

STRUCTURE OF INORGANIC COMPOUNDS

Crystal Structures of Rb- and Ag-Substituted Forms of Natural Zeolite Amicite

O. N. Kazheva^{a,*}, N. V. Chukanov^{a,b}, N. A. Chervonnaya^a, D. A. Varlamov^{a,c},
V. N. Ermolaeva^c, and G. V. Shilov^a

^a Institute of Problems of Chemical Physics, Russian Academy of Sciences, Moscow oblast, Chernogolovka, 142432 Russia

^b Moscow State University, Moscow, 119234 Russia

^c Institute of Experimental Mineralogy, Russian Academy of Sciences, Moscow oblast, Chernogolovka, 142432 Russia

*e-mail: koh@icp.ac.ru

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Abstract—The crystal structures of ion-exchange products of the zeolite-group mineral amicite from Khibiny Alkaline Massif with silver and rubidium salts have been studied. The investigated samples are monoclinic (sp. gr. $P2_1$ and $I2/a$); their crystallochemical formulas ($Z = 1$) are $\text{Ag}_8(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 10.6\text{H}_2\text{O}$ and $\text{K}_{0.4}\text{Na}_{0.7}\text{Rb}_{6.9}(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 4.5\text{H}_2\text{O}$; the unit cell parameters are $a = 9.272(2)$ and $10.043(2)$ Å, $b = 9.997(2)$ and $9.748(2)$ Å, $c = 10.380(3)$ and $10.265(2)$ Å, $\beta = 90.821(8)^\circ$ and $90.09(3)^\circ$, $V = 962.0(4)$ and $1005.0(3)$ Å³, respectively. In the Ag-amicite structure, 22 partially occupied sites of the extra-framework components (Ag and H₂O) are localized. In the Rb-amicite structure, most of rubidium atoms are located in two sites with the occupancies of 0.414(6) and 0.389(5). The cross-sectional areas of the zeolite channels are 3.5×4.5 and 2.3×6.3 Å² for Ag-amicite and 3.0×4.3 and 3.0×3.9 Å² for Rb-amicite.

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INTRODUCTION

Among the zeolites belonging to the gismondine subgroup, which includes topologically identical minerals garronite $\text{NaCa}_{2.5}(\text{Al}_6\text{Si}_{10}\text{O}_{32}) \cdot 14\text{H}_2\text{O}$ [1], gobbinsite $\text{Na}_5(\text{Al}_5\text{Si}_{11}\text{O}_{32}) \cdot 12\text{H}_2\text{O}$ [2], gismondine $\text{Ca}_4(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 18\text{H}_2\text{O}$ [3], and amicite $\text{K}_4\text{Na}_4(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 10\text{H}_2\text{O}$ [1], the latter is the rarest one. It was described for the first time on the material from postmagmatic hydrothermalites of the Höwenegg paleovolcano (Hegau, Germany) [4]. Later on, larger amounts of amicite were found in several alkaline pegmatites of Khibiny Massif on Kola Peninsula [5, 6].

The tetrahedral aluminosilicate frameworks of all these minerals contain double wave-shaped bent chains of (Al, Si) tetrahedra (a crankshaft configuration). The structures of Ag- and Rb-substituted amicites are formed in a similar way. Si and Al atoms are ordered in the amicite and gismondine crystal structures, while in the garronite and gobbinsite tetrahedral frameworks these atoms are disordered. In addition, the gismondine-subgroup minerals differ in the content and distribution of extra-framework components (large cations and water molecules). These structural features may lead to symmetry lowering from orthorhombic or tetragonal (gobbinsite, sp. gr. $Pmn2_1$, unit-cell parameters $a = 10.108(1)$ Å, $b = 9.766(1)$ Å, and $c = 10.171(1)$ Å [2]; garronite, sp. gr. $I4m2$, unit-cell

parameters $a = 9.9266(2)$ Å and $c = 10.3031(3)$ Å [1]) to monoclinic (amicite, sp. gr. $I2$, unit-cell parameters $a = 10.226(1)$ Å, $b = 10.422(1)$ Å, $c = 9.884(1)$ Å, $\beta = 88.19(1)^\circ$ [7]).

The ion-exchange properties of gismondine were investigated for the reactions with aqueous solutions of Ag, Cs, Ba, Li, Na, K, and Rb salts at a temperature of 368 K [8]. However, any attempts to obtain ion-substituted gismondine in the form of single crystals suitable for structural examination were unsuccessful: in all experiments, crystals were dispersed as a result of the effect of stresses at the interfaces between zones with different compositions. Therefore, the crystal structures of the ion-exchange products were studied by X-ray powder diffraction using the Rietveld method. The ion-exchange properties of MAP zeolite (a purely sodium synthetic analogue of amicite) were also investigated; it was shown that this material is highly selective to cations of some alkali and alkaline-earth elements [9, 10].

The ion-exchange properties of amicite have not been studied previously. There are data of single-crystal X-ray diffraction study of amicite from Kola Peninsula, which was performed in a wide temperature range for the initial zeolite $\text{K}_4\text{Na}_4(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 11\text{H}_2\text{O}$, partially dehydrated derivatives $\text{K}_8(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 4\text{H}_2\text{O}$ and $\text{Na}_8(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 2\text{H}_2\text{O}$, and completely dehy-

drated phases. In particular, it was found that above 75°C amicite partially degrades into two individual but intergrown phases: $K_8(Al_8Si_8O_{32}) \cdot 4H_2O$ and $Na_8(Al_8Si_8O_{32}) \cdot 2H_2O$; they both crystallize in the sp. gr. $I2/a$. Upon further heating, both phases lose the rest of water they retained and become completely anhydrous at 175 and 375°C, respectively, without decomposition up to 425°C [11]. In addition, there are data on dehydration of amicite from Höwenegg (Germany), which are indicative of a high degree of its framework elasticity [12]. In this work, the products of ion exchange of natural amicite with silver and rubidium salt solutions were studied for the first time by X-ray spectral microanalysis and single-crystal X-ray diffraction analysis.

EXPERIMENTAL

In the ion-exchange experiments, isometric fragments of amicite crystals 0.7–0.9 mm in size from Khibiny Massif were used. The reactions were carried out with 0.1 M $AgNO_3$ and $RbNO_3$ solutions at 363 K for 24 h. Then, the ion-exchange products were washed with distilled water and dried at 333 K.

The chemical composition was investigated by X-ray spectral microanalysis on a Tescan Vega-II XMU scanning electron microscope (EDS mode, 20 kV, 400 pA) and an INCA Energy 450 system for X-ray microanalysis and sample composition calculation. The electron beam was 157–180 nm in diameter. The signal accumulation time was 100 s. The working sample-to-detector distance was 25 mm. The references in use were albite for Na, sanidine for K, Al_2O_3 for Al, SiO_2 for Si, metallic silver for Ag, and Rb_2ReCl_6 for Rb. The water content was determined from the weight loss after the sample calcination to a temperature of 1070 K.

The empirical formulas of the investigated samples are as follows: $H_{20.20}Na_{3.62}K_{4.06}(Al_{7.71}Si_{8.29}O_{32})O_{10.09}$ for the initial amicite, $H_{8.64}Na_{0.77}K_{0.44}Rb_{6.55}(Al_{7.86}Si_{8.14}O_{32})O_{4.27}$ for Rb-amicite, and $H_{27.90}Ag_{8.00}(Al_{7.96}Si_{8.04}O_{32})O_{13.97}$ for Ag-amicite.

The X-ray diffraction analysis of Ag-substituted amicite (**1**) crystal fragments $0.24 \times 0.20 \times 0.18$ mm in size and Rb-substituted amicite (**2**) crystal fragments $0.19 \times 0.17 \times 0.15$ mm in size was performed on an Xcalibur diffractometer (MoK_{α} radiation) at 100 K. An experimental set for the structure determination was obtained in a region exceeding reciprocal space hemisphere. The data were processed using the CrysAlis program [13]. The crystal structures of **1** and **2** were determined by direct methods and refined in the SHELXT software package [14, 15]. The coordinates of hydrogen atoms were not localized. Unfortunately, the insufficient quality of the Ag-amicite crystal (microblock structure with slightly misoriented blocks) did not allow us to obtain a low divergence factor: the final R value was 9.2% for 5380 independent

reflections with $I > 2\sigma(I)$. The satisfactory values of thermal atomic displacements and interatomic distances are indicative of the general correctness of the structural model. The final atomic coordinates correspond to the crystallochemical formula $Ag_8(Al_8Si_8O_{32}) \cdot 10.6H_2O$ for Ag-amicite and $K_{0.4}Na_{0.7}Rb_{6.9}(Al_8Si_8O_{32}) \cdot 4.5H_2O$ for Rb-amicite. The crystallographic characteristics, details of the experiment, and results of refinement of Ag- and Rb-amicite structures are listed in Table 1. The atomic coordinates, equivalent atomic displacements, site occupancy factors, and site compositions are given in Table 2 for the Ag-amicite structure and in Table 3 for the Rb-amicite structure. The detailed crystallographic data on the structures of **1** and **2** were deposited in the Inorganic Crystal Structure Database (ICSD) (nos. 2006215 and 2006216).

RESULTS OF THE X-RAY DIFFRACTION ANALYSIS AND DISCUSSION

Ag-Amicite Structure

Si and Al atoms are ordered and occupy general tetrahedral sites. The Si–O interatomic distances in silicon-oxygen tetrahedra are within 1.61(1)–1.64(1) Å for Si1, 1.61(2)–1.64(1) Å for Si2, 1.55(2)–1.67(2) Å for Si3, and 1.59(1)–1.66(1) Å for Si4; the Al–O interatomic distances lie within 1.71(1)–1.76(1) Å for Al1, 1.73(1)–1.75(1) Å for Al2, 1.73(2)–1.77(2) Å for Al3, and 1.71(2)–1.78(2) Å for Al4 (Table 4).

The extra-framework Ag^+ cations occupy general sites and are highly disordered: there are 13 localized sites with partial occupancy, which are closely spaced. Ag1 and Ag2 sites have the highest occupancies: 0.60(3) and 0.68(1), respectively. The occupancies of the sites of closely spaced (at a distance of 0.549(6) Å) Ag4 and Ag5 atoms, determined at the initial stage of refinement, were later fixed as 0.52 and 0.48, respectively, in order to exclude negative values of thermal fluctuations and excess of their total occupancy above unity, which was observed in refinement without fixation.

The chemical-composition data suggest that the sites Ag3, Ag8, Ag12, and Ag13 contain also a certain (probably, dominant) amount of water. The occupancy of each of these mixed sites was obtained by a step-by-step variation in composition, with allowance for the minimum divergence factor and the validity of heat corrections. In addition to the mixed sites, nine more extra-framework sites were localized, which are closely spaced and occupied by water molecules with occupancy factors from 20 to 60%.

Since the X-ray diffraction study yielded the number of water molecules smaller by almost four than that found in gravimetric measurements, one can suggest that non-localized water molecules are partially spread over other Ag sites and extra-framework sites with a low occupancy.

Table 1. Crystallographic characteristics, details of X-ray experiment, and results of refinement of the Ag- and Rb-amicite structures

Mineral	Ag-amicite	Rb-amicite
Formula	$\text{Ag}_8(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 10.6\text{H}_2\text{O}$	$\text{K}_{0.4}\text{Na}_{0.7}\text{Rb}_{6.9}(\text{Al}_8\text{Si}_8\text{O}_{32}) \cdot 4.5\text{H}_2\text{O}$
System, sp. gr., Z	Monoclinic, $P2_1, 1$	Monoclinic, $I2/a, 1$
$a, b, c, \text{\AA}$	9.272(2), 9.997(2), 10.380(3)	10.043(2), 9.748(2), 10.265(2)
β , deg	90.821(8)	90.09(3)
$V, \text{\AA}^3$	962.0(4)	1005.0(3)
Radiation; $\lambda, \text{\AA}$	Mo K_α : 0.71073	
$D_x, \text{g/cm}^3$	3.454	2.735
μ, mm^{-1}	4.551	8.907
T, K	100	
Diffractionmeter	Xcalibur EoS (CCD)	
Scanning type	ω	
Absorption-correction technique	Multi-scan (empirical method using spherical harmonics and the SCALE3 ABSPACK algorithm)	
$\theta_{\text{max}}, \text{deg}$	34.06	29.06
Ranges of indices h, k, l	$-14 \leq h \leq 14$ $-15 \leq k \leq 15$ $-16 \leq l \leq 16$	$-13 \leq h \leq 11$ $-12 \leq k \leq 13$ $-11 \leq l \leq 14$
Number of reflections:		
measured,	13 108	4153
independent (N_1),	7142	1343
with $I > 2\sigma(I)$ (N_2),	5380	860
R_{int}	0.0494	0.1165
Refinement method	Full-matrix least-squares refinement on F^2	
Number of refined parameters	423	117
Weight scheme	$1/[\sigma^2(F_o^2) + (0.0820P)^2 + 28.9787P]$, $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0805P)^2 + 7.6858P]$, $P = (F_o^2 + 2F_c^2)/3$
Reliability factors:		
R_1, wR_2 for N_1 ,	0.1228, 0.2399	0.1291, 0.1946
R_1, wR_2 for N_2 ,	0.0917, 0.2156	0.0775, 0.1716
S	1.061	1.068
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}, \text{e/\AA}^3$	-3.111/2.299	-0.653/0.806
Program	SHELXL-2018/3	

The Ag1 coordination polyhedron (CP) is a distorted trigonal bipyramid (the Ag–O distances range from 2.34(5) to 2.54(3) Å) with mutually exclusive sites of the OW2 and OW6 atoms having a total occupancy of 0.85 at one of the apical vertices. The occupancy of these sites is such that the maximum total number of Ag1-coordinating water molecules per unit cell is 4.6. A similar CP is formed by the Ag8 site (the

Ag–O distances range from 2.33(2) to 2.74(2) Å). The maximum total number of Ag8-coordinating water molecules is 4.6.

The Ag2 CP is a distorted tetragonal pyramid with mutually exclusive sites of OW1 and OW7 atoms with a total occupancy of 0.86 in the apex. The total number of Ag2-coordinating water molecules is 4.54 at

Table 2. Atomic coordinates (x, y, z), equivalent atomic displacement parameters ($U_{\text{eq}}, \text{\AA}^2$), multiplicities (Q), site occupancy factors (s.o.f.), and composition of sites in the Ag-amicitite structure

Site	x/a	y/b	z/c	$U_{\text{eq}}, \text{\AA}^2$	s.o.f., site composition	Q
Extra-framework components						
Ag1	0.7895(9)	0.4422(7)	-0.0700(6)	0.026(2)	0.60(3)	2
Ag2	0.7160(2)	0.7222(3)	0.0668(2)	0.0212(7)	0.68(1)	2
Ag3	0.7853(6)	0.4327(7)	0.5697(5)	0.0165(8)	Ag _{0.49} OW3* _{0.38}	2
Ag4	0.7244(4)	0.7160(4)	0.4468(3)	0.0170(6)	0.52*	2
Ag5	0.7102(6)	0.7561(5)	0.4129(5)	0.034(1)	0.48*	2
Ag6	0.7818(9)	0.5283(8)	0.017(1)	0.023(3)	0.172(9)	2
Ag7	0.6583(9)	0.7851(7)	0.1046(8)	0.014(2)	0.169(8)	2
Ag8	0.792(1)	0.437(1)	0.6018(6)	0.016(1)	Ag _{0.3} OW8* _{0.25}	2
Ag9	0.717(1)	0.6801(7)	-0.012(1)	0.028(3)	0.19(1)	2
Ag10	0.834(2)	0.4221(8)	-0.102(2)	0.023(3)	0.22(3)	2
Ag11	0.775(1)	0.489(2)	0.531(1)	0.019(4)	0.12(1)	2
Ag12	0.796(2)	0.582(2)	0.259(2)	0.036(4)	Ag _{0.04} OW12* _{0.68}	2
Ag13	0.713(2)	0.594(2)	-0.249(2)	0.029(4)	Ag _{0.01} OW13* _{0.75}	2
OW1	0.747(3)	0.887(2)	0.248(2)	0.025(7)	0.61(7)	2
OW2	0.780(3)	0.263(3)	0.757(3)	0.022(8)	0.52(7)	2
OW4	0.467(4)	0.867(4)	0.245(4)	0.04(1)	0.51(8)	2
OW5	0.536(6)	0.919(6)	0.286(6)	0.03(2)	0.30(8)	2
OW6	0.644(5)	0.351(5)	0.768(5)	0.03(1)	0.31(6)	2
OW7	0.624(7)	0.922(6)	0.222(5)	0.03(2)	0.27(7)	2
OW9	0.781(5)	0.445(5)	0.200(4)	0.02(1)	0.28*	2
OW10	1.120(9)	0.357(10)	-0.284(9)	0.03(2)	0.20*	2
OW11	0.703(4)	0.741(4)	-0.291(4)	0.01(1)	0.24*	2
Tetrahedral framework						
Si1	0.8866(6)	0.9361(5)	0.5952(5)	0.0159(9)	1	2
Si2	1.0519(6)	0.6638(6)	-0.0960(6)	0.0198(10)	1	2
Si3	0.6118(6)	0.2500(5)	0.4030(5)	0.0171(10)	1	2
Si4	0.4499(5)	0.5234(5)	0.0960(5)	0.0139(9)	1	2
Al1	0.4442(6)	0.5257(5)	0.3986(5)	0.0129(9)	1	2
Al2	0.8814(6)	0.9393(6)	-0.1029(5)	0.0150(10)	1	2
Al3	1.0566(7)	0.6601(6)	0.6017(6)	0.0188(11)	1	2
Al4	0.6185(7)	0.2465(6)	0.1018(6)	0.0176(11)	1	2
O1	0.4418(17)	0.5846(12)	0.2392(14)	0.018(3)	1	2
O2	0.6988(13)	0.9510(15)	-0.0652(13)	0.018(3)	1	2
O3	0.9222(15)	0.9898(14)	0.7413(13)	0.018(2)	1	2
O4	0.4895(17)	0.6478(13)	-0.0027(15)	0.017(2)	1	2
O5	0.9196(14)	0.7708(14)	-0.0811(15)	0.021(3)	1	2
O6	0.9176(16)	0.7782(14)	0.5826(14)	0.020(3)	1	2
O7	0.5819(16)	0.4156(12)	0.0790(14)	0.019(3)	1	2
O8	0.7161(13)	0.9519(12)	0.5625(13)	0.014(2)	1	2
O9	0.7744(17)	0.2316(16)	0.4337(17)	0.028(4)	1	2
O10	1.2043(16)	0.7335(16)	-0.0597(14)	0.023(3)	1	2
O11	1.0160(16)	0.5414(16)	0.0012(15)	0.022(3)	1	2
O12	1.0518(19)	0.605(2)	-0.2402(16)	0.030(4)	1	2
O13	1.0163(16)	0.5236(14)	0.5017(15)	0.020(3)	1	2
O14	0.4860(16)	0.6625(14)	0.4919(15)	0.018(2)	1	2
O15	0.5781(15)	0.4098(14)	0.4196(14)	0.019(3)	1	2
O16	0.5744(17)	0.1940(18)	0.2599(14)	0.027(3)	1	2

* Fixed during refinement.

Table 3. Atomic coordinates (x, y, z), equivalent atomic displacement parameters ($U_{\text{eq}}, \text{\AA}^2$), multiplicities (Q), site occupancy factors (s.o.f.), and composition of sites in the Rb-amicite structure

Site	x/a	y/b	z/c	$U_{\text{eq}}, \text{\AA}^2$	s.o.f., site composition	Q
Extra-framework components						
Rb1	0.9158(4)	0.0177(2)	0.0498(2)	0.045(1)	0.414(6)	8
Rb2	0.7930(3)	-0.2686(3)	-0.1623(4)	0.056(1)	0.389(5)	8
K1(Rb3)	0.75	-0.25	-0.25	0.030(3)	$\text{K}_{0.1}\text{Rb}_{0.04}^*$	4
Rb4	0.783(2)	-0.281(2)	-0.077(2)	0.035(5)	0.04*	8
Na1	1	0	0	0.024(5)	$\text{Na}_{0.1}\text{OW5}_{0.125}^*$	4
Na2	0.834(2)	0.039(2)	0.051(2)	0.026(4)	$\text{Na}_{0.035}\text{OW6}_{0.25}^*$	8
OW7	0.648(5)	-0.032(5)	-0.109(6)	0.06(1)	0.15*	8
OW8	0.75	-0.269(7)	0	0.07(2)	0.2*	4
Tetrahedral framework						
Si1	0.92696(2)	0.15669(2)	0.3683(2)	0.0167(5)	1	8
Al1	0.8808(2)	0.0994(2)	0.66702(19)	0.0170(5)	1	8
O1	0.9328(5)	0.1829(5)	0.5250(5)	0.0228(11)	1	8
O2	0.7926(5)	0.0777(5)	0.3255(5)	0.0215(11)	1	8
O3	0.9403(5)	0.3070(5)	0.2988(5)	0.0219(11)	1	8
O4	1.0534(5)	0.0654(5)	0.3212(5)	0.0206(11)	1	8

* Fixed during refinement.

most. The Ag–O distances range from 2.33(1) to 2.70(8) Å.

The Ag3 CP is a distorted tetragonal pyramid with Ag–O distances ranging from 2.44(2) to 2.59(5) Å and mutually exclusive sites of the OW2 and OW6 atoms with a total occupancy of 0.85 at the vertex. The maximum total number of Ag3-coordinating water molecules is 4.6.

The Ag4 CP is a distorted tetragonal pyramid (the Ag–O distances range between 2.33(2)–2.68(2) Å), whose apical vertex contains mutually exclusive OW1 and OW10 atomic sites with a total occupancy of 0.8. The total number of Ag4-coordinating water molecules is 4.48. A similar CP is formed by the Ag7 site. In this CP, one of the base vertices is formed by a pair of mutually exclusive OW4 and OW5 atomic sites with a total occupancy of 0.79, for which the maximum number of Ag7-coordinating water molecules is 4.07. The Ag7–O distances range from 1.97(2) to 2.87(2) Å.

The Ag5 CP is a distorted tetragonal bipyramid with two equatorial vertices occupied by pairs of mutually exclusive atomic sites (OW5 + OW7) and (OW1 + OW10), the total occupancies of which are 0.52 and 0.8, respectively. The total maximum number of Ag5-coordinating water molecules is 5.02. The Ag–O distances lie in the range of 2.17(2)–2.70(8) Å.

The Ag6 CP is a distorted uncapped trigonal prism (CN = 7) with Ag6–O distances ranging from 2.04(5) to 2.97(2) Å. The total maximum number of Ag6-coordinating water molecules is 5.71.

The Ag9 CP is a flattened tetrahedron (the Ag9–O distances range from 2.14(2) to 2.76(2) Å) and the Ag10 CP is a distorted square (the Ag10–O distances are in the range of 2.21(3)–2.56(2)) with one of the vertices containing mutually exclusive OW2 and OW6 atomic sites with a total occupancy of 0.85. The total maximum numbers of water molecules coordinating the Ag9 and Ag10 cations are 3.75 and 3.6, respectively.

The Ag11 CP is a distorted tetragonal pyramid with Ag11–O distances ranging from 2.28(2) to 2.98(3) Å. The maximum number of Ag11-coordinating water molecules is 4.43.

Rb-Amicite Structure

In the Rb-substituted amicite structure, Si and Al atoms of the polyhedral framework are ordered and occupy general tetrahedral sites. In the silicon–oxygen tetrahedra, the interatomic distances range from 1.614(5) to 1.635(5) Å; the Al–O framework interatomic distances are from 1.737(5) to 1.757(5) Å (Table 4).

Table 4. Main interatomic distances in the Ag- and Rb-amicite structures (Å)

Ag-amicite							
<i>T</i> tetrahedra	<i>d</i> , Å	<i>T</i> tetrahedra	<i>d</i> , Å	Ag polyhedra	<i>d</i> , Å	Ag polyhedra	<i>d</i> , Å
Si1–O3	1.64(1)	Al3–O6	1.76(1)	–Ag13	2.58(2)	Ag7–O4	2.35(1)
–O6	1.61(1)	–O9	1.77(2)	–OW2	2.58(3)	–OW4	2.45(4)
–O8	1.61(1)	–O12	1.73(2)	–OW6	2.59(5)	–O2	2.45(1)
–O13	1.61(1)	–O13	1.75(1)	Ag4–O14	2.33(2)	–OW5	2.59(5)
Si2–O5	1.64(1)	Al4–O7	1.74(1)	–O6	2.35(1)	–Ag12	2.87(2)
–O10	1.61(2)	–O4	1.73(1)	–O8	2.65(1)	Ag8–Ag13	2.33(2)
–O11	1.62(2)	–O10	1.71(2)	–Ag12	2.46(2)	–OW2	2.37(3)
–O12	1.61(2)	–O16	1.78(2)	–OW1	2.68(2)	–OW6	2.38(5)
Si3–O9	1.55(2)	Ag polyhedra	<i>d</i> , Å	–OW10	2.64(9)	–O13	2.49(2)
–O14	1.67(2)	Ag1–O11	2.43(2)	Ag5–OW1	2.17(2)	–O9	2.69(2)
–O15	1.64(2)	–O10	2.48(2)	–OW10	2.31(5)	–O15	2.74(2)
–O16	1.62(2)	–Ag13	2.49(2)	–O14	2.43(2)	Ag9–O2	2.76(2)
Si4–O2	1.59(1)	–O7	2.50(2)	–Ag12	2.49(2)	–O4	2.14(2)
–O1	1.61(1)	–OW2	2.54(3)	–O8	2.50(1)	–O5	2.21(2)
–O4	1.66(1)	–OW6	2.34(5)	–O6	2.60(1)	–Ag13	2.60(2)
–O7	1.64(1)	Ag2–O4	2.33(1)	–OW5	2.64(5)	Ag10–OW2	2.21(3)
Al1–O1	1.76(1)	–O2	2.67(1)	–OW7	2.70(8)	–OW6	2.32(5)
–O8	1.71(1)	–O5	2.50(2)	Ag6–OW9	2.04(5)	–O11	2.32(2)
–O14	1.71(1)	–OW1	2.51(3)	–O11	2.18(2)	–Ag13	2.54(2)
–O15	1.71(1)	–OW7	2.70(8)	–O4	2.97(2)	–O10	2.56(2)
Al2–O2	1.75(1)	–Ag12	2.54(2)	–O5	2.93(2)	Ag11–O9	2.77(2)
–O3	1.74(1)	Ag3–O13	2.44(2)	–O7	2.27(2)	–O13	2.28(2)
–O5	1.73(1)	–O9	2.46(2)	–Ag12	2.58(2)	–O15	2.29(2)
–O11	1.74(1)	–O15	2.47(1)	–Ag13	2.90(2)	–Ag13	2.58(2)
				Ag7–OW1	1.97(2)	–Ag12	2.98(3)
Rb-amicite							
<i>T</i> tetrahedra	<i>d</i> , Å	Rb polyhedra	<i>d</i> , Å	Rb polyhedra	<i>d</i> , Å	K, Rb polyhedra	<i>d</i> , Å
Si1–O2	1.614(5)	Rb1–O1	2.935(5)	Rb2–O4	2.905(5)	K1–O4	2.771(5) × 2
–O4	1.625(5)	–O3	2.953(5)	–O4	2.996(6)	–O3	3.200(5) × 2
–O1	1.629(5)	–O3	3.103(5)	–O2	3.016(6)	–O2	3.315(5) × 2
–O7	1.635(5)	–O4	3.142(5)	–O1	3.128(6)	Rb4–O1	2.92(2)
Al1–O3	1.737(5)	–O2	3.145(5)	–O3	3.048(6)	–O4	2.94(2)
–O4	1.741(5)	–O1	3.682(5)	–O3	3.639(6)	–O2	3.06(2)
–O1	1.750(5)	–Ow7	3.18(6)	–Ow7	2.78(6)	–O4	3.43(2)
–O2	1.757(5)	–Ow7	2.85(6)	–Ow7	3.10(6)	–O3	3.60(2)
		–Ow8	3.29(6)	–Ow8	3.51(6)	–O4	3.67(2)
		–Ow6	2.72(2)	–Ow6	3.46(3)	–O1	3.68(2)
		–Ow6	2.78(3)	–Ow6	3.74(3)	–O3	3.77(2)
				–Ow5	3.73(3)		

The Ag3, Ag8, Ag12, and Ag13 sites are included in the coordination sphere of the rest Ag sites under the assumption that these sites contain many H₂O molecules. For weakly occupied K1 and Rb4 sites, only the distances to the framework-forming O atoms are given.

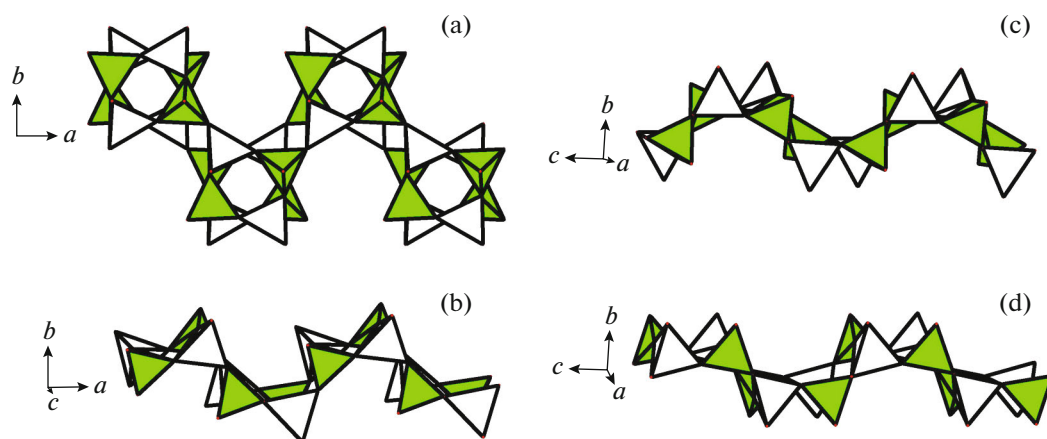


Fig. 1. Double chains of (Al, Si) tetrahedra (a, b) along the *a* axis and (c, d) along the *c* axis in the Rb- and Ag-amicite structures, respectively. Closed and open tetrahedra are SiO₄ and AlO₄, respectively.

The extra-framework Rb⁺ cations are disordered over two main general sites Rb1 and Rb2 with occupancies of 0.414(6) and 0.390(5), respectively. The center of symmetry connects these sites in such a way that the distances between them are Rb1–Rb1' = 2.008(7) and Rb2–Rb2' = 2.027(8) Å.

The refinement revealed two weakly occupied sites: special centrosymmetric K1 site with a coordination number of 6 and the occupancy K_{0.10}Rb_{0.04} and general Rb4 site with the occupancy Rb_{0.04}. The presence of potassium in the Rb3 site is consistent with the low coordination number of this site and the K1–O distances.

Four sites (three general and one special centrosymmetric) containing water molecules, with occupancies from 0.125 to 0.25, were localized in the Rb-amicite structure. According to the chemical-composition data, two of these sites were refined as mixed with Na⁺ cations in H₂O : Na ratios of 0.25 : 0.035 (the site Na2OW6) and 0.125 : 0.1 (the special site Na1OW5). The concurrent occupation of these two sites by Na⁺ cations and water molecules was indicated by the underestimated values of their thermal parameters. The occupancy of each of these mixed sites was obtained by a stepwise change in the compositions under the conditions of the minimum divergence factor and correctness of thermal parameters.

The Rb1 and Rb2 cations have the coordination numbers of 11 and 12, respectively. The Rb1 site is bonded to six O atoms at distances from 2.935(5) to 3.682(5) Å and five water molecules at distances from 2.72(2) to 3.29(6) Å. The degree of occupancy of these sites is such that the total number of Rb1-coordinating water molecules is 7. The Rb2 site is bonded to six O

atoms at distances from 2.905(5) to 3.639(6) Å and six water molecules at distances from 2.78(6) to 3.74(3) Å. The total number of Rb2-coordinating water molecules is 7.125.

The Ag- and Rb-substituted amicitite structures are generally similar to the Ag- and Rb-gismondine structures [8]: the chains of four-membered rings evolving along the *a* and *c* axes form a two-dimensional system of bent zeolite channels (Fig. 1).

In the Rb-substituted amicitite structure, the cross sections of the channels formed by eight-membered rings are 3.0 × 4.3 Å² in the projection along the *a* axis and 3.0 × 3.9 Å² in the projection along the *c* axis (the measurements were performed through the channel center with regard to the oxygen ionic radius of 1.35 Å) (Figs. 2a, 2b).

In the Ag-substituted amicitite structure, the cross-sectional areas of the channels formed by eight-membered rings are 3.5 × 4.5 Å² in the projection along the *a* axis and 2.3 × 6.3 Å² in the projection along the *c* axis (Figs. 2c, 2d). Among the investigated amicitite derivatives (K-, Cs-, [16], Rb-, and Ag-substituted), the Ag-substituted amicitite is characterized by channels have the largest ratio of major and minor radii of the ellipses approximating their gaps in the projection along the *c* axis. A similar feature was observed in gismondine derivatives [8].

CONCLUSIONS

The structural study of the ion-exchange products of amicitite zeolite from Khibiny Alkaline Massif with silver and rubidium salt solutions showed that their crystal structures are similar to the analogous gismondine derivatives: the tetrahedral aluminosilicate frameworks contain double wave-shaped chains of

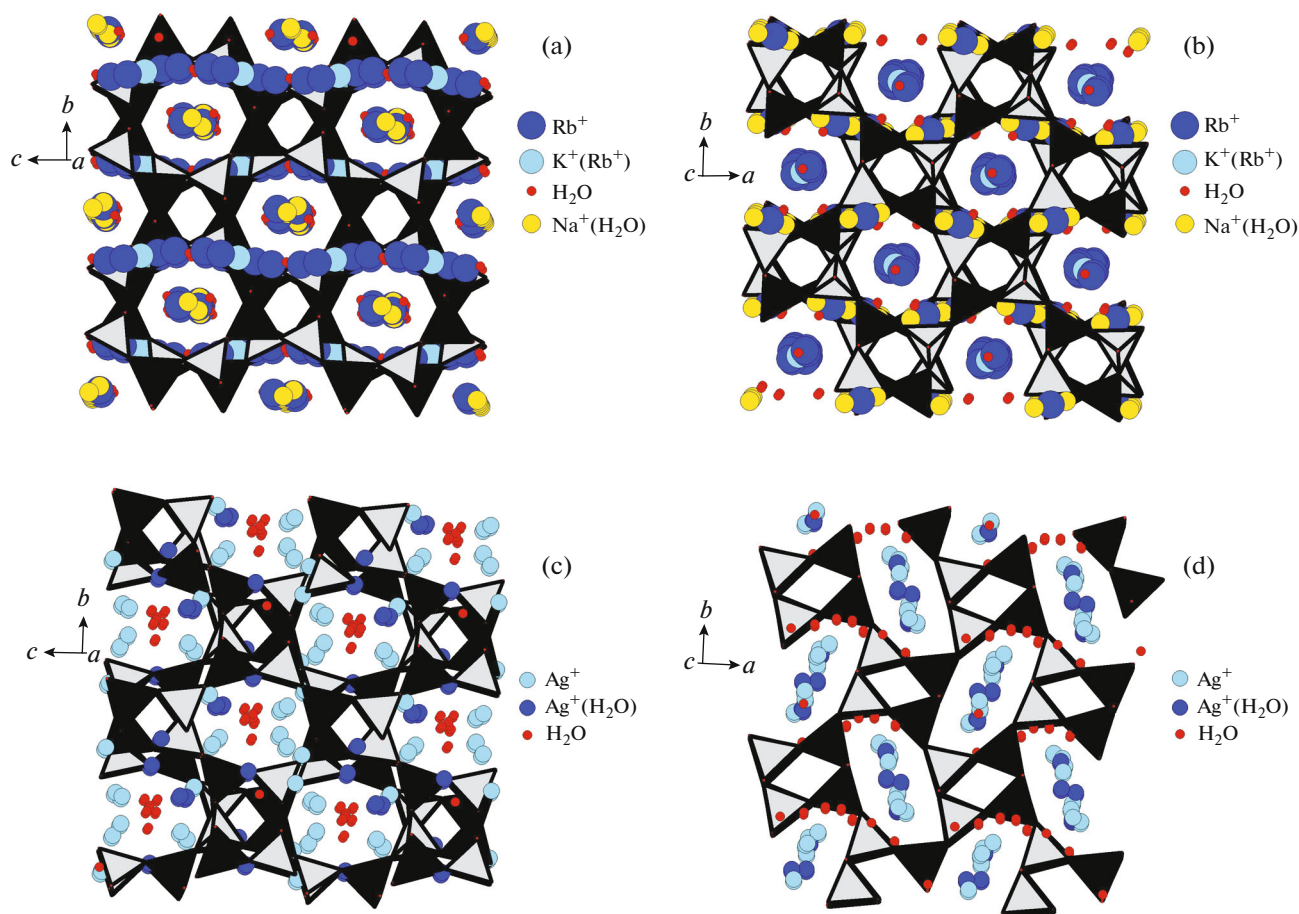


Fig. 2. (a, b) Rb- and (c, d) Ag-amicite crystal structures in projections along the (a, c) [100] and (b, d) [001] directions. Gray and black tetrahedra are SiO₄ and AlO₄, respectively.

(Al, Si) tetrahedra. The Si and Al atoms in these tetrahedra are ordered, while the extra-framework components exhibit a significant degree of disordering: 22 partially occupied sites of cations and H₂O molecules are localized in the Ag-substituted amicitite structure and 8 such sites are localized in the Rb-substituted amicitite structure. The significant dependence of the cross-sectional areas of zeolite channels on the type of metal used in the ion exchange are indicative of a high degree of framework elasticity.

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