07

Luminescent ceramics LuGdAG:Ce with high color rendering index: Effect of thermal annealing on luminescent properties

© A.A. Kravtsov[1], V.A. Lapin[1], E.V. Medyanik[1], L.V. Tarala[1], O.V. Devitsky[1,2]

[1] North Caucasus Federal University, Stavropol, Russia
[2] Federal Research Center Southern Scientific Center of the Russian Academy of Sciences, Rostov-on-Don, Russia
E-mail: v2517@rambler.ru

The optical properties of LuGdAG:Ce ceramics with gadolinium content ranging from 0 to 100 atomic percent were investigated. The study demonstrated that as the gadolinium content increases, the light transmittance of the ceramics also rises, while the luminescence spectrum shifts toward the red region. Additionally, the color temperature decreases, luminescence efficiency declines, but the color rendering index (R_a) improves. Following annealing in air, a significant enhancement in luminescence was observed in ceramics with high gadolinium content, although this was accompanied by a reduction in R_a. These findings indicate that LuGdAG:Ce ceramics hold promise for use in warm white light sources with a high color rendering index.

Keywords: Ceramics, luminescence, LuGdAG:Ce, thermal annealing, solid solution, garnet.

Yellow phosphors, which convert blue or ultraviolet radiation into longer-wavelength radiation [1], are used to produce white LEDs. At present, YAG:Ce is most commonly used for the production of white luminescent converters [2]. However, YAG:Ce-based LEDs emit white light with a high correlated color temperature (CCT) and a low color rendering index (R_a) due to the deficiency of red and green components in the spectrum [3]. Lighting with a low color rendering index has obvious disadvantages, since such light is perceived as unnatural by humans and may be harmful in long-term use. A variety of different approaches to this problem have been tested. Specifically, modification of the YAG:Ce matrix for the purpose of enhancing the red and green spectral components has been discussed multiple times. Co-doping of YAG:Ce with ions producing red emission (Cr^{3+}, Pr^{3+}, and Mn^{2+}) [4–6] and substitution of a fraction of garnet-forming cations with Lu^{3+} and Ga^{3+} have been proposed as a means to enhance the green component [7,8]. However, the introduction of impurity ions inevitably leads to a reduction in thermal conductivity and thermal stability of the material as a result of disordering of crystalline media. The synthesis of luminescent ceramics based on solid solutions is one of the promising ways to obtain a material with a wide luminescence spectrum and a high color rendering index coupled with a high thermal stability. For example, lutetium aluminum garnet (LuAG) features pronounced luminescence with a maximum in the green spectral region, while the spectrum shifts toward the red region as the gadolinium aluminum garnet (GdAG) content increases [9].

The aim of the present study is to examine the optical properties of LuGdAG:Ce ceramics based on LuAG and GdAG solid solutions and assess the effect of annealing on their luminescent properties.

A ceramic powder was synthesized by reverse coprecipitation [10]. The cerium content in all samples was 0.01 formula units (0.33 at.%). The Gd content in LuGdAG:Ce varied from 0 to 100 at.% (nominal compositions are listed in the table). Ceramic disk-shaped blanks were produced by uniaxial pressing under a pressure of 50 MPa and sintered in a vacuum furnace at a temperature of 1740 °C for 10 h. Finally, ceramic samples were ground to a uniform thickness of 0.80 ± 0.05 mm and polished on both sides. The approximate diameter of the obtained ceramic disks was 15 mm (LG series). Following the study of optical properties, these ceramics were annealed in air in a muffle furnace at a temperature of 1300 °C for 120 min (LGA series). The annealing temperature was chosen based on the data for YAG:Ce ceramics reported in [11].

An SF-56 spectrophotometer (OKB Spektr, Russia) was used to record the transmittance spectra within the wavelength range of 200–1100 nm. They were measured in 0.5 nm steps with an integration time of 0.1 s. The luminescence spectra of LuGdAG:Ce ceramics were recorded with a Lisun LMS-9000C spectroradiometer fitted with an integrating sphere. A blue laser with a wavelength of 445 nm and a power of 190 mW was the excitation source.

Compositions of LuGdAG:Ce ceramic samples

Sample designation	Nominal composition
LG1	$Ce_{0.01}Lu_{2.99}Al_5O_{12}$
LG2	$Ce_{0.01}Lu_{2.39}Gd_{0.6}Al_5O_{12}$
LG3	$Ce_{0.01}Lu_{1.79}Gd_{1.2}Al_5O_{12}$
LG4	$Ce_{0.01}Lu_{1.49}Gd_{1.5}Al_5O_{12}$
LG5	$Ce_{0.01}Lu_{1.19}Gd_{1.8}Al_5O_{12}$
LG6	$Ce_{0.01}Lu_{0.59}Gd_{2.4}Al_5O_{12}$
LG7	$Ce_{0.01}Gd_{2.99}Al_5O_{12}$
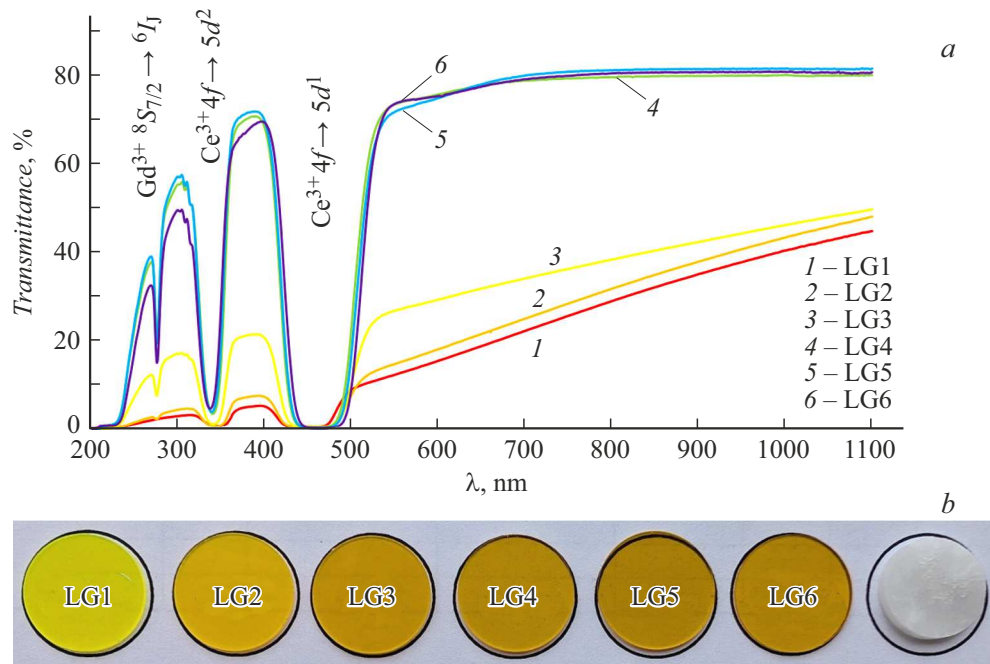
Figure 1. a — Transmittance spectra of LuGdAG:Ce ceramics. b — Photographic image of ceramic samples 15 mm in diameter and 0.8 mm in thickness). The far right ceramic sample has nominal composition LG7 ($Ce_{0.01}Gd_{2.99}Al_5O_{12}$). It is unstable at the vacuum sintering temperature and decomposes into a mixture of $GdAlO_3$ and Al_2O_3.
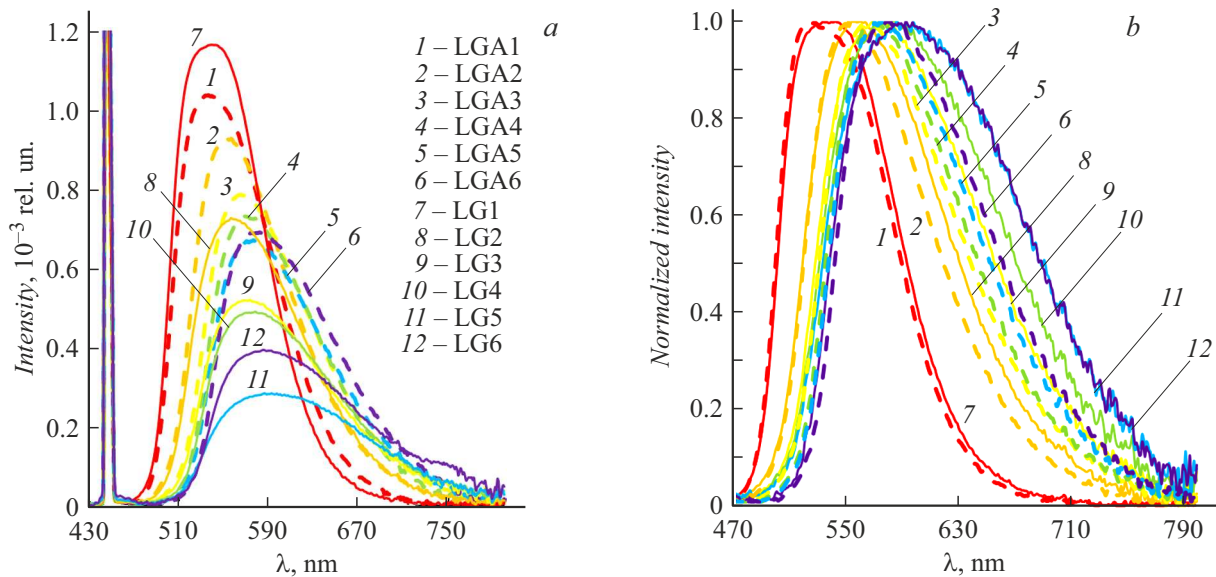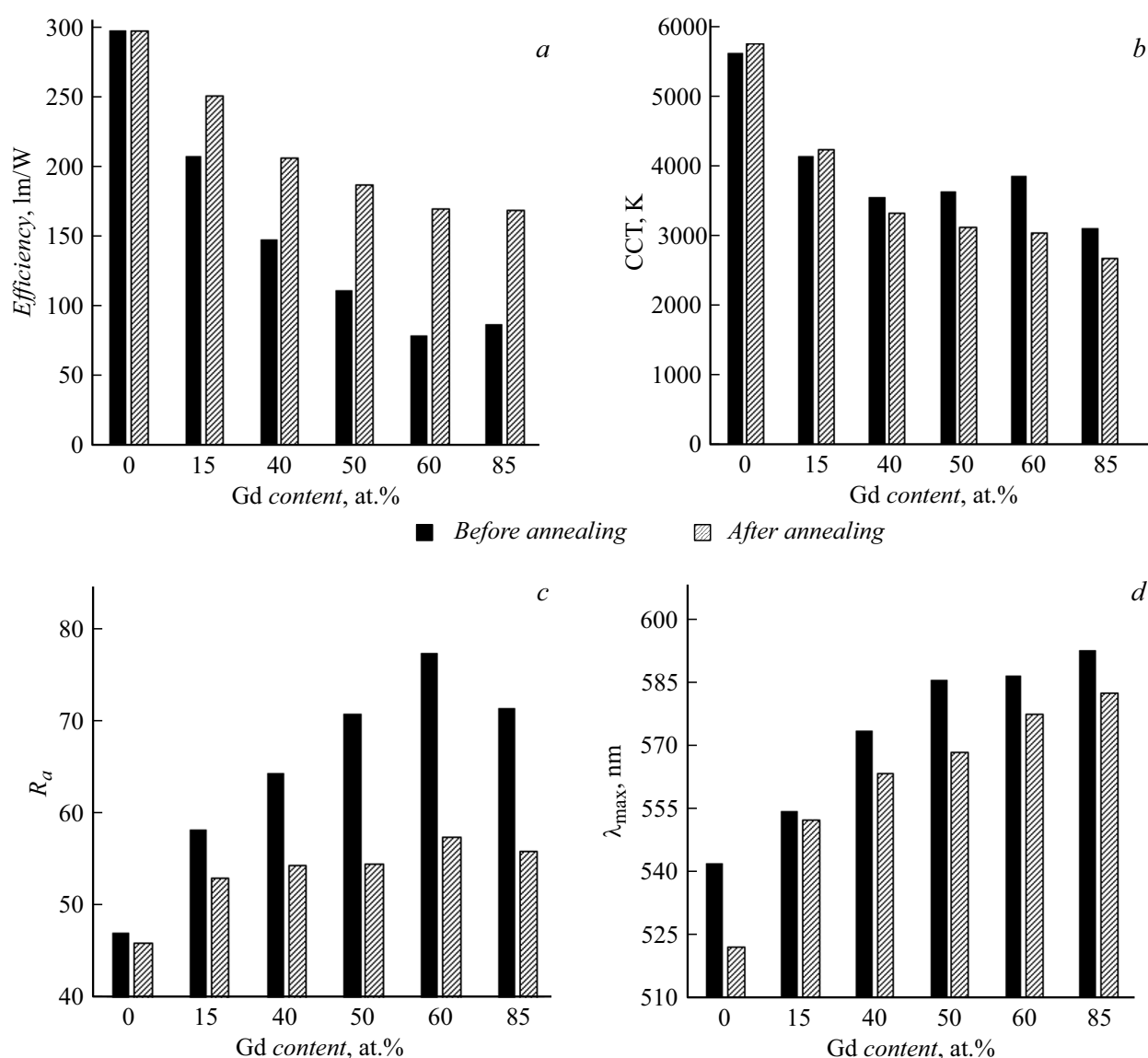

Figure 2. Luminescence spectra of LuGdAG:Ce ceramics (a) and normalized luminescence spectra of LuGdAG:Ce ceramics (b).

The diameter of the laser beam spot on the sample was ~ 3 mm. The luminescence spectra were measured within the range of 350−800 nm with a resolution of 1 nm.

The transmittance spectra for ceramic samples LG1–LG6 are shown in Fig. 1, a. All of them feature two absorption bands with centers at 345 and 450 nm induced by the $^4f \rightarrow {}^5d_2$ and $^4f \rightarrow {}^5d_1$ transitions, respectively, of Ce^{3+} ions [9]. The Ce^{3+} absorption band attributed to the $^4f \rightarrow {}^5d_1$ transition had a red shift that increased

with increasing gadolinium content, while the band associated with the $^4f \rightarrow {}^5d_2$ transition shifted toward shorter wavelengths. The spectra of samples LG2−LG6 also had a narrow absorption band around 275 nm associated with the $^8S_{7/2} \rightarrow {}^6I_J$ transition of Gd^{3+} ions [12]. The transmittance of ceramic samples at a wavelength of 1000 nm varied depending on the composition from 40 % (for LG1) to 80 % (for LG6). It is important to note that the light transmittance of the examined ceramics increased significantly with

Figure 3. Dependences of luminescence efficiency (*a*), CCT (*b*), color rendering index (*c*), and λ_{max} (*d*) on the gadolinium content in LuGdAG:Ce ceramics.

increasing gadolinium content. This is attributable to the fact that LuAG requires higher vacuum sintering temperatures than GdAG. The nominal composition of LG7 amounted to cerium-doped GdAG (see the table). This was the end point in the LuGdAG:Ce series. It is known that GdAG is unstable and decomposes to form the GdAlO$_3$ phase and Al$_2$O$_3$ [13] at temperatures above $1300\,^\circ$C. Owing to this, the LG7 sample differed in its external appearance from the other compositions and was non-luminescent (Fig. 1, *b*).

All the studied ceramic compositions had pronounced luminescence in the visible region of the spectrum (Figs. 2, *a, b*). The luminescence intensity decreased as the gadolinium content increased from 0 to 1.8 formula units. It is important to note that the shape of luminescence spectra varied significantly with composition. An increase in gadolinium content resulted in appreciable

suppression of the green component and enhancement of the red component. The introduction of Gd^{3+} into the LuAG matrix leads to more intense distortions of the local environment of Ce^{3+} cations and splitting of energy level 5*d*. Energy gaps $\Delta E_1\,(5d^1 \rightarrow {}^2F_{5/2})$ and $\Delta E_2\,(5d^1 \rightarrow {}^2F_{7/2})$ become narrower as a result. Consequently, the energy of emitted photons decreases, which amounts to a bathochromic shift [9]. The normalized luminescence spectra reveal that the spectra of ceramics with a high gadolinium content become narrower after annealing due to suppression of the red component (Fig. 2, *b*).

Let us now consider the dependence of the key luminescence parameters (efficiency, CCT, R_a, and λ_{max}) on the gadolinium content and examine the effect of annealing on these parameters (Fig. 3). It was found

that the luminescence efficiency decreases significantly (from 300 to 100 lm/W) with increasing gadolinium content in the ceramics; however, the luminescence efficiency of the LG2−LG6 compositions increased after annealing (Fig. 3, *a*), and the relative enhancement of efficiency was proportional to the gadolinium content. The CCT value was inversely proportional to the Gd content and decreased from 5500 to 3000 K (Fig. 3, *b*). In contrast, the color rendering index rose from 46 to 77 as the Gd content increased; however, R_a for ceramics with a high Gd content dropped to 52−56 after annealing (Fig. 3, *c*). The position of the luminescence band maximum shifted toward the red region with an increase in Gd content (Fig. 3, *d*), but a slight blue shift was observed upon annealing. This is associated with suppression of the red component (Fig. 2, *b*). The observed effects are attributable to the significant crystallographic difference between LuAG and GdAG. The introduction of large Gd cations into the LuAG lattice induces significant distortions, which facilitate the formation of crystal structure defects (such as oxygen vacancies) and establishes the conditions for valence transition $Ce^{3+} \rightarrow Ce^{4+}$. These factors contribute to a reduction in luminescence efficiency. However, annealing induces the relaxation of defects and redistribution of Lu^{3+} and Gd^{3+} cations in the local environment of cerium atoms, raising the efficiency of light conversion, but reducing the intensity of the red component.

Thus, highly transparent luminescent LuGdAG:Ce ceramics were obtained at gadolinium concentrations ranging from 50 to 80 at.%. One may adjust the color rendering index within the range from 46 to 77, the color temperature (from 5500 to 3000 K), and the position of the maximum of the ceramic luminescence band (from 513 to 571 nm) by varying the gadolinium content in LuGdAG:Ce. At the same time, the luminescence efficiency decreased as the gadolinium concentration increased. However, the light conversion efficiency of LuGdAG:Ce ceramics with a high concentration of gadolinium increases significantly after annealing. The presented results demonstrate that optimized LuGdAG:Ce ceramics may serve as an efficient color converter for warm LED lighting with a high color rendering index. These materials may be used in the production of spotlights, car headlights, and specialized lighting with a controlled spectrum.

Funding

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Y. Liu, M. Zhang, L. Xu, W. Xia, J. Lumin., **216**, 116698 (2019). DOI: 10.1016/j.jlumin.2019.116698

[2] O.V. Devitsky, A.A. Kravtsov, Tech. Phys. Lett., **49** (2), 69 (2023). DOI: 10.21883/TPL.2023.02.55376.19420.

[3] J. Ling, W. Xu, J. Yang, T. Mu, Y. Zhang, Y. Zhou, M. Hong, J. Eur. Ceram. Soc., **41**, 5967 (2021). DOI: 10.1016/j.jeurceramsoc.2021.05.005

[4] S. Feng, H. Qin, G. Wu, H. Jiang, J. Zhao, Y. Liu, Z. Luo, J. Qiao, J. Jiang, J. Eur. Ceram. Soc., **37**, 3403 (2017). DOI: 10.1016/j.jeurceramsoc.2017.03.061

[5] Y. Ma, L. Zhang, T. Zhou, B. Sun, Y. Wang, J. Kang, P. Gao, J. Huang, F.A. Selim, C. Wong, M. Li, H. Chen, J. Mater. Chem. C, **8**, 4329 (2020). DOI: 10.1039/d0tc00032a

[6] J. Ling, Y. Zhou, W. Xu, H. Lin, S. Lu, B. Wang, K. Wang, J. Adv. Ceram., **9**, 45 (2020). DOI: 10.1007/s40145-019-0346-0

[7] J. Huang, Y. Ni, Y. Ma, Y. Li, Z. Sun, X. Zhu, R. Wang, T. Li, X. Xi, G. Huang, T. Zhou, M. Li, H. Ren, L. Zhang, H. Chen, Ceram. Int., **47**, 11415 (2021). DOI: 10.1016/j.ceramint.2020.12.268

[8] A.A. Kravtsov, V.A. Lapin, L.V. Tarala, V.E. Suprunchuk, E.V. Medyanik, O.M. Chapura, F.F. Malyavin, Glass Ceram., **80**, 364 (2024). DOI: 10.1007/s10717-023-00616-3.

[9] J. Ling, Y. Zhou, C. Lin, H. Zhang, W. Xu, M. Hong, J. Eur. Ceram. Soc., **44**, 6430 (2024). DOI: 10.1016/j.jeurceramsoc.2024.04.014

[10] A.A. Kravtsov, E.V. Medyanik, V.A. Tarala, V.A. Lapin, F.F. Malyavin, I.S. Chikulina, D.S. Vakalov, O.M. Chapura, L.V. Tarala, V.E. Suprunchuk, A.V. Blinov, J. Am. Ceram. Soc., **107**, 1020 (2024). DOI: 10.1111/jace.19497

[11] B. Sun, L. Zhang, T. Zhou, C. Shao, L. Zhang, Y. Ma, Q. Yao, Z. Jiang, F.A. Selim, H. Chen, J. Mater. Chem. C, **7**, 4057 (2019). DOI: 10.1039/C8TC06600K

[12] P. Gupta, A.K. Bedyal, V. Kumar, Y. Khajuria, V. Sharma, O.M. Ntwaeaborwa, H.C. Swart, Mater. Res. Exp., **2**, 076202 (2015). DOI: 10.1088/2053-1591/2/7/076202

[13] J. Li, J.-G. Li, Z. Zhang, X. Wu, Sh. Liu, X. Li, X. Sun, Y. Sakka, J. Am. Ceram. Soc., **95**, 931 (2012). DOI: 10.1111/j.1551-2916.2011.04991.x

Translated by D.Safin