



Research article

Lanthanoid-doped quaternary garnets as phosphors for high brightness cathodoluminescence-based light sources



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ABSTRACT

Gadolinium-yttrium- aluminum-gallium garnets (GYAGG) doped and codoped with Eu, Tb, and Ce were manufactured as ceramics to develop long-wavelength phosphors for high-brightness white light sources based on cathodoluminescence (CL). The CL light yield (LY) of Tb-doped ceramics at high-intensity electron beam excitation is shown to be more than twice as high as that of the conventional phosphor YAG:Ce, whereas codoping with Eu to redshift the chromaticity results in reducing the LY approximately to the level of YAG:Ce. The LY might be substantially improved by using a mix of Tb- and Eu-doped GYGAG powders instead of a single codoped GYGAG to produce ceramic phosphor. The high LY is explained by favorable contribution of Gd sublattice in excitation transfer to activator ions. Chromaticity of phosphors GYGAG:Tb, Eu can be tuned in a wide range by varying the ratio of Tb to Eu concentration. They are radiation resistant and stable in the temperature range from 300 to 450 K.

1. Introduction

During the two decades after the breakthrough in the production of InGaN-based high-brightness light emitting diodes (LEDs) [1], the penetration of LED-based white light lamps into the global general lighting market is already above 50% [2] and has a good acceleration to expand further. Currently, commercial white LED-based lamps contain phosphor-conversion white LEDs with YAG:Ce as a sole phosphor to provide a high efficiency at a moderate price, though at a lower color rendering of the cool white light, or with a phosphor combination to emit warm-white light with improved color rendering [3]. Unfortunately, the increased driving current for the InGaN-based white LEDs to increase their brightness results in a substantial efficiency droop of InGaN emission [4]. To mitigate the problem, using laser diodes (LD) instead of LEDs is suggested [5], and this approach is being successfully implemented in such niche applications of white light as automotive headlamps [6] and digital projection [7] as well as for general lighting [8]. It is worth noting that the power conversion efficiency of blue LDs is approximately 30%,

i.e., more than twice lower than that of blue LEDs at low driving current [9]. Moreover, phosphor degradation becomes an issue under intense illumination by LD emission [10]. Therefore, radiation-hard phosphors are in especial demand for coupling with LDs to develop high-brightness white light sources.

Excitation of the radiation-hard phosphors by electron beam is another alternative for the development of the extremely bright white light sources. The conventional sources like electron guns and cathode ray tubes (CRTs) are too bulky and expensive for being exploited in light sources, however, cold electron-emitting cathodes might be an appropriate option. In particular, the cold electron emitters based on carbon nanotubes (CNT) are quite compact, require moderate voltages, and emit electrons at a high efficiency [11]. This excitation source might be an attractive alternative to semiconductor LDs for certain lighting applications. Lighting lamps with CNT emitters were reported two decades ago [12, 13]. Phosphors exploited in CRT-based television (Y₂O₃:Eu for red, ZnS:Cu, Al for green, and ZnS:Ag for blue) have been used for the first lamps with CNT cathode and ensured stable performance for 10000 h

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Table 1. Composition of GYAGG-based phosphors studied.

Sample number	Sample label	Composition
1	GYGAG:Tb	$Gd_xY_{2.85-x}Tb_{0.15}Al_2Ga_3O_{12}$ ($x = 1.13$)
2	GYGAG:Ce	$Gd_xY_{2.97-x}Ce_{0.03}Al_2Ga_3O_{12}$ ($x = 1.19$)
3	YAG:Ce	$Y_{2.97}Ce_{0.03}Al_5O_{12}:Ce$
4	GYGAG:Eu	$Gd_xY_{2.85-x}Eu_{0.15}Al_2Ga_3O_{12}$ ($x = 1.2$)
5	GYGAG:Tb, Eu-1	$Gd_xY_{2.85-x}Eu_{0.075}Tb_{0.075}Al_2Ga_3O_{12}$ ($x = 1.2$)
6	GYGAG:Tb, Eu-2	$Gd_xY_{2.7-x}Eu_{0.15}Tb_{0.15}Al_2Ga_3O_{12}$ ($x = 1.2$)
7	GYGAG:Tb, Eu-3	$Gd_{1.2}Y_{1.65}Tb_{0.15}Al_2Ga_3O_{12} + Gd_{1.2}Y_{1.65}Eu_{0.15}Al_2Ga_3O_{12}$

[12]. The white cathodoluminescence (CL) lamps with higher brightness and longer lifetime require phosphors with substantially higher tolerance to high-intensity electron beam.

Among phosphors, the scintillators are a family of materials providing a high tolerance to ionizing radiation. Radiation hardness is one of the key properties of scintillating materials in many applications, especially in high-energy physics experiments. In particular, radiation hard cerium-doped garnet-type single crystals are currently being successfully developed as scintillators for high-energy physics applications (see [14] for review). The garnet-type structure has cubic crystal symmetry and is flexible to accept high concentrations of dopants without substantial distortion of the crystalline structure. The concentration of dopants acting as the centers of radiative recombination and, consequently, the light emission efficiency might be further increased by exploiting ceramics instead of single crystals. Recently, transparent garnet ceramics

were produced by hot pressing [15] and translucent by 3D printing [16]. Recently, $Gd_3Al_4GaO_{12}:Ce^{3+}$ (GAGG:Ce) ceramics is suggested as a phosphor for high-power white light sources based on LEDs and LDs [17].

The phosphor-conversion CL-based white light sources require at least two phosphors of appropriate chromaticity. Blue phosphors are presumably available [3] and are out of scope of this paper. The flexibility in tuning the phosphor chromaticity in long-wavelength range is demonstrated in photoexcited quaternary single-crystal garnets $Gd_3Ga_3Al_2O_{12}$ codoped by Eu, Tb, and Ce [18], whereas GAGG:Ce transparent ceramics are demonstrated to be promising color converters for LED- and LD-based white lamps [17]. In this paper, we study Eu-, Tb-, and Ce-doped ceramic garnets under high-intensity electron beam and X-ray excitations in order to develop prospective CL phosphors. Yttrium-containing $(Gd,Y)_3Al_2Ga_3O_{12}$ (GYAGG) was used as the host matrix for the phosphors under study, since the scintillation properties of phosphors with such quaternary host garnet composition were found to be superior to those achieved in Gd-based ternary garnets [19] and efficient Tb emission is demonstrated in GYAGG:Tb ceramics [20].

The surface morphology of the phosphors has been characterized by scanning electron microscopy. Spectroscopy of the emission by the phosphors with different doping and matrix composition has been performed at electron beam and X-ray excitation, chromaticity of the phosphors has been estimated using the emission spectra. The stability of emission properties has been studied in the range from 300 to 425 K.

2. Experimental

2.1. Samples

A set of ceramic samples containing garnets GYAGG activated by RE (Ce, Tb, and Eu) was fabricated to vary chromaticity of these phosphors

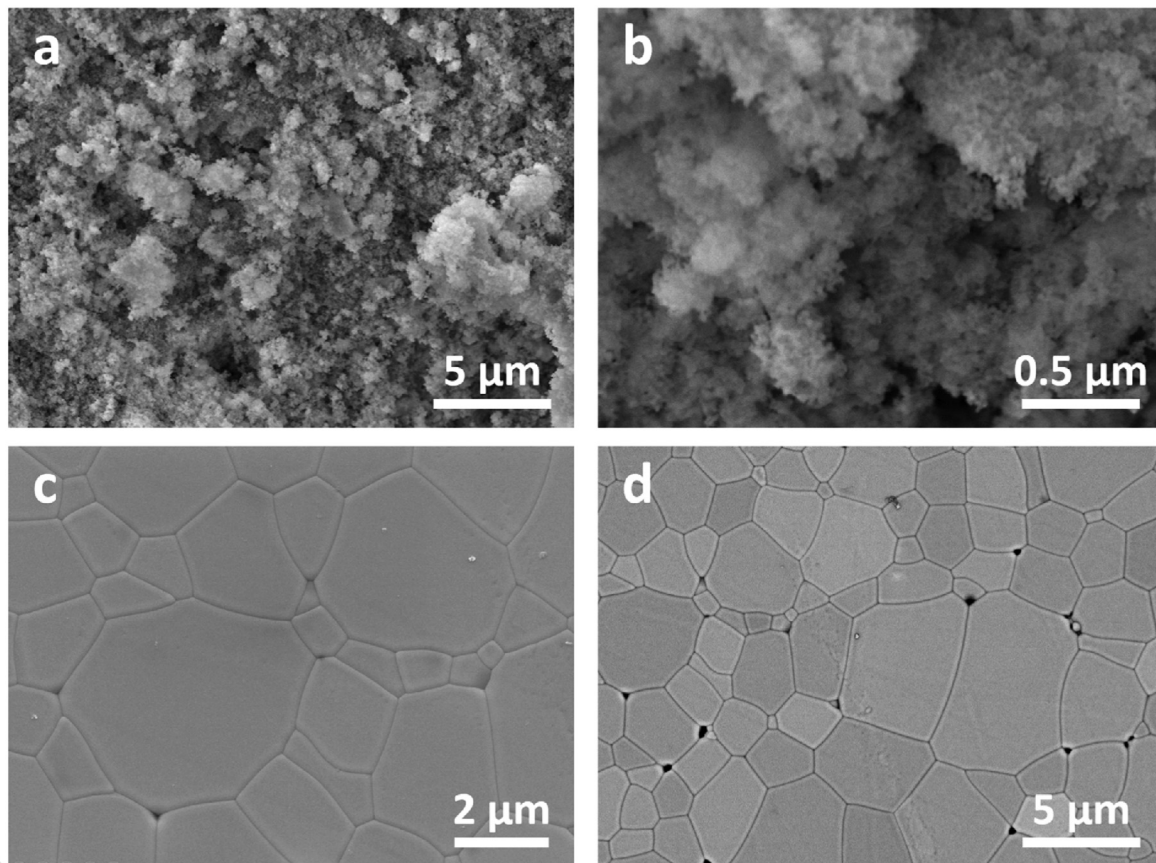


Figure 1. Scanning electron microscopy images of $Gd_xY_{2.85-x}Eu_{0.075}Tb_{0.075}Al_2Ga_3O_{12}$ ($x = 0.83$), precipitate calcined at 900 °C (a,b), and mirror-polished ceramics thermally etched at 1250 °C and recorded in secondary electrons (c) and backscattered electrons (d) modes.

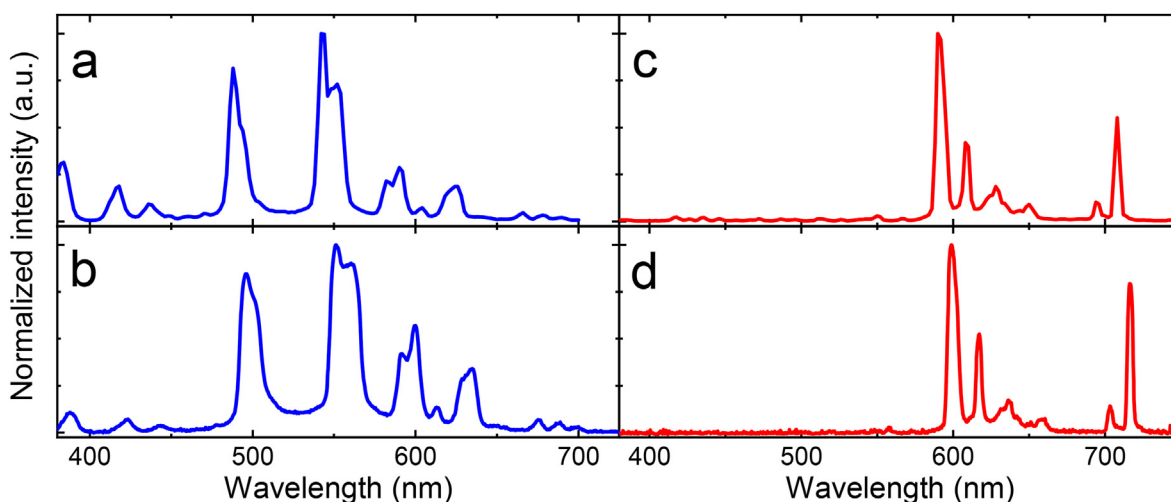


Figure 2. Room temperature luminescence spectra of samples GYGAG:Tb (a,b) and GYGAG:Eu (c, d) under X-ray (a, c) and electron beam (b, d) excitation.

and to test their efficiency and resistance to irradiation by electrons. Starting powders were fabricated by coprecipitation method. The coprecipitation provides a product with a homogeneous element distribution, allowing the formation of the garnet phase at temperatures low enough to avoid Ga evaporation. To produce samples corresponding to formulas listed in Table 1, the mixed nitrate solutions containing Gd, Y, Tb, Eu, Al, Ga, and Ce in appropriate ratios were prepared. Individual nitrate solutions were made by dissolving Gd (4N5), Y (5N), Tb (4N), and Eu (4N) oxides and aluminum hydroxide (5N) in high-purity nitric acid and Ga (4N5) and Ce (3N5) nitrates in high-purity water. A slow addition of the solution to a 2 mol/L solution of NH_4HCO_3 under constant stirring was used to produce precipitate. The precipitates were filtered, washed with water twice and with isopropyl alcohol once, dried in an air-ventilated oven (100 °C, 8 h) and calcined (900 °C, 2 h) to prepare samples 1–6. A planetary ball mill containing corundum grinding medium was used to produce particles with a median particle size of 1.0–1.5 μm . A uniaxial pressing at 64 MPa was used to create 1.5 mm-thick green bodies of 20 mm in diameter. The tablets were sintered in an air

environment at 1600 °C. The resulting ceramic samples were translucent and had a density of $\sim 98\%$ of the theoretical value.

In addition, to avoid a luminescence quenching interaction of different dopants, one sample was prepared as a mix of two phosphors containing either Tb or Eu in the GYAGG host. The GYAGG:Tb and GYAGG:Eu powders were calcined individually at 1300 °C, separately ball-milled, then mixed at the ratio of 1:1 in a ball mill for 15 min. The resulting powder was uniaxially pressed and sintered as described above.

Scanning electron microscopy (SEM) images demonstrating the major steps in the sample production recorded using microscope Jeol JSM 7100 F in secondary electrons and backscattered electrons modes at 6 kV are presented in Fig.1 (a-d).

GYGAG ceramics heavily doped by Ce, Tb, and Eu and ceramic YAG:Ce for comparison were fabricated as the first set of samples. The cerium concentration in the samples was approximately a factor of ten higher than the typical concentration (~ 1000 ppm) in single-crystalline garnets pulled from the melt by the Czochralski method. The Tb index in different samples was in the range 0.075–0.15, close to the value providing the highest luminescence yield in Al-based ternary garnets, as reported in [21]. Two GYAGG samples containing Tb and Eu at different proportions and one more sample containing a mix of two GYAGG doped either by Tb or Eu were prepared in the second sample set. All the samples were translucent, which is common in practice of the materials for different kinds of illumination.

2.2. Characterization techniques

The luminescence properties were studied under excitation by X-rays and a 150 keV electron beam. The X-ray source URS-55A equipped with the X-ray tube BSV-2 (Cu anode, 30 kV, 10 mA) was utilized to obtain the X-ray excited luminescence (XRL) spectra. The luminescence was measured with a spectral resolution 2 nm by MDR-23 (LOMO) coupled to photomultiplier FEU-106 in a photon counting mode.

The 150 keV pulsed electron beam was provided by a small-size pulsed accelerator MIRA-2D (electron tube IMA-2-150E, current density 1 A/cm², pulse duration ~ 20 ns), which was used for CL excitation. The spectrograph FICS 77443 (Oriel Instruments) coupled to a CCD detector had a spectral resolution of 2.4 nm and was used to record the CL spectra. The luminescence was collected at $\sim 45^\circ$ to the direction of electron beam. The 0.18 mm-thick Al filter was installed at the output of the electron tube to avoid signal saturation in the detection system. The certified film dosimeter SO PD (E)-1/10 (VNIIFTRI) was used to measure the absorbed dose during the exposure. It was established that an absorbed dose rate of 0.5 kGy/s corresponds to an absorbed dose of 2.0 kGy.

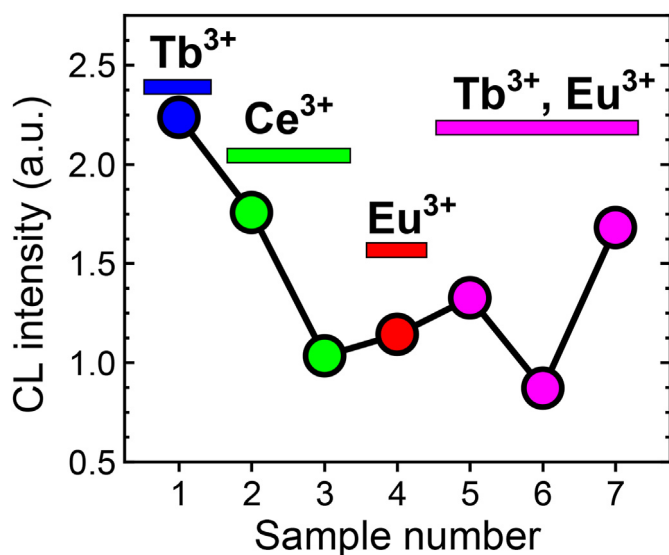


Figure 3. Cathodoluminescence intensity spectrally integrated in the range 300–800 nm measured at high flux of electron beam for the samples listed in Table 1. The dopants are indicated by horizontal bars, the intensity is normalized to that of YAG:Ce.

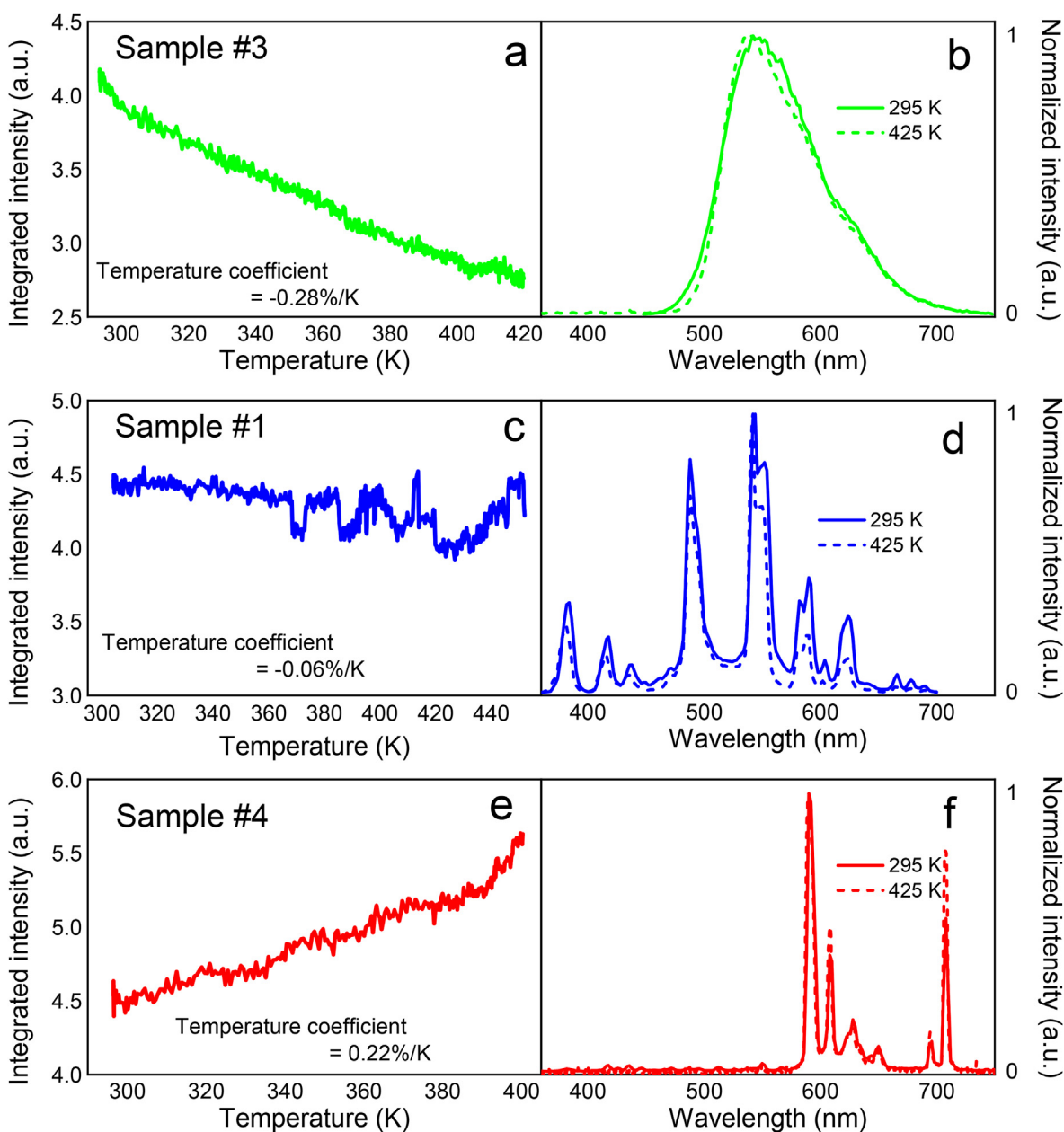


Figure 4. Temperature dependence of the intensity of X-ray luminescence integrated in spectral range 300–700 nm (a, c, e) and luminescence spectra at room (295 K) and elevated (425 K) temperatures (b, d, f) of YAG:Ce (a,b), GYGAG:Tb (c,d), and GYGAG:Eu (e,f).

3. Results

Figure 2(a,b) demonstrates the XRL and CL spectra of GYGAG:Tb. The spectra consisting of lines distributed over the entire visible range are typical of Tb^{3+} ions in garnet-type crystals [20]. The $^5D_3 \rightarrow ^7F_j$ transitions cause the blue part of the spectrum, whereas the luminescence bands in the green-red range are due to the transitions $^5D_4 \rightarrow ^7F_j$. The XRL and CL spectra of Eu-doped GYAGG (see Figure 2 (c, d)) consist of several lines in the red region and are quite similar to the photoluminescence spectra observed in Eu-doped ternary garnet GYAG [22]. Thus, the combination of the spectra of GYGAG:Tb and GYGAG:Eu enables fine tuning of the chromaticity of the composite phosphor.

The studied phosphors exhibited a high cathodoluminescence light yield (LY) under high-intensity electron beam excitation, in spite of possible light yield saturation [23], which is typical of phosphors with slow luminescence decay [24, 25]. The relative LY of these samples was measured as the ratio of the spectrally-integrated CL normalized to the

intensity of the electron beam. The data are compared in Figure 3 to that of YAG:Ce, which was used as a reference sample.

GYGAG:Tb phosphor exhibited the highest CL yield, which is by a factor of 2.25 higher than that in YAG:Ce. The enhancement factor of GYGAG:Ce is 1.75, whereas the yield of GYGAG:Eu is similar to that in YAG:Ce. The CL yield in GYAGG codoped with Tb and Eu is also close to that of YAG:Ce. Note that the yield of sample #7 fabricated using two powders containing the same host matrix doped by either Tb or Eu is substantially higher than that of samples #5 and #6 prepared using one powder of a Tb- and Eu-codoped host.

The intended utilization of the phosphor at a high excitation energy deposition requires thermal stability of the yield and the luminescence spectrum. The temperature stability of XRL spectrum and spectrally-integrated intensity are compared with these parameters of YAG:Ce in Fig. 4. As for YAG:Ce garnet, GYAGG doped with Tb or Eu shows a fairly good spectral stability as the temperature is increased from room temperature up to 425 K. The LY temperature coefficient of GYAGG:Tb in the

temperature range 300–400 K equals $-0.06\%/K$, i.e., is substantially smaller than that for the conventional phosphor YAG:Ce ($-0.28\%/K$). GYGAG:Eu has a small positive LY temperature coefficient of $+0.22\%/K$. Meanwhile, the coefficient of GYAGG:Ce is by a factor of three larger than that in YAG:Ce. These results show that the emission of Tb^{3+} and Eu^{3+} in quaternary matrix GYAGG is quite stable in the temperature range important for exploitation of these phosphors under electron beam excitation, in contrast to the emission of Ce^{3+} GYAGG.

4. Discussion

The measured luminescence spectra can be explained by the energy spectrum of levels for ions Tb^{3+} , Eu^{3+} , and Ce^{3+} compiled in accordance with the “zig-zag” diagram reflecting the relative positions of the levels of trivalent ions [26]. The scheme is presented in Figure 5. The luminescence spectrum and efficiency in Gd-containing quaternary garnets are strongly affected by the formation of a sublattice of Gd ions in the crystal structure. The sublattice results in the formation of energy levels inside the band gap, the lowest of which is built by Gd state $6P(2f)$, as depicted in Figure 5 by taking into account the position of the ground state of Gd in the valence band [27]. At high Gd concentrations, the sublattice might serve as an efficient channel for excitation transfer. The excitation of matrix-building Gd^{3+} ion can be transferred from site to site in the sublattice as Frenkel exciton.

The excitation transfer through the Gd sublattice is of especial importance for Eu-doped GYAGG. There is a substantial difference between the trivalent europium and two other activator ions, Ce and Tb. Contrary to Ce^{3+} and Tb^{3+} ions, Eu^{3+} ion has no interconfigurational states $4f^{n-1}5d$ in the band gap of oxide garnets. Such states are favorable for excitation capturing from the matrix host [28]. Nevertheless, we found that GYAGG:Eu phosphor exhibits a high CL yield even slightly exceeding that of YAG:Ce. Apparently, the excitation of Eu^{3+} ions occurs via the gadolinium sublattice as a result of Frenkel exciton migration. Charge transfer transitions $O^{2-} \rightarrow Eu^{3+}$ indicated in Figure 5 are feasible in garnets [29] and might also contribute to the populating of Eu^{3+} .

A substantial role of Gd^{3+} subsystem in the excitation transfer to Ce and Tb activators is discussed in detail in [20]. The Gd subsystem might serve as a reservoir for the accumulation of nonequilibrium electrons at the lowest $6P$ state. The radiative recombination time for the electrons at $6P$ is in a wide time domain, from micro-to milliseconds [30], thus, a

long-range migration of Frenkel excitons as excitation along to states $6P$ and $8S$ is expected. When the optical transitions in Gd^{3+} subsystem and the electronic transitions of activator levels are in resonance, the excitation transfer from Frenkel exciton becomes an effective tool to increase the LY of Gd-based phosphors. The fine tuning of the resonance conditions can be accomplished by the variation of Gd/Y ratio in the material composition, as demonstrated for Ce- and Tb-doped scintillators [20]. In Ce-doped Gd-containing garnets, the Gd sub-system contributes to the population of the radiative level of Ce^{3+} via the interaction between Frenkel exciton and transition $2F_{5/2} \rightarrow 5d_2$. When holes are quickly delocalized from state $8S$ to the top of the valence band, the resonant transfer processes $2F_{5/2} \rightarrow 5d_1$ and $6P \rightarrow VB_{top}$ (top of the valence band) contribute to the population of the radiative level of ion Ce^{3+} .

In GYAGG doped with Eu, only charge transfer transition may be in a good resonance with Frenkel excitons. The delocalization of holes to the top of the valence band opens another channel due to transfer between $7F_0 \rightarrow 5D_1$ and $6P \rightarrow VB_{top}$. Due to poor resonance conditions, however, this transfer is less effective than that in the same host matrix doped with Ce, so the resulting LY of CL in Eu-doped sample #5 is smaller. In GYAGG:Tb, a few levels are in a good resonance: $8S \rightarrow 6P$ and $7F_0 \rightarrow 4f^7 [8S]5d_1$ [HS], $7F_0 \rightarrow 5D_4$ (Tb^{3+}) and $6P$ (Gd^{3+}) $\rightarrow VB_{top}$. As a result, Tb-doped samples exhibit the highest LY even at a high-intensity excitation by electron beam.

It is worth noting that codoping with Eu quenches the Tb emission, as evident in the LY results provided in Figure 4 (compare sample 1 with samples 5, 6). However, no exceptional quenching of transitions $5D_3 \rightarrow 7F_j$ of Tb^{3+} , which was observed at photoexcitation in ternary garnet [18], was detected in the CL spectra of the samples under study. Moreover, we demonstrate that the quenching effect can be substantially suppressed in the ceramic phosphor fabricated by using a mix of GYAGG doped by either Tb or Eu instead of a single GYAGG codoped by the ions. The CL light yield of the mixed ceramics (Figure 5, sample #7) was twice as high as that of the codoped ceramics (sample #6) containing approximately the same content of Tb and Eu.

The CIE chromaticity coordinates corresponding to the emission spectra of Ce- and Tb-doped GYAGG and YAG:Ce, for comparison, are plotted on the chromaticity diagram in Figure 6(a). The incorporation of gadolinium and gallium into the Ce-doped matrix redshifts the chromaticity point. Doping of GYAGG by Tb instead of Ce shifts the chromaticity point into the green region.

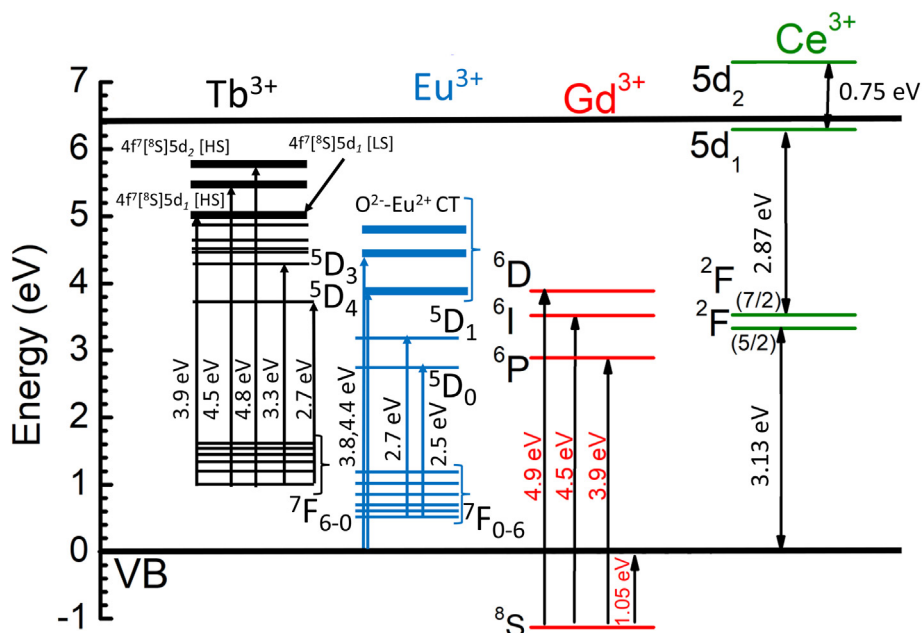


Figure 5. Scheme of the electronic energy levels of Tb^{3+} , Eu^{3+} , Gd^{3+} , and Ce^{3+} in gadolinium-yttrium-aluminum-gallium garnets.

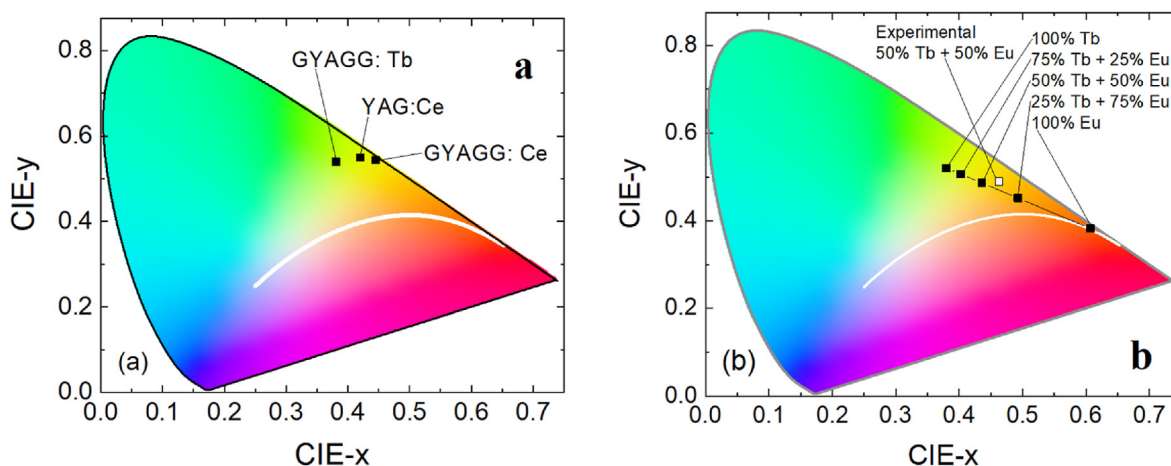


Figure 6. CIE chromaticity diagram with points corresponding to Ce- and Tb-doped garnets under study (a), points calculated for different Tb/Eu ratios in GYAGG matrix (black squares), and the point (white square) corresponding to the ceramic phosphor produced using a 50/50 mix of GYAGG:Tb and GYAGG:Eu (b). White line shows the Planckian locus.

To shift the chromaticity of GYAGG-based phosphors to the red region, europium was used as codopant for the phosphors. Changing the ratio between Tb and Eu ions enables tuning the chromaticity point in a wide range along the line connecting the points corresponding to GYAGG doped solely with Tb and Eu. Several intermediate points corresponding to different Tb/Eu ratios were calculated and plotted on the line connecting the terminal points in Figure 6(b). This wide-range tunability enables easy matching the chromaticity of GYAGG:Tb, Eu CL phosphor with an appropriate blue phosphor to produce white light. The chromaticity point of the ceramic phosphor prepared as a mix of GYAGG:Tb and GYAGG:Eu is shown in Figure 6(b) by a white square. It lays quite close to the corresponding point calculated using the spectra of GYAGG:Tb and GYAGG:Eu.

The XRL spectra measured above room temperature up to 425 K evidence thermal stability of the phosphors, both solely doped with Eu or Tb and codoped ones. The good spectral and intensity stability of the lanthanoid-doped garnets under study at elevated temperatures enables exploitation of these ceramic materials as phosphors in white light sources of extremely high brightness. Such sources might have a niche application for illumination of stadiums, museums, and other large spaces. These applications were targeted by sulfur electrodeless discharge lamps, which were introduced decades ago [31] but are being used with changeable and limited success up to now despite some gradual improvements [32, 33, 34]. On the other hand, the efficient and radiation hard phosphors might be prospective for the development of indirect energy converters of radioisotope radiation. Radioisotope thermoelectric generators containing Pu-238 fuel and ~6% efficient PbTe thermoelectric converters were exploited in space missions from 1961 to 1975 and were followed by improved versions of these generators and by radioisotope thermophotovoltaic energy converters producing electricity directly from radiant heat by means of infrared-sensitive photovoltaic cells ensuring a higher specific power [35]. A tradeoff between the losses in efficiency due to heating of the cell and the weight of the heat rejection radiator to keep the temperature at acceptable level is the key problem of these conventional converters. A two-step device first converting the ionizing radiation of the radioisotope to light in a radiation-hard and temperature-tolerant phosphor, then transforming the light to electric current using a remote photodetector might be an attractive solution in space and certain ground applications. GYAGG (Ce) ceramics is already recognized to be very radiation hard material [36]. The high-light-yield ceramic mix of GYAGG:Eu and GYAGG:Tb and ceramic GYAGG:Eu with the emission spectrum in red region well-matched with the sensitivity spectrum of mature photodetectors is a good candidate for such two-step radioisotope photovoltaic converter.

5. Conclusions

Ceramic garnets $(\text{Gd,Y})_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ (GYAGG) doped and codoped by Eu, Tb, and Ce were fabricated by coprecipitation and future sintering, and their spectra, light yield, and emission stability in the temperature range from room temperature to 425 K were studied at electron beam and X-ray excitation. The cathodoluminescence light yield of Tb- and Eu-doped GYAGG ceramics is shown to be more than twice higher and approximately equal to that of the conventional phosphor YAG:Ce. The high light yield is interpreted by the contribution of Gd-based sublattice in the energy transfer to the activator ions. The quenching of Tb emission by Eu ions introduced as codopant to redshift the chromaticity of the phosphor might be substantially suppressed in ceramics fabricated by mixing powders of GYAGG solely doped either with Tb or Eu instead of producing a single codoped GYAGG:Tb, Eu ceramic phosphor. The irradiation-tolerant phosphors might be exploited in extremely bright white light lamps for illumination of large spaces and in radioisotope photovoltaic converters with radiation-light-current conversion enabling a spatial separation of radiation-sensitive conversion devices from radiation source and easing the radiation shielding.

Declarations

Author contribution statement

M. Korjik, G. Dosovitskiy, V. Retivov: Conceived and designed the experiments; Wrote the paper.

A. Bondarau, V. Dubov, K. Gordienko, P. Karpuk, V. Mechinsky, D. Tavrunov: Performed the experiments.

I. Komendo, V. Pustovarov: Analyzed and interpreted the data.

D. Kuznetsova: Analyzed and interpreted the data; Wrote the paper.

V. Smyslova: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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