CrystEngComm



PAPER

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Cite this: *CrystEngComm*, 2020, **22**, 2621

Influence of the Sc cation substituent on the structural properties and energy transfer processes in GAGG:Ce crystals[†]

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The influence of the Sc cation substituent on the structural and luminescence properties of GAGG:Ce crystals was studied. Unit cell parameters and space groups were obtained using XRD analysis. The chemical compositions of the crystals were determined using SEM-EDX and TEM-EDX techniques. Structures were refined by the Rietveld method and the distribution of Al/Ga/Sc cations between octahedral and tetrahedral sites was obtained. The influence of Sc on the electronic band structure and the energy of the 4f and 5d Ce³⁺ levels is shown. The modification of the band structure induced by the Sc electronic states results in the suppression of Gd emission and enhancement of Ce³⁺ emission at low temperatures. The Ce³⁺ emission decay is accelerated under high-energy excitation of the Sc-containing GAGG compound.

Received 26th January 2020, Accepted 25th February 2020

DOI: 10.1039/d0ce00122h

rsc.li/crystengcomm

1. Introduction

 $Gd_3Al_2Ga_3O_{12}$:Ce³⁺ (GAGG:Ce) crystals are promising for scintillator applications in medicine (SPECT, PET) and highenergy physics.¹⁻³ GAGG:Ce is a high-density (6.63 g cm⁻³) chemically stable compound which demonstrates the highest scintillation yield among oxide-based scintillators (~60 000 ph MeV⁻¹). The main disadvantage of this crystal is that upon excitation by ionizing radiation, besides the decay component typical for the 5d–4d Ce³⁺ emission (~60 ns), additional slow decay components with $\tau > 200$ ns emerge in its scintillation response, which deteriorate the scintillation performance.^{3,4} The presence of slow decay components is related to the intermediate localization of charge carriers at traps during the energy transfer process from the host to the emission centers as well as to energy migration *via* the Gd sublattice.^{5,6} Nowadays two strategies are applied for the improvement of the scintillation characteristics of GAGG:Ce:

(i) Co-doping of the crystal with divalent ions (Mg^{2+}, Ca^{2+}) has been shown to suppress slow decay components in GAGG:Ce.^{4,7} The co-doping accelerates energy transfer to emission centers by altering the Ce ion valency from 3+ to 4+ (ref. 5 and 8) or by modification of the trap level structure.⁹ However, a side effect of such co-doping is the decrease of scintillation light yield.¹⁰

(ii) The method of bandgap engineering allows fine tailoring of physical properties by gradual change of crystal composition.^{11,12} A wide range of compositional variation of garnet solid solutions enables the optimization of their optical properties aimed at specific applications.¹³

The application of the bandgap engineering method for the improvement of luminescence and scintillation properties is usually focused on the modification of electronic states at the top of the valence band and at the bottom of the conduction band as well as on the shift of the relative energy position of the activator and trap levels in the bandgap. Alongside with this, the band structure modification caused

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^h Institute of Physics, University of Tartu, W. Ostwald str. 1, 50411 Tartu, Estonia † Electronic supplementary information (ESI) available: Selected distances (Å) in Gd₃Al_{2.3}Ga_{2.7}O₁₂ and Gd₃Sc_{1.3}Al_{1.6}Ga_{2.1}O₁₂ (Table S1). Example photo of the grown Ce-doped Gd₃Al_{2.3}Ga_{2.7}O₁₂ single crystal (Fig. S1). EDX spectra of Gd₃Al_{2.3}Ga_{2.7}O₁₂ and Gd₃Sc_{1.3}Al_{1.6}Ga_{2.1}O₁₂ samples from selected area (Fig. S2). TSL curves for Gd₃Al_{2.3}Ga_{2.7}O₁₂: Ce measured at λ_{irr} = 460 nm (2.7 eV) (Fig. S2). TSL curves for Gd₃Al_{2.3}Ga_{2.7}O₁₂: Ce measured at λ_{irr} = 460 nm (2.7 eV) (Fig. S3). TSL curves for GAGG:Ce measured at λ_{irr} = 340 nm (3.65 eV) (Fig. S4). CCDC 1979928 (Gd₃Al_{2.3}Ga_{2.7}O₁₂), CCDC 1979929 (Gd₃Sc_{1.3}Al_{1.6}Ga_{2.1}O₁₂). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ d0ce00122h

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by the bandgap engineering also alters the pathways of energy relaxation in a scintillator. The electronic states of Sc considerably change the conduction band structure in garnets. Band structure calculations for $Gd_3Sc_2Ga_3O_{12}$ and $Gd_3Sc_2Al_3O_{12}$ have shown that 3d Sc electronic states are located at the bottom of the conduction band, forming a localized subband with a high density of electronic states.¹⁴ For this reason, the modification of cation composition by partial substitution of the Al and Ga cations with Sc is expected to influence the relaxation of high-energy excitations and energy transfer to Ce^{3+} emission centers in GAGG:Ce crystals.

The influence of Sc on the scintillation and luminescence properties of gadolinium garnets has been previously studied for the $Gd_3Sc_2Al_3O_{12}$ composition.^{6,15-18} The larger ionic radius of Sc in comparison to Al increases the unit cell parameters and results in increased solubility of Ce^{3+} in garnets and higher external quantum efficiency.¹⁵ The positive influence of even small additions of Sc on garnet transparency has been reported in ref. 6. Along with the positive influence of Sc on the luminescence properties of garnets, adverse effects such as strong thermal quenching of emission and the presence of long rise time in scintillation response have been reported as well.^{15,17}

Here we present the study of the modification of structural properties and energy transfer to emission centers caused by partial substitution of Al and Ga cations by Sc in GAGG:Ce crystals.

2. Experimental section

Single crystals of Gd₃Ga₃Al₂O₁₂ (GAGG), Gd_{2.97}Ce_{0.03}Ga₃Al₂O₁₂ (GAGG:Ce) and Gd_{2.97}Ce_{0.03}Ga_{2.5}Sc₁Al_{1.5}O₁₂ (GASGG:Ce) were grown by the Czochralski method. GAGG:Ce and GASGG:Ce crystals were co-doped with 150 ppm CaCO₃. The crystals were grown in Fomos-Materials, Moscow. A small (100) oriented single crystal bar was used as a seed. Yellow crystals with up to 40 mm diameter and 80 mm height were grown at a pulling rate of 0.5–1 mm h⁻¹ and a rotating rate of 10–15 rpm in an Ar atmosphere with O₂ addition up to 2 vol% (see Fig. S1 of the ESI†). The weight of the grown crystals was not less than 30% of the melt weight. All single crystals were optically transparent without cracks and phase inclusions. Crystal slices with a thickness of approximately 2 mm were cut perpendicular to the growth axis from the top part of the crystal and then optically polished to obtain parallel faces.

Powder X-ray diffraction (XRD) patterns for phase determination were collected on a Thermo ARL X'TRA powder diffractometer (Cu K α radiation, λ = 1.5418 Å, Bragg–Brentano geometry, Peltier-cooled CCD detector). The XRD data were collected at room temperature over the 10–80° 2 θ range with steps of 0.02°. To determine the lattice parameters, Le Bail decomposition¹⁹ was applied using the JANA2006 software.²⁰

Powder XRD patterns for GAGG and GASGG crystal structure refinement were collected on a Huber G670 Guinier diffractometer (Cu K α_1 radiation, curved Ge(111)

monochromator, transmission mode, image plate detector). PXRD data were collected over the $3-100^{\circ} 2\theta$ range with steps of 0.005°. Rietveld refinements were performed using the JANA2006 software.²⁰

The cation composition of crushed GAGG and GASGG samples was determined by energy-dispersive X-ray spectrometry (EDXS) using a JEOL JSN-6490LV scanning electron microscope equipped with an EDX spectrometer (Oxford Instruments).

Samples for transmission electron microscopy (TEM) were made by crushing the powders in an agate mortar and dispersing them in methanol. After treatment in an ultrasonic bath to disperse the crystallites, a few drops of the solution were put on a copper grid with a holey carbon film. Selected area electron diffraction (SAED) patterns of selected areas were recorded for GASGG using a Tecnai G^2 F20 transmission electron microscope operating at 200 kV. The elemental composition of the GAGG and GASGG samples was confirmed using energy-dispersive X-ray (EDX) analysis on the Tecnai G^2 F20 microscope with an EDAX attachment (TEM-EDX), using the Gd_L, Sc_K, Ga_K and Al_K lines. TEM-EDX analyses at 3 points for 10 different crystallites of each sample were linked with the SAED analysis of the crystallites.

For the measurements of optical and luminescence characteristics, polished plates with a thickness of ~900 µm were prepared. Absorption spectra were measured using an Agilent Technologies Cary-5000 spectrophotometer at 300 K and a PerkinElmer Lambda 950 spectrophotometer in the temperature region 80-500 K. The samples were placed into an optical vacuum cryostat (CRYOTRADE LN-120) equipped with a LakeShore 335 temperature controller. Luminescence and excitation spectra as well as thermostimulated luminescence (TSL) curves under UV excitation were measured using a laboratory setup. For the measurements of TSL glow curves the samples were placed into a CRYOTRADE LN-120 cryostat equipped with a LakeShore 335 temperature controller. Samples were irradiated with a wavelength of 460 or 340 nm for 3 min at a given temperature and then heated to 500 K at a linear rate of 20 K min⁻¹. The TSL signal was detected using an H7732-11 photosensor module. Luminescence spectra in the range of 400-800 nm and excitation spectra under UV excitation in the energy range of 2.5-6.0 eV were measured using a 150 W Xe lamp. Excitation wavelengths were selected using an MDR-206 monochromator. Luminescence spectra were detected using an Oriel MS 257 spectrograph equipped with a Marconi CCD detector. The excitation spectra were corrected for spectral distribution of incident light using yellow Lumogen.

Luminescence excitation and emission spectra under excitation in the UV-VUV region were measured using the photoluminescence endstation²¹ of the FinEstBeAMS undulator beamline,²² which was recently constructed at the 1.5 GeV storage ring of the MAX IV synchrotron facility (Lund, Sweden). The excitation range from 4.5 to 40 eV was chosen from the full energy range provided by the beamline. A set of optical (fused silica, MgF₂) and thin-film (In, Sn) filters was utilized to suppress higher orders of excitation. The excitation

spectra were corrected using the excitation flux curve obtained by means of a factory-calibrated AXUV-100G diode. The measurement chamber was equipped with a closed-cycle helium cryostat and a LakeShore 325 temperature controller that allowed changing the temperature in the range from 10 to 350 K. A fiber-coupled Andor Shamrock SR-303i spectrometer was used as a secondary monochromator. The spectrometer contained two diffraction gratings (300 l mm⁻¹) optimized for different spectral regions (300 and 500 nm blaze). In order to detect the luminescence signal in a wide spectral range, interchangeable photon counting heads (Hamamatsu H8259 or H8259-01) were mounted on one exit port of the spectrometer and a CCD camera was mounted on the other exit port. The described sets of gratings and detectors allowed recording of emission spectra in the range from 190 to 900 nm. All presented luminescence spectra were corrected for the spectral sensitivity of the registration channel.

Cathodoluminescence decay curves were measured at the pulsed cathodoluminescence setup described in detail in ref. 23. An electron beam with a broad energy spectrum ($E_{\text{max}} \sim 120 \text{ keV}$), pulse FWHM of 200 ps, and peak electron current of 15 A cm⁻² was used for excitation. An Andor Shamrock SR303-i spectrograph equipped with a Hamamatsu R3809U-50 MCP-PMT was used to record decay curves in pulsed current mode. Its output was digitized using a LeCroy SDA 760Zi-A oscilloscope (6 GHz, 40 Gs s⁻¹).

3. Results and discussion

3.1. Elemental composition

Using SEM-EDX, the Gd:Al:Ga and Gd:Sc:Al:Ga ratios were found to be $\sim 3:2.3:2.7$ (36.3 ± 1.8 at% Gd, 29.1 ± 4.0 at% Al, 34.6 ± 2.6 at% Ga) and $\sim 3:1.3:1.6:2.1$ (34.6 ± 1.7 at% Gd, 17.6 ± 1.3 at% Sc, 20.6 ± 2.8 at% Al, 27.2 ± 1.3 at% Ga) in GAGG and GASGG samples, respectively. GAGG and GASGG compositions calculated according to the formula A₃B₅O₁₂ were Gd₃Al_{2.3}Ga_{2.7}O₁₂ and Gd₃Sc_{1.3}Al_{1.6}Ga_{2.1}O₁₂. Representative SEM-EDX spectra for both samples are shown in Fig. S2 of the ESI.[†]

In order to verify the results of the SEM-EDS analysis, a local chemical composition in GAGG and GASGG crystallites was evaluated by EDX analysis performed using a transmission electron microscope (TEM-EDX). The Al:Ga ratio in GAGG was found to vary from 1.5:3.5 to 2:3 for a probe diameter of 60–90 nm. This variation in composition may be explained in terms of the formation of a solid solution $Gd_3Al_xGa_{5-x}O_{12}$ (1.5 $\leq x \leq 2$). A local composition analysis performed using TEM-EDX for GASGG (33.1 ± 1.7 at% Gd, 18.8 ± 1.4 at% Sc, 20.0 ± 1.3 at% Al, 28.1 ± 0.9 at% Ga) agreed with the results obtained using SEM-EDX.

3.2. XRD characterization

The determination of GAGG and GASGG unit cell parameters from PXRD patterns using Le Bail decomposition revealed that reflections could be indexed in the space group $Ia\bar{3}d$ with the unit cell parameters a = 12.2654(4) Å and a = 12.4396(5) Å for GAGG and GASGG, respectively.

GAGG and GASGG are representatives of the garnet structure crystal group described by the $A_3B_2(CO_4)_3$ formula. The structure of the most studied $Ca_3Al_2(SiO_4)_3$ garnet is made up of CaO_8 polyhedra, AlO_6 octahedra and SiO_4 tetrahedra.²⁴ The Gd³⁺ cations in Gd₃Ga₅O₁₂ garnets (GGG) occupy the Ca positions of the $Ca_3Al_2(SiO_4)_3$ structure, while gallium cations are located in octahedral and tetrahedral sites. The substitution of Ga³⁺ by Al³⁺ in GAGG is accompanied by the decrease of lattice parameters and unit cell volume in accordance with ionic radii difference ($r_{IV} = 0.47$ Å and $r_{VI} = 0.62$ Å for Ga³⁺ and $r_{IV} = 0.39$ Å and $r_{VI} = 0.535$ Å for Al³⁺ (ref. 25)).

 Sc^{3+} cations can replace both Gd^{3+} in the GdO_8 polyhedra $(r_{\text{VIII}} = 0.870 \text{ Å for Sc}^{3+}$ and $r_{\text{VIII}} = 1.053 \text{ Å for Gd}^{3+})$ and Ga^{3+} in the octahedra of the garnet-type structure $(r_{\text{VI}} = 0.745 \text{ Å for Sc}^{3+} (\text{ref. 25}))$. In the first case, this should lead to a decrease in the unit cell parameters due to the smaller size of scandium compared to gadolinium, while in the second case the unit cell would increase. On the contrary, upon the substitution of Ga^{3+} for Al^{3+} , the introduction of Sc^{3+} in the garnet-type structure leads to an increase in unit cell parameters even in comparison with GGG (a = 12.3829 Å (ref. 26)). Thus, Sc^{3+} cations preferably substitute Ga^{3+} in the structure sites with an octahedral oxygen coordination.

3.3. Electron diffraction study

The [100], [$\overline{1}10$] and [$\overline{1}11$] ED patterns of GASGG are shown in Fig. 1. All ED patterns are completely indexed on a cubic unit cell with lattice parameters determined from XRD and space group $Ia\overline{3}d$. The general reflection conditions for the space group $Ia\overline{3}d$ are as follows: hkl: h + k + l = 2n; 0kl: k, l =2n; hhl: 2h + l = 4n; h00: h = 4n. The [100] and [$\overline{1}11$] ED patterns show the reflections $h00: h \neq 4n$ (h00: 200 and 600) and $hhl: 2h + l \neq 4n$ (hhl: 110, 330 and 550), which should be extinct according to the $Ia\overline{3}d$ symmetry. These reflections are due to multiple diffraction. This is also confirmed by the absence of the $h00: h \neq 4n$ and $hhl: 2h + l \neq 4n$ reflections in the [$\overline{1}10$] zone.

3.4. Crystal structure refinement

The structural data for $Gd_3Ga_5O_{12}$ (ref. 26) were used as a starting model for the refinements of GAGG and GASGG structures. At the first stage, the *f* curves for Gd^{3+} (A site) and Ga^{3+} (B and C sites) were used, and all parameters of the chosen model were refined. According to the refinement, the Gd^{3+} ions occupy A sites in GAGG and GASGG structures. At the second stage, the *f* curves for Al^{3+} (B and C sites) were used and all parameters of the chosen model were refined. The analysis of the occupancies demonstrated (Table 1, n_{f-Ga} and n_{f-Al}) that Ga^{3+} and Al^{3+} cations are distributed between the B and C sites in the GAGG structure. The distribution of Ga^{3+} and Al^{3+} over the B and C positions in the GAGG structure was refined considering their multiplicities (B =

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Fig. 1 ED patterns along the main zone axes for GASGG.

 $mGa^{3+} + (1 - m)Al^{3+}$, C = $nGa^{3+} + (1 - n)Al^{3+}$) with stoichiometric constraints on the global Gd/Ga/Al ratio determined by SEM-EDX.

According to XRD characterization (section 3.2) the B sites with an octahedral oxygen environment were preferably occupied by the Sc^{3+} cations while the Ga^{3+} and Al^{3+} cations were distributed between the B and C sites in the GASGG structure (Table 2). It is worth noting that the Ga^{3+} cations preferably occupy tetrahedral C sites despite their larger ionic

Table 1	Crystallographic data for Gd ₃ Al _{2.3} Ga _{2.7} O ₁₂ and Gd ₃ Sc _{1.3} Al _{1.6} Ga _{2.1} -
O12 (SG /	$a\bar{3}d, Z = 8)$

Composition	Gd ₃ Al _{2.3} Ga _{2.7} O ₁₂	Gd ₃ Sc _{1.6} Al _{1.3} Ga _{2.1} O ₁₂
Lattice parameters: <i>a</i> , Å	12.2615(1)	12.4372(1)
Unit cell volume, Å ³	1843.44(3)	1923.83(3)
Calculated density, $g \text{ cm}^{-3}$	6.59(8)	6.34(9)
$R, R_{\rm w}$ (%) for Bragg	4.95, 5.84	4.82, 5.70
reflections		
$R_{\rm P}$ and $R_{\rm wP}$; $R_{\rm exp}$ (%)	1.77, 3.81, 0.95	2.21, 4.54, 0.82
Goodness of fit (ChiQ)	4.00	5.52
Selected crystal structure data		
n _{f-Gd} A	~ 1	~1
n _{f-Ga} B	0.602(6)	0.637(6)
n _{f-Al} B	1.51(2)	1.60(2)
n _{f-Sc} B		~1
n _{f-Ga} C	0.737(4)	0.717(4)
n _{f-Al} C	1.85(1)	1.80(1)
v		

radius in comparison to Al³⁺ in the GAGG structure. The observed distribution can be explained by a greater covalency of the Ga–O bond in comparison to Al–O as has been proposed for yttrium garnets.^{27,28}

The reliability factors (*R*-factors) show a good agreement between the calculated and the experimental XRD patterns. Fig. 2 displays a portion of the observed, calculated, and difference XRD patterns for GAGG and GASGG. Other numerical characteristics illustrating the quality of the structure refinements are presented in Table 1. The fractional atomic coordinates, isotropic atomic displacement parameters, cation occupancies and main relevant interatomic distances for GAGG and GASGG are listed in Tables 2 and S2 of the ESI.[†]

3.5. Luminescence properties of GAGG:Ce and GASGG:Ce under UV excitation

In this part, we consider the influence of Sc on the luminescence properties of GAGG under UV excitation. The Ce^{3^+} luminescence arises due to electron transitions from the lowest of the 5d levels usually denoted as $5d^1$ to 4f and is represented by a broad emission band peaking around 550 nm in GAGG:Ce. The energy of the UV excitation is sufficient to cause intracenter electron transitions within the Ce^{3^+} ions and ionization of Ce^{3^+} with electron transfer to the conduction band as well as interband electron transitions in the region of the fundamental absorption edge. The partial substitution of Al and Ga with Sc results in the modification of luminescence characteristics due to the change of the (i) energies of the 4f–5d transitions in Ce^{3^+} , (ii) bandgap energy E_g and (iii) energy gap between the conduction band bottom and the $5d^1$ level of Ce^{3^+} .

The energies of the $4f-5d^1$ and $4f-5d^2$ transitions of the Ce³⁺ ions were determined from the absorption spectra (Fig. 3). The related absorption bands were observed at 2.82 and 3.64 eV in GAGG:Ce and 2.86 and 3.62 eV in GASGG:Ce. The decrease of the energy difference Δ_{12} between the 5d¹ and the 5d² levels in GASGG indicates the decrease of the crystal field splitting with scandium introduction into GAGG: Ce.¹³ Sharp absorption peaks at 3.92–4.14, 4.51, 4.9 and 5.02 eV are related to the ${}^{8}S_{7/2}-{}^{6}P_{I}$, ${}^{8}S_{7/2}-{}^{6}I_{I}$ and ${}^{8}S_{7/2}-{}^{6}D_{I}$ transitions in Gd³⁺. A broad absorption peak at 5.3 eV in Cedoped samples arises due to the overlap of the absorption bands related to electron transitions from the 4f to the highenergy 5d levels of Ce3+ and those connected with crystal structure defects and Ce⁴⁺ centers. The transparency cutoff is observed at 5.85 eV in GAGG:Ce, while it is shifted by 0.15 eV to lower energies in GASGG:Ce.

The bandgap energy can be estimated using a simple empirical formula:

$$E_{\rm g} \sim 1.08 \times E_{\rm ex},$$
 (1)

where E_{ex} is an exciton peak position in the luminescence excitation spectrum.²⁹ The excitation spectra peaks connected with exciton creation are observed at 6.18 eV and 6.05 eV for

Table 2 Fractional atomic coordinates, site symmetry, isotropic displacement atomic parameters (U_{iso}) and site occupation for Gd₃Al_{2.3}Ga_{2.7}O₁₂ and Gd₃Sc_{1.3}Al_{1.6}Ga_{2.1}O₁₂

	Atom	x	У	Z	$U_{ m iso}$	Occupancy
GAGG	А	0.125	0	0.25	0.005	Gd^{3^+}
	В	0	0	0	0.005	0.442(7)Ga ³⁺ + $0.558(7)$ Al ³⁺
	С	0.375	0	0.25	0.005	$0.605(5)Ga^{3+} + 0.395(5)Al^{3+}$
	0	0.2812(5)	-0.1006(7)	0.3087(5)	0.005	0
GASGG	А	0.125	0	0.25	0.005	Gd^{3+}
	В	0	0	0	0.005	0.815(9)Sc ³⁺ + $0.185(9)$ Ga ³⁺
	С	0.375	0	0.25	0.005	$0.576(6)Ga^{3+} + 0.424(6)Al^{3+}$
	0	0.2806(6)	-0.0971(7)	0.3140(5)	0.005	0

GAGG:Ce and GASGG:Ce, respectively (T = 10 K, see Fig. 7). Thus, the corresponding bandgap values were estimated as 6.67 eV and 6.53 eV.

Additional studies were performed to verify the E_g value. The absorption coefficient in the region of the fundamental absorption edge is an exponential function of photon energy and can be described by the Urbach formula:

$$\alpha(h\omega) = \alpha_0 \, \exp\left(-\sigma \frac{E_0 - E}{k_{\rm B}T}\right),\tag{2}$$

where α_0 and E_0 are the parameters characteristic of the given compound, σ is the temperature-dependent steepness



Fig. 2 Fragments of the observed, calculated and difference XRD patterns for $Gd_3Al_{2.3}Ga_{2.7}O_{12}$ (a) and $Gd_3Sc_{1.3}Al_{1.6}Ga_{2.1}O_{12}$ (b). Tick marks denote the peak positions of possible Bragg reflections.

parameter, $k_{\rm B}$ is the Boltzmann constant and T is temperature.^{30,31} The fit of eqn (2) to the experimental data is presented in Fig. 4. We used the data obtained for the undoped GAGG crystal because the fundamental absorption edge was distorted in the Ce-doped crystals by the intensive absorption bands related to activator and structural defects. The extrapolations of the fitting lines for different temperatures intersect at a point with $\alpha_0 = 0.7 \times 10^5 \text{ cm}^{-1}$ and $E_0 = 6.52$ eV. The value of E_0 corresponds to the energy of an exciton peak in a given compound.³¹ This value can also be used for the estimation of the bandgap of GAGG taking into account that a more reliable value of E_{g} should be slightly higher, differing by the value of the exciton binding energy.32 Indeed, the bandgap value of 6.67 eV obtained using an empirical formula (1) is higher by 0.17 eV than E_0 that validates the performed bandgap estimation.

Parameter σ in formula (2) is the temperature-dependent steepness parameter, which can be represented as:

$$\sigma(T) = \sigma_0 \frac{2kT}{\omega_{\rm p}} \tanh\left(\frac{\omega_{\rm p}}{2kT}\right),\tag{3}$$

where $\hbar \omega_{\rm p}$ is the average energy of the interacting phonons and σ_0 is the limit of σ at high temperatures. The fit of eqn (3) to the experimental data is presented in the inset to Fig. 4



Fig. 3 Absorption spectra of GAGG (1), GAGG:Ce (2) and GASGG:Ce (3), measured at 300 K.



Fig. 4 Temperature dependence of the absorption coefficient for GAGG, d = 0.9 mm (open dots). The lines represent the fit of eqn (1) to the experimental data. Inset: Temperature dependence of the steepness parameter σ (squares) and its fit by eqn (2) (line).

for $\sigma_0 = 0.39$. The phonon energy was taken as 50 meV that corresponds to typical vibration energies according to the data of Raman spectroscopy in garnets.³³ The σ_0 parameter characterizes the strength of the electron–phonon interaction and allows one to predict whether the self-trapping of excitons may be expected in a given compound. The σ_0 value below unity is a criterion for exciton self-trapping, while the higher value may indicate the existence of free excitons. The obtained value is less than unity, suggesting a strong electron–phonon interaction and exciton self-trapping in GAGG crystals.

The gap between the $5d^1 \text{ Ce}^{3+}$ level and the conduction band bottom depends on the garnet composition.^{34,35} If the gap is narrow (a few tens of eV), electrons can be further transferred from the 5d¹ level to the conduction band due to interaction with the phonons (thermal ionization of Ce^{3+}). The thermal ionization is accompanied by luminescence quenching because electrons transferred to the conduction band can be captured by traps or recombine non-radiatively. This is the most probable process to explain thermal quenching of luminescence in GAGG:Ce and GASGG:Ce. We have measured TSL curves in crystals irradiated with 2.8 eV photons. The irradiation energy corresponds to the 4f-5d¹ transitions within Ce³⁺, whereas both levels are located in the bandgaps of the GAGG:Ce and GASGG:Ce crystals. Upon crystal irradiation at low temperature (80 K) the TSL signal is not detectable, thus demonstrating that the excitation remains on Ce³⁺ ions and no energy transfer to the host takes place (see Fig. S3 and S4 of the ESI[†]). However, the irradiation at elevated temperatures (starting from 250 K in GAGG and 200 K in GASGG) results in the appearance of the TSL signal. The effect is connected with thermally induced electron transitions from the 5d¹ level to the conduction band followed by electron capture by traps. The rise of the TSL signal is accompanied by Ce³⁺ luminescence quenching (Fig. 5), which also supports the conclusion about the thermal ionization of the Ce^{3+} center. This conclusion holds for both GAGG:Ce and GASGG:Ce crystals. The activation energy of the quenching process can be calculated using Mott's formula:³⁶

$$I = \frac{1}{1 + A \exp\left(-\frac{E_{\text{act}}}{kT}\right)},\tag{4}$$

where *T* is the temperature, *A* is the coefficient representing the product of luminescence decay time ($\sim 10^{-8}$ s in case of GAGG:Ce) and Debye frequency ($\sim 10^{13}$ s⁻¹), E_{act} is the quenching activation energy and *k* is the Boltzmann constant. The calculated values were $E_{act} = 0.32$ eV and A =17 180 for GAGG:Ce and $E_{act} = 0.26$ eV and $A = 23\,900$ for GASGG:Ce. As the thermal quenching is connected with the thermal ionization of Ce³⁺, the process activation energy E_{act} was adopted as the energy gap between the 5d¹ level and the bottom of the conduction band.

It is worth noting that the dependence of TSL intensity on irradiation temperature under irradiation with 3.65 eV photons is similar to that obtained for irradiation with 2.8 eV photons (see Fig. 5(b), curve 3). The irradiation energy of 3.65 eV corresponds to the electron transitions from the 4f to the $5d^2$ level of Ce³⁺. The $5d^2$ level is located within the conduction band, so there is no energy barrier for electron



Fig. 5 Temperature dependence of the Ce³⁺ luminescence intensity measured for $\lambda_{\rm em} = 550$ nm at excitation $E_{\rm ex} = 2.7$ eV (curve 1, dots) and its fit using Mott's formula (red line). Curves 2 and 3 represent the dependence of the intensity of the high-temperature TSL peak (440 K for GAGG:Ce and 400 K for GASGG:Ce) on irradiation temperature ($E_{\rm irr} = 2.7$ eV (2) and 3.65 eV (3)). Data are presented in plot (a) for GAGG: Ce and plot (b) for GASGG:Ce.



Fig. 6 Energy level diagram for the GAGG:Ce (left) and GASGG:Ce (right) crystals.

delocalization even at low temperatures. A relatively lowintensity TSL was detected also after irradiation at low temperatures (see Fig. S5 of the ESI†); however, a drastic increase of the TSL intensity after irradiation at higher temperatures and a general similarity of its dependence on irradiation temperature to that obtained for the 2.8 eV irradiation indicates that electron escape from the 5d² level to the conduction band is much less probable than its relaxation to the 5d¹ level.

The energy level diagram for GAGG:Ce and GASGG:Ce is presented in Fig. 6. Based on the diagram it is possible to demonstrate that the lower thermal stability of Ce^{3+} luminescence in GASGG:Ce crystal is connected with a cumulative effect of bandgap decrease and lower crystal field splitting of the 5d levels.

3.6. Influence of Sc on relaxation processes in GAGG under VUV excitation

The excitation in the VUV spectral region corresponds to interband electron transitions in GAGG and allows creating primary electron excitations with energies high enough for the relaxation through inelastic scattering with the creation of secondary e-h pairs relaxing through the thermalization process. The final distribution of the secondary electrons and holes created at the stage of inelastic scattering and possessing energies insufficient to cause further interband transitions is largely determined by the peculiarities of the electronic density of states in the depth of the conduction and valence bands.³⁷ For this reason, the modification of the GAGG band structure connected with scandium introduction is expected to reveal itself in the experimental investigation of energy relaxation processes in the material.

The excitation spectra of Ce^{3+} emission in GAGG and GASGG are presented for the UV-VUV spectral regions in Fig. 7. The intracenter transitions $4f-5d^1$ and $4f-5d^2$ in Ce^{3+} and ${}^8S_{7/2}-{}^6I_{3/2}$ in Gd^{3+} are responsible for the excitation peaks at 2.7, 3.5, and 4.6 eV, respectively. A non-elementary broad

excitation band at 5.3 eV is due to the superposition of the 4f-5d³⁻⁵ Ce³⁺ intracenter transitions with the ligand to metal charge-transfer transition from the O²⁻ levels to the Ce³⁺ ground state.^{8,34} In the region of the fundamental absorption edge, a peak around 5.9-6.2 eV is connected with the direct creation of excitons. The peak shifts to a high-energy region by 0.2 eV with temperature decrease from 300 to 10 K because of the shift of the absorption edge (see Fig. 4 and the discussion in the previous paragraph). The interband electron transitions start at $E \ge E_g$. The most distinctive feature, which differentiates the excitation spectrum of GASGG:Ce from that of GAGG:Ce in this region, is an intensive peak at 6.75 eV. The peak is attributed to electron transitions from the valence band to the 3d Sc states in the conduction band of GASGG:Ce. The position of the peak right above E_{g} indicates that the 3d Sc states participate in the formation of the conduction band bottom. This conclusion is also supported by the results of band structure calculations performed for compounds with similar compositions -Gd₃Sc₂Ga₃O₁₂ and Gd₃Sc₂Al₃O₁₂.¹⁴ It has been shown that the 3d Sc subband with a high density of electronic states is located at the bottom of the conduction band.

Upon further increase of excitation energy, the intensity in the excitation spectrum decreases till 11 eV. The excitation



Fig. 7 Luminescence excitation spectra of GAGG:Ce (a) and GASGG: Ce (b) measured for $\lambda_{em} = 530$ nm at 300 K (1) and 10 K (2). The excitation band denoted as Ce⁴⁺ is ascribed to a superposition of the charge-transfer transitions from the O²⁻ levels to the Ce³⁺ ground state with the 4f-5d³⁻⁵ Ce³⁺ intracenter transitions. The weak peaks denoted as MEE are ascribed to the impact ionization of the Ce³⁺ center in the process of multiplication of electronic excitations (e \rightarrow e + Ce³⁺*).

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with photon energies exceeding E_{g} creates separated electrons and holes, which can be transferred to Ce³⁺ by consecutive capture of hole ($Ce^{3+} + h \rightarrow Ce^{4+}$) and electron $(Ce^{4+} + e \rightarrow Ce^{3+*})$ or by the creation of an exciton as an intermediate stage of relaxation (e + h + Ce³⁺ \rightarrow ex + Ce³⁺ \rightarrow Ce³⁺*). The former mechanism has low probability because the hole cannot be captured by Ce³⁺ due to the large energy distance from the 4f Ce³⁺ level to the top of the valence band in GAGG:Ce and GASGG:Ce (>3 eV, see Fig. 6), which cannot be covered by a multiphonon process.³⁸ Therefore, the energy transfer occurs mainly though excitons. The probability of exciton creation decreases when the excitation energy increases because of the increase of the mean distance between thermalized electrons and holes.^{39,40} This is the reason for the drop of intensity in the excitation spectra of the Ce^{3+} emission in the region from E_g to 11 eV. Temperature also influences the excitation spectra behavior. The intensity of the excitation spectra in the region above E_{α} increases with temperature decrease. The effect is due to the increase of exciton creation probability at low temperatures.⁴¹ The rise of intensity at higher energies (>11 eV) is connected with the multiplication of electronic excitations.⁴² The process is usually observed at $E_{ex} > 2E_g$ when the excitation energy allows electron transitions to the depth of the conduction band, where the energy of hot electrons is high enough for inelastic scattering with the creation of secondary e-h pairs ($e \rightarrow e + e + h$). The rise of the intensity in the excitation spectra of GAGG:Ce and GASGG:Ce starts at ~11 eV, *i.e.* below the $2E_g$ threshold. This allows one to ascribe it to the impact ionization of the Ce³⁺ centers by hot electrons.43,44 The energy difference between the lowintensity peaks at 12.2 and 13.4 eV (1.2 eV) perfectly corresponds to the difference between the 5d¹ and the 5d² Ce^{3+} levels, thus supporting the hypothesis.

The luminescence spectra under the 40 eV excitation at 11 K are represented by a broad emission band peaking at 540–560 nm related to the $5d^{1}$ -4f transitions in Ce^{3+} and narrow emission lines at ~313 nm related to the ${}^{6}P_{j}-{}^{8}S_{7/2}$ transitions in Gd^{3+} (Fig. 8(a)). Additional narrow emission lines supposedly related to the presence of uncontrolled rare-earth impurities were also observed in the 680–720 nm region. Scandium introduction into GAGG:Ce results in the (i) increase of integrated emission intensity in the 290–750 nm region by 25% and in (ii) intensity redistribution between the emission bands related to Gd^{3+} and Ce^{3+} . The intensity of the Gd^{3+} emission at 313 nm is suppressed, while the intensity of the Ce^{3+} emission is increased in GASGG:Ce.

The relaxation of primary e-h pairs created by the 40 eV photons comprises the stages of inelastic scattering with the creation of secondary e-h pairs, thermalization and energy migration to the Ce^{3+} and Gd^{3+} emission centers. The excitation energy exceeds $6E_g$ and allows creation of up to 6 e-h pairs due to the inelastic scattering of primary hot electrons. The higher density of electronic states at the bottom of the conduction band due to the contribution of the 3d Sc states increases the relative number of secondary



Fig. 8 Luminescence spectra of GAGG:Ce (1) and GASGG:Ce (2) at E_{ex} = 40 eV at T = 11 K (a) and 300 K (b).

electrons with low kinetic energy after the scattering. As a result, this reduces energy losses for the thermalization of charge carriers and increases the total number of e-h pairs created at the stage of inelastic scattering of primary hot electrons. This is the reason for the integrated emission intensity increase in GASGG:Ce.

The origin of the electronic states forming the bottom of the conduction band is crucial for the competition between the Gd³⁺ and the Ce³⁺ emission centers for the thermalized charge carriers. In gadolinium garnets, the bottom of the conduction band is formed mainly by the 5d states of Gd³⁺ with a small admixture of electronic states of other cations.¹⁴ Therefore, the migration of thermalized electrons to the Ce³⁺ emission centers occurs through the Gd³⁺ electronic states that favors energy transfer to the Gd³⁺ emission centers as well. The participation of the 3d Sc states in the formation of the conduction band bottom causes the redistribution of energy transfer efficiencies between the two radiative relaxation channels in GASGG:Ce. On the one hand, it prevents electron migration via Gd states leading to the suppression of the Gd3+ emission. On the other hand, the increase of the Ce3+ emission intensity in GASGG:Ce indicates that 3d Sc electronic states facilitate energy transfer to the Ce³⁺ emission centers.

When temperature is increased up to 300 K the influence of Sc on the energy transfer processes in GASGG:Ce is mitigated by the thermal quenching effect. The luminescence spectra measured under the VUV excitation at 295 K are presented in Fig. 8b. The emission of Gd^{3+} is completely quenched at RT.^{45,46} Only the Ce³⁺ emission band is observed, whereas its intensity in GASGG:Ce is lower by \sim 35% than that in GAGG:Ce. The decrease is explained by partial thermal quenching of the Ce³⁺ luminescence in GASGG:Ce (see Fig. 5).

The luminescence decay curves measured under electron beam excitation are presented in Fig. 9. The curves can be approximated by the sum of four exponential functions (see Table 3). The decrease of decay times in a Ca-co-doped GAGG:Ce crystal is due to the presence of Ce⁴⁺ ions stabilized by the Ca²⁺ impurity. The energy transfer to cerium emission centers becomes faster as no sequential trapping of hole and electron by a Ce³⁺ ion is necessary in such a case. This may lead to a considerable shortening of luminescence rise time as well as to some acceleration of the emission decay (see also ref. 4, 8, 10 and 47). Partial substitution of Al and Ga cations with Sc also results in the acceleration of decay processes even without Ca co-doping. However, in this case, the acceleration is mainly attributed to a moderate thermal quenching of Ce³⁺ emission at 300 K (see Fig. 5). In particular, thermal quenching is responsible for the acceleration of decay times, which is characteristic for 5d-4f electron transitions in Ce^{3+} (τ_{dec} < 60 ns). The decay components with τ_{dec} >60 ns are caused by the delay in energy transfer to Ce³⁺ connected with intermediate capture of charge carriers at shallow traps. The energy migration via the Gd sublattice is responsible for the appearance of slow components in the scintillation response of Gd-containing scintillators as well.⁶ The delayed decay components become faster and their amplitude decreases in GASGG:Ce. The introduction of Sc into GAGG:Ce suppresses energy transfer to the Gd³⁺ emission centers and may also prevent energy migration via the Gd sublattice, thus improving the scintillation response in GASGG:Ce.



Fig. 9 The decay curves for GAGG:Ce (black), GAGG:Ce,Ca (red curve), GASGG:Ce (green curve) and GASGG:Ce,Ca (blue curve) under electron beam excitation at RT. The enlarged initial part of decay curve is presented in the inset.

Table 3 Decay times (in ns) derived from the approximation of decay curves presented in Fig. 9 by four exponential components. The amplitude ratio of component *i* is calculated as $A_i/(A_1 + A_2 + A_3 + A_4) \times 100\%$ and is presented in brackets

Crystal	GAGG:Ce	GAGG:Ce,Ca	GASGG:Ce	GASGG:Ce,Ca
$ \begin{array}{c} \overline{\tau_1} \\ \overline{\tau_2} \\ \overline{\tau_3} \\ \overline{\tau_4} \end{array} $	65 (63%)	34 (50%)	4 (15%)	3 (25%)
	145 (33%)	90 (47%)	28 (54%)	23 (42%)
	322 (2%)	357 (3%)	111 (28%)	91 (30%)
	624 (2%)	677 (<1%)	486 (3%)	446 (3%)

It is worth noting that the decay times obtained in the current study for the GASGG:Ce crystals are considerably shorter than those reported earlier for crystals with rather similar composition – $Gd_{2.97}Ce_{0.03}Sc_2Al_3O_{12}$. The decay curve with 122 ns decay time and 60 ns rise time under gamma excitation has been reported in ref. 17. Better decay characteristics in our samples may be connected with the slightly different composition of the gadolinium garnet as well as with the lower concentration of defects which slow down energy transfer to the Ce³⁺ emission centers.

Conclusions

The structural and luminescence properties of Gd_{2.97}Ce_{0.03}-Ga₃Al₂O₁₂ (GAGG:Ce) and Gd_{2.97}Ce_{0.03}Ga_{2.5}Sc₁Al_{1.5}O₁₂ (GASGG: Ce) crystals were studied. Elemental analysis allowed determination of the real composition of the studied crystals as Gd₃Al_{2.3}Ga_{2.7}O₁₂ and Gd₃Sc_{1.3}Al_{1.6}Ga_{2.1}O₁₂. Both crystals are characterized by the space group $Ia\bar{3}d$. Unit lattice parameters were determined as a = 12.2654(4) Å and a =12.4396(5) Å for GAGG and GASGG, respectively. Crystal structure refinement was performed using the Rietveld method. The distribution of Al/Ga/Sc cations between octahedral and tetrahedral sites was determined, whereas Ga was shown to preferably occupy tetrahedral sites in the garnet structure. Partial substitution of Al and Ga with Sc results in the decrease of the bandgap value from 6.67 eV in GAGG to 6.53 eV in GASGG and in the lower crystal field splitting of the 5d Ce³⁺ levels. It is shown that the 3d Sc states participate in the formation of the conduction band bottom. A pronounced peak at 6.75 eV appearing in the excitation spectrum of GASGG:Ce is related to electron transitions from the valence band to 3d Sc states at the conduction band bottom. The modification of the conduction band structure influences energy relaxation processes and energy transfer to emission centers. It results in the enhancement of the intensity of the Ce³⁺ emission centers while the Gd³⁺ emission intensity decreases at 11 K. However, the light output of GASGG:Ce under ambient conditions is lower than in GAGG:Ce due to the thermal quenching effect connected with the thermal ionization of the $5d^1 \text{ Ce}^{3+}$ level. The acceleration of emission decay in GASGG:Ce is observed and attributed to the partial thermal quenching of Ce³⁺ emission and to the suppression of energy transfer via the Gd³⁺ sublattice.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from the grant RFBR 20-02-00688, from Ministry of Science and Higher Education of the Russian Federation, State Contracts 3.2794.2017/4.6, 11.5583.2017/7.8, from STSM Grant from the COST Action TD1401 "FAST" as well as from the Estonian Research Council (project PUT PRG111) and ERDF funding in Estonia granted to the Centre of Excellence TK141 (Project No. 2014-2020.4.01.15-0011) is gratefully acknowledged. The measurements at MAX-lab were performed within the proposals 20180411 and 20190244. The research leading to this result has been supported by the project CALIPSOplus under the Grant Agreement 730872 from the EU Framework Programme for Research and Innovation HORIZON 2020. We are grateful to Dr. V. Pankratov for his help during experiments at MAX-lab.

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