MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE IVAN FRANKO NATIONAL UNIVERSITY OF LVIV NATIONAL ACADEMY OF SCIENCES OF UKRAINE WESTERN SCIENTIFIC CENTER UKRAINIAN CRYSTALLOGRAPHIC COMMITTEE

XIV INTERNATIONAL CONFERENCE ON CRYSTAL CHEMISTRY OF INTERMETALLIC COMPOUNDS



LVIV, UKRAINE SEPTEMBER 22-26, 2019

COLLECTED ABSTRACTS

SPONSORED BY LVIV CITY COUNCIL INTERNATIONAL CENTRE FOR DIFFRACTION DATA (ICDD) MATERIAL PHASES DATA SYSTEM (MPDS) SCC "STRUCTURE-PROPERTIES" Collected Abstracts of the XIV International Conference on Crystal Chemistry of Intermetallic Compounds, Lviv, Ukraine, 22-26 September 2019, Ivan Franko National University of Lviv, 2019, 169 p.

INTERNATIONAL ADVISORY COMMITTEE

R. Ben Hassen	Tunisia	Z. Naz
G. Borzone	Italy	H. No
R. Černý	Switzerland	V. Peo
T. Fässler	Germany	R. Pöt
D. Fruchart	France	K. Ric
H. Fuess	Germany	C. Rö
A.P. Gonçalves	Portugal	A. Sac
Yu. Grin	Germany	A. Szy
L. Havela	Czech Republic	T. Ve
D. Kaczorowski	Poland	P. Vil
M.G. Kanatzidis	USA	

zarchuk Ukraine ël France charsky USA Germany ttgen chter Austria hr Germany Italy ccone Poland vtuła likanova Ukraine Switzerland lars

LOCAL ORGANIZING COMMITTEE

R. Gladyshevskii (<i>chairman</i>)	
B. Belan S	. Pukas
K. Cenzual L	. Romaka
Ya. Kalychak N	. Semuso
M. Konyk Y	a. Tokaychuk
V. Pavlyuk V	. Zaremba

Department of Inorganic Chemistry Ivan Franko National University of Lviv Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine telephone: +380 32 2600388, fax: +380 32 2616048 e-mail: imc@lnu.edu.ua web site: http://chem.lnu.edu.ua/about/departments/imc-conference

PROGRAM

ORGANIZERS

The XIV International Conference on Crystal Chemistry of Intermetallic Compounds is organized by the Ministry of Education and Science of Ukraine, the Ivan Franko National University of Lviv, the National Academy of Sciences of Ukraine, the Western Scientific Center, and the Ukrainian Crystallographic Committee.

SPONSORS

The organizers acknowledge with gratitude the financial support of Lviv City Council, Ukraine, International Centre for Diffraction Data (ICDD), USA, Material Phases Data System (MPDS), Vitznau, Switzerland, and SCC "Structure-Properties", Lviv, Ukraine.

INTERNATIONAL ADVISORY COMMITTEE

R. Ben Hassen (Tunisia), G. Borzone (Italy), R. Černý (Switzerland), T. Fässler (Germany),
D. Fruchart (France), H. Fuess (Germany), A.P. Gonçalves (Portugal), Yu. Grin (Germany),
L. Havela (Czech Republic), D. Kaczorowski (Poland), M.G. Kanatzidis (USA),
Z. Nazarchuk (Ukraine), H. Noël (France), V. Pecharsky (USA), R. Pöttgen (Germany),
K. Richter (Austria), C. Röhr (Germany), A. Saccone (Italy), A. Szytuła (Poland),
T. Velikanova (Ukraine), P. Villars (Switzerland)

LOCAL ORGANIZING COMMITTEE

R. Gladyshevskii (*chairman*), B. Belan, K. Cenzual, Ya. Kalychak, M. Konyk, V. Pavlyuk, S. Pukas, L. Romaka, N. Semuso, Ya. Tokaychuk, V. Zaremba

Department of Inorganic Chemistry Ivan Franko National University of Lviv e-mail: imc@lnu.edu.ua http://chem.lnu.edu.ua/about/departments/imc-conference

GENERAL INFORMATION

Conference sites

On Monday, *September 23*, the conference sessions will take place in the *Main Building* of the Ivan Franko National University of Lviv. On Tuesday, *September 24*, and Wednesday, *September 25*, they will take place in the nearby *Bank Hotel*.

Registration – Conference secretariat

Registration will start on Sunday, *September 22*. From Monday, *September 23*, the secretariat will be situated at the conference site and remain open during the conference.

Sunday, *September 22*, 14⁰⁰-18⁰⁰: *Department of Inorganic Chemistry*, Ivan Franko National University of Lviv.

Monday, *September 23*, 8⁰⁰-18⁰⁰: *Main Building* of the Ivan Franko National University of Lviv.

Tuesday, *September 24*, and Wednesday, *September 25*, 8⁰⁰-18⁰⁰: *Bank Hotel*.

Proceedings

Proceedings will be published in the journal *Chemistry of Metals and Alloys* (http://chemetal-journal.org). An electronic version of the manuscript should be submitted to the journal office (chemetal@lnu.edu.ua; subject: IMC-XIV proceedings) before *October 15, 2019*.

Oral presentations

Equipment for computer presentation is available for the speakers. Please contact the secretariat before your presentation, in order to check your CD / flash-drive.

Poster presentations

The posters will be displayed on Tuesday, *September 24* (posters P1-P52) and Wednesday, *September 25* (posters P53-P104). The authors are kindly requested to be present near their posters during the poster sessions $(14^{00}-15^{30})$.

SATELLITE MEETING

VII School for Young Scientists "X-ray Diffraction: Single-Crystal Methods"

The School will take place on September 19-21, 2019 at the *Department of Inorganic Chemistry* of the Ivan Franko National University of Lviv. There will be lectures on modern experimental methods and novel software for refinements of crystal structures and practical exercises (see <u>http://chem.lnu.edu.ua/about/departments/young-researchers-school</u>).

SOCIAL PROGRAM

Sunday, September 22	18^{00}	Guided walk in the Old town
Monday, September 23	17^{00}	Concert
Monday, September 23	18^{00}	Get-together party
Tuesday, September 24	19 ⁰⁰	Conference dinner
Wednesday, September 25	18 ³⁰	Musical event
Thursday, September 26	9 ⁰⁰	Bus excursion "Lviv and Surroundings"

EXCURSIONS FOR ACCOMPANYING PERSONS

Monday, September 23	9 ³⁰	Art and history
Tuesday, September 24	9 ⁰⁰	Coffee and chocolate
Wednesday, September 25	9 ⁰⁰	Ecotourism

Tuesday

Bank Hotel (Lystopadovogo Chynu St. 8) Chairpersons: **R. Ben Hassen, P. Villars, V. Zaremba**

SESSIONS: CRYSTAL STRUCTURES, DATABASES AND SOFTWARE

9 ⁰⁰	A. Haffner, V. Weippert, Dirk Johrendt : SUPERTETRAHEDRAL NETWORKS AND PROPERTIES OF NEW PHOSPHIDOSILICATES AND ARSENIDOGALLATES	L6
9 ³⁵	Vitaliy V. Romaka , A. Grytsiv, Yu.V. Stadnyk, G. Rogl, L. Romaka, P. Rogl: DETERMINATION OF STRUCTURAL DISORDER IN HEUSLER-TYPE PHASES	O6
9 ⁵⁰	F. Abdel-Hamid, K. Anand, M.C. de Weerd, C. Allio, G. Krellner, H.D. Nguyen, M. Baitinger, Y. Grin, J. Ledieu, E. Gaudry, Vincent Fournée : INTERPLAY BETWEEN THE 3D CAGE NETWORK AND 2D SURFACES IN INTERMETALLIC CAGE COMPOUNDS	L7
10^{25}	Coffee break	
1100	Peter Y. Zavalij , B.W. Eichhorn: CRYSTALLOGRAPHY OF INTERMETALLIC CLUSTERS: STRUCTURE, SYMMETRY AND DISORDER	L8
11^{35}	T. Braun, Viktor Hlukhyy: NEW NICKEL SILICIDES	O7
11 ⁵⁰	Fermin Cuevas , J. Zhang, C. Nervi, M. Baricco, M. Latroche: STRUCTURAL AND HYDROGENATION PROPERTIES OF THE TiCo INTERMETALLIC AND ITS HYDRIDES	08
12 ⁰⁵	Myroslava Horiacha , F. Stegemann, R. Pöttgen, G. Nychyporuk, V. Zaremba: QUATERNARY INTERMETALLIC COMPOUNDS $REPt_2Ga_3In$ ($RE = Y$, Gd-Yb)	O9
12^{20}	Lunch break	
13 ³⁰	POSTER SESSION I P1-P52	
15 ⁰⁰	Pierre Villars : THE IMPORTANCE OF THE PERIODIC (MEDELEEV) NUMBER IN CRYSTAL STRUCTURE PREDICTION – A DATA-CENTRIC APPROACH USING THE PAULING FILE	L9
15 ³⁵	Matthias Kotsch , Yu. Prots, Yu. Grin: Ba ₆ Li ₂ Ga ₁₀ , A NEW INTERMETALLIC PHASE WITH PYRAMIDAL Ga ₅ CLUSTERS	O10
15 ⁵⁰	Julia-Maria Hübner , W. Carrillo-Cabrera, Yu. Prots, M. Bobnar, U. Schwarz, Yu. Grin: UNCONVENTIONAL METAL-FRAMEWORK INTERACTION IN MgSi ₅	011
16 ⁰⁵	Coffee break	
16 ⁴⁰	Yibin Xu: MATERIALS DATABASE AS FUNDAMENTAL OF MATERIALS INFORMATICS	L10
17 ¹⁵	Oleksandra Koloskova , V. Buturlim, P. Minárik, L. Havela: MAGNETIC PROPERTIES OF $(UH_3)_{1-x}T_x$: IS STRUCTURE TYPE IMPORTANT?	012
17 ³⁰	Vira M. Shved , V.M. Hreb, L.O. Vasylechko: PrCo _{0.5} Fe _{0.5} O ₃ ELECTRONIC STRUCTURE FROM FIRST PRINCIPLES	013
19 ⁰⁰	Conference dinner (departure 18^{40})	

Wednesday

Bank Hotel (Lystopadovogo Chynu St. 8) Chairpersons: **D. Fruchart, V. Pavlyuk, A. Szytula**

SESSIONS: PHYSICAL PROPERTIES, CRYSTAL CHEMICAL FEATURES

9 ⁰⁰	Mauro Giovannini : INVESTIGATION ON Ce AND Yb INTERMETALLICS: THE ROLE OF CRYSTAL CHEMISTRY	L11
9 ³⁵	Nataliya E. Skryabina : OSCILLATION BEHAVIOR OF METAL ATOMS IN HYDROGENATED INTERMETALLICS	O14
9 ⁵⁰	Daniel Fruchart , O. Fruchart, G. Girard, L. Ortega, N.E. Skryabina, M.G. Shelyapina: HYDROGENATION/DEHYDROGENATION OF EPITAXIAL DEPOSITS INTERFACING Mg TO Nb LAYERS	L12
10^{25}	Coffee break	
11 ⁰⁰	B. Penc, St. Baran, A. Hoser, Andrzej Szytula: STRUCTURAL AND MAGNETIC PROPERTIES OF R_2T Ge ₆ COMPOUNDS	L13
11 ³⁵	Ihor Yu. Zavaliy , A.R. Kytsya, Yu.V. Verbovytskyy, P.Yu. Zavalij, Yu.O. Kulyk, V.V. Berezovets, P.Ya. Lyutyy: HYDROGENATION PROPERTIES OF Ni-BASED NANOPOWDERS AND MH–NANO-Ni COMPOSITE MATERIALS	015
11 ⁵⁰	Silvie Maskova-Cerna , A.V. Andreev, H. Nakotte, K. Kothapalli, A.V. Kolomiets, L. Havela: MAGNETIC AND LATTICE ANISOTROPIES IN U-COMPOUNDS: U ₂ Ni ₂ Sn	O16
12 ⁰⁵	Alexandre V. Kolomiets, S. Mašková, I. Halevy, J. Prchal, J. Valenta, L. Havela, A. Andreev: INFLUENCE OF PRESSURE ON THE RESISTIVITY OF U_2Ni_2Sn	O17
12^{20}	Lunch break	
13 ³⁰	POSTER SESSION II P53-P104	
15 ⁰⁰	Ladislav Havela , M. Divis, T. Gouder, D. Legut: URANIUM HYDRIDES: MYTHOLOGY AND REALITY	L14
15 ³⁵	Iryna Antonyshyn , U. Burkhardt, O. Sichevych, A. Ormeci, K. Rasim, S. Titlbach, S.A. Schunk, Yu. Grin: CHEMICAL REACTIVITY OF Ca–Ag INTERMETALLIC COMPOUNDS	O18
15 ⁵⁰	Eleonora V. Afanasenko , I.I. Seifullina, E.E. Martsinko, E.A. Chebanenko, V.V. Dyakonenko, S.V. Shishkina: SYNTHESIS AND INVESTIGATION OF TARTRATOGERMANATE Cu(II), Ni(II), Fe(II) COMPLEXES WITH 2,2'-BIPYRIDINE	O19
16^{05}	Coffee break	
1640	Jing-Tai Zhao : TUNING OF THE THERMOELECTRIC PROPERTIES OF QUATERNARY COMPOUNDS, $ABZnSb$ ($A = Sr$, Ba AND RARE EARTH ELEMENTS; $B = F$ AND O) WITH THE ZrCuSiAs STRUCTURE TYPE	L15
17 ¹⁵	Closing of the XIV International Conference on Crystal Chemistry of Intermetallic Compounds	
	Ĩ	

POSTER SESSION I

Tuesday

September 24

Bank Hotel (Lystopadovogo Chynu St. 8)

Kostyantyn Ye. Korniyenko , V.G. Khoruzhaya, O.V. Zaikina, T.Ya. Velikanova: TERNARY COMPOUNDS OF THE Al–Ti–Pt SYSTEM AND PHASE EQUILIBRIA WITH THEIR PARTICIPATION	P1
Olena L. Semenova, V.I. Ivashchenko: ON THE TRANSFORMATION IN ZrNi	P2
Mariya Konyk, L. Romaka, V.V. Romaka, Yu. Stadnyk, P. Demchenko, A. Horyn: ISOTHERMAL SECTION AT 800°C OF THE PHASE DIAGRAM OF THE Er–Cr–Ge TERNARY SYSTEM	P3
Ivanna Romaniv , L. Romaka, V.V. Romaka, Yu. Stadnyk, M. Konyk: INTERACTION OF THE COMPONENTS IN THE Ho-{Fe,Co}-Sn TERNARY SYSTEMS	P4
M. Fedyna, A. Popovych, Bohdan Stelmakhovych : INVESTIGATION OF THE La–Cu–Al SYSTEM (0-25 AT.% La) AT 870 K	Р5
Lyubov Romaka , V.V. Romaka, Yu. Stadnyk, A. Horyn: FORMATION OF THERMOELECTRIC HALF-HEUSLER PHASES IN THE {Y,Tm}–Ni–Sb TERNARY SYSTEMS	P6
Y.M. Kogut , L.V. Piskach, I.D. Olekseyuk, O.V. Parasyuk: PHASE EQUILIBRIA IN THE QUASI-TERNARY SYSTEMS $A_2^I X - PbX - D^{IV}X_2$ ($A^I - Cu$, Ag; $D^{IV} - Si$, Ge, Sn; $X - S$, Se) AT 300 K	P7
Khrystyna O. Melnychuk , O.V. Smitiukh, O.V. Marchuk, L.V. Piskach: THE PbS–In ₂ S ₃ –SiS ₂ SYSTEM AT 770 K	P8
Valery Plechystyy , I. Shtablavyi, S. Winczewski, K. Rybacki, S. Mudry, J. Rybicki: MOLECULAR DYNAMICS SIMULATION OF SILICIDE FORMATION AT INTERLAYER BOUNDARIES IN THE Cu–Si SYSTEM	P9
M.V. Bulanova, Iuliia V. Fartushna , K.A. Meleshevich: PHASE EQUILIBRIA IN THE TERNARY Zr–Co–Sn SYSTEM	P10
Zinoviya Shpyrka , O. Soludchyk, N. German, V. Pavlyuk: THE Nd–Si–Ge SYSTEM AT 870 K	P11
V.S. Sudavtsova, A.S. Dudnik , V.G. Kudin, N.V. Podoprigora: THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF THE In–Tb SYSTEM	P12
Valentyna S. Sudavtsova, M.O. Shevchenko, V.G. Kudin, A.S. Kozorezov: THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF THE Sn-Ho SYSTEM	P13
Nastasia Klymentiy , S. Pukas, R. Gladyshevskii: THE TERNARY SYSTEM V–Cu–Al AT 800°C	P14
Khrystyna O. Melnychuk , O.V. Marchuk, I.D. Olekseyuk, L.D. Gulay, M. Daszkiewicz: THE La ₂ S ₃ –CoS–SiS ₂ SYSTEM AT 770 K	P15
Larysa Marushko, I. Ivashchenko, L. Piskach: PHASE EQUILIBRIA IN THE SYSTEM Cu ₂ ZnGeSe ₄ -Cu ₂ CdGeSe ₄ AT 720 K	P16
Lyudmyla Piskach , O. Tsisar, L. Marushko, V. Pankevych, O. Parasyuk: QUATERNARY COMPOUNDS $PbGa_2MX_6$ ($M = Si, Ge; X = S, Se$)	P17

Roman Dankevych , Ya. Tokaychuk, R. Gladyshevskii: PHASE EQUILIBRIA IN THE TERNARY SYSTEM Gd–Ge–Sn at 600°C	P18
Taras Slivinskyi , Ya. Tokaychuk, R. Gladyshevskii: ISOTHERMAL SECTIONS OF THE PHASE DIAGRAMS OF THE SYSTEMS Sm–B–Al AND B–Al–Ga AT 600°C	P19
Sergiy I. Levkovets , O.V. Smitiukh, B.A. Tataryn, L.V. Piskach: PHASE EQUILIBRIA IN THE TIPb ₂ Br ₅ –KPb ₂ Br ₅ SYSTEM	P20
Lyudmila S. Kriklya , K.Ye. Korniyenko, V.G. Khoruzhaya: PHASE CONSTITUENTS OF Hf–Rh–Ir ALLOYS IN AS-CAST STATE AND ANNEALED AT SUBSOLIDUS TEMPERATURES	P21
Anastasiya M. Storchak, T.Ya. Velikanova, L.V. Artyukh, V.M. Petyukh, M.A. Turchanin, P.G. Agraval: PHASE EQUILIBRIA IN THE Cu–Ti–Zr SYSTEM AT SUBSOLIDUS TEMPERATURES	P22
Vasyl Kordan , I. Tarasiuk, V. Nytka, O. Zelinska, R. Serkiz, V. Pavlyuk: CRYSTAL STRUCTURE AND ELECTROCHEMICAL HYDROGENATION OF THE $La_2Mg_{17-x}M_x$ ($M = Sn$, Sb, Ni) PHASES	P23
M. Dzevenko, Yaroslava Lomnytska , V. Babizhetskyy: HIGHER PHOSPHIDES WITH OsGe ₂ -TYPE STRUCTURE	P24
Olha V. Zhak , T.P. Zdorov, O.R. Karychort: CRYSTAL STRUCTURE OF THE NEW TERNARY PHOSPHIDE Ho ₅ Pd ₁₉ P ₁₂	P25
Anna I. Tursina , S.N. Nesterenko, K.B. Kalmykov, D. Kaczorowski: NEW ALUMINIDES $RE_3Ni_4Al_2$ ($RE = La$, Ce, Pr, Nd) OF THE La ₃ Ni ₄ Ga ₂ -TYPE	P26
D. Kowalska, Bohdana Belan , M. Manyako, Ya. Kalychak: SINGLE-CRYSTAL INVESTIGATION OF THE SmMn _{6.8} Ni _{5.2} COMPOUND	P27
Volodymyr Babizhetskyy , J. Köhler, R. Krutjak, Y. Tyvanchuk: $GdFe_{1-x}Si_2$ ($x = 0.32$) – A NEW TERNARY REPRESENTATIVE OF THE TbFeSi ₂ STRUCTURE TYPE	P28
V. Pavlova, Elena Murashova : THE INTERMETALLIC COMPOUND Sm ₂ Ru ₃ Sn ₅ WITH A NEW STRUCTURE TYPE	P29
I. Grekhov, Zh. Kurenbaeva, Elena Murashova : NEW GALLIDES OF RUTHENIUM AND RARE-EARTH ELEMENTS	P30
Y. Grishina, D. Sedelnikov, Zhanafiya Kurenbaeva , A. Tursina, E. Murashova: COMPOUNDS IN THE SYSTEMS RE -Ru- X (RE = Dy-Lu, X = Ga, In) WITH CsCl STRUCTURE TYPE	P31
Volodymyr Levytskyi , GL. Păşcuț, R. Gumeniuk, V. Babizhetskyy, O. Isnard, B. Kotur: NPD STUDIES OF THE NOVEL HELICAL FERRIMAGNET $Dy_{11}Ni_{60}C_6$	P32
Yulia S. Morozova , A.I. Tursina, E.V. Murashova: NEW TERNARY INTERMETALLIC Ce ₉ Pt ₂₅ Al ₃₇	P33
O. Sichevych, Lev Akselrud, E. Svanidze, Yu. Grin: SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF Y_3Pt_4	P34
Bogdan Kotur , V. Babizhetskyy, V. Smetana: CRYSTAL STRUCTURE OF THE NEW TERNARY SILICIDE Sc ₁₂ Co _{43.2} Si ₂₇	P35
V. Babizhetskyy, V. Levytskyy, V. Smetana, Lyudmyla Piskach, O. Tsisar, O. Parasyuk: A NEW CATION-DISORDERED QUATERNARY SELENIDE Tl ₂ Ga ₂ SnSe ₆	P36

Olha V. Zhak, T.S. Horetska: NEW TERNARY PHASES IN THE Er-Ag-Al SYSTEM	P37
Pavlo Ya. Lyutyy , V.V. Berezovets, I.Yu. Zavaliy: Zr ₃ Ni(Co) COMPOUNDS STABILIZED BY NITROGEN AND THEIR HYDRIDES	P38
L. Fedyna, A. Fedorchuk, V. Mykhalichko, Mykhajlo Fedyna : CRYSTAL STRUCTURE OF THE NEW TERNARY ANTIMONIDE Ce ₆ Cu ₄₃ Sb ₂₄	P39
Igor V. Oshchapovsky , I.Yu. Zavaliy, V.V. Pavlyuk: DFT CALCULATIONS OF THE HYDROGEN SUBLATTICE IN Mg_2NiH_x AND $Mg_3AlNi_2H_y$ HYDRIDES	P40
Vasyl M. Hreb , L.O. Vasylechko: HIGH-TEMPERATURE BEHAVIOR OF $GdCo_{0.5}Cr_{0.5}O_3$ PROBED BY X-RAY SYNCHROTRON POWDER DIFFRACTION	P41
Sever Flipo , M. Kohout, F. Roth, T. Weigel, W. Schnelle, M. Bobnar, A. Ormeci, U. Burkhardt, C. Hennig, T. Leisegang, DC. Meyer, A. Leithe-Jasper, R. Gumeniuk: $CeMo_2B_5$: A NEW TYPE OF ARRANGEMENT OF PUCKERED BORON HEXAGONAL RINGS	P42
Iryna Voloshyn , Z. Shpyrka, V. Pavlyuk: CRYSTAL STRUCTURE OF THE TERNARY $Ce_{0.75}Y_{0.25}Ge$ COMPOUND	P43
Nataliya Semuso , S. Pukas, Ya. Tokaychuk, R. Gladyshevskii: NEW MULTICOMPONENT COMPOUNDS R_5 Ni _{1.5} Co _{1.5} Al ₃ Ge ₄ (R = RARE-EARTHS)	P44
A. Broda, Oksana Matselko , R. Gladyshevskii: A TERNARY PHASE WITH THE Nb ₂ Cr ₄ Si ₅ STRUCTURE TYPE IN THE Hf–V–Ge SYSTEM	P45
Yu. Plyatsko, Svitlana Pukas , R. Gladyshevskii: NEW REPRESENTATIVES OF THE STRUCTURE TYPE Er ₅ Ni ₃ Al ₃ Ge ₄	P46
Taras Delenko , Ya. Tokaychuk, R. Gladyshevskii: CRYSTAL STRUCTURE OF THE COMPOUND Dy ₄ Ga _{1.4} Ge _{5.6}	P47
Danylo Maryskevych , Ya. Tokaychuk, Yu. Prots, L. Akselrud, R. Gladyshevskii: CRYSTAL STRUCTURE OF THE COMPOUND Zr ₅ AlGe ₃	P48
V. Topertser, Nataliya Muts , Ya. Tokaychuk, P. Demchenko, R. Gladyshevskii: CRYSTAL STRUCTURE OF THE DyNi ₃ Ga ₉ AND ErNi ₃ Ga ₉ COMPOUNDS	P49
Yuriy B. Tyvanchuk , A.O. Oliynyk: CRYSTAL STRUCTURE OF NOVEL TERNARY INDIDES RE_{23} Ni ₇ In ₄ ($RE = $ Gd, Tb, Dy)	P50
Nazar Zaremba , V. Hlukhyy, V. Pavlyuk: YbNi _{2.31} Al _{2.69} – A NEW DERIVATIVE OF THE YCo ₃ Ga ₂ AND YNi ₂ Al ₃ STRUCTURES	P51
Valentyna Kozak , L. Gulay, I. Ivashchenko, P. Tyshchenko, I. Olekseyuk: CRYSTAL STRUCTURE OF AgGa ₂ Se ₃ Cl	P52

POSTER SESSION II

Nazar Pavlyuk, G. Dmytriv, V. Pavlyuk, G. Cichowicz, M.K. Cyrański, H. Ehrenberg: NEW CUBIC PHASES IN THE Mg-Ni-Ga SYSTEM Yurii I. Slyvka, M.Yu. Luk'yanov, M.G. Mys'kiv: BIMETALLIC Cu(I)/Fe(II) π-COORDINATION COMPOUNDS BASED ON **3-ALLYLSULFANYL-**4-ALLYL-5-PHENYL-4H-1,2,4-TRIAZOLE AND **5-ALLYLSULFANYL-**1,3,4-THIADIAZOL-2-AMINE Khrystyna O. Melnychuk, O.V. Marchuk, I.D. Oleksevuk, L.D. Gulav, M. Daszkiewicz: CRYSTAL STRUCTURE OF R₃Fe_{0.5}SnS₇ (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Y, AND Ho) L.V. Piskach, Andrij O. Selezen, O.V. Smitiukh, I.D. Olekseyuk: $Tl_2B^{II}D^{IV}X_4$ COMPOUNDS WITH TETRAGONAL STRUCTURE Zakharii M. Oliinyk, A.V. Korolyshyn, S.I. Mudry: RAPID QUENCHING OF **INTERMETALLICS** Vasvl R. Kozer, O.V. Parasyuk, I.D. Olekseyuk: PHASE EQUILIBRIA IN THE $Cu_2ZnD'X_4$ - $Cu_2ZnD'X_4$ SYSTEMS (D – Si, Ge, Sn; X – S, Se) Stepan S. Milyovich, V.I. Gomonaj, V.V. Pavlyuk, I.P. Stercho, I.E. Barchiy: CRYSTAL STRUCTURE OF CLINOPTILOLITE 1.4(Na,K)₂O×(Ca,Mg)O×3Al₂O₃× $28SiO_2 \times 22H_2O$ Romana Perun, M. Horiacha, R. Pöttgen, G. Nychyporuk, V. Zaremba: INVESTIGATION OF THE GdNiAl_{4-x}In_x (x = 0-2) SYSTEM Natalia Chorna, O. Zelinska, G. Dmytriv, V. Pavlyuk, A. Zelinskiy, V. Kordan, CRYSTAL STRUCTURE OF NEW ZINC-RICH TERNARY A. Mar: COMPOUNDS $Gd_2Zn_{17-x}M_x$ (*M* = Mn, Fe) Oksana Zaremba, V. Hrytsan, R. Gladyshevskii: PEROVSKITE PHASES IN AO-R₂O₃-Fe₂O₃ SYSTEMS (A – ALKALINE-EARTH METAL, R – RARE-EARTH METAL) Bohdana Belan, D. Kowalska, O. Bardin, M. Manyako, R. Gladyshevskii: SINGLE-CRYSTAL **INVESTIGATION** OF THE $Ce_5Ag_{0.1}Ge_{3.9}$ PHASE WITH Sm₅Ge₄ TYPE Bohdana Belan, D. Kowalska, M. Manyako, R. Gladyshevskii: SINGLE-CRYSTAL INVESTIGATION OF THE EuNi₉Si₄ COMPOUND O. Kasaraba, S. Pukas, Bohdana Belan, M. Manyako, R. Gladyshevskii: REINVESTIGATION OF THE CRYSTAL STRUCTURE OF LaNi₉Si₄ Bohdana Belan, M. Manyako, R. Gladyshevskii, R. Černý: A NEW MEMBER OF THE AlB₂ STRUCTURE TYPE FAMILY

September 25

P53

P54

P55

P56

P57

P58

P59

P60

P61

P62

P63

P64

P65

P66

Bank Hotel (Lystopadovogo Chynu St. 8)

Wednesday

Yurii Prots, J. Kadok, M. Schmidt, M. Coduri, M. Mihalkovič, V. Fournée,
J. Ledieu, Yu. Grin: NEW FEATURES OF THE $Al_{2.75}$ Ir STRUCTUREP67Jakub Miśtal, V. Pavlyuk, G. Kowalczyk, A. Balińska, N. Pavlyuk, G. Dmytriv,
S. Indris, B. Schwarz, H. Ehrenberg: LITHIATION, SODIATION AND
MAGNESIATION OF $Gd_{1-x}La_xSn_{2-y}Sb_yM_z$ (M = Li, Na, Mg) HIGH DISORDER –
HIGH ENTROPY PHASES (HD-HEP)P68

V. Shtender, Valérie Paul-Boncour, JC. Crivello, R.V. Denys, K. Provost,	P69
F. Couturas, I.Yu. Zavaliy: CRYSTAL STRUCTURE, HYDROGENATION AND	
I V Fesych Oleksiv V Ivanov N A Liedienov S A Nedilko O G Dziazko	P70
A.V. Pashchenko, G.G. Levchenko: MAGNETOCALORIC EFFECT IN NANOCRYSTALLINE La _{0.8-x} $K_{0.2}Mn_{1+x}O_{3\pm\delta}$ ($0 \le x \le 0.2$) MANGANITES	170
Yuriy Stadnyk , V.V. Romaka, L. Romaka, P. Demchenko, A. Horyn: CRYSTAL AND ELECTRONIC STRUCTURES, AND PHYSICAL PROPERTIES OF THE $Ti_{1-x}Sc_xCoSb$ SOLID SOLUTION	P71
Volodymyr Babizhetskyy , V. Levytskyy, O. Isnard: Dy ₄ B ₃ C ₄ : PREPARATION, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES	P72
I.I. Bulyk, V.V. Chabanenko, A. Nabiałek, T. Zajarniuk, A. Szewczyk, R. Puźniak, V.V. Burkhovetskyi, V.Yu. Tarenkov, Ihor V. Borukh : THE INFLUENCE OF RECOMBINATION CONDITIONS ON THE PHASE CONTENT, MICROSTRUCTURE, AND MAGNETIC PROPERTIES OF SmCo ₅ -BASED SINTERED MAGNETS	P73
Andriy Horyn , V.A. Romaka, Yu. Stadnyk, L. Romaka, M. Rokomanyuk, V. Krayovskyy: FEATURES OF ELECTRICAL CONDUCTIVITY MECHANISMS OF THE Ti _{1-x} Mo _x CoSb SOLID SOLUTION	P74
Yuriy V. Verbovytskyy , Yu.V. Kosarchyn, P.Ya. Lyutyy, V. Paul-Boncour, I.Yu. Zavaliy: SOLID-GAS AND ELECTROCHEMICAL HYDROGENATION PROPERTIES OF $R_{1-x}R'_xMgNi_{4-y}M_y$ ($R, R' = Y$, La, Pr, Nd; $M = Fe$, Mn) ALLOYS	P75
Anatoliy Zelinskiy , L. Romaka, L. Akselrud, R. Gladyshevskii, O. Sichevych, M. Bobnar, Yu. Grin: INFLUENCE OF SUBSTITUTION ON THE STRUCTURE AND MAGNETIC PROPERTIES OF THE Dy _{1-x} Ho _x Cu ₅ Sn SOLID SOLUTION	P76
Iryna Stetskiv , V. Kordan, I. Tarasiuk, V. Pavlyuk: ELECTROCHEMICAL SYNTHESIS OF THE $TbCo_{4.8}Mg_{0.1}Al_{0.1}H_x$ HYDRIDE	P77
Marta Dufanets, Yu. Plevachuk, V. Sklyarchuk: VISCOSITY AND ELECTROPHYSICAL PROPERTIES OF THE Cu–Pb SYSTEM – A COMPONENT FOR MODELLING HIGH-ENTROPY ALLOYS	P78
Olha Tkach , Yu. Plevachuk, V. Sklyarchuk: INFLUENCE OF NANO Ni ADDITIONS ON STRUCTURE-SENSITIVE PROPERTIES OF Sn–Ag–Cu LIQUID ALLOYS	P79
Ihor M. Kobasa , Yu.V. Kropelnytska, V.M. Fedoriv: SENSITIZATION OF TITANIUM DIOXIDE WITH AN ANIONIC POLYMETHINE DYE IN THE PHOTOCATALYTIC REDUCTION OF METHYLENE BLUE	P80
Ihor M. Kobasa , O.V. Sema, M.M. Vorobets: REGULARITIES OF FORMATION AND SOME PHYSICO-CHEMICAL PROPERTIES OF COPPER AND SILVER FILMS ON CdTe, CdSb, In ₂ Hg ₃ Te ₆	P81
S. Baran, Yuriy Tyvanchuk , B. Penc, Ya. Kalychak, A. Szytula: CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF R_{11} Pd ₄ In ₉ COMPOUNDS ($R = $ Gd-Er)	P82
Ana María Barrios Jiménez , S. Flipo, O. Sichevych, K. Höfer, S. Altendorf, A. Leithe-Jasper, R. Gumeniuk, I. Antonyshyn, Y. Grin: ELECTROCATALYTIC PROPERTIES OF THE Hf ₂ Ir ₅ B ₂ BORIDE	P83

Viktoriia Milashius , V. Kordan, I. Tarasiuk, G. Dmytriv, V. Pavlyuk: INFLUENCE OF BORON ON THE ELECTROCHEMICAL DELITHIATION OF Li _x Al _y PHASES	P84
M.D. Koterlyn, Orest I. Babych , G.M. Koterlyn: SPECIFICITIES OF THE BEHAVIOR OF THERMOELECTRIC POWER IN $CeNi_4X$ ($X = Cu$, Al, Ga) WITH UNSTABLE VALENCE OF Ce	P85
Bogdan Sokoliuk , Yu. Plevachuk, V. Sklyarchuk, M. Dufanets: ELECTROPHYSICAL PROPERTIES OF Ga–Sn–Zn EUTECTIC ALLOY WITH ADMIXTURES OF ELEMENTS OF GROUPS I-IV	P86
Bogdan Kuzhel , L. Salamakha, L. Romaka, B. Belan, R. Gladyshevskii: PECULIARITIES OF THE RESISTIVITY OF <i>RE</i> ₃ (Ce,Nd,Sm)Cu ₄ Sn ₄ , <i>RE</i> (Gd,Tb,Ho)NiSn ₂ , DyNiSi, AND DyNiSi ₃ IN MAGNETIC FIELDS	P87
Oleksandra S. Berezhnytska , O.K. Trunova, I.O. Savchenko, Ya.V. Fedorov, N.V. Rusakova: LUMINESCENT PROPERTIES OF SOME β -DICARBONYL COMPLEXES OF LANTHANIDES	P88
Oleksandra S. Berezhnytska , N.B. Ivakha, O.K. Trunova, S.S. Smola, O.O. Rohovtsov: LUMINESCENT PROPERTIES OF POLYMERS AND COPOLYMERS OF Nd(III) AND Yb(III)	P89
Makhsuda N. Abdusalyamova , M.A. Badalova, F.A. Makhmudov, I.G. Vasilyeva, S.M. Kauzlarich: PREPARATION AND INVESTIGATION OF SOME PROPERTIES OF Pr-DOPED Yb ₁₄ MnSb ₁₁	P90
T. Prikhna, V. Shaternik, V. Moshchil, V. Sverdun, Anton Shaternik: PINNING IN MAGNESIUM DIBORIDE THIN FILMS AND BULK SAMPLES WITH HIGH CRITICAL CURRENT DENSITIES j_c	P91
Romana-Iryna Martyniak , N. Muts, M. Bobnar, L. Akselrud, R. Gladyshevskii: CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF Cr-{Ru,Pd}-Ni-Si PHASES	P92
Khrystyna Miliyanchuk , L. Havela, O. Lavriv, S. Maskova-Cerna, R. Gladyshevskii: STABILIZATION OF A Mo ₂ FeB ₂ -TYPE PHASE IN THE SYSTEM Ho–Ni–In AND ITS HYDROGENATION	P93
Khrystyna Miliyanchuk , N. Saidov, S. Maskova-Cerna, Ya. Tokaychuk, L. Havela, R. Gladyshevskii: HYDROGENATION OF STRUCTURALLY RELATED PHASES $Tb_m T_m Ga (T = Co, Ni; m = 2, 3)$	P94
Sergey A. Nedilko , T.A. Voitenko, I.V. Fesych, O.G. Dziazko, M.A. Zelenko, D.D. Naumova: TI-CONTAINING HTSC CUPRATES	P95
Karolina Kluziak , V. Pavlyuk: STRUCTURAL AND HYDROGENATION PROPERTIES OF $Gd_{1-x}T_xNi$ (0 < x < 1) ALLOYS	P96
Volodymyr N. Shevchuk , I.V. Kayun: CALCULATION OF CATION MIGRATION CHANNELS IN CRYSTALS WITH SCHEELITE-TYPE STRUCTURE	P97
Georgiy S. Firstov , T.A. Kosorukova, A.N. Timoshevskii, Yu.N. Koval, V.V. Odnosum, Yu. Matviychuk, G. Gerstein, H.J. Maier: MULTICOMPONENT INTERMETALLIC COMPOUNDS WITH DISTORTED B2 STRUCTURE: PHASE STABILITY AND STRUCTURE-PROPERTIES RELATIONSHIP	P98
Gregory Gerstein , G. Firstov, T. Kosorukova, Y. Koval, V. Odnosum, A. Dalinger, H.J. Maier: STRUCTURAL CHANGES DRIVEN BY PULSED MAGNETIC FIELDS: COMPARISON OF NON-STOICHIOMETRIC CoNiGa AND CoNiCuAlGaIn INTERMETALLIC COMPOUNDS	P99

Martyn A. Sozanskyi, P.Yo. Shapoval, V.E. Stadnik, Yo.Yo. Yatchyshyn,	P100
V.M. Kordan: HYDROCHEMICAL SYNTHESIS AND X-RAY INVESTIGATION	
OF CdS_xSe_{1-x} FILMS	
Liudmila I. Sliusarchuk, L.I. Zheleznova, T.V. Pavlenko, O.O. Rogovtsov:	P101
SYNTHESIS OF COMPLEX OXIDES ON GRANULES OF ALUMINUM OXIDE	
FROM β-DIKETONATE COMPLEXES OF 3 <i>d</i> -4 <i>f</i> -METALS	
Olha V. Pirozhok, E.E. Martsinko, I.I. Seifullina, E.A. Chebanenko,	P102
V.V. Dyakonenko, S.V. Shishkina: SYNTHESIS AND STRUCTURE OF Ge(IV)	
AND Cu(II) COMPLEXES WITH CITRIC ACID AND 2,2'-BIPYRIDINE	
Liana Zinko, O. Matselko, G. Nychyporuk, R. Gladyshevskii: A NEW	P103
HEXAGONAL PHASE IN THE Hf-Al-Re SYSTEM	
L. Ben Amor, B. Belgacem, J.S. Filhol, ML. Doublet, M. Ben Yahia, Rached Ben	P104
Hassen: COMBINED DENSITY FUNCTIONAL THEORY AND EXPERIMENTAL	
STUDY TO UNDERSTAND THE OPTOELECTRONIC PROPERTIES OF THE	
NEW p-TYPE PEROVSKITE SrSnO3:Al	

ADDRESSES

Department of Inorganic Chemistry, Ivan Franko National University of Lviv
Kyryla i Mefodiya St. 6; telephone: +380 32 2600388
Main Building of the Ivan Franko National University of Lviv
Universytetska St. 1; telephone: +380 32 2394325
Bank Hotel
Lystopadovogo Chynu St. 8; telephone: +380 32 2534293
Hotel Atlas DeLuxe
Shevchenka Ave. 27; telephone: +380 32 2614764
Hotel Dnister
Mateyka St. 6; telephone: +380 32 2613483
Hotel Ibis Styles
Shukhevycha St. 3; telephone: +380 32 2546767
University Guesthouse
Gertsena St. 7 / Stetska St. 3; telephone: +380 32 2394076
Restaurant "Navariya Nova"
Navariya Village, Pustomyty District, Lviv Region
telephone: +380 32 2272727

Martyn A. Sozanskyi, P.Yo. Shapoval, V.E. Stadnik, Yo.Yo. Yatchyshyn,	P100
V.M. Kordan: HYDROCHEMICAL SYNTHESIS AND X-RAY INVESTIGATION	
OF CdS_xSe_{1-x} FILMS	
Liudmila I. Sliusarchuk, L.I. Zheleznova, T.V. Pavlenko, O.O. Rogovtsov:	P101
SYNTHESIS OF COMPLEX OXIDES ON GRANULES OF ALUMINUM OXIDE	
FROM β-DIKETONATE COMPLEXES OF 3 <i>d</i> -4 <i>f</i> -METALS	
Olha V. Pirozhok, E.E. Martsinko, I.I. Seifullina, E.A. Chebanenko,	P102
V.V. Dyakonenko, S.V. Shishkina: SYNTHESIS AND STRUCTURE OF Ge(IV)	
AND Cu(II) COMPLEXES WITH CITRIC ACID AND 2,2'-BIPYRIDINE	
Liana Zinko, O. Matselko, G. Nychyporuk, R. Gladyshevskii: A NEW	P103
HEXAGONAL PHASE IN THE Hf-Al-Re SYSTEM	
L. Ben Amor, B. Belgacem, J.S. Filhol, ML. Doublet, M. Ben Yahia, Rached Ben	P104
Hassen: COMBINED DENSITY FUNCTIONAL THEORY AND EXPERIMENTAL	
STUDY TO UNDERSTAND THE OPTOELECTRONIC PROPERTIES OF THE	
NEW p-TYPE PEROVSKITE SrSnO3:Al	

ADDRESSES

Department of Inorganic Chemistry, Ivan Franko National University of Lviv
Kyryla i Mefodiya St. 6; telephone: +380 32 2600388
Main Building of the Ivan Franko National University of Lviv
Universytetska St. 1; telephone: +380 32 2394325
Bank Hotel
Lystopadovogo Chynu St. 8; telephone: +380 32 2534293
Hotel Atlas DeLuxe
Shevchenka Ave. 27; telephone: +380 32 2614764
Hotel Dnister
Mateyka St. 6; telephone: +380 32 2613483
Hotel Ibis Styles
Shukhevycha St. 3; telephone: +380 32 2546767
University Guesthouse
Gertsena St. 7 / Stetska St. 3; telephone: +380 32 2394076
Restaurant "Navariya Nova"
Navariya Village, Pustomyty District, Lviv Region
telephone: +380 32 2272727

INVITED LECTURES

VALUE-ADDED CYCLES ON MATERIALS DATA IN THE ERA OF INCLUSIVE WEALTH -NEW ROLES OF WORLD MATERIALS DATA-

Shuichi Iwata¹ and Pierre Villars²

¹ The University of Tokyo / Materials Phases Data System / The Graduate School of Project Design / The University of Science and Technology Beijing / The Ecoethica Laboratory ² Material Phases Data System (MPDS), Unterschwanden 6, Vitznau, CH-6354 Luzern, Switzerland iwatacodata@mac.com

Based on the recent enrichment of scientific data and models, a draft towards social innovation based on materials data is given. Through various types of manufacturing process, raw materials become parts of engineering products with values for customers, changing dynamically their chemistries and structures, and corresponding properties, performances and functions, in each engineering product. Thanks to the progress of science and technology, we have great freedom in controlling the chemistry and structure of materials with fine characterization, if we use time and energy properly. Manufacturing cycle efficiency measures the proportion of production time spent on value-added activities basically endorsed by materials data. A business can use this information to pare away non value-added activities, thereby reducing costs and shortening the time required to manufacture a product. Both outcomes can be used as competitive advantages in the market, since a business can then lower its prices while maintaining robust profits, while also offering faster turnaround times to its customers. It has been an important guideline for sustainable business activities under mass production and mass consumption paradigms in these centuries.

About half a century ago, in 1968, we, about 3.6 G human beings, got the Earth Rise photo to share one Earth *existere* object. However, we have not yet shared the *existentia* of this object in terms of materials with a seamless resolution for the sustainability until now. In the next 50 years, about 10 G people of digital and analogue hybrid minds are about to be connected in the cloud, inter-subjectively as well as inter-objectively, at more than Gigabit connection speeds, and at near zero-cost. As a natural consequence, the positive spiral of mass production-mass consumption-mass waste disposal is driven together with an ICT agenda of "Big Data, IoT, AI, smart cities, and others". It needs to be controlled properly with sustainability, taking advantage of materials data, if we think we are sharing one Earth.

The total cycle time of an engineering product is not only the aggregate amount of all process time, operation time, inspection time, queue time and move time, but also the inverse manufacturing time for several Rs (reduce, reuse, recycle, repair, rethink, ...) with large diversities. The former part has been managed successfully on the basis of curiosity-driven approaches, but the latter part, comprising an inordinately large part of the total cycle time, may require wholesome scientific data for dealing with the large diversities in the long term.

Taking into account the above issues to derive basic procedures for dealing with materials data, new paradigm shifts towards a sustainability of our society will be started, where properly balanced utilizations of materials are required. Two basic viewpoints are introduced to navigate associated challenges concerning materials data, namely, at first on the rich diversity of engineering products on the basis of exponentially advancing materials engineering, and, secondly, visualizing materials complexity and their mass flows and positioning tons of associated, but fragmented data sets on the basis of scientific data, scientific models and engineering standards. Perspectives to navigate collective challenges are discussed as a series of converging communications between these two viewpoints through materials data, expecting intelligent processing concerning our activities in the future.

MAGNESIOTHERMY: AN EFFICIENT ROUTE TO MESOSTRUCTURED THERMOELECTRIC INTERMETALLICS... AND MORE

S. Le Tonquesse¹, E. Alleno², D. Berthebaud³, V. Demange¹, V. Dorcet¹, Q. Guo³, H. Huynh³, T. Mori⁴, <u>M. Pasturel¹</u>, and C. Prestipino¹

¹ Univ Rennes, CNRS, ISCR – UMR6226, F-35042 Rennes, France

² Université Paris-Est, ICMPE, UMR7182 – UPEC, 94320 Thiais, France

³ CNRS – Saint-Gobain – NIMS, UMI3629 LINK, NIMS, Ibaraki 305-0044, Japan

⁴ National Institute for Materials Sciences, WPI-MANA and CFSN, Tsukuba, Japan

mathieu.pasturel@univ-rennes1.fr

Thermoelectric (TE) devices belong to the bunch of alternative "green" energy technologies enabling direct conversion of (wasted) heat into electricity and vice-versa. Their efficiency is related to the TE materials figure-of-merit defined as $ZT = \alpha^2 / (\rho(\kappa_e + \kappa_L))T$, where α is the Seebeck coefficient, ρ the electrical resistivity, and κ_e and κ_L the charge carrier and lattice thermal conductivities, respectively. Semiconducting intermetallics are among the best performing materials, whatever the temperature range considered from room temperature (Bi₂Te₃ and derivatives) to high temperature (Zintl phases or Si-Ge alloys above 1000 K). At intermediate temperatures, from about 600 to 800 K corresponding to the car engine exhaust gases, two families are of particular interest: (i) CoSb₃-based skutterudites, where the numerous possibilities of chemical substitution and/or insertion of heavy rattlers in the large cages of the structure make it possible to reach ZT values much above 1 for bulk samples [1], and (ii) transition metal silicides (MnSi_v with $\gamma \approx 1.7$, also known as higher manganese silicides or HMS, and β -FeSi₂), which have already been tested in industrial demonstrators, despite their moderate ZT, due to the availability and low cost of the constituting elements [2]. Both families are characterized by two common features: (i) the necessity to decrease the thermal conductivity to improve the TE properties and (ii) the not straightforward synthesis due to the non-congruent melting of the phases.

To address both problems, we recently applied a magnesioreduction process, inspired by the industrial Kroll process [3], for the synthesis of (Ni-doped and In-inserted) CoSb₃ [4], (V-doped) MnSi_{1.74}, and (Co-doped) β -FeSi₂. Starting from cheap and air-stable oxides, we showed that after short and low-temperature annealing, high-purity submicron powders are obtained, leading, after spark plasma sintering, to mesostructured materials with significantly reduced thermal conductivities. Additionally, the high crystallinity of the powders enabled structural characterization of the composite chimney-ladder structure of HMS and of the stacking faults in β -FeSi₂.

After a description of the experimental procedures, the different synthesis reaction mechanisms identified by powder X-ray diffraction will be presented. A careful examination of the microstructure of the materials by electron backscattering diffraction and transmission electron microscopy will be used to discuss its influence on the thermal conductivity and overall TE behavior of the materials. The discussion will be opened to the applicability of this synthesis route to other classes of intermetallics for energy conversion or storage.

- [1] G. Rogl, P. Rogl, Curr. Opin. Green Sustain. Chem. 4 (2018) 50-57.
- [2] G. Skomedal et al., Energy Convers. Manage. 110 (2016) 13-21.
- [3] W. Kroll, Z. Anorg. Allg. Chem. 234 (1940) 42-50.
- [4] S. Le Tonquesse et al., J. Alloys Compd. 796 (2019) 176-184.

INTERMETALLIC ALUMINUM COMPOUNDS – STRUCTURES AND PROPERTIES

O. Janka

Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 28/30, 48149 Münster, Germany ocjanka@uni-muenster.de

Intermetallic compounds are, especially with respect to their numerous applications in everyday life, an important class of materials. Amongst them, aluminum-containing intermetallics are an interesting field of research, since aluminum is used as pure element or as alloys in all sorts of technical products. The most important field, amongst many, is probably the transport sector. In the case of aluminum alloys, the handling of the material during preparation and annealing plays an important role with respect to the mechanical properties of the final product. Modern solid-state chemistry usually follows an opposite approach. Its goal is to synthesize novel binary, ternary or even multinary compounds and investigate their structures and physical properties.

The talk will cover our endeavors in the field of intermetallic aluminum compounds from different viewpoints, namely structural and crystal chemistry, as well as spectroscopic and physical properties. These compounds exhibit a large structural diversity that can be examined with respect to their crystal structures, but also probed by *e.g.* solid-state ²⁷Al NMR spectroscopy. One of the compounds that encouraged us to dig deeper into NMR spectroscopic methods was Ba₃Pt₄Al₄ [1]. This material crystallizes in a new structure type and exhibits heterocubane [Pt₄Al₄] entities. Due to the absence of localized magnetic moments, the compound is Pauli-paramagnetic and therefore ²⁷Al NMR spectra could be recorded. They exhibit two signals, in line with the crystal structure. In addition, even the different crystal chemical environments could be observed in the line shape of the NMR signals. We continued this research and soon realized that X-ray photoelectron spectroscopy (XPS) is another powerful tool that can be used to correlate structures and properties, and to investigate the electron transfer in these materials. By this, we could prove in a number of compounds, that the term 'aluminides', often used in the literature, is misleading. In fact, many of these compounds should rather be considered as 'metallides'.

During these investigations, once in a while compounds with extraordinary properties could be found. One example is $Eu_2Pt_6Al_{15}$ [2]. Magnetic measurements of this material revealed an anomaly in the susceptibility data, which was also observed as λ -type anomaly in heat capacity measurements. The shape of the observed anomaly, however, contradicted a classical magnetic ordering phenomenon. Subsequently, temperature-dependent powder X-ray diffraction experiments were conducted, indicating a drastic shortening of the *c* axis, while the *a* axis remained nearly the same. The observed anomalies in both the diffraction experiments and physical property measurements can only be explained by a temperature-driven first-order valence change from Eu²⁺ at higher temperatures to Eu³⁺ at low temperatures. This proposed valence change was subsequently proven by temperature-dependent ¹⁵¹Eu Mößbauer spectroscopic investigations.

- [1] F. Stegemann, C. Benndorf, T. Bartsch, R.S. Touzani, M. Bartsch, H. Zacharias, B.P.T. Fokwa, H. Eckert, O. Janka, *Inorg. Chem.* 54 (2015) 10785-10793.
- [2] M. Radzieowski, F. Stegemann, T. Block, J. Stahl, D. Johrendt, O. Janka, J. Am. Chem. Soc. 140 (2018) 8950-8957.

DESIGN OF TI-ALLOY BY INTEGRATING HIGH-THROUGHPUT EXPERIMENTS AND CALCULATIONS

Libin Liu¹, Ji-Cheng Zhao², Zhanpeng Jin¹, Lilong Zhu¹, and Di Wu¹ ¹ Central South University, School of Materials Science and Engineering, Changsha, Hunan 410083, China ² Ohio State University, Department of Materials Science and Engineering, Columbus, OH 43210 | 614-292-Ohio, USA Ibliu@csu.edu.cn

The speed of the development of new materials is too slow and has emerged as a bottleneck for the innovation of manufacturing technology. However, on the one hand, application of computer and information technology to materials science and engineering has made it possible for us to estimate the properties of single phases, model microstructure evolutions, and predict material properties. On the other hand, in order to verify the results of the calculations, we should develop and use high-throughput methods. In this work, we introduce some new progress in materials calculations and high-throughput experiments, especially highthroughput determination of phase diagrams, diffusion coefficients, and thermal-physical properties, and high-throughput verification of the response of the microstructure and properties of the materials to different compositions and heat treatment temperatures. Some preliminary results on attempts to develop high-strength and high-toughness Ti alloy will be presented.



Fig. Prediction of pseudospinodal decomposition with the CALPHAD method.

[1] A. Boyne, D. Wang, R. Shi, Y. Zheng, A. Behera, S. Nag, J. Tiley, H.L. Fraser, R. Banerjee, Y. Wang, *Acta Mater.* 64 (2014) 188-197.

FROM CURIOSITY-DRIVEN EXPLORATION OF CHALLENGING INTERMETALLICS TO NOVEL MATERIALS DESIGN

<u>Pavlo Solokha</u>, Serena De Negri, Riccardo Freccero, and Adriana Saccone Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale, Via Dodecaneso 31, I-16146 Genova, Italy pavlo.solokha@unige.it

The chemistry of intermetallics (IMC) is still one of the most complicated topics in materials science, mainly due to the strong and almost continuous variation with the composition and nature of the elements involved. Almost 2 % of the IMCs known up to date are structurally complex [1]. Among these, the family of quasicrystals (QCs) is particularly challenging, due also to the difficulties related to structural studies of aperiodic matter through interpretation of 3D diffraction data.

Fortunately, QCs frequently have compositionally close "satellites", called approximants (ACs), which are 3D periodic structures composed of the same onion-like clusters. The discovery of novel approximants and their structures may help to unveil not only the structure of new building blocks for QCs, but, hopefully, some rules that crystalline matter follows during crystallization.

In this work, the following combined theoretical and experimental investigation is presented, targeting novel materials design:

(i) Topologically based data mining of databases of inorganic structures [2] to select a set of compounds containing the Mackay cluster as building block;

(ii) Generation of phenomenological maps on the group of gathered IMCs to discern the factors involved in their formation;

(iii) Selection of the most promising QCs/ACs candidates, followed by experimental work and structural/theoretical studies aimed at confirming the reliability and robustness of the proposed scheme.

As a result of this route, a new orthorhombic 1/1 Sc-rich AC was successfully obtained. During an accurate single-crystal X-ray diffraction analysis, fine structural peculiarities were revealed, such as smeared out electron densities corresponding to some crystallographic sites assigned to the outer shell of the Mackay nanocluster. These features were studied more in detail through comprehensive density functional theory modeling, based on a combination of point defects, such as vacancies and substitutions. It was confirmed that structural disorder exclusively occurs in the shell enveloping the classical Mackay cluster. As a result, the real structure can be viewed as an assemblage of slightly different, locally ordered 131-atom nanoclusters.

One of the main strengths of the proposed modeling is the possibility to generate structural models covering a small compositional range and evaluate them on the basis of thermodynamics. This approach can be exploited for developing efficient machine learning for new QCs/ACs discovery.

- [1] J. Dshemuchadse, W. Steurer, Acta Crystallogr. A 71 (2015) 335-345.
- [2] V.A. Blatov, Acta Crystallogr. A 56 (2000) 178-188.

SUPERTETRAHEDRAL NETWORKS AND PROPERTIES OF NEW PHOSPHIDOSILICATES AND ARSENIDOGALLATES

A. Haffner, V. Weippert, and <u>D. Johrendt</u> Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstr. 9-13 (D), 81377 München, Germany johrendt@lmu.de

Given the immense interest in new materials with potential lithium or sodium ion conductivity, we addressed the systems Li–Si–P and Na–Si–P and came across a series of new compounds with fascinating new structures based on interpenetrating networks of T2 to T5 supertetrahedral clusters [1]. Li₂SiP₂ ($I4_1/acd$, Z = 32) contains two interpenetrating diamond-analogue supertetrahedral networks made of corner-sharing T2 supertetrahedra. Sphalerite-like interpenetrating networks of bridged T4 and T5 clusters occur in the complex structure of LiSi₂P₃ ($I4_1/a$, Z = 100), shown in Fig. 1. Impedance spectroscopy data indicated Li⁺ ion conductivities of up to 6×10^{-4} Scm⁻¹ at 300°C. The structures of new sodium-phosphidosilicates are likewise hierarchical variants of the diamond-type with interpenetrating networks of T3 to T5 supertetrahedra [2]. Within the series Na₂₃Si_{9n+19}P_{12n+33} (n = 0-3), we found that the Na⁺ ion conductivity increases with the size of the supertetrahedral clusters up to 4×10^{-4} Scm⁻¹ at 25°C in Na₂₃Si₄₆P₆₉ with a network of T5 clusters. This effect results from the dilution of the Na⁺ ions between larger, and thus less charged, polyanionic cluster networks.

With the new arsenidogallates $A_3Ga_6As_8$ (A = Sr, Eu; C2/c, Z = 32) we have found the first GaAs-based supertetrahedral structures [3]. These represent hierarchical variants of the layered HgI₂-type structure, and contain the so far largest supertetrahedra (T6), made of 56 GaAs₄ tetrahedra without vacancies (Fig. 2). Optical band gap and Hall-effect measurements revealed semiconducting properties remarkably similar to those of binary GaAs.



Fig. 1. Interpenetrating networks of T4 and T5 supertetrahedra in LiSi₂P₃.



Fig. 2. Layers of fused T6 supertetrahedra in Sr₃Ga₆As₈.

- [1] A. Haffner, T. Bräuniger, D. Johrendt, Angew. Chem. Int. Ed. 55 (2016) 13585-13588.
- [2] A. Haffner, A.-K. Hatz, I. Moudrakovski, B.V. Lotsch, D. Johrendt, Angew. Chem. Int. Ed. 57 (2018) 6155-6160.
- [3] V. Weippert, A. Haffner, A. Stamatopoulos, D. Johrendt, J. Am. Chem. Soc. (2019). DOI: 10.1021/jacs.9b04712.

INTERPLAY BETWEEN THE 3D CAGE NETWORK AND 2D SURFACES IN INTERMETALLIC CAGE COMPOUNDS

F. Abdel-Hamid¹, K. Anand¹, M.C. de Weerd¹, C. Allio², G. Krellner², H.D. Nguyen³, M. Baitinger³, Y. Grin³, J. Ledieu¹, E. Gaudry¹, and <u>V. Fournée¹</u>
¹ Institut Jean Lamour, UMR 7198 CNRS-Université de Lorraine, Nancy, France
² Physikalisches Institut, Goethe-Universität, Frankfurt, Frankfurt am Main, Germany ³ Max-Plank-Institut für Chemische Physik fester Stoffe, Dresden, Germany

vincent.fournee@univ-lorraine.fr

Intermetallic cage compounds have crystal structures characterized by three-dimensional (3D) frameworks of host atoms forming cages that may be filled with guest atoms. They can be considered as a class of complex metallic alloys (CMAs), a broad family of crystalline materials having large or giant unit cells, in which a cluster substructure exists. The bulk physical properties of cage compounds have attracted interest in recent years, particularly as several of them are considered as promising thermoelectric materials. As a different type of CMA, they may exhibit interesting surface properties as well, which have not been explored until now. Here, we report a structural analysis of some low-index surfaces of two cage compounds - namely the Ce₃Pd₂₀Si₆ phase and the Ba₈Au_{5.25}Ge_{40.75} clathrate [1-3]. The surfaces were investigated under ultrahigh vacuum conditions by low-energy electron diffraction, photoelectron spectroscopy and scanning tunneling microscopy (STM). This experimental approach was complemented with theoretical calculations based on the density functional theory. The results allow describing the relationship between the 3D cage framework and the 2D surface in these compounds. We will show that it leads to highly corrugated surfaces with a subnanometric periodicity that is directly linked to the cage framework. This approach thus provides an ultimate way for surface nanostructuration.



Fig. STM image of the Ce₃Pd₂₀Si₆-(100) surface and bulk model showing the cage network in this compound.

- [1] F. Abdel-Hamid, M.C. de Weerd, J. Ledieu, E. Gaudry, V. Fournée, *J. Phys. Chem. C* 123 (2019) 12355-12366.
- [2] K. Anand, C. Allio, C. Krellner, H.D. Nguyen, M. Baitinger, Yu. Grin, J. Ledieu, V. Fournée, É. Gaudry, J. Phys. Chem. C 122 (2018) 2215-2220.
- [3] K. Anand, H.D. Nguyen, M. Baitinger, C. Allio, C. Krellner, Yu. Grin, J. Ledieu, V. Fournée, É. Gaudry, J. Phys. Chem. C 122 (2018) 29298-29306.

CRYSTALLOGRAPHY OF INTERMETALLIC CLUSTERS: STRUCTURE, SYMMETRY AND DISORDER

Peter Y. Zavalij and Bryan W. Eichhorn Department of Chemistry and Biochemistry, University of Maryland, 091 Chemistry Bldg., College Park, MD 20832, USA pzavalij@umd.edu

Reaction of intermetallic group 14 and 15 Zintl ion precursors, with subvalent group 13 compounds, and low oxidation state transition metal complexes, under various conditions, leads to formation of novel clusters. The intermetallic clusters are often formed with high, and sometimes non-crystallographic local symmetry. Thus, K₅Sb₄ and K₃Sb₇ react with Pd(PPh₃)₄ and Ni(cyclooctadiene)₂ to form the icosahedral metal clusters $[SbPd_{12}Sb_{20}]^{n}$ and $[SbNi_{12}Sb_{20}]^{n}$ [1], which are constructed of interpenetrating platonic solids – a M_{12} icosahedron enclosed by a Sb₂₀ dodecahedral shell. In this case the symmetries of the inner and outer shells match. However, it is not always the case. For example, the metalloid cluster $[Al_{77}{N(SiMe_3)_2}_{20}]^{2-}$ consists of three shells – Al_{20} , Al_{44} and Al_{12} , with very different symmetry, which causes disorder of the shells in multiple orientations. To stabilize crystal formation, the negative charge of the metallic clusters is usually balanced by large positive ions, such as [K(18-crown-6)]⁺, [K(cryptand-222)]⁺, [P(Butyl)₄]⁺, etc. Mismatch in symmetry between the clusters and the large cations and the often near spherical shape of the clusters result in irregular or faulty packing. As a result, the majority of these structures show disorder of the metallic clusters or the large cations, or both. In this presentation we discuss several dozen clusters, emphasizing their structural aspects, symmetry and the disorder it causes.

[1] Y. Wang, M. Moses-DeBusk, L. Stevens, J. Hu, P.Y. Zavalij, K.H. Bowen, B.I. Dunlap, E.R. Glaser, B.W. Eichhorn, J. Am. Chem. Soc. 139 (2017) 619-622.

THE IMPORTANCE OF THE PERIODIC (MEDELEEV) NUMBER IN CRYSTAL STRUCTURE PREDICTION – A DATA-CENTRIC APPROACH USING THE PAULING FILE

Pierre Villars

Material Phases Data System (MPDS), Unterschwanden 6, Vitznau, CH-6354 Luzern, Switzerland villars.mpds@bluewin.ch

The atomic number (AN) of the elements together with their periodic number (PN_{MD} Mendeleev) were found to form an efficient pair for the discussion of metallurgical and structural experimental facts. The periodic number PN_{MD} represents a different enumeration of the elements, emphasizing the role of the valence electrons. In contrast to the atomic number, PN_{MD} depends in details on the underlying Periodic Table of the elements. As a first result, we describe the elemental-property parameters 'atomic size SZ_a ' and 'atomic reactivity RE_a ', derived from fits to various experimental and theoretical data sets. These two parameters can be approximated as simple functions of AN and PN_{MD} . We argue that all elemental-property parameter patterns are derived from AN and PN_{MD} , which are independent from each other.

On the example of compound formers/non-formers in binary, ternary and quaternary chemical systems we demonstrate that a quantitative link exists between material properties (experimental metallurgical facts) and AN, PN_{MD} (or simple functions of both) of the constituent elements.

Crystallographic structures (structural experimental facts) can be classified within the prototype classification (based on symmetry), as well as within the atomic environment types (AET) classification (based on the coordination polyhedron of each atom). We analyzed all binary compounds at the equi-atomic composition based on a comprehensive set of literature data, using the PAULING FILE. The periodic number (PN_{MD}) was successfully used to classify all *AB* binary compounds by developing prototype structure maps, as well as atomic environment type maps, both leading to clear stability domains within the maps. The maps also show clear separation between chemical systems where binary *AB* compounds form and those where no compounds form. These maps make it possible to predict the existence of compounds that have not yet been investigated (prototype/atomic environment).

The PAULING FILE is a relational database for materials scientists, grouping crystallographic data, phase diagrams, and physical properties of inorganic crystalline substances under the same frame. Focus is on experimental observations and the data are processed from the original publications, covering world literature from 1900 to present date, for further details see <u>www.paulingfile.com</u>. The recently developed platforms called AtomWork-adv (NIMS) and Materials Platform for Data Science (MPDS) (see <u>www.crystbd.nims.go.jp</u> and <u>www.mpds.io</u>), aim to give easy access to large amounts of different kinds of critically analyzed experimental data (over 1 mio. data), and by this propose a general overview on crystalline inorganic substances (also called distinct phases), offering possibilities to reveal yet undiscovered patterns among data and facilitate a sensible and efficient search for new materials with tailored properties. In combination with different data mining and simulation (CHALPHAD, DFT, USPEX) techniques, it provides guidelines for **Materials Design and Accelerated Development** by giving holistic views on inorganic crystalline substances, confirming that "*the whole is greater than the sum of its parts*".

L10

MATERIALS DATABASE AS FUNDAMENTAL OF MATERIALS INFORMATICS

<u>Yibin Xu</u>

National Institute for Materials Science, Tsukuba, Japan XU.Yibin@nims.go.jp

Through some examples of design of thermal management materials based on data and data science methods, we show the advantages and potential of material informatics to study material issues that are too complicated or time-consuming for conventional theoretical and experimental methods. Materials big data is the fundamental of material informatics. However, the volume and complexity of big data make it difficult for the traditional data capturing and processing methods to deal with them. To construct materials big data, we face challenges of data capture, data storage, data analysis, search, sharing, visualization, information privacy, and data source. Some of these challenges are expected to be solved by progresses in information technology, however, some of them are problems of material science. In this presentation, we focus our discussion on some issues specific to materials data, including materials identification, linking from single-phase material to complex material systems, and data quality control. Some strategies are proposed as the results of our experiences to construct NIMS materials databases.

INVESTIGATION ON Ce AND Yb INTERMETALLICS: THE ROLE OF CRYSTAL CHEMISTRY

M. Giovannini

Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, I-16146 Genova, Italy mauro.giovannini@unige.it

Strongly correlated electron systems are among the most intriguing and versatile materials. In the context of rare-earth intermetallic compounds, and in particular in the case of Ce- and Ybbased compounds and alloys, the hybridization of *f*- and conduction electrons can cause a number of outstanding low-temperature features. Chemical compositions, pressure and magnetic field can play an important role in the competition between Kondo and RKKY interactions and, consequently, in the ground state evolution of these compounds. Moreover, there is growing evidence that magnetic frustration is an important additional tuning parameter in the Kondo lattice model of heavy fermion materials.

In this talk a few examples of Ce and Yb compounds, which have recently been investigated by us, are discussed, with the aim to show the role of crystal chemistry in the challenging activity of synthesis and characterization of novel promising strongly correlated electron intermetallics.

HYDROGENATION/DEHYDROGENATION OF EPITAXIAL DEPOSITS INTERFACING Mg TO Nb LAYERS

D. Fruchart¹, O. Fruchart², G. Girard¹, L. Ortega³, N.E. Skryabina⁴, and M.G. Shelyapina⁵ ¹ Institut Néel, CNRS & UGA, BP166, 38042 Grenoble Cedex 9, France ² UGA, CNRS, Institut Néel 38042 Grenoble & CEA, SPINTEC, 38054 Grenoble, France

³ LPS, UMR 8502, Université de Paris Sud, 91405 Orsay Cedex, France

⁴ Faculty of Physics, Perm State University, Bukireva St. 15, 614990 Perm, Russia

⁵ St. Petersburg State University, Universitetskaya St. 7/9, 199034 St. Petersburg, Russia daniel.fruchart@neel.cnrs.fr

With a high hydrogen storage capacity (7.6 wt.%), magnesium hydride (MgH₂) is considered as an attractive material for solid-state hydrogen storage. However, both the hydride stability and the slow sorption kinetics are limiting characteristics for specific applications. Here we report a study of a model system, with a view to shed light on the complex nucleation Mg \leftrightarrow MgH₂ processes. We like to distinguish between a so-called catalytic process and a stress-absorbing layer at the Nb/Mg interface promoting changes of the crystal structure.

The sample considered here consisted of stacks of single-crystal metal layers, epitaxially grown by Pulsed Laser Deposition on a Al₂O₃(11-20) substrate. It consisted of layers of Mo(110)/Pd(111)/Nb(110)/Mg(001)/Mo(110). It was characterized before and after hydrogenation, by using many different techniques, such as REED, AFM and XRD (normal and grazing incidence), texture analysis, in-operando diffraction versus temperature. RHEED, AFM and XRD at high and grazing incidence allowed us to perfectly characterize the multilayer system, e.g. the excellent single crystalline state of each of the layers, and to well interpret the epitaxy rules governing the interactions between bcc, fcc, and hcp systems. Hydrogenation of the nano-tank was readily operated at 40°C under 2 MPa hydrogen pressure, as confirmed by the grazing incidence XRD experiments, where Pd, Nb and Mg hydrides were identified. Epitaxy rules leading to the development of specific twinning effects at the crystal interfaces were found to be coherent with the phase transformations. In fact, the initial twinning, modified after hydrogenation, was recovered when the hydrogen was fully evacuated from the nano-tank. In-operando XRD experiments allowed us to study the thermally induced desorption process following the evacuation of the Mg- and Nb-based layers. The mechanism was found to be in agreement with the well-known Nb-H phase diagram, putting into evidence out of equilibrium hydrogenation states. This aspect fully confirms our previous results obtained from neutron diffraction experiments on Nb-doped ball-milled Mg powders [1]. In order to better understand the rapid activation mechanisms taking place at the Nb-Mg interface, one has to consider the scheme of distortions taking place at the interface of the Mg-hcp lattice to form a local fcc (or then bcc) stacking mode, where hydrogen can diffuse fast, leading to formation of the strongly covalent MgH₂ rutile structure, as already suggested in [2,3]. This could be achieved via a martensitic distortion mode. The twinning modes and their "memory" effect corroborate the early analyses in [4]. However, studies of the desorption process by XRD indicate that a metal interface forming hydrides could contribute to accelerate even more the kinetics of hydrogen transfer via a β -NbH_{~0.6} state.

- [1] P. de Rango et al., J. Alloys Compd. 446 (2007) 52-57.
- [2] N.E. Skryabina et al., Solid State Phenom. 194 (2013) 237-244.
- [3] M.G. Shelyapina et al., J. Alloys Compd. 644 (2015) 371-377.
- [4] S.X. Tao et al., Fuel Energy Abstr. 36(18):11802-11809.

STRUCTURAL AND MAGNETIC PROPERTIES OF R₂TGe₆ COMPOUNDS

B. Penc¹, St. Baran¹, A. Hoser², and <u>A. Szytula¹</u> ¹ M. Smoluchowski Institute of Physics, Jagiellonian University, Lojasiewicza 11, 30-348 Krakow, Poland ² Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner Platz 1, D-14109 Berlin, Germany andrzej.szytula@uj.edu.pl

The lecture reports the results of X-ray and neutron diffraction, as well as magnetic measurements, of R_2T Ge₆ compounds (R = rare-earth element, T = Ni, Cu, Pd). The compounds with T = Cu were for the first time obtained at the University of Lviv [1]. Compounds with different T elements are reported in [2].

The diffraction experiments indicate that the compounds with T = Ni and Cu crystallize in the orthorhombic Ce₂CuGe₆-type structure (space group *Amm*2) [1], and those with T = Pdin the orthorhombic Yb₂CuGe₆-type structure (space group *Cmce*) [3]. Magnetic data for the Ni- and Cu-compounds confirm previous results [4,5]. The R_2PdGe_6 compounds are antiferromagnets with Néel temperaturs ranging from 6.2 K for R = Er up to 48 K for R = Tb. Based on neutron diffraction data the magnetic structures were determined for R_2TGe_6 (T =Ni, Cu; R = Nd, Tb, Ho, Er) and R_2PdGe_6 (R = Tb, Ho). In the majority of these compounds the magnetic moments localized on the rare-earth elements form a collinear magnetic structure. In most cases the magnetic unit cell is equal to the crystallographic cell. For R_2CuGe_6 the magnetic order is described by the propagation vector $\mathbf{k} = (\frac{1}{2}, 0, 0)$ (R = Ho, Er) and $\mathbf{k} = (\frac{1}{2}, 0.28, 0)$ (R = Tb). The differences between the determined magnetic structures result from the competition between RKKY-type interactions and the influence of the Crystal Electric Field (CEF). The influence of these factors is discussed.

- [1] M.B. Konyk et al., Kristallografia 33 (1988) 838-840.
- [2] O. Sologub et al., J. Alloys Compd. 227 (1995) 37-39.
- [3] M.L. Fornasini et al., Z. Kristallogr. New Cryst. Struct. 217 (2002) 173-174.
- [4] M. Konyk et al., J. Alloys Compd. 398 (2005) 8-11.
- [5] D. Kaczorowski et al., Solid State Sci. 10 (2008) 1891-1894.

URANIUM HYDRIDES: MYTHOLOGY AND REALITY

Ladislav Havela¹, M. Divis¹, T. Gouder², and D. Legut³ ¹ Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 12116 Prague 2, Czech Republic ² European Commission, Joint Research Centre (JRC), Karlsruhe, Germany ³ IT4Innovations Center, VSB-Technical University of Ostrava, Czech Republic havela@mag.mff.cuni.cz

The electronic properties of the actinides depend on the situation of the 5f electronic states, the character of which varies between localized, analogous to the 4f states in the lanthanides, and band-like, resembling the transition metals. Uranium metal is a weak Pauli paramagnet, as the 5f states form a broad band. The reason is the too short distance between nearest U neighbors. A magnetic ground state can be reached for U-U spacing exceeding the limit of 340-360 pm, called the Hill limit. The U lattice can easily be expanded (by ~60%) by hydrogen. Lattice expansion due to H absorption has been taken as a natural reason why both known UH₃ hydrides are ferromagnets. A closer inspection shows the rather surprising fact that the distance between nearest U-U neighbors in one of the variants of UH₃, β -UH₃, can be only 331 pm, far below the Hill limit, but the Curie temperature, $T_{\rm C} = 165$ K, is relatively high. α -UH₃, with an entirely different crystal structure and U-U distances, has identical T_C. *Mutatis mutandis* we tried alloying with *d*-elements, which led to even slightly higher $T_{\rm C}$, which is also unusual, as 5f-band magnetism is easily disrupted by atomic disorder. To compare with another U hydride would be even more exciting. However, although most of the f-elements form, besides the trihydride, also the dihydride with uniform CaF2 structure type, no such compound was known for U.

We eventually succeeded in synthesizing UH₂ in the CaF₂ structure as metastable in the form of a thin film [1]. Larger U-U spacing (378 pm) does not lead to higher $T_{\rm C}$, which would most likely happen in a band case. T_C of UH₂ is lower, ~120 K. A comparison of the crystal structures of α - and β -UH₃ and UH₂ reveals that in all these cases there are practically identical U tetrahedra accommodating H atoms, and the U-H distance (232 pm) is therefore the same. Naturally, the three species differ by the arrangement of these tetrahedra, which play a role of "molecules". This actually stresses the role of the U-H interaction. Insight into the bonding can naturally be obtained from *ab initio* calculations. The problem is that fully relativistic GGA of LSDA calculations may not be adequate under the conditions of strong electron-electron correlations, *i.e.* close to the verge of 5f localization. Therefore, a feedback from experiment is necessary. The calculations suggest that H in the hydrides accepts additional electrons from electropositive U. The density of states indicates that the H-1s states strongly hybridize with U-5f states, which are thus withdrawn from the 5f-6d hybridization, present in the U metal. This can also explain the relatively strong magnetism of U hydrides and suggests a general route to enhance $T_{\rm C}$ in U-based systems. Fingerprints of mixed ioniccovalent bonding were indeed found by photoelectron spectroscopy. However, details around the Fermi level are not well reproduced, indicating the prominence of e-e correlations. The agreement was improved within the GGA+U framework. The main conclusion is that U hydrides are not expanded U metals, but details of U-H bonding are essential.

This work was supported by the Czech Science Foundation under the grant No. 18-02344S.

[1] L. Havela et al., Inorg. Chem. 57 (2018) 14727-14732.

TUNING OF THE THERMOELECTRIC PROPERTIES OF QUATERNARY COMPOUNDS, *AB*ZnSb (*A* = Sr, Ba AND RARE-EARTH ELEMENTS; *B* = F AND O) WITH THE ZrCuSiAs STRUCTURE TYPE

Jing-Tai Zhao

School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China jtzhao1962@gmail.com

The quaternary, layered compounds ABZnSb (A = Sr, Ba and rare-earth elements; B = F and O) adopt tetragonal ZrCuSiAs-type structures (P4/nmm), consisting of [AB] layers and [ZnSb] layers, alternately stacked along the *c* axis. In the [ZnSb] layer, Zn is tetrahedrally coordinated by four Sb atoms, forming edge-sharing tetrahedrons [ZnSb_{4/4}]. The [ZnSb] layer has been viewed as a promising carrier tunnel, due to weak scattering and high carrier mobility, and can be tuned by replacement of both Zn and Sb atoms by other elements that can modify the carrier concentration and mobility. Similar effects have been studied in the Zintl systems of AZn_2Sb_2 and related systems. The [AB] layers, matched with the ZnSb layers, will play an important role in lowering the thermal conductivity, acting as some sort of thermal barrier, resulting in overall potential optimization of the thermal properties. The flexibility of the chemical adjustments in these layered compounds provides great potential for tuning of the electronic conductivity, thermal conductivity, carrier concentration and mobility, and structural anisotropy.

The phase stability of a series of rare-earth compounds was predicted and confirmed experimentally. Samples of the title compounds and substitutional variants were prepared and their thermoelectric parameters characterized. The so far maximal thermoelectric figure of merit *ZT* for NdOZn_{0.96}Ag_{0.04}Sb reached 0.44 at 725 K. Further optimization of the electrical and thermal transport properties of other compounds is undergoing.

ORAL PRESENTATIONS
INFLUENCE OF THE H(D) CONTENT ON THE MAGNETOCALORIC PROPERTIES OF $Y_{0.9}R_{0.1}Fe_2$ HYDRIDES AND DEUTERIDES (R = Pr, Nd, Gd)

V. Paul-Boncour¹, V. Shtender¹, O. Isnard², T. Mazet³, K. Provost¹, and F. Couturas¹

 ¹ ICMPE (UMR 7182), CNRS, UPEC, 2 rue H. Dunant, 94320 Thiais, France paulbon@icmpe.cnrs.fr, vitalik.shtender@gmail.com, provost@u-pec.fr, couturas@icmpe.cnrs.fr
 ² Institut Néel, Univ. Grenoble Alpes and CNRS, 25 rue des Martyrs, BP 166X, F-38042 Grenoble, France olivier.isnard@neel.cnrs.fr
 ³ Université de Lorraine, CNRS, IJL, F-54000 Nancy, France thomas.mazet@univ-lorraine.fr

Magnetic refrigeration is a promising green technology to replace classical refrigeration systems using refrigerants contributing to global warming, and progressively forbidden by different climate protocols. However, it requires finding materials that have considerable magnetocaloric effects near room temperature. Development of efficient magnetocaloric effect (MCM) has become a challenge since the discovery of a giant magnetocaloric effect (MCE) near room temperature (RT) in Gd(Ge,Si)₅ compounds [1].

A significant MCE was discovered in the monoclinic YFe₂D_{4,2} compound, related to a first-order ferro-antiferromagnetic (FM-AFM) transition [2]. However, the transition temperature $T_{\text{F-AF}}$ is only 84 K, and should be increased for magnetic refrigeration applications near room temperature (RT). $T_{\text{F-AF}}$ can be increased by replacing D by H (large isotope effect) [3] or by replacing Y by another rare earth R of larger size (R = Pr, Nd, Gd) [3,4]. But to reach room temperature it is also necessary to play on the H content, which modifies the crystal structure of the material. A recent study of the structural properties of $Y_{0.9}Gd_{0.1}Fe_2H_v$ (3 $\leq y \leq 4.5$), using synchrotron radiation, versus temperature has shown a correlation between structural changes and magnetic properties. For example, in $Y_{0.9}Gd_{0.1}Fe_2H_{\nu}$ ferrimagnetic behavior with a Curie temperature near RT was found in monoclinic and cubic phases with $3.3 \le y \le 3.9$. But to fully solve the crystal structure (determine the positions of the H(D) atoms), as well as the magnetic order responsible for the transition, it is necessary to perform neutron powder diffraction (NPD) experiments. As Gd is too absorbent, we measured the NPD patterns of Y_{0.9}Pr_{0.1}Fe₂D_{3.5} to follow its crystal and magnetic structure versus temperature. The crystallographic and magnetic properties, as well as a comparison of the magnetocaloric properties of $Y_{0.9}R_{0.1}Fe_2$ hydrides and deuterides (R = Pr, Nd, Gd), will be presented and discussed in order to propose the most interesting magnetocaloric materials near room temperature.

- [1] V.K. Pecharsky, K.A. Gschneidner, *Phys. Rev. Lett.* 78 (1997) 4494-4497.
- [2] V. Paul-Boncour, T. Mazet, J. Appl. Phys. 105 (2009) 013914.
- [3] V. Paul-Boncour, M. Guillot, T. Mazet, J. Appl. Phys. 111 (2012) 07A934.
- [4] V. Paul-Boncour, S. Voyshnis, K. Provost, J.C. Crivello, *Chem. Met. Alloys* 6 (2013) 130.

INTERACTION OF THE COMPONENTS IN THE SYSTEMS {Dy,Yb}-Ga-{Si,Ge}

<u>T. Delenko</u>, Ya. Tokaychuk, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine tarasdelenko@gmail.com

Interaction of the components in the ternary systems {Dy,Yb}–Ga–{Si,Ge} was investigated in the full concentration range. The phase equilibria were determined and isothermal sections of the phase diagrams at 600°C were constructed. The alloys were synthesized by arc melting of the metals under a purified argon atmosphere, annealed at 600°C under vacuum in quartz tubes for 720 h, and subsequently quenched in cold water. Phase analysis was carried out on X-ray powder diffraction patterns collected at room temperature on a DRON-2.0M diffractometer (Fe $K\alpha$ -radiation). The crystal structures of the binary and ternary compounds were refined by the Rietveld method, using the FullProf Suite program package, on X-ray powder diffraction patterns collected on DRON-2.0M (Fe $K\alpha$ -radiation) and STOE Stadi P (Cu $K\alpha_1$ -radiation) diffractometers. For the confirmation of some of the equilibria and the determination of the compositions of the phases, local X-ray spectral analysis was performed, using a raster electron microscope REMMA-102-02 equipped with an energy-dispersive X-ray spectrometer EDAR.

The existence and crystal structures of 50 binary compounds in the systems $Dy-{Ga,Si,Ge}$ and $Yb-{Ga,Si,Ge}$ at 600°C were confirmed. Between the isotypic TII-type binary compounds in the systems $Dy-Ga-{Si,Ge}$, a continuous solid solution is formed. The largest limited solubility of the third component was observed for the silicide $DySi_{1.75}$ (16 at.% Ga), and the gallide $DyGa_2$ (15 at.% Si and 15 at.% Ge). The common feature for all these systems is the formation of substitutional solid solutions based on the Mn_5Si_3 -type binary rare-earth silicides and germanides: 15 at.% Ga in Dy_5Si_3 and Dy_5Ge_3 , 10 at.% Ga in Yb_5Ge_3 , 5 at.% Ga in Yb_5Si_3 .

The existence of 22 ternary compounds with constant or variable compositions in the systems {Dy,Yb}-Ga-{Si,Ge} at 600°C was established. Their crystal structures belong to 17 structure types. The Ge-containing systems are richer in ternary compounds than the Si-containing systems: 17 compounds in the systems {Dy,Yb}-Ga-Ge and 5 compounds in the systems {Dy,Yb}-Ga-Si. The largest number of ternary compounds (10) exists in the system Dy–Ga–Ge. They are located in a narrow concentration range with 22.2-37.5 at.% Dy. The structure of the ternary phase with the smallest Dy content (22.2 at.%) belongs to a homologous series of structures formed by linear intergrowth of slabs characteristic of the simple structure types $BaAl_4$, AlB_2 , and α -Po, and is characterized by trigonal-prismatic and square-antiprismatic coordination of the small *p*-element atoms. The crystal structures of three ternary compounds Dy(Ga,Ge)₃ (25 at.% Dy) belong to close-packed structure types (Mg₃In, PuAl₃, and Cu₃Au) and are characterized by cuboctahedral and anticuboctahedral coordination of the atoms. An increase of the Ge content in the phases of the system $DyGa_{3-x}Ge_x$ is accompanied by a decrease of the hexagonality of the close-packed structures. In the structures of the other six ternary compounds with higher Dy content (33.3-37.5 at.%) trigonal-prismatic coordination of the smaller atoms dominates. Trigonal prisms are generally the main coordination polyhedra of the *p*-element atoms in the structures of the ternary compounds forming in the systems {Dy,Yb}-Ga-{Si,Ge}. Due to the strong interaction between these atoms, they are often arranged in chains, planes, slabs, or isolated cluster-like groups of atoms.

PECULIARITIES OF THE INTERACTION OF *d*-METALS WITH LITHIUM AND *p*-METALS AND SEMIMETALS

<u>Grygoriy Dmytriv</u> and Volodymyr Pavlyuk Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine grygroriy.dmytriv@lnu.edu.ua

The level of investigation of T-Li-X systems (where T is a transition metal and X a p-element) is very unequal. Isothermal sections of the phase diagrams have been built for 31 systems in the whole concentration range, and for 7 systems in part of it. In total 282 ternary compounds form in these systems. There are some transition metals for which no data on the interaction of the components in the ternary systems is available: Cr, Mo, Ta, W, Re, Os, or only information about existing compounds: Nb, Ru, Rh, Pd, Hf, Ir, Pt, Hg. Concerning the p-elements, the situation is much better: only for Tl we did not find any information about investigations of isothermal sections of the phase diagrams, but we know about compounds in Tl-containing systems with Pd, Ag, Cd, Au, Hg. The most thoroughly investigated systems are with Ag: for this transition metal isothermal sections of six phase diagrams, and information about compounds in four additional T-Li-X systems, have been reported. The most compound-rich system is Cu-Li-Al: 10 ternary compounds are known in this system. Cu is the transition element for which the largest number of ternary compounds has been published: 38 compounds in 8 systems.

The known compounds of the T-Li-X systems crystallize in 114 structure types, but the crystal structures of the majority of the intermetallics belong to a few related cubic structure types, which are Heusler or Zintl phases: Cu₂MnAl (space group Fm-3m, Pearson symbol cF16) - 51 representatives, Li₂AgSb (Fm-3m, cF16) - 48, BiF₃ (F-43m, cF16) - 18, NaTl (Fd-3m, cF16) - 9. On the other hand, some of the intermetallics of the T-Li-X systems crystallize in own structure types (including Li₂AgSb): LiCuAl₂, Li₁₂Cu_{16+x}Al_{26-x}, $Li_{18}Cu_{15}Al_7$, $Li_8Cu_{12+x}Al_{6-x}$, $Li_{13}Cu_6Ga_{21}$, $Li_{68}Zn_{16}Ga_{133}$, $Li_{38}(Ga_xZn_{1-x})_{101}$, $Li_{77-x}Ni_{20}Si_{135-y}$, Li₁₃Ni₄₀Si₃₁, Li_{0.6}Ni_{5.4}Si₆, LiCu₃Si₂, Li₇Cu₇Si₅, Li₁₄₅Cu₁₁₉Si₁₇₇, Li₁₁₃Cu₅₄Si₅₇, Li₇CuSi₂, Li_{7.3}CuSi₃, Li₁₃(Cu_{0.53}Si_{0.47})₂₇, Li₂ZnSi, Li₂MnGe, LiFe₆Ge₄, LiFe₆Ge₅, LiFe₆Ge₅, LiFe₆Ge₆, LiZnGe, Li₈Zn₂Ge₃, LiCu₂Sn, LiCu₂Sn, $Li_3Zn_2Sn_4$, Li₅Cu₂Ge₂, Li_{1,15}MnAs, $Li_{1,35}(Li_{0.25}Mn_{0.75})As$, $Li_{2.7}(Li_{0.5}Mn_{0.5})MnAs_2$, $Li_{2.15}(Li_{0.67}Mn_{0.33})_3As_2$, Li_2CuAs , $LiCu_{0.93}As$, Li₂₉Cd₈Ga₆₄, Li₂Y₅In₉, Li_{2-x}Ag_{1+x}In₃, Li_{13.7}Rh₈Si_{18.3}, Li_{4.82}Pd_{2.90}Si_{2.2}, Li₁₃Pd₁₂Si₁₂, Li₃Ag₂Si₃, Li₁₃Ag₅Si₆, Li₁₂Ag_{1-x}Si₄, Li₄ZrGe₂, Li₂Pd_{2.7}Ge_{2.3}, Li_{2.53}AgGe₂, LiYSn, LiRuSn₄, Li₈Rh₇Sn₈, Li₈Rh₇Sn₈, Li_{1.42}Pd₂Sn_{5.58}, Li₁₇Ag₃Sn₆, Li₂IrSi₃, Li₄Pt₃Si, Li₈La₇Ge₁₀, Li_{0.69}LaSn₂, Li₃Pt₂Sn₃, LiAu₃Sn₄, Li₂AuSn₂, and Li₃LaSb₂.

FORMATION OF INTERMETALLIC COMPOUNDS BY FRICTION STIR WELDING OF ALUMINUM AND TITANIUM

Mayerling Martinez¹, Florent Picot², Florent Moisy¹, and Eric Hug¹

¹ Laboratoire de Cristallographie et Sciences de Matériaux, Normandie Université, ENSICAEN, CNRS UMR 6508, 6 Boulevard du Maréchal Juin, 14050 Caen, France ² Sominex, 13 rue de la Résistance, 14400 Bayeux, France mayerling.martinez@ensicaen.fr

Friction Stir Welding (FSW) is a solid-state assembly technique widely employed in industry, initially used for joining aluminum alloys [1]. Application of this technique for joining two types of alloy having very different properties has been spreading recently. However, details of the change of microstructure in the welded zone are still poorly understood, due to their complex nature (strongly inhomogeneous deformation and heating). Hence, understanding the influence of FSW parameters on the microstructure and the phases formed in the welded region remains an important challenge for understanding the mechanical properties [2].

In the present work dissimilar FSW was used to join aluminum and titanium using the lap joining configuration. We examined FSW with different process parameters (such as rotation and translation speeds), which mainly affect the heat input. The microstructure of the welded region was studied by means of X-ray diffraction, hardness measurements, and electron microscopy. The analysis of the interface region shows, besides inhomogeneous intermixed Ti and Al metal areas, also formation of the TiAl₃ intermetallic compound, which is a line phase forming below $T = 1400^{\circ}$ C. No other Ti–Al phases from the complicated phase diagram (5 phases) were identified. The amount of TiAl₃, which appears as 1-2 µm thick slabs, interlaced with slabs of Ti (forming a multilayer), increases with the heat input from the FSW process [3].

Results will be confronted with the approach based on the effective heat of formation [4].

- [1] R. Nandan, T. DebRoy, H.K.D.H. Bhadeshia, Prog. Mater. Sci. 53 (2008) 980-1023.
- [2] M.A. Mofi, A. Abdollah-zadeh, F. Malek Ghaini, Mater. Des. 36 (2012) 161-167.
- [3] F. Picot, A. Gueydan, E. Hug, AIP Conf. Proc. 1896 (2017) 050008-1-050008-6.
- [4] R. Pretorius, A.M. Vredenberg, F.W. Saris, R. De Reus, J. Appl. Phys. 70 (1991) 3636-3646.

CRYSTAL STRUCTURES OF M₂P₂Se₆-TYPE COMPOUNDS

I. Barchiy¹, V. Tovt¹, M. Piasecki², O. Khyzhun³, V. Pavlyuk⁴, and A. Fedorchuk⁵

Department of Chemistry, Uzhhorod National University,

Pidgirna St. 46, 88000 Uzhhorod, Ukraine

² Institute of Physics, Jan Dlugosz University,

Armii Krajowej St. 13/15, 42200 Częstochowa, Poland

³ I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences

of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine

⁴ Department of Inorganic Chemistry, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

⁵ Department of Inorganic and Organic Chemistry, Lviv National University of Veterinary

Medicine and Biotechnologies, Pekarska St. 50, 79010 Lviv, Ukraine

igor.barchiy@uzhnu.edu.ua

 $M_2P_2Se_6$ -type compounds have a number of promising properties – ferroelectric, piezoelectric, electro-optic, and thermoelectric. To expand the range of compounds and improve the properties, compounds of compositions related to $M_2P_2Se_6$ were obtained by replacing the M^{2+} metal ions, which form the cation sublattice of the structure, by four M^{1+} ions, or by $M1^{1+}$ and $M2^{3+}$ ions.

According to the investigation of the physical-chemical interactions, the Tl₂Se-In₂Se₃-"P₂Se₄" system is characterized by the formation of intermediate complex selenides that melt congruently: $Tl_4P_2Se_6$ (758 K), $In_4(P_2Se_6)_3$ (880 K), and $TlInP_2Se_6$ (875 K). The crystal structures of the $M_2P_2Se_6$ compounds were studied by X-ray powder diffraction (DRON-4, Cu Ka radiation, Ni filter) with the software package WinCSD. The results of the structure investigation are shown in the Table.

Table Lattice parameters of the $M_2P_2Se_6$ compounds in the Tl₂Se-In₂Se₃-"P₂Se₄" system.

Compound	Space group	Lattice parameters
$Tl_4P_2Se_6$	$P12_1/c1$	$a = 12.239(2), b = 9.055(2), c = 12.328(2) \text{ Å}, \beta = 98.83(1)^{\circ}$
$In_4(P_2Se_6)_3$	<i>R</i> 3 h	$a = 6.308(8), c = 20.014(4) \text{ \AA}$
TlInP ₂ Se ₆	<i>P</i> -1	<i>a</i> = 6.4488(7), <i>b</i> = 7.5420(9), <i>c</i> = 12.166(2) Å, <i>a</i> = 100.72(0), β = 93.63(0), γ = 113.32(0)°



Fig. The structure of the anionic group $[P_2Se_6]^{4-}$.

In the multilayer structures of the $M_2P_2Se_6$ compounds one can distinguish the anionic group $[P_2Se_6]^{4-}$, which takes the form of two fused tetrahedra (Fig.), the P-P pair of phosphorus atoms occupying the octahedral voids between planes of selenium atoms. The metal cations occupy octahedral voids between the layers of anionic groups. In the structure of the $\tilde{T}IInP_2Se_6$ compound, the TI^+ and In^{3+} cations have an asymmetric arrangement.

Within the series $In_4(P_2Se_6)_3 \rightarrow TlInP_2Se_6 \rightarrow Tl_4P_2Se_6$, with increasing number of cations per $[P_2Se_6]^{4-}$ group, the P-P distances within the pair of phosphorus atoms decrease: 3.302 Å \rightarrow 2.278 Å \rightarrow 2.217 Å (2.108 Å), like the P-Se bonds: 2.286÷2.303 Å \rightarrow 2.184÷2.235 Å \rightarrow 2.100÷2.246 Å (2.101÷2.323 Å), which indicates increasing stability of the anionic group $[P_2Se_6]^{4-}$.

The layered structure of the $M_2P_2Se_6$ compounds contributes to the dipole moment between atoms of anion and cation groups. Replacing the metal cations M^{2+} by other metal cations $(M^+ \text{ and } M^{3+} \text{ or } 4M^+)$ leads to deformations of the structure, a change of the value of the dipole moment and, therefore, to changes of the electro-optical properties.

DETERMINATION OF STRUCTURAL DISORDER IN HEUSLER-TYPE PHASES

V.V. Romaka^{1,2}, A. Grytsiv², Yu.V. Stadnyk³, G. Rogl², L. Romaka³, and P. Rogl² ¹Lviv Polytechnic National University, Ustyyanovycha St. 5, 79013 Lviv, Ukraine ²Institute of Materials Chemistry, University of Vienna, Währingerstrasse 42, A -1090 Wien, Austria ³Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine romakav@lp.edu.ua

In recent years complex intermetallic systems have triggered interest as thermoelectric and magnetic materials, mainly because of their unconventional physical properties. To such materials belong the family of the Heusler-type phases, which includes both full-Heusler and half-Heusler compounds. Traditional high-throughput DFT calculations, which are used to discover new Heusler-type phases, are usually performed for compounds with stoichiometric point composition. However, a number of Heusler-type phases, e.g. TiNi₂Sn, TiNiSb, ZrNiSn, TiFeSb, and NbCoSb, which, for a long time, were considered as stoichiometric with point compositions, are, in fact, characterized by homogeneity regions and/or off-stoichiometry. The challenges that arise during the investigation of Heusler-type phases can be described as problems related to their constitution, structural disorder, and physical properties, however, the proper structural model of Heusler-type phases supplies a key for understanding their constitution and physical properties. In order to extend the application of DFT methods to the determination of structural disorder in half-Heusler and full-Heusler phases, we propose a new multi-way approach. It is based on an evaluation of the crystal structure model that is used in the DFT calculations by obtaining the best agreement between a set of theoretical and experimental data (e.g. concentration dependence of the lattice parameter, homogeneity region, physical and mechanical properties). This approach allows determining the model of structural disorder in Heusler-type phases, and can explain or predict the presence of homogeneity regions or off-stoichiometry, and reveal the mechanisms of solid-solution formation.

NEW NICKEL SILICIDES

T. Braun and V. Hlukhyy

Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, DE-85747 Garching, Germany viktor.hlukhyy@lrz.tum.de

Nickel silicides are intermetallics that have attracted interest because of their electronic (binary silicides) [1], thermoelectric (*e.g.* clathrates $Ba_8Ni_xSi_{46-x-y}$) [2-4], or superconducting (Sr(Ni_xSi_{1-x})₂ and $Ba_8Ni_xSi_{46-x-y}$) [2,5] properties. Compared to the alkaline-earth (Ca, Sr, Ba) nickel germanides, the corresponding ternary systems with silicon are less investigated. Only a few alkaline-earth nickel silicides are known so far. In the ternary systems *Ae*–Ni–Si (*Ae* = Ca, Sr, Ba) the existence of the following compounds has been reported: CaNi₂Si, Ca₃Ni₃Si₂, Ca(Ni_xSi_{1-x})₂, CaNi₂Si₂, Ca₂Ni₂Si₇, Sr(Ni_xSi_{1-x})₂, SrNiSi₃, SrNi_{9-x}Si_{4+x}, BaNi₂Si₂, Ba₂NiSi₃, and Ba₈Ni_xSi_{46-x-y} [6]. Our exploratory investigations of these systems in the Ni-rich region have revealed the existence of five new ternary silicides: CaNi₃Si₂ (ErRh₃Si₂ structure type), SrNiSi (BaPdP structure type), SrNi₅Si₃ (LaCo₅P₃ structure type), SrNi₂Si [7], BaNi₂Si (BaNi₂Ge structure type) [7], and one binary phase, Ni₂3Si₉ (own structure type).

The new silicides were synthesized from the pure elements by different methods: (i) arc-melting technique, (ii) melting in an induction furnace, (iii) special thermal treatment in a resistance furnace. Arc-welded Ta/Nb ampoules were used for (ii) and (iii), in order to prevent the evaporation of alkaline-earth metal at high temperature.

In analogy to the Zintl phases, the structures of these alkaline-earth nickel silicides can be considered as constructed of polyanionic units $[Ni_nSi_m]^{p-}$ and encapsulated cations. Increasing of the *Ae* content leads to a change of the polyanionic substructure from a three-dimensional network to two-dimensional layers.



Fig. Polyanionic fragments of a) CaNi₃Si₂, b) Sr(Ba)Ni₂Si, c) SrNi₅Si₃, and d) SrNiSi.

- [1] H. Iwai, T. Ohguro, S. Ohmi, *Microelectron. Eng.* 60 (2002) 157.
- [2] U. Aydemir, C. Candolfi, A. Ormeci, H. Borrmann, U. Burkhardt, Y. Oztan, N. Oeschler, M. Baitinger, F. Steglich, Y. Grin, *Inorg. Chem.* 51 (2012) 4730.
- [3] M. Falmbigl, M.X. Chen, A. Grytsiv, P. Rogl, E. Royanian, H. Michor, E. Bauer, R. Podloucky, G. Giester, *Dalton Trans.* 41 (2012) 8839.
- [4] J.H. Roudebush, M. Orellana, S. Bux, T. Yi, S.M. Kauzlarich, J. Solid State Chem. 192 (2012) 102.
- [5] S. Pyon, K. Kudo, M. Nohara, J. Phys. Soc. Jpn. 81 (2012) 023702.
- [6] SpringerMaterials. The Landolt-Börnstein Database.
- [7] T. Braun, S. Zeitz, V. Hlukhyy, Z. Anorg. Allg. Chem. 645(3) (2019) 388-395.

STRUCTURAL AND HYDROGENATION PROPERTIES OF THE TICO INTERMETALLIC AND ITS HYDRIDES

<u>F. Cuevas</u>¹, J. Zhang¹, C. Nervi², M. Baricco², and M. Latroche¹ ¹ Université Paris Est, ICMPE (UMR 7182), CNRS, UPEC, 94320 Thiais, France ² Department of Chemistry and NIS, University of Turin, Via P. Giuria 7, 10125 Torino, Italy cuevas@icmpe.cnrs.fr

AB-type intermetallic compounds (A = Ti and B = Fe, Co or Ni), all crystallizing with a simple CsCl-type structure, have remarkable properties for hydrogen storage at room temperature (*e.g.* TiFe) and as negative electrodes for Ni-MH batteries (*e.g.* TiNi) [1]. In this work, we are interested in the hydrogenation properties of the less-studied TiCo compound. This binary alloy has very singular hydrogenation properties, highlighted by a multi-plateau behavior in the pressure-composition-temperature (PCT) isothermal curves, evidencing the formation of several hydride phases.

The TiCo compound was synthesized by co-melting pure elements, and characterized from chemical and structural viewpoints by electron microprobe (EPMA) and X-ray diffraction (XRD) analyses. The thermodynamic properties of hydrogen absorption and desorption were determined by PCT measurements. The shape of the PCT curves demonstrates the formation of three TiCoH_x hydrides of distinct compositions (β , γ and δ , with x = 0.9, 1.2, 1.5, respectively). Their structures were determined by *ex-situ* neutron diffraction using deuterated samples. These measurements were carried out at LLB (France) using the beamline 3T2. The structural evolution as a function of temperature was also analyzed by Temperature Programmed Desorption (TPD) coupled to *in-situ* neutron diffraction at PSI (Switzerland) using the beamline HRPT. To illustrate the results of this study, the figure below shows the three successive structural transitions $\delta \rightarrow \gamma \rightarrow \beta \rightarrow \alpha$ observed during hydrogen desorption by heating from RT to 320°C, from the phase with the highest concentration of hydrogen, δ -TiCoH_{1.5}, to the intermetallic compound α -TiCo.



2D representation of the *in-situ* neutron diffractograms collected during TPD of the compound δ -TiCoD_{1.5} on heating from RT to 320°C (one pattern every 12°C). Three successive structural transitions $\delta \rightarrow \gamma \rightarrow \beta \rightarrow \alpha$ are observed.

[1] F. Cuevas, In: E. Burzo (Ed.), *Hydrogen Storage Materials*, Vol. 8, Springer-Verlag, Berlin Heidelberg, 2018, pp. 40-72.

QUATERNARY INTERMETALLIC COMPOUNDS *REPt*₂Ga₃In (*RE* = Y, Gd-Yb)

 <u>M. Horiacha</u>^{1,2}, F. Stegemann², R. Pöttgen², G. Nychyporuk¹, and V. Zaremba¹
 ¹Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ² Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, 48149 Münster, Germany goryacha_muroslava@ukr.net

Polycrystalline samples $REPt_2Ga_3In$ (RE = Y, Gd-Yb) with the ideal 1:2:3:1 atomic ratio were arc-melted and characterized by powder X-ray diffraction with an Enraf-Nonius FR552 Guinier camera using the image plate technique (Fuji Film, BAS-READER 1800) and Cu $K\alpha_1$ radiation (Table). Small single crystals of GdPt_2Ga_3In and TbPt_2Ga_3In were grown by induction heating in sealed tantalum ampoules, using a special temperature mode. The crystal structures were investigated by single-crystal X-ray analysis (STOE IPDS II diffractometer, Mo $K\alpha$ radiation) and refined with the JANA2006 [1] software package.

Compound	a (pm)	<i>b</i> (pm)	<i>c</i> (pm)	$V(nm^3)$				
YPt ₂ Ga ₃ In	1753.3(2)	429.9(1)	673.6(1)	0.5077				
GdPt ₂ Ga ₃ In	1755.6(2)	428.7(1)	673.1(1)	0.5066				
TbPt ₂ Ga ₃ In	1758.8(4)	426.8(1)	672.9(2)	0.5051				
DyPt ₂ Ga ₃ In	1763.0(3)	425.9(1)	672.9(1)	0.5053				
HoPt ₂ Ga ₃ In	1763.7(2)	425.9(1)	672.9(1)	0.5055				
ErPt ₂ Ga ₃ In	1764.0(5)	425.8(1)	672.7(1)	0.5053				
TmPt ₂ Ga ₃ In	1764.2(3)	425.8(1)	672.3(1)	0.5050				
YbPt ₂ Ga ₃ In	1764.6(5)	425.6(1)	672.1(1)	0.5048				

Table Lattice parameters of the intermetallic compounds *RE*Pt₂Ga₃In.

GdPt₂Ga_{2.95}In_{1.05} and TbPt₂Ga_{3.14}In_{0.86} crystallize in the NdRh₂Sn₄ structure type [2], space group *Pnma*: a = 1760.28(4), b = 429.09(5), c = 675.37(14) pm, $wR_2 = 0.0618$, 1104 F^2 values and 45 refined parameters, and a = 1746.56(3), b = 427.05(5), c = 672.69(13) pm, $wR_2 = 0.0554$, 1086 F^2 values and 45 refined parameters, respectively. The refined compositions were confirmed by EDX analysis. Refinement of the crystal structure of GdPt₂Ga_{2.95}In_{1.05} showed that one of the four *p*-element positions is occupied by indium, and a small degree of Ga/In mixing on one of the 4*c* gallium sites. For the Tb-based crystal, the 4*c* indium site showed in addition a small degree of In/Ga mixing.

Temperature-dependent magnetic susceptibility data of GdPt₂Ga₃In showed Curie-Weiss paramagnetism with an anomaly at T = 12.7(1) K, proven to be intrinsic by zero-field heat capacity measurements, pointing towards a stable canted antiferromagnetic ground state. An effective magnetic moment of $\mu_{eff} = 8.03(1) \mu_B/Gd$ atom and a paramagnetic Curie temperature of $\theta_P = -8.7(3)$ K were revealed. The experimental magnetic moment slightly exceeds the theoretical value of the free Gd³⁺ ion.

The small degree of Ga/In mixing is similar to that observed for the previously investigated quaternary intermetallic compound $GdNi_2Ga_{2.89}In_{1.11}$ [3].

M. Horiacha is indebted to DAAD for a research scholarship.

- [1] V. Petříček, M. Dušek, L. Palatinus, Z. Kristallogr. Cryst. Mater. 229 (2014) 345-352.
- [2] M. Méot-Meyer, G. Venturini, B. Malaman, B. Roques, *Mater. Res. Bull.* 20 (1985) 913-919.
- [3] Ya.V. Galadzhun, M.M. Horiacha, G.P. Nychyporuk, U.C. Rodewald, R. Pöttgen, V.I. Zaremba, Z. Anorg. Allg. Chem. 642 (2016) 896-901.

Ba₆Li₂Ga₁₀, A NEW INTERMETALLIC PHASE WITH PYRAMIDAL Ga₅ CLUSTERS

<u>M. Kotsch</u>, Yu. Prots, and Yu. Grin Max-Planck-Instut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany kotsch@cpfs.mpg.de

In the field of intermetallics, compounds containing discrete gallium cluster units are mainly found in binary MGa_n phases, where M is an alkali or alkaline-earth metal, europium or uranium, as established by Belin and Tillard-Charbonnel [1]. In our previous work [2], which yielded $Eu_3Li_{5+x}Ga_{5-x}$, a phase with unique bell-like $[Ga_n]$ (n = 5) cluster units, it was shown that ternary compounds with discrete clusters can also be obtained. Interestingly, in $Eu_3Li_{5+x}Ga_{5-x}$ the lithium is not only incorporated into the cationic substructure, but also into the bell-like Ga_5 cluster units as a 0.15/0.85 Li/Ga mixed occupation of a Ga position, which had not been observed before. In order to establish a possible region for the formation of Ga cluster units, we analyzed the size of the cations in comparison with the valence electron concentration per gallium atom. From this, we were able to estimate boundary conditions, which can be applied to various different Ga systems. In the following, we used this to extend our work to the Ba–Li–Ga system, since it shares many features with the Eu–Li–Ga system, making it eminently suitable for further experiments concerning the addition of lithium. As a result, we succeeded in the synthesis of the compound $Ba_6Li_2Ga_{10}$.

The synthesis was performed from a suitable ratio of the constituent elements in a Ta crucible equipped with a small intermediate sieve. After the primary reaction at 923 K, the sample was slowly cooled to 748 K and held there for several days to allow formation of single crystals. The formation temperature was estimated from dynamic scanning calorimetry (DSC), and the excess lithium was separated by high-temperature centrifugation-aided filtration.

The structure was characterized by single crystal X-ray diffraction, as well as by powder X-ray and neutron diffraction. $Ba_6Li_2Ga_{10}$ (space group *Immm*, Pearson symbol *oI*20, a = 6.2720(2) Å, b = 6.5872(2) Å, c = 12.6878(8) Å). The Ga/Ba ratio was confirmed by EDX and the complete composition by chemical analysis.

The structure of Ba₆Li₂Ga₁₀ contains Ga₅ square pyramids, the quadrangular face of which is capped by a single lithium atom, resulting in a Ga₅Li octahedron. Due to the crystal symmetry, the orientation of the pyramids cannot be determined, leading to a $\frac{1}{2}$: $\frac{1}{2}$ mixed occupation of Li and Ga at the 4g position above and below the mirror plane, at the apexes of the pyramid. Each pyramid is connected to four adjacent pyramids parallel to {100}, forming 2D nets. The interatomic Ga-Ga distances range from 2.609 Å to 2.803 Å. Each pyramid is furthermore surrounded by 12 Ba atoms forming a nearly ideal cuboctahedron with Ba-Ba distances between 4.479 Å and 4.559 Å.

Susceptibility, resistivity, heat capacity and Hall effect were analyzed and are in good agreement with the results of quantum chemical calculations, proving that $Ba_6Li_2Ga_{10}$ is a semi-conductor, as well as a Zintl phase. For the quantum chemical calculations a variety of different ordered models were developed, using the group-subgroup approach.

- [1] C. Belin, M. Tillard-Charbonnel, *Prog. Solid State Chem.* 22 (1993) 59-109.
- [2] A. Fedorchuk, Yu. Prots, W. Schnelle, Yu. Grin, *Eur. J. Inorg. Chem.* 26 (2011) 3904-3908.

UNCONVENTIONAL METAL-FRAMEWORK INTERACTION IN MgSi5

J.-M. Hübner, W. Carrillo-Cabrera, Yu. Prots, M. Bobnar, U. Schwarz, and Yu. Grin Chemical Metals Science, Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany julia.huebner@cpfs.mpg.de

Intermetallic framework compounds constitute a class of materials that has attracted significant interest, because several members possess beneficial thermoelectric or superconducting properties [1]. In these structures, a majority of framework atoms enclose a minority of guest atoms. The three-dimensional framework is usually based on four-bonded tetrel atoms like Si, Ge and Sn, whereby the connectivity of the network atoms is related to the electron count by the 8-N rule, although silicon compounds may tolerate a certain electron excess [2]. Typically, members of the alkaline, alkali-earth or rare-earth metal groups act as cationic guest species. However, magnesium seems to be an exceptional case, as the metal tends to participate in the anionic network, e.g. in TiNiSi-type CaMgSi or BaAl₄-type phases like EuGa_{4-x}Mg_x [3]. At ambient pressure, the only phase in the binary system Mg–Si is (anti-)fluorite-type Mg₂Si [4], and also ternary magnesium-silicon compounds tend to evade clathrate-like frameworks [3,5]. However, high-pressure synthesis techniques provide valuable tooling equipment for advancing the spectrum of accessible tetrel frameworks, regarding network topology and chemical composition [6,7].

The silicon-rich cage compound MgSi₅ was synthesized by high-pressure hightemperature methods. The initial crystal structure determination was accomplished by electron diffraction tomography, setting the stage for phase analysis in the process of synthesis optimization that resulted in the growth of single crystals suitable for X-ray diffraction experiments. The crystal structure of MgSi₅ (space group *Cmme*, oS24, a = 4.4868(2) Å, b = 10.1066(5) Å, c = 9.0753(4) Å) represents a new type of framework of four-bonded silicon atoms forming Si₁₅ cages enclosing the Mg atoms. Two types of smaller Si₈ cage remain empty. The atomic interactions within the silicon framework are characterized by twocenter two-electron bonds. In addition, there is evidence for multi-center Mg-Si bonding in the large cavities of the framework and for lone-pair-like interactions in the smaller empty voids.

- (a) S. Stefanoski, M. Beekman, G.S. Nolas, In: G.S. Nolas (Ed.), *The Physics and Chemistry of Inorganic Clathrates*, Springer, Dordrecht, 2014, pp. 169-191; (b) S. Yamanaka, In: G.S. Nolas (Ed.), *The Physics and Chemistry of Inorganic Clathrates*, Springer, Dordrecht, 2014, pp. 193-226; (c) J.-A. Dolyniuk, B. Owens-Baird, J. Wang, J.V. Zaikina, K. Kovnir, *Mater. Sci. Eng.* 108 (2016) 1-46R; (d) K.A. Kovnir, A.V. Shevelkov, *Russ. Chem. Rev.* 73 (2004) 923-938; (e) A.M. Guloy, J.D. Corbett, *Inorg. Chem.* 30 (1991) 4789-4794; (f) F. Kneidinger, H. Michor, A. Sidorenko, E. Bauer, I. Zeiringer, P. Rogl, C. Blaas-Schenner, D. Reith, R. Podloucky, *Phys. Rev. B* 88 (2013) 104508.
 [2] A. Bhattacharya, C. Carbogno, B. Böhme, M. Baitinger, Yu. Grin, M. Scheffler, *Phys. Rev. Lett.* 118 (2017) 236401
- 236401

- [12] A. Bhattachalya, C. Carbogho, B. Bohme, M. Battinger, Fu. Grini, M. Schenner, *Phys. Rev. Lett.* 118 (2017) 236401.
 [3] (a) H. Axel, B. Eisenmann, H. Schäfer, A. Weiss, *Z. Naturforsch. B* 24 (1969) 815-817; (b) B. Eisenmann, H. Schäfer, A. Weiss, *Z. Anorg. Allg. Chem.* 391 (1972) 241-254; (c) F. Merlo, M. Pani, M.L. Fornasini, *J. Alloys Compd.* 196 (1993) 145-148; (d) S.J. Andersen, C.D. Marioara, A. Froseth, R. Vissers, H.W. Zandbergen, *Mater. Sci. Eng. A: Struct. Mater.* 390 (2005) 127-138; (e) A.O. Fedorchuk, Yu. Prots, Yu. Grin, *Z. Kristallogr. New Cryst. Struct.* 220 (2005) 317-318.
 [4] X.Y. Yan, Y.A. Chang, F. Zhang, *J. Phase Equilib.* 21 (2000) 379-384.
 [5] (a) H. Witte, *Metallwirtschaft* 18 (1939) 459-463; (b) R.J. LaBotz, D.R. Mason, D.F. O'Kane, *J. Electrochem. Soc.* 110 (1963) 127-134; (c) B. Eisenmann, N. May, W. Mueller, H. Schäfer, A. Weiss, J. Winter, G. Ziegleder, *Z. Naturforsch. B* 25 (1970) 1350-1352; (d) F. Wrubl, M. Pani, P. Manfrinetti, P. Rogl, *J. Solid State Chem.* 182 (2009) 716-724; (e) A. Currao, J. Curda, R. Nesper, *Z. Anorg. Allg. Chem.* 622 (1996) 85-94; (f) R. Nesper, S. Wengert, F. Zuercher, A. Currao, *Chem. Eur. J.* 5 (1999) 3382-3389; (g) I. Schellenberg, M. Eul, C. Schwickert, C.M. Kubata, E.C. Reyes, R. Nesper, U.C. Rodewald, R. Pöttgen, *Z. Anorg. Allg. Chem.* 638 (2012) 1976-1985.
 [6] (a) S. Yamanaka, S. Maekawa, *Z. Naturforsch. B* 61 (2006) 1493-1499; (b) A. Wosylus, Y. Prots, U. Burkhardt, W. Schnelle, U. Schwarz, Y. Grin, *Z. Naturforsch. B* 61 (2006) 1485-1492; (c) A. Wosylus, Y. Prots, U. Burkhardt, W. Schnelle, U. Schwarz, Yu. Grin, *Solid State Sci.* 8 (2007) 73-781.
 [7] (a) H. Fukuoka, S. Yamanaka, *Phys. Rev. B* 67 (2003) 094501; (b) U. Schwarz, A. Wosylus, H. Rosner, W. Schnelle, A. Ormeci, K. Meier, A. Baranov, M. Nicklas, S. Leipe, C.J. Müller, Y. Grin, *J. Am. Chem. Soc.* 134 (2012) 13558-13561.

MAGNETIC PROPERTIES OF $(UH_3)_{1-x}T_x$: IS STRUCTURE TYPE IMPORTANT?

<u>Oleksandra Koloskova</u>¹, Volodymyr Buturlim¹, Peter Minárik², and Ladislav Havela¹ ¹Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 12116 Prague 2, Czech Republic ²Department of Physics of Materials, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 12116 Prague 2, Czech Republic koloskova.alexandra@gmail.com

Uranium hydride UH₃, the first known material with ferromagnetism purely based on the 5*f* electronic states [1], has a Curie temperature of around 165 K for both structure modifications, transient α -UH₃ and stable β -UH₃. The use of fast-cooled U-*T* (*T* = transition metals) alloys as precursors for hydrides leads to certain changes of the structure and properties of the resulting hydrides. Adding *T* = Zr results in a stable crystalline α -UH₃ type hydride; other elements provide nanocrystalline materials with β -UH₃ type structure. All the studied (UH₃)_{1-x}*T_x* hydrides show higher *T*_C values, exceeding 200 K in the case of Mo alloying, with a maximum corresponding to 12-15 at.% of the alloying element [2]. The reason for such a general increase has so far been unclear, but could be attributed either to an effect of electronic states of the alloying elements or to an impact of crystal structure changes.

Vanadium was chosen as a new alloying element for further studies. Unlike the other U-*T* hydrides, UH₃-V crystallizes in a regular β -UH₃ type structure, except for high V concentrations (20 %), where the grain size decreases and reaches nanocrystallinity. The lattice parameters slightly decrease with increasing V concentration (*a* = 6.6444 Å, 6.6616 Å, 6.6429 Å, and 6.6416 Å, for pure UH₃, 10 %, 15 %, and 20 % V, respectively). Introductory

magnetization studies indicated an increase of $T_{\rm C}$ to ~190 K for 15 at.% V, followed by saturation, related to a tendency to segregate excessive V in small clusters (~100-250 nm), preventing dissolution of more than ~15 % V in the uranium hydride phase.

If further studies prove the preliminary results, it can be concluded that $T_{\rm C}$ of alloyed U hydrides has nothing to do with a particular crystal structure, but is an electronic effect.

Basic magnetic (temperature and field dependencies of the magnetization) data on the hydrides will be presented, as well as a study of their microstructure and the impact of the synthesis conditions (hydrogen pressure and time of exposure) on these properties.



Fig. Concentration dependence of the Curie temperature in the series $(UH_3)_{1-x}(Zr-Mo-V)_x$.

This work was supported by the Czech Science Foundation under the grant No. 18-02344S and by the Czech Ministry of Education under the COST project scheme, project No. LTC18024.

- [1] N.-T.H. Kim-Ngan et al., J. Nucl. Mater. 479 (2016) 287-294.
- [2] L. Havela et al., J. Magn. Magn. Mater. 400 (2016) 130-136.

PrCo_{0.5}Fe_{0.5}O₃ ELECTRONIC STRUCTURE FROM FIRST PRINCIPLES

<u>V.M. Shved</u>, V.M. Hreb, and L.O. Vasylechko Semiconductor Electronics Department, Lviv Polytechnic National University, S. Bandera St. 12, 79013 Lviv, Ukraine shvedvira@gmail.com

Rare-earth cobaltite and ferrite perovskites are intensively studied strongly correlated materials. In particular, $RFeO_3$ perovskites are known as canted antiferromagnets that possess magneto-optical and multiferroic properties, and exhibit magnetization reversal and spin switching phenomena. The magnetic and transport properties of $RCoO_3$ cobaltites strongly depend on the spin state of the cobalt ions.

The electronic structure and magnetic properties of mixed praseodymium cobaltiteferrites were studied on the example of $PrCo_{0.5}Fe_{0.5}O_3$, which adopts a GdFeO₃-type perovskite structure with pseudo-tetragonal lattice metrics $a_p \approx c_p < b_p$ in space group *Pbnm* [1]. *Ab-initio* calculations were performed within the projector augmented-wave method implemented in the ABINIT software package [2]. For a correct treatment of the strongly correlated Co-3*d*, Fe-3*d* and Pr-4*f* electrons, the PBE0 hybrid functional was adopted [3]. All the calculations were performed using experimental lattice parameters (a = 5.4299 Å, b = 5.4462 Å, c = 7.6757 Å) and the atomic positions in the structure of $PrCo_{0.5}Fe_{0.5}O_3$ at room temperature reported in [1]. An energy cutoff of 545 eV was used to expand the wave functions. The Brillouin zone was sampled on a $6 \times 6 \times 4$ Monkhorst-Pack grid.

The PBE0 hybrid functional band structure calculations predict an indirect band gap of 1.44 eV in PrCo_{0.5}Fe_{0.5}O₃. The conduction band minimum occurs at the Y point and the valence band maximum at the X point. Calculations of the spin-polarized total and partial density of states revealed that the contributions of the spin up and spin down states are equal, indicating an antiferromagnetic ground state in $PrCo_{0.5}Fe_{0.5}O_3$. The bottom of the conduction band mainly consists of Co-d and some Fe-d, O-p and Pr-f states. The valence band is located between -7.6 and 0 eV; the top of this band is mainly formed by Pr-f states. The Fe-d states significantly contribute to the bottom of the valence band. The calculated magnetic moments of Fe³⁺ and Co³⁺ in this mixed cobaltite-ferrite are 4.12 μ_B and 0.12 μ_B , respectively. According to literature data for the parent compounds, at low temperature PrCoO₃ is a nonmagnetic insulator with low-spin state of the Co³⁺ ions, while PrFeO₃ exhibits G-type antiferromagnetic ordering with a magnetic moment of 4.14 μ_B per Fe³⁺ ion. Our calculations for PrCo_{0.5}Fe_{0.5}O₃ also agree well with the results of neutron powder diffraction investigations of the isostructural lanthanum cobaltite-ferrite, which show that the magnetic structure of LaCo_{0.5}Fe_{0.5}O₃ at low temperature is similar to that of "pure" LaFeO₃. It was also assumed that the low-spin Co³⁺ ions do not actively participate in the magnetic interactions and the antiferromagnetism of $LaCo_{1-x}Fe_xO_3$ is induced by interactions between Fe^{3+} ions.

The work was funded by the Ministry of Education and Science of Ukraine under project No. 0118U000264 (DB/Feryt).

- [1] O.V. Kharko, L.O. Vasylechko, *Visn. Lviv Polytech. Nat. Univ. Electron.* 734 (2012) 119-126 (in Ukrainian).
- [2] X. Gonze et al., Comput. Phys. Commun. 180 (2009) 2582-615.
- [3] E. Tran et al., Phys. Rev. B 74 (2006) 155108 (10 p.).

014

OSCILLATION BEHAVIOR OF METAL ATOMS IN HYDROGENATED INTERMETALLICS

N.E. Skryabina

Department of Chemistry, Perm State University, Bukireva St. 15, 614990 Perm, Russian Federation natskryabina@mail.ru

These studies led us to discover that hydrogen penetrating into the structure of intermetallics can provoke a redistribution of the alloy components, just after and even a long time after achievement of the hydrogenation process. Earlier, this phenomenon (multi phase transitions) had been mentioned for Pd-based alloys by Katsnelson and coworkers. Later, we detected fluctuations of the metal atom concentration in amorphous/nano-crystalline iron-based alloys, and more recently in crystallized $(TiCr_{1.8})_{1-x}V_x$ and $(TiCr_{1.8})_{1-x}V_x + 5 \text{ wt.\%}$. Zr₇Ni₁₀, where x = 20-40-60 at.%. It was proven that addition of 5 wt.% Zr–Ni alloy to Ti–Cr–V leads to a significant improvement of the hydrogen sorption properties of the alloy, due to the net localization of the admixture at the grain boundaries, thus serving as paths for hydrogen diffusing deeply into the grains of the alloy. We evidenced that hydrogen insertion causes marked fluctuations of the element concentrations of variable intensity, at and near the grain boundaries.

In this communication, we analyze the reasons for the changes occurring in the atom concentrations over time, after hydrogen saturation. It appears that this phenomenon could have theoretical and applied scientific impacts. In particular, it should be accounted for when selecting compositions for hydrogen storage applications, since the stability of the alloys during absorption/desorption cycling should be especially high.

HYDROGENATION PROPERTIES OF Ni-BASED NANOPOWDERS AND MH–NANO-NI COMPOSITE MATERIALS

<u>I.Yu. Zavaliy</u>¹, A.R. Kytsya^{1,2}, Yu.V. Verbovytskyy¹, P.Yu. Zavalij³, Yu.O. Kulyk⁴, V.V. Berezovets¹, and P.Ya. Lyutyy¹

¹ Karpenko Physico-Mechanical Institute, National Academy of Sciences of Ukraine, Naukova St. 5, 79060 Lviv, Ukraine

² Department of Physical Chemistry of Fossil Fuels InPOCC, National Academy of Sciences

of Ukraine, Naukova St. 3a, 79060 Lviv, Ukraine

³ Department of Chemistry and Biochemistry, University of Maryland,

College Park, MD, 20742, USA

⁴ Faculty of Physics, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 8, 79005 Lviv, Ukraine

zavaliy@ipm.lviv.ua

Hydrogen and hydrogen-containing materials are important alternative energy sources. Development of chemical power sources (*e.g.* Li-ion or Ni-MH) with enhanced parameters is one of the most attractive directions in this field. Hydrides of intermetallic compounds are used as negative electrodes in rechargeable Ni-MH batteries [1]. For this application, *RE*–Ni and *RE*–Mg–Ni alloys [2] are often studied as composites with Ni or Cu powders as a binder. The understanding of the influence of their dispersed state on the working parameters of the electrodes is very important.

In this work, we studied different types of nanopowder (Ni, Cu and their alloys). It was early demonstrated that the hydrogenation properties are critically dependent on the structure of the particles. Therefore, the crystal structures of the Ni-based nanopowders were thoroughly studied by SEM, XRD and SAXS. X-ray diffraction and SEM analysis showed that the size of the obtained nickel nanoparticles covered the range from 20 to 200 nm. The particles consisted of crystallites, which were characterized by a size of about 5-20 nm. The complicated structure of the particles was confirmed by the SAXS method [3]. The gas hydrogenation was studied using a Sieverts type apparatus. Electrochemical charge-discharge characteristics were studied using PGStat-8 equipment.

The hydrogenation properties of the Ni and Ni-based nanopowders (Ni-NP or Ni-based NP) were studied individually, or as additives to hydrogen storage or electrode materials. It was revealed that the nano-state substantially enhances gas or electrochemical hydrogenation of Ni powders. The hydrogenation of the nanosized Ni–Cu alloys showed interesting peculiarities depending on the Ni/Cu ratio. The nanopowders prepared in [3] and commercial Ni-NP were used for the preparation of composites (RE–Mg–Ni + Ni-NP), and their charge-discharge properties were studied. Substantial enhancement of the discharge capacity of the MH-electrodes was observed due to the addition of Ni-NP. It was shown that the discharge capacity of Ni-NP itself in some cases reached up to 100 mA×h/g. Ni-NP and Ni-based NP also evidenced an ability to absorb hydrogen gas at ambient conditions. Possible explanations for the observed hydrogenation behavior of the studied nanomaterials will be proposed.

- [1] P. Notten, M. Latroche, *Encyclopedia of Electrochem. Power Sources* (2009) 502-521.
- [2] Yu. Verbovytskyy, I. Zavaliy, Mater. Sci. 51/4 (2016) 443-456.
- [3] I. Zavaliy, A. Kytsya, Yu. Verbovytskyy, et al., Proc. IEEE 8th Int. Conf. Nanomaterials: Applications & Properties (NAP-2018), Zatoka, 2018, Part 1, pp. 148-151.

MAGNETIC AND LATTICE ANISOTROPIES IN U-COMPOUNDS: U2Ni2Sn

<u>S. Maskova-Cerna</u>¹, A.V. Andreev², H. Nakotte³, K. Kothapalli^{3,4}, A.V. Kolomiets⁵, and L. Havela¹

¹ Department of Condensed Matter Physics, Charles University, Prague, Czech Republic ² Institute of Physics, Academy of Sciences, Prague, Czech Republic

³ Department of Physics, New Mexico State University, Las Cruces, NM, USA

⁴ College of Arts and Sciences, King University, Bristol, TN, USA

⁵ Department of Physics, Lviv Polytechnic National University, Lviv, Ukraine maskova@mag.mff.cuni.cz

 U_2Ni_2Sn represents an important example for studying the origin of magnetic anisotropy in U intermetallics. The majority of the U_2T_2X compounds, crystallizing in tetragonal Mo₂FeB₂-type structures, have the shortest U-U spacing along the *c*-axis. The magnetic moments are, as a rule, located in the basal plane. In U_2Ni_2Sn , the U-U spacing in the basal plane is smaller than along *c*.

Existing reports on the magnetic structure of U_2Ni_2Sn are contradictory. A powder neutron diffraction experiment led to the conclusion that the known antiferromagnetic order $(T_N = 26 \text{ K})$ has the propagation vector $\mathbf{k} = (0,0,\frac{1}{2})$ and AF coupling also within each unit cell [1]. The magnetic structure should be collinear with basal-plane orientation of the U-moments $(\mu_U = 1.05 \mu_B)$. Later and never published neutron diffraction data on an allegedly singlecrystalline sample pointed to *c*-axis orientation [2].

We successfully prepared a single crystal of U₂Ni₂Sn by the Czochralski method, studied the anisotropy of the bulk magnetic properties and performed neutron diffraction. The temperature dependence of the crystal structure parameters was studied by means of X-ray diffraction. For U₂Ni₂Sn, the shortest U-U distances perpendicular to the *c*-axis (d_{U-U}) are considerably shorter than the corresponding shortest U-U distances along the *c*-axis (d_{U-U}) = 3.61 Å, d_{U-U} = 3.69 Å at room temperature). Contrary to the expectations from usual thermal-expansion behavior, d_{U-U} increases with decreasing temperature, while d_{U-U} decreases with decreasing temperature.

The temperature dependence of the magnetic susceptibility was measured with the field along the *c*-axis and in the basal plane. It revealed that the *c*-axis is the easy axis of magnetization, *i.e.* indeed perpendicular to the shortest U-U distances. The field dependence of the magnetization showed three metamagnetic transitions at approx. 30, 39 and 50 T. The magnetization did not show any tendency to saturation in the highest fields.

A low-temperature neutron diffraction experiment at ORNL, USA, was performed in order to determine the magnetic structure. Our data indicate a clear preference for a collinear antiferromagnetic structure with *c*-axis direction of the U moments with alternating orientation within each unit cell and the propagation vector $\mathbf{k} = (0,0,\frac{1}{2})$. No Ni moments were considered. The magnetic structure of U₂Ni₂Sn is fully compatible with the 5*f*-5*f* two-ion anisotropy model dominant in most U band systems.

- [1] F. Bourée, B. Chevalier, L. Fournès, F. Mirambet, T. Roisnel, V.H. Tran, Z. Zolnierek, *J. Magn. Magn. Mater.* 138 (1994) 307.
- [2] D. Laffargue, B. Chevalier, S.F. Matar, F. Bourée, 1996, private communication.

INFLUENCE OF PRESSURE ON THE RESISTIVITY OF U2Ni2Sn

<u>A.V. Kolomiets</u>^{1,2}, S. Mašková², I. Halevy³, J. Prchal², J. Valenta², L. Havela², and A. Andreev⁴

¹ Department of Physics, Lviv Polytechnic National University, Lviv, Ukraine

² Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic

³ Department of Physics, IAEC-NRCN, Beer-Sheva, Israel

⁴ Institute of Physics, Academy of Sciences, 18221 Prague, Czech Republic

kolomiet@gmail.com

The electrical resistivity of a U₂Ni₂Sn single crystal was studied under pressures up to 3.3 GPa, in order to establish the evolution of the magnetic interactions in this compound. Since U₂Ni₂Sn is a uniaxial antiferromagnet ($T_N = 25$ K) with pronounced anisotropy, indicated by an anisotropy field of well above 60 T, the measurements were performed with the electric current both along and perpendicular to the easy magnetization axis, which is the [001] direction in U₂Ni₂Sn [1]. The resistivity curves for the two current orientations are similar in shape and magnitude, the $\rho(T)$ for *i* // [110] running somewhat higher (Fig.).



Fig. Zero-field resistivity of U₂Ni₂Sn for different electric current directions. The inset shows the transition region.

The shape of the resistivity curves and relatively low residual resistivity, excluding the effect of structural disorder, point to scattering of the conduction electrons on spin fluctuations. The bump around 25 K is associated with the AFM ordering.

The low-temperature resistivity can be approximately expressed by the sum of the Fermi-liquid AT^2 and magnon $(BT)^{-\Delta/T}$ terms, where A and B are constants and Δ represents the excitation gap. The **300** application of hydrostatic pressure increasing from the ambient value till 3.3 GPa results in a monotonous increase of the excitation gap Δ from about 30 K to 50 K. The Δ values for the i // [110]geometry are consistently higher than for

i // [001] by about 15 %, yet the shapes of the $\Delta(p)$ dependencies are similar for both current directions. This difference increases further, due to the decrease of Δ for i // [001], if a magnetic field is applied. The gaps for the other geometry remain unchanged. The Néel temperature at first increases with increasing pressure till p = 3 GPa, but then drops upon further pressurization.

The absence of low-lying magnetic excitations, as well as the anisotropic field effect on the effective spin gap, are consistent with the uniaxial anisotropy of the magnetic structure of U_2Ni_2Sn .

[1] S. Mašková et al., Phys. Rev. B 99 (2019) 064415.

CHEMICAL REACTIVITY OF Ca-Ag INTERMETALLIC COMPOUNDS

<u>I. Antonyshyn</u>¹, U. Burkhardt¹, O. Sichevych¹, A. Ormeci¹, K. Rasim¹, S. Titlbach², S.A. Schunk², and Yu. Grin¹ ¹ Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany ² hte GmbH, Kurpfalzring 104, 69123 Heidelberg, Germany Iryna.Antonyshyn@cpfs.mpg.de

The chemical properties of intermetallic compounds (IMCs) are mainly represented by corrosion studies, or hidden in catalysis research. On the one hand, catalysis is the perfect playground to study the behavior of intermetallic compounds under different reaction conditions, on the other hand, intermetallic compounds represent an interesting class of materials for catalytic applications [1-3]. Considering this, Ca–Ag compounds were investigated as catalysts for industrially valuable ethylene epoxidation processes [4-6].

Contrary to the increased sensitivity of Ca–Ag compounds towards air with increasing Ca content, their reactivity under ethylene epoxidation conditions follows another trend and the five compounds forming in the system can formally be divided into three groups. The Ag-rich compounds, namely Ca₂Ag₇ (Yb₂Ag₇-type, *Cmcm*) and CaAg₂ (KHg₂-type, *Imma*), undergo oxidation with formation of Ag particles embedded in a complex Ca-containing matrix (CaO, Ca(OH)₂ and CaCO₃). The equiatomic compound CaAg (α -TII type, *Cmcm*) remains stable in bulk over 600 h on stream. This stability originates from the formation of a highly ordered, stable and dense CaO passivation layer with a small amount of embedded Ag atoms on the (010) surface, which is also the preferred cleavage surface upon sample crushing. The *post mortem* characterization of the Ca-rich compounds, Ca₅Ag₃ (Cr₅B₃-type, *I4/mcm*) and Ca₃Ag (Fe₃C-type, *Pnma*), reveals only very slow oxidation and correspondingly traces of oxidation products. The chemical properties of the Ca-Ag compounds under ethylene epoxidation conditions are governed by the crystal structure and chemical bonding features. To evaluate such diverse chemical reactivity, a multitude of experimental and computational techniques was used.

- [1] M. Armbrüster, R. Schlögl, Yu. Grin, Sci. Technol. Adv. Mater. 15 (2014) 034803.
- [2] A.P. Tsai, S. Kameoka, K. Nozawa, et al., Acc. Chem. Res. 50 (2017) 2879-2885.
- [3] S. Furukawa, T. Komatsu, ACS Catal. 7 (2017) 735-765.
- [4] I. Antonyshyn, O. Sichevych, K. Rasim, et al., Eur. J. Inorg. Chem. (2018) 3933-3941.
- [5] I. Antonyshyn, O. Sichevych, K. Rasim, et al., Inorg. Chem. 57 (2018) 10821-10831.
- [6] I. Antonyshyn, O. Sichevych, A. Ormeci, *et al.*, *submitted*.

SYNTHESIS AND INVESTIGATION OF TARTRATOGERMANATE Cu(II), Ni(II), Fe(II) COMPLEXES WITH 2,2'-BIPYRIDINE

<u>E.V. Afanasenko¹</u>, I.I. Seifullina¹, E.E. Martsinko¹, E.A. Chebanenko¹, V.V. Dyakonenko², and S.V. Shishkina^{2,3}

¹ Department of General Chemistry and Polymers, Odesa I.I. Mechnikov National University, Dvoryanska St. 2, 65082 Odesa, Ukraine

² SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine, Nauky Ave. 60, 61001 Kharkiv, Ukraine

³ V.N. Karazin Kharkiv National University, Svobody Sq. 4, 61077 Kharkiv, Ukraine afanasenkoeleonora@gmail.com

New heterometallic multiligand compounds are of special scientific and practical interest, because they are highly perspective for the creation of novel drugs, nutritional supplements and growth stimulants on their basis, with the consequent introduction in medicine and agriculture. Scientists at the Department of General Chemistry and Polymers recently developed a novel synthesis strategy, which provides a combination of the biological properties of Ge(IV) (p-element) and Cu(II), Ni(II) or Fe(II) (d-elements), and two types of ligand: polydentate tartaric acid and chelating heterocyclic 2,2'-bipyridine. It involves preparation of a working solution of tartratogermanic acid by dissolving GeO₂ and tartaric acid in hot water in the first step of the synthesis, and adding ethanol mixtures of 2,2'-bipyridine with $CuCl_2$ (I), $NiCl_2$ (II) or $FeSO_4$ (III) to three portions of the working solution in the second step. This method allowed obtaining $[CuCl(bipy)_2]_2[Ge_2(OH)_2(Tart)_2] \cdot 4H_2O$ (I), $[Ni(bipy)_3]_4[\{Ge_2(OH)_2(Tart)_2\}_3Cl_2] \cdot 15H_2O$ (II), and $[Fe(bipy)_3]_2[{Ge(H_2O)(\mu-Tart)_2Ge(H_2Tart)}(S_2O_7)] \cdot 9H_2O$ (III). The complexes were characterized by elemental analysis, mass-spectrometry, IR-spectroscopy, thermogravimetry, and X-ray diffraction.

According to the X-ray data, I and II are cation-anion compounds; they contain similar dimeric anions $[Ge_2(OH)_2(Tart)_2]^{2^-}$, and all the carboxyl and hydroxyl groups of the two molecules of tartaric acid are fully deprotonated and bonded to Ge. This was confirmed by the results of the IR-spectroscopy: stretching vibrations of free carboxyl groups $v(C=O)\sim1738 \text{ cm}^{-1}$ are absent. In the mass-spectra of I and II the same peak with the half-mass of the complex anion $[Ge_2(OH)_2(Tart)_2]^{2^-} - 235.76$, is present. The coordination polyhedron of Ge is a trigonal bipyramid. The molecular structures of the cations $[CuCl(bipy)_2]^{1+}$ in I and $[Ni(bipy)_3]^{2+}$ in II are different, despite the anion being the same. The coordination polyhedron of Cu(II) is a distorted trigonal bipyramid, that of Ni(II) is an octahedron.

The Ge atoms in the complex anion $[Ge(H_2O)(\mu-Tart)_2Ge(H_2Tart)]^{2-}$ (III) have different types of coordination: distorted square bipyramid and distorted octahedron. Two molecules of tartaric acid are fully deprotonated, bridging ligands, while the third molecule is a terminal ligand with one hydroxyl and one carboxylate group, which are not bonded to Ge. A particular feature of the compound III is the presence of a second anion – $S_2O_7^{2-}$, which is formed in acidic solution *via* the reaction $2SO_4^{2-} + 2H^+ \rightarrow 2HSO_4^{--} \rightarrow S_2O_7^{2-} + H_2O$. The total charge of the anions is compensated by two cations $[Fe(bipy)_3]^{2+}$.

In conclusion, despite the fact that the chosen d-metals are characterized by similar properties, different structures of cations and anions are present in their tartratogermanate complexes. This can be explained by the diversity of the electronic structures of the 3d-elements and their preferred coordination polyhedrons.

POSTER PRESENTATIONS

TERNARY COMPOUNDS OF THE AI-TI-Pt SYSTEM AND PHASE EQUILIBRIA WITH THEIR PARTICIPATION

<u>K.Ye. Korniyenko</u>, V.G. Khoruzhaya, O.V. Zaikina, and T.Ya. Velikanova I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine korniyenkok@ukr.net

In the Al–Ti–Pt system, the existence of three ternary compounds at 950°C, namely τ_1 (Al₆₇Ti₂₆Pt₇) with a structure of type Cu₃Au, τ_2 (Al₅₀Ti₂₅Pt₂₅) – Th₆Mn₂₃₊₁-type, and τ_3 (Al₄₂Ti₄₄Pt₁₄ ÷ Al_{43.2}Ti_{37.8}Pt_{19.0}) – MgZn₂-type, has been established [1-3]. In the range 0-50 at.% Pt at 1100°C, in addition to the above-mentioned phases, for the first time seven more ternary phases were found [4]. For three of them the type of crystal structure was established: τ_4 (Al_{33.3}Ti_{33.3}Pt_{33.3}) – ZrBeSi-type, τ_5 (Al₁₄Ti₅₈Pt₂₈ ÷ Al₂₁Ti₆₃Pt₁₆) – FeCr-type, and τ_6 (Al₂₅Ti₅₅Pt₂₀) – Au₄Al-type [5,6].

We have studied the phase equilibria in the Al–Ti–Pt system (0-50 at.% Pt) experimentally and constructed the phase diagram, represented by the liquidus and solidus surface projections, melting diagram and reaction scheme, as well as by a series of vertical sections. The existence of a continuous series of solid solutions between the isostructural (CsCl-type) phases based on TiPt and the high-temperature modification of AlPt (β_0 phase) allows triangulating this ternary system along the isopleth at 50 at.% Pt. The alloys were produced by arc or levitation melting and studied by metallography, scanning electron microscopy, electron microprobe and differential thermal analyses, and X-ray diffraction.

According to the results, 10 of the 11 ternary phases (the exception being the phase labeled τ_{10}) take part in the equilibria observed during alloy crystallization. The existence of a new ternary phase, τ_{11} , was established, but its structure was not determined. There are 31 isothermal planes on the solidus surface, formed with participation of ternary compounds and solid solutions based on binary compounds existing in the boundary systems. The liquidus surface consists of 23 primary crystallization fields, corresponding to the ternary phases $\tau_1 \div \tau_9$ and τ_{11} , binary phases formed in the boundary systems and to solid solutions based on the elements. The highest temperatures on the solidus and liquidus surfaces correspond to the congruent melting of TiPt (1830°C), and the lowest ones to the eutectic in the binary Al-Pt system (655°C). It was established that the ternary compounds τ_3 , τ_4 , and τ_8 form congruently with participation of the liquid phase, and the phases τ_1 , τ_2 , τ_5 , τ_6 , τ_7 , τ_9 , and τ_{11} by peritectic reactions. 31 four-phase and 28 three-phase invariant equilibria with participation of the liquid phase exist at temperatures from 1410 to 660°C. Vertical temperature-composition sections along the isopleths at 7, 25 and 35±1 at.% Pt were constructed. The congruent crystallization of the phases τ_3 , τ_4 , and τ_8 , and the incongruent one of the phases τ_2 and τ_5 , were confirmed unambiguously.

- [1] J.J. Ding, P. Rogl, B. Chevalier, J. Etourneau, Intermetallics 8 (2000) 1377-1384.
- [2] X. Yan, A. Grytsiv, P. Rogl, *et al.*, *Intermetallics* 17 (2009) 336-342.
- [3] A. Grytsiv, P. Rogl, H. Schmidt, et al., Intermetallics 12 (2004) 563-577.
- [4] O.V. Zaikina, V.G. Khorujaya, D. Pavlyuchkov, et al., J. Alloys Compd. 509 (2011) 7565-7571.
- [5] O. Zaikina, D. Pavlyuchkov, V. Khorujaya, et al., Powder Diffr. 23 (2008) 360-362.
- [6] S. Samuha, D. Pavlyuchkov, O.V. Zaikina, et al., J. Alloys Compd. 621 (2015) 47-52.

ON THE TRANSFORMATION IN ZrNi

O.L. Semenova¹ and V.I. Ivashchenko² ¹ Department of Physical Chemistry of Inorganic Materials, I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine olenasemenova45@gmail.com ² Department of Refractory Materials, I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine ivashchenko@icnanotox.org

The absence of a solid-state transformation in the ZrNi compound distinguishes it from the other binary nickelides formed with the participation of metals belonging to the same group of the Periodic Table, *i.e.* titanium and hafnium. Both TiNi and HfNi crystallize at high temperatures with the cubic CsCl-type structure. TiNi undergoes a martensitic transformation at 83°C into a monoclinic phase, whereas HfNi transforms at 1150°C into an orthorhombic CrB-type phase [1,2]. Zirconium is the metallochemical analogue of titanium and hafnium, but as it follows from literature data on the Ni–Zr system, the ZrNi compound retains the CrB-type structure in a wide temperature range [3-5]. To our knowledge, there are no works devoted to the study of a polymorphic transformation in ZrNi. Direct evidence of a high-temperature modification of ZrNi is difficult to obtain, because of the lack of noticeable solubility of the components in ZrNi, according to the phase diagram [3-5].

For the Ni–Zr system, we investigated the phase equilibria near the equiatomic composition, and the results point to the appearance of a phase with cubic crystal structure close to the solidus temperature. This indicates the possible formation of a high-temperature CsCl-type modification of ZrNi. To investigate the phase transformations in ZrNi, we calculated the enthalpies of formation of CrB- and CsCl-type ZrNi at 0 K, as a function of pressure, using a first-principles approach. It was found that a first-order phase transition from the CrB-type Structure to the CsCl-type structure takes place at 64.6 GPa, which indicates that the CrB-type ZrNi phase is unstable under extreme conditions. This enables us to suppose that a similar phase transition can take place at high temperature, as suggested by our experimental investigations.

- [1] V.G. Pushin, V.V. Kondratiev, V.N. Khachin, *Izv. VUZ, Fiz.* 5 (1985) 5-19.
- [2] V.N. Yeremenko, E.L. Semenova, L.A. Tretyachenko, V.M. Petyukh, J. Alloys Compd. 191 (1993) 117-119.
- [3] M.E. Kirkpatrick, W.L. Larsen, ASM Trans. Q. 54 (1961) 580-590.
- [4] H. Okamoto, J. Phase Equilib. Diffus. 28 (2007) 409. DOI: 10.1007/s11669-007-9120-z.
- [5] N. Bochvar, O. Abdulov, T. Dobatkina, M. Kareva, O. Semenova, In: G. Effenberg (Ed.), *Materials Science International*, Eureka, Stuttgart, 2015. Document ID: 20.11406.1.2.

<u>M. Konyk</u>¹, L. Romaka¹, V.V. Romaka^{2,3}, Yu. Stadnyk¹, P. Demchenko¹, and A. Horyn¹ ¹ Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Institute for Solid State Research, IFW-Dresden, Helmholtzstr. 20, 01069 Dresden, Germany ³ Lviv Polytechnic National University, Ustyyanovycha St. 5, 79013 Lviv, Ukraine mariya.konyk@lnu.edu.ua

Intermetallics with rare-earth metals (*R*), transition elements and germanium are of great interest, due to the large variety of their structural and physical properties. The Cr-containing ternary systems with rare-earth metals and germanium are not yet completely studied; a phase equilibrium diagram has already been established for Y at 600°C [1]. Two series of isotypic compounds, RCr_6Ge_6 (MgFe₆Ge₆ structure type) [2] and $RCr_{0.3}Ge_2$ (CeNiSi₂ structure type) [3] have been reported. The aim of our work was the complete investigation of the Er–Cr–Ge system at 800°C.

The samples were prepared by direct arc melting of the elements, and were annealed at 800°C in evacuated quartz tubes for 720 h, after which they were quenched in ice water. The annealed samples were examined by X-ray powder diffraction and electron probe microanalysis. The crystal structures of the ternary compounds were studied by powder X-ray diffraction (STOE STADI P diffractometer, Cu $K\alpha_1$ radiation).

Four compounds were confirmed in the Cr–Ge binary system: $Cr_{11}Ge_{19}$ ($Mn_{11}Si_{19}$ -type), CrGe (FeSi-type), $Cr_{11}Ge_8$ ($Cr_{11}Ge_8$ -type), and Cr_3Ge (Cr_3Si -type). In the Er–Ge system, the ErGe_{2.83} (DyGe_3-type), Er_2Ge_5 (Er_2Ge_5 -type), $ErGe_{1.83}$ (DyGe_{1.85}-type), $ErGe_{1.5}$ (AlB₂-type), Er_3Ge_4 (Er_3Ge_4 -type), ErGe (CrB-type), $Er_{11}Ge_{10}$ (Ho₁₁Ge₁₀-type), Er_5Ge_4 (Sm₅Ge₄-type), and Er_5Ge_3 (Mn₅Si_3-type) binaries were confirmed. The binary germanide Cr_5Ge_3 (W_5Si_3 -type) was not observed at the temperature of annealing. The sample of this composition contained two binaries in equilibrium: Cr_3Ge and $Cr_{11}Ge_8$. The Cr_5Ge_3 phase is stable only at higher temperatures [4]. Under the conditions used here, the solubility of the third component in the binary phases was less than 1-2 at.%.

The interaction of the components in the Er–Cr–Ge system at 800°C results in the formation of two ternary compounds: ErCr₆Ge₆ (MgFe₆Ge₆ type, space group *P6/mmm*, Pearson symbol *hP*13, *a* = 5.15149(3), *c* = 8.26250(7) Å; $R_{\text{Bragg}} = 0.0493$, $R_F = 0.0574$) and ErCr_{0.28}Ge₂ (CeNiSi₂ type, space group *Cmcm*, Pearson symbol *oS*16, *a* = 4.10271(5), *b* = 15.6652(1), *c* = 3.99017(4) Å; $R_{\text{Bragg}} = 0.0473$, $R_F = 0.0433$). The ErCr_{1-x}Ge₂ compound is characterized by a homogeneity range of $0.62 \le x \le 0.72$, which was confirmed by X-ray diffraction and EPMA data. Differential thermal analysis showed that the ErCr₆Ge₆ compound is stable up to ~850°C.

An analysis of the results showed that the reduced number of ternary phases formed in the Er–Cr–Ge system does not differ from the related Y–Cr–Ge system [5]; both systems are characterized by the formation of RCr_6Ge_6 and $RCr_{1-x}Ge_2$ ternary compounds. According to literature data, isotypic compounds RCr_6Ge_6 and $RCr_{1-x}Ge_2$ also exist with other heavy rare earths (R = Gd, Tb, Dy, Ho).

- [1] O.I. Bodak, E.I. Gladyshevskii, *Rare-Earth Metal Ternary Systems*, Lvov, Vyshcha Shkola, 1985, 328 p. (in Russian).
- [2] J.H.V.J. Brabers, K.H.J. Buschow, F.R. de Boer, J. Alloys Compd. 205 (1994) 77-80.
- [3] H. Bie, A. Tkachuk, A. Mar, J. Solid State Chem. 182(1) (2009) 122-128.
- [4] I. Jandl, K.W. Richter, J. Alloys Compd. 500 (2010) L6-L8.
- [5] M. Konyk, L. Romaka, L. Orovčik, V.V. Romaka, Yu. Stadnyk, Visn. Lviv. Univ., Ser. Khim. 60(1) (2019) 38-47.

INTERACTION OF THE COMPONENTS IN THE Ho-{Fe,Co}-Sn TERNARY SYSTEMS

I. Romaniv¹, L. Romaka¹, V.V. Romaka^{2,3}, Yu. Stadnyk¹, and M. Konyk¹

¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

² Department of Materials Engineering and Applied Physics, Lviv Polytechnic National University, Ustyyanovycha St. 5, 79013 Lviv, Ukraine

³ Institute for Solid State Research, IFW-Dresden, Helmholtzstr. 20, 01069 Dresden, Germany ivona6250@gmail.com

Studies of the phase diagrams of metallic systems provide useful information about the interaction of the elements, temperature and composition stability of the intermediate phases. The interaction of the components in the Ho–Fe–Sn and Ho–Co–Sn ternary systems was studied over the whole concentration range, using X-ray diffraction, metallography and electron microprobe analysis. Isothermals sections of the phase diagrams of the Ho–Fe–Sn and Ho–Co–Sn systems were constructed at 670 K and 770 K, respectively. The samples for the investigation were prepared by direct twofold arc melting of the constituent elements under high-purity Ti-gettered argon atmosphere on a water-cooled copper crucible. The alloys were then annealed at 770 K (Ho–Co–Sn system, for 8 weeks) and 670 K (Ho–Fe–Sn system, for 4 weeks) in evacuated quartz glass tubes. At the end the tubes were quenched in cold water.

Ho–Fe–Sn. The interaction of the components in the Ho–Fe–Sn system at 670 K, according to X-ray phase and electron microprobe analyses, results in the existence of one ternary compound, HoFe₆Sn₆ with YCo₆Ge₆-type structure (space group *P6/mmm*, a = 0.5495(3), c = 0.4461(3) nm). An interstitial-type solid solution HoFe_xSn₂ (up to 8 at.% Sn), based on the HoSn₂ (ZrSi₂ structure type) binary compound, was also found. The solubility of Sn in the HoFe₂ binary (MgCu₂-type) extends up to 5 at.%.

Ho–Co–Sn. At the temperature of investigation, 770 K, the Ho–Co–Sn system is characterized by the existence of eight ternary compounds: Ho₆Co₂Sn (Ho₆Co₂Ga-type), Ho₃Co₈Sn₄ (Lu₃Co_{7.77}Sn₄-type), HoCoSn (TiNiSi-type), Ho₃Co₆Sn₅ (Dy₃Co₆Sn₅-type), Ho₁₁₇Co_{57.3}Sn_{111.5} (Dy₁₁₇Co₅₇Sn₁₁₂-type), HoCo₆Sn₆ (YCo₆Ge₆-type), Ho₅Co₆Sn₁₈ (Er₄Rh₆Sn₁₉-type), and Ho₇Co₆Sn₂₃ (Ho₇Co₆Sn₂₃-type). According to the XRD and EPM analyses the Ho₃Co₈Sn₄ compound has a small homogeneity range along the isoconcentrate of Ho up to 4 at.% Sn. The formation of an interstitial-type solid solution HoCo_xSn₂, based on the HoSn₂ (ZrSi₂-type) binary compound, was found up to 8 at.% Co.

The studies showed that substitution of Co for Fe leads to more complex phase relations and a higher number of ternary compounds in the Ho–Co–Sn system. Only compounds with stoichiometry HoM_6Sn_6 (YCo₆Ge₆-type) are formed in both systems.

INVESTIGATION OF THE La-Cu-Al SYSTEM (0-25 AT.% La) AT 870 K

M. Fedyna¹, A. Popovych², and <u>B. Stelmakhovych²</u>

¹ Department of Chemistry, National University of Forest and Wood Technology of Ukraine, Chuprynky St. 103, 79057 Lviv, Ukraine, fmf@ua.fm

² Department of Analytical Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine, bstelmakhovych@gmail.com

The ternary system La–Cu–Al has been investigated by means of X-ray diffraction in the region up to 25 at.% La. The isothermal section of the phase equilibria diagram has been mapped at the temperature of 870 K.

48 ternary alloys with a mass of ~1 g were synthesized by arc-melting on a cooled copper hearth under purified argon, using a tungsten electrode. Metals of the following purity were used: La 99.5 wt.%, Cu 99.99 wt.%, Al 99.9 wt.%. Titanium sponge was used as a getter. The samples were annealed at 870 K for 900 h, with subsequent water-quenching. Phase analysis was performed using powder X-ray diffraction patterns recorded on DRON-3M and DRON-2.0 diffractometers (Cu K α and Fe K α radiation, respectively). All the calculations were performed using WinCSD software [1].

At the investigated temperature copper dissolves up to 18 at.% aluminum, whereas the latter dissolves nearly 2 at.% copper. The existence of four previously known phases in the binary Cu–Al system was confirmed: β -phase (W-type structure, space group (SG) *Im-3m*, Pearson symbol (PS) *cI*2), γ -phase (Cu₉Al₄-type structure, SG *P*-43*m*, PS *cP*52), η -phase (CuAl-type structure, SG *C2/m*, PS *mS*20), and θ -phase (CuAl₂-type structure, SG *I4/mcm*, PS *tI*12). The existence of three previously reported binary compounds in the La–Al system was confirmed: La₃Al₁₁ (own structure type, SG *Immm*, PS *oI*28), LaAl₃ (Ni₃Sn-type structure, SG *P*6₃/*mmc*, PS *hP*8), and LaAl₂ (Cu₂Mg-type structure, SG *Fd-3m*, PS *cF*24). Two compounds form in the binary La–Cu system: LaCu₆ (ht) (CeCu₆-type structure, SG *Pnma*, PS *oP*28) and LaCu₅ (CaCu₅-type structure, SG *P6/mmm*, PS *hP*6). The latter dissolves up to 47 at.% Al. The lattice parameters for the limiting composition of the solid solution, LaCu_{2.2}Al_{2.8}, were refined as *a* = 0.54123(7) nm, *c* = 0.41490(8) nm.

Crystallographic data for the ternary compounds found in the La–Cu–Al system at 870 K are presented in the table below.

Phase composition	ST	SG	PS	Lattice parameters, nm		
i nase composition				а	С	
LaCu _{6.0-11.2} Al _{7.0-2.8}	NaZn ₁₃	Fm-3c	<i>cF</i> 112	1.1944(2)-1.17738(6)	_	
LaCu _{4.9-3.1} Al _{7.1-8.9}	ThMn ₁₂	I4/mmm	<i>tI</i> 26	0.88816(9)-0.8884(2)	0.51772(6)-0.5175(1)	
LaCu _{0.7-1.4} Al _{3.3-2.6}	BaAl ₄	I4/mmm	<i>tI</i> 10	0.43194(2)-0.42958(2)	1.09050(7)-1.06898(7)	

Table Crystallographic characteristics of the ternary phases of the La–Cu–Al system.

The compositions of the compounds with $NaZn_{13}$ - and $BaAl_4$ -type structures are in good correlation with the results previously reported in [2]. According to our investigation, the ternary compound with $ThMn_{12}$ -type structure forms at a slightly higher copper content and is characterized by a small homogeneity range.

[1] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.

[2] I. Yunusov, I.N. Ganiev, Izv. Akad. Nauk SSSR, Met. 2 (1990) 215-217.

FORMATION OF THERMOELECTRIC HALF-HEUSLER PHASES IN THE {Y,Tm}–Ni–Sb TERNARY SYSTEMS

L. Romaka¹, V.V. Romaka^{2,3}, Yu. Stadnyk¹, and A. Horyn¹

 ¹ Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ² Lviv Polytechnic National University, Ustyyanovycha St. 5, 79013 Lviv, Ukraine
 ³ Institute for Solid State Research, IFW-Dresden, Helmholtzstr. 20, 01069 Dresden, Germany lyubov.romaka@lnu.edu.ua

Half-Heusler compounds with semiconducting properties have proven remarkably high efficiency in the thermoelectric conversion of (waste) heat into electricity. The thermoelectric properties of half-Heusler compounds strongly depend on the heat treatment, impurities, and the presence of structural disorder. The half-Heusler *R*NiSb phases (R = rare-earths) are good candidates for high-efficiency *p*-type thermoelectric materials. Recent investigations of (Gd,Lu)NiSb half-Heuslers [1] revealed off-stoichiometry, which had a noticeable impact on their thermoelectric properties. In order to check the constitution of other *R*NiSb phases, the corresponding systems with Y and Tm were examined.

The phase equilibria in the {Y,Tm}–Ni–Sb ternary systems were studied at 870 K in the whole concentration range by means of X-ray powder diffraction (XPD) and electron probe microanalysis of binary and ternary alloys. The samples were prepared by arc-melting of the constituent elements under purified, Ti-gettered argon atmosphere, with a non-consumable tungsten electrode on a water-cooled copper hearth. To compensate for the evaporative losses of antimony during arc-melting, 3-5 wt.% excess Sb, depending on the composition, was added. The alloys were annealed at 870 K for 720 h in evacuated quartz ampoules, and finally quenched in cold water. The Y–Ni–Sb system is characterized by the existence of four ternary compounds: Y_5Ni_2Sb (Mo₅SiB₂-type), $Y_5Ni_xSb_{3-x}$ (Yb₅Sb₃-type), YNiSb (MgAgAs-type), and $Y_3Ni_6Sb_5$ (Y₃Ni₆Sb₅-type). The off-stoichiometry of the YNiSb half-Heusler phase was revealed by EPMA and confirmed by Rietveld refinement and DFT modeling.

The Tm–Ni–Sb system is characterized by the existence of two ternary antimonides at 870 K: Tm₅Ni₂Sb (Mo₅SiB₂-type) and TmNiSb (MgAgAs-type). The formation of a Tm₅Ni_xSb_{3-x} substitutional solid solution based on Tm₅Sb₃ (Yb₅Sb₃-type) up to ~6 at.% Ni was observed. In contrast to other isotypic *R*NiSb (R = Gd, Lu) compounds [1], which are characterized by deviations from the equiatomic composition toward lower Ni content, the TmNiSb antimonide is a fully stoichiometric compound.

Electrical transport studies (resistivity and Seebeck coefficient) of the YNiSb and TmNiSb half-Heusler compounds were performed in the temperature range 80-380 K and showed that both compounds exhibit hole-type conductivity and are doped and compensated semiconductors. Band structure calculations performed for the off-stoichiometric model of p-YNiSb are in a good agreement with the results of the electrical transport studies.

[1] V.V. Romaka, L. Romaka, A. Horyn, P. Rogl, Yu. Stadnyk, N. Melnychenko, M. Orlovskyy, V. Krayovskyy, *J. Solid State Chem.* 239 (2016) 145-152.

PHASE EQUILIBRIA IN THE QUASI-TERNARY SYSTEMS $A^{I}_{2}X$ -PbX- $D^{IV}X_{2}$ (A^{I} - Cu, Ag; D^{IV} - Si, Ge, Sn; X - S, Se) AT 300 K

Y.M. Kogut, L.V. Piskach, I.D. Olekseyuk, and O.V. Parasyuk

Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine luchanyn@yahoo.com

Investigation of the quasi-ternary systems $A_2^{I}X-B^{II}X-D^{IV}X_2$ (A = Cu, Ag Tl; $B^{II} = Zn$, Cd, Hg; $D^{IV} = Si$, Ge, Sn; X = S, Se) revealed many new semiconductor phases with promising physical properties. One of the ways to modify the composition is to replace the double-charged element by lead, which produced a group of quaternary compounds of a new type, Ag_{0.5}Pb_{1.75}GeS₄. These are likely to form large solid solution ranges, which would allow modifying the physical properties by changing the composition.

Isothermal sections of 12 quasi-ternary systems $A_2^I X$ -PbX- $D^{IV} X_2$ were investigated by XRD (DRON 4-13 diffractometer, Cu K α radiation). The sections are presented at room temperature, due to the existence in most of the systems of compounds of the argyrodite Ag₈GeS₆ family, which have low-temperature (below 500 K) polymorphic transitions and relatively extended solid solutions at 670 K and cannot be quenched from this temperature.

The interaction of the components in the $Cu_2S-PbS-SiS_2$ system yielded the quaternary sulfides Cu_2PbSiS_4 and $Cu_4PbSi_2S_7$. The existence of a compound in the $Cu_2Se-PbSe-SiSe_2$ system was known, and its composition was ascertained as $CuPb_{1.5}SiSe_4$. The isothermal section of the $Ag_2S-PbS-SiS_2$ system contains a new compound of approximate composition $Ag_{1.43}PbSi_{1.14}S_4$. The existence of a quaternary compound of $Ag_{0.5}Pb_{1.75}SiSe_4$ was confirmed in the analogous selenide system.

The study of the copper-containing sections with germanium only revealed the known quaternary compound in the Cu₂S–PbS–GeS₂ system. Its composition was refined as Cu_{0.9}Pb_{1.55}GeS₄. The study of isothermal sections of the Ag₂X–PbX–GeX₂ systems found the known quaternary compounds Ag_{0.5}Pb_{1.75}GeS₄ and Ag_{0.5}Pb_{1.75}GeSe₄, and for the first time we obtained the Ag₂PbGeS₄ compound.

No quaternary compounds were found in the tin-containing systems. Four-phase fields exist in the selenide systems because the PbSe–SnSe₂ section is non-quasi-binary.

Thus, quaternary compounds exist in the majority of the considered quasi-ternary systems $A_2^I X - PbX - D^{IV}X_2$ (seven systems *vs*. five where no such compounds were found), with the number of compounds decreasing in the series $S \rightarrow Se$, $Ag \rightarrow Cu$, $Si \rightarrow Ge \rightarrow Sn$. We observed the formation of five quaternary compounds in the systems with silicon: $Cu_4PbSi_2S_7$, Cu_2PbSiS_4 (space group $P3_221$), $CuPb_{1.5}SiSe_4$ (SG *I*-43*d*), $Ag_{1.43}PbSi_{1.14}S_4$, $Ag_{0.5}Pb_{1.75}SiSe_4$ (SG *I*-43*d*), four compounds in the systems with germanium: $Cu_{0.9}Pb_{1.55}GeS_4$, $Ag_{0.5}Pb_{1.75}GeS_4$ (SG *I*-43*d*), $Ag_{2.2}PbGeS_4$ (SG *Ama2*), $Ag_{0.5}Pb_{1.75}GeSe_4$ (SG *I*-43*d*), but no quaternary tin-containing compounds.

The compositions of the quaternary compounds vary. The majority of the quaternary compounds are formed at 33.33 mol.% of the $D^{IV}X_2$ component. The largest number of compounds, five, are isostructural analogues of Ag_{0.5}Pb_{1.75}GeS₄ that crystallize in cubic symmetry, space group *I*-43*d*. The copper-containing compounds of this type have somewhat different stoichiometry. The compounds of the $A_2^I B^{II} D^{IV}X_4$ composition, which are very common in the analogous quasi-ternary systems with $B^{II} = Zn$, Cd, and Hg, were only found in two cases, Ag₂PbGeS₄ and Cu₂PbSiS₄.

THE PbS-In₂S₃-SiS₂ SYSTEM AT 770 K

<u>Kh.O. Melnychuk</u>, O.V. Smitiukh, O.V. Marchuk, and L.V. Piskach Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine Marchuk.Oleg@eenu.edu.ua

Modern scientific and technological progress is associated with the creation of new materials that have functionally controlled properties. Investigation of the relationship between composition, structure and properties of materials, as well as the establishment of the thermodynamic conditions for their existence, contribute to the development of materials science and semiconductor technologies.

The study of the PbS–In₂S₃–SiS₂ system (investigation of phase diagrams, crystal structures of the quaternary phases, and their physical properties) is part of a systematic study of the quasi-ternary chalcogenide systems PbX– $C^{III}_{2}X_{3}$ – $D^{IV}X_{2}$ (C^{III} = Ga, In; D^{IV} = Si, Ge; X = S, Se). At present, the gallium-containing systems are the most studied ones. They are characterized by the formation of quaternary chalcogenides with stoichiometric compositions, PbGa₂ $D^{IV}X_{6}$ and Pb₄Ga₄ $D^{IV}X_{12}$ [1,2], and promising non-linear optical properties. Materials based on these chalcogenides can be used in many fields, such as optical communication, laser surgery, molecular spectroscopy, *etc*.

The PbS–In₂S₃–SiS₂ system was studied on 50 alloys that were prepared by co-melting semiconductor-purity components in evacuated quartz containers. The synthesis was carried out in an MP-30 programmable muffle furnace. The maximum synthesis temperature was 1420 K; homogenizing annealing lasted 500 h at 770 K. The phase analysis was based on X-ray diffraction patterns recorded on a DRON 4-13 diffractometer in the 2θ range 10-80° (Cu K α radiation, scan step 0.05°, 4 s exposure at each point). Data processing utilized WinCSD software package [3].

The existence of two ternary compounds, $PbIn_2S_4$ (space group *Pnma* [4]) and Pb_2SiS_4 (space group $P2_1/c$ [5]), was confirmed in the system after annealing at 770 K. It was found that the $PbIn_2S_4$ – Pb_2SiS_4 system is a quasi-binary section of the quasi-ternary system PbS– In_2S_3 – SiS_2 . The solid solution range of the ternary phase Pb_2SiS_4 extends to a boundary composition of 30 mol.% $PbIn_2S_4$ at 770 K.

The performed research allows us to assert the formation of a new quaternary phase of approximate composition $Pb_{1.5}In_3SiS_8$ in the $PbIn_2S_4$ -SiS₂ section. The study of its crystal structure is the next stage of the study.

- Z.-Z. Luo, C.-S. Lin, H.-H. Cui, W.-L. Zhang, H. Zhang, H. Chen, Z.-Z. He, W.-D. Cheng, *Chem. Mater.* 27 (2015) 914-922.
- [2] Y.K. Chen, M.C. Chen, L.J. Zhou, L. Chen, L.M. Wu, *Inorg. Chem.* 52(15) (2013) 8334-8341.
- [3] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.
- [4] V. Krämer, K. Berroth, Mater. Res. Bull. 18 (1980) 299-308.
- [5] J.E. Iglesias, H. Steinfink, J. Solid State Chem. 6 (1973) 93-98.

MOLECULAR DYNAMICS SIMULATION OF SILICIDE FORMATION AT INTERLAYER BOUNDARIES IN THE Cu–Si SYSTEM

<u>V. Plechystyy</u>^{1,2}, I. Shtablavyi², S. Winczewski¹, K. Rybacki¹, S. Mudry², and J. Rybicki¹ ¹ Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza St. 11/12, 80-233 Gdansk, Poland ² Physics of Metals Department, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 8, 79005 Lviv, Ukraine

 $ihor. shtablavyi @ {\it lnu.edu.ua}$

The properties of metal silicides are of interest in a number of areas in applied science, including catalysis, high-temperature applications, and microelectronics. Some Cu silicides, in particular Cu₃Si, have shown potential as catalysts, with clear evidence that the oxidation of silicon is catalyzed by Cu₃Si, and some evidence that Cu₃Si serves as an efficient catalyst in other reactions. In microelectronics, the use of Cu metallization depends on the prevention of the formation of Cu silicides. When Cu is directly deposited onto Si crystals, Cu₃Si readily forms at moderate temperatures (*e.g.* 470 K). As reported, the reaction of Cu with Si results in the formation of Cu₃Si, which forms by diffusion of Cu atoms through the silicide toward the Cu₃Si–Si interface [1,2]. However, there are currently no detailed studies on the kinetics of the copper-silicon interaction at the atomic level.

In this work, a study of the formation of intermetallics on the interface of copper-silicon by molecular dynamics simulation has been carried out. The interaction of copper with silicon was investigated for different numbers of atomic layers of copper (2-10 ML) on the (111) silicon surface. Using the methods of geometric-statistical analysis, the mechanism of formation of the Cu_3Si intermetallic compound at the boundary between the phases was revealed.

- [1] A. Cros, M.O. Aboelfotoh, K.N. Tu, J. Appl. Phys. 67 (1990) 3328-3336.
- [2] S.Q. Hong, C.M. Comrie, S.W. Russell, J.W. Mayer, J. Appl. Phys. 70 (1991) 3655-3660.

PHASE EQUILIBRIA IN THE TERNARY Zr-Co-Sn SYSTEM

M.V. Bulanova, I.V. Fartushna, and K.A. Meleshevich

I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine juliefart81@gmail.com

Information on the phase equilibria in the ternary Zr–Co–Sn system is limited to the isothermal section at 497°C [1]. No experimental data on the crystallization of the alloys are available. Therefore, the goal of the present research was to study the phase equilibria in the Zr–Co–Sn system at crystallization over the concentration range up to 50 at.% Sn, using scanning electron microscopy (SEM), electron probe microanalysis (EPMA), differential thermal analysis (DTA), and X-ray diffraction (XRD).

The existence of two ternary compounds, $ZrCo_2Sn(\tau_1)$ (MnCu₂Al-type structure, *Fm*-3*m*, a = 6.234 Å) and ZrCoSn(τ_2) (ZrNiAl-type structure, *P*-62*m*, a = 7.133, c = 3.571 Å), so-called full-Heusler and half-Heusler phases, respectively, reported earlier in [2], was confirmed in our study. It was shown that at the solidus temperatures the Heusler phase (τ_1) has a wide homogeneity range, which extends from 44 to 50 at.% Co along the line 50Zr50Sn–Co. The homogeneity range of the half-Heusler phase (τ_2) does not exceed 1 at.%. Both ternary compounds melt congruently at about 1400°C.

In addition to τ_1 and τ_2 , in the investigated region of the Zr–Co–Sn system, one more ternary compound takes part in the phase equilibria, Zr₄CoSn (τ_3). In [1] the structure of this compound was found to be a superstructure of the Fe₂P-type structure, *P*-62*m* with the lattice parameters *a* = 7.971, *c* = 3.453 Å, and the composition was reported to be Zr₆Co_{1.65}Sn_{1.35}. It was shown by us that this compound melts incongruently at 1270°C and has a rather wide homogeneity range, which at the solidus temperatures extends from 11 to 20 at.% Sn.

Additionally, solid solutions based on the binary phases Zr_5Sn_{3+x} , Zr_2Co , $ZrCo_2$, $ZrCo_4$, Zr_2Co_{11} , and βCo_3Sn_2 , and on the chemical elements (βZr) and (αCo) take part in phase equilibria. Among the binary compounds, the Laves phase $ZrCo_2$ (MgCu₂ type structure, *Fd*-3*m*) has the widest homogeneity region at solidus temperatures and, according to the EPMA data, dissolves up to 15 at.% Sn. The Zr_5Sn_{3+x} phase (Mn₅Si₃ type structure, *P*6₃/*mcm*) also has a wide homogeneity region and dissolves up to 9 at.% Co. The homogeneity regions of the remaining phases are narrow.

The liquidus surface of the Zr–Co–Sn system is characterized by twelve areas of primary crystallization of the above phases, separated by the corresponding monovariant curves, and eleven four-phase invariant equilibria.

The solidus surface is characterized by the following three-phase fields: β + Zr₅Sn_{3+x} + τ_3 , β + Zr₂Co + τ_3 , τ_3 + Zr₂Co + ZrCo, τ_3 + Zr₅Sn_{3+x} + ZrCo, Zr₅Sn_{3+x} + ZrCo + ZrCo₂, Zr₅Sn_{3+x} + τ_1 + ZrCo₂, Zr₅Sn_{3+x} + τ_1 + τ_2 , τ_1 + ZrCo₂ + β Co₃Sn₂, (Co) + ZrCo₂ + β Co₃Sn₂, (Co) + ZrCo₂ + ZrCo₂ + ZrCo₄ + Zr₂Co₁₁, which result from invariant four-phase equilibria; seven are of the eutectic type (E) and four of the transition type (U).

- [1] Yu.V. Stadnyk, L.P. Romaka, V.K. Pecharskii, R.V. Skolozdra, *Inorg. Mater.* 31(11) (1995) 1290-1293.
- [2] R.V. Skolozdra, Yu.V. Stadnyk, E.E. Starodynova, Ukr. Fiz. Zh. 31(8) (1986) 1258-1262.

THE Nd-Si-Ge SYSTEM AT 870 K

Z. Shpyrka, O. Soludchyk, N. German, and V. Pavlyuk Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine z.shpyrka@gmail.com

The interaction of the components in the Nd–Si–Ge ternary system was investigated by X-ray diffraction and energy-dispersive X-ray spectroscopy in the whole concentration range, and the isothermal section of the phase diagram at 870 K was built.

The alloys were synthesized by arc melting of pure metals (all with stated purity better than 99.9 wt.%) in an arc furnace under argon atmosphere. The alloys were annealed at 870 K in evacuated quartz ampoules for 720 h, subsequently quenched in ice water, and then examined by powder X-ray diffraction (DRON-4.07 diffractometer, Fe $K\alpha$ radiation).

The existence of a continuous substitutional solid solution with Mn_5Si_3 -type structure $(Nd_5(Si,Ge)_3)$ was found. The solubility of germanium in the binary silicide Nd_5Si_4 (Zr_5Si_4 -type structure) is 0.20 at.part, and that in NdSi (FeB-type structure) is 0.10 at.part. The solubility of silicon in the binary germanide NdGe (CrB-type structure) is 0.20 at.part, and that in Nd₅Ge₄ (Sm₅Ge₄-type structure) is 0.05 at.part.

A continuous solid solution $NdSi_xGe_{2-x}$ between the binary disilicide and digermanide of neodymium, which crystallize in the related structure types α -ThSi₂ and α -GdSi₂, was observed in the Nd–Si–Ge system.

Within this solid solution there is a change in the symmetry of the crystal structure at the transition α -ThSi₂ $\leftrightarrow \alpha$ -GdSi₂. The number of atoms in the cell is the same. Similar solid solutions are formed in the *R*–Si–Ge systems where *R* = La, Ce, Pr, Sm, and Gd [1-5]. In the homogeneity region of the solid solutions *R*Si_xGe_{2-x}, when the composition is changed, continuous transitions of the tetragonal α -ThSi₂ structure into the orthorhombic α -GdSi₂ structure are observed. These solid solutions have wide areas of homogeneity, which are divided into two or three fields of existence of the orthorhombic and tetragonal structures.

No ternary compounds form in the Nd–Si–Ge system.

- [1] L.A. Muratova, Visn. Lviv. Univ., Ser. Khim. 16. (1974) 15-18 (in Ukrainian).
- [2] O.I. Bodak, L.A. Muratova, Vestn. Lvov. Univ., Ser. Khim. 21. (1979) 55-57 (in Russian).
- [3] Z. Shpyrka, J. Stepien-Damm, G. Kyrchiv, P. Starodub, Coll. Abstr. VII Int. Conf. Cryst. Chem. Intermet. Compd., Lviv, 1999, p. B21.
- [4] Z. Shpyrka, O. Bodak, O. Safiyanyk, J. Konzyk, B. Marciniak, *Coll. Abstr. XII Int. Sem. Phys. Chem. Solids.*, Lviv, 2006, p. 135.
- [5] Z.M. Shpyrka, S.Ya. Pukas, R.E. Gladyshevskii, *Coll. Abstr. XVII Conf. Inorg. Chem.*, Lviv, 2008, p. 228 (in Ukrainian).

P12

THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF THE In-Tb SYSTEM

V.S. Sudavtsova¹, <u>A.S. Dudnik¹</u>, V.G. Kudin², and N.V. Podoprigora¹

¹ I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine

² Taras Shevchenko National University of Kyiv, Volodymyrska St. 64, 01033 Kyiv, Ukraine sud.materials@ukr.net

Indium and indium alloys with *d*- and *f*-metals are used as fusible, heat-conducting semiconductor materials, as well as lead-free solders. Data on the thermodynamic properties of the various phases and, in particular, the liquid, are necessary for scientifically sound development of methods of obtaining said materials and alloys. The purpose of this study was to investigate the enthalpy of mixing of melts of the In–Tb system in the composition range $0 < x_{Tb} < 0.4$ at a temperature of 1625 ± 1 K.

Partial terbium and integral enthalpy of mixing of alloys of the In–Tb system, obtained at $T = 1625\pm1$ K, are shown in Fig. The parameters were approximated by polynomials by which the thermochemical properties at rounded concentrations were evaluated.

The first partial terbium and the minimal integral enthalpy of mixing of the In–Tb system are -145 ± 7 and -40.1 ± 0.2 kJ/mol, respectively. These parameters are similar to those previously established for liquid alloys of the In–La(Ce) systems, but differ slightly from those obtained for In–Eu(Yb). Based on this, it is possible to predict the thermochemical properties of the melts of In–*REM* systems that have not yet been fully investigated. It can be seen that this dependence is almost monotonous, due to the close values of the mole volumes and the electronegativities.



Fig. Partial and integral enthalpy of mixing of alloys of the In–Tb system at $T = 1625 \pm 1$ K.

The enthalpy of formation of the $TbIn_3$ compound, -44.6 kJ/mol, was determined. A comparison of this value with the enthalpy of mixing of a melt of the corresponding composition, shows that the former is more exothermic, as one would expect.

We have come to the conclusion that the activities of the components, and the entropy of mixing, will be similar to those characteristic of the melts of the systems In–La(Ce). This significantly expands the information on the nature of the interatomic interaction in the melts under consideration. Thermodynamic properties of alloys of binary Sn(Sb)–*REM* melts were compared. It was found that the interaction energy between the *p*-element and the *REM* increases in the following order: In–*REM* \rightarrow Sn–*REM* \rightarrow Sb–*REM*. This is due to the fact that antimony is the best electron acceptor.

THERMODYNAMIC PROPERTIES OF LIQUID ALLOYS OF THE Sn-Ho SYSTEM

V.S. Sudavtsova¹, M.O. Shevchenko¹, V.G. Kudin², and A.S. Kozorezov¹

¹ I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine

² Taras Shevchenko National University of Kyiv, Volodymyrska St. 64, 01033 Kyiv, Ukraine sud.materials@ukr.net

Alloys and intermetallics consisting of rare-earth metals and tin exhibit magnetic properties. To obtain such materials, it is important to know both the phase equilibria and the thermodynamic properties, because they are obtained by melting.

The phase equilibria in Sn–Ho alloys were studied by thermal and metallographic analysis. The existence of five intermetallic phases was established: Ho₅Sn₃, Ho₁₁Sn₁₀, HoSn₂, Ho₂Sn₅, and HoSn, the first of them being very refractory ($T_m = 2288$ K). In [1], partial and integral enthalpies of mixing of liquid alloys of this system were determined by calorimetry at 1473 K in the composition range $0 < x_{Ho} < 0.4$. It was established that the partial enthalpy of mixing of holmium has a complex character, and the value of ΔH at $x_{Ho} = 0.4$ equals -78.1 kJ/mol. In this paper, the enthalpy of mixing of melts of the Sn–Ho system in the entire concentration range at 1640 and 1870 K was investigated by the same method. It is seen from Fig. 1 that the minimum value of the integral enthalpy of mixing is -71.8±0.9 kJ/mol at $x_{Ho} = 0.5$. Comparison of the data obtained here with the indicated literature shows that there is qualitative agreement only for the integral enthalpy (ΔH).

Using own and literature data for melts and intermetallics of this system, we calculated the thermodynamic properties of alloys and compounds using the IAS model. Fig. 2 shows the enthalpy of formation of tin stannides (calculated and experimentally determined). It can be seen that the calculated and experimental data agree well. This supports the reliability of the enthalpies of Sn–Ho melt mixing obtained in this work.







 $\Delta_{f}H$, kJ/mole

Fig. 2. The enthalpy of formation of Ho stannides (calculated and experimental data).

[1] M.V. Bulanova, V.N Eremenko, V.M. Petjukh, V.R. Sidorko, J. Phase Equilib. 19 (1998) 136-141.

THE TERNARY SYSTEM V-Cu-Al AT 800°C

<u>N. Klymentiy</u>, S. Pukas, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine nastasia.klymentiy@lnu.edu.ua

The aim of our investigation was to construct the isothermal section of the phase diagram of the V–Cu–Al system at 800°C. The interaction of the components in the V–Cu–Al system at 600°C and 900°C has earlier been investigated in the whole concentration range [1,2]. No ternary phases were found. V₃Al was not observed by [1] and is not included in the phase equilibria in [1,2]. The phases V₅Al₈, VAl₃ and Cu₉Al₄ were found to exhibit significant solubility of the third component [2].

Alloys of the system V–Cu–Al were synthesized from the metals (purity for $V \ge 99.99$, $Cu \ge 99.99$, $Al \ge 99.998$ mass%) by arc melting in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere (using Ti as a getter). The ingots were annealed at 800°C under vacuum in quartz ampoules for one week and quenched in cold water. Phase and structural analyses were performed using X-ray powder diffraction data.

The isothermal section at 800°C of the phase diagram of the ternary system V–Cu–Al was constructed in the whole concentration range using X-ray powder diffraction data. The four ternary solid solutions with variable composition at 800°C exhibit the following homogeneity ranges: 10 at.% Cu for V_{1-x}Cu_xAl₃ (x = 0-0.40(3), TiAl₃ type), 6.5 at.% Cu for V_{5-x}Cu_xAl₈ (x = 0-0.85(3), Cu₅Zn₈ type), 8.9 at.% V for V_xCu_{1.7-x}Al (x = 0-0.24(2), Co_{1.75}Ge type), and 7.2 at.% for V_xCu_{9-x}Al₄ (x = 0-0.94(4), Cu₉Al₄ type). The table shows the unit-cell parameters as a function of the Cu or V content. In all cases the unit-cell parameters decrease with increasing Cu content and decreasing V content, in agreement with the difference between the atomic radii of V ($r_V = 1.34$ Å) and Cu ($r_{Cu} = 1.28$ Å).

Nominal composition	x	<i>a</i> , Å	<i>c</i> , Å	$V, Å^3$				
$V_{1,x}Cu_xAl_3, x = 0.0.40(3) \text{ (structure type TiAl_3)}$								
V ₂₅ Al ₇₅	0	3.777(1)	8.330(6)	118.56(1)				
V ₂₀ Cu ₅ Al ₇₅	0.2	3.767(2)	8.364(2)	118.06(5)				
$V_{15}Cu_{10}Al_{75}$	0.40	3.756(3)	8.367(8)	117.86(2)				
$V_{25}Cu_{10}Al_{65}$	0.40	3.754(2)	8.356(8)	117.80(2)				
$V_{5-x}Cu_xAl_8, x = 0.0.85(3)$ (structure type Cu_5Zn_8)								
V _{38.46} Al _{61.54}	0	9.207(2)	_	780.4(3)				
V ₃₆ Cu _{2.46} Al _{61.54}	0.33	9.199(3)	_	778.5(4)				
V _{33.3} Cu ₅ Al _{61.50}	0.65	9.191(3)	_	776.3(4)				
V ₃₃ Cu _{5.46} Al _{61.54}	0.85	9.189(2)	—	776.0(3)				
$V_x Cu_{1.7-x} Al, x = 0-0.24(2)$ (structure type $Co_{1.75} Ge$)								
Cu _{62.96} Al _{37.04}	0	4.1080(1)	5.0110(1)	73.26(3)				
$V_2Cu_{62}Al_{36}$	0.11	4.1095(6)	5.0285(8)	73.27(3)				
$V_4Cu_{60}Al_{36}$	0.11	4.1076(8)	5.0360(1)	73.28(2)				
$V_9Cu_{53}Al_{38}$	0.24	4.1086(6)	5.0351(1)	73.39(3)				
V_x Cu _{9-x} Al ₄ , $x = 0-0.94(4)$ (structure type Cu ₉ Al ₄)								
Cu _{69.23} Al _{30.77}	0	8.6940(1)	—	657.1(1)				
$V_2Cu_{65}Al_{33}$	0.24	8.7000(2)	—	658.6(2)				
$V_4Cu_{65}Al_{31}$	0.51	8.7020(2)	—	659.1(2)				
$V_4Cu_{63}Al_{33}$	0.48	8.7140(1)	—	661.6(1)				
V ₉ Cu ₅₅ Al ₃₆	0.94	8.7120(1)	—	661.6(1)				

[1] A.P. Prevarskyy, R.V. Skolozdra, Visn. Lviv. Univ., Ser. Khim. 12 (1971) 14-16.

[2] A. Raman, K. Schubert, Z. Metallkd. 56 (1965) 44-52.
THE La₂S₃-CoS-SiS₂ SYSTEM AT 770 K

 <u>Kh.O. Melnychuk</u>¹, O.V. Marchuk¹, I.D. Olekseyuk¹, L.D. Gulay², and M. Daszkiewicz³
 ¹ Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine
 ² Department of Ecology and Protection of the Environment, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine
 ³ Institute of Low Temperature and Structure Research, Polish Academy of Sciences,

P.O. Box 1410, 50-950 Wrocław 2, Poland

Melnychuk.Khrystyna@eenu.edu.ua

The basis for the development of materials science is the experimental data on the nature of formation, thermodynamic conditions of existence, and crystal structure of new compounds. Here we present the results of a study of the interaction of the components in the quasi-ternary La_2S_3 -CoS-SiS₂ system at 770 K and the crystal structure of the new quaternary compound $La_3Co_{0.5}SiS_7$.

An appropriate number of alloys was synthesized from high-purity elements in evacuated quartz containers in an MP-30 programmable electric muffle furnace. The maximum synthesis temperature was 1370 K, and homogenizing annealing was carried out for 500 h at 770 K.

Phase analysis using Powder Cell software [1] was performed on X-ray diffraction patterns recorded on a DRON 4-13 diffractometer. The isothermal section of the investigated system was constructed according to the results of the X-ray phase analysis (Fig.).



Fig. Isothermal section of the La_2S_3 -CoS-SiS₂ system at 770 K.

X-ray diffraction data for $La_3Co_{0.5}SiS_7$ was recorded on an X'calibur automatic single-crystal diffractometer (Mo *K* α radiation, graphite monochromator). The determination and refinement of the structure utilized SHELXL-2014 software [2].

found that We the structure of the La₃Co₀ ₅SiS₇ belongs compound to the structural type $La_3Mn_{0.5}SiS_7$ (space group P6₃, Pearson symbol hP23[3]). The compound crystallizes in hexagonal symmetry with the cell parameters a = 1.03121(8) nm and c = 0.57432(6) nm.

- [1] W. Kraus, G. Nolze, *Powder Cell for Windows (version 2.4)*, Federal Institute for Materials Research and Testing, Berlin, 1999.
- [2] G.M. Sheldrick, Acta Crystallogr., Sect. C: Struct. Chem. 71(1) (2015) 3-8.
- [3] G. Collin, P. Laruelle, C. R. Seances Acad. Sci., Ser. C 270 (1970) 410-412.

P16

PHASE EQUILIBRIA IN THE SYSTEM Cu2ZnGeSe4-Cu2CdGeSe4 AT 720 K

L. Marushko, I. Ivashchenko, and L. Piskach

Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine marushko.larissa@eenu.edu.ua

According to XRD results, a continuous solid solution series with tetragonal structure forms in the Cu₂ZnGeSe₄–Cu₂CdGeSe₄ system at 720 K, which represents an example of isovalent substitution. Cu₂ZnGeSe₄ and LT-Cu₂CdGeSe₄ crystallize in the stannite structure (space group *I*-42*m*), with the unit-cell parameters a = 0.5607, c = 1.1042 nm, and a = 0.5749, c = 1.1055 nm, respectively, which is in good agreement with the literature data [1,2]. The crystal structures of two compositions of the solid solution were refined, with the results presented in the Table and Fig. The lattice parameters of the Cu₂Zn_{1-x}Cd_xGeSe₄ solid solutions vary depending on the Zn/Cd ratio. The variation of the *c*-parameter shows deviation from linearity, with a maximum at $x \approx 0.7$ (70 mol.% Cu₂CdGeSe₄). However, the unit-cell volume is a linear function of Cd²⁺ (0.092 nm) for Zn²⁺ (0.074 nm) [3].

Table Results of the refinement of the crystal structure of the solid solution	utions
$Cu_2Zn_2 Cd_2 Ce_2 Cu_2Zn_2 Cd_2 Ce_2 Cu_2Zn_2 Cd_2 Ce_2 Cu_2 Cu_2 Cu_2 Cu_2 Cu_2 Cu_2 Cu_2 Cu$	

$Cu_2 \Sigma II_{0.5} Cu_{0.5} CeSe_4$ and $Cu_2 \Sigma II_{0.3} Cu_{0.7} CeSe_4$.						
Formula	$Cu_2Zn_{0.5}Cd_{0.5}GeSe_4$	$Cu_2Zn_{0.3}Cd_{0.7}GeSe_4$				
Formula units per unit cell	2	2				
Space group	I-42m	I-42m				
a (nm), c (nm)	0.56831(3), 1.10904(6)	0.56940(1), 1.11248(3)				
Unit-cell volume (nm ³)	0.35820(5)	0.36068(3)				
Number of atoms in the cell	16	16				
Density, calculated (g/cm ³)	5.6033(8)	5.6513(4)				
Absorption coefficient (1/cm)	519.46	556.43				
Radiation and wavelength	Cu 0.154185 nm	Cu 0.154185 nm				
Diffractometer	DRON 4-13	DRON 4-13				
Computation method	Full profile	Full profile				
Number of atomic positions	4	4				
Number of free parameters	9	9				
2θ , $\sin\theta/\lambda$ (max)	100.02; 0.497	100.02; 0.497				
$R_I; R_P$	0.0683; 0.1426	0.0782; 0.1092				
Texture axis; texture parameter	[011]; 2.49(9)	[110]; 1.31(4)				



 2Θ (degree) 2Θ (degree) **Fig.** Experimental and calculated diffraction patterns and their difference for the solid solutions 'Cu₂Zn_{0.5}Cd_{0.5}GeSe₄' and 'Cu₂Zn_{0.3}Cd_{0.7}GeSe₄'.

- [1] O.V. Parasyuk, L.D. Gulay, Ya.E. Romanyuk, L.V. Piskach, J. Alloys Compd. 329 (2001) 202-207.
- [2] L.D. Gulay, Ya.E. Romanyuk, O.V. Parasyuk, J. Alloys Compd. 347 (2002) 193-197.
- [3] N. Wiberg, *Lehrbuch der anorganischen Chemie*, Walter de Gruyter, Berlin, New York, 1995, pp. 1838-1841.

QUATERNARY COMPOUNDS PbGa₂ MX_6 (M = Si, Ge; X = S, Se)

L. Piskach, O. Tsisar, L. Marushko, V. Pankevych, and O. Parasyuk Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine lyuda0760@ukr.net

Quaternary compounds $PbGa_2MX_6$ (M = Si, Ge; X = S, Se) are among the most promising materials for non-linear optical devices in the mid-IR spectral region [1-3]. The development of the manufacture technology of high-quality crystals of these compounds requires the knowledge of the phase diagrams of the PbGa_2S(Se)_4-Si(Ge)S(Se)_2 systems.

The samples were synthesized by the single-temperature method, co-melting the elementary substances lead, gallium, germanium/silicon, and sulfur/selenium in evacuated quartz ampoules in a shaft-type furnace. The maximum synthesis temperature was 1120-1350 K, depending on the composition, with 200 h annealing at 670 K. The alloys were investigated by DTA (Paulik-Paulik-Erdey derivatograph, Pt/Pt-Rh thermocouple) and XRD (DRON 4-13 diffractometer, Cu Ka radiation).

The physico-chemical interaction of PbGa₂S(Se)₄ and GeS(Se)₂ was presented in [4]. The quaternary compounds PbGa₂GeS(Se)₆ melt congruently at 998 K and 960 K, respectively. The analogous silicon-containing compounds PbGa₂SiS(Se)₆ of the PbGa₂S(Se)₄–SiS(Se)₂ systems form incongruently in peritectic reactions $L + \alpha \leftrightarrow$ PbGa₂SiX₆ (α are the solid solutions of the ternary chalcogenides) at 975 K (PbGa₂SiS₆) and 936 K (PbGa₂SiS₆). Both phases have two polymorphous modifications, with phase transitions at 830 K (PbGa₂SiS₆) and 735 K (PbGa₂SiSe₆). The PbGa₂SiS₆ compound was observed for the first time [5,6].

The lattice parameters, assuming the orthorhombic space group Fdd2, are a = 4.5199(2), b = 0.72838(2), c = 1.16019(4) nm for PbGa₂GeS₆ [2], and a = 4.7147(5), b = 0.75775(6), c = 1.21648(9) nm for PbGa₂GeSe₆ [1]. PbGa₂SiSe₆ crystallizes in the monoclinic space group Cc with the unit cell parameters a = 0.7188(5), b = 2.3171(19), c = 0.7044(5) nm, $\beta = 116.25^{\circ}$ [1].

The $PbGa_2S(Se)_4$ -Si(Ge)S(Se)₂ sections are triangulating in the quasi-ternary systems PbS(Se)-Ga₂S(Se)₃-Si(Ge)S(Se)₂ (in the entire temperature range for the sulfur-containing systems, for the selenides below the temperatures of primary crystallization of the ternary selenide $PbGa_2Se_4$, due to the incongruent type of formation).

Analysis of the phase diagrams and of the properties of the complex chalcogenides shows that the most acceptable methods for the growth of single crystal are the melt methods, including the Bridgman-Stockbarger method. The congruent melting and narrow homogeneity ranges of the quaternary compounds PbGa₂GeS₆ and PbGa₂GeSe₆ make easy the selection of the method and conditions for crystal growth. Single crystals of 11 mm diameter and up to 50-55 mm length were obtained for the first time.

- [1] Z.-Z. Luo, C.-S. Lin, H.-H. Cui, et al., Chem. Mater. 27 (2015) 914-922.
- [2] A.O. Fedorchuk, O.V. Parasyuk, O. Cherniushok, et al., J. Alloys. Compd. 740 (2018) 294-304.
- [3] Y.-Z. Huang, H. Zhang, C.-S. Lin, et al., Cryst. Growth Des. 18 (2018) 1162-1167.
- [4] O.V. Parasyuk, O.I. Cherniushok, O.P. Vronska, et al., Proc. IX Int. Sci. Conf. RNAOPM'2018, Lutsk-Shatsk Lakes, 2018, p. 81.
- [5] O.V. Tsisar, L.V. Piskach, L.P. Marushko, et al., Proc. III Int. Sci. Conf. APFS'2019, Lutsk-Shatsk Lakes, 2019, p. 103-104.
- [6] O.V. Tsisar, L.V. Piskach, L.P. Marushko, et al., Proc. XX Int. Conf. Stud. PhD Stud. Modern Chemistry Problems, Kyiv, 2019, p. 83.

PHASE EQUILIBRIA IN THE TERNARY SYSTEM Gd-Ge-Sn at 600°C

<u>R. Dankevych</u>, Ya. Tokaychuk, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine roman.dankevych@gmail.com

70 two- and three-component alloys were synthesized from high-purity metals (Gd \geq 99.8 mass%; Ge \geq 99.99 mass%; Sn \geq 99.9 mass%) by arc melting under argon atmosphere, using a water-cooled copper hearth, a tungsten electrode and Ti sponges as a getter. The alloys were wrapped into tantalum foil, sealed in quartz ampoules under vacuum, annealed at 600°C for 1 month, and finally quenched into cold water. Phase analysis and structure refinements were performed using X-ray powder diffraction data collected at room temperature on diffractometers DRON-2.0M (Fe K α -radiation) and STOE Stadi P (Cu K α ₁-radiation). The profile and structural parameters were refined by the Rietveld method, using the FullProf Suite program package [1]. Some phase equilibria and the compositions of the phases were confirmed by local X-ray spectral analysis, performed on a raster electron microscope REMMA-102-02, equipped with an energy dispersion X-ray spectrometer EDAR.

The isothermal section of the phase diagram of the ternary system Gd–Ge–Sn at 600°C was constructed in the whole concentration range. The existence of 15 compounds at 600°C was confirmed in the boundary binary systems Dy–Ge and Dy–Sn. Between the isotypic Mn₅Si₃-type binary compounds Dy₅Ge₃ and Dy₅Sn₃, a continuous solid solution is formed. The other binary compounds do not dissolve noticeable amounts of the third component, except GdSn₃ and GdSn₂, which form solid solutions of substitution type up to 5 at.% Ge. Three ternary compounds exist in the system Gd–Ge–Sn at 600°C. The existence and crystal structures of Gd₂Ge_{2.94}Sn_{0.82} [2] and GdGeSn [3] were confirmed, and for the latter the homogeneity range at 600°C, GdGe_{1.00-0.75}Sn_{1.00-1.25}, was determined. A new ternary compound, Gd₂Ge_{3.85}Sn_{0.93}, was found. Crystallographic data for the ternary compounds in the system Gd–Ge–Sn are summarized in the Table. The structure types MoAlB, Nd₂Sn_{1.24}Ge_{3.55}, and Gd₂Ge_{2.94}Sn_{0.82} belong to the structures with trigonal-prismatic coordination of the small atoms and are built by the stacking of layers of trigonal prisms and planar square nets of atoms along the crystallographic direction [010].

Compound	Structure type	Pearson	Space	Unit-cell parameters, Å		
Compound		symbol	group	а	b	С
Gd ₂ Ge _{3.85} Sn _{0.93}	Nd ₂ Ge _{3.55} Sn _{1.24}	oS40	Cmcm	4.0434(6)	35.284(6)	4.1724(6)
Gd ₂ Ge _{2.94} Sn _{0.82}	Gd ₂ Ge _{2.94} Sn _{0.82}	oS32	Cmcm	4.2226(8)	30.451(6)	4.0003(7)
GdGe _{1.00-0.75} ×	MaAlD	oC12	Current	4.2982(4)-	16.4371(16)-	4.0935(4)-
$\times Sn_{1.00-1.25}$	MOAID	0512	Cmcm	4.3206(4)	16.4824(15)	4.1270(4)

Table Crystallographic data for the ternary compounds in the system Gd–Ge–Sn at 600°C.

- [1] J. Rodrigues-Carvajal, Commission on Powder Diffraction (IUCr), Newsletter 26 (2001) 12-19.
- [2] P.H. Tobash, S. Bobev, F. Ronning, J.D. Thompson, J.L. Sarrao, J. Alloys Compd. 488 (2009) 1511-517.
- [3] P.H. Tobash, J.J. Meyers, G. DiFilippo, S. Bobev, F. Ronning, J.D. Thompson, J.L. Sarrao, *Chem. Mater.* 20 (2008) 2151-2159.

ISOTHERMAL SECTIONS OF THE PHASE DIAGRAMS OF THE SYSTEMS Sm–B–Al AND B–Al–Ga AT 600°C

<u>T. Slivinskyi</u>^{1,2}, Ya. Tokaychuk¹, and R. Gladyshevskii¹ ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Scientific Consulting Company "Structure-Properties", Sakharova St. 33, 79026 Lviv, Ukraine taras.slivinskiy@gmail.com

During a systematic investigation of the interaction between the components in the quaternary system Sm–B–Al–Ga, the isothermal sections of the phase diagram of the ternary systems Sm–B–Al and B–Al–Ga at 600°C were constructed.

The samples were synthesized from bulk elements (\geq 99.8 mass%) by arc-melting under purified argon atmosphere, annealed at 600°C in quartz ampoules for 720 h under vacuum, and subsequently quenched in cold water. Phase and structure analyses were performed using X-ray powder diffraction data obtained on a diffractometer DRON-2.0M (Fe K α -radiation). The crystallographic and profile parameters were refined by the Rietveld method, using the program package FullProf Suite [1].

The isothermal section of the phase diagram of the ternary system Sm–B–Al at 600°C contains 12 single-phase, 29 two-phase and 13 three-phase fields. The highest numbers of equilibria (6) are formed with the phase SmB₄. The binary compounds of the systems Sm–B, Sm–Al and B–Al do not dissolve noticeable amounts of the third component. One ternary compound, Sm₃AlB_x with filled Cu₃Au-type structure, was found at 600°C.

The isothermal section of the phase diagram of the ternary system B–Al–Ga at 600°C contains 5 single-phase, 7 two-phase and 3 three-phase fields. The binary compounds of the systems B–Al, Al–Ga and B–Ga do not dissolve significant amounts of the third component, and no ternary compounds were found in this system at 600°C.



Fig. Isothermal sections of the phase diagram of the ternary systems Sm–B–Al and B–Al–Ga at 600°C.

[1] J. Rodrigues-Carvajal, Commission on Powder Diffraction (IUCr), Newsletter 26 (2001) 12-19.

PHASE EQUILIBRIA IN THE TIPb2Br5-KPb2Br5 SYSTEM

<u>S.I. Levkovets</u>, O.V. Smitiukh, B.A. Tataryn, and L.V. Piskach Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine ya.hhhggg@yandex.ua

Ternary lead-containing halides are promising materials for use as solid-state laser hosts, laser-cooling materials, scintillators, and γ -radiation detectors. Most studies have focused on the ternary halides APb_2X_5 (A = K, Rb; X = Cl, Br) for use in solid-state lasers [1-4]. TlPb₂Br₅ is a promising material for safe solid-state lasers and optical communication [5,6]. The study of the interaction in the TlPb₂Br₅–KPb₂Br₅ system is of interest in terms of finding complex phases with new sets of parameters.

The compounds KPb_2Br_5 and TlPb_2Br_5 form congruently at 655 and 668 K, respectively, the latter having a polymorphic transformation at 580 K. KPb_2Br_5 and LT-TlPb}_2Br_5 are isostructural and crystallize in monoclinic symmetry, space group $P2_1/c$.

The physico-chemical interactions in the $TlPb_2Br_5$ -KPb₂Br₅ system were studied on eleven alloys in the entire concentration range. The samples were synthesized by heating to 1070 K at the rate of 20 K/h. After 6 h exposure, the alloys were gradually cooled at the rate of 20 K/h to room temperature.

The obtained alloys were investigated by X-ray diffraction (DRON 4-13 powder diffractometer, Cu $K\alpha$ radiation) and differential thermal analysis (Paulik-Paulik-Erdey derivatograph, Pt/Pt-Rh thermocouple).

The TlPb₂Br₅–KPb₂Br₅ system belongs to Type III of the Roozeboom classification, with a minimum at 73 mol.% KPb₂Br₅ and 645 K. According to XRD data, a continuous solid solutions series is formed in the system. The unit cell parameters, except the parameter a, gradually increase from TlPb₂Br₅ to KPb₂Br₅.

The conditions for growth of single crystals of TlPb₂Br₅, Tl_{0.5}K_{0.5}Pb₂Br₅, and KPb₂Br₅ were selected taking into account their physico-chemical properties and crystallization characteristics from the analysis of the obtained phase diagram. The directional crystallization method with a Bridgman-Stockbarger set-up was used. 20 g-batches were prepared from appropriate amounts of binary bromides, and loaded into quartz ampoules that were evacuated and sealed. After the preliminary synthesis, the obtained alloys were ground into powder and loaded into quartz ampoules with pear-shaped bottom. The temperature in the upper zone was 710 K, and the lower zone was held at 570 K. The furnace gradient at the solid-melt interface was 12 K/cm. Compact single-crystalline samples were obtained, which varied in color from light gray (TlPb₂Br₅) to pale green (KPb₂Br₅).

- [1] L. Isaenko, A. Yelisseyev, A. Tkachuk, et al., Mater. Sci. Eng. B 81 (2001) 188-190.
- [2] K. Rademaker, F.W. Krupke, H.R. Page, et al., J. Opt. Soc. Am. B 21 (2004) 2117-2129.
- [3] U.N. Roy, R.H. Hawrami, Y. Cui, et al., Appl. Phys. Lett. 86 (2005) 151911.
- [4] A.Y. Tarasova, L. I. Isaenko, V. G. Kesler, et al., J. Phys. Chem. Solids 73 (2012) 674-682.
- [5] P. Demchenko, O.Y. Khyzhun, P.M. Fochuk, et al., Opt. Mater. 49 (2015) 94-99.
- [6] S.B. Trivedi, U. Hömmerich, A.A. Kabir, A.G. Bluiett, *Proc. SPIE 10981, Laser Technology for Defense and Security XV*, 1098105. Doi.org/10.1117/12.2521674.

PHASE CONSTITUENTS OF Hf–Rh–Ir ALLOYS IN AS-CAST STATE AND ANNEALED AT SUBSOLIDUS TEMPERATURES

L.S. Kriklya, K.Ye. Korniyenko, and V.G. Khoruzhaya

I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine lkriklya2017@ukr.net

The investigation of the Hf–Rh–Ir system was started in connection with a study of the phase equilibria in quaternary systems of group IV transition metals with refractory platinum group metals. This system is a boundary system of the quaternary Hf–Ru–Rh–Ir system and there is no information about experimental studies in the literature. We have previously constructed the other boundary ternary systems [1-3]. Hafnium alloys with these metals are of interest both from a scientific point of view and because of their possible use as heat-resistant structural materials, catalysts, hydrogen adsorbents, for coating of gas turbine parts, and in semiconductor technology.

The alloys of the Hf–Rh–Ir system were prepared from the components by arc melting, and investigated, in the as-cast state and annealed at subsolidus temperatures, by differential thermal (DTA) and electron microprobe (EMPA) analyses, light optical microscopy (LOM), X-ray diffraction (XRD), and the Pirani-Alterthum melting point determination technique.

It was found that continuous series of solid solutions exist between the isostructural chemical elements (Rh and Ir), as well as between the isostructural phases based on the compounds HfRh₃ and HfIr₃ (AuCu₃-type structure, ε phase), high-temperature modifications of HfRh and HfIr (CsCl-type, δ phase), and Hf₂Rh and Hf₂Ir (Ti₂Ni-type, γ phase). Ternary compounds were not found. The surfaces of primary crystallization of the continuous series of the solid solutions (<Rh, Ir>, ε , δ , and γ phase), β -hafnium solid solution, and phases based on Hf₃Rh₅ (Ge₃Rh₅-type structure, θ phase) and Hf₅Ir₃ (Mn₅Si₃-type, η phase), form the liquidus surface of the Hf–Rh–Ir system. The δ and ε phases have the largest liquidus surface area, and the smallest liquidus surfaces correspond to the θ and η phases.

Several congruent processes exist in the Hf–Rh–Ir system. Three of them, namely $L \rightleftharpoons \varepsilon + \langle Rh, Ir \rangle$, $L \rightleftharpoons \delta + \varepsilon$ and $L \rightleftharpoons \gamma + \langle \beta - Hf \rangle$, occur along monovariant curves that originate from the boundary Hf–Ir system. Others, in particular $L \rightleftharpoons \varepsilon + \theta$ and $L \rightleftharpoons \delta + \gamma$, start at *U*-type points and arrive to the Hf–Rh system. The incongruent processes $L + \delta \rightleftharpoons \theta$, $L + \delta \rightleftharpoons \eta$ and $L + \eta \rightleftharpoons \gamma$ are directed toward the ternary system from the boundary Hf–Rh and Hf–Ir systems.

The solidus surface of the system, besides the seven single-phase surfaces corresponding to <Rh, Ir>, < β -Hf>, the ε , δ , θ , η , and γ phases, is formed by two isothermal planes, $\delta\theta\varepsilon$ and $\delta\gamma\eta$, which correspond to invariant four-phase equilibria of the transition type with participation of liquid: $L_{U1} + \delta \rightleftharpoons \varepsilon + \theta$ and $L_{U2} + \eta \rightleftharpoons \delta + \gamma$, as well as by the linear surfaces <Rh, Ir> ε , $\delta\varepsilon$, $\theta\varepsilon$, $\delta\theta$, $\eta\delta$, $\delta\gamma$, $\eta\gamma$, and <Hf> γ . These surfaces limit the corresponding two-phase volumes. The highest temperature on the liquidus and solidus surfaces is 2470°C, corresponding to congruent melting of the HfIr₃ phase, and the lowest one (1350°C) corresponds to the eutectic process $L \rightleftharpoons \gamma + <\beta$ -Hf> in the Hf–Rh system.

- [1] V.N. Eremenko, L.S. Kriklya, V.G. Khoruzhaya, Sov. Powder Metall. Met. Ceram. 31 (1992) 339-343.
- [2] L.S. Kriklya, K.Ye. Korniyenko, V.G. Khoruzhaya, et al., Powder Metall. Met. Ceram. 55 (2016) 201-209.
- [3] L.S. Kriklya, K.Ye. Korniyenko, V.G. Khoruzhaya, Coll. Abstr. 6 Int. Samsonov's Conf. Material Sciences of Refined Compounds, Kyiv, 2018, p. 24.

PHASE EQUILIBRIA IN THE Cu–Ti–Zr SYSTEM AT SUBSOLIDUS TEMPERATURES

<u>A.M. Storchak</u>¹, T.Ya. Velikanova¹, L.V. Artyukh¹, V.M. Petyukh¹, M.A. Turchanin², and P.G. Agraval²

 ¹ I.M. Frantsevich Institute for Problems in Materials Science, National Academy of Sciences of Ukraine, Krzyzhanovsky St. 3, 03142 Kyiv, Ukraine
 ² Donbass State Engineering Academy, Shkadinov St. 72, 84313 Kramatorsk, Ukraine

asvasf@bigmir.net

The Cu–Ti–Zr system has attracted interest due to the formation of bulk metallic glasses in a wide concentration range. The system has been studied in some experimental and theoretical works [1-8], but there are no experimental data on the phase equilibria at subsolidus temperatures. The aim of the present work was to plot the solidus surface experimentally.



Fig. The solidus surface projection of the Cu–Ti–Zr system.

The Cu–Ti–Zr ternary alloys were prepared from the components by arc melting and investigated, in the as-cast state and after annealing at 750°C, by X-ray diffraction scanning (XRD), electron microscopy (SEM), electron microprobe (EPMA) and differential thermal (DTA) analyses. As a result the solidus surface projection of the Cu-Ti-Zr system was constructed (Fig.). It turned out that the character of the solidus projection is the same as that of the isothermal section 750°C. at The difference involves a wider homogeneity range of the ternary τ_1 phase toward higher titanium content at the solidus temperatures, in comparison with the section at 750°C.

- [1] C.G. Woychik, T.B. Massalski, Z. Metallkd. 79(3) (1988) 149-153.
- [2] V.N. Chebotnikov, V.V. Molokanov, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 26(5) (1990) 960-964.
- [3] Y.K. Kovneristyj, A.G. Pashkovskaya, Amorfnye (Stekloobraznye) Met. Mater., 1992, pp. 153-157.
- [4] R. Arroyave, T.W. Eagar, L. Kaufman, J. Alloys Compd. 351 (2003) 158-170.
- [5] U.E. Klotz, C. Liu, P.J. Uggowitzer, J.F. Löffler, Intermetallics 15 (2007) 1666-1671.
- [6] X. Yan, X.-Q. Chen, A. Grytsiv, P. Rogl, et al., Intermetallics 16 (2008) 651-657.
- [7] A.M. Storchak-Fedyuk, L.V. Artyukh, L.A. Duma, *et al.*, *Poroshk. Metall. (Kiev)* (1/2) (2017) 102-114.
- [8] A.M. Storchak-Fedyuk, L.V. Artyukh, A.V. Grytsiv, *et al.*, *Poroshk. Metall. (Kiev)* (3/4) (2017) 131-142.

CRYSTAL STRUCTURE AND ELECTROCHEMICAL HYDROGENATION OF THE La₂Mg_{17-x} M_x (M = Sn, Sb, Ni) PHASES

V. Kordan¹, I. Tarasiuk¹, V. Nytka¹, O. Zelinska¹, R. Serkiz², and V. Pavlyuk¹ ¹Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Scientific-Technical and Educational Centre of Low Temperature Studies, Ivan Franko National University of Lviv, Drahomanova St. 50, 79005 Lviv, Ukraine kordan50@gmail.com

During a systematic investigation of the interaction between the metallic components in the systems La–Mg–{Sn,Sb}, we observed the formation of solid solutions of substitution on the basis of the binary phase La₂Mg₁₇ (structure type Th₂Ni₁₇, space group $P6_3/mmc$) with a homogeneity range of up to 4-5 at.% Sn or Sb. This structure is suitable for hydrogen storage and can serve as negative electrode material in Ni-MH batteries.

The crystal structure of the La₂Mg_{17-x}Sn_x solid solution was investigated by singlecrystal X-ray diffraction (diffractometer Xcalibur Oxford Diffraction, CCD-detector, Mo $K\alpha_1$ -radiation). The single crystal was selected from an alloy with the composition La_{10.5}Mg_{85.5}Sn₄. The crystal structure was refined in the anisotropic approximation to the reliability factors $R_1 = 0.0092$, $wR_2 = 0.0230$. The results of the crystal structure refinement are listed in the Table. All the sites in the structure are fully occupied by atoms according to the structure type, except the position 4*f* where a statistical mixture (Mg,Sn) was found. This position is also partially defect.

Atom	Site	A	$II \overset{\circ}{\lambda}^2$		
Atom	Site	x/a	y/b	z/c	$U_{\rm eq}, A$
La1	2b	0	0	1⁄4	0.0209(8)
La2	2c	1/3	2/3	1⁄4	0.0080(8)
M	4f	1/3	2/3	0.6020(7)	0.0309(17)
Mg1	6 <i>g</i>	1/2	0	0	0.0124(12)
Mg2	12 <i>j</i>	0.3616(4)	0.0337(6)	1⁄4	0.0171(12)
Mg3	12 <i>k</i>	0.16366(17)	0.3273(3)	0.0205(4)	0.0154(11)

Table Atomic coordinates and isotropic displacements parameters for the La₂Mg_{16.74}Sn_{0.14} single crystal (a = 10.3911(3) Å, c = 10.2702(3) Å, V = 960.36(5) Å³).

M = 87% Mg + 7% Sn

Samples with the compositions $La_{10.5}Mg_{89.5}$, $La_{10.5}Mg_{85.5}Sn_4$, $La_{10.5}Mg_{85.5}Sb_4$, and $La_{10.5}Mg_{85.5}Ni_4$ were synthesized for electrochemical investigations. Before and after the electrochemical processes, the alloys were examined by X-ray powder diffraction (diffractometer DRON-2.0M, Fe K α -radiation) and EDX-analysis (scanning electron microscope REMMA 102-02). Electrochemical hydrogenation was carried out in two-electrode Swagelok-type cells. Hydrogen intercalation occurs in the octahedral voids 6*h* of the structure. The reversible content of hydrogen is 1.36 H/f.u. for La₂Mg_{16.2}Sn_{0.8}-, 1.70 H/f.u. for La₂Mg_{16.2}Sb_{0.8}- and 1.73 H/f.u. for La₂Mg_{16.2}Ni_{0.8}-based electrodes. The electrochemical properties of these electrode materials depend on the corrosion stability of the alloys in the electrolyte solution (6M KOH).

Funding for this research was provided by the grant No. 0117U007192.

HIGHER PHOSPHIDES WITH OsGe₂-TYPE STRUCTURE

M. Dzevenko, <u>Ya. Lomnytska</u>, and V. Babizhetskyy Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine yalomnytska@gmail.com

The investigation of the ternary system Ta–V–P led to the question concerning the thermal stability of the phosphides TaP₂ and VP₂ (both isotypic to OsGe₂ [1,2]). Several pressed samples, prepared from mixtures of tantalum, vanadium, and phosphorus powders, were annealed in evacuated silica tubes at 870, 1010, and 1170 K. The binary phosphides TaP₂ and VP₂ exist at 870 K, but decompose into TaP or VP and P at higher temperatures. In order to determine the values of the decomposition temperatures of TaP₂ and VP₂, a differential thermal analysis was performed on the samples prepared at 870 K. The results of the investigations showed that TaP₂ decomposes in the temperature range 940-1040 K, and VP₂ in the range 970-1030 K.

The existence of ternary phosphides with $OsGe_2$ -type at 1070 K has earlier been reported in the Ta–Ti–P [3], Ta–Cr–P [4], and Ta–Mn–P [5] systems. Therefore, we expected to find isostructural compounds in other, related systems. Samples $Ta_{1-x}M_xP_2$ (M = transition metals, except noble metals) were synthesized at 1070 K with a content of 4-6 at.% M. New isostructural compounds were found with V, Fe, Co, Ni, Cu, Zr, Hf, Nb, Mo, W, and Re. Complete crystal structure determinations were performed by X-ray powder diffraction for the majority of them.

Compound	Lat	tice parameters	ßo	VÅ ³	
Compound	а	b	С	ρ ,	V, A
$Ta_{0.93(3)}Ti_{0.07(3)}P_2$	8.8556(9)	3.2654(4)	7.4846(8)	119.307(2)	188.73(7)
$Ta_{0.94(4)}V_{0.06(4)}P_2$	8.8532(5)	3.2648(1)	7.480(3)	119.306(2)	188.54(4)
$Ta_{0.92(2)}Cr_{0.08(2)}P_2$	8.8586(3)	3.2670(1)	7.4871(2)	119.315(1)	188.93(2)
$Ta_{0.91(2)}Mn_{0.09(2)}P_2$	8.8591(3)	3.2667(1)	7.4873(2)	119.310(1)	188.95(2)
$Ta_{0.83(5)}Fe_{0.17(5)}P_2$	8.855(2)	3.2634(5)	7.482(1)	119.33(1)	188.5(3)
$Ta_{0.82(4)}Co_{0.18(4)}P_2$	8.862(2)	3.2674(6)	7.486(2)	119.33(2)	188.99(3)
$Ta_{0.91(1)}Ni_{0.09(1)}P_2$	8.85716(5)	3.26529(3)	7.48572(4)	119.310(1)	188.78(4)
$Ta_{0.92(3)}Cu_{0.08(3)}P_2$	8.8585(4)	3.2649(3)	7.4862(3)	119.304(2)	188.81(3)
$Ta_{0.86(8)}Zr_{0.14(8)}P_2$	8.8546(8)	3.2651(3)	7.4831(5)	119.312(3)	188.65(3)
$Ta_{0.9(2)}Hf_{0.1(2)}P_2$	8.8478(9)	3.2628(4)	7.4781(7)	119.321(3)	188.22(6)
$Ta_{0.81(4)}Nb_{0.19(4)}P_2$	8.8471(5)	3.2619(2)	7.4764(4)	119.308(2)	188.14(4)
$Ta_{0.9}Mo_{0.1}P_2$	8.8585(2)	3.255(1)	7.4752(4)	119.04(7)	188.81(3)
$Ta_{0.9}W_{0.1}P_2$	8.837(3)	3.260(1)	7.467(3)	119.280(9)	187.63(3)
$Ta_{0.96(6)}Re_{0.04(6)}P_2$	8.8536(6)	3.2649(3)	7.4810(5)	119.302(2)	188.57(4)

The content of the transition metal is small, and the lattice parameters of the phases differ little. This indicates that all the ternary phosphides are actually the biphosphide TaP_2 , stabilized at high temperature by small admixtures of another transition metal. We did not detect such a phenomenon of stabilization near the VP₂ binary compound.

- [1] F. Hulliger, *Nature* 204 (1964) 775.
- [2] M. Goelin, B. Carlsson, S. Rundqvist, Acta Chem. Scand. A 29 (1975) 706-708.
- [3] Ya. Lomnytska, M. Dzevenko, V. Babizhetskyy, et al., J. Alloys Compd. 732 (2018) 777-783.
- [4] Ya. Lomnytska, V. Babizhetskyy, A. Oliynyk, et al., J. Solid State Chem. 235 (2016) 50-57.
- [5] Ya. Lomnytska, M. Dzevenko, V. Babizhetskyy, J. Köhler, J. Solid State. Chem. 277 (2019) 77-82.

CRYSTAL STRUCTURE OF THE NEW TERNARY PHOSPHIDE H05Pd19P12

O.V. Zhak, T.P. Zdorov, and O.R. Karychort Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine olha.zhak@lnu.edu.ua

Among the ternary systems RE-Pd-P, where RE is a heavy rare-earth metal, phase diagrams in the whole concentration region have been constructed only for the systems Er-Pd-P [1] and Yb-Pd-P [2]. The existence of seven and six ternary phases, respectively, was discovered in these systems, and the crystal structures of most of them were established using X-ray single-crystal or powder diffraction data.

The phase diagram of the Ho–Pd–P ternary system has not yet been constructed, but the formation of three ternary phases has been reported: $HoPd_2P_2$ (BaAl₄-type structure) [3], HoPdP (TiNiSi-type structure) [4], and $Ho_3Pd_{20}P_6$ (Cr₂₃C₆-type structure) [2]. The main goal of our research was the synthesis of new ternary holmium palladium phosphides and investigation of their crystal structures.

The sample used for the investigation was prepared by a double sintering procedure of a pressed pellet, obtained from a mixture of the starting materials (powders of holmium, palladium, and red phosphorus, all with a stated purity better than 99.9 wt.%) in the atomic ratio Ho:Pd:P = 20:40:40. The sintered sample was further heat-treated in an evacuated fused-silica tube at 1070 K for 2 months and quenched in cold water without breaking the tube. The homogenized sample was studied by X-ray diffraction. The powder diffraction intensity data were collected on an automatic powder diffractometer STOE STADI P: transmission mode; curved germanium (111) monochromator; linear PSD detector; Cu K α_1 radiation; $\lambda = 0.154056$ nm; 2θ -range $6.000 \le 2\theta \le 110.625^\circ$, 2θ -step 0.015° , scan time 270 s/step. The WinCSD software [5] was used for all the calculations, including the Rietveld refinement of the crystal structure.

The crystal structure of the new ternary phosphide Ho₅Pd₁₉P₁₂ was established using powder X-ray diffraction data: Ho₅Ni₁₉P₁₂-type structure, space group *P*-62*m*, *a* = 1.31342(4), c = 0.39839(2) nm; $R_I = 0.0652$, $R_p = 0.0821$, $wR_p = 0.1159$. This is the first representative of the Ho₅Ni₁₉P₁₂ type among ternary phosphides of rare-earth metals and palladium.

The interatomic distances in the structure of the new phosphide are nearly the same as the sums of the atomic radii of the pure components, indicating predominantly metallic type of bonding. However, several short distances between phosphorus and palladium atoms indicate contribution of covalent interaction.

- [1] M.V. Zelinska, *Thesis*, Ivan Franko National University of Lviv, 2007.
- [2] S.L. Budnyk, *Thesis*, Ivan Franko National University of Lviv, 2002.
- [3] W. Jeitschko, W.K. Hofmann, J. Less-Common Met. 95 (1983) 317-322.
- [4] D. Johrendt, A. Mewis, Z. Naturforsch. B 45 (1990) 1262-1266.
- [5] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.

NEW ALUMINIDES *RE*₃Ni₄Al₂ (*RE* = La, Ce, Pr, Nd) OF THE La₃Ni₄Ga₂-TYPE

A.I. Tursina¹, S.N. Nesterenko¹, K.B. Kalmykov¹, and D. Kaczorowski² ¹ Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russian Federation ² Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław 2, Poland anna-tursina@yandex.ru

Novel intermetallics $RE_3Ni_4Al_2$ (RE = La, Ce, Pr, Nd) were synthesized by arc-melting stoichiometric amounts of the elemental constituents, and subsequent annealing at 650°C for 50 days followed by quenching in cold water. The crystal structures were determined from single-crystal X-ray diffraction (XRD) data collected on a CAD4 Enraf Nonius diffractometer with Ag Ka radiation.

The new compounds crystallize with the monoclinic La₃Ni₄Ga₂-type structure [1] in space group C2/m, alike the recently reported aluminide La₃Ni₄Al₂ [2]. The main crystal data of the phases RE_3 Ni₄Al₂ (RE = Ce, Pr, Nd) are given in the Table, while more detailed information on the crystal structure refinements, and the obtained structural parameters are available in the CCDC/FIZ Karlsruhe database *via* www.ccdc.cam.ac.uk, quoting reference numbers 1940541, 1939606, 1940590, respectively.

Compound	Cel	ll dimensions (Å	$V(^{3})$	P/wP	
Compound	а	b	С	$V(\mathbf{A})$	$\Lambda / W\Lambda$
Ce ₃ Ni ₄ Al ₂	10.111(3)	4.2074(14)	8.2493(19)	347.37(18)	2.97 / 7.46
		$\beta = 98.17(2)$			
Pr ₃ Ni ₄ Al ₂	10.1088(13)	4.1873(11)	8.2873(7)	347.00(11)	2.95 / 6.69
		$\beta = 98.432(9)$			
Nd ₃ Ni ₄ Al ₂	9.996(3)	4.1702(9)	8.2692(18)	340.89(15)	4.14 / 10.36
		$\beta = 98.55(2)$			

The $RE_3Ni_4Al_2$ compounds were also obtained as polycrystalline samples with small or negligible amounts of admixtures. The unit cell parameters derived from Rietveld refinements of powder XRD patterns are as follows:

La₃Ni₄Al₂ – a = 10.3831(16), b = 4.2240(7), c = 8.3876(11) Å, $\beta = 98.770(15)^{\circ}$; Ce₃Ni₄Al₂ – a = 10.1475(18), b = 4.2074(8), c = 8.2575(12) Å, $\beta = 98.206(17)^{\circ}$; Pr₃Ni₄Al₂ – a = 10.1230(11), b = 4.1928(5), c = 8.3005(8) Å, $\beta = 98.413(11)^{\circ}$; Nd₃Ni₄Al₂ – a = 10.0164(19), b = 4.1734(11), c = 8.2808(15) Å, $\beta = 98.540(19)^{\circ}$.

Preliminary examinations of the low-temperature magnetic and electrical transport properties of the new compounds are currently in progress.

This study was supported by the Russian Foundation for Basic Research (Grant No. 18-03-00656a and 19-03-00135).

- [1] Y. Grin, Y.P. Yarmolyuk, *Kristallografiya* 25 (1980) 613-616.
- [2] N. Zaremba, Y. Schepilov, G. Nychyporuk, V. Hlukhyy, V. Pavlyuk, Z. Kristallogr. *Cryst. Mater.* DOI: 10.1515/zkri-2019-0011.

SINGLE-CRYSTAL INVESTIGATION OF THE SmMn_{6.8}Ni_{5.2} COMPOUND

D. Kowalska¹, <u>B. Belan²</u>, M. Manyako², and Ya. Kalychak³

¹ Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław 2, Poland

 ² Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ³ Department of Analytical Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

bohdanabelan@gmail.com

The ternary compound $\text{SmMn}_{6.8}\text{Ni}_{5.2}$ was found during an investigation of the isothermal section of the ternary system Sm-Mn-Ni in the whole concentration range at 600°C by X-ray diffraction phase analysis. Here we present the results of a crystal structure investigation using X-ray single-crystal diffraction.

A single crystal suitable for X-ray investigation $(0.069 \times 0.035 \times 0.026 \text{ mm})$ was obtained from a sample of nominal composition $\text{Sm}_{7.7}\text{Mn}_{52.3}\text{Ni}_{40}$, which had been synthesized from high-purity elements by arc-melting under a purified argon atmosphere. The alloy was annealed at 600°C in an evacuated quartz ampoule for 720 h. X-ray diffraction data were collected on an Xcalibur Atlas CCD diffractometer using Mo Ka radiation. The crystal structure was refined using the program SHELXL-97 [1]. The chemical composition of the crystal was checked with a field-emission scanning electron microscope equipped with an EDS analyzer.

The present investigation revealed the following data for the crystal structure of SmMn_{6.8}Ni_{5.2}: structure type ThMn₁₂, Pearson symbol *tI*26, space group *I*4/*mmm*, a = 8.6528(3), c = 4.8635(3) Å, V = 364.13(3) Å³, Z = 2, R = 0.0195, $R_w = 0.0387$. The refined atomic coordinates and displacement parameters are given in the Tables.

Site	Wyckoff position	x	У	Z.	G	$U_{ m iso}({ m \AA}^2)$
Sm	2 <i>a</i>	0	0	0	1	0.0149(2)
Ni1 Mn1	8 <i>f</i>	1⁄4	1⁄4	1⁄4	0.76(3) 0.24(3)	0.0080(3)
Mn	8 <i>i</i>	0.35615(10)	0	0	1	0.0097(2)
Ni2 Mn2	8 <i>j</i>	0.22011(10)	1⁄2	0	0.54(3) 0.46(3)	0.0098(3)

Table 1 Atomic coordinates and displacement parameters for SmMn_{6.8}Ni_{5.2}.

Table 2 Anisotropic displacement parameters (A) for $\text{Smin}_{6.8}$ N ₁₅	Table 2 Anisotro	oic displacement	t parameters	(\AA^2) for	SmMn _{6.8} Ni ₅
--	------------------	------------------	--------------	----------------------	-------------------------------------

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm	0.0101(2)	0.0101(2)	0.0245(4)	0	0	0
Ni1	0.0000(3)	0.0000(3)	0.0058(4)	0.00087(10)	0.00087(10)	0.0005(3)
Mn1	0.0090(3)	0.0090(3)	0.0038(4)	0.00087(19)	0.00087(19)	0.0003(3)
Mn	0.0090(4)	0.0086(4)	0.0115(4)	0	0	0
Ni2	0.0064(4)	0.0142(5)	0.0087(4)	0	0	0
Mn2	0.0004(4)	0.0142(3)	0.0007(4)	0	0	0

[1] G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3-8.

GdFe_{1-x}Si₂ (x = 0.32) – A NEW TERNARY REPRESENTATIVE OF THE TbFeSi₂ STRUCTURE TYPE

<u>V. Babizhetskyy</u>¹, J. Köhler², R. Krutjak¹, and Y. Tyvanchuk¹ ¹ Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, Postfach 800665, 70569 Stuttgart, Germany v.babizhetskyy@googlemail.com

Several ternary compounds with the approximate composition $RT_{1-x}Si_2$ (R = rare earth, T = transition element) have been reported over the last decades. Their crystal structures are characterized by a stacking of BaAl₄ and AlB₂ slabs. The early rare-earth manganese $RMn_{1-x}Si_2$ (R = La-Sm) and iron (R = La-Nd, Tb-Lu) silicides $RFe_{1-x}Si_2$ crystallize in the TbFeSi₂-type structure, a structure closely related to that of the CeNiSi₂-type structure and characterized by site exchange between transition-metal and main-group elements within the BaAl₄ block [1-3]. The stoichiometric rare-earth iron silicides $RFeSi_2$ (R = Nd, Sm, Gd, Tb) crystallize in the NdRuSi₂-type structure [4].

The new ternary rare-earth iron silicide was synthesized by arc-melting stoichiometric amounts of the constituent elements under argon atmosphere. The alloy was annealed at 1070 K in an evacuated quartz tube for 4 weeks, followed by quenching in cold water. It was found that $GdFe_{1-x}Si_2$ only exists above 1070 K, since after annealing, only the $Gd_2Fe_3Si_5$ and $GdSi_2$ phases were found.

Intensity data from a single crystal was collected using a Stoe IPDS II image-plate diffractometer. EDX analysis of the single crystal revealed the composition $Gd_{27.3(3)}Fe_{19.1(3)}Si_{53.6(3)}$, which is in good accordance with the results obtained for the bulk sample. The crystal structure of $GdFe_{1-x}Si_2$ (x = 0.32(2)) was determined from the X-ray single-crystal data. The new silicide crystallizes in the orthorhombic space group *Cmcm*, Pearson symbol oS16, a = 4.0496(8), b = 16.416(2), c = 3.9527(6) Å, $R_1 = 0.041$ ($wR_2 = 0.088$ for 225 reflections with $I_0 \ge 2\sigma(I_0)$). In the crystal structure of $GdFe_{1-x}Si_2$ (x = 0.32) all the atoms are in Wyckoff position 4(c) 0 y ¹/₄: Gd (y = 0.39603(5)), $U_{eq} = 0.0089(5)$), Fe (y = 0.7501(3), $U_{eq} = 0.016(2)$, G = 0.68(2)), Si1 (y = 0.0412(6), $U_{eq} = 0.022(1)$), Si2 (y = 0.1850(5), $U_{eq} = 0.024(1)$).

Formation of the stoichiometric compound $GdFeSi_2$ (NdRuSi₂-type structure) was also confirmed in the course of systematic studies of the phase equilibria of the Gd–Fe–Si system at 1070 K.

- [1] V.I. Yarovets, Yu.K. Gorenlenko, Visn. Lviv. Univ., Ser. Khim. 23 (1981) 20-23.
- [2] G. Venturini et al., Rev. Chim. Miner. 23 (1986) 162-182.
- [3] L. Paccard, D. Paccard, J. Allemand, J. Less-Common Met. 161 (1990) 295-298.
- [4] I. Ijjaali, G. Venturini, B. Malaman, J. Alloys Compd. 282 (1999) 153-157.

THE INTERMETALLIC COMPOUND Sm₂Ru₃Sn₅ WITH A NEW STRUCTURE TYPE

V. Pavlova and <u>E. Murashova</u> Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russian Federation murashovaev@rambler.ru

Among the group of known silicides, germanides, gallides, and stannides with the element ratio 2:3:5, six main structural types are known: $Sc_2Fe_3Si_5$ (*P4/mnc*), $Lu_2Co_3Si_5$ (*C2/c*), $Y_2Rh_3Sn_5$ (*Cmc2*₁), $Yb_2Pt_3Sn_5$ (*Pnma*), $U_2Co_3Si_5$ (*Ibam*), and $Yb_2Ir_3Ce_5$ (*Pmmn*). According to a review by Sebastian *et al.* [1], the structures of all these types contain anionic frameworks with variations due to the introduction of rare-earth elements. There is information in the literature that compounds with these structural types exhibit anomalous magnetic properties. We present one more compound of the same element ratio, $Sm_2Ru_3Sn_5$, with a new structure type.

The sample $Sm_2Ru_3Sn_5$ was synthesized by arc-melting pure elements, Sm (99.9 %), Ru (99.99 %), and Sn (99.99 %), in a purified argon atmosphere. To reach homogeneity the fused mass was re-melted several times. After melting, the alloy was annealed at 600°C for 30 days. The microstructure of $Sm_2Ru_3Sn_5$ was investigated with the use of a scanning electron microscope Carl Zeiss LEO EVO 50VXP. X-ray powder diffraction data was collected on a STOE STADI P transmission diffractometer. The X-ray single-crystal diffraction experiment was carried out using a Bruker APEX3 diffractometer with Mo $K\alpha$ radiation.

The compound $\text{Sm}_2\text{Ru}_3\text{Sn}_5$ crystallizes with a cubic unit cell, a = 9.4606(8) Å, space group I-43m, Z=4, and a structure of a new type, derived from the Ru₃Sn₇ type $(a_{Ru3Sn7} = 9.3735(8) \text{ Å}$, space group Im-3m) [2]. The crystal structure was determined by means of X-ray powder ($R_F = 0.013$, $R_B = 0.017$, $\chi^2 = 1.47$) and single-crystal (R1/wR2 = 0.043/0.114) diffraction data. The structure of Sm₂Ru₃Sn₅ is characterized by four crystallographically independent atom sites: Sm(8c), Ru(12e) and two sites occupied by tin atoms, Sn1(8c) and Sn2(12d). The loss of the inversion center in space group I-43m $(Sm_2Ru_3Sn_5)$, compared to Im-3m (Ru_3Sn_7), causes the position 16f to split into two positions 8c, which are occupied by samarium and tin atoms in an ordered manner. The coordination polyhedra of the samarium (CN = 13) and tin (CN = 10) atoms differ noticeably in shape, which is associated with a change of the interatomic distances inside the polyhedra. The Sm-Ru distances increase (3.034 Å), whereas the Sn-Ru distances decrease (2.702 Å), compared to the corresponding distances in the prototype Ru_3Sn_7 (2.745 Å). Six Sn2 atoms are situated at a distance of 3.441 Å from the central samarium atom, while they are 4.002 Å away from the Sn1 atom (in the prototype, the same distance is 3.613 Å). The structure of $Sm_2Ru_3Sn_5$ can also be described as a three-dimensional framework of ruthenium and tin atoms, since these atoms form the shortest interatomic distances with each other (2.702-2.759 Å), in the large voids of which the samarium atoms are located.

The work was supported by the RFBR under research grant No. 19-03-00135.

- [1] C.P. Sebastian et al., Inorg. Chem. 49 (2010) 10468-104744.
- [2] B.C. Chakoumakos, D. Mandrus, J. Alloys Compd. 281 (1998) 157-159.

NEW GALLIDES OF RUTHENIUM AND RARE-EARTH ELEMENTS

I. Grekhov, Zh. Kurenbaeva, and <u>E. Murashova</u> Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russian Federation murashovaev@rambler.ru

Gallides of Ru and rare-earth (RE) elements with a high content of the latter have been studied for RE = Ce and La [1]. These compounds exhibit extremely interesting physicochemical properties. Compounds with other rare-earth elements have not been studied, although indides of Ru and rare-earth elements are known and possess curious properties at low temperatures [2-4].

In the region with high content of rare-earth metal, compounds with the ratio 4-2-3 were obtained for the series RE = Pr, Nd, Sm, Gd, Tb, Dy, Er. Compounds of this composition do not form in other RE–Ru–X systems (X = Al, In; RE = La, Ce). All the compounds of the $RE_4Ru_2Ga_3$ series crystallize in a new type of structure with a monoclinic cell, space group C2; the unit-cell parameters are presented in the Table.

Compound	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	β , °	$V, Å^3$
$Pr_4Ru_2Ga_3$	10.930(3)	4.2380(15)	9.660(3)	111.03(3)	417.68(2)
$Nd_4Ru_2Ga_3$	10.908(5)	4.1904(16)	9.635(4)	111.44(5)	409.9(2)
$Sm_4Ru_2Ga_3$	10.870(6)	4.081(3)	9.735(5)	111.13(5)	402.8(3)
$Gd_4Ru_2Ga_3$	10.830(2)	4.0145(8)	9.717(2)	111.24(2)	393.8(1)
Tb ₄ Ru ₂ Ga ₃	10.762(7)	3.981(3)	9.710(6)	111.24(6)	387.8(3)
Dy ₄ Ru ₂ Ga ₃	10.732(3)	3.9593(10)	9.698(3)	111.33(2)	383.9(1)
$Er_4Ru_2Ga_3$	10.626(2)	3.9248(8)	9.667(2)	111.42(2)	375.3(1)

High-purity metals (more than 99.8 at.%) were used as reagents for the preparation of the alloys. Fusion of the samples was carried out under argon atmosphere in an electric arc furnace. After melting, the samples were annealed to establish equilibrium, at a temperature of 600° C for 89 days. Then the samples were quenched in ice water.

All the obtained samples were studied by powder X-ray diffraction. The structure of $Nd_4Ru_2Ga_3$ was determined from single-crystal data: R1/wR2 = 0.043/0.084, 1198 reflections

with $I > 2\sigma(I)$, 46 variable parameters. The structure of the Nd₄Ru₂Ga₃ compound is constructed from the stacking of alternating corrugated layers of two types: Nd-layers and Ru/Ga layers, along the [100] direction. The structure can also be described as built from distorted fragments of AlB₂ and CsCl, but the arrangement of these fragments differs from that in the isoformular compound RE_4 Co₂Mg₃ [5]. The interatomic distances Nd-Ru and Ru-Ga are close to the sum of the covalent radii, and the remaining distances (Nd-Nd, Ga-Ga, Nd-Ga) are close to the sum of the atomic radii.



This work was supported by the RFBR, project No. 19-03-00135.

- [1] K. Shablinskaya et al., J. Alloys Compd. 575 (2013) 183-189.
- [2] V. Gribanova et al., J. Alloys Compd. 711 (2017) 455-461.
- [3] L. Sojka et al., Intermetallics 49 (2014) 14-17.
- [4] A. Szytuła et al., J. Alloys Compd. 589 (2014) 622-627.
- [5] S. Tuncel et al., Z. Naturforsch. B 62 (2007) 162-168.

Y. Grishina, D. Sedelnikov, <u>Zh. Kurenbaeva</u>, A. Tursina, and E. Murashova Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russian Federation kurenbaeva@mail.ru

Among the aluminides, gallides and germanides of ruthenium and rare-earth (*RE*) elements of the beginning of the series (mainly Ce), compounds of the composition RE_2RuX , or close to it, are known [1-3]. They do not form isostructural series, but crystallize in different structural types, and exhibit interesting magnetic and electrical properties at low temperatures. Intermetallic compounds with magnesium as the *p*-element, RE_2RuMg (RE = Sc, Y, Er, Tm, Lu) with structures derived from CsCl, are described in the literature [4]. On the contrary, indides with the stoichiometric ratio of components RE_2RuIn have not been reported previously with early *RE* elements. The gallides with *RE* of the end of the *RE* series have not been studied, except for HoRu_{0.6}Ga_{0.4} [5]. Therefore, in this work we focused on the compounds RE_2RuGa (RE = Er, Tm, Lu) and RE_2RuIn (RE = Dy-Lu).

High-purity metals (more than 99.8 at.%) were used as reagents for the preparation of the alloys. Fusion of the samples was carried out under argon atmosphere in an electric arc furnace. After melting, the samples were annealed to establish equilibrium, at a temperature of 600°C for 89 days. Then the samples were quenched in ice water.

In the system Lu–Ru–Ga, a compound of the composition LuRu_{0.5}Ga_{0.5} is formed, and in the systems with Er and Tm, compounds of the compositions $\text{ErRu}_{0.4}\text{Ga}_{0.6}$ and $\text{TmRu}_{0.4}\text{Ga}_{0.6}$. All the three compounds are of the structural type CsCl. It should be noted that the *RE* atoms occupy the Cl positions, while the Ru and Ga occupy the Cs positions statistically. The parameters of the cubic cells decrease within the series Er (3.4629(2) Å) – Tm (3.4433(4) Å) – Lu (3.4068(3) Å), which is associated with the decrease of the radius of the rare-earth element due to the lanthanoid compression. The boundaries of the homogeneity regions were established.

RE	<i>a</i> , Å	<i>c</i> , Å	$V, \text{\AA}^3$
Dy	3.4616(8)	7.596(3)	91.02(2)
Ho	3.4550(16)	7.561(8)	90.25(6)
Er	3.4474(19)	7.504(4)	89.18(6)
Tm	3.4261(11)	7.402(5)	86.88(6)
Lu	3.4219(3)	7.411(1)	86.77(1)

The obtained indides RE_2RuIn (RE = Dy-Lu) crystallize in the tetragonal system, space group P4/mmn, with structures derived from CsCl with doubling of the parameter c. The doubling is due to the ordered arrangement of the Ru and In atoms at the Cs positions. The Cl positions are occupied by the *RE* atoms. Due to the large difference in size between Ru (r = 1.60 Å) and In (r = 1.34 Å), these atoms are not statistically distributed, but each element has its own position.

This work was supported by the RFBR, project No. 19-03-00135.

- [1] K. Shablinskaya et al., J. Alloys Compd. 575 (2013) 183-189.
- [2] E. Murashova et al., J. Alloys Compd. 580 (2013) 55-60.
- [3] E. Murashova et al., J. Alloys Compd. 802 (2019) 437-444.
- [4] M. Kersting et al., Z. Kristallogr. 230(3) (2015) 151-155.
- [5] O. Myakush et al., Neorg. Mater. 34(6) (1998) 688-691.

NPD STUDIES OF THE NOVEL HELICAL FERRIMAGNET Dy11Ni60C6

V. Levytskyi^{1,2}, G.-L. Păşcuț³, R. Gumeniuk², V. Babizhetskyy¹, O. Isnard⁴, and B. Kotur¹

¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

² Institute of Experimental Physics, TU Bergakademie Freiberg,

Leipziger St. 23, 09596 Freiberg, Germany

³ MANSiD Research Center and Faculty of Forestry, Stefan Cel Mare University (USV),

720229 Suceava, Romania

⁴ Institut Néel, University Grenoble Alpes and CNRS,

25 rue des Martyrs, BP 166, Cedex 9, Grenoble 38042, France

volodymyr.levytskyi@physik.tu-freiberg.de

Among related *M*-rich compounds (M = 3d-element), ternary nickel *R*–Ni–C carbides (R = rare earth) crystallize in original structure types. $R_{11}Ni_{60}C_6$ (R = Y, Tb-Lu) revealed a unique structure arrangement, known as the Yb₁₁Ni₆₀C₆ type. Due to the high *d*-element content in such compounds, a variety of useful magnetic properties is expected, similar to those observed in the boundary RNi_5 and R_2Ni_{17} phases [1,2]. Recently, the crystal structure, thermal dependence of magnetic susceptibility, and field dependence of magnetization of the $R_{11}Ni_{60}C_6$ carbides with R = Tb, Dy were reported [3]. The value of the effective magnetic moment and the low ordering temperatures indicated that most probably only the R atoms carry magnetic moments. However, from these experiments the origin of the observed transition was unclear.

To determine the detailed magnetic structure, we performed a neutron powder diffraction (NPD) study of $Dy_{11}Ni_{60}C_6$. Both the nuclear and magnetic structures were solved and refined.

The magnetic unit cell (Shubnikov space group R-3m', a = 17.5511(5) Å, c = 10.7478(5) Å, $R_I = 3.5$ %, $R_p = 2.9$ %, $R_{wp} = 3.9$ %) is commensurate with the nuclear one (*Im-3m*, a = 12.424(1) Å, $R_I = R_{mag} = 3.0$ %, $R_p = 3.8$ %, $R_{wp} = 5.0$ %). The magnetic structure of Dy₁₁Ni₆₀C₆ consists of three different Dy sublattices, and due to peculiarities of the alignment of the magnetic moments, it represents a helical ferrimagnetic phase (see Fig.). The thermal dependence of the unit cell parameters, electronic structure calculations and magnetic parameters are discussed in details.



Fig. *Left: ab* projection of the magnetic unit cell of Dy₁₁Ni₆₀C₆; *Right:* view of the alignment of magnetic moments along the [001] direction and 3-fold screw axes, the (1-100) cross-section is shown (red line). The magnetic vectors are drawn as red arrows, the Dy atoms as blue balls, and nearest-border Dy-Dy atoms are connected by solid lines.

- [1] N.A. de Oliveira, J. Phys. Chem. Solids 103 (2017) 13-15.
- [2] O. Moze, J.M. Cadogan, S.J. Kennedy, K.H.J. Buschow, *Physica B* 319 (2002) 35-44.
- [3] V. Levytskyi, O. Isnard, V. Babizhetskyy, B. Kotur, J. Phys. Chem. Solids 122 (2018) 189-197.

NEW TERNARY INTERMETALLIC Ce₉Pt₂₅Al₃₇

<u>Yu.S. Morozova</u>, A.I. Tursina, and E.V. Murashova Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russian Federation yu.s.morozova@gmail.com

In the course of our systematic investigation of the Ce–Pt–Al system, a novel ternary intermetallic phase was identified. The compound Ce₉Pt₂₅Al₃₇ was synthesized by melting the elemental constituents (purity: Ce 99.85 wt.%, Pt 99.99 wt.%, Al 99.999 wt.%) in an arc furnace under ultra-pure argon atmosphere. Homogenizing annealing was performed in an evacuated quartz tube at 700°C for 1 month, followed by quenching in cold water. The crystal structure was determined by single-crystal X-ray diffraction (Nonius KappaCCD diffractometer, Mo K α radiation). The compound crystallizes in the hexagonal space group *P*-6*m*2, lattice parameters: *a* = 18.6550(5) Å, *c* = 4.1370(10) Å, *Z* = 1, *R*1 = 0.045.

The unit cell contains as many as three inequivalent positions of Ce atoms, seven positions of Pt atoms, and nine positions of Al atoms. The structure of Ce₉Pt₂₅Al₃₇ can be considered as a three-dimensional network constructed from infinite hexagonal channels of Pt and Al atoms, with the Ce atoms located inside the channels, forming a stacking of Ce-polyhedra characterized by common hexagonal bases in the [001] direction. The condensation of three Ce2 polyhedra *via* lateral faces forms the basic unit for triple channels (see Fig.). The stacking of the hexagonal prisms centered by the Ce1 or Ce3 atoms forms single channels.



Fig. Projection of the network in the crystal structures of Ce₉Pt₂₅Al₃₇ in the direction along the smallest unit cell parameter.

Three hexagonal prisms centered by Ce3 atoms are grouped around an infinite chain of empty face-connected Pt_3Al_3 octahedra. Three hexagonal prisms centered by Ce1 atoms are joined around an infinite chain of Al_6 trigonal prisms centered by Pt atoms. Similar structural fragments were observed in the structure of Ce₄Pt₉Al₁₃ [1].

This study was supported by the Russian Foundation for Basic Researches (Grant No. 19-03-00135).

[1] Yu.S. Morozova et al., J. Alloys Compd. 767 (2018) 496-503.

SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF Y₃Pt₄

O. Sichevych¹, <u>L. Akselrud</u>^{1,2}, E. Svanidze¹, and Yu. Grin¹ ¹ Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany ² Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

The title compound was prepared by arc melting under argon atmosphere of a mixture of elemental components, followed by thermal treatment in a closed tantalum tube. Phase analysis was performed using energy-dispersive X-ray spectroscopy (EDXS, system Quantax

400, Bruker). The crystal structure of Y_3Pt_4 (space group R-3, a = 13.1186(2), c = 5.6745(1) Å, Z = 6) was elucidated from X-ray powder diffraction data (Guinier camera Huber G670, Cu $K\alpha_1$ radiation, $\lambda = 1.540598$ Å). The crystal structure solution by a dual-space technique and the Rietveld refinement were performed by using the program package WinCSD [1]. The magnetic behavior of the Y₃Pt₄ intermetallic was studied bv magnetic susceptibility (χ) measurements in the temperature range 1.8-400 K in a static magnetic field.



Element	Wyckoff Position	x	у	Z.	$B_{\rm iso}$, Å ²
Y	18 <i>f</i>	0.0452(1)	0.2109(1)	0.2316(2)	0.75(3)
Pt1	3 <i>a</i>	0	0	0	0.59(5)
Pt2	3 <i>b</i>	0	0	1/2	0.65(3)
Pt3	18 <i>f</i>	0.27354(5)	0.21982(5)	0.2807(1)	0.66(1)

Table Atomic coordinates and isotropic displacement parameters for Y₃Pt₄.

The coordination polyhedron of Y contains 16 atoms. The coordination numbers of the Pt atoms are 12 and 14. The shortest interatomic distances observed in the structure of Y_3Pt_4 are: d(Y-Y) = 3.40-3.95 Å, d(Y-Pt) = 2.84-3.23 Å, d(Pt-Pt) = 2.84-2.93 Å.

The compound Y_3Pt_4 crystallizes with the Pu_3Pd_4 structure type (Pearson symbol *hR*42) [2] and is geometrically related to the CsCl type [3].

- [1] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.
- [2] D.T. Cromer, A.C. Larson, R.B. Roof, Acta Crystallogr. B 29 (1973) 564-567.
- [3] K. Cenzual, J.L. Jorda, E. Parthé, Acta Crystallogr. C 44 (1988) 14-18.

CRYSTAL STRUCTURE OF THE NEW TERNARY SILICIDE Sc12C043.2Si27

<u>B. Kotur</u>¹, V. Babizhetskyy¹, and V. Smetana²

 ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ² Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius väg 16C, 10691 Stockholm, Sweden

bohdan.kotur@lnu.edu.ua

The existence of a ternary phase with approximate composition ~Sc₄Co₁₄Si₉ was established during an investigation of the phase equilibria at 800°C in the Sc-Co-Si system [1,2]. Recently we obtained a single crystal from an arc-melted sample homogenized at 800°C, and determined its crystal structure from X-ray single-crystal diffraction data (Bruker Venture diffractometer, Mo Ka radiation). The starting atomic parameters, derived by direct methods, using the program SIR 97, were refined with anisotropic displacement parameters, using the program SHELXL-97 in the WinGX program package [3]. The refined composition Sc₁₂Co_{43.2}Si₂₇ was confirmed by EDX. The compound crystallizes in an original hexagonal structure: Pearson symbol hP165, space group P6/mmm, a = 17.2909(14), c = 8.0293(8) Å, R1 = 0.048 for 1124 $F_0 > 4\sigma(F_0)$, 0.060 for all the 1293 data, and 107 refined parameters, including anisotropic displacement parameters. The scandium, cobalt and silicon atoms occupy 3, 13 and 6 crystallographically independent positions, respectively. The crystal structure of Sc₁₂Co_{43.2}Si₂₇ is closely related to two other hexagonal structures, Sc_{12.3}Ni_{40.7}Ge₃₁ (hP168, P6/mmm, a = 17.865, c = 8.220 Å) and $Li_{13}Ni_{40}Si_{31}$ (hP168, P6/mmm, a = 17.092, c = 17.092)c = 7.848 Å) [4]. These structures are derivatives of the close-packed atomic structures. They differ from each other by different atomic occupations of positions along the 3-fold and 6-fold axes. Some of these positions are partially occupied. This leads to slight differences in the composition. The structures are formed by three types of atomic layer: flat layers at z = 0(layer A) and z = 0.5 (layer C) and corrugated layers at z = 0.16-0.33 and z = 0.67-0.84(layer B). The atomic composition of the layers is slightly different in each of the three structures. The structures are formed by the following stacking of the indicated layers: ABCB along the z direction and, therefore, this series of structures can be described as four-layered structures. The layers and their stacking ensure close packing of the three different types of atom in this series of hexagonal structures.

The coordination numbers of the atoms in the structure of $Sc_{12}Co_{43.2}Si_{27}$ are 14 (Sc), 12 (Co, Si), 11 (Co), 10 (Co, Si), 9 (Co), and 8 (Co). The coordination polyhedra are icosahedra, distorted icosahedra, and polyhedra derived from icosahedra, while the atoms on the 3-fold axes have trigonal prismatic coordination [Co₆] and [Si₆] with three additional Sc atoms centering the lateral faces. The cobalt atoms occupying 2*e* positions (0, 0, *z*) along the 6-fold axes are located inside hexagonal dipyramids [Co₈] and [Co₂Si₆]. The majority of the interatomic distances Co-Si, Co-Co, and Co-Sc in the structure are shorter than the sums of the metallic radii of the atoms.

- [1] B.Ya. Kotur, O.I. Bodak, E.I. Gladyshevskii, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* 7 (1977) 664-666.
- [2] B.Ya. Kotur, E. Gratz, In: K.A. Gschneidner, Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 27, Ch. 175, Elsevier, Amsterdam, North-Holland, 1999, pp. 339-533.
- [3] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837-838.
- [4] O.I. Bodak, V.V. Pavlyuk, R.I. Andrusyak, B.Ya. Kotur, V.K. Pecharsky, V.A. Bruskov, *Kristallografiya* 35 (1990) 312-315 [*Sov. Phys.-Crystallogr.* 35 (1990) 173-175].

A NEW CATION-DISORDERED QUATERNARY SELENIDE Tl₂Ga₂SnSe₆

V. Babizhetskyy¹, V. Levytskyy¹, V. Smetana², <u>L. Piskach</u>³, O. Tsisar³, and O. Parasyuk³ ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

 ² Department of Materials and Environmental Chemistry, Stockholm University, Svante Arrhenius väg 16C, 10691 Stockholm, Sweden
 ³ Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European

National University, Potapova St. 9, 43021 Lutsk, Ukraine

lyuda0760@ukr.net

The family of TlX (X = S, Se, Te) compounds and their derivatives are well known as optical and semiconducting materials. Derivative ternary compounds Tl MX_2 (M = Al, Ga, In) form with ordering and different coordination environments of the metal atoms in the structure, in which the heavy metal atoms exhibit oxidation state +1, whereas +3 is typical for the light ones [1]. This offers a possibility to investigate the formation of solid solutions or quaternary compounds, resulting from aliovalent metal substitution, in the Tl MX_2 - $M'X_2$ (M' = Si, Ge, Sn) systems.

In the course of systematic studies of the quasiternary system $TIGaSe_2-SnSe_2$, a new quaternary compound, $Tl_2Ga_2SnSe_6$, was found. The starting atomic parameters, obtained by direct methods using the program SIR 97, were refined using the program SHELXL-97. The refined single-crystal composition is close to the composition of the initial sample, $Tl_2Ga_2SnSe_6$, and indicates a narrow homogeneity range of the compound, confirmed by EDX analysis.

The new compound Tl₂Ga₂SnSe₆ crystallizes in the tetragonal crystal system, Pearson symbol *tI*16, space group *I*4/*mcm*, *a* = 8.095(1), *c* = 6.402(1) Å, *R*₁ = 0.028 for 122 *I* > $2\sigma(I)$ and 0.043 for all the 167 data, and 10 refined parameters, including anisotropic displacement parameters. The thallium atoms occupy Wyckoff position 4*a* (0, 0, ¹/₄), the selenium atoms are in 8*h* sites (0.16418(11), ¹/₂+*x*, 0), and the *M* (0.655(5)Ga + 0.345(5)Sn) atoms occupy the 4*b* position (0, ¹/₂, ¹/₄), respectively. The unit cell and atomic coordination polyhedra of the crystal structure of Tl₂Ga₂SnSe₆ are shown in Fig.



The crystal structure of $Tl_2Ga_2SnSe_6$ is composed of one-dimensional chains of edgesharing [Ga/SnSe₄] tetrahedra along the [0 0 1] direction, with Tl^+ cations occupying voids. The observed interatomic distances indicate that thallium is monovalent, gallium is trivalent, and selenium is divalent in the structure of $Tl_2Ga_2SnSe_6$.

[1] K.-J. Range, G. Mahlberg, S. Obenland, Z. Naturforsch. B 32 (1977) 1354-1355.

NEW TERNARY PHASES IN THE Er-Ag-Al SYSTEM

<u>O.V. Zhak</u> and T.S. Horetska Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine olha.zhak@lnu.edu.ua

Among the ternary systems RE-Ag-Al, where RE is heavy rare-earth metal, phase diagrams in the whole concentration region have been constructed for the systems Y-Ag-Al [1], Gd-Ag-Al [2], Dy-Ag-Al [3], and Tb-Ag-Al [4]. Other ternary RE-Ag-Al systems have been studied for the synthesis of ternary aluminides and investigation of their crystal structures. The existence of three ternary phases, namely $Er_{1.75}Ag_{8.1}Al_{9.2}$ (Th₂Ni₁₇-type structure), $Er_8Ag_{17}Al_{49}$ (Yb₈Cu₁₇Al₄₉-type structure), and $ErAg_{2.5}Al_{2.5}$ (DyAg_{2.4}Al_{2.6}-type structure), has been reported in the Er-Ag-Al system, whereas in related systems from six to eight ternary phases are known. The main aim of our research was the synthesis of new ternary erbium silver aluminides and determination of their crystal structures.

Samples for the investigation were prepared by arc melting of weighted pieces of pure elements (all with a stated purity better than 99.9 wt.%) in a purified argon atmosphere. The alloys were placed into evacuated silica tubes, heat-treated at 600°C for 700 h, and subsequently quenched in cold water without breaking the tubes. All the samples were studied by X-ray diffraction using powder diffractometers STOE STADI P and DRON-3M. The WinCSD software [6] was used for the calculations, including the Rietveld refinement of the crystal structure.

A solid solution of substitution on the basis of the binary compound $ErAl_3$ with cubic AuCu₃-type structure was observed. The solubility of silver in $ErAl_3$ reaches up to 0.13 mol.part Ag, and the limiting composition of the solid solution is described by the formula $ErAl_{1.47}Ag_{0.53}$. The existence of the earlier reported ternary compounds $Er_{1.75}Ag_{8.1}Al_{9.2}$, $Er_8Ag_{17}Al_{49}$, and $ErAg_{2.5}Al_{2.5}$ was confirmed; in addition a new ternary aluminide, $Er(Ag_{0.5}Al_{0.5})_{12}$, with a tetragonal structure of the ThMn₁₂-type, was obtained (space group *I4/mmn*, refined lattice parameters *a* = 0.91195(6) nm, *c* = 0.54514(6) nm. The new aluminide $Er(Ag_{0.5}Al_{0.5})_{12}$ was found to be in two-phase equilibrium with the ternary phase $Er_{1.75}Ag_{8.1}Al_{9.2}$ (hexagonal Th₂Ni₁₇-type structure).

- [1] T.M. Gumenyuk, Yu.B. Kuz'ma, B.M. Stel'makhovych, J. Alloys Compd. 299 (2000) 213-216.
- [2] B.M. Stel'makhovych, O.V. Zhak, N.R. Bilas, Yu.B. Kuz'ma, J. Alloys Compd. 363 (2004) 243-248.
- [3] B.M. Stel'makhovych, Yu.B. Kuz'ma, *Dopov. Akad. Nauk Ukr.* 3 (1994) 86-89 (in Ukrainian).
- [4] R.V. Gumeniuk, Yu.B. Kuz'ma, B.M. Stel'makhovych, J. Alloys Compd. 237 (2001) 3-7.
- [5] P. Villars, *Pearson's Handbook Desk Edition, Crystallographic Data for Intermetallic Phases*, ASM International, Materials Park (OH 44073), 1997.
- [6] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.

Zr₃Ni(Co) COMPOUNDS STABILIZED BY NITROGEN AND THEIR HYDRIDES

<u>P.Ya. Lyutyy</u>, V.V. Berezovets, and I.Yu. Zavaliy Karpenko Physico-Mechanical Institute, National Academy of Sciences of Ukraine, Naukova St. 5, 79060 Lviv, Ukraine pavlo_lyutyy@ukr.net

The influence of low concentrations of light elements such as oxygen, nitrogen and carbon on the crystal structures of intermetallic compounds and their stabilization is a well-known feature of *d*-metal systems. Moreover, the impact of the O, N and C content on the hydrogen absorption/desorption properties of $A_4B_2O_x$ and $A_3B_3O_x$ phases (so-called η -phases with Ti₂Ni- or W₃Fe₃C-type structure) [1-4], as well as of A_3B phases with Re₃B-type structure, has been described in a number of publications [5-6].

Samples with starting compositions $Zr_3NiN_{0.5}$, Zr_3NiN , $Zr_3CoN_{0.5}$, and Zr_3CoN were synthesized by direct arc-melting of the elements (at least 99.8 % metal/metalloid-based purity). Nitrogen was introduced into the alloys in the form of zirconium nitride (ZrN). Calculated appropriate amounts of the elements were weighed to an accuracy of 0.01 mg, and then arc-melted on a water-cooled copper plate under an argon atmosphere, using titanium as a getter material. The obtained pellets, each with a mass of approximately 1 g, were re-melted three times for homogenization, and then re-weighed, in order to check for possible mass losses. No significant mass losses (more than 1 %) were observed. Further homogenization of the samples was performed by annealing at 600°C for 14 days.

The hydrogen absorption-desorption properties of the alloys were characterized using a Sieverts-type apparatus. The samples were activated by heating up to 473 K in dynamic vacuum, cooled to 293 K, and then hydrogenated with high-purity H₂ gas (99.999 %) at a pressure of 1.25 atm. X-ray powder diffraction data was collected using a DRON-3.0M diffractometer (Cu Ka radiation). Indexing, structure solution and full-profile refinement to obtain the structural parameters, were performed with the WinCSD [7] program package.

In the present study, crystallographic data for the $Zr_3NiN_{0.5}$, Zr_3NiN , $Zr_3CoN_{0.5}$, and Zr_3CoN compounds, and of the $Zr_3CoNH_{5.62}$ and $Zr_3NiN_{0.5}H_{5.64}$ hydrides, were determined. It was shown that the hydrides retain the structure of the parent compounds. The influence of the nature of the interstitial atoms (O,N,C) and their concentration on the hydrogen sorption properties was analyzed.

- [1] B. Rupp, J. Less-Common Met. 104 (1984) 51-63.
- [2] M.H. Mintz, Z. Hadari, M.P. Dariel, J. Less-Common Met. 63 (1979) 181-191.
- [3] I.Yu. Zavaliy, J. Alloys Compd. 291 (1999) 102-109.
- [4] I.Yu. Zavaliy, W.B. Yelon, P.Yu. Zavalij, et al., J. Alloys Compd. 309 (2000) 75-82.
- [5] H. Boller, Monatsh. Chem. 104 (1973) 545-551.
- [6] R. MacCay, H.F. Franzen, J. Alloys Compd. 186 (1992) L7-L10.
- [7] L.G. Akselrud, Yu.M. Grin. J. Appl. Crystallogr. 47 (2014) 803-805.

CRYSTAL STRUCTURE OF THE NEW TERNARY ANTIMONIDE Ce6Cu43Sb24

L. Fedyna¹, A. Fedorchuk², V. Mykhalichko³, and <u>M. Fedyna⁴</u>

¹ Lviv Institute of Economics and Tourism, Mentsynskoho St. 8, 79007 Lviv, Ukraine

² S.Z. Gzhytskyj Lviv National University of Veterinary Medicine

and Biotechnologies, Pekarska St. 50, 79010 Lviv, Ukraine

³ Lviv Polytechnic National University, Bandera St. 12, 79013 Lviv, Ukraine

⁴ National University of Forest and Wood Technology of Ukraine,

Chuprynky St. 103, 79057 Lviv, Ukraine

fmf@ua.fm

A new structure type of intermetallic compounds, Ce₆Cu₄₃Sb₂₄ (space group *P*-43*m*, Pearson code *cP*292, *a* = 17.28662(7) Å; *Z* = 4, *R*_B = 0.0796, *R*_F = 0.0905), was established by X-ray powder diffraction. Samples for the investigation, of a total weight of 1 g, were prepared from pieces of pure metals (cerium (99.88 wt.%), copper (99.99 wt.%), antimony (99.99 wt.%)) by arc melting under purified argon atmosphere at a pressure of $1.1 \cdot 10^5$ Pa (with Ti as a getter). To ensure homogeneity, the samples were remelted twice. During the sample preparation the weight losses were less than 1 % of the total mass. The samples were annealed in quartz ampoules under vacuum at 870±10 K for 740 h, and quenched in cold water. The alloys were stored under a layer of purified oil.

Phase analysis was carried out using X-ray powder diffraction data collected on DRON-3M and HZG-4a powder diffractometers (Cu K α radiation). All the samples were single-phased. The crystal structure of the ternary compounds was refined from X-ray powder diffraction data obtained with a Huber G670 Imaging Plate Guinier camera (Cu K α 1 radiation). All the procedures, including indexing, refinement of the lattice and atomic parameters, and calculations of the interatomic distances, were performed using the WinCSD [1] program package. The composition of the ternary compound was determined by X-ray diffraction and electron microprobe analysis (REMMA 102-02), and confirmed by inductively coupled plasma-optical emission spectrometry (Spectroblue FMS 26).

Isostructural $R_6Cu_{43}Sb_{24}$ compounds only form with La (a = 17.34702(7) Å). The structure type $Dy_3Cu_{20+x}Sb_{11-x}$ ($x \approx 2$) was observed with the other rare-earth metals, except for Eu, Yb



Fig. The space filling by polyhedra around the least electronegative atoms of Ce in the structures of compounds $Ce_6Cu_{43}Sb_{24}$.

and Lu.

Peculiarities of the coordination polyhedra were considered. The crystal structure of Ce₆Cu₄₃Sb₂₄ belongs to the icosahedral and cuboctahedral structures, according to the coordination of the smallest atoms. The relationship of the investigated structure with those of BaHg₁₁, Dy₃Cu_{20+x}Sb_{11-x} ($x \approx$ 2), and Eu₄Cu₄₄As₂₃ was analyzed. The coordination polyhedra formed around the least electronegative atoms in all of these structures are similar to the polyhedra in the ThMn₁₂-type structure.

The structure type $Ce_6Cu_{43}Sb_{24}$ can be derived from the simple structure of α -Po *via* the following structure types: Mo₂N, TmRuGa₃, Fe₁₃Ge₃, two hypothetical structures X1 and X2, and BaHg₁₁, by periodic doubling of the unit-cell parameter and by including both single atoms and groups of atoms (cubes and cuboctahedra).

[1] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.

DFT CALCULATIONS OF THE HYDROGEN SUBLATTICE IN Mg₂NiH_x AND Mg₃AlNi₂H_y HYDRIDES

I.V. Oshchapovsky^{1,2}, I.Yu. Zavaliy¹, and V.V. Pavlyuk²

 ¹ Karpenko Physico-Mechanical Institute, National Academy of Sciences of Ukraine, Naukova St. 5, 79060 Lviv, Ukraine
 ² Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine romaniuk@ua.fm

Magnesium alloys attract significant attention, due to their high specific hydrogen absorption capacity. They can form both complex and metallic intercalation hydrides. Complex hydrides have high specific capacity, but also high enthalpy of hydrogenation, which is an obstacle for their practical application, as the dehydrogenation requires high temperatures. In contrast to these, intercalation hydrides have lower enthalpy of hydrogenation, but also lower capacity. Moreover, the information about the structure of the hydrogen sublattice in hydrides is not always unambiguous.

Hydrogenation of the Mg₂Ni compound with hexagonal structure leads to formation of the solid solution Mg₂NiH_{0.3}, and finally transformation into the hydride Mg₂NiH₄ with cubic structure. The structure of Mg₂NiH_{0.3} is not completely clear, as several models are described in the literature [1,2]. Partial replacement of Mg by another metal leads to the formation of intermetallides Mg₃*M*Ni₂ (M = Al, Ti, Mn). These form typical metallic intercalation hydrides with much easier dehydrogenation, but also much lower capacity. The present, computational work is an effort to identify the factors governing the formation of complex (Mg₂NiH₄) or metallic hydrides (Mg₂NiH_{0.3}, Mg₃*M*Ni₂H_{*x*}), as well as to reveal the most probable structure models.

Four different models for the structure of $Mg_2NiH_{0.3}$ are described. They share the same motif, made of Mg and Ni atoms, but propose different filling of voids by hydrogen. The free energies of hydrogenation for several optimized ordered models for Mg_2NiH_x (x = 0.167, 0.333, 0.5) were calculated by the program JDFTx [3]. The results of the calculations show that the model of the $Mg_2NiH_{0.3}$ structure with partial occupation of trigonal and tetrahedral voids is the most likely.

The structure of the hydrogen sublattice of the hydride Mg₃AlNi₂H_x (x = 2.7) has not been studied by neutron diffraction. The structure of the related compound Mg₃MnNi₂D_{3-x} was investigated in [4], and it was shown that deuterium occupies $16d (\frac{1}{2} \frac{1}{2})$ and 32e(0.289 0.289 0.289) voids. Several models for the structure of Mg₃AlNi₂H_x with full occupation of 16d, 32e, as well as $8a (\frac{1}{8} \frac{1}{8})$ and $8b (\frac{5}{8} \frac{5}{8} \frac{5}{8})$ voids were tested. Niggli cell reduction was used in order to speed up the calculations. The model with full occupation of both 16d + 32e voids showed the highest energy of hydrogenation and proved that hydrogen occupies these voids in Mg₃AlNi₂H_x (x = 2.7) too.

- [1] D. Noreus, P.-E. Werner, Acta Chem. Scand., Ser. A 36 (1982) 847-851.
- [2] B. Darriet, J.L. Soubeyroux, M. Pezat, D. Fruchart, J. Less-Common Met. 103 (1984) 153-162.
- [3] R. Sundararaman, K. Letchworth-Weaver, K.A. Schwarz, D. Gunceler, Y. Ozhabes, T.A. Arias, *SoftwareX* 6 (2017) 278-284.
- [4] R.V. Denys, A.R. Riabov, V.V. Berezovets, I.V. Koval'chuk, R. Cerný, I.Yu. Zavaliy, *Intermetallics* 19 (2011) 1563-1566.

<u>V.M. Hreb</u> and L.O. Vasylechko

Semiconductor Electronics Department, Lviv Polytechnic National University, S. Bandera St. 12, 79013 Lviv, Ukraine wasiahreb@meta.ua

Perovskite-type oxides based on $RCoO_3$ and $RCrO_3$ (R – rare-earth element) are perspective materials for diverse applications in fuel cells, thermoelectrics, multiferroics, catalysts, and sensory materials, due to their high electrical conductivity, specific magnetic properties, as well as significant electrochemical and catalytic activity.

The mixed gadolinium cobaltite-chromite $GdCo_{0.5}Cr_{0.5}O_3$ with orthorhombic perovskite structure was prepared from stoichiometric amounts of Gd_2O_3 , Co_3O_4 and Cr_2O_3 by solidstate reaction in air at 1573 K for 25 h with intermediate regrinding of the product. Laboratory X-ray powder diffraction examination (Huber image plate Guinier camera G670, Cu $K\alpha_1$ radiation) of the as-prepared material revealed a single phase with orthorhombic perovskite structure isotypic with GdFeO₃ (space group *Pbnm*). The structural parameters of GdCo_{0.5}Cr_{0.5}O₃ agree well with those of the parent GdCoO₃ and GdCrO₃ compounds, thus proving formation of a continuous solid solution in the GdCoO₃–GdCrO₃ system.

The thermal behavior of the structure of $GdCo_{0.5}Cr_{0.5}O_3$ was studied in the temperature range 298-1173 K by *in situ* X-ray synchrotron powder diffraction at the B2 beamline of the synchrotron laboratory HASYLAB@DESY. Anomalous behavior of the lattice expansion was found, which is reflected in a sigmoidal temperature dependence of the unit-cell dimensions, and in a significant increase of the thermal expansion coefficients (TECs), with a broad maximum near 900 K (Fig.). The observed anomalies in the mixed cobaltite-chromite $GdCo_{0.5}Cr_{0.5}O_3$ are less pronounced than in "pure" $GdCoO_3$: the increment of the thermal expansion coefficients is 1.3 times lower and the maximum of the TEC curve is shifted toward higher temperatures. Analysis of selected interatomic distances and angles allowed detecting additional structural anomalies, such as increasing deformation of the [Co/CrO₆] octahedra and saturation of the octahedral tilt angles above 800 K (Fig., inset), which evidently are caused by spin cross-over phenomena occurring in the system.



Fig. Temperature dependencies of the linear thermal expansion coefficients in different crystallographic directions, average interatomic distances inside the $[Co/CrO_6]$ octahedra and octahedral tilt angles (inset) in the structure of $GdCo_{0.5}Cr_{0.5}O_3$.

The work was supported in parts by the Ukrainian Ministry of Education and Sciences under project No. 0118U000264 (DB/Feryt) and an ICDD Grant-in-Aid program.

CeM02B5: A NEW TYPE OF ARRANGEMENT OF PUCKERED BORON HEXAGONAL RINGS

<u>Sever Flipo^{1,2}</u>, Miroslav Kohout², Friedrich Roth¹, Tina Weigel¹, Walter Schnelle²,

Matej Bobnar², Alim Ormeci^{1,2}, Ulrich Burkhardt², Christoph Hennig³, Tilmann Leisegang¹, Dirk-Carl Meyer¹, Andreas Leithe-Jasper², and Roman Gumeniuk¹

¹Institut für Experimentelle Physik, TU Bergakademie Freiberg,

Leipziger Straße 23, 09596 Freiberg, Germany

² Max-Planck-Institut für Chemische Physik fester Stoffe,

Nöthnitzer Straße 40, 01187 Dresden, Germany

³ ESRF, 71, Avenue des Martyrs, Grenoble, France

sever.flipo@physik.tu-freiberg.de

 $REMo_2B_5$ (RE = Ce, Pr, Nd) and CeW_2B_5 were synthesized by arc melting, followed by annealing at 1300°C. $CeMo_2B_5$ represents a new structure type; it crystallizes with space group *Pnma*, a = 11.0298(2) Å, b = 3.12080(5) Å, c = 9.9594(2) Å, Z = 4. Its structure contains puckered [B₆]-hexagonal rings, trigonal-prismatic and empty pyramidal-tetrahedral slabs. The structure can be related to derivatives of the AlB₂ and CrB prototypes. The boron atoms form a two-dimensional network of corrugated ribbons, infinitely extending along the *b* axis, the width of which is composed of four edge-linked [B₆] rings.

CeMo₂B₅ is a Pauli paramagnet. Electrical transport measurements, together with the calculated density of states (DOS) at the Fermi level of 3.81 states eV^{-1} f.u.⁻¹, indicate that CeMo₂B₅ is a typical metallic system. Electronic structure calculations revealed important hybridization of Ce 4*f*5*d* states with Mo 4*d* states. The chemical bonding scenario is dominated by chains of [Ce₂Mo₂] clusters with multi-center bonds. The clusters are connected *via* metallic Mo-Mo bonds. This metal framework is in turn stabilized by bonding interactions with the boron ribbons to which it donates electrons [1].

 S. Flipo, M. Kohout, F. Roth, T. Weigel, W. Schnelle, M. Bobnar, A. Ormeci, U. Burkhardt, C. Hennig, T. Leisegang, D.-C. Meyer, A. Leithe-Jasper, R. Gumeniuk, *Eur. J. Inorg. Chem.* (2019) 3572-3580. Doi: 10.1002/ejic.201900411.

P42

CRYSTAL STRUCTURE OF THE TERNARY Ce0.75Y0.25Ge COMPOUND

I. Voloshyn, Z. Shpyrka, and V. Pavlyuk Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine volosinira_@ukr.net

The ternary compound $Ce_{0.75}Y_{0.25}Ge$ was found during an investigation of the Ce–Y–Ge system [1]. The crystal structure of this compound has now been determined from X-ray powder diffraction data (DRON-4.07, Fe K α -radiation). Rietveld refinements of the powder diffraction data were performed with the FullProf program [2]. Details of the structure refinement for Ce_{0.75}Y_{0.25}Ge are given in Table 1. Atomic coordinates, isotropic displacement parameters and site occupancies for Ce_{0.75}Y_{0.25}Ge are listed in Table 2.

Table 1 Details of the structure refinement for the $Ce_{0.75}Y_{0.25}Ge$ compound.

Compound	Ce _{0.75} Y _{0.25} Ge
Structure type	CrB
Space group	Стст
Pearson symbol	oS8
Lattice parameters, Å	a = 4.4676(7), b = 11.067(1), c = 4.0499(6)
Cell volume V, $Å^3$	200.24
Formula units per cell Z	4
FWHM parameters U, V, W	-0.10706, 0.02634, 0.10714
Mixing parameter η	0.26(4)
Asymmetry parameter $C_{\rm M}$	-0.13(2)
Reliability factors	$R_{\rm B} = 0.119, R_{\rm p} = 0.0424, R_{\rm wp} = 0.0582, R_{\rm exp} = 0.0213$

	Ta	abl	le :	27	Atomi	coord	inates	and	isotro	pic	disp	lacement	parameters	for	Ce _{0.75}	Y_0	25Ge.	Cmcm.
--	----	-----	------	----	-------	-------	--------	-----	--------	-----	------	----------	------------	-----	--------------------	-------	-------	-------

Atom	Site	G	x/a	y/b	z/c	$B_{\rm iso},{\rm \AA}^2$
Ce Y	4 <i>c</i>	0.75 0.25	0	0.3631(3)	1⁄4	1.06(2)
Ge	4c	1.0	0	0.0765(1)	1⁄4	1.6(1)

Isostructural compounds are formed with Dy, Ho, Er, and Tm. Unit-cell parameters of the $R_{0.75}Y_{0.25}$ Ge compounds are listed in Table 3.

Compound	U	Volume Å ³		
Compound	a	b	С	vorunie, m
Ce _{0.75} Dy _{0.25} Ge	4.4691(2)	11.068(4)	4.052(2)	200.4
Ce _{0.75} Ho _{0.25} Ge	4.468(1)	11.067(4)	4.050(1)	200.3
Ce _{0.75} Er _{0.25} Ge	4.470(4)	11.074(6)	4.062(3)	201.2
Ce _{0.75} Tm _{0.25} Ge	4.467(3)	11.065(8)	4.049(5)	200.1

Table 3 Unit-cell parameters of $R_{0.75}$ Y_{0.25}Ge compounds.

[1] Z.M. Shpyrka, O.I. Bodak, I.R Mokra, J. Alloys Compd. 247 (1997) 217-222.

[2] J. Rodriguez-Carvajal, Program FullProf. 2k (Version 2.90. 2004. LLB JRC).

NEW MULTICOMPONENT COMPOUNDS *R*₅Ni_{1.5}Co_{1.5}Al₃Ge₄ (*R* = RARE-EARTHS)

<u>N. Semuso</u>, S. Pukas, Ya. Tokaychuk, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine nataliya.semuso@lnu.edu.ua

Three new multicomponent compounds were found in the *R*–Ni–Co–Al–Ge (R = Tb, Ho, Er) systems with the simultaneously presence of two *d*-elements, at the ratio Ni:Co = 1:1. Alloys of nominal composition $R_{0.33}$ Ni_{0.10}Co_{0.10}Al_{0.20}Ge_{0.27} were synthesized by arc melting under an Ar atmosphere and annealed at 600°C for 1800 h. The crystal structures were studied by X-ray powder diffraction (diffractometers DRON-2.0M, Fe K α radiation and STOE STADI P, Cu $K\alpha_1$ radiation). The compounds crystallize in the orthorhombic structure type Er₅Ni₃Al₃Ge₄: Pearson symbol *oP*30, space group *Pmmn*. Up to now, the type-defining compound was the only known representative of this structure type [1].

Table Crystallographic parameters of the compounds *R*₅Ni_{1.5}Co_{1.5}Al₃Ge₄.

Carro Paran	receipe of the compo		
<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	$V, \text{\AA}^3$
4.1995(7)	19.375(4)	6.9029(8)	561.7(1)
4.1666(5)	19.216(2)	6.8478(6)	548.3(1)
4.1559(6)	19.158(3)	6.8203(7)	543.1(1)
4.1556	19.082	6.8392	542.3
	<i>a</i> , Å 4.1995(7) 4.1666(5) 4.1559(6) 4.1556	a, Å b, Å 4.1995(7) 19.375(4) 4.1666(5) 19.216(2) 4.1559(6) 19.158(3) 4.1556 19.082	a, Å $b, Å$ $c, Å$ $4.1995(7)$ $19.375(4)$ $6.9029(8)$ $4.1666(5)$ $19.216(2)$ $6.8478(6)$ $4.1559(6)$ $19.158(3)$ $6.8203(7)$ 4.1556 19.082 6.8392



Fig. Stacking of trigonal prisms in the structure of Er₅Ni₃Al₃Ge₄.

The cell parameters of the isotypic compounds $R_5Ni_{1.5}Co_{1.5}Al_3Ge_4$ are listed in the Table; they decrease with decreasing atomic radius of the rare-earth metal from Tb to Er.

In the structure of the $R_5Ni_{1.5}Co_{1.5}Al_3Ge_4$ compounds, one of the two *T* sites (Ni or Co atoms) and both Ge sites are characterized by trigonal-prismatic coordination, but with different compositions: Al₆ (*T*), R_4T_2 (Ge1) and R_6 (Ge2), respectively.

The structure can be considered as a three-dimensional framework of infinite columns of trigonal prisms of composition R_6 and R_4T_2 sharing common bases, which are interconnected by edges and form hexagonal rings. The channels in this framework contain isolated columns formed by the Al₆ trigonal prisms (Fig.).

[1] P. Demchenko, J. Konczyk, G. Demchenko, R. Gladyshevskii, V. Pavlyuk, Acta Crystallogr. C 62 (2006) i29-i31.

A TERNARY PHASE WITH THE Nb₂Cr₄Si₅ STRUCTURE TYPE IN THE Hf–V–Ge SYSTEM

A. Broda, <u>O. Matselko</u>, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine oksana.matselko@lnu.edu.ua

The isothermal section of the phase diagram of the Hf–V–Ge system has been constructed at 900°C, and the formation of three ternary compounds has been reported: $Hf_{10.8-21.7}V_{36.0-42.8}Ge_{42.3-46.4}$, HfVGe, and Hf_2V_3Ge . The crystal structures have only been determined for HfVGe and Hf_2V_3Ge [1].

In order to define the crystal structure parameters of the not yet characterized phase, samples in the region $Hf_{10.8-21.7}V_{36.0-42.8}Ge_{42.3-46.4}$ were synthesized from pure elements by arc melting, annealed in evacuated quartz tube at 900°C for 1000 h, and subsequently quenched in water. Phase and structural analyses were performed using X-ray powder diffraction data (STOE STADI P diffractometer, Cu $K\alpha_1$ radiation) and the WinCSD program package [2].

A sample of composition $Hf_{12}V_{42}Ge_{46}$ was chosen for detailed structural investigations. The reflections of the main phase in the sample were indexed with an orthorhombic lattice, and the Nb₂Cr₄Si₅ structural model was used for the crystal structure refinement: Pearson symbol *oI*44, space group *Ibam*, *a* = 7.8527(2), *b* = 16.6460(4), *c* = 5.1431(1) Å.

The crystal structure of the title phase, refined composition $Hf_{2.05(2)}V_{3.95(2)}Ge_5$, is characterized by the statistical mixtures of V and Hf atoms in two of the 8*j* positions. Isostructural compounds are known in related systems: {Nb,Ta}–V–Si, {Sc,Ti,Zr,Hf,Nb,Ta}–Cr–Si, {Nb,Ta}–Mn–Si, Hf–Cr–Ge, and Sc–Nb–Sn [3].

111 2.05(2) v 3.95(2	005 (102014015	, 0144, 10 <i>um</i> , a =	-7.0527(2), b =	10.0+00(+), t = 10.0+00(+)	5.1+51(1) A).
Site	Wyckoff position	X	у	Z.	$B_{\rm iso}$, Å ²
<i>M</i> 1	8 <i>j</i>	0.1162(4)	0.1425(3)	0	0.78(3)
M2	8 <i>j</i>	0.2414(10)	0.4355(5)	0	0.82(4)
V	8g	0	0.3101(6)	1⁄4	0.82(4)
Ge1	8 <i>j</i>	0.2986(9)	0.2853(5)	0	0.86(4)
Ge2	8 <i>j</i>	0.4044(10)	0.0661(5)	0	0.80(4)
Ge3	4 <i>a</i>	0	0	1⁄4	0.80(4)
3.64 0.054 (6)3					

Table Atomic coordinates, site occupancies, and isotropic displacement parameters for $Hf_{2.05(2)}V_{3.95(2)}Ge_5$ (Nb₂Cr₄Si₅, *oI*44, *Ibam*, *a* = 7.8527(2), *b* = 16.6460(4), *c* = 5.1431(1) Å).

M1 = 0.951(6)Hf + 0.049(6)V; M2 = 0.925(7)V + 0.075(7) Hf.

- [1] Yu.D. Seropegin, M.V. Rudometkina, *Moscow Univ. Chem. Bull.* 54 (1999) 32-41.
- [2] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.
- P. Villars, K. Cenzual (Eds.), Pearson's Crystal Data Crystal Structure Database for Inorganic Compounds, Release 2016/17, ASM International, Materials Park (OH), 2016.

NEW REPRESENTATIVES OF THE STRUCTURE TYPE Er₅Ni₃Al₃Ge₄

Yu. Plyatsko, <u>S. Pukas</u>, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine svitlana.pukas@lnu.edu.ua

The aim of the present work was to search for new representatives of the structure type $Er_5Ni_3Al_3Ge_4$ (*oP30*, *Pmmn*) [1] in *R*–Ni–Al–Ge systems. Two new rare-earth nickel aluminogermanides, Ho₅Ni₃Al₃Ge₄ and Tm₅Ni₃Al₃Ge₄, were synthesized by arc melting, and their crystal structures were refined from X-ray powder diffraction data (diffractometer STOE STADI P, Cu Ka₁ radiation; program DBWS-9708). The cell parameters of the *R*₅Ni₃Al₃Ge₄ aluminides decrease with increasing atomic number of *R* from Ho to Tm (Table).

Compound	<i>a</i> , Å	b, Å	<i>c</i> , Å	$V, \text{\AA}^3$
Ho ₅ Ni ₃ Al ₃ Ge ₄	4.1632(8)	19.114(5)	6.8563(9)	545.6(2)
Er5Ni3Al3Ge4 [1]	4.1561	19.069	6.8369	541.8
Tm ₅ Ni ₃ Al ₃ Ge ₄	4.1360(7)	18.974(4)	6.7908(9)	532.9(2)

Table Crystallographic parameters of the compounds *R*₅Ni₃Al₃Ge₄.

In the $Er_5Ni_3Al_3Ge_4$ -type structure the atoms of the rare-earth metal occupy three sites, whereas the Ni, Al, and Ge atoms occupy two sites each. The coordination polyhedra of the Er atoms are pentagonal prisms ($Er_2Ni_2Al_2Ge_4$, $Ni_2Al_4Ge_4$, and Al_6Ge_4) with 8 additional atoms (Er, Ni, and Ge). The Al atoms are situated at the centers of cuboctahedra ($Er_6Ni_2Al_2Ge_2$) and the Ge atoms at the centers of tricapped trigonal prisms (Ho_4Ni_2 and Ho_6 prisms with three additional atoms, HoNiAl and Al_2Ni , respectively). The Ni atoms are characterized by two types of polyhedron: tricapped trigonal prisms (Al_6 prism with three additional Ho atoms) and tetrahedra (Ge_4).

The structure of $Er_5Ni_3Al_3Ge_4$ can be considered as a stacking of trigonal prisms. The Ni-centered Al₆ trigonal prisms form infinite columns (common triangular faces) along the short translation period (*x* axis). The Ge-centered prisms are connected *via* prism edges, forming infinite slabs with 6-membered rings (two Ho₄Ni₂ prisms and four Ho₆ prisms). This way hexagonal channels are formed, inside which the isolated columns of Ni-centered Al₆ prisms are situated.

[1] P. Demchenko, J. Konczyk, G. Demchenko, R. Gladyshevskii, V. Pavlyuk, Acta Crystallogr. C 62 (2006) i29-i31.

P46

CRYSTAL STRUCTURE OF THE COMPOUND Dy4Ga14Ge5.6

<u>T. Delenko</u>, Ya. Tokaychuk, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine tarasdelenko@gmail.com

A new ternary compound, Dy₄Ga_{1.4}Ge_{5.6}, was found during a systematic investigation of the phase equilibria in the system Dy-Ga-Ge at 600°C. The crystal structure was refined by the Rietveld method, using the X-ray powder diffraction pattern of an alloy of nominal composition $Dy_{40}Ga_{15}Ge_{45}$, collected on a powder diffractometer STOE STADI P (Cu Ka₁) radiation). The sample was synthesized from the elements by arc melting under a purified argon atmosphere, annealed at 600°C under vacuum for 720 h and subsequently quenched in cold water. Refinement of the profile and structural parameters was performed using the software package FullProf Suite [1]. The compositions of the individual phases in the sample were determined by local X-ray spectral analysis, performed on a raster electron microscope REMMA-102-02 equipped with an energy-dispersion X-ray spectrometer EDAR. The positions of the small atoms were assumed to be occupied by statistical mixtures of Ga and Ge atoms. Due to the similarity of the scattering factors of Ga and Ge, the compositions of the statistical mixtures were not refined, but fixed to the ratio M = 0.2Ga + 0.8Ge, given by the results of the EDX spectroscopy. Beside the main phase, the sample contained 17.7(5) wt.% of the ternary phase Dy₃Ga_{2.4}Ge_{2.6} (structure type Pu₃Pd₅, Pearson symbol oS32, space group *Cmcm*, a = 9.359(2), b = 7.4790(19), c = 9.415(2) Å) [2] and 7.3(3) wt.% of the TII-type phase DyGa_{0.2}Ge_{0.8} (oS8, Cmcm, a = 4.2777(13), b = 10.679(4), c = 3.9345(12) Å) which is part of the continuous solid solution $DyGa_{1-x}Ge_x$ existing in the system Dy-Ga-Ge at 600°C.

The crystal structure of the ternary compound Dy₄Ga_{1.4}Ge_{5.6} belongs to the structure type Er₄(Ga_{0.19}Ge_{0.81})₇, which is a vacancy ordering derivative of the structure type AlB₂. The shortest distances in the structure of Dy₄Ga_{1.4}Ge_{5.6} are the distances between the positions of the statistical mixture of Ga and Ge atoms: $\delta_{M1-M2} = 2.440(13)$ and $\delta_{M1-M3} = 2.446(18)$ Å, indicating strong interaction between the *p*-elements in the planar nets stacked along the crystallographic direction [001].

a = 7.5507(17), c = 4.1202(5) A, AB = 0.0714, AF = 0.0071, M = 0.20a + 0.0002).									
Site	Wyckoff position	x	У	Z.	$B_{\rm iso},{\rm \AA}^2$				
Dy1	3 <i>k</i>	0.8352(6)	0.1648(6)	1/2	0.43(2)				
Dy2	1d	1/3	2/3	1/2	0.41(3)				
<i>M</i> 1	3 <i>j</i>	0.1766(18)	0.8234(18)	0					
<i>M</i> 2	3 <i>j</i>	0.5240(11)	0.4760(11)	0	1.83(17)				
<i>M</i> 3	1 <i>a</i>	0	0	0					

Table Atomic coordinates and isotropic displacement parameters for Dy₄Ga_{1.4}Ge_{5.6} (structure type Er₄(Ga_{0.19}Ge_{0.81})₇, Pearson symbol *hP*11, space group *P*-6*m*2, a = 7.9967(17), c = 4.1202(9) Å $R_{\rm P} = 0.0714$, $R_{\rm F} = 0.0871$, M = 0.2Ga + 0.8Ge)

[1] J. Rodriguez-Carvajal, Commission on Powder Diffraction (IUCr), Newsletter 26 (2001) 12-19.

[2] T. Delenko, Ya. Tokaychuk, R. Gladyshevskii, *Visn. Lviv. Univ., Ser. Khim.* 60 (2019) 91-102 (in Ukrainian).

CRYSTAL STRUCTURE OF THE COMPOUND Zr₅AlGe₃

<u>D. Maryskevych</u>¹, Ya. Tokaychuk¹, Yu. Prots², L. Akselrud¹, and R. Gladyshevskii¹ ¹Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Max Planck Institute for Chemical Physics of Solids, Nöthnitzer St. 40, 01187 Dresden, Germany danylo.maryskevych @gmail.com

The new ternary compound Zr₅AlGe₃ was found during an investigation of the interaction between the components in the system Zr–Al–Ge at 600°C. An alloy of nominal composition Zr_{55.6}Al_{11.1}Ge_{33.3} was synthesized from pure metals (\geq 99.99 wt.%) by arc melting under argon atmosphere, and annealed under vacuum at 600°C for 720 h. A prism-like single crystal was extracted from the alloy, mounted on a glass fiber and X-ray diffraction data were collected with a Rigaku AFC7 diffractometer, equipped with a Mercury CCD detector (graphite monochromator, Mo K α radiation, $\lambda = 0.71073$ Å) at room temperature. An absorption correction was performed with a multi-scan procedure.

The structure was solved by direct methods in the centrosymmetric hexagonal space group $P6_3/mcm$; the positional and anisotropic displacement parameters were refined by the full-matrix least-squares method, using the program package WinCSD [1]. The structure of the ternary compound Zr₅AlGe₃ belongs to the structure type Hf₅CuSn₃ (Pearson symbol *hP*18, space group $P6_3/mcm$), which represents a ternary ordered variant of the structure type Ti₅Ga₄, which is a filled derivative of the structure type Mn₅Si₃ (*hP*16, *P6*₃/*mcm*).

Site	Wyckoff position	, x	x		у		Z.	$B_{\rm iso}$, Å ²
Zr1	6 <i>g</i>	0.256	7(2)	0			1⁄4	1.21(4)
Zr2	4 <i>d</i>	1/3	1/3		2/3		0	0.87(3)
Al	2b	0	0		0		0	1.27(14)
Ge	6 <i>g</i>	0.610	0(2)	2) 0			1⁄4	1.05(4)
~ .			_				_	
Site	B_{11}	B_{22}	B	33	B_{12}		B_{13}	B_{23}
Zr1	1.25(4)	0.87(5)	1.0	9(5)	0.43(2)	0	0
Zr2	0.86(3)	0.86(3)	0.5	9(5)	0.43(2)	0	0
Al	1.4(2)	1.4(2)	0.6	0.69		9)	0	0
Ge	0.96(4)	0.94(5)	0.9	4(5)	0.47(3)	0	0

Table Atomic coordinates and displacement parameters for Zr ₅ AlGe ₃
(structure type Hf ₅ CuSn ₃ , $hP18$, $P6_3/mcm$, $a = 8.104(3)$, $c = 5.654(2)$ Å,
R = 0.0357, wR = 0.0375).

In the structure of Zr_5AlGe_3 the Al atoms occupy Wyckoff position 2*b* at the origin of the unit cell and center Zr_6 octahedra, which are connected *via* common faces, forming columns along the crystallographic direction [001]. These columns fill the channels in the 3D-framework of Zr-centered Ge₆ octahedra.

[1] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.

CRYSTAL STRUCTURE OF THE DyNi₃Ga₉ AND ErNi₃Ga₉ COMPOUNDS

V. Topertser, <u>N. Muts</u>, Ya. Tokaychuk, P. Demchenko, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine natalia.muts@gmail.com

The *R*–Ni–Ga systems, where *R* is a rare-earth metal (Sc, Y, La-Lu), are rich in intermetallic compounds: more than 270 ternary compounds, crystallizing with 53 structure types, have been reported in these systems [1]. Our investigations in the Gd–Ni–Ga system showed the existence of a new ternary compound in the Ga-rich region – GdNi₃Ga₉ [2].

 $R_{7.7}$ Ni_{23.1}Ga_{69.2} (R = Dy, Er) samples were synthesized by arc-melting of elements with the following purities: $R \ge 99.89$ wt.%, Ni ≥ 99.89 wt.%, and Ga ≥ 99.89 wt.%. The alloys were annealed at 600°C for 88 days in evacuated quartz ampoules, and subsequently quenched in cold water. The crystal structures of the DyNi₃Ga₉ and ErNi₃Ga₉ compounds were refined, using the program package FullProf Suite, from X-ray powder diffraction patterns recorded with a STOE STADI P diffractometer (Cu K α_1 radiation).

The crystal structure of the compounds RNi_3Ga_9 (R = Dy, Er) belongs to the structure type DyNi_3Al₉ (Pearson symbol *hR*99, space group *R*32): a = 0.72455(2), c = 2.74346(7) nm for DyNi_3Ga₉ and a = 0.72351(2), c = 2.74087(9) nm for ErNi_3Ga₉), which is a partially disordered variant of the ordered ErNi_3Al₉-type structure (*hR*78, *R*32), and of the disordered Yb_{0.67}Ni_2Al₆-type structure (*hP*11, *P*-6*m*2).

(structure type D y113/19, 1 carson symbol <i>mxyy</i> , space group <i>myz</i>).									
Atom	Wyckoff	At	comic coordinat	Occupancy	$B_{\rm iso.}$				
Atom	position	x	У	z	Occupancy	(10^{-2} nm^2)			
Dy1	6 <i>c</i>	0	0	0.3333(4)	0.809(4)	1.46(12)			
Dy2	3a	0	0	0	0.424(4)	1.46(12)			
Ni	18 <i>f</i>	0.3233(18)	0.0088(19)	0.0822(1)	1	1.14(11)			
Ga1	18 <i>f</i>	0.3213(15)	0.3310(16)	0.0664(1)	1	1.42(7)			
Ga2	9e	0.213(3)	0	0	0.576(5)	1.42(7)			
Ga3	9 <i>d</i>	0.3495(14)	0	1⁄2	1	1.42(7)			
Ga4	6 <i>c</i>	0	0	0.4514(5)	1	1.42(7)			
Ga5	6 <i>c</i>	0	0	0.2176(7)	1	1.42(7)			
Ga6	6 <i>c</i>	0	0	0.1144(6)	1	1.42(7)			
Ga7	18 <i>f</i>	0.008(8)	0.207(6)	0.3275(12)	0.190(4)	1.42(7)			

Table Atomic coordinates, site occupancies and displacement parameters for DyNi₃Ga₆ (structure type DyNi₃Al₉, Pearson symbol *hR*99, space group *R*32).

[1] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data – Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, USA, Release 2016/17.

[2] V. Topertser, R.-I. Martyniak, N. Muts, Ya. Tokaychuk, R. Gladyshevskii, *Coll. Abstr. XVII Sci. Conf. Lviv Chem. Readings*, Lviv, 2019, p. H1.

CRYSTAL STRUCTURE OF NOVEL TERNARY INDIDES $RE_{23}Ni_7In_4$ (RE = Gd, Tb, Dy)

<u>Yu.B. Tyvanchuk¹ and A.O. Oliynyk²</u>

 ¹ Department of Analytical Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ² Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2 yuriy.tyvanchuk@lnu.edu.ua

A systematic investigation of the phase equilibria in the Dy–Ni–In system at 870 K [1] revealed 13 ternary compounds, three of them in the dysprosium-rich region. Along with the Ho_6Co_2Ga - and $Lu_{14}Co_3In_3$ -type compounds, a phase with composition $\sim Dy_{67}Ni_{22}In_{11}$ and unknown hexagonal structure was found.

Polycrystalline samples of $Dy_{67}Ni_{22}In_{11}$ and $RE_{62.5}Ni_{25}In_{12.5}$ (RE = Gd, Tb) were synthesized by arc-melting stoichiometric amounts of the elements under argon atmosphere. The samples were annealed at 870 K for 720 h in evacuated quartz tubes, and finally quenched in cold water, without breaking the tubes.

Phase analysis and Rietveld refinements on powder data (STOE STADI P, Cu $K\alpha_1$ radiation) were performed using the FullProf program package. Intensity data from a Dy₆₇Ni₂₂In₁₁ single crystal, which was isolated from an annealed sample, were collected using a Bruker PLATFORM diffractometer with an APEX II detector. The crystal structure was determined by direct methods, using SHELX-2018 package programs. The compound adopts a Yb₂₃Cu₇Mg₄-type structure (space group *P*6₃/*mmc*, *hP*68) [2] with the lattice parameters a = 9.533(5) and c = 21.890(13) Å. The refined composition of the compound was Dy₂₃Ni₇In₄, or Dy_{67.6}Ni_{20.6}In_{11.8}, which agrees well with the composition established by EDX analysis – Dy_{64.0}Ni_{19.3}In_{16.7}. Based on 393 independent reflections [$I > 2\sigma(I)$] the crystal structure was refined to the reliability factors R1 = 0.0328 and wR2 = 0.0547 with anisotropic displacement parameters for all of the atoms.

The largest, dysprosium atoms are surrounded by 13-15 nearest neighbors, *viz*. $[Dy1Dy_{10}Ni_2In_2]$, $[Dy2Dy_{10}Ni_4In]$, $[Dy3Dy_{10}Ni_2In_2]$, $[Dy4Dy_{10}NiIn_2]$, $[Dy5Dy_9Ni_3In_3]$. The indium atoms are surrounded by 12 atoms forming icosahedra $[In1Dy_{10}In_2]$ and $[In2Dy_{12}]$. The smallest, nickel atoms are surrounded by trigonal prisms of dysprosium atoms with three additional atoms capping the lateral faces, $[Ni1Dy_8Ni]$ and $[Ni2Dy_9]$.

Isotypic $RE_{23}Ni_7In_4$ compounds were also found for RE = Gd (a = 9.6394(6), c = 22.115(2) Å) and RE = Tb (a = 9.5732(6), c = 21.984(2) Å).

The Yb₂₃Cu₇Mg₄-type structure was found for the first time in ternary indides. It is related to the structure types $Pr_{23}Ir_7Mg_4$ (*P*6₃*mc*, *hP*68, *a* = 10.012, *c* = 22.572 Å) and Gd₄RhIn (*F*-43*m*, *cF*96, *a* = 13.707 Å) [3].

- [1] Yu.B. Tyvanchuk, V.I. Zaremba, L.G. Akselrud, A. Szytula, Ya.M. Kalychak, J. Alloys Compd. 704 (2017) 717-723.
- [2] S. De Negri, A. Saccone, P. Rogl, G. Giester, Intermetallics 16 (2008) 1285-1291.
- [3] P. Solokha, S. De Negri, V. Pavlyuk, A. Saccone, Chem. Met. Alloys 2 (2009) 39-48.
P51

<u>Nazar Zaremba^{1,2}</u>, Viktor Hlukhyy², and Volodymyr Pavlyuk^{1,3}

¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

² Department of Chemistry, Technische Universität München,

Lichtenbergstr. 4, 85747 Garching, Germany

³ Częstochowa Jan Długosz University, Institute of Chemistry, Environmental Protection and

Biotechnology, al. Armii Krajowej 13/15, 42200, Częstochowa, Poland

nazar.zaremba@gmail.com

During an investigation of the interaction of the components in the Yb–Ni–Al ternary system at 970 K, the existence of a new ternary compound, YbNi_{2+x}Al_{3-x} (x = 0.31), was established. Good-quality single crystals of the title compound were isolated from an annealed alloy of composition Yb_{16.6}Ni_{41.7}Al_{41.7}. Intensity data of YbNi_{2.31}Al_{2.69} were collected at room temperature on a STOE StadiVari diffractometer, equipped with a Mo K α microfocus source and a Pilatus 300K detector. The YbNi_{2.31}Al_{2.69} compound crystallizes in space group *P6/mmm* (a = 8.2723(12) Å, c = 4.0672(8) Å; $R_1 = 0.0100$, w $R_2 = 0.0212$, 212 F^2 values, 18 variables). The refined atomic parameters are given in Table 1. The structure of YbNi_{2.31}Al_{2.69} can be derived from the hexagonal YCo₃Ga₂ [1] and YNi₂Al₃ [2] types. The difference between the three structures is in the different distribution of transition metal (Co and Ni) and *p*-element (Al and Ga) atoms on the crystallographic sites (see Table 2).

Similarly to the recently reported $YNi_{2+x}Al_{3-x}$ compound [3], the $YbNi_{2+x}Al_{3-x}$ compound can be considered as a good candidate for hydrogenation.

101 101 (12.5)1 12.09							
Atom	Wyckoff position	X	у	Z.	$U_{ m eq}$		
Yb1	1 <i>a</i>	0	0	0	0.00793(9)		
Yb2	2d	1/3	2/3	1/2	0.00716(8)		
Al1	3f	1/2	0	0	0.0060(2)		
Ni1	61	0.18215(3)	0.36431(6)	0	0.00547(9)		
М	6 <i>k</i>	0.29669(10)	0	1⁄2	0.0070(2)		

 Table 1 Atomic coordinates and isotropic equivalent displacement parameters

 for YbNi2 21Al2 60.

M = 0.154(5)Ni + 0.846(5)Al

Table 2 Distribution of atoms on the crystallographic sites in YbNi_{2.31}Al_{2.69}, YNi₂Al₃ and YCo₃Ga₂.

Wyckoff position	YNi ₂ Al ₃	YbNi _{2.31} Al _{2.69}	YCo ₃ Ga ₂			
1a	Y1	Yb1	Y1			
2d	Y2	Yb2	Y2			
3 <i>f</i>	Al1	Al1	Co1			
6 <i>k</i>	A12	М	Ga			
61	Ni1	Ni1	Co2			

This work was supported by DAAD, Germany (No. 91619802).

- [1] M.A. Fremy, D. Gignoux, J.M. Moreau, D. Paccard, L. Paccard, *J. Less-Common Met.* 106 (1985) 251-255.
- [2] O.S. Zarechnyuk, R.M. Rykhal', Visn. Lviv. Derzh. Univ., Ser. Khim. 23 (1981) 23-45.
- [3] B. Sorgic, Z. Blazina, A. Drasner, J. Alloys Compd. 265 (1998) 185-189.

CRYSTAL STRUCTURE OF AgGa₂Se₃Cl

 <u>V. Kozak</u>¹, L. Gulay², I. Ivashchenko¹, P. Tyshchenko¹, and I. Olekseyuk¹
 ¹ Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine
 ² Department of Ecology and Environmental Protection, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine inna.ivashchenko05@gmail.com

The investigation of the crystal structure was performed by X-ray powder diffraction. Experimental intensities from a polycrystalline sample were obtained using a diffractometer DRON-4-13 (Cu K α -radiation, range $10^{\circ} \le 2\theta \le 100^{\circ}$, scan step 0.05°, counting time at each step 20 s). Solution and refinement of the structure were performed using WinCSD computer programs. The results are shown in the Tables.

Sample composition	AgGa ₂ Se ₃ Cl
Space group	<i>I</i> -4
a (nm)	0.59789(3)
<i>c</i> (nm)	1.08592(7)
$V(nm^3)$	0.38818(6)
Number of atoms in the unit cell	14
Calculated density (g/cm ³)	4.4454(6)
Absorption coefficient (1/cm)	499.53
Radiation; wavelength (nm)	Cu <i>K</i> α; 0.154185
Diffractometer	DRON 4-13
Computation mode	full profile
Number of free parameters	10
$R_I; R_p$	0.0932; 0.2028
Scale factor	1.170(8)
Texture axis and parameter	[1 0 0]; 0.4154

Atom	Wyckoff position	x/a	y/b	z/c	Occupation	$B_{\rm iso} \times 10^2$ (nm ²)
Ga1	2 <i>a</i>	0	0	0	0.8	0.4(4)
Ga2	2c	0	1/2	1⁄4	0.8	1.1(5)
<i>M</i> 1	2 <i>b</i>	0	0	1/2	0.5 Ag + 0.2 Ga	1.7(8)
<i>M</i> 2	2d	0	1⁄2	3⁄4	0.5 Ag + 0.2 Ga	0.4(4)
X	8g	0.2161(15)	0.270(3)	0.1236(10)	0.75 Se + 0.25 Cl	2.4(2)

NEW CUBIC PHASES IN THE Mg-Ni-Ga SYSTEM

<u>Nazar Pavlyuk</u>¹, Grygoriy Dmytriv¹, Volodymyr Pavlyuk^{1,2}, Grzegorz Cichowicz³, Michał K. Cyrański³, and Helmut Ehrenberg⁴

¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

² Jan Długosz University, al. Armii Krajowej 13/15, 42200 Częstochowa, Poland

³ Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

⁴ Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Hermann-

von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

nazar.pavlyuk@gmail.com

All steps of the preparation of the alloys were performed in a glove box under dried argon atmosphere. Melting of the metals was carried out in sealed tantalum crucibles in an induction furnace at 1100°C. Single crystals were investigated by means of a Bruker APEX-II diffractometer with a CCD area detector and graphite-monochromatized Mo $K\alpha$ radiation. The crystal structures of the Mg₃Ni₂Ga and Mg₆Ni₉Ga₁₄ compounds were successfully solved by direct methods, and both were refined in space group Fd-3m. The refined lattice parameters are: for Mg₃Ni₂Ga a = 11.4886 Å, for Mg₆Ni₉Ga₁₄ a = 19.8621 Å. The starting atomic parameters were taken from an automatic interpretation of direct methods, followed by difference Fourier syntheses, using the SHELX-97 program package. Atomic coordinates and thermal displacement parameters are listed in the Table. All the parameters for the Mg₃Ni₂Ga alloy were refined to $R_1 = 0.0179$ and $wR_2 = 0.0201$ using 115 independent reflections with $I > 2\sigma(I)$, and for the Mg₆Ni₉Ga₁₄ alloy to $R_1 = 0.0240$ and w $R_2 = 0.0295$ using 429 independent reflections with $I > 2\sigma(I)$. Both structures can be described as three-shell cluster compounds. In the structure of Mg₆Ni₉Ga₁₄ a [Ni₆Ga₆] icosahedron is encapsulated into a $[Mg_{20}]$ dodecahedron, which is then encapsulated into a $[Ni_{18}Ga_{42}]$ fullerene-like truncated icosahedron. Hence, the composition of the cluster is [Ni₆Ga₆@Mg₂₀@Ni₁₈Ga₄₂]. In the structure of Mg₃Ni₂Ga a $[Mg_6]$ octahedron is encapsulated into a $[Ni_{12}Ga_6]$ hexagonal antiprism with six additional atoms centering the bases and edges, which is encapsulated into a [Mg₃₆] cluster, so that the composition of the Mg₃Ni₂Ga three-shell cluster becomes $[Mg_6@Ni_{12}Ga_6@Mg_{36}].$

Atoms	Sites	x/a	y/b	z/c	$U_{\rm eq}$				
	Mg ₃ Ni ₂ Ga								
Mg	48f	0.43139	1/8	1/8	0.00479				
Ni	32e	0.20622	0.20622	0.20622	0.00441				
Ga	16 <i>c</i>	0	0	0	0.00474				
	Mg ₆ Ni ₉ Ga ₁₄								
Gal	96g	0.07835	0.07835	0.26831	0.01530				
Ga2	96g	0.08029	0.08029	0.48703	0.01748				
Ga3	96g	0.03942	0.03942	0.03942	0.02146				
Ni4	32e	0.03975	0.03975	0.37919	0.02796				
Mg5	8a	0.28003	0.28003	0.28003	0.01875				
Mg6	8b	3/8	3/8	3/8	0.02002				
Mg7	96g	0.31561	0.31561	0.12987	0.01739				
Mg8	32e	1/8	1/8	1/8	0.01391				

Table Atomic parameters for the Mg₃Ni₂Ga and Mg₆Ni₉Ga₁₄ compounds.

Financial support from the National Science Center, Poland (No. 2017/25/B/ST8/02179) is gratefully acknowledged.

BIMETALLIC Cu(I)/Fe(II) π-COORDINATION COMPOUNDS BASED ON 3-ALLYLSULFANYL-4-ALLYL-5-PHENYL-4*H*-1,2,4-TRIAZOLE AND 5-ALLYLSULFANYL-1,3,4-THIADIAZOL-2-AMINE

<u>Yu.I. Slyvka</u>, M.Yu. Luk'yanov, and M.G. Mys'kiv Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine yurii.slyvka@lnu.edu.ua

Copper(I) π -coordination compounds have received considerable theoretical and practical interest because of their remarkable catalytic, luminescent, nonlinear optical, and other useful properties [1,2]. The key role of allyl azoles in crystal engineering of copper π -compounds with extremely rarely occurring inorganic fragments, was found recently.

In the present work we focused on the synthesis and study of bimetallic Cu(I)/Fe(II) π -coordination compounds with allyl azoles, such as 3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole (*Triaz*) and 5-allylsulfanyl-1,3,4-thiadiazol-2-amine (*Thiaz*). The ligand *Thiaz* was synthesized from commercially available 5-amino-1,3,4-thiadiazole-2-thiol by reaction with allyl chloride in ethanol solution. *Triaz* was obtained in several steps, starting from benzoyl hydrazine. The corresponding bimetallic π -coordination compounds 1 and 2 (Table) in crystalline form were prepared by the alternating-current electrochemical technique under different conditions, starting from an acetonitrile (or methanol/acetonitrile) solution of the organic azole ligand, copper(II) chloride and iron(III) chloride, on a copper electrode, using an alternating current of 50 Hz (voltage 0.56 & 0.60 V). The obtained complexes were studied by single-crystal X-ray diffraction and IR spectroscopy.

	Composition	Space group	$V, \text{\AA}^3$	Ζ	Density, g/cm ³	Coordination		
1	$[Cu_2(Triaz)_2Fe^{II}Cl_4]\cdot 2CH_3CN$	$P2_1/n$	3886(2)	4	1.575	π, σ		
2	$[Cu_2Fe^{II}(Thiaz)_4Cl_2](Fe^{II}Cl_4)$	C2/c	3981(2)	4	1.910	π, σ		

Table Selected crystal data for π -complexes 1 & 2.

In the structure of **1** the organometallic part is represented by $\{Cu_2(Triaz)_2\}^{2+}$ dimers, which are formed due to the π,σ -chelating-bridging coordination behavior of the ligand *Triaz*. The inorganic part is represented by the tetrahedral anion $\{FeCl_4\}^{2-}$, which binds two copper(I) ions of the $\{Cu_2(Triaz)_2\}^{2+}$ dimer in a bridging mode. A study of the magnetic properties of **1** ($\mu_{eff} = 5.58 \mu_B$, $\theta_p = 0.8 \text{ K}$) indicates very weak character of magnetic interactions of the ferromagnetic (positive) type.

The crystal structure of **2** is built of centrosymmetric cationic fragments $\{Cu_2Fe^{II}(Thiaz)_4Cl_2\}^{2+}$ and tetrahedral $FeCl_4^{2-}$ anions. Within the cation, the Fe(II) atom of a linear FeCl₂ fragment is attached to four N atoms of four neighboring 1,3,4-thiadiazole rings of *Thiaz* molecules. Two copper(I) atoms additionally stitch *Thiaz* pairs through π,σ -coordination.

- [1] Yu. Slyvka, E. Goreshnik, G. Veryasov, D. Morozov, A.A. Fedorchuk, N. Pokhodylo, I. Kityk, M. Mys'kiv, *J. Coord. Chem.* 72 (2019) 1049-1063.
- [2] Yu. Slyvka, A.A. Fedorchuk, E. Goreshnik, G. Lakshminarayana, I.V. Kityk, P. Czaja, M.G. Mys'kiv, *Chem. Phys. Lett.* 694 (2018) 112-119.
- [3] O.R. Hordiichuk, Yu.I. Slyvka, V.V. Kinzhybalo, E.A. Goreshnik, T.J. Bednarchuk, O. Bednarchuk, J. Jedryka, I. Kityk, M.G. Mys'kiv, *Inorg. Chim. Acta* 495 (2019) 119012.

CRYSTAL STRUCTURE OF R₃Fe_{0.5}SnS₇ (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Y, AND Ho)

<u>Kh.O. Melnychuk</u>¹, O.V. Marchuk¹, I.D. Olekseyuk¹, L.D. Gulay², and M. Daszkiewicz³ ¹ Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine

² Department of Ecology and Environmental Protection, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine

³ Institute of Low Temperature and Structure Research, Polish Academy of Sciences,

P.O. Box 1410, 50-950 Wrocław, Poland

Melnychuk.Khrystyna@eenu.edu.ua

Multicomponent chalcogenides are characterized by complex crystal structures and rich chemical and physical properties, which make them good materials for multifunctional devices.

Alloys of composition R_3 Fe_{0.5}SnS₇ were obtained by co-melting high-purity elementary substances in quartz containers evacuated to 10^{-2} Pa. The synthesis was performed in a programmable muffle furnace, with maximum synthesis temperature 1420 K and annealing at 770 K for 500 h.

X-ray diffraction data sets for R_3 Fe_{0.5}SnS₇ (R = La, Ce, Pr, Nd, Sm, Tb, Dy, and Y) were recorded on an X'calibur automatic single-crystal diffractometer (Mo K α radiation, graphite monochromator). The determination and refinement of the structures were performed using SHELXL-2014 software [1]. X-ray diffraction data for the quaternary phases R_3 Fe_{0.5}SnS₇ with R =Gd and Ho were obtained on a DRON 4-13 diffractometer. The crystal structures of Gd₃Fe_{0.5}SnS₇ and Ho₃Fe_{0.5}SnS₇ were determined and refined using the WinCSD software package [2].

The performed researches established that the crystal structures of the ten new chalcogenide phases R_3 Fe_{0.5}SnS₇ belong to the structural type La₃Mn_{0.5}SiS₇ (space group $P6_3$, Pearson symbol hP23 [3]). The lattice parameters of the compounds were determined:

J L J	1 1	1 .	
a = 1.029119(19) nm,	c = 0.600220(12) nm,	$V = 0.55052(2) \text{ nm}^3$	$(La_{3}Fe_{0.5}SnS_{7});$
a = 1.017333(12) nm,	c = 0.601116(8) nm,	$V = 0.538784(15) \text{ nm}^3$	$(Ce_{3}Fe_{0.5}SnS_{7});$
a = 1.00943(2) nm,	c = 0.600764(13) nm,	$V = 0.53013(2) \text{ nm}^3$	$(Pr_{3}Fe_{0.5}SnS_{7});$
a = 0.999378(19) nm,	c = 0.605675(12) nm,	$V = 0.52388(2) \text{ nm}^3$	$(Nd_{3}Fe_{0.5}SnS_{7});$
a = 0.98215(9) nm,	c = 0.61301(6) nm,	$V = 0.51210(8) \text{ nm}^3$	$(Sm_{3}Fe_{0.5}SnS_{7});$
a = 0.97220(2) nm,	c = 0.61762(2) nm,	$V = 0.50555(4) \text{ nm}^3$	$(Gd_{3}Fe_{0.5}SnS_{7});$
a = 0.96651(8) nm,	c = 0.61674(6) nm,	$V = 0.49894(8) \text{ nm}^3$	$(Tb_{3}Fe_{0.5}SnS_{7});$
a = 0.96093(9) nm,	c = 0.61815(6) nm,	$V = 0.49432(8) \text{ nm}^3$	$(Dy_{3}Fe_{0.5}SnS_{7});$
a = 0.95948(10) nm,	c = 0.61888(8) nm,	$V = 0.49341(10) \text{ nm}^3$	$(Y_{3}Fe_{0.5}SnS_{7});$
a = 0.95799(2) nm,	c = 0.61870(2) nm,	$V = 0.49174(3) \text{ nm}^3$	$(Ho_3Fe_{0.5}SnS_7).$

[1] G.M. Sheldrick, Acta Crystallogr. C 71(1) (2015) 3-8.

- [2] Y. Grin, L. Akselrud, J. Appl. Crystallogr. 47 (2014) 803-805.
- [3] G. Collin, P. Laruelle, C. R. Seances Acad. Sci., Ser. C 270 (1970) 410-412.

Tl₂B^{II}D^{IV}X₄ COMPOUNDS WITH TETRAGONAL STRUCTURE

L.V. Piskach, <u>A.O. Selezen</u>, O.V. Smitiukh, and I.D. Olekseyuk Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine andrijandrij1993@gmail.com

One of the challenges of modern chemical research is the search for new materials, which requires studying physico-chemical systems. For instance, studies of the quasi-ternary systems $Tl_2X-HgX-D^{IV}X_2$ revealed the equimolar compounds $Tl_2HgD^{IV}X_4$ ($D^{IV} = Ge$, Sn; X = S, Se) [1-3]. The crystal structures of four representatives, Tl_2HgGeS_4 , $Tl_2HgSiSe_4$, $Tl_2HgGeSe_4$, and $Tl_2HgSnSe_4$, were found to have non-centrosymmetric tetragonal symmetry (space group *I*-42*m*); the compounds are isostructural to $Tl_2CdGeTe_4$ [4]. Studies of the crystal structures of five more quaternary telluride analogs ($Tl_2CdGeTe_4$, $Tl_2CdSnTe_4$, $Tl_2HgGeTe_4$, $Tl_2HgSnTe_4$, $Tl_2MnGeTe_4$, and $Tl_2MnSnTe_4$) have also been reported.

The existence of analogous compounds of the same composition, Tl₂CdGe(Sn)Se₄, was found in the quasi-ternary systems Tl₂Se–CdSe–Ge(Sn)Se₂ at 520 K. Each compound has a polymorphous transformation. The crystal structures of the low-temperature modifications also belong to space group *I*-42*m* with the parameters a = 0.80145(9), c = 0.67234(9) nm (Tl₂CdGeSe₄), and a = 0.80490(6), c = 0.68573(8) nm (Tl₂CdSnSe₄) [5]. The diffraction patterns of the investigated tellurides Tl₂CdSiTe₄ and Tl₂HgSiTe₄ also pointed to this series of compounds, which was confirmed by refinement of their crystal structures in space group *I*-42*m*. The lattice periods are a = 0.84121(6), c = 0.70289(9) nm for Tl₂CdSiTe₄, and a = 0.83929(4), c = 0.70396(5) nm for Tl₂HgSiTe₄.



Fig. Unit cell and coordination polyhedra of the atoms in the structure of $Tl_2HgSiTe_4$.

The spatial arrangement and coordination polyhedra of the atoms and atom groups is shown on the example of the Tl₂HgSiTe₄ compound (Fig.). The Tl atoms are coordinated by eight Te atoms forming deformed tetragonal antiprisms. The symmetry of the coordination environment of the indicates Tl atoms isostructural stereochemical inactivity of the lone pair of the Tl⁺-ions. The Hg atoms have tetrahedral surrounding, and the Si atoms are also located at the centers of tetrahedra of Te atoms. The coordination polyhedra of the Te atoms are trigonal prisms formed by 1Hg, 1Si and 4Tl atoms.

- [1] M.Yu. Mozolyuk, L.V. Piskach, A.O. Fedorchuk, et al., Mater. Res. Bull. 47 (2012) 3830-3834.
- [2] L.V. Piskach, A.O. Fedorchuk, I.D. Olekseyuk, O.V. Parasyuk, *Chem. Met. Alloys* 6 (2013) 55-62.
- [3] L. Piskach, M. Mozolyuk, A. Fedorchuk, et al., Chem. Met. Alloys 10 (2017) 136-141.
- [4] M.A. McGuire, Th.J. Scheidemantel, J.V. Badding, F.J. DiSalvo, Chem. Mater. 17 (2005) 6186-6191.
- [5] L. Piskach, A. Selezen, Coll. Abstr. XVII Sci. Conf. Lviv Chem. Readings, Lviv, 2019, p. 321 (in Ukrainian).

RAPID QUENCHING OF INTERMETALLICS

Z.M. Oliinyk, A.V. Korolyshyn, and S.I. Mudry Faculty of Physics, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 8, 79005 Lviv, Ukraine zachar908@gmail.com

Rapid quenching of materials is widely used to extend the solubility of alloys in which, in the equilibrium phase diagram, such solubility is extremely limited. For instance, many conventional Al-based alloys contain limited amount of other metals and rapid quenching is commonly used to increase their solubility, in order to improve the mechanical properties. Improved properties can also be obtained if intermetallic compounds precipitate in the alloy. For this reason it is of great importance to study the influence of rapid quenching from the liquid on the micro- and nanoscale structure of solidified alloys, which, depending on the cooling rate, can be in amorphous or crystalline state.

In this work the influence of rapid cooling on the structure of Cu_3Si intermetallics was investigated by means of X-ray diffraction. Diffraction patterns were obtained at different temperatures within a wide temperature range, including both the solid and liquid state. The structure data in the liquid state were analyzed and used to determine the main short-range order structure parameters, interatomic distances, number of neighbors, and size of structural units (clusters). Parameters of chemical ordering were also determined for the liquid phase.

Similar structure parameters were obtained for rapidly cooled crystalline Cu₃Si intermetallics and compared with the data for the liquid alloy.

PHASE EQUILIBRIA IN THE $Cu_2ZnD'X_4$ - $Cu_2ZnD''X_4$ SYSTEMS (*D* – Si, Ge, Sn; *X* – S, Se)

<u>V.R. Kozer</u>, O.V. Parasyuk, and I.D. Olekseyuk Department of Inorganic and Physical Chemistry, Lesya Ukrainka Eastern European National University, Potapova St. 9, 43021 Lutsk, Ukraine uakozer@gmail.com

Chalcogenides of composition $Cu_2ZnD^{IV}X_4$ have been known for a long time. Despite the similarity of the composition, they crystallize in different crystal structures. The germanium-containing compounds Cu_2ZnGeS_4 and Cu_2ZnGeS_4 crystallize in space group *I*-4, the tincontaining Cu_2ZnSnS_4 and Cu_2ZnSnS_4 in space group *I*-42*m*, and the silicon-containing Cu_2ZnSiS_4 and Cu_2ZnSiS_4 in space group *Pmn2*₁. The sections Cu_2ZnGeS_4 – Cu_2ZnSnS_4 , Cu_2ZnGeS_4 – Cu_2ZnSiS_4 , Cu_2ZnSiS_4 , Cu_2ZnSiS_4 , Cu_2ZnSiS_4 , Cu_2ZnSiS_4 , Cu_2ZnSiS_4 , Cu_2ZnGeS_4 – Cu_2ZnSiS_4 , Cu_2ZnSiS_4 , Cu_2ZnSiS_4 , Cu_2ZnGeS_4 – Cu_2ZnSiS_4 , $Cu_2ZnSiS_$

The challenge in studying these systems is to obtain homogeneous alloys. Direct hightemperature synthesis by co-melting the elements in evacuated ampoules does not provide satisfactory results. The samples are non-uniform. The main reason is the high melting points of the intermediate and starting compounds. In most cases, the process stops with the formation of a large share of binary compounds, which complicates the synthesis of quaternary compounds. To obtain samples of satisfactory quality, pre-synthesized batches were ground to powder and re-melted in evacuated ampoules at high temperature (1373 K). The process of powdering and melting was then repeated. Final annealing of the alloys was performed at 1273 K. X-ray diffraction spectra of the samples were obtained on a DRON 4-13 diffractometer, using Cu $K\alpha$ radiation. The diffraction patterns were processed using CSD software.

The investigated systems are characterized by modest solid-state solubility of the starting compounds. The boundaries of the solid solutions were determined by the variation of the lattice parameters. In most cases the solid solutions extend to 5-15 mol.%. A notable exception is the Cu₂ZnGeS₄–Cu₂ZnSiS₄ section, where the solid solubility based on Cu₂ZnSiS₄ reaches ~50 mol.% Cu₂ZnGeS₄. The mechanism of formation of solid solutions in this system was studied on the example of Cu₂ZnSi_{0.5}Ge_{0.5}S₄. The silicon atoms were found to substitute for germanium atoms in the crystallographic site 2*a*. In the other studied systems, the mechanism of formation of solid solutions is similar and consists in replacement of Si, Ge, and Sn by other *D*^{IV}-element atoms in the same crystallographic site.

CRYSTAL STRUCTURE OF CLINOPTILOLITE 1.4(Na,K)₂O×(Ca,Mg)O×3Al₂O₃×28SiO₂×22H₂O

 <u>S.S. Milyovich</u>¹, V.I. Gomonaj¹, V.V. Pavlyuk², I.P. Stercho¹, and I.E. Barchiy¹
 ¹ Department of Chemistry, Uzhhorod National University, Pidgirna St. 46, 88000 Uzhhorod, Ukraine
 ² Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine stepan.milyovich@uzhnu.edu.ua

Currently, inorganic clinoptilolites are used as ionic exchangers characterized by low cost, good adsorption and ion-exchange properties, and the possibility of modification. The largest field of clinoptilolite (zeolite type HEU) in Ukraine, is located in the v. Sokirnytsia, Transcarpathian region. The composition of the sample of clinoptilolite, determined by the SIMS method, was $1.4(Na,K)_2O\times(Ca,Mg)O\times3Al_2O_3\times28SiO_2\times22H_2O$ (Fe admixture $\approx 0.1\div1.5$ wt.%). The study of the crystal structure of clinoptilolite showed that it crystallizes in monoclinic symmetry, space group C2/m (12), lattice parameters a = 17.595, b = 17.593, c = 7.415 Å, $\beta = 117.01^{\circ}$.

A comparison of the interatomic distances in the individual oxides and clinoptilolite (Table) shows that the transition from the individual oxides of Na, K, and Ca to clinoptilolite increases the interatomic M-O distances for these metals, which indicates an increase of the ionicity of the chemical bond. The opposite pattern is observed in the transition from Al and Si oxides to clinoptilolite – the interatomic distances are reduced, indicating an increase of the covalent component of the corresponding bonds. We also observed an alignment of the Al-O and Si-O chemical bond lengths in the [AlO₄] and [SiO₄] tetrahedra, which form the anionic framework of clinoptilolite by sharing vertices.



Fig. Crystal structure of clinoptilolite.

Bonds	Clinoptilolite	$\Sigma r_{\rm ion}$, Å	$\Sigma r_{ m cov}$, Å	Oxide
Na-O	2.242-2.795	2.42	2.285	2.403
K-O	2.793-2.896	2.78	2.705	2.787
Ca-O	2.423-2.629	2.40	2.385	2.408
Al-O	1.616-1.635	1.94	1.945	1.866-1.974
Si-O	1.603-1.642	1.80	1.915	1.592-1.618

Table Interatomic distances in individual oxides and clinoptilolites

The change of the interatomic M-O distances and the coordination environment of the metal atoms confirm the formation of clinoptilolite as an individual compound, in which the Al and Si atoms act as the central atoms of anionic groups [AlO₄] and [SiO₄]; the Na, K, Ca atoms form a cationic group, located in the cavities (tunnels) of the framework of the anionic groups.

INVESTIGATION OF THE GdNiAl_{4-x}In_x (x = 0-2) SYSTEM

 <u>R. Perun</u>¹, M. Horiacha^{1,2}, R. Pöttgen², G. Nychyporuk¹, and V. Zaremba¹
 ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ² Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, 48149 Münster, Germany perun.roma98@gmail.com

The interaction between the components in the quasi-ternary GdNiAl_{4-x}In_x system in the concentration range x = 0.2 was investigated by means of X-ray diffraction and EDX analysis at 873 K. The limit of the solubility of indium in the GdNiAl₄ compound was determined (up to 16.7 %) and the unit-cell parameters of the solid solution were refined: GdNiAl_{4.0-3.0}In_{0-1.0} (YNiAl₄ structure type, space group *Cmcm*, a = 0.40744(5)-0.41110(4), b = 1.54838(16)-1.56434(13), c = 0.66098(7)-0.66949(5) nm, V = 0.41700(8)-0.43054(6) nm³).

Single crystals of the GdNiAl_{3.80}In_{0.20} compound were grown by a heating/cooling procedure of an arc-melted alloy of the composition $Gd_{0.167}Ni_{0.167}Al_{0.633}In_{0.033}$ in a sealed Ta container in a muffle furnace, using a special heat treatment. The crystal structure was investigated by single-crystal X-ray diffraction (Stoe IPDS II diffractometer, Mo *K* α radiation) and refined with programs from the JANA2006 package [1].

GdNiAl_{3.80}In_{0.20} crystallizes in the YNiAl₄ [2] structure type (orthorhombic, space group *Cmcm*, oS24, a = 0.40890(4), b = 1.55508(15), c = 0.66408(6) nm, $R_1 = 0.0146$, w $R_2 = 0.0248$, 546 F^2 values, 25 variables). All the atom sites in the refined structure are completely occupied, including Wyckoff position 4*b*, which was found to be occupied by a statistical mixture of aluminum and indium. The atomic coordinates and displacement parameters of the structure are listed in the Table. The refined composition was confirmed by the results of the EDX analysis (Zeiss EVO MA10 scanning electron microscope).

Atom	W yckoff position	X	У	Z.	$U_{ m eq}$
Gd	4 <i>c</i>	0	0.11748(1)	1⁄4	0.0073(1)
Ni	4 <i>c</i>	0	0.77401(4)	1⁄4	0.0068(1)
Al	4 <i>c</i>	0	0.92225(10)	1⁄4	0.0116(4)
Al	8 <i>f</i>	0	0.69015(7)	0.55344(16)	0.0080(2)
М	4b	0	1/2	0	0.0104(3)
3.6 0.00(4) 1.1	0.00(1) -				

Table Atomic coordinates and displacement parameters of the GdNiAl_{3.80}In_{0.20} structure.

M = 0.80(1) Al + 0.20(1) In

A similar character of the interaction of the components was observed in the quasiternary systems $YNiAl_{4-x}In_x$ [3], $TbNiAl_{4-x}In_x$, and $TbNiGa_{4-x}In_x$ [4], which are also characterized by solid solutions of insignificant length with the $YNiAl_4$ structure type.

M. Horiacha is indebted to DAAD for a research scholarship.

- [1] V. Petříček, M. Dušek, L. Palatinus, Z. Kristallogr. 229 (2014) 345-352.
- [2] R.M. Rykhal', O.S. Zarechnyuk, Ya.P. Yarmolyuk, *Kristallografiya* 17 (1972) 521-524.
- [3] M. Horiacha, G. Nychyporuk, R. Pöttgen, V. Zaremba, *Coll. Abstr. XXI Int. Sem. Phys. Chem. Solids Adv. Mater.*, Częstochowa, Poland, 2018, p. 80.
- [4] O. Panakhyd, G. Nychyporuk, Ya. Galadzhun, V. Hlukhyy, R. Pöttgen, V. Zaremba, *Coll. Abstr. III All-Ukr. Conf. Young Sci. Stud.*, Lutsk, 2014, p. 86-87.

CRYSTAL STRUCTURE OF NEW ZINC-RICH TERNARY COMPOUNDS $Gd_2Zn_{17-x}M_x$ (M = Mn, Fe)

<u>N. Chorna</u>¹, O. Zelinska¹, G. Dmytriv¹, V. Pavlyuk¹, A. Zelinskiy¹, V. Kordan¹, and A. Mar² ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Department of Chemistry, University of Alberta, T6G 2G2 Edmonton, Canada nata.chorna15@gmail.com

Rare-earth transition-metal alloys have attracted much attention for decades due to their interesting magnetic behavior. Recent scientific activity around these alloys has been motivated by promising hydrogen storage and electrochemical properties.

A systematic study of the phase equilibria in the Gd–{Mn,Fe}–Zn systems confirmed that the binary phase Gd₂Zn₁₇ is characterized by hexagonal symmetry, a Th₂Ni₁₇-type structure and negligible solubility of the third component (Mn or Fe) at 500°C. Along the same isoconcentrate of gadolinium and a concentration of zinc of ~79 at.%, we observed the formation of new ternary compounds with rhombohedral Th₂Zn₁₇-type structure. Isostructural compounds have previously been reported in similar systems to have a composition $R_2M_2Zn_{15}$ [1-3] or $R_2M_3Zn_{14}$ [4]. The main difference between these compositions is in the atom site occupied by the *M* atoms: in the case of $R_2M_2Zn_{15}$ they occupy a site 6*c*, and in the case of $R_2M_3Zn_{14}$ a site 9*d*.

The samples for investigation were synthesized by direct reaction of the metals in the molar ratio Gd:*M*:Zn = 11:11:78 in evacuated fused-silica ampoules heated to 900°C, slowly cooled to 500°C, annealed at this temperature for 2 weeks, and quenched in cold water. The crystal structures of the compounds were investigated by single-crystal X-ray diffraction (Bruker PLATFORM / SMART APEX II CCD diffractometer). Structure solution and refinement were carried out using the SHELXTL program package.

The title compounds crystallize with rhombohedral Th₂Zn₁₇-type structures (space group *R*-3*m*, Pearson code *hR*57). The lattice parameters of the Mn-containing phase are the following: a = 9.0076(2) Å, c = 13.2629(6) Å, V = 931.94(5) Å³. Replacing the larger Mn-atoms ($r_{Mn} = 1.35$ Å) by the smaller Fe-atoms ($r_{Fe} = 1.26$ Å) leads to a decrease of the lattice parameters for the Fe-containing phase (a = 9.0025(10) Å, c = 13.160(3) Å, V = 923.6(3) Å³). In the structures of these compounds the Gd atoms fully occupy a position 6c, and the Zn atoms fully occupy two positions 18*f* and 18*h*. The second site in Wyckoff position 6c and the site in 9*d* are occupied by Zn and Mn or Fe statistically, which makes it possible to consider these compounds as disordered derivatives of Th₂Zn₁₇.

- [1] I.M. Opainych, V.V. Pavlyuk, O.I. Bodak, R. Cerny, K. Yvon, *Cryst. Rep.* 41 (1996) 809-812.
- [2] O.Ya. Zelinska, V.V. Pavlyuk, A.V. Zelinskyy, V.M. Davydov, J. Alloys Compd. 343 (2002) 132-134.
- [3] N. Dychko, O. Zelinska, A. Zelinskiy, V. Pavlyuk, Visn. Lviv. Univ., Ser. Khim. 56(1) (2015) 46-52.
- [4] N. Gross, G. Block, W. Jeitschko, Chem. Mater. 14 (2002) 24-32.

PEROVSKITE PHASES IN $AO-R_2O_3$ -Fe₂O₃ SYSTEMS (A – ALKALINE-EARTH METAL, R – RARE-EARTH METAL)

<u>O. Zaremba</u>, V. Hrytsan, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine oksanazaremba@gmail.com

 ABO_3 phases belonging to the well-known perovskite family constitute an important class of functional materials. Many of them are already used as catalysts, electrodes, sensors, *etc.* However, a systematic study of perovskite phases remains topical, taking into account the huge tolerance of the CaTiO₃ structure type and its derivatives, as well as the wide range of physical properties. We have previously [1] shown that Sr_{1-x}R_xFeO₃ (structure type CaTiO₃, Pearson symbol *cP*5, space group *Pm*-3*m*) and *R*_{1-x}Sr_xFeO₃ phases (GdFeO₃, *oP*20, *Pnma*) are formed in the SrO–*R*₂O₃–Fe₂O₃ systems. In the case of the cubic perovskite, the solid solution extends up to $x \sim 0.20$, for the orthorhombic perovskite up to $x \sim 0.10$. In this work we focused on a search for four-component perovskites in systems with calcium and barium.

Ceramic samples of nominal composition $A_{0.5}R_{0.5}$ FeO₃, where A = Ca or Ba, and R = Pr, Gd, Tb or Lu, were prepared by solid-state reaction, using high-purity CaCO₃ and BaCO₃ carbonates, and Gd₂O₃, Tb₂O₃, Lu₂O₃, and Fe₂O₃ oxides. At first the reagents were mixed manually and heated in corundum crucibles for decomposition of the carbonates. After cooling to room temperature, the samples were ground to achieve homogeneity, pressed into pellets, and sintered again. Each stage was carried out at 1000°C under air for 24 h. X-ray powder diffraction was performed on a DRON 2.0M diffractometer (Fe K α radiation).

The investigation of samples in the CaO– R_2O_3 –Fe₂O₃ systems confirmed the existence of four-component phases with GdFeO₃ perovskite structure for R = Pr and Gd [2]: a = 0.5540(2), b = 0.7756(3), c = 0.5468(1) nm, $R_B = 0.109$ for the Ca_{0.15}Pr_{0.85}FeO₃ phase and a = 0.5583(1), b = 0.7647(1), c = 0.5348(1) nm, $R_B = 0.108$ for the Ca_{0.15}Gd_{0.85}FeO₃ phase. The formation of Ca_{0.15}Tb_{0.85}FeO₃ (a = 0.5579(1), b = 0.7628(1), c = 0.5318(1) nm, $R_B = 0.110$) and Ca_{0.15}Lu_{0.85}FeO₃ (a = 0.5554(1), b = 0.7549(1), c = 0.5217(1) nm, $R_B = 0.063$) with the same structure type was established for the first time. The cell volume of the perovskite phases decreases regularly on going from Pr to Lu.

The phase analysis of the $Ba_{0.5}Pr_{0.5}FeO_3$ and $Ba_{0.5}Gd_{0.5}FeO_3$ samples revealed equilibria between the three-component perovskite phases {Pr,Gd}FeO₃ (orthorhombic perovskite with the GdFeO₃ structure type) and BaFeO₃ (cubic perovskite with CaTiO₃ structure type). The study of the $Ba_{0.5}Tb_{0.5}FeO_3$ sample showed the presence of more than three phases. The re-grinding and sintering procedure did not influence the phase composition.

The interaction of the components in the BaO–Lu₂O₃–Fe₂O₃ system is different. The sample of nominal composition Ba_{0.5}Lu_{0.5}FeO₃ contained 62 wt.% of the BaFe₂O₄ phase (own structure type, *oS*56, *Cmc*2₁, *a* = 0.8448(1), *b* = 1.9002(3), *c* = 0.5380(1) nm, *R*_B = 0.119) and 38 wt.% of the Lu₂O₃ phase ((Mn_{0.5}Fe_{0.5})₂O₃, *cI*80, *Ia*-3, *a* = 1.0377(1) nm, *R*_B = 0.068). No traces of a perovskite phase were observed.

- [1] V. Hrytsan, O. Zaremba, R. Gladyshevskii, *Coll. Abstr. XVII Sci. Conf. Lviv Chem. Readings*, Lviv, 2019, p. H23 (in Ukrainian).
- [2] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data Crystal Structure Database for Inorganic Compounds, Release 2017/18*, ASM International, Materials Park, OH, 2017.

P62

SINGLE-CRYSTAL INVESTIGATION OF THE Ce₅Ag_{0.1}Ge_{3.9} PHASE WITH Sm₅Ge₄ TYPE

<u>B. Belan¹</u>, D. Kowalska², O. Bardin¹, M. Manyako¹, and R. Gladyshevskii¹

 ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ² Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław 2, Poland bohdanabelan@gmail.com

We have previously reported the crystal structure of the phase Ce₅Ag_{1.08}Ge_{2.92} with the Sm₅Ge₄ type (a = 7.107, b = 15.28, c = 7.953 Å) [1]. During an investigation of the Ce–Ag–Ge system we obtained a single crystal from an alloy of composition Ce₅₆Ag₁₂Ge₃₂. The alloy had been synthesized by arc melting under an argon atmosphere, and then annealed at 500°C for 1 month. X-ray diffraction data were collected on a diffractometer Xcalibur Atlas CCD operating in kappa geometry, using Mo Ka radiation. The crystal structure was refined using the program SHELXL [2]. The chemical composition of the selected crystal was checked with a field-emission scanning electron microscope (FEINovaNanoSEM 230). Crystallographic data for Ce₅Ag_{0.1}Ge_{3.9}: structure type Sm₅Ge₄, Person symbol *oP*36, space group *Pnma*, a = 7.9632(2), b = 15.2693(5), c = 8.0803(2) Å, R = 0.0261, $R_w = 0.0460$ for 1224 reflections. The atomic coordinates and displacement parameters are listed in the Table.

Site	Wyckoff position	x	у	Ζ.	G	$U_{ m eq},{ m \AA}^2$
Ce1	8 <i>d</i>	0.01918(4)	0.10066(2)	0.68166(4)	1	0.01322(10)
Ce2	8 <i>d</i>	0.37909(4)	0.11545(2)	0.33836(4)	1	0.01287(10)
Ce3	4 <i>c</i>	0.20835(6)	1⁄4	0.00117(6)	1	0.01536(12)
Ge1	81	0.21844(8)	0.04363(4)	0.03340(7)	0.978(6)	0.0145(2)
Ag1	<i>6u</i>	0.21044(8)	0.04303(4)	0.03349(7)	0.022(6)	0.0143(2)
Ge2	10	0.08/13(11)	1/4	0.30//8(10)	0.972(9)	0.0130(3)
Ag2	τc	0.00413(11)	/4	0.39440(10)	0.028(9)	0.0139(3)
Ge3	4c	0.31651(11)	1⁄4	0.63112(10)	1	0.01251(19)

Table Atomic coordinates and equivalent displacement parameters for Ce₅Ag_{0.1}Ge_{3.9}.

It was established that an interstitial solid solution of up to 12 at.% Ag is formed on the basis of the binary compound Ce_5Ge_4 with Sm_5Ge_4 type.

- [1] J. Stepen-Damm, B. Belan, L. Kryvulya, O. Bodak, L. Muratova, G. Mykhalichko, *Coll. Abstr. VI Int. Conf. Crystal Chem. Intermet. Compd.*, Lviv, 1995, p. 99.
- [2] G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3-8.

SINGLE-CRYSTAL INVESTIGATION OF THE EuNi₉Si₄ COMPOUND

<u>B. Belan</u>¹, D. Kowalska², M. Manyako¹, and R. Gladyshevskii¹ ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław 2, Poland bohdanabelan@gmail.com

During a study of the isothermal section of the ternary system Eu–Ni–Si in the range 0-33.3 at.% by X-ray diffraction at 400°C we found the compounds $EuNi_{3.7-5.9}Si_{9.3-7.1}$, $EuNi_{6.6-6.9}Si_{6.4-6.1}$, and $EuNi_{7.6-8.3}Si_{5.4-4.7}$ [1]. The crystal structures within the homogeneity ranges are related to the tetragonal CeNi_{8.5}Si_{4.5} type [2]. The crystal structures were refined on X-ray powder diffraction data.

During an investigation of alloys along the isoconcentrate 7.14 at.% Eu, we obtained a single crystal in an alloy of composition $Eu_{7.14}Ni_{64.28}Si_{28.58}$, which had been prepared by arc melting and annealing at 400°C for 350 h. X-ray diffraction data were collected on a diffractometer Xcalibur Atlas CCD operating in kappa geometry, using Mo *K* α radiation. The crystal structure was refined using the program SHELXL [3]. The chemical composition of the selected crystal was checked with a field-emission scanning electron microscope (FEINovaNanoSEM 230).

The present investigation gave the following data for the crystal structure of EuNi₉Si₄: structure type CeNi_{8.5}Si_{4.5}, Pearson symbol *tI*56, space group *I*4/*mcm*, a = 7.8348(2), c = 11.4656(6) Å, R = 0.0162, $R_w = 0.0190$ for 277 independent reflections. The refined atomic coordinates and displacement parameters are presented in the Table.

Site	Wyckoff position	X	у	Z.	$U_{ m eq}$, Å ²
Eu	4a	0	0	1⁄4	0.0072(1)
Ni1	16 <i>l</i>	0.62990(4)	0.12990(4)	0.18411(4)	0.0075(1)
Ni2	16 <i>k</i>	0.06931(6)	0.20294(6)	0	0.0072(1)
Ni3	4d	0	1/2	0	0.0069(2)
Si	16 <i>l</i>	0.17068(9)	0.67068(9)	0.11856(9)	0.0073(2)

Table Atomic coordinates and equivalent displacement parameters for EuNi₉Ni₄.

[1] B.D. Belan, *Thesis*, Lvov State University, 1988 (in Russian).

[2] B. Belan, S. Pukas, M. Manyako, R. Gladyshevskii, *Coll. Abstr. XVI Sci. Conf. Lviv Chem. Readings*, Lviv, 2017, p. H50 (in Ukrainian).

[3] G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3-8.

REINVESTIGATION OF THE CRYSTAL STRUCTURE OF LaNi₉Si₄

O. Kasaraba, S. Pukas, <u>B. Belan</u>, M. Manyako, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine bohdanabelan@gmail.com

The interaction of lanthanum with nickel and silicon has been studied at 400°C [1]. According to [2] three compounds form along the isoconcentrate 7.14 at.% La: LaNi_{11.6-9.5}Si_{1.4-3.5}, LaNi_{8.8-8.4}Si_{4.2-4.6}, and LaNi_{7.8-4.5}Si_{5.2-8.5}. We have previously reported the crystal structure of LaNi₉Si₄, investigated by X-ray powder diffraction data: structure type CeNi_{8.5}Si_{4.5} (a = 7.86415(6), c = 11.5101(1) Å) [3].

During a systematic investigation of alloys in the La–Ni–Si system 12 ternary samples along the isoconcentrate 7.14 at.% La were synthesized by arc melting and annealed at 600°C (720 h). We confirmed the existence of the LaNi₉Si₄ compound. X-ray diffraction data were collected on a diffractometer STOE IP (Mo *K* α radiation). The crystal structure was solved by the Patterson method and refined by the full-matrix least-squares method, using the program SHELX [4]. After the data collection, the single crystal was analyzed by EDX spectroscopy with a Leica420i scanning electron microscope.

Crystallographic data and parameters for the data collection and refinement for the compound LaNi₉Si₄ (structure type CeNi_{8.5}Si_{4.5}, Pearson symbol *tI*56) are shown in the Table. The refined atomic coordinates and displacement parameters are the following: La 4*a* 0 0 ¹/₄, $U_{eq} = 0.0039(2)$ Å²; Ni1 16*l* 0.63048(7) 0.13048(7) 0.18442(6), $U_{eq} = 0.0070(2)$ Å²; Ni2 16*k* 0.06884(10) 0.20317(9) 0, $U_{eq} = 0.0065(2)$ Å²; Ni3 4*d* 0 ¹/₂ 0, $U_{eq} = 0.0061(3)$ Å²; Si 16*l* 0.17072(14) 0.67072(14) 0.11833(14), $U_{eq} = 0.0066(3)$ Å².

Crystallographic data	Data collection	Refinement	
Space group <i>I</i> 4/ <i>mcm</i>	T = 295(2) K	24 refined parameters	
a = 7.83933(17),	2177 measured reflections	343 reflections with $I > 2\sigma(I)$	
c = 11.4472(5) Å			
$V = 703.49(4) \text{ Å}^3$	352 independent reflections	$R = 0.0220 \ (0.0209)$	
Z = 4	$R_{\rm int} = 0.0632$	$wR = 0.0734 \ (0.0703)$	
$D_{\rm X} = 7.361 {\rm Mg \cdot m^{-3}}$	ω-scan	S = 1.053	
linear absorption coefficient	$-11 \le h \le 11, -9 \le k \le 10,$	analytical absorption	
$\mu = 30.005 \text{ mm}^{-1}$	$-16 \le l \le 17$	correction	

Table 1 Crystallographic data and parameters for the data collection and refinement.

The crystal structure of the LaNi₉Si₄ compound was redetermined by X-ray singlecrystal diffraction. The structural parameters are in good agreement with those obtained by X-ray powder diffraction.

- [1] O.I. Bodak, E.I. Gladyshevskii, *Rare-Earth Metal Ternary Systems*, Lvov, Vyshcha Shkola, 1985, 328 p. (in Russian).
- [2] P. Villars, K. Cenzual (Eds.), *Pearson's Crystal Data Crystal Structure Database for Inorganic Compounds*, ASM International, Materials Park, OH, Release 2017/18.
- [3] O. Kasaraba, B. Kuzhel, S. Pukas, B. Belan, M. Manyako, R. Gladyshevskii, *Coll. Abstr. XIII Int. Conf. Cryst. Chem. Intermet. Compd.*, Lviv, 2016, p. 137.
- [4] G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3-8.

A NEW MEMBER OF THE AIB₂ STRUCTURE TYPE FAMILY

<u>B. Belan</u>¹, M. Manyako¹, R. Gladyshevskii¹, and R. Černý² ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Department of Quantum Matter Physics, University of Geneva, 24, quai Ernest-Ansermet, CH 1211 Geneva 4, Switzerland bohdanabelan@gmail.com

During an investigation of the ternary system Lu–Ni–Si, we obtained the binary silicide Lu₃Si₅. The crystal structure of Lu₃Si₅, which represents a new structure type, was determined from single-crystal X-ray diffraction.

Alloys were prepared by melting the components under argon in an arc furnace, and were annealed at 870 K under vacuum for 1 month. Single crystals were found in a sample of nominal composition $Lu_{33,3}Si_{66,7}$. Integrated intensities were measured with graphitemonochromatized Mo K α radiation on an Agilent SUPER NOVA CCD diffractometer. Crystallographic data and parameters for the data collection and refinement are shown in Table 1. The structure was refined by the full-matrix least-squares method on F^2 , using SHELXL [1]. The refined atomic coordinates and displacement parameters are given in Table 2. The structure type Lu_3Si_5 is a new, partly ordered vacancy derivative of the structure type AlB₂.

Crystallographic data	Data collection	Refinement	
Space group $P6_222$	T = 180 K	46 refined parameters	
a = 6.4815(4),	13447 measured	523 reflections with	
c = 24.241(3) Å	reflections	$I > 2\sigma(I)$	
$V = 881.92(12) \text{ Å}^3$	793 independent	$R = 0.0543 \ (0.0429)$	
	reflections		
Z = 6	$R_{\rm int} = 0.0357$	$wR = 0.130 \ (0.119)$	
$D_{\rm X} = 7.517 {\rm ~Mg \cdot m^{-3}}$	$\theta_{\rm max} = 29.39^{\circ}$	S = 1.137	
linear absorption coefficient	$-8 \le h \le 8, -8 \le k \le 8,$	analytical absorption	
$\mu = 50.855 \text{ mm}^{-1}$	$-32 \le l \le 30$	correction	

Table 1 Crystallographic data and parameters for the data collection and refinement.

Table 2 Atomic coordinates and equivalent displacement parameters for Lu₃Si₅.

					5 5
Site	Wyckoff position	x	у	Z.	$U_{ m eq},{ m \AA}^2$
Lu1	6 <i>j</i>	0.66378(5)	0.32756(11)	1/2	0.0089(3)
Lu2	6 <i>i</i>	0.31842(9)	0.63685(17)	0	0.0072(3)
Lu3	3 <i>b</i>	0	0	1/2	0.0095(3)
Lu4	3 <i>a</i>	0	0	0	0.0192(4)
Si1	12k	0.0358(9)	0.3359(6)	0.25045(11)	0.0246(13)
Si2	12k	0.3354(6)	0.0406(9)	0.24943(11)	0.0240(12)
Si3*	12k	0.5970(16)	0.0049(13)	0.08142(19)	0.0035(19)

* occ. = 0.485(14)

[1] G.M. Sheldrick, Acta Crystallogr. C 71 (2015) 3-8.

NEW FEATURES OF THE Al_{2.75}Ir STRUCTURE

<u>Yu. Prots</u>¹, J. Kadok^{1,2}, M. Schmidt², M. Coduri³, M. Mihalkovič⁴, V. Fournée², J. Ledieu², and Yu. Grin¹ ¹ Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany ² Institut Jean Lamour UMR7198 CNRS, Université de Lorraine, Parc de Saurupt, 54011 Nancy Cedex, France

³ European Synchrotron Radiation Facility, 71, avenue des Martyrs,

CS 40220, 38043 Grenoble Cedex 9, France

⁴ Institute of Physics, Slovak Academy of Sciences,

Dúbravská cesta 9, 84511 Bratislava 45, Slovak Republik

prots@cpfs.mpg.de

The cubic Al_{2.75}Ir phase was reported to crystallize in space group *P*23 (a = 7.674 Å) with a strongly disordered Al sublattice [1]. Recent studies (X-ray powder diffraction, transmission electron microscopy and theoretical calculations [2-5]) indicated the existence of super-structure reflections and concluded that Al_{2.75}Ir may crystallize with a doubled lattice parameter a = 15.345 Å (for a cubic cell). Nevertheless, no structural model was proposed.

In the present study, we focused on the optimization of the synthesis procedure and on the crystal structure determination of Al_{2.75}Ir using different X-ray diffraction techniques. The crystal structure of Al_{2.75}Ir was investigated using powder and single-crystal X-ray diffraction, performed at ambient conditions as well as at high temperature (*in situ*). Above 630°C, this phase adopts the already reported primitive cubic structure (strongly disordered). Below this temperature, the appearance of a doubled lattice parameter was observed. A partially disordered crystal structure was established by investigating a twinned single-crystal specimen (with three diffraction domains): space group *Fmmm*, a = 15.3506(3) Å, b = 15.3334(4) Å, c = 15.3283(4) Å, $R_F = 0.029$ for 2494 observed reflections and 86 refined parameters with twin component ratio 0.712(2):0.148:0.140. However, a set of very weak reflections compatible with a *C*-lattice was well detectable on both the powder and singlecrystal patterns. Based on the *Fmmm* model, the crystal structure of Al_{2.75}Ir was optimized and further developed using DFT calculations and group-subgroup relationships. The obtained structural model (space group *Cmc*2₁) is completely ordered and agrees with both X-ray diffraction data.

The pronounced features of the crystal structure are Al icosahedral clusters centered by Ir atoms. The remaining Ir atoms are coordinated by 8 to 10 Al atoms. The formation of the superstructure originates from Ir displacements and reconfiguration of the IrAl₉ coordination polyhedrons into mono-capped tetragonal antiprisms. The mechanism of the transformation of the Al_{2.75}Ir phase, manifested by the (dis)appearance of superstructure reflections, is discussed.

- [1] Yu. Grin, K. Peters, U. Burkhard, K. Gotzmann, M. Ellner, Z. Kristallogr. 212 (1997) 439-444.
- [2] T. Dotera, S. Bekku, P. Ziherl, *Nat. Mater.* 16 (2017) 987-993.
- [3] A. Oishi, K. Nishimoto, R. Tamura, Z. Kristallogr. 224 (2009) 115-118.
- [4] M. Mihalkovič, C.L. Henley, *Phys. Rev. B* 88 (2013) 064201.
- [5] K. Nishimoto, N. Yamaguci, R. Tamura, J. Phys. Conf. Series 809 (2017) 012010.

LITHIATION, SODIATION AND MAGNESIATION OF $Gd_{1-x}La_xSn_{2-y}Sb_yM_z$ (*M* = Li, Na, Mg) HIGH DISORDER – HIGH ENTROPY PHASES (HD-HEP)

<u>J. Miśtal</u>¹, V. Pavlyuk^{1,2}, G. Kowalczyk¹, A. Balińska¹, N. Pavlyuk², G. Dmytriv², S. Indris³, B. Schwarz³, and H. Ehrenberg³

¹ Institute of Chemistry, Environmental Protection and Biotechnology, Jan Dlugosz University in Częstochowa, Armii Krajowej Al. 13/15, 42200 Częstochowa, Poland ² Department of Inorganic Chemistry, Ivan Franko National University of Lviv,

Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

³ Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany jakubmistal01@gmail.com

High Disorder – High Entropy Phases (HD-HEP) of the $Gd_{1-x}La_xSn_{2-y}Sb_yM_z$ (M = Li, Na, Mg) system were prepared by lithiation, sodiation and magnesiation of the $Gd_{1-x}La_xSn_{2-y}Sb_y$ solid solution phases and were studied by XRD, SEM, EPMA, ⁷Li MAS NMR, Sn Mössbauer spectroscopy, and electrochemical techniques. The formation of $Gd_{1-x}La_xSn_{2-y}Sb_yLi_z$ and $Gd_{1-x}La_xSn_{2-y}Sb_yMg_z$ HD-HEP phases, as a result of the insertion of Li/Mg into tetragonal antiprismatic voids, was observed during electrochemical lithiation and magnesiation, respectively.



The $Gd_{1-x}La_xSn_{2-y-z}Sb_yNa_z$ phase was formed by partial substitution of Na atoms for tin atoms.

The total lithiation process occurs in two stages. The first one is the insertion of lithium into structural voids, and the second stage is the decomposition of the hexagonal phase into new phases and substitution of lithium atoms for tin atoms. This process is reversible, so we can introduce a process of lithiation/delithiation:

I.
$$(Gd/La)(Sn/Sb)_2 + zLi \xleftarrow{\text{insertion}} (Gd/La)(Sn/Sb)_2Li_z$$

II. $(Gd/La)(Sn/Sb)_2Li_z + (k+m)Li \xleftarrow{decomposition-substitution} (Gd/La)(Sn/Sb)_{2-k}Li_{z+k} + Li_m(Sn/Sb)_k$ The same processes are observed during magnesiation/demagnesiation.

The total sodiation process will be presented as:

 $(Gd/La)(Sn/Sb)_2 + (k+m)Na \xleftarrow{decomposition-}{substitution} (Gd/La)(Sn/Sb)_{2-k}Na_k + Na_m(Sn/Sb)_k$ The comparatively larger size of the sodium atom is apparently the reason why it is not inserted into the tetragonal antiprism.

Financial support from the National Science Center, Poland (No. 2017/25/B/ST8/02179) is gratefully acknowledged.

CRYSTAL STRUCTURE, HYDROGENATION AND MAGNETIC PROPERTIES IN THE TbMgNi_{4-x}Co_x-(H,D)₂ SYSTEM

V. Shtender^{1,3}, <u>V. Paul-Boncour</u>¹, J.-C. Crivello¹, R.V. Denys²,

K. Provost¹, F. Couturas¹, and I.Yu. Zavaliy³

¹ ICMPE (UMR 7182), CNRS, UPEC, rue H. Dunant 2, 94320 Thiais, France ² HYSTORSYS AS, P.O. Box 45, Kjeller NO-2027, Norway

³ Karpenko Physico-Mechanical Institute, National Academy of Sciences of Ukraine,

Naukova St. 5, 79060 Lviv, Ukraine

paulbon@icmpe.cnrs.fr

Research on metal hydrides focuses on improving hydrogenation capacities, hydrogen absorption/desorption kinetics and thermodynamics of potential hydrogen storage materials [1]. Substantial work has been carried out on the improvement of the thermodynamic properties of Mg-based compounds. It is known that substitution of Mg for the rare-earth in the binary RT_2 , RT_3 , R_2T_7 and R_5T_{19} (R = rare-earth and T = d-transition metals) intermetallic compounds increases their stability against hydrogenation-induced amorphization [2]. Moreover, such Mg-modified compounds can display interesting magnetic properties: Mg substitution induces ferromagnetism in Ce_{3-x}Mg_xCo₉ compounds and increases the Curie temperature in Nd₂MgCo₉ compared with NdCo₃ [3,4]. Various approaches have been applied in order to enhance favorable properties: partial replacement of R by another rare-earth metal or by Mg; different combinations of d-transition metals, or even replacement of H by D (significant isotope effect [5]).

R-Mg-Co(Ni) compounds have recently attracted substantial interest due to their outstanding hydrogenation properties. For instance, it has been shown that $RMgCo_4$ (R = Y, La, Pr, Nd) compounds absorb ~50% more hydrogen, and at lower pressures, than $RMgNi_4$.

In this work, TbMgNi_{4-x}Co_x (x = 0-4) intermetallics with SnMgCu₄-type cubic structure were synthesized. Their hydrogenation properties were studied in detail. Increase of the Co content increases the stability of the TbMgNi_{4-x}Co_x hydrides, as demonstrated by the experimental results and confirmed by first-principles calculations. The structural investigation of the alloys and their hydrides (deuterides) showed that the crystal structure changes with the (H,D) content. The influence of both the Ni/Co ratio and the (H,D) content on the magnetic properties will be presented and discussed in detail.

- [1] J.B. von Colbe, J.-R.Ares, J. Barale, *et al.*, *Int. J. Hydrogen Energy* 44 (2019) 7780-7808.
- [2] R.V. Denys, A.B. Riabov, V.A. Yartys, et al., J. Solid State Chem. 181 (2008) 812-821.
- [3] T.N. Lamichhane, V. Taufour, A. Palasyuk, et al., Phys. Rev. Appl. 9 (2018) 024023.
- [4] V.V. Shtender, R.V. Denys, V. Paul-Boncour, et al., J. Alloys Compd. 695 (2017) 1426-1435.
- [5] V. Paul-Boncour, M. Guillot, T. Mazet, et al., J. Appl. Phys. 111 (2012) 07A934.

MAGNETOCALORIC EFFECT IN NANOCRYSTALLINE La_{0.8-x}K_{0.2}Mn_{1+x}O_{3± δ} (0 ≤ x ≤ 0.2) MANGANITES

I.V. Fesych¹, <u>O.V. Ivanov</u>¹, N.A. Liedienov^{2,3}, S.A. Nedilko¹, O.G. Dziazko¹, A.V. Pashchenko^{2,3}, and G.G. Levchenko^{2,3}

 ¹ Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska St. 64/13, 01601 Kyiv, Ukraine
 ² State Key Laboratory of Superhard Materials, International Center of Future Science of Jilin University, Qianwei Road 10, 130012 Changchun, China
 ³ O.O. Galkin Donetsk Institute for Physics and Engineering, National Academy of Sciences of Ukraine, Nauky Ave. 46, 03028 Kyiv, Ukraine snedilko@ukr.net

Currently, the scientific and practical interest in the search for new oxide ferromagnetics has increased. The application field of these materials is the development of systems for magnetic cooling in a wide temperature range. This is possible thanks to the magnetocaloric effect. Among the variety of such materials, nanocrystalline manganites of the composition $La_{0.8-x}K_{0.2}Mn_{1+x}O_{3\pm\delta}$ ($0 \le x \le 0.2$) were investigated in this work.

Lanthanum-potassium manganites were synthesized using the citrate sol-gel method. A mixed solution of lanthanum, potassium and manganese nitrates, taken in a stoichiometric ratio, was evaporated in a water bath. Preliminarily a complexing agent (citric acid) had been added to the solution. It was evaporated until the formation of a homogeneous gel-like mass, then this gel was calcined in a furnace at 200-500°C. The obtained black powder was ground in an agate mortar and placed into platinum crucibles, followed by annealing at 850°C for 20 h.

Investigations by X-ray diffraction were carried out at room temperature. The study was performed by means of a Shimadzu LabX XRD-6000 spectrometer (Cu K α radiation, $\lambda = 1.54178$ Å). The average size of the nanocrystallites (D_{012}) was determined from the broadening of the reflection with Miller indices (012), using the Debye-Scherrer formula.

The homogeneity region of the solid solutions of the $La_{0.8-x}K_{0.2}Mn_{1+x}O_{3\pm\delta}$ system is limited to the interval $0 \le x \le 0.1$. All the samples crystallized in the space group *R*-3*c* of rhombohedral symmetry. Further substitution caused the appearance of traces of manganese oxides (Mn₃O₄ and MnO₂). Increasing the lanthanum deficiency led to a decrease of the X-ray density of the samples with respect to the stoichiometric $La_{0.8}K_{0.2}MnO_{3-\delta}$ manganite. The average oxidation state of manganese was practically independent of the substitution degree *x* and was equal to +3.33±0.02. Powder X-ray diffraction data and transmission electron microscopy confirmed the formation of nanoparticles of substituted lanthanum-potassium manganites. The average size of the nanocrystallites was not larger than 40 nm.

According to the magnetic data, all the La_{0.8-x}K_{0.2}Mn_{1+x}O_{3± δ} samples were ferromagnetic materials at room temperature, and showed typical behavior for an ensemble of magnetic particles in a single domain state. The Curie temperature, calculated from $\left|\partial M / \partial T\right|_{T=T_c} = \max$, hardly changed with increasing *x*: 330 K (*x* = 0), 333 K (*x* = 0.05), 332 K (*x* = 0.10), 331 K (*x* = 0.15), and 329 K (*x* = 0.20). The composition La_{0.7}K_{0.2}Mn_{1.1}O₃ showed the highest magnetocaloric effect, $\Delta S_M = 3.154 \text{ J kg}^{-1} \text{ K}^{-1}$ at *H* = 3 T, which makes it suitable for room-temperature refrigeration application.

Yu. Stadnyk¹, V.V. Romaka^{1,2,3}, L. Romaka¹, P. Demchenko¹, and A. Horyn¹

¹Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

² Department of Materials Engineering and Applied Physics, Lviv Polytechnic National

University, Ustyyanovycha St. 5, 79013 Lviv, Ukraine

³ Institute for Solid State Research, IFW-Dresden, Helmholtzstr. 20, 01069 Dresden, Germany stadnykyu@gmail.com.ua

The demand for energy is dramatically increasing. Meanwhile, most of the energy generated from burning fossil fuels is dissipated as waste heat. It is of great importance to recover some of the wasted heat and convert it into useful energy. At present, numerous research centers and laboratories are working on the discovery and improvement of materials for thermoelectric generators. Compounds with MgAgAs-type structure (half-Heusler phases) are used as basic alloys for obtaining high-performance thermoelectric materials. Significant improvement of the thermoelectric properties of the half-Heusler phases may be achieved by doping the basic compounds with various elements at different crystallographic sites. In particular, this applies to the phase TiCoSb [1,2].

Samples of the Ti_{1-x}Sc_xCoSb solid solution ($0.005 \le x \le 0.20$) were synthesized by arcmelting, annealed at 1070 K, and examined by X-ray powder diffraction (STOE STADI P diffractometer, Cu K α_1 radiation) and scanning electron microscopy with energy-dispersive X-ray analysis (Carl Zeiss DSM 962 and REMMA-102-02). The electrical resistivity and Seebeck coefficient were measured in the temperature range 80-380 K. The magnetic susceptibility was measured by the Faraday method at room temperature in magnetic fields up to 1.0 T.

X-ray diffraction phase and structure analyses of the as-cast and annealed samples showed the presence of a single phase with MgAgAs-type cubic structure (space group F-43m) up to a Sc-content of x = 0.15. The Ti_{0.80}Sc_{0.20}CoSb sample contained an additional phase, ScCoSb with the orthorhombic TiNiSi-type. The lattice parameter of the alloys of the Ti_{1-x}Sc_xCoSb solid solution increases monotonously as atoms of smaller size ($r_{Ti} = 0.145$ nm) are replaced by larger Sc atoms ($r_{Sc} = 0.161$ nm). The compositions of the samples determined from EPMA data confirmed the substitution of Sc atoms for Ti in the TiCoSbbased compound.

The investigated Ti_{1-x}Sc_xCoSb solid solution shows a semiconductor to metal transition. Substitution of Sc for Ti increases the number of charge carriers, which results in a decrease of the electrical resistivity, and holes become the main charge carriers. All the samples of the Ti_{1-x}Sc_xCoSb ($x \ge 0.03$) solid solution are Pauli paramagnets. DFT calculations revealed that the maximum solubility of the Ti_{1-x}Sc_xCoSb solid solution reaches $x \approx 0.35$ at 800 K, due to the configuration entropy of mixing term of the thermodynamic potential. With increasing Sc content, the Fermi level drifts towards the valence band. Both the calculated density of states at the Fermi level and the Seebeck coefficient are in good agreement with the experimental transport properties.

- [1] Yu. Stadnyk, Yu. Gorelenko, A. Tkachuk, A. Goryn, V. Davydov, O. Bodak, J. Alloys Compd. 329 (2001) 37-41.
- [2] V.A. Romaka, V.V. Romaka, Yu.V. Stadnyk, *Intermetallic Semiconductors: Properties and Applications*, Lvivska Politekhnika, Lviv, 2011, 488 p. (in Ukrainian).

P72

Dy₄B₃C₄: PREPARATION, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES

<u>V. Babizhetskyy</u>¹, V. Levytskyy¹, and O. Isnard² ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Institut Néel, University Grenoble Alpes and CNRS, 25 rue des Martyrs, BP 166, Cedex 9, F-38042 Grenoble, France v.babizhetskyy@googlemail.com

The structures of the ternary rare-earth metal boride carbides $R_x B_y C_z$ display a variety of different arrangements with boron carbon substructures ranging from zero-dimensional units to one- and two-dimensional networks alternating with metal atom sublattices. The dimensionality of the anionic nonmetal substructures is strongly dependent on the valence electron concentration (VEC) per main group atom considering a Zintl-Klemm approach. Compounds with 2D boron-carbon layers have a VEC slightly larger than 4. With a VEC around 5, 1D ribbons are found, whereas compounds with a VEC larger than 5 contain finite (0D) units [1].

Dy₄B₃C₄ crystallizes in the triclinic Gd₄B₃C₄ structure type [2], space group *P*-1, *Z* = 1, *a* = 3.5545(6), *b* = 3.599(1), *c* = 11.739(1) Å, *a* = 93.23(1), *β* = 96.74(1), *γ* = 90.11(1)°, according to X-ray powder diffraction ($R_B = 0.069$, $R_p = 0.145$). The crystal structure of Dy₄B₃C₄ contains linear CBC units, as well as one-dimensional planar ribbons (BC)_∞ formed from zigzag chains of boron atoms to which carbon atoms are attached. The boron atoms in the ribbons exhibit slight bond alternation with two crystallographically different B2-B2 distances, 1.95(5) Å and 2.03(6) Å. The CBC units, formed by B1 and C1 atoms, have short B-C distances of 1.478(8) Å, indicative of double bond character.

Magnetic susceptibility measurements of the Dy₄B₃C₄ sample were performed in the temperature range 2 < T < 300 K at B = 1 T. The sample undergoes an antiferromagnetic transition at $T_{\rm N} = 26$ K, and, at low field (B = 0.1 T), in addition a metamagnetic transition corresponding to spin reorientation was detected at $T_{\rm sr} = 14.4$ K. The magnetic susceptibility of Dy₄B₃C₄ at T > 40 K is described by the Curie-Weiss model with a Curie-Weiss temperature obtained from a curve fit: $\theta_{\rm p} = 14.3(3)$ K, indicating predominance of ferromagnetic nearest-neighbor exchange interactions. The estimated effective paramagnetic moment (40 < T < 300 K), $\mu_{\rm eff} = 10.4 \,\mu_{\rm B}$ /Dy-atom, is close to the theoretical value of 10.65 $\mu_{\rm B}$ for Dy³⁺ (ground state term ${}^{6}H_{15/2}$).

- V. Babizhetskyy, J. Bauer, R. Gautier, K. Hiebl, A. Simon, J.-F. Halet, In: J.C. Bünzli, V. Pecharsky (Eds.), *Handbook on the Physics and Chemistry of the Rare Earths including Actinides*, Vol. 53, Elsevier, North-Holland, 2018, pp. 145-269.
- [2] C. Jardin, O. Oeckler, Hj. Mattausch, A. Simon, J.-F. Halet, J.-Y.Saillard, J. Bauer, *Inorg. Chem.* 39 (2000) 5895-5900.

THE INFLUENCE OF RECOMBINATION CONDITIONS ON THE PHASE CONTENT, MICROSTRUCTURE, AND MAGNETIC PROPERTIES OF SmC05-BASED SINTERED MAGNETS

I.I. Bulyk¹, V.V. Chabanenko^{2,3}, A. Nabiałek³, T. Zajarniuk³, A. Szewczyk³, R. Puźniak³, V.V. Burkhovetskyi², V.Yu. Tarenkov², and <u>I.V. Borukh¹</u>

¹ Karpenko Physico-Mechanical Institute, National Academy of Sciences of Ukraine, Naukova St. 5, 79060 Lviv, Ukraine
² O.O. Galkin Donetsk Institute for Physics and Engineering, National Academy of Sciences of Ukraine, Nauky Ave. 46, 03028 Kyiv, Ukraine ³ Institute of Physics, Polish Academy of Sciences, Lotników Al. 32/46, 02-668 Warsaw, Poland

ihor.borukh@gmail.com

Permanent magnets based on rare-earth – transition metals (*REM–TM*) intermetallics have been widely applied in fields such as electric motors, wind power generators, electroacoustics, computer peripherals, medical equipment, and magnetomechanics [1]. The production volume of such magnets is increasing at a rapid pace [2]. This is why studies aimed at looking for new magnetic materials [3] and improving the magnetic properties of known ones, *e.g.* by grinding their microstructure down to nanoscale, are stimulated. Hydrogen treatment of ferromagnetic materials is a perspective method for grinding the microstructure. The hydrogenationdisproportionation-desorption-recombination (HDDR) process is the physical base. A method of hydrogen treatment based on the HDDR-process was developed for grinding the microstructure of ferromagnetic alloys to nanoscale [4]. It is based on the dependence of the dispersity of the microstructure of the HDDR-processed materials on the dispersity of the microstructure of the products of disproportionation. This method has been used for obtaining sintered nanoscale anisotropic Nd₂Fe₁₄B-, SmCo₅-, and Sm₂Co₁₇-based magnets.

The influence of the phase recombination conditions on the phase content, microstructure, and magnetic properties of sintered SmCo₅-based alloys was studied by X-ray diffraction, scanning electron microscopy, and magnetic hysteresis loop measurements. Recombination of the disproportionation products, SmH_{2±x} and Co and remains of SmCo₅ phase, was carried out by heating in vacuum to 850°C, with and without holding for 1 h, and by heating to 950°C. The coercivity of the magnet (μ_0H_c) changed in the range 4.90-4.97 T after recombination. The remanent magnetization was increased from 27.7 to 43.5 and up to 46.7 emu/g, by increasing the holding time during recombination from 0 to 1 h at 850°C, and by increasing the recombination temperature up to 950°C. The hysteresis loop rectangularity changed from 77 to 74.6 and 78.8 % for the same conditions.

- [1] O. Gutfleisch, M.A. Willard, E. Brück, C.H. Chen, S.G. Sankar, J.P. Liu, *Adv. Mater*. 23 (2011) 821-842.
- [2] Y. Yang, A. Walton, R. Sheridan, K. Güth, R. Gauß, O. Gutfleisch, M. Buchert, B.-M. Steenari, T.V. Gerven, P.T. Jones, K. Binnemans, J. Sustain. Metall. (2016). Doi: 10.1007/s40831-016-0090-4 (open access).
- [3] J. Cui, M. Kramer, L. Zhou, F. Liu, A. Gabay, G. Hadjipanayis, B. Balasubramanian, D. Sellmyer, *Acta Mater*. 158 (2018) 118-137.
- [4] I.I. Bulyk, V.V. Burkhovetskyy, *Powder Metall. Met. Ceram.* 54 (2016) 614-623.

FEATURES OF ELECTRICAL CONDUCTIVITY MECHANISMS OF THE Ti_{1-x}Mo_xCoSb SOLID SOLUTION

<u>A. Horyn</u>¹, V.A. Romaka², Yu. Stadnyk¹, L. Romaka¹, M. Rokomanyuk², and V. Krayovskyy²

¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Lviv Polytechnic National University, S. Bandera St. 12, 79013 Lviv, Ukraine andriv.horvn@lnu.edu.ua

Thermoelectric materials based on the semi-Heusler phases demonstrate high efficiency of transformation of thermal energy into electric energy. Uncontrolled changes in the crystalline and electronic structures when optimizing the characteristics by doping, constrain broad application of these materials. Previous studies of the TiCo_{1-x}Ni_xSb, TiCo_{1-x}Cu_xSb and Ti_{1-x}V_xCoSb substitutional solid solutions [1-3] showed that doping of the TiCoSb half-Heusler phase by Ni, Cu or V atoms, with higher number of *d*-electrons than Co or Ti, generates structural defects of donor nature. The investigation of the electrokinetic, magnetic, and energy state characteristics and electronic structure of the Ti_{1-x}Mo_xCoSb (x = 0.005-0.10) solid solution is a continuation of our previous work [1-3]. It is an integrated study of the mechanisms and conditions for the inclusion of impurity atoms into the matrix of the TiCoSb compound, in order to establish the conditions for obtaining efficient thermoelectric materials.

Based on the electronic configuration of the Ti $(3d^24s^2)$ and Mo $(4d^55s^1)$ atoms, it was predicted that substitution of Mo for Ti in the TiCoSb compound will generate structural defects of donor nature, and a donor band ϵ_D^2 will be formed in the band gap of the semiconductor. Since in the *n*-TiCoSb compound the Fermi level ε_F is located near the middle of the band gap ε_g , at a small Mo concentration it will be displaced to the conduction band ε_C , which will be crossed at $x \approx 0.03$ (dielectric-metal transition of conductivity). The maximal values of the thermoelectric power factor are expected for concentrations $x \le 0.03$, when the Fermi level ε_F approaches the conduction band ε_C .

The presence of high-temperature activation in the $\ln\rho(1/T)$ dependencies for all the studied $\text{Ti}_{1-x}\text{Mo}_x\text{CoSb}$ samples was unexpected. Such activation confirms the location of the Fermi level ε_{F} in the energy band gap. The negative values of the thermopower coefficient $\alpha(x,T)$ for $\text{Ti}_{1-x}\text{Mo}_x\text{CoSb}$ indicate location of the Fermi level ε_{F} in the band gap near the conduction band ε_{C} . Doping of TiCoSb with a low Mo content changes the position of the Fermi level ε_{F} , bringing it closer to the conduction band, at a distance of Fermi level ε_{F} , bringing it closer to the conduction band, at a distance of $\varepsilon_{n}^{\rho}(x=0.01)=14.6 \text{ meV}$. At concentrations x=0.05-0.1, the Fermi level is drifted from the edge of the conduction band to a distance of 37.4 meV, indicating the appearance of acceptors of unknown nature. However, even at higher concentrations of donor impurity, $N_{\text{D}}^{\text{V}} \approx 1.1 \cdot 10^{21} \text{ cm}^{-3}$ (x=0.07), the Fermi level is still located in the band gap of the semiconductor. The reason for the "inhibition" of the Fermi level in $\text{Ti}_{1-x}\text{Mo}_x\text{CoSb}$ could be, simultaneously with the presence of donors, the generation of acceptors that capture free electrons, decreasing their number. The conditions for the generation of structural defects of acceptor nature in $\text{Ti}_{1-x}\text{Mo}_x\text{CoSb}$ are given in the present work.

- [1] Yu. Stadnyk, V. Romaka, M. Shelyapina, Yu. Gorelenko, L. Romaka, D. Fruchart, A. Tkachuk, V. Chekurin, *J. Alloys Compd.* 421 (2006) 19-23.
- [2] V. Romaka, Yu. Stadnyk, L. Akselrud, V. Romaka, D. Fruchart, P. Rogl, V. Davydov, Yu. Gorelenko, *Semiconductors* 42(7) (2008) 753-760.
- [3] V.A. Romaka, Yu.V. Stadnyk, D. Fruchart, J. Tobola, Yu.K. Gorelenko, L.P. Romaka, V.F. Chekurin, A.M. Horyn, *Ukr. Fiz. Zh.* 52(5) (2007) 453-457.

SOLID-GAS AND ELECTROCHEMICAL HYDROGENATION PROPERTIES OF $R_{1-x}R'_x$ MgNi_{4-v} M_v (R, R' = Y, La, Pr, Nd; M = Fe, Mn) ALLOYS

<u>Yu.V. Verbovytskyy</u>¹, Yu.V. Kosarchyn¹, P.Ya. Lyutyy¹, V. Paul-Boncour², and I.Yu. Zavaliy¹

¹ Karpenko Physico-Mechanical Institute, National Academy of Sciences of Ukraine, Naukova St. 5, 79060 Lviv, Ukraine

² Institut de Chimie et des Matériaux Paris Est, CMTR, UMR 7182 CNRS UPEC,

2-8 rue H. Dunant, 94320 Thiais, France

yuryvv@bigmir.net

Rare earth - magnesium - nickel based hydrogen storage alloys have gained increasing interest as one of the most promising materials for negative electrodes in Ni-MH batteries. The electrochemical discharge capacity of electrode materials based on La-Mg-Ni-Co alloys reaches 400 mAh/g, which is 30 % higher than the capacity of commercial LaNi₅-based electrodes. However, the poor cyclic stability (degradation during the cyclic process) is the main problem that hinders its practical application. Several methods have been adopted to improve the cyclic stability of the alloys. Metal substitution, mechanical milling and various preparation techniques are some of them [1]. In most cases the studied alloys are multi-phase and contain compounds with structures of the Laves AB_2 , Haucke AB_5 and/or composed/ superlattice $(AB_2)_n(AB_5)_m$ types. Single-phase intermetallics with the composition R_2 MgNi₉ and PuNi₃ structure type (n = 1 and m = 1) are well explored and briefly discussed in [2]. The RMgNi₄, or so-called 1:1:4 phases (n = 2 and m = 0) are characterized by good electrochemical properties [3] and can easily be prepared by the sintering method [4,5]. In the present work, which continues our previous research on such alloys, a series of hydrogen storage alloys $R_{1-x}R'_{x}MgNi_{4-v}M_{v}$ (R, R' = Y, La, Pr, Nd; M = Fe, Mn) were prepared, and the effect of multiple metal substitution on gas and electrochemical hydrogenation was systematically studied.

The above mentioned samples were prepared by the powder metallurgy route, using pure magnesium and AB_2 alloy powder precursors. Hydrogenation curves were obtained using a Sieverts type apparatus. Electrochemical charging-discharging properties were studied by galvanostatic measurements, using a GStat-8 workstation. Powder X-ray diffraction and microprobe analysis were used for the sample characterization.

The X-ray diffraction analysis showed that the $R_{1-x}R'_xMgNi_{4-y}M_y$ (x = 0 or 0.5, y = 0, 0.5 and 1) phases belong to the MgCu₄Sn structure type. The synthesized alloys absorb hydrogen at room temperature and hydrogen pressures below 10 bar. The formation of hydrides with cubic, orthorhombic, or amorphous structures was observed. Electrochemical studies showed that the Fe- or Mn-doped electrode materials have slightly higher maximum discharge capacity than $R_{1-x}R'_xMgNi_4$, but the doping influenced in a different manner the cyclic stability. For example, the highest discharge capacity was equal to 236 mAh/g for LaMgNi_{3.5}Mn_{0.5}, 271 mAh/g for PrMgNi_{3.5}Mn_{0.5} and 263 mAh/g for NdMgNi_{3.5}Mn_{0.5} at a current density of 50 mA/g.

- [1] Y. Liu, Y. Cao, L. Huang, M. Gao, H. Pan, J. Alloys Compd. 509 (2011) 675-686.
- [2] Yu.V. Verbovytskyy, I.Yu. Zavaliy, *Mater. Sci.* 51 (2016) 443-456.
- [3] Yu.V. Verbovytskyy, I.Yu. Zavaliy, Mater. Sci. 52 (2017) 747-759.
- [4] Yu.V. Verbovytskyy, V.V. Shtender, et al., J. Alloys Compd. 741 (2018) 307-314.
- [5] V.O. Oprysk, Yu.V. Verbovytskyy, et al., Solid State Sci. 2018 (84) 112-119.

INFLUENCE OF SUBSTITUTION ON THE STRUCTURE AND MAGNETIC PROPERTIES OF THE Dy_{1-x}Ho_xCu₅Sn SOLID SOLUTION

<u>A. Zelinskiy</u>¹, L. Romaka¹, L. Akselrud^{1,2}, R. Gladyshevskii¹, O. Sichevych², M. Bobnar², and Yu. Grin² ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187, Dresden, Germany anatoliy.zelinskiy@lnu.edu.ua

Several samples from the homogeneity range of the solid solution $Dy_{1-x}Ho_xCu_5Sn$ ($x = 0 \div 0.1$) were prepared by arc melting of the elements and annealed at 1100 or 870 K. Structure and profile parameters were refined by the Rietveld method, using powder X-ray diffraction data (image-plate Guinier camera Huber G670, Cu $K\alpha_1$ radiation) with LaB₆ as an internal standard. Magnetic measurements were carried out in magnetic fields of up to 10 T, using an automatic extraction magnetometer.



Fig. Composition dependence of the paramagnetic Curie temperature and unit-cell volume of $Dy_{1-x}Ho_xCu_5Sn$ (a); and temperature dependence of the inverse magnetic susceptibility of $Dy_{0.9}Ho_{0.1}Cu_5Sn$ (b).

The Dy_{1-x}Ho_xCu₅Sn phase crystallizes with the structure type CeCu₅Au (an ordered variant of the CeCu₆ type). The replacement of Dy by Ho is accompanied by a decrease of the volume of the unit cell, but, depending on the annealing time, the decrease has a different character. The magnetic behavior of the Dy_{1-x}Ho_xCu₅Sn intermetallic was studied by magnetic susceptibility (χ) measurements in the temperature range 1.8-400 K in a static magnetic field. From the $1/\chi(T)$ dependence the paramagnetic Curie temperature Θ_p was determined and the effective magnetic moment μ_{eff} was calculated. The magnetic behavior of the sample Dy_{0.9}Ho_{0.1}Cu₅Sn, with a critical temperature ≈ 0 K, can be described by a quantum phase transition associated with an antiferromagnetic transformation.

ELECTROCHEMICAL SYNTHESIS OF THE TbCo_{4.8}Mg_{0.1}Al_{0.1}H_x HYDRIDE

I. Stetskiv, V. Kordan, I. Tarasiuk, and V. Pavlyuk Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ira.stetskiv95@gmail.com

In the modern world, the attention of many scientists is attracted by the emergency to develop various types of alternative fuels. One of the most promising types of alternative fuel is hydrogen. The most suitable solution for multiple tasks is the use of metal hydrides, since the cost of conversion and liquefaction of hydrogen disappears, and the volume of the system decreases by a factor of about 3, compared with the volume of storage in cylinders. AB_5 -type hydrogen storage is widely used nowadays. Continuing our previous research, we tried to dope the TbCo₅ intermetallic compound with magnesium and aluminum to increase the hydrogen sorption properties of the phase.

An alloy was synthesized by arc melting and annealed in a sealed evacuated quartz ampoule in a resistance furnace at 400°C for 1 month. X-ray diffraction phase analysis was carried out by means of an X-ray diffractometer DRON-2.0M (Fe $K\alpha$ radiation). The phase composition and cell parameters of the material, before and after hydrogenation, were determined by energy-dispersive X-ray spectroscopy (EDX) and X-ray powder diffraction. Electrochemical synthesis of the hydride was carried out in a two-electrode Swagelok-type cell, using a galvanostat MTech G410-2. Powder of a TbCo_{4.8}Mg_{0.1}Al_{0.1} alloy was used as the negative electrode (anode). A mixture of Ni(OH)₂ and graphite (9:1) was used as the positive electrode (cathode), and a 6 M KOH solution as electrolyte. The charge and discharge processes were studied in a galvanostatic regime at 1.0 mA/cm².

X-ray phase analysis of the investigated alloy showed the formation of a main phase with CaCu₅-type structure (space group *P6/mmm*, Pearson symbol *hP*6) and minor amounts of a phase with PuNi₃-type structure (space group *R-3m*, Pearson symbol *hR*36). The cell parameters of the TbCo_{4.8}Mg_{0.1}Al_{0.1} phase changed after hydrogenation: a = 4.94176(5)-4.9577(3) Å, c = 3.9884(7)-3.9902(8) Å, V = 83.35(2)-84.93(7) Å³. Scanning electron microscopy also showed the existence of two phases with 1:5 and 1:3 stoichiometries. The X-ray powder pattern of the sample after electrochemical hydrogenation is characterized by slightly broadened peak profiles and amorphous halo in the low-angle region. The composition of the main phase changed from Tb_{15.8}Co_{79.6}Mg_{2.4}Al_{2.2} before hydrogenation, to Tb_{12.7}Co_{78.7}Mg_{4.7}Al_{3.9} after hydrogenation. We observed an improvement of the hydrogen absorption for the TbCo_{4.8}Mg_{0.1}Al_{0.1} sample and an increase of the discharge capacity (0.25 H/f.u.) as compared to the TbCo₅ binary intermetallic compound under the same experimental conditions (0.23 H/f.u.). The nominal discharge voltage increased from 1.00-1.15 V for the TbCo₅-based, to 1.20-1.30 V for the TbCo_{4.8}Mg_{0.1}Al_{0.1}-based electrode.

VISCOSITY AND ELECTROPHYSICAL PROPERTIES OF THE Cu–Pb SYSTEM – A COMPONENT FOR MODELLING HIGH-ENTROPY ALLOYS

<u>M. Dufanets</u>, Yu. Plevachuk, and V. Sklyarchuk Department of Metal Physics, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 8, 79005 Lviv, Ukraine marta_dufanets@ukr.net

The concept of multicomponent high-entropy alloys (HEAs), according to which high entropy of mixing can stabilize the formation of solid solutions during solidification, is described in [1]. HEAs can have increased strength and thermal stability, in combination with good resistance to oxidation and corrosion. HEAs must contain 5 or more elements (for example, the CuBiSnInPb and CuBiSnGaPb systems).

Viscosity, electrical conductivity and thermoelectric power of Cu–Pb alloys, as a subsystem of the above mentioned high-entropy alloy systems, are reported. The Cu–Pb phase diagram shows a non-mixing region in the range of 33-85 at.% Cu. The critical temperature of the phase separation is 990°C at a concentration of 65.5 at.% Cu. Based on this, all the experimental measurements were performed above 1000°C. The experimental viscosity curve is described by an exponential dependence on the activation energy of a viscous flux of 45.8 kJ/mol for Cu–Pb. The absolute values of the viscosity range from 2.3 mPa·s, just after melting, to 1.5 mPa·s at 1200°C. Based on the experimental viscosity data, the preexponential factor η_0 was determined, which allowed calculating the entropy of the melt – 18 J/K.

The electrical conductivity of the CuPb melt at 1000°C was about 10'000 S/cm, and decreased almost linearly to 9'700 S/cm at 1200°C. The thermoelectric power reached – $1.12 \,\mu$ V/K at 1000°C and increased linearly (decreased in absolute values) to +0.15 μ V/K at 1200°C. The metallic behavior of the studied properties, in the case of high entropy, may indicate the formation of statistically stable solutions.

[1] J.W. Yeh, Y.L. Chen, S.J. Lin, et al., Mater. Sci. Forum 3 (2007) 1-9.

INFLUENCE OF NANO NI ADDITIONS ON STRUCTURE-SENSITIVE PROPERTIES OF Sn-Ag-Cu LIQUID ALLOYS

<u>O. Tkach,</u> Yu. Plevachuk, and V. Sklyarchuk Department of Metal Physics, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 8, 79005 Lviv, Ukraine ntkacholga@gmail.com

Sn–Ag–Cu alloys are widely used as lead-free solders (LFS) in the electronics industry, and numerous studies intended to enhance their characteristics have been carried out. Addition of minor amounts of a fourth element, such as metals in bulk or nanosized form, ceramic or carbon nanoparticles, is a widespread method to improve the mechanical properties of the solder joints. The constant development towards miniaturization and purposeful densification needs much smaller solder joints and fine-pitch interconnections for microelectronic packaging in electronic devices. The miniaturization of the electronic devices demands better solder-joint reliability, but much research is based on bulk solder properties only. However, to meet the needs of miniaturization in the electronics industry, nanoparticle reinforcements are often added to provide the mechanical integrity needed with LFS, while keeping the solder environmentally friendly. Hence, nanoscale solder alloys have been identified as a potential route for yielding higher microstructural stability and better mechanical and thermophysical properties [1-3].

The electrical conductivity of nanocomposite Sn-3.0Ag-0.5Cu alloys with various weight percentages of Ni nanoparticles (from 1.0 to 2.0 wt.%) was measured in a wide temperature range. The samples were prepared using a cold-pressing method: Sn-3.0Ag-0.5Cu powder and Ni nanopowder were mechanically mixed and pressed into 8 mm-diameter rods. The Ni nanoparticles were synthesized *via* the chemical reduction method and exhibited a core/shell structure. The temperature dependence of the electrical conductivity showed a hysteresis between the heating and cooling curves in a wide temperature range above the melting point. This fact is connected with structure transformations, accompanied by dissolution of the Ni nanoparticles, which should be decelerated due to formation of an oxide/hydroxide shell on the surface of the nanoparticles. A microstructure analysis of the investigated samples showed a fine distribution of intermetallic compounds in the Sn-based matrix, while the Ni atoms had substituted for Cu atoms in the Cu₆Sn₅ compound, forming a (Cu,Ni)₆Sn₅ phase in the solid state.

- [1] L. Sun, L. Zhang, Adv. Mater. Sci. Eng. (2015) 639028.
- [2] E.E.M. Noor, A. Singh, T.C. Yap, Soldering Surf. Mount Technol. 25 (2013) 229-241.
- [3] A. Sharma, B.G. Baek, J.P. Jung, Mater. Des. 87 (2015) 370-379.

SENSITIZATION OF TITANIUM DIOXIDE WITH AN ANIONIC POLYMETHINE DYE IN THE PHOTOCATALYTIC REDUCTION OF METHYLENE BLUE

I.M. Kobasa¹, Yu.V. Kropelnytska², and V.M. Fedoriv¹

 Yu. Fedkovych National University of Chernivtsi, Kotsyubynsky St. 2, 58012 Chernivtsi, Ukraine
 ² Bukovinian State Medical University, Teatralna Sq. 2, 58002 Chernivtsi, Ukraine i.kobasa@chnu.edu.ua

Photocatalysis has attractive prospects for solar energy conversion, environmental protection, registration and reproduction of information, *etc*. But, to satisfy the requirements, the highest quantum yields of the photocatalytic processes involving known photocatalysts, in particular TiO_2 , are not sufficient. Therefore, one of the most important challenges in photocatalysis is the creation of highly efficient photocatalytic systems, and finding opportunities for their practical application.

A perspective method that can increase the photocatalytic activity (PA) consists in constructing heterostructures (HS) containing microparticles of a semiconductor photocatalyst and a dye-sensitizer (D), which is attached to the surface of a film of electron-permeable material (P). HS of this type are active in the photocatalytic processes of decomposition of water and oxidation of iodide ions. It is important to determine the general nature of this approach to create efficient light systems and evaluate the possibility of using it to create sensitized photocatalytic blocks, using other dyes as block components. For this purpose we synthesized new HS based on TiO₂ and anionic polymethine dyes, and investigated them in the photocatalytic process of restoring methylene blue (MB). To obtain the HS we used anionic polymethine dyes 1-3, titanium dioxide and as polymer polyepoxypropylcarbazole. The PA of the HS P/D/TiO₂ was evaluated for speed bleaching of a solution of MB formaldehyde.



The studies of the effect of the HS on the process of photoreduction of MB showed that the HS behave differently, depending on which spectral area of light is used for the photoexcitation. During irradiation of the reaction mixture with visible light, the light was absorbed by the dye sensitizer, which is part of HS, and MB, which is in the solution. The restoration of MB is the result of the photocatalytic activity of HS. Research has shown that on replacing P/D/TiO₂ by TiO₂ a similar reaction does practically not take place under the same conditions. In the systems containing HS with increasing contents of dye, PA initially increases and then, having reached a certain threshold, is reduced. A completely different dependence of the activity on the quantitative composition of the HS is observed if the system is irradiated with ultraviolet light, which is absorbed, mainly, by the titanium dioxide. The highest activity was observed for the original sample that did not contain any dye-sensitizer.

In conclusion, we have created a new heterostructure, consisting of titanium dioxide, polymethine dye-sensitizer and polymers, which is sensitive to light of the visible spectral area.

REGULARITIES OF FORMATION AND SOME PHYSICO-CHEMICAL PROPERTIES OF COPPER AND SILVER FILMS ON CdTe, CdSb, In₂Hg₃Te₆

I.M. Kobasa, O.V. Sema, and M.M. Vorobets Yu. Fedkovych National University of Chernivtsi, Kotsyubynsky St. 2, 58012 Chernivtsi, Ukraine i.kobasa@chnu.edu.ua

The presentation summarizes and reports some theoretical and experimental results related to the acid-base and redox processes occurring at the interphase "semiconductor/solution of Me^{n+n} and some regularities of the formation of copper and silver films on the surface of CdTe, CdSb, and In₂Hg₃Te₆. The results were obtained by thermodynamic analysis of the system "CdSb (CdTe, Hg₃In₂Te₆)–solution of Me^{n+n} , potentiometric investigation of the contact deposition of copper and silver, chemical and analytical identification of the transformation products, and by analysis of particular features of the formation of copper and silver films on the surface of the semiconducting materials.

A thermodynamic analysis of the contact exchange processes taking place in the system $CdSb-Cu^{2+}-H_2O$ was performed and Pourbaix diagrams were built for this system, using methods of chemical thermodynamics and acid-base equilibriums. Analysis of the diagrams, taking into account the distribution of the ionic forms of copper and cadmium, proved that the contact exchange in the system $CdSb-Cu^{2+}-H_2O$ in acidic solutions is conditioned by stoichiometric dissolution of the semiconducting components. It was found that the ion exchange processes taking place in the system $CdSb-Cu^{2+}-H_2O$ are controlled by the following physico-chemical parameters: pH, concentration of the metal cation and crystallochemical state of the semiconductor surface. As seen from the results of the calculations, contact exchange is allowed in the system and, therefore, further technological solutions related to the formation of copper contact spots on the surface of CdSb can be elaborated.

The kinetics of the contact deposition of Cu^{2+} and Ag^+ on the surface of crystalline CdSb (CdTe) and their electrode behavior in acidic aqueous solutions were also investigated. It was found that the surface condition and ion exchange processes in the systems "CdSb(CdTe)– $Cu^{2+}(Ag^+)$ – H_2O " are the parameters that control the contact deposition of copper and silver. The deposition process is driven by the difference between the standard electrode potentials of the semiconductor and the metal-carburizer. Some parameters and regularities of the formation of silver and copper contact spots on the surface of crystalline CdSb, CdTe and Hg₃In₂Te₆ were found, and the structure and chemical composition of the spot areas were determined.

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF R_{11} Pd₄In₉ COMPOUNDS (R = Gd-Er)

 S. Baran¹, <u>Yu. Tyvanchuk</u>², B. Penc¹, Ya. Kalychak², and A. Szytula¹
 ¹ M. Smoluchowski Institute of Physics, Jagiellonian University, Lojasiewicza 11, 30-348 Krakow, Poland
 ² Department of Analytical Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya 6, 79005 Lviv, Ukraine yuriy.tyvanchuk@lnu.edu.ua

The work reports the results of X-ray diffraction and magnetometric measurements of the $R_{11}Pd_4In_9$ (R = Gd-Er) compounds. These compounds adopt the orthorhombic Nd₁₁Pd₄In₉-type structure (space group *Cmmm*) [1], a complex crystal structure in which the rare-earth atoms occupy five non-equivalent crystallographic positions.

The results of the magnetic measurements, performed using the vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform, indicate complex magnetic properties.

At high temperature, the reciprocal magnetic susceptibility obeys the Curie-Weiss law. The values of the effective magnetic moments are close to the free R^{3+} ion values. The positive values of the paramagnetic Curie temperature indicate that ferromagnetic interactions are predominant. With decreasing temperature the magnetic susceptibility sharply increases, which indicates a change of the magnetic properties, firstly to a ferri- and next to an antiferromagnetic state. These properties are in agreement with the temperature and magnetic field dependence of the primary magnetization curves and hysteresis loops.

For $Ho_{11}Pd_4In_9$, additional ac and neutron diffraction measurements were performed, which confirmed a change of the magnetic order with increasing temperature.

The complex magnetic properties are connected with the crystal structure, in which rare-earth atoms with localized magnetic moment occupy five distinct sublattices. The interactions between the moments, within the sublattices and between the different sublattices, lead to different magnetic orders. The *R*-*R* interatomic distances between rare-earth atoms occupying the same atom site, and between atoms at different sublattices, are near 3.6 Å, suggesting that the magnetic interactions between rare-earth moments are of the RKKY-type. However, the dependence of the critical temperature of the magnetic ordering does not obey the de Gennes relation. This suggests strong influence of the crystalline electric field on the formation of the magnetic state.

The results obtained here are compared with those for isostructural $R_{11}Ni_4In_9$ compounds [2-6].

- [1] L. Sojka et al., Intermetallics 16 (2008) 625-628.
- [2] A. Szytula et al., J. Alloys Compd. 601 (2014) 238-244.
- [3] Yu. Tyvanchuk et al., J. Alloys Compd. 587 (2014) 573-577.
- [4] A. Provino et al., Acta Mater. 73 (2014) 27-36.
- [5] A. Provino et al., Acta Mater. 91 (2015) 128-140.
- [6] C. Ritter et al., J. Phys.: Condens. Matter 27 (2015) 476001.

ELECTROCATALYTIC PROPERTIES OF THE Hf₂Ir₅B₂ BORIDE

<u>A. Barrios Jiménez</u>¹, S. Flipo¹, O. Sichevych¹, K. Höfer¹, S. Altendorf¹, A. Leithe-Jasper¹, R. Gumeniuk², I. Antonyshyn¹, and Y. Grin¹ ¹ Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straβe 40, 01187 Dresden, Germany ² Technische Universität Bergakademie Freiberg, Akademiestraβe 6, 09599 Freiberg, Germany Ana.Barrios@cpfs.mpg.de

The new boride $Hf_2Ir_5B_2$ (*Pbam*, a = 5.62185(7) Å, b = 11.2442(2) Å, c = 3.82872(3) Å) was synthesized as bulk by arc-melting. The crystal structure represents a distorted derivative of the α -Fe structural pattern with single iridium atoms and boron dumbbells located at the centers of cubes formed by Ir and Hf.

 $Hf_2Ir_5B_2$ was investigated as electrocatalyst for oxygen evolution reaction (OER), which is the anode half-reaction of water splitting. The latter is one of the possible routes towards production of hydrogen as a clean fuel [1]. The electrochemical activity of $Hf_2Ir_5B_2$, with an overpotential of 300 mV in 0.1 M H_2SO_4 , is comparable to that of the parent metal Ir (270 mV in 0.1 M H_2SO_4), which is one of the best catalysts for this reaction [2]. Furthermore, $Hf_2Ir_5B_2$ possesses an outstanding bulk stability under harsh oxidative conditions. The electrochemical results were supported by characterization of the material (PXRD, SEM, XPS) and the electrolyte (ICP-OES).

- [1] M. Carmo, D.L. Fritz, J. Mergel, D. Stolten, *Int. J. Hydrogen Energy* 38 (2013) 4901-4934.
- [2] S. Cherevko, A.R. Zeradjanin, A.A. Topalov, N. Kulyk, I. Katsounaros, K.J.J. Mayrhofer, *ChemCatChem* 6 (2014) 2219-2223.

INFLUENCE OF BORON ON THE ELECTROCHEMICAL DELITHIATION OF Li_xAl_y PHASES

<u>V. Milashius</u>, V. Kordan, I. Tarasiuk, G. Dmytriv, and V. Pavlyuk Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine milashys@gmail.com

Alloys based on light metals such as Li, Al, and B will always be interesting as constructive materials or electrode materials for batteries. The purpose of this work was to study the electrochemical behavior of alloys on the basis of binary (Li_3Al_2 and Li_9Al_4) or ternary ($Li_3Al_{2-x}B_x$ and $Li_9Al_{4-x}B_x$) phases. In addition, we calculated the electron localization function (ELF) and density of states (DOS) to explain the influence of boron on the crystal structure and properties of the intermetallic compounds.

Lithium and aluminum with a nominal purity of more than 99.8 wt.%, and boron with a nominal purity of more than 95.0 wt.%, were used as starting materials for the synthesis of the alloys. Samples with the nominal compositions $L_{i_{60}}Al_{40}$, $L_{i_{69}}Al_{31}$, $L_{i_{60}}Al_{35}B_5$, and $L_{i_{69}}Al_{26}B_5$ were prepared by arc melting of pressed pellets (mixtures of Al and B powders). Electrochemical delithiation/lithiation was carried out in two-electrode Swagelok-type cells that consisted of a negative electrode containing 0.1 g of the alloy and a positive electrode containing $LiCoO_2$ powder. A separator (pressed cellulose), soaked in an electrolyte (1 M solution of $Li[PF_6]$ in a mixture of ethylenecarbonate / dimethylcarbonate 1:1), was placed between the electrodes. Delitiation/lithiation of the electrodes was carried out in a galvanostatic regime (0.1-0.2 mA/cm²) over 50 cycles. The electron localization function (ELF) and the density of states (DOS) were calculated using the TB-LMTO-ASA method. At the experimental conditions we observed that Li_3Al_2 delithiated 10.3 at.% Li (0.52 Li/f.u.), $Li_3Al_{2-x}B_x - 12.2$ at.% (0.61 Li/f.u.). For the Li-rich alloys the amount of mobile Li was higher: $Li_9Al_4 - 12.5$ at.% Li (1.6 Li/ f.u.) and $Li_9Al_{4-x}B_x - 13.8$ at.% Li (1.8 Li/f.u.).

The Li₉Al₄ binary compound (own structure type) has an interesting crystal structure, since there are two crystallographic positions for the Li-atoms (4i and 2a). We observed a high value for the interaction energy between Al atoms (-iCOHP = 2.285 eV), which confirms the particular interaction between *p*-element atoms. Probably the Al-Al chemical bond contains some covalent interaction. The energy of the Li-Al interaction is small (-iCOHP = 0.435 eV), confirming the higher diffusion and mobility of the Li-atoms of this position in the crystal structure. The ELF is concentrated around the Al atoms, while the Liatoms give valence electrons to the electron gas. The DOS demonstrated the existence of populated energy states in the valence area and conductivity area for the lithium and aluminum atoms. The general aspect indicated typical metallic behavior, since at the Fermi level (E = 0 eV) the energy states are populated. We can explain this since metallic bonding is dominating in the structure; the existence of partially covalent interactions between Al atoms is minor. As a result, we confirm that the crystal structure of the intermetallic and the distribution of the electron density on the atoms play a dominant role. Components with acceptor-ability, such as boron, contribute to a redistribution of the charges on the atoms, which is related to the formation of a partial positive δ + charge on the Li-atoms, and further influence the mobility of these atoms. For this reason the ternary phases showed better results than the binary ones.

M.D. Koterlyn¹, <u>O.I. Babych²</u>, and G.M. Koterlyn³

¹ Institute of Physics, K. Wielkiego University,

Weyssenhoffa Sq. 11, 85-072 Bydgoszcz, Poland

² Faculty of Electronics and Computer Systems, Ivan Franko National University of Lviv,

Dragomanova St. 50, 79005 Lviv, Ukraine

³ Western Scientific Center of the National Academy of Sciences and Ministry of Education

and Science of Ukraine, Mateyka St. 4, 79007 Lviv, Ukraine

koterlyn@mail.lviv.ua

The results of studies in a wide temperature range (4-900 K) of the thermoelectric power (TEP) of CeNi₄X (X = Cu, Al, Ga,) compounds with a structure of the CaCu₅ type (space group *P6/mmm*), containing cerium in a state of valence instability, are presented. We analyzed the contribution of the *f*-states of cerium to the total TEP, taking into account the transport properties of the crystal matrix containing the *f*-electron subsystem, for the compounds with X = Cu and Ga. The isostructural compounds LaNi₄X were used as matrix.

It was shown that the specificities of the temperature behavior of the TEP of CeNi₄X are caused by a joint manifestation of the effects of incoherent Kondo scattering of conduction electrons on localized *f*-centers and scattering on the spin fluctuations in the narrow *d*-band of the nickel sublattice. The anomalously low Kondo contribution to the total TEP for the compounds with Ga and Al, observed in this case, is suggested to be associated with possible weakening of the Kondo-compensation of the magnetic moment of the cerium ions, due to structural atomic disorder in its immediate environment. The temperature dependencies of the Kondo component of the TEP (*S*_K) of CeNi₄X in the temperature range *T* < 500 K are well described within the framework of the model of a narrow peak of the density of states $g_f(E)$ of lorentzian shape near the Fermi level E_F [1], associated with Kondo screening (so-called Kondo resonance), characterized by a Kondo temperature of $T_K \approx 0.5 \cdot 10^3$ K for X = Ga and $\approx 1.8 \cdot 10^3$ K for X = Cu.

The $S_{\rm K}(T)$ dependence is well described within the framework of the model proposed in [2], taking into account the temperature dependence of the position of the peak $g_f(E)$ above the Fermi level, $\varepsilon_f(E)$, and its width, $\Gamma_f(E)$, in the temperature range 500-900 K. Fitting of the calculated curve $S_{\rm K}(T)$ to the experimental data was carried out under the assumption of a temperature dependence of the peak width according to the relation $\Gamma_f(E) = A + BT^n$ where n = 0, 0.5, 1, 2, and A, B are fitting parameters. It was found that good agreement between the theoretical and experimental curves $S_{\rm K}(T)$ is achieved when the temperature dependence of the parameter ε_f is described by the relation $\varepsilon_f(T) = a + bth((-T + c)/d)$, where a, b, c, d are fitting parameters. The choice of the type of dependence for $\Gamma_f(T)$ does not significantly affect the overall nature of the behavior of $\varepsilon_f(T)$. In general, the Kondo resonance in CeNi₄Ga, in comparison with CeNi₄Cu, is more stable in the region of T < 500 K, and less stable at T > 700 K.

[1] M.D. Koterlyn, O.I. Babych, G.M. Koterlyn, J. Alloys Compd. 325 (2001) 6-11.

[2] M. Koterlyn, B. Morokhivskii, R. Yasnitskii, *Chem. Met. Alloys* 4 (2011) 107-112.

ELECTROPHYSICAL PROPERTIES OF Ga–Sn–Zn EUTECTIC ALLOY WITH ADMIXTURES OF ELEMENTS OF GROUPS I-IV

<u>B. Sokoliuk</u>, Yu. Plevachuk, V. Sklyarchuk, and M. Dufanets Department of Metal Physics, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 8, 79005 Lviv, Ukraine jetforfirefly@gmail.com

The growing possibility of application of liquid metals in thermal transport systems has prompted the development of new materials based on Ga, which could work at room temperature and are non-toxic. Among such materials is the Ga–Sn–Zn eutectic, which is characterised by higher thermal conductivity, density, surface tension, viscosity and electrical conductivity, than water. This study presents the temperature dependence of density, surface tension, viscosity, electrical conductivity, thermoelectric power, and thermal conductivity for the Ga–Sn–Zn eutectic, and the influence of Bi, In, Al, and Pb doping.

The measurements conducted here showed higher melting temperature and surface tension, but lower thermal expansion coefficient, density, viscosity, electrical conductivity, and thermal conductivity, compared to the Ga–In–Sn eutectic [1]. Small amounts of Bi, In, Al, and Pb were added with the purpose to enhance the thermal conductivity, electrical conductivity, and viscosity. We observed that addition of In or Al led to an increase of the thermal conductivity and viscosity, while the thermoelectric power decreased [2,3]. Bi and Pb doping led to decreasing of the thermal and electrical conductivity [4,5]. The results obtained here confirm the assumption that the addition of admixtures decreases the electrical conductivity, and Linde's rule, but a weak, negligible increase of the electrical conductivity was observed for Al doping [3]. Admixtures caused the solidification temperature to decrease, which may extend the applications of these alloys.

The measurements agreed well with the theoretical predictions and showed good results in comparison with usual liquid metal coolants, so Ga–Sn–Zn is a good candidate for thermal transport purposes. Bi, In, Al, and Pb admixtures can be used for tuning of the physical properties, and may extend the application of the alloys for specific purposes.

The obtained experimental results will be part of a thermophysical database, which could be useful for the application of liquid alloys in cooling systems for different purposes.

- [1] B. Sokoliuk, A. Dobosz, Yu Plevachuk, V. Sklyarchuk, T. Gancarz, *Fluid Phase Equilib.* 465 (2018) 1-9.
- [2] B. Sokoliuk, A. Dobosz, Yu. Plevachuk, V. Sklyarchuk, O. Tkach, T. Gancarz, J. Mol. Liq. 271 (2018) 942-948.
- [3] B. Sokoliuk, A. Dobosz, Yu. Plevachuk, V. Sklyarchuk, T. Gancarz, *Int. J. Heat Mass Transfer* 126 (2018) 414-420.
- [4] B. Sokoliuk, A. Dobosz, Yu. Plevachuk, V. Sklyarchuk, O. Tkach, T. Gancarz, *J. Chem. Eng. Data* 64 (2019) 404-411.
- [5] B. Sokoliuk, A. Dobosz, Yu. Plevachuk, V. Sklyarchuk, O. Tkach, T. Gancarz, J. Mol. Liq. 281 (2019) 542-548.
PECULIARITIES OF THE RESISTIVITY OF *RE*₃(Ce,Nd,Sm)Cu₄Sn₄, *RE*(Gd,Tb,Ho)NiSn₂, DyNiSi, AND DyNiSi₃ IN MAGNETIC FIELDS

<u>B. Kuzhel</u>¹, L. Salamakha², L. Romaka¹, B. Belan¹, and R. Gladyshevskii¹ ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Institute of Solid State Physics, Vienna University of Technology, Wiedner Hauptstrasse 8-10, 1040 Wien, Austria kuzhelb@gmail.com

The resistivity of intermetallic ternary compounds with different crystalline structures: $RE_3Cu_4Sn_4$ (RE = Ce, Nd, Sm; Gd_3Cu_4Ge_4 type, space group *Immm*), $RENiSn_2$ (RE = Gd, Tb, Ho; LuNiSn_2 type, space group *Pnma*), DyNiSi (TiNiSi type, space group *Pnma*), DyNiSi₃ (ScNiGe₃ type, space group *Cmmm*), which exhibit clear anomalies in the temperature dependence of the electrical resistivity at low temperatures, was studied under magnetic fields up to 12 T and at temperatures down to 0.3 K. The anomalies in the temperature dependencies of the resistivity observed in the absence of external magnetic field correspond to magnetic phase transitions. The transition temperatures are related to ordering of the magnetic moments and can, according to publications on magnetic investigations and neutron diffraction, be interpreted as Néel temperatures.



Fig. Temperature dependence of the electrical resistivity of HoNiSn₂ at various values of magnetic field. Arrows point to the transitions.

The effect of the magnetic field on the nature of the temperature dependence of the electrical resistivity of the investigated compounds is considered to be a result of the influence on the strength of hybridization between (sd)-conduction electrons and localized *f*-electrons, including a change of mobility of the charge carriers due to possible compensation of spin interaction. The electron transport properties revealed peculiarities of the crystalline structure and magnetic state of the compound.

LUMINESCENT PROPERTIES OF SOME β-DICARBONYL COMPLEXES OF LANTHANIDES

O.S. Berezhnytska^{1,2}, O.K. Trunova¹, I.O. Savchenko³, Ya.V. Fedorov¹, and N.V. Rusakova⁴ V.I. Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences

of Ukraine, Akad. Palladina Ave. 32/34, 03142 Kyiv, Ukraine

² National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Peremohy Ave. 37, 03056 Kyiv, Ukraine

 ³ Taras Shevchenko National University of Kyiv, Volodymyrska St. 64/13, 01601 Kyiv, Ukraine
 ⁴ O.V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, Lustdorf Road 86, 65000 Odessa, Ukraine

olekberez@gmail.com

Modern industry requires new multifunctional materials of a certain composition with predicted properties, in particular luminescent ones. The lanthanides exhibit luminescence over a wide spectral range, depending on the electronic structure of the metal, which has attracted considerable attention. The disadvantages of the existing materials are: heterogeneity of the structure, weak luminescence intensity, poor solubility, low stability, and limited temperature range. These problems can be avoided by using metal-polymer compounds as fluorescent materials. Polymer complexes have high stability, can be used in a wide temperature range, and facilitate the production of ultrathin devices, thanks to the conductivity of the polymers. Metal-polymer and hybrid materials have attracted attention, due to the wide range of their properties, and, accordingly, areas of application. They can be used as solutions or powders, as well as films of different thicknesses. An important aspect, both from a fundamental and applied point of view, is to study the influence of the nature of the ligands on the spectral-luminescent properties of the compounds. Therefore, the synthesis and study of the physicochemical properties of lanthanide coordination compounds based on β -diketones with multiple bonds, which make it possible to obtain new polymeric materials based on them, is a relevant study of modern chemical science.

A number of β -diketones obtained by Claisen condensation are shown below:



Lanthanide complexes were obtained on the basis of the above ligands. Radical homopolymerization produced metal polymers. In order to determine the composition and structure, all the synthesized compounds were investigated by physico-chemical methods of analysis. It was shown that the coordination number of the lanthanide ions in the synthesized compounds is 8. It was further established that polymerization does not cause significant changes in the coordination polyhedron. Studies of the luminescent properties showed that the luminescence intensities of the complexes based on **mbphpd** and **mphpd** are the highest ones, due to both the harder structure of these molecules and the additional antenna effect created by the phenyl substituents. The maximum luminescence efficiency was observed for the metal polymers of Eu(III) and Tb(III).

LUMINESCENT PROPERTIES OF POLYMERS AND COPOLYMERS OF Nd(III) AND Yb(III)

O.S. Berezhnytska^{1,2}, N.B. Ivakha¹, O.K. Trunova¹, S.S. Smola³, and O.O. Rohovtsov¹

¹ V.I. Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Akad. Palladina Ave. 32/34, 03142 Kyiv, Ukraine

² National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Peremohy Ave. 37, 03056 Kyiv, Ukraine

³ O.V. Bogatsky Physico-Chemical Institute, National Academy of Sciences of Ukraine, Lustdorf Road 86, 65000 Odessa, Ukraine olekberez@gmail.com

The interest in lanthanide coordination compounds emitting in the IR band is increasing. However, complexes with low molecular weight are of limited use due to their low thermal and chemical resistance, and tendency to aggregation. It is necessary to create materials that, in addition to having excellent luminescent characteristics, will exhibit high durability. From this point of view metal-containing polymeric materials are of interest. The aim of this study was to synthesize neodymium and ytterbium complexes with β -dicarbonyl ligands containing unsaturated substituents in chelating rings.

Most studies are based on the preparation of metal polymers by intercalating metal salts into polymer matrices. This method does not allow obtaining a homogeneous chemical composition of the compound, which causes both heterogeneity of the materials and aggregation during the production of films. We offer another approach to solve this problem.

As ligands, β -dicarbonyl compounds containing unsaturated substituents in chelate rings are proposed. The presence of a double bond in the molecule allows the use of these compounds as monomers in a polymerization reaction. In this way, the coordination compounds of the lanthanides can act as precursors in the reactions of radical homo- and copolymerization. The production of copolymers of lanthanide complexes with industrial monomers (methyl methacrylate, styrene, vinyl carbazole, unsaturated carboxylic acids) will improve the physico-chemical characteristics (thermal stability, flexibility) and reduce the cost of the final products. The variation of the composition of the copolymer allows expanding the spectrum of practical applications, and will increase the functionality of the material.

Nd(III) and Yb(III) complexes of 2,6-dimethyloctene-1-3,5-dione (*dmokd*), 2,7-dimethylheptene-1-3,5-dione (*dmhpd*), 2-methyl-5-phenylpentene-1-3,5-dione (*mphpd*), and 3-allyloxobutanoate (*alacac*) were synthesized. Based on the synthesized metal complexes, homo- and copolymers were obtained by a free-radical mechanism. The composition and structure of the synthesized compounds were determined. The lanthanide ion coordinates three ligand molecules. The coordination sphere is completed by water molecules. The complexes are characterized by tetragonal symmetry, and the coordination polyhedron is a square antiprism.

Studies of the luminescent properties indicated higher luminescence intensity for the polymers than for the monomers. The luminescence intensity of the copolymers depends on the structure of the industrial monomer and the nature of the ligand. In the case of the β -diketones (*dmokd*, *dmhpd*, *mphpd*), the styrene-based copolymers exhibited the highest luminescence intensity, and the methylacetylate-based copolymers were most efficient for *alacac*. Hence, this method of obtaining new metal polymers allows the synthesis of compounds of a given composition with predicted properties.

PREPARATION AND INVESTIGATION OF SOME PROPERTIES

<u>M.N. Abdusalyamova¹</u>, M.A. Badalova¹, F.A. Makhmudov¹, I.G. Vasilyeva², and

OF Pr-DOPED Yb₁₄MnSb₁₁

S.M. Kauzlarich³

 ¹ V.I. Nikitin Institute of Chemistry, Tajik Academy of Sciences, Ajni St. 299/2, 734063 Dushanbe, Republic of Tajikistan
 ² Nikolaev Institute of Inorganic Chemistry, Russian Academy of Sciences, Lavrentieva Ave. 3, 630090 Novosibirsk, Russian Federation
 ³ Department of Chemistry, University of California, One Shields Ave., Davis, CA 95616, USA amahsuda@mail.ru

One of the new classes of materials for utilization as high-temperature thermoelectric materials is composed of Zintl phases that are pnictides of rare-earth elements and have the $Ca_{14}AlSb_{11}$ structure type. In this work single crystals of $Yb_{14-x}Pr_xMnSb_{11}$ were prepared and the melting temperature and thermal dilatation were measured.

Single crystals of $Yb_{14-x}Pr_xMnSb_{11}$ were grown from a molten Sn flux in a glassy carbon crucible, using powders of Yb, Pr (99.9 %, Aldrich), and Mn (99.99 %, Aldrich), and ingots of Sb (99.9999 %, Aldrich).

The materials were characterized by X-ray diffraction and microprobe analysis. All the solid solutions had the tetragonal structure of $Ca_{14}AlSb_{11}$. Thermal analysis of 2-3 mg specimens was repeated 3-5 times for each sample. Two procedures were developed to study the thermal stability of the samples. The first one consisted in heating at a rate of 3000°C/min up to 1900°C in an apparatus with a He pressure equal to 7 atm. Thermal expansion measurements were made on a dilatometer. Cylindrical samples with a diameter of 4 mm, and a length of 10-13 mm, were placed into a quartz ampoule that was firmly attached by screws to the upper flange of the apparatus. The sample was heated in the range of 25-750°C, at a rate of 5-6°/min.

Pr, <i>x</i>	<i>a</i> , Å	<i>c</i> , Å	V, Å ³	Melting point, °C	Thermal expansion coefficient, $\alpha \cdot 10^6$, K ⁻¹	Debye temperature, $\theta_{\rm D}$, K
0.1	16.641(8)	22.031(11)	6100.89	1714	16.8	147
0.3	16.648(8)	22.035(11)	6107.13	1719	17.7	143
0.5	16.652(8)	22.041(11)	6111.73	1765	15.5	153
0.7	16.659(8)	22.041(11)	6116.87	1764	18.0	142
0.9	16.666(8)	22.063(11)	6128.12	1785	18.1	142

Table Some data of Yb_{14-x}Pr_xMnSb₁₁.

The work was conducted under financial support of ISTC (project T-2067).

P90

PINNING IN MAGNESIUM DIBORIDE THIN FILMS AND BULK SAMPLES WITH HIGH CRITICAL CURRENT DENSITIES j_c

Tatiana Prikhna¹, Vladimir Shaternik², Viktor Moshchil¹, Vladimir Sverdun¹, and Anton Shaternik¹

 ¹ Institute for Superhard Materials, National Academy of Sciences of Ukraine, Avtozavodskaya St. 2, 07074 Kyiv, Ukraine
 ² G.V. Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, Akad. Vernadsky Blvd. 36, 03680 Kyiv, Ukraine shanton855@gmail.com

It was shown that the pinning of Abrikosov vortices in oxygen-enriched magnesium diboride (MgB_2) thin films and bulk samples depends on the type and spatial distribution of oxygenenriched nanoscale inclusions of the Mg–B–O system. The observation of a higher critical current density j_c in MgB₂ thin films, compared to bulk samples, is explained by the presence in the film structure of a higher concentration of oxygen-enriched nanosized Mg–B–O inhomogeneities.

The results of calculations of the density of states (DOS) of $MgB_{2-x}O_x$ solid solutions showed that these compounds are conductors with metallic type of conductivity and are characterized by high coupling energy. The presence of a relatively high content of impurity oxygen in the structure does not result in a significant decrease of the critical temperature T_c of the MgB₂-based superconducting materials.

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF Cr-{Ru,Pd}-Ni-Si PHASES

<u>R.-I. Martyniak¹</u>, N. Muts¹, M. Bobnar², L. Akselrud^{1,2}, and R. Gladyshevskii¹

Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany martyniak241@gmail.com

Sustainability of data storage technologies is critical for further development in the information age. Modern information storage devices, relying on magnetic domain memory, may soon be superseded by novel and more efficient technologies. Magnetic skyrmions are nanometer-sized quasiparticles existing in ferromagnets with broken inversion symmetry. Due to their compact size and simplicity of nucleation and annihilation, they bear a potential to once become the ultimate information carriers. This research is a continuation of our previous investigations [1,2], where we focused on the synthesis of compounds with chiral structures. Our previous results suggest that the magnetic characteristics of phases with Au₄Al-type structures (Pearson symbol *cP*20, space group *P*2₁3) in the Cr–{Fe,Co,Cu}–Ni–Si systems are a function of the isomorphic atom substitution. The aim of this work was the investigation of the crystal structures and magnetic properties of isotypic phases in the Cr–{Ru,Pd}–Ni–Si systems.

Samples of nominal compositions Cr₂₆Ru₉Ni₄₇Si₁₈ and Cr₂₆Pd₉Ni₄₇Si₁₈ were synthesized by arc melting of pure (\geq 99.9 wt.%) elements with subsequent 35 day-annealing at 900°C. The crystal structures were refined from X-ray powder diffraction patterns recorded with a Huber Image Plate Camera - G670 diffractometer (Cu $K\alpha_1$ radiation), using the WinCSD-2000 program. The investigated samples were single-phase and contained a phase with Au₄Al-type structure: unit cell parameter a = 0.614549(3) nm for the $(Cr_{0.324}Ru_{0.113}Ni_{0.563})_4(Si_{0.837}Ni_{0.163})$ phase and a = 0.618384(6) nm for the $(Cr_{0.324}Pd_{0.113}Ni_{0.563})_4(Si_{0.837}Ni_{0.163})$ phase.

The temperature dependence of the magnetic susceptibility for the $Cr_{26}Ru_9Ni_{47}Si_{18}$ and $Cr_{26}Pd_9Ni_{47}Si_{18}$ samples was investigated on a SQUID magnetometer (MPMSXL7, Quantum Design) in a $\mu_0H = 10.0$ T magnetic field. All of the samples were found to be paramagnets described by the modified Curie-Weiss law:

 $\chi_0 = 195 \cdot 10^{-6}$ emu g-at.⁻¹, $C = 1.44 \cdot 10^{-3}$ emu g-at.⁻¹ K⁻¹, $\theta_p = -6.46$ K for Cr₂₆Ru₉Ni₄₇Si₁₈, $\chi_0 = 187 \cdot 10^{-6}$ emu g-at.⁻¹, $C = 3.98 \cdot 10^{-3}$ emu g-at.⁻¹ K⁻¹, $\theta_p = -3.4$ K for Cr₂₆Pd₉Ni₄₇Si₁₈.

- [1] R.-I. Martyniak, N. Muts, O. Sichevych, H. Borrmann, M. Bobnar, L. Akselrud, R. Gladyshevskii, *Solid State Phenom.* 289 (2019) 108-113.
- [2] R.-I. Martyniak, N. Muts, M. Bobnar, L. Akselrud, R. Gladyshevskii, *Abstr. Int. Conf. Stud. Young Res. Theor. Exp. Phys. "HEUREKA-2019"*, Lviv, 2019, p. A14.

STABILIZATION OF A M02FeB2-TYPE PHASE IN THE SYSTEM H0-Ni-In AND ITS HYDROGENATION

<u>K. Miliyanchuk</u>¹, L. Havela², O. Lavriv¹, S. Maskova-Cerna², and R. Gladyshevskii¹ ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine ² Department of Condensed Matter Physics, Charles University, Ke Karlovu St. 5, 12116 Prague, Czech Republic khrystyna.miliyanchuk@lnu.edu.ua

The Mo₂FeB₂ type (Pearson symbol *tP*10, space group *P*4/*mbm*) is the most common structure type (ST) for compounds with the stoichiometry R_2T_2M (where *R* is a rare-earth metal or U, *T* is a *d*-metal, and *M* is a main-group element). A large number of compounds with this ST tend to form hydrides, which allows clarifying the role of the nature of the constituent elements in the hydrogenation properties of isotypical compounds. The ST of a specific R_2T_2M compound is determined by the atomic size factor and/or valence electron concentration. Within the series R_2Ni_2In , at the annealing temperature 600°C the compounds adopt the ST Mo₂FeB₂ for *R* = La-Nd and Mn₂AlB₂ (space group *Cmmm*) for *R* = Sm-Lu. For the compounds $R_2Ni_{2-x}In$, the ST Mo₂FeB₂ is observed throughout the whole rare-earth series [1].

Samples of compositions $Ho_2Ni_{2-x}In$ (x = 0, 0.1, 0.7) and $Ho_2Ni_2In_{0.9}X_{0.1}$ (X = AI, Ga, Sn, Sb) were synthesized by arc melting in argon atmosphere, and X-ray diffraction phase analysis was performed both in the as-cast state, and after annealing at $T = 600^{\circ}C$ for six weeks. Mo_2FeB_2 -type phases were found in the as-cast samples of $Ho_2Ni_{1.7}In$ and $Ho_2Ni_2AI_{0.1}In_{0.9}$. Differential scanning calorimetry showed that the tetragonal $Ho_2Ni_2AI_{0.1}In_{0.9}$ phase exists above the temperature 919°C. In the case of all the other substitutions, the phase with the ST Mn_2AIB_2 was observed also in the as-cast samples.

Hydrides of the samples $Ho_2Ni_{1.7}In$ and $Ho_2Ni_2Al_{0.1}In_{0.9}$ were synthesized at room temperature and a hydrogen pressure of 820 mbar by direct interaction of the intermetallics with hydrogen gas. The reaction started ~15 min after the exposure of $Ho_2Ni_2Al_{0.1}In_{0.9}$ to hydrogen and saturation was reached after another 30 min. The process was substantially slower for $Ho_2Ni_{1.7}In$: it started after ~1 h and it took another 2 h to complete. The final pressure drop in the system yielded the amount of absorbed hydrogen. In both cases, hydrogenation led to anisotropic lattice expansion, prevailing in the *ab* plane (Table).

The results will be discussed in terms of correlations between the composition of the intermetallic and peculiarities of its hydrogenation.

Compound	<i>a</i> (Å)	<i>c</i> (Å)	$V(\text{\AA}^3)$	$\Delta a/a~(\%)$	$\Delta c/c \ (\%)$	$\Delta V/V(\%)$	
Ho ₂ Ni _{1.7} In	7.3493(2)	3.6267(1)	195.89(1)	—	_	—	
Ho ₂ Ni _{1.7} InH _{2.7}	7.5974(7)	3.6819(4)	212.52(4)	3.4	1.5	8.5	
Ho ₂ Ni ₂ Al _{0.1} In _{0.9}	7.3428(3)	3.6359(2)	196.03(1)	—	_	_	
Ho ₂ Ni ₂ Al _{0.1} In _{0.9} H _{3.4}	7.6102(9)	3.6848(5)	213.40(5)	3.6	1.3	8.9	

Table Unit-cell parameters *a*, *c*, *V* for Mo₂FeB₂-type phases before and after hydrogenation, and relative lattice expansion $\Lambda a/a$, $\Lambda c/c$, $\Lambda V/V$ upon hydrogenation.

[1] Ya.M. Kalychak, V.I. Zaremba, V.M. Baranyak, P.Y. Zavalii, V.A. Bruskov, L.V. Sysa, O.V. Dmytrakh, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 26 (1990) 94-96.

HYDROGENATION OF STRUCTURALLY RELATED PHASES $Tb_m T_m Ga$ (T = Co, Ni; m = 2, 3)

<u>K. Miliyanchuk</u>¹, N. Saidov¹, S. Maskova-Cerna², Ya. Tokaychuk¹, L. Havela², and R. Gladyshevskii¹

 ¹ Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
 ² Department of Condensed Matter Physics, Charles University, Ke Karlovu St. 5, 12116 Prague, Czech Republic

khrystyna.miliyanchuk@lnu.edu.ua

Intermetallic compounds of composition R_2T_2M (*R* is a rare-earth metal, *T* is a *d*-metal, and *M* is a main-group element) with the structure type W₂CoB₂ (Pearson symbol *oI*10, space group *Immm*) are known to exhibit unique hydrogenation properties, absorbing up to 6 H at./f.u. at extremely low pressures [1]. The structure types W₂CoB₂ and W₃CoB₃ (Pearson symbol *oS*28, space group *Cmcm*) belong to a series of intergrowth structures R_xT_xM (x = 2, 3, 4, ...), formed by various combinations of TII-type and UPt₂-type related slabs: 1TII:1UPt₂ in W₂CoB₂-type compounds and 2TII:1UPt₂ in W₃CoB₃-type compounds.

Tb₂Co₂Ga, Tb₂Ni₂Ga, and Tb₃Co₃Ga were synthesized by arc-melting under argon atmosphere, with further annealing for two months at $T = 600^{\circ}$ C. The crystal structure of the samples, before and after hydrogenation, was studied by X-ray powder diffraction.

The hydrides were synthesized at room temperature and a hydrogen pressure of 530 mbar. The compositions of the hydrides and the lattice expansion upon hydrogenation are given in the Table. The cobalt compounds showed faster hydrogenation than Tb₂Ni₂Ga. The thermal decomposition curves for Tb₂Co₂GaH_{6.2} and Tb₃Co₃GaH_{9.7} revealed several peaks of hydrogen desorption, suggesting several inequivalent hydrogen positions. The lower hydride of Tb₃Co₃Ga was obtained by heating Tb₃Co₃GaH_{9.7} in dynamic vacuum up to 260°C.

A common feature of the W₂CoB₂- and W₃CoB₃-type compounds after hydrogenation is the shrinkage of the trigonal prisms forming infinite columns along a ($\Delta a/a < 0$). In the *bc* plane, the hydrogenation affects the TII-type slabs to a greater extent. These experimental results will serve as a ground for discussing possible models for the crystal structures of the hydrides.

hydrogenation, and relative fattice expansion $\Delta a/a$, $\Delta b/b$, $\Delta c/c$, $\Delta v/v$ upon hydrogenation.								
Compound	$a(\mathring{A})$ $b(\mathring{A})$	$h(\mathring{A})$	$c(\mathring{A})$	$V(\text{\AA}^3)$	$\Delta a/a$	$\Delta b/b$	$\Delta c/c$	$\Delta V/V$
Compound	<i>u</i> (A)	$v(\mathbf{A})$	C (A)		(%)	(%)	(%)	(%)
Tb ₂ Co ₂ Ga	4.092(1)	5.414(1)	8.431(1)	186.78(5)	—	—	—	-
Tb ₂ Co ₂ GaH _{6.2}	3.760(4)	6.425(8)	9.214(10)	222.6(4)	-8.1	18.7	9.3	19.2
Tb ₂ Ni ₂ Ga	4.184(1)	5.372(1)	8.309(1)	186.76(3)	_	_	_	_
Tb ₂ Ni ₂ GaH _{5.1}	3.751(5)	6.521(10)	9.119(10)	223.1(5)	-10.3	21.4	9.7	19.4
Tb ₃ Co ₃ Ga	4.123(1)	10.091(1)	12.949(2)	538.8(1)		-	-	_
Tb ₃ Co ₃ GaH _{9.7-x}	3.776(3)	11.065(8)	14.789(14)	617.9(9)	-8.4	9.6	14.2	14.7
Tb ₃ Co ₃ GaH _{9.7}	3.743(2)	11.331(7)	15.225(10)	645.8(7)	-9.2	12.3	17.6	19.9

Table Unit-cell parameters a, b, c, V for Tb₂ T_2 Ga and Tb₃Co₃Ga before and after hydrogenation, and relative lattice expansion $\Lambda a/a$, $\Lambda b/b$, $\Lambda c/c$, $\Lambda V/V$ upon hydrogenation

 K. Miliyanchuk, L. Havela, Y. Tsaruk, S. Mašková, R. Gladyshevskii, J. Alloys Compd. 647 (2015) 911.

TI-CONTAINING HTSC CUPRATES

S.A. Nedilko, T.A. Voitenko, I.V. Fesych, O.G. Dziazko, M.A. Zelenko, and D.D. Naumova Faculty of Chemistry, Taras Shevchenko National University of Kyiv, Lva Tolstogo St. 12, 01033 Kyiv, Ukraine snedilko@ukr.net

The possibility of practical applications of high-temperature superconducting materials has opened new opportunities for microelectronics, medicine, production of efficient energy storage and power transmission systems, and industry as a whole. The discovery of high-temperature superconductivity in the system Tl–Ba–Ca–Cu–O initiated active research on the structure and properties of this class of superconductors. It was determined that the system consists of two homologous phases, Tl and T2, with the basic stoichiometric formulas TlBa₂Ca_{*n*-1}Cu_{*n*}O_{2*n*+3} and Tl_{2.2}Ba₂Ca_{*n*-1}Cu_{*n*</sup>O_{2*n*+4} (*n* = 1-5). These phases have intergrowth structures consisting of active layers of superconductors have been obtained with transition temperatures to the superconducting state of 80-135 K. However, in structural terms, several questions concerning the nature of the defects in the structures of the thallium phases remain open: the availability of vacancies, isomorphic substitution, displacement of atoms in the cation or anion sublattice, and others. The electrical properties of ceramics of the same stoichiometry are quite sensitive to the conditions of preparation and may vary from characteristic of a superconductor with $T_c = 135$ K, to characteristic of a dielectric.}

The purpose of this work was the study of possible correlations between the properties, in particular the grain size, crystallographic parameters, electrophysical properties, oxygen stoichiometry, and cation substitutions, of complex-oxide HTSC materials, such as $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$ ($n = 2, 3; 0 \le x \le 0.5$).

The lattice parameters and phase composition were determined by powder X-ray diffraction (Shimadzu LabX XRD-6000; λ (Cu $K\alpha_1$) = 1.54056 Å, Ni filter).

Infrared absorption spectra of the annealing products were recorded on a spectrophotometer Spectrum BX FT-IR (Perkin Elemer) in the range 1200-1800 cm⁻¹, using the method of pellet compression with KBr.

Resistivity measurements were conducted in the temperature range 300-78 K by the standard four-contact method, using indium-gallium eutectic.

The oxygen content was determined by iodometry.

The microstructure of the obtained samples was studied with an electronic microscope Hitachi S-2400.

The samples $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$ ($n = 2, 3, 0 \le x \le 0.5$) were obtained by the solid-state method.

The microstructure, homogeneity region, unit-cell parameters, electrophysical descriptions, and oxygen stoichiometry of the systems $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$ (n = 2, 3; $0 \le x \le 0.5$) were investigated. The influence of the heat treatment conditions on the grain size, oxygen content and critical temperature was studied. The size and shape of the particles forming the ceramics were determined. The size of the prepared particles was D = 0.5-1.5 µm. It was shown that the transition temperature to the superconducting state decreases with the addition of bismuth ions.

STRUCTURAL AND HYDROGENATION PROPERTIES OF $Gd_{1-x}T_xNi$ (0 < x < 1) ALLOYS

K. Kluziak¹ and V. Pavlyuk^{1,2}

¹ Faculty of Mathematics and Natural Sciences, Jan Dlugosz University in Częstochowa, Armii Krajowej Al. 13/15, 42200 Częstochowa, Poland
² Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine karolina_kluziak@o2.pl

In recent years, the demand for devices for storing electric energy has increased significantly. Metal hydride batteries seem to provide the necessary features. Currently, Ni/MH cells are equipped with negative electrodes that are usually produced from intermetallic compounds. These alloys are capable of absorbing hydrogen into their structure, which leads to the formation of metal hydrides. Along with the growing demand for energy, new intermetallic compounds have been developed that offer a promising future for these batteries. Electrode materials based on the LaNi compound (*AB*-type alloys) have competitive parameters in comparison with the *AB*₅ materials used at present. The replacement of lanthanum by titanium or zirconium has a significant impact on the stability of the charge-discharge cycles and the corrosion potential, and reduces the cost by reducing the amount of the more expensive rare-earth metals. In this short report, we present the results of structural and hydrogen absorption studies for Gd_{1-x}Ti_xNi (0 < x < 1). The samples, each with a total weight of about 1 g, were prepared by melting arched stoichiometric mixtures of the elements in a stream of pure argon. A comprehensive study, using X-ray diffraction, scanning electron microscopy, gas and electrochemical hydrogenation, was conducted.



The obtained isotherms do not exhibit the shape typical for metal-hydrogen systems. The main difference is the lack of hydrogen pressure plateau segments (in Fig. 1 marked as *Desorption*) at values less than 0.26 wt.% (for the curve at 200°C) and 0.60 wt.% (for the curve at 30°C), which usually reflect the presence of a well-defined metal hydride phase in the material.

Financial support from the National Science Center, Poland NCN (No. 2017/25/B/ST8/02179).

CALCULATION OF CATION MIGRATION CHANNELS IN CRYSTALS WITH SCHEELITE-TYPE STRUCTURE

V.N. Shevchuk and I.V. Kayun

Department of Electronics and Computer Technologies, Ivan Franko National University of Lviv, Drahomanova St. 50, 79005 Lviv, Ukraine shevchuk@electronics.lnu.edu.ua

Crystals with scheelite-type structure are important, widely known, modern materials, used as work elements in detector systems. But the electrical conductivity of AMO_4 crystals where A is Ba, Ca, Pb, or Sr, and M is Mo or W, is by far not sufficiently investigated. The mechanism of ionic conductivity and the migration paths of the mobile ions in the AMO_4 crystals are still pending questions.

The electrical properties of tungstate crystals of divalent metal ions have been investigated in our previous papers [1-3]. Some first visualization data of the migration paths of the Mo or W ions, obtained by using the TOPOS program, were presented in [4-6]. The visualization of possible migration ways of ionic charge carriers is an important method for the determination of the micro-mechanism of their moves through the crystalline lattice. But the calculation of the probable migration way of the *M* ions in AMO_4 crystals represents only the first step of the investigation.

For ion migration modeling and visualization of ion pathways in different oxide,s we utilized *ab initio* techniques (see *e.g.* brief reviews in [5,7-8]). In [7,8] the procrystal analysis is presented as a valuable tool for the visualization of ion migration pathways in solids. In the present study we used the program package TOPOS [9] with the aim to analyze the microstructure of the migration ways of the W ions in AWO_4 . For this we considered a substantial amount of published structural data on AMO_4 compounds and own results. We studied the W-migration ways and the temperature dependence of the characteristic elementary parameters of the cationic transference, in particular the length of the migration of the unit cell parameters of the compounds.

- [1] V.N. Shevchuk, I.V. Kayun, Acta Phys. Pol. A 117 (2010) 150-154.
- [2] V.N. Shevchuk, I.V. Kayun, Chem. Met. Alloys 4 (2011) 72-76.
- [3] V.N. Shevchuk, I.V. Kayun, Funct. Mater. 18 (2011) 165-170.
- [4] V.N. Shevchuk, I.V. Kayun, Proc. Int. Conf. Oxide Materials for Electronic Engineering Fabrication, Properties and Applications, Lviv, 2014, pp. 117-118.
- [5] V.N. Shevchuk, I.V. Kayun, Chem. Met. Alloys 9 (2016) 128-124.
- [6] V.N. Shevchuk, I.V. Kayun, Proc. X Int. Scint and Pract. Conf. Electronics and Information Technologies, Lviv, 2018, pp. B82-B84.
- [7] M.O. Filsoe, E. Eikeland, B.B. Iversen, Proc. AIP Conf. 1765, 2016, p. 020010-1-020010-5.
- [8] M.O. Filsoe, M.J. Turner, G.V. Gibbs, S. Adams, M.A. Spackman, B.B. Iversen, Chem Eur. J. 19 (2013) 15535-15544.
- [9] V.A. Blatov, IUCr CompComm Newsletter 7 (2006) 4-38.

MULTICOMPONENT INTERMETALLIC COMPOUNDS WITH DISTORTED B2 STRUCTURE: PHASE STABILITY AND STRUCTURE-PROPERTIES RELATIONSHIP

<u>G.S. Firstov</u>¹, T.A. Kosorukova¹, A.N. Timoshevskii¹, Yu.N. Koval¹, V.V. Odnosum¹, Yu. Matviychuk¹, G. Gerstein², and H.J. Maier²

¹ G.V. Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, Akad. Vernadsky Blvd. 36, 03680 Kyiv, Ukraine

² Institut für Werkstoffkunde (Materials Science), Leibniz Universität Hannover,

An der Universität 2, 30823 Garbsen, Germany FirstovGS@nas.gov.ua, yuri.firstov@gmail.com

The NiTi intermetallic occupies a special place amongst compounds possessing a B2 type structure, due to the shape memory effect, which was initially discovered on this material. Since this discovery, it has remained the most widely used shape memory alloy (SMA). Its key application is the medical sector. In industry, R&D on NiTi and other conventional SMAs has slowed down, following the significant disenchantment of industrial leaders with SMAs, because of functional and structural fatigue phenomena. These effects appear due to plastic deformation and/or diffusion processes. To cope with these, the so-called high entropy approach was employed with some success on as-cast multicomponent TiZrHfCoNiCu compounds, using binary NiTi as a prototype [1,2]. The martensitic transformation (MT), which can be described in this system as $B2 \leftrightarrow B19'$, results in exceptionally stable shape memory behavior. The peculiar crystal and electronic structures result in severe distortions of the B2 lattice [3], transmitted during the MT, and provide high strength that favors the martensitic deformation, while suppressing the plastic one. A similar structure transformation was confirmed for CoNiCuAlGaIn intermetallics that were engineered after the binary NiAl compound, but exhibit a B2 \leftrightarrow L1₀ MT [4]. The present report will include the latest developments, which represent a major improvement in the knowledge of the structure property relationships of these novel shape memory materials; their application perspectives will also be discussed.

- G.S. Firstov, T.A. Kosorukova, Yu.N. Koval, V.V. Odnosum, *Mater. Today: Proc.* 2S (2015) S499-S504.
- [2] G.S. Firstov, T.A. Kosorukova, Yu.N. Koval, P.A. Verhovlyuk, *Shape Mem. Superelasticity* 1 (2015) 400-407.
- [3] G. Firstov, A. Timoshevskii, T. Kosorukova, Yu. Koval, Yu. Matviychuk, P. Verhovlyuk, *MATEC Web Conf.* 33 (2015) 06006.
- [4] G. Gerstein, G.S. Firstov, T.A. Kosorukova, Yu.N. Koval, H.J. Maier, *Shape Mem. Superelasticity* 4(3) (2018) 360-380.

<u>Gregory Gerstein</u>¹, Georgiy Firstov², Tetiana Kosorukova², Yuri Koval², Valeriy Odnosum², Andrej Dalinger¹, and Hans Jürgen Maier¹

¹ Institut für Werkstoffkunde (Materials Science), Leibniz Universität Hannover, An der Universität 2, 30823 Garbsen, Germany

² G.V. Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine,

Akad. Vernadsky Blvd. 36, 03680 Kyiv, Ukraine

gerstein@iw.uni-hannover.de

Fine magnetic and microstructure in CoNiGa magnetic shape-memory-alloy single crystals were generated, applying pulsed magnetic fields up to 0.7 T. The observed effects could be attributed to changes in the dynamics of the interaction process between the magnetic field and the microstructure of this non-stoichiometric intermetallic compound. This report addresses the impact of pulsed and permanent magnetic fields on the structure and phase composition of CoNiGa and multicomponent CoNiCuAlGaIn intermetallic compounds. A pulsed magnetic field can result in different microstructural accommodation processes in stress-induced martensite, as compared to the application of mechanical stress or a permanent magnetic field. In a pulsed magnetic field the development of new nano twin systems in the martensitic structure of the CoNiGa alloy, and the formation of fine magnetic domains at the microscale, as well as evolution of this process in CoNiCuAlGaIn, were observed. The ramifications of exploiting pulsed magnetic fields for magnetic shape memory in these compounds will be discussed.

HYDROCHEMICAL SYNTHESIS AND X-RAY INVESTIGATION OF CdS_xSe_{1-x} FILMS

<u>M.A. Sozanskyi</u>¹, P.Yo. Shapoval¹, V.E. Stadnik¹, Yo.Yo. Yatchyshyn¹, and V.M. Kordan² ¹Department of Physical, Analytical and General Chemistry, Lviv Polytechnic National University, S. Bandera St. 12, 79013 Lviv, Ukraine ²Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine martyn.a.sozanskyi@lpnu.ua

Films of cadmium sulfide-selenide (CdS_xSe_{1-x}) solid solutions were chemically deposited from a working solution composed of aqueous solutions of cadmium chloride $(CdCl_2)$, tri-sodium citrate $(Na_3C_6H_5O_7)$, as a complex-forming reagent for Cd^{2+} , ammonium hydroxide (NH_4OH) , as pH regulator, thiourea $((NH_2)_2CS)$, as a source of S²⁻, and sodium selenosulfate (Na_2SeSO_3) , as a source of Se²⁻. The concentrations of the reagents were: 0.005 M of CdCl₂, 0.2 M of Na₃C₆H₅O₇, 0.14 M of NH₄OH, 0.05 M of $(NH_2)_2CS$, and from 0.001 to 0.025 M of Na₂SeSO₃.

The deposited CdS_xSe_{1-x} films had orange-red color with a mirror hue. Adhesion of the films to the glass surface was strong at $C(Na_2SeSO_3) = 0.001$ M, but decreased with increasing sodium selenosulfate concentration, as in this case the films were partially washed off the substrate surface during cleaning by a jet of distilled water.

X-ray diffraction of the CdS_xSe_{1-x} film samples (diffractometer DRON-2.0M, Fe Ka radiation) was carried out (Fig. 1*a*). It was established that the films were crystalline and consisted of a cubic phase of CdS_xSe_{1-x} substitutional solid solution ($x \approx 0.30-0.85$) (structure type ZnS, space group *F*-43*m*). The lattice parameters were determined by the Rietveld method, using the FullProf Suite package [1]. It was found that, with an increase of the Na₂SeSO₃ concentration from 0.001 to 0.025 M in the working solution, the diffraction peaks of the CdS_xSe_{1-x} phase shifted toward lower 2 θ values and the lattice parameter *a* increased from 0.5826(2) to 0.5971(2) nm (Fig. 1*b*). This is a result of the rise of the Se content, which has substituted for S in the films.



Fig. 1 X-ray diffractograms (*a*) and lattice parameter of the phase (*b*) in CdS_xSe_{1-x} films, deposited at different concentrations of Na₂SeSO₃ in the working solution.

[1] J. Rodriguez-Carvajal, Commission on Powder Diffraction (IUCr), Newsletter 26 (2001) 12-19.

SYNTHESIS OF COMPLEX OXIDES ON GRANULES OF ALUMINUM OXIDE FROM β-DIKETONATE COMPLEXES OF 3d-4f-METALS

L.I. Sliusarchuk, L.I. Zheleznova, T.V. Pavlenko, and O.O Rogovtsov V.I. Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences

of Ukraine, Akad. Palladina Ave. 32/34, 03142 Kyiv, Ukraine

soleillyuda@gmail.com

Deposition of complex oxide structures onto granules of aluminum oxide was performed. Dispersed aluminum oxide powders with highly developed surfaces are widely used as catalysts, sorbents and raw materials for production of ceramics. The idea of fixing various nanoparticles on the surface of microgranules is of interest. Such microgranules can significantly alter the physical and chemical properties of nanoparticles [1].

Thermolysis of a mixture of complexes $Ln(AA)_3 \cdot nH_2O + M(AA)_2 \cdot nH_2O$ (Ln = La, Nd; M = Co, Ni, Zn) was carried out. The metal ratio of the sample was Ln:M = 1:1. A series of experiments was carried out to determine the optimum temperatures and times for the pyrolysis. The samples were heated at different rates (20°C/min, 10°C/min, 5°C/min) up to 800°C and held at this temperature for one, three and five hours.

The composition of the obtained oxide powders was controlled by X-ray powder diffraction (Fig. 1). The conditions for the synthesis of this sample were heating at a rate of 20°C/min and holding at 800°C for one hour. The phase composition of the formed oxide corresponds to lanthanum cobaltite (LaCoO₃).





Fig. 2 SEM micrographs of the coating by complexes $La(AA)_3 \cdot nH_2O + Zn(AA)_2 \cdot nH_2O$ on a powder of aluminum oxide.

The deposition of the complex oxide structures onto granules of aluminum oxide was performed by impregnation of the sample with a solution of the precursor with further annealing. The obtained samples were examined by energy-dispersive X-ray spectroscopy (EDX). SEM micrographs (Fig. 2) show that the particles are hexagonal-shaped macros with hexagons at the base, which are combined into structured macro objects resembling "clusters". This may indicate the ability of such systems to crystallize, *i.e.* the hexagonal shape can indicate the presence of long-range order of the atoms and confirm the existence of a crystalline structure. The formation of crystalline structures is then responsible for the large particle size (0.5-2 μ m). The large spherical particles of a size of 50-100 μ m on Fig. 2 are aluminum oxide, and the bright spots on their surface are nanoclusters of metal oxides with a particle size of 25-50 nm.

[1] A.I. Gerasymchuk, L.I. Zheleznova, O.O. Rogovtsov, O.K. Trunova, Ukr. Khim. Zh. 81 (2014) 9-13.

P102

SYNTHESIS AND STRUCTURE OF Ge(IV) AND Cu(II) COMPLEXES WITH CITRIC ACID AND 2,2'-BIPYRIDINE

O.V. Pirozhok¹, E.E. Martsinko¹, I.I. Seifullina¹, E.A. Chebanenko¹, V.V. Dyakonenko², and S.V. Shishkina^{2,3}

¹ Department of General Chemistry and Polymers, Odesa I.I. Mechnikov National University, Dvoryanska St. 2, 65082 Odesa, Ukraine

² SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine, Nauky Ave. 60, 61001 Kharkiv, Ukraine

³ V.N. Karazin Kharkiv National University, Svobody Sq. 4, 61077 Kharkiv, Ukraine olyapirozhok94@gmail.com

Citric acid is the most interesting vital biological ligand for a range of metal ions in coordination chemistry. It is a direct participant of the Krebs cycle (a cycle of three carboxylic acids) and is present in blood plasma. This acid has many useful properties and applications in medicine, pharmaceutical and food industries. A number of mixed-ligand and mixed-metal coordination compounds of germanium(IV) with citric acid have been synthesized and studied. The pharmacological activity of some of these compounds has been approved.

The crystalline compounds $(Hbipy)_2[Ge(HCit)_2]\cdot 2H_2O(1), [CuCl(bipy)_2]_2[Ge(HCit)_2]\cdot$ 8H₂O (2), and $[{Cu(bipy)_2}_2Ge(\mu-Cit)_2] \cdot 12H_2O$ (3) (where H₄Cit is citric acid and bipy is 2,2'-bipyridine) were obtained for the first time and their structures were determined by the single-crystal X-ray diffraction method. The compounds were further characterized by IR spectroscopy, thermogravimetric (TGA) and chemical analyses.

The compounds 1 and 2, which were obtained using $CuCl_2$ as precursor, both contain the complex bis(citrato)germanate anion [Ge(HCit)₂] (Fig. 1), and protonated 2,2'-bipyridine or $[Cu(bipy)_2Cl]^+$ (Fig. 2) as cations. In the centrosymmetric anion of the complexes 1 and 2, the coordination polyhedron of the Ge atom is a distorted octahedron, which is formed by three pairs of three different types of O atom from two tridentate bis(chelating) $HCit^{3-}$ ligands: hydroxyl, α -carboxylate, and β -carboxylate.



 $[Cu(bipy)_2Cl]^+$ cation in **2**.

According to the X-ray diffraction analysis of compound 3, which was obtained using $Cu(CH_3COO)_2$ as precursor, it is a three-core mixed-ligand complex, in which Cit^{4-} acts as a bridge and links germanium(IV) with two copper(II) atoms. The square-bipyramidal coordination polyhedron of copper(II) is formed through bidentate coordination of a carboxylate group and two bipy molecules.

A NEW HEXAGONAL PHASE IN THE Hf-Al-Re SYSTEM

L. Zinko, O. Matselko, G. Nychyporuk, and R. Gladyshevskii Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine lianazinko@gmail.com

A new hexagonal ternary phase was revealed during a systematic investigation of the Hf–Al–Re system at 1000°C. The samples were synthesized from pure elements by arc melting, annealed in evacuated quartz tubes at 1000°C for 1 week, and subsequently quenched in water. Characterization of the samples was performed by means of X-ray powder diffraction (XRPD; diffractometer DRON-2.0M, Fe $K\alpha$ radiation) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDXS; scanning electron microscope REMMA-102-02).

The crystal structure of the new phase was refined from the XRPD data, using the WinCSD program package [1] and the MgZn₂ type as structural model: refined composition HfAl_{0.82(3)}Re_{1.18(3)}, Pearson symbol *hP*12, space group *P*6₃/*mmc*, *a* = 5.2408(3), *c* = 8.5287(7) Å. The composition of the phase as obtained from the crystal structure refinement is in agreement with the EDXS results.

It should be noted that among the binary phases of the boundary phase diagrams of the Hf–Al–Re system, only the Hf–Re compounds are characterized by homogeneity ranges and, thus, formation of statistical mixtures of Hf and Re atoms [2]. In the crystal structure of the ternary phase $HfAl_{0.82}Re_{1.18}$, the Re and Al atoms form statistical mixtures (in contrast to the binary phases) and occupy the Zn sites (2*a* and 6*h*) of the prototype MgZn₂, while the Hf atoms are located in the positions of Mg (4*f*).

Isotypic hexagonal phases with extended homogeneity ranges are also known in several related systems {Ti,Zr,Hf}–Al–Mn and {Zr,Hf}–Ga–Mn [3].

111110.621001.16 (1152112, 1112, 105/10000, $u = 5.2000(5)$, $v = 0.5207(7)11$).						
Site	Wyckoff position	x	у	Z.	$B_{\rm iso}$, Å ²	
Hf1	4f	1/3	2/3	0.5628(9)	0.4(2)	
M1	2a	0	0	0	1.3(4)	
M2	6 <i>h</i>	0.168(2)	0.336(4)	1⁄4	1.5(3)	

Table Atomic coordinates, site occupancies, and isotropic displacement parameters for $HfAl_{0.82}Re_{1.18}$ (MgZn₂, *hP*12, *P*6₃/*mmc*, *a* = 5.2408(3), *c* = 8.5287(7) Å).

M1 = 0.56(3)Re + 0.44(3)Al; M2 = 0.60(2)Re + 0.40(2) Al.

[1] L. Akselrud, Yu. Grin, J. Appl. Crystallogr. 47 (2014) 803-805.

- [2] P. Villars, K. Cenzual, J.L.C. Daams, F. Hulliger, T.B. Massalski, H. Okamoto, K. Osaki, A. Prince, S. Iwata (Eds.), *Pauling File. Inorganic Materials Database and Design System.* Binaries Edition, Crystal Impact, Bonn, 2001.
- [3] P. Villars, K. Cenzual (Eds.), Pearson's Crystal Data Crystal Structure Database for Inorganic Compounds, Release 2016/17, ASM International, Materials Park (OH), 2016.

COMBINED DENSITY FUNCTIONAL THEORY AND EXPERIMENTAL STUDY TO UNDERSTAND THE OPTOELECTRONIC PROPERTIES OF THE NEW p-TYPE PEROVSKITE SrSnO₃:Al

Leila Ben Amor¹, Besma Belgacem¹, Jean Sébastien Filhol², Marie-Liesse Doublet², Mouna Ben Yahia², and <u>Rached Ben Hassen¹</u>

¹ Laboratoire de Recherche de Chimie des Matériaux et de l'Environnement pour le Développement Durable (LR18ES10), ISSBAT, Université de Tunis El Manar ² Equipe Chimie Théorique, Méthodologies et Modélisation (CTMM), ICGM, Université de Montpellier

A combination of experimental and computational studies was undertaken to investigate the crystal structure and optoelectronic properties of a novel and promising perovskite, $SrSn_{1-x}Al_xO_3$ (x = 0, 0.20, and 0.50). These new materials were successfully synthesized *via* the sol-gel method, then sintered at 1350°C for 6 h. The synthesized phases were identified by X-ray diffraction (XRD), which pointed out an orthorhombic perovskite structure (space group: *Pbnm*) as major constituent. The morphological behavior was studied from SEM images, and the chemical constituents of the synthesized materials were identified by EDX analysis. Optical properties were measured by UV-visible spectroscopy. The experimental band gaps (E_g) were estimated by applying the Tauc relation, and UV-visible characterization indicated that the band gaps increase with increasing Al content. First-principles calculations within the density functional theory (DFT) are provided to explore the effect of Al incorporation on the optoelectronic properties of SrSnO₃. The calculations confirmed the increase of E_g and the creation of holes in the valence band, and announced a stable p-doped behavior when partly replacing Sn by Al.

INDEX OF AUTHORS

Abdel-Hamid F.	25	Buturlim V.	48
Abdusalyamova M.N.	148	Carrillo-Cabrera W.	47
Afanasenko E.V.	55	Černý R.	124
Agraval P.G.	80	Chabanenko V.V.	131
Akselrud L.	92 , 106, 134, 150	Chebanenko E.A.	55, 160
Alleno E.	20	Chorna N.	119
Allio C.	25	Cichowicz G.	111
Altendorf S.	141	Coduri M.	125
Anand K.	25	Couturas F.	37, 127
Andreev A.V.	52, 53	Crivello JC.	127
Antonyshyn I.	54 , 141	Cuevas F.	44
Artyukh L.V.	80	Cyrański M.K.	111
Babizhetskyy V.	82, 86 , 90, 93, 94,	Dalinger A.	157
	130	Dankevych R.	76
Babych O.I.	143	Daszkiewicz M.	73, 113
Badalova M.A.	148	De Negri S.	23
Baitinger M.	25	de Weerd M.C.	25
Balińska A.	126	Delenko T.	38, 105
Baran S.	31, 140	Demange V.	20
Barchiy I.E.	41 , 117	Demchenko P.	61, 107, 129
Bardin O.	121	Denys R.V.	127
Baricco M.	44	Divis M.	32
Barrios Jiménez A.M.	141	Dmytriv G.	39 , 111, 119, 126,
Belan B.	85, 121-124 , 145		142
Belgacem B.	162	Dorcet V.	20
Ben Amor L.	162	Doublet ML.	162
Ben Hassen R.	162	Dudnik A.S.	70
Ben Yahia M.	162	Dufanets M.	136 , 144
Berezhnytska O.S.	146, 147	Dyakonenko V.V.	55, 160
Berezovets V.V.	51,96	Dzevenko M.	82
Berthebaud D.	20	Dziazko O.G.	128, 153
Bobnar M.	47, 100, 134, 150	Ehrenberg H.	111, 126
Borukh I.V.	131	Eichhorn B.W.	26
Braun T.	43	Fartushna I.V.	68
Broda A.	103	Fedorchuk A.	41, 97
Bulanova M.V.	68	Fedoriv V.M.	138
Bulyk I.I.	131	Fedorov Ya.V.	146
Burkhardt U.	54, 100	Fedyna L.	97
Burkhovetskyi V.V.	131	Fedyna M.	63, 97

Fesych I.V.	128, 153	Hübner JM.	47
Filhol J.S.	162	Hug E.	40
Firstov G.S.	156 , 157	Huynh H.	20
Flipo S.	100 , 141	Indris S.	126
Fournée V.	25 , 125	Isnard O.	37, 90, 130
Freccero R.	23	Ivakha N.B.	147
Fruchart D.	30	Ivanov O.V.	128
Fruchart O.	30	Ivashchenko I.	74, 110
Gaudry E.	25	Ivashchenko V.I.	60
German N.	69	Iwata S.	19
Gerstein G.	156, 157	Janka O.	21
Giovannini M.	29	Jin Z.	22
Girard G.	30	Johrendt D.	24
Gladyshevskii R.	38, 72, 76, 77, 102-	Kaczorowski D.	84
	107, 120-124, 134,	Kadok J.	125
	145, 150-152, 161	Kalmykov K.B.	85
Gomonaj V.I.	117	Kalychak Ya.	85, 140
Gouder T.	32	Karychort O.R.	83
Grekhov I.	88	Kasaraba O.	123
Grin Yu.	25, 46, 47, 54, 92,	Kauzlarich S.M.	148
	125, 134, 141	Kayun I.V.	155
Grishina Y.	89	Khoruzhaya V.G.	59, 79
Grytsiv A.	42	Khyzhun O.	41
Gulay L.D.	73, 110, 113	Kluziak K.	154
Gumeniuk R.	90, 100, 141	Klymentiy N.	72
Guo Q.	20	Kobasa I.M.	138, 139
Haffner A.	24	Kogut Y.M.	65
Halevy I.	53	Köhler J.	86
Havela L.	32 , 48, 52, 53, 151,	Kohout M.	100
	152	Kolomiets A.V.	52, 53
Hennig C.	100	Koloskova O.	48
Hlukhyy V.	43 , 109	Konyk M.	61 , 62
Höfer K.	141	Kordan V.M.	81 , 119, 135, 142,
Horetska T.S.	95		158
Horiacha M.	45 , 118	Korniyenko K.Ye.	59 , 79
Horyn A.	61, 64, 129, 132	Korolyshyn A.V.	115
Hoser A.	31	Kosarchyn Yu.V.	133
Hreb V.M.	49, 99	Kosorukova T.A.	156, 157
Hrytsan V.	120	Koterlyn G.M.	143

Koterlyn M.D.	143	Marchuk O.V.	66, 73, 113
Kothapalli K.	52	Martinez M.	40
Kotsch M.	46	Martsinko E.E.	55, 160
Kotur B.	90, 93	Martyniak RI.	150
Koval Yu.N.	156, 157	Marushko L.	74 , 75
Kowalczyk G.	126	Maryskevych D.	106
Kowalska D.	85, 121, 122	Maskova-Cerna S.	52 , 53, 151, 152
Kozak V.	110	Matselko O.	103 , 161
Kozer V.R.	116	Matviychuk Yu.	156
Kozorezov A.S.	71	Mazet T.	37
Krayovskyy V.	132	Meleshevich K.A.	68
Krellner G.	25	Melnychuk K.O.	66, 73, 113
Kriklya L.S.	79	Meyer DC.	100
Kropelnytska Yu.V.	138	Mihalkovič M.	125
Krutjak R.	86	Milashius V.	142
Kudin V.G.	70, 71	Miliyanchuk K.	151, 152
Kulyk Yu.O.	51	Milyovich S.S.	117
Kurenbaeva Zh.	88, 89	Minárik P.	48
Kuzhel B.	145	Miśtal J.	126
Kytsya A.R.	51	Moisy F.	40
Latroche M.	44	Mori T.	20
Lavriv O.	151	Morozova Yu.S.	91
Le Tonquesse S.	20	Moshchil V.	149
Ledieu J.	25, 125	Mudry S.I.	67, 115
Legut D.	32	Murashova E.V.	87 , 88 , 89, 91
Leisegang T.	100	Muts N.	107 , 150
Leithe-Jasper A.	100, 141	Mykhalichko V.	97
Levchenko G.G.	128	Mys'kiv M.G.	112
Levkovets S.I.	78	Nabiałek A.	131
Levytskyy V.	90 , 94, 130	Nakotte H.	52
Liedienov N.A.	128	Naumova D.D.	153
Liu L.	22	Nedilko S.A.	128, 153
Lomnytska Ya.	82	Nervi C.	44
Luk'yanov M.Yu.	112	Nesterenko S.N.	84
Lyutyy P.Ya.	51, 96 , 133	Nguyen H.D.	25
Maier H.J.	156, 157	Nychyporuk G.	45, 118, 161
Makhmudov F.A.	148	Nytka V.	81
Manyako M.	85, 121-124	Olekseyuk I.D.	65, 73, 110, 113,
Mar A.	119		114, 116

Odnosum V.V.	156, 157	Puźniak R.	131
Oliinyk Z.M.	115	Rasim K.	54
Oliynyk A.O.	108	Rogl G.	42
Ormeci A.	54, 100	Rogl P.	42
Ortega L.	30	Rogovtsov O.O.	147, 159
Oshchapovsky I.V.	98	Rokomanyuk M.	132
Pankevych V.	75	Romaka L.	42, 61, 62, 64 , 129,
Parasyuk O.V.	65, 75, 94, 116		132, 134, 145
Pășcuț GL.	90	Romaka V.A.	132
Pashchenko A.V.	128	Romaka V.V.	42 , 61, 62, 64, 129
Pasturel M.	20	Romaniv I.	62
Paul-Boncour V.	37 , 127 , 133	Roth F.	100
Pavlenko T.V.	159	Rusakova N.V.	146
Pavlova V.	87	Rybacki K.	67
Pavlyuk N.	111 , 126	Rybicki J.	67
Pavlyuk V.V.	39, 41, 69, 81, 98,	Saccone A.	23
	101, 109, 111, 117,	Saidov N.	152
	119, 126, 135, 142,	Salamakha L.	145
	154	Savchenko I.O.	146
Penc B.	31, 140	Schmidt M.	125
Perun R.	118	Schnelle W.	100
Petyukh V.M.	80	Schunk S.A.	54
Piasecki M.	41	Schwarz B.	126
Picot F.	40	Schwarz U.	47
Pirozhok O.V.	160	Sedelnikov D.	89
Piskach L.V.	65, 66, 74, 75 , 78,	Seifullina I.I.	55, 160
	94 , 114	Selezen A.O.	114
Plechystyy V.	67	Sema O.V.	139
Plevachuk Yu.	136, 137, 144	Semenova O.L.	60
Plyatsko Yu.	104	Semuso N.	102
Podoprigora N.V.	70	Serkiz R.	81
Popovych A.	63	Shapoval P.Yo.	158
Pöttgen R.	45, 118	Shaternik A.	149
Prchal J.	53	Shaternik V.	149
Prestipino C.	20	Shelyapina M.G.	30
Prikhna T.	149	Shevchenko M.O.	71
Prots Yu.	46, 47, 106, 125	Shevchuk V.N.	155
Provost K.	37, 127	Shishkina S.V.	55, 160
Pukas S.	72, 102, 104 , 123	Shpyrka Z.	69 , 101

Shtablavyi I.	67	Trunova O.K.	146, 147
Shtender V.	37, 127	Tsisar O.	75, 94
Shved V.M.	49	Turchanin M.A.	80
Sichevych O.	54, 92, 134, 141	Tursina A.I.	84 , 89, 91
Sklyarchuk V.	136, 137, 144	Tyshchenko P.	110
Skryabina N.E.	30, 50	Tyvanchuk Yu.B.	86, 108 , 140
Sliusarchuk L.I.	159	Valenta J.	53
Slivinskyi T.	77	Vasilyeva I.G.	148
Slyvka Y.I.	112	Vasylechko L.O.	49, 99
Smetana V.	93, 94	Velikanova T.Ya.	59, 80
Smitiukh O.V.	66, 78, 114	Verbovytskyy Yu.V.	51, 133
Smola S.S.	147	Villars P.	19, 27
Sokoliuk B.	144	Voitenko T.A.	153
Solokha P.	23	Voloshyn I.	101
Soludchyk O.	69	Vorobets M.M.	139
Sozanskyi M.A.	158	Weigel T.	100
Stadnik V.E.	158	Weippert V.	24
Stadnyk Yu.V.	42, 61, 62, 64, 129 ,	Winczewski S.	67
	132	Wu D.	22
Stegemann F.	45	Xu Y.	28
Stelmakhovych B.	63	Yatchyshyn Yo.Yo.	158
Stercho I.P.	117	Zaikina O.V.	59
Stetskiv I.	135	Zajarniuk T.	131
Storchak A.M.	80	Zaremba N.	109
Sudavtsova V.S.	70, 71	Zaremba O.	120
Svanidze E.	92	Zaremba V.	45, 118
Sverdun V.	149	Zavalij P.Yu.	26 , 51
Szewczyk A.	131	Zavaliy I.Yu.	51 , 96, 98, 127, 133
Szytula A.	31 , 140	Zdorov T.P.	83
Tarasiuk I.	81, 135, 142	Zelenko M.A.	153
Tarenkov V.Yu.	131	Zelinska O.	81, 119
Tataryn B.A.	78	Zelinskiy A.	119, 134
Timoshevskii A.N.	156	Zhak O.V.	83, 95
Titlbach S.	54	Zhang J.	44
Tkach O.	137	Zhao JC.	22
Tokaychuk Ya.	38, 76, 77, 102,	Zhao JT.	33
	105-107, 152	Zheleznova L.I.	159
Topertser V.	107	Zhu L.	22
Tovt V.	41	Zinko L.	161

Підп. до друку 12.09.2019. Формат 30×42. Папір офсет. Друк. арк. 21. Тираж 150. Зам.

Видавництво Львівського національного університету імені Івана Франка 79000 Львів, вул. Дорошенка, 41