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Radiation synthesis and luminescent properties of $Y_3Al_xGa_{5-x}O_{12}:Ce$ ceramics

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$Y_3Al_xGa_{5-x}O_{12}:Ce$ ceramics with an Al/Ga ratio from 5/0 to 0/5 was synthesized for the first time by direct impact of a powerful electron beam with an energy of 1.4 MeV on a charge of stoichiometric composition. The study results of dependence of the spectral properties and the conversion efficiency the excitation energy into luminescence on the ceramic composition are presented. A difference was found between the dependences of the efficiency of transformation of the excitation energy into luminescence on the Al/Ga ratio upon excitation of cerium ions at 450 and 337 nm.

Keywords: yttrium-aluminum-gallium garnet, radiation synthesis, luminescence, spectra, transformation efficiency of excitation energy into luminescence.

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1. Introduction

Cerium-doped luminophores, yttrium-aluminum garnet (YAG:Ce) based ceramics are the most common materials used in light-emitting diodes. With these luminophores the LED's maximum luminous efficiency has been achieved. One of the ways available for changing the luminescence spectrum of YAG:Ce luminophores is partial replacement of Al with Ga in the crystal lattice (YAGG:Ce). The first studies of these systems produced by methods of solid-phase synthesis were carried out in [1]. Synthesis of refractory YAG:Ce ceramics is a complicated process, the synthesis uses additional substances promoting the formation of ceramics [2–4]. This makes it difficult to determine the dependencies of properties of the produced material on the composition of feed materials, synthesis process modes. It seems to be promising to use the method of radiation synthesis to produce samples of the ceramics in order to study the dependencies of their properties on the initial feed composition. The possibility to use radiation to synthesize ceramics from refractory oxides was demonstrated by the example of yttrium-aluminum garnet YAG:Ce [5–6]. The radiation synthesis of ceramics is realized in a short time from a mix of metal oxides with a stoichiometric composition that does not require complex preparation. This provides for the possibility to study a large number of synthesis variants. In this work, we have reported the results of studies of several series of YAGG:Ce ceramics samples with different Al/Ga ratios.

2. Experimental methods. Synthesis of ceramics

We used commercially available powders of Y, Al, Ga, Ce oxides for the synthesis. For the purpose of synthesis, the powders were mixed in a stoichiometric ratio shown in the table. No other substances were added to the feed. The resulted feed was poured into a massive copper crucible to provide for the heat from the ceramic material to be formed, with the following dimensions: base area $120 \times 50\,mm^2$ height 40 mm. The synthesis was performed by direct exposure of the feed to an electron beam with an energy of 1.4 MeV and a power density of $18-25\,kW/cm^2$ generated by the ELV-6 accelerator at the Institute of Nuclear Physics of the Siberian Branch of the RAS. The electron beam with Gaussian flux distribution of had a diameter of 1 cm on the feed surface. The beam was scanning in the direction normal to the long side of the crucible along the feed surface with a frequency of 50 Hz. The crucible moved in relation to the scanning beam with a speed of $1\,cm \cdot s^{-1}$. Thus, every area of the feed surface was exposed to the radiation beam for about 1 s. The total time of feed exposure to the electron beam in the crucible was 10 s.

3. Results and discussion

The table shows initial feed compositions for the synthesis. The last column shows the ratio of Al and Ga element numbers in the feed. For Al/Ga ratios of 4/1 and 1/4, several series of samples were synthesized.

Feed composition for YAGG synthesis:Ce

№	Sample	Feed composition	Al/Ga
124	$Y_3Al_5O_{12}:Ce$	$Al_2O_3(42\%) + Y_2O_3\ (57\%) + Ce_2O_3\ (1\%)$	5/0
125	$Y_3Al_4GaO_{12}:Ce$	$Al_2O_3\ (32\%) + Y_2O_3\ (52\%) + Ga_2O_3(1)\ (15\%) + Ce_2O_3\ (1\%)$	4/1
126	$Y_3Al_4GaO_{12}:Ce$	$Al_2O_3\ (32\%) + Y_2O_3\ (52\%) + Ga_2O_3(1)\ (15\%) + Ce_2O_3\ (1\%)$	4/1
127	$Y_3Al_3Ga_2O_{12}:Ce$	$Al_2O_3(23\%) + Y_2O_3\ (50\%) + Ga_2O_3(1)\ (26\%) + Ce_2O_3\ (1\%)$	3/2
128	$Y_3Al_2Ga_3O_{12}:Ce$	$Al_2O_3(14\%) + Y_2O_3\ (47\%) + Ga_2O_3(1)\ (38\%)\ + Ce_2O_3\ (1\%)$	2/3
129	$Y_3AlGa_4O_{12}:Ce$	$Al_2O_3\ (7\%) + Y_2O_3\ (44\%) + Ga_2O_3(1)\ (48\%) + Ce_2O_3\ (1\%)$	1/4
130	$Y_3AlGa_4O_{12}:Ce$	$Al_2O_3(7\%) + Y_2O_3\ (44\%) + Ga_2O_3(1)\ (48\%) + Ce_2O_3\ (1\%)$	1/4
131	$Y_3Ga_5O_{12}:Ce$	$Y_2O_3\ (54\%) + Ga_2O_3(1)\ (45\%) + Ce_2O_3\ (1\%)$	0/5
132	$Y_3Al_4GaO_{12}:Ce$	$Al_2O_3\ (32\%) + Y_2O_3\ (52\%) + Ga_2O_3(1)\ (15\%) + Ce_2O_3\ (1\%)$	4/1
133	$Y_3Al_4GaO_{12}:Ce$	$Al_2O_3(32\%) + Y_2O_3\ (52\%) + Ga_2O_3(2)(15\%) + Ce_2O_3\ (1\%)$	4/1
134	$Y_3AlGa_4O_{12}:Ce$	$Al_2O_3(7\%) + Y_2O_3\ (44\%) + Ga_2O_3(2)\ (48\%) + Ce_2O_3\ (1\%)$	1/4
135	$Y_3AlGa_4O_{12}:Ce$	$Al_2O_3(7\%) + Y_2O_3\ (44\%) + Ga_2O_3(2)\ (48\%) + Ce_2O_3\ (1)$	1/4

Note. Numbers in the table correspond to sequential numbers of series of samples synthesized by the authors.

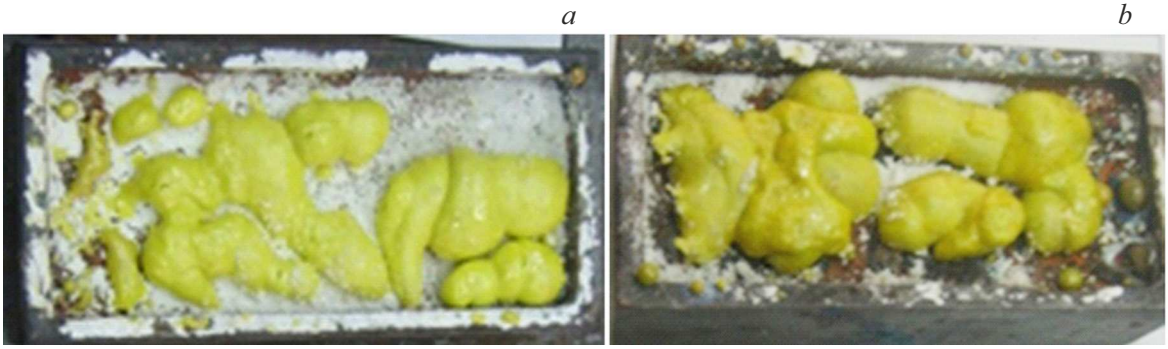

Figure 1. Photos of series 124 and 133 of samples of the synthesized ceramics.

Fig. 1 shows examples of photos of synthesized material samples.

In the process of synthesis series of droplike samples of ceramics with irregular shape and dimensions of up to $30 \times 20 \times 5\,mm^3$ are formed in the crucible. Quantity, shapes, and arrangement of samples in the crucibles are not the same in different experiments. The number of samples of different shapes in the one crucible could be as high as 15–20 pieces. The samples are colored in yellow, which is typical for cerium-doped luminophores.

3.1. Photoluminescence

Luminescence excitation spectra of samples of the synthesized ceramics were measured by a Cary Eclipse „Adgilent" spectrophotometer. The luminescence in all samples is excited by the radiation in spectral ranges of 450, 340 nm, and the UV range with a wavelength of less than 250 nm. Typical excitation spectrum is shown in Fig. 2.

The excitation at 450 and 340 nm results in the electron transition $4F^{5/2} \rightarrow 5D^0$, $5D^1$ in the cerium ion. The reverse transition $5D^0 \rightarrow 4F^{5/2}$, $4F^{7/2}$ causes the luminescence at 520 and 580 nm. [7]. In the UV range at $\lambda < 250$ nm, the excitation energy is absorbed by the matrix in the region of luminescence center [8], then it is transferred to the luminescence center.

The luminescence spectra were measured using an Avantes AvaSpec-2048L spectrophotometer. The luminescence spectra were studied in the range of 400–750 nm in the condition of excitation by radiations of a chip with $\lambda_{ex} = 450$ nm, a nitrogen laser with $\lambda_{ex} = 337$ nm. The samples of ceramics were powdered for the measurement in order to average the possible compositional heterogeneity in the ceramics volume. The produced powder was placed in cuvettes to measure luminescence spectra.

Fig. 3 shows results of photoluminescence (PL) spectra measurements for the YAGG:Ce ceramic material with different Al/Ga ratios. Spectra are shown for the selected

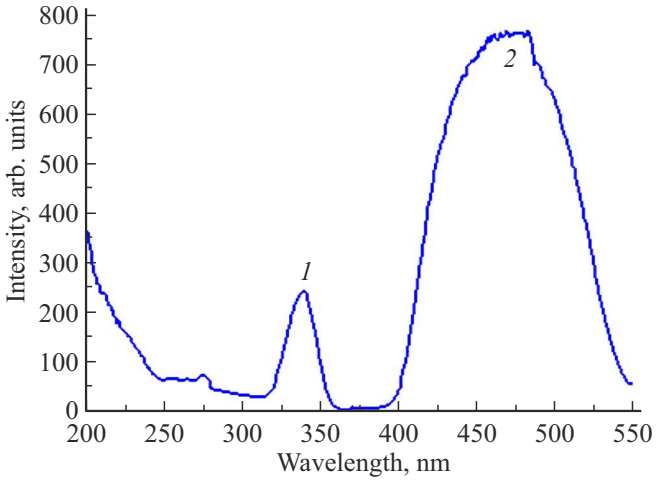

Figure 2. Excitation spectrum of YAGG:Ce when the luminescence is recorded at a wavelength of 550 nm.

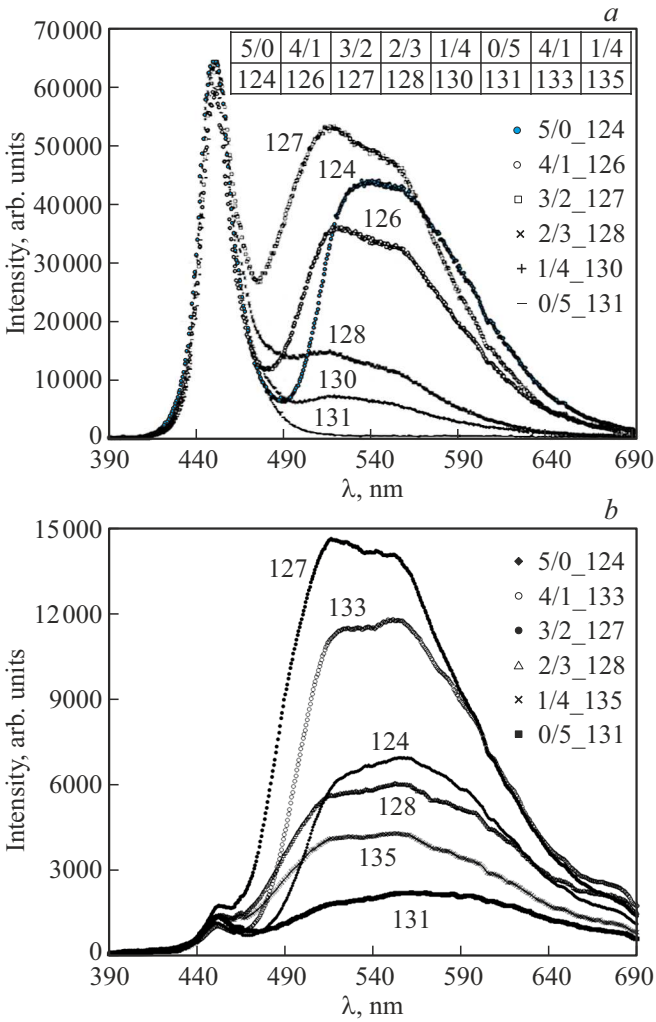

Figure 3. Luminescence spectra of YAGG:Ce-ceramic samples with different Al/Ga ratios excited by radiation of: *a* — chip at 450 nm, *b* — nitrogen laser at 337 nm.

samples from a set in a form, which is convenient for the demonstration of changes in shape and (indicatively) intensity. Digits near the spectra show numbers of the selected samples with the Al/Ga ratio shown in the top part of the table.

Fig. 3, *a* shows results of PL spectra measurements for YAGG:Ce ceramics with different Al/Ga ratios under excitation by radiation of a chip with maximum at 450 nm. In the range of 400–490 nm a typical peak of chip radiation reflected from the sample surface is observed. A change in shape of activation luminescence bands takes place. It can be seen from the presented results, that maximum of the luminescence band shifts towards the short-wave domain from 540 to 510 nm with decrease in the Al/Ga ratio.

Basically the luminescence spectra of YAGG:Ce ceramics excited by laser radiation at 337 nm are similar to those measured under the excitation at 450 nm. There is a shift of luminescence band from 540 to 510 nm, a decrease in luminescence intensity.

The described behaviors match well with the behaviors known for YAGG:Ce materials produced by conventional methods [1]. With decrease in Al/Ga ratio the luminescence intensity decreases.

3.2. Efficiency of radiation transformation

To estimate the efficiency of excitation radiation transformation into luminescence, brightness of ceramic powders was measured using a CS-200 luminance meter. Brightness of a lighting body $L(\omega)$ is directly related to luminosity M and light flux to hemisphere Φ_v as follows:

$$M = \int_0^{2\pi} L(\omega)d\omega, \quad \Phi_v = MS, \tag{1}$$

where S is area of the lighting surface.

The light flux, in turn, is related to the radiation flux by the following relationships:

$$\Phi_e = \int_0^{\infty} \varphi_\lambda d\lambda = \varphi_{\lambda m} \int_0^{\infty} \varphi(\lambda)d\lambda, \tag{2}$$

$$\Phi_v = \int_0^{\infty} \varphi_\lambda v_\lambda d\lambda = 683\varphi_{\lambda m} \int_0^{\infty} v(\lambda)\varphi(\lambda)d\lambda, \tag{3}$$

where φ_λ, v_λ, $\varphi(\lambda)$, $\varphi_{\lambda m}$ spectral density and luminous efficiency (at 555 nm $v_{\lambda m} = 683$ lm/W), their relative and maximum values.

In can be seen from relationships 1–3, that the radiation flux is related directly to the brightness provided that the luminophore surface is equally bright under the excitation. This assumption is quite realizable for a medium such as the luminophore powder and provided that the excitation source is located at a sufficiently long distance from the luminophore $l \gg d$, where d being diameter of

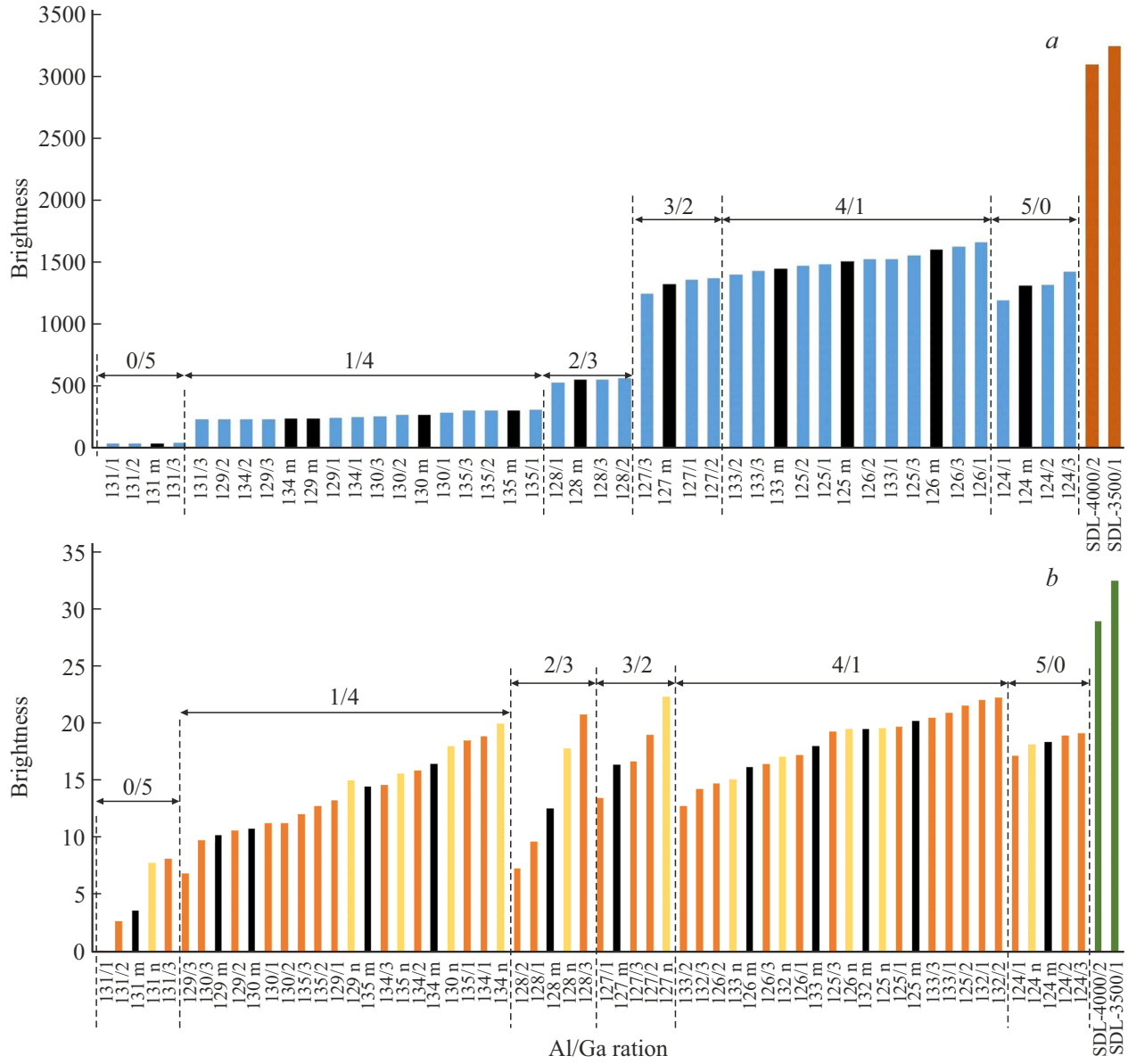

Figure 4. Luminescence brightness of YAGG:Ce-ceramic samples with different Al/Ga ratios excited by radiation of: *a* — chip at 450 nm, *b* — nitrogen laser at 337 nm.

the luminophore surface area. The area of luminophore surface, whose brightness is to be measured, is set by the telescopic system of the luminance meter. In the performed measurements the relative positions of optical setup elements, and hence the area of luminophore surface were unchanged. Therefore, we can write the following:

$$M = 2\pi L. \tag{4}$$

In the case if luminophores of one type are studied, for example those based on YAG:Ce, then spectra of their radiation $\varphi(\lambda)$ can be considered similar to each other. Then the ratio of radiation fluxes Φ_{e1} and Φ_{e2} from two sources with similar radiation spectra, $\varphi_1(\lambda) = \varphi_2(\lambda)$, Lambert distribution of brightness, and equal areas of lighting surfaces is as follows:

$$\frac{\Phi_{e1}}{\Phi_{e2}} = \frac{\Phi_{\nu_1} \int\limits_0^\infty \varphi_1(\lambda)d\lambda \int\limits_0^\infty \varphi_1(\lambda)\nu(\lambda)d\lambda}{\Phi_{\nu_2} \int\limits_0^\infty \varphi_2(\lambda)d\lambda \int\limits_0^\infty \varphi_2(\lambda)\nu(\lambda)d\lambda} = \frac{\Phi_{\nu_1}}{\Phi_{\nu_2}} = \frac{L_1}{L_2}. \tag{5}$$

Thus, with the use of luminance meter an express estimation is possible for the luminescence flux of the luminophore under study in relation to a reference (or standard) luminophore adopted for comparison.

We have investigated relative efficiency of the excitation radiation transformation (chip with $\lambda = 450$ nm and nitrogen laser with $\lambda = 337$ nm) to the luminescence ceramic samples with different Al/Ga ratios synthesized in the radiation field. We selected commercially available SDL 3500,

SDL 4000 luminophores (by „Platan“ Scientific Production Center, The Russian Federation) as reference (standard) luminophores for the brightness measurement of samples under study.

Results of measurements of the relative efficiency of chip radiation transformation to luminescence are shown in Fig. 4. Also, the same figure shows results of brightness measurements of SDL luminophores. Brightness was measured multiple times for each sample and each sample series produced within one experiment. The figure shows brightness measurement results for samples of various series with different Al/Ga ratios.

Fig. 4, *a* shows results of luminescence brightness studies for ceramic samples of various series with different Al/Ga ratios excited by the chip radiation at 450 nm. In the legend numbers of series and some randomly selected samples of series are specified. The measurement results are grouped by the Al/Ga ratio in the composition. The highest luminescence brightness is observed in samples with a ratio of 4/1, samples without Ga have slightly lower brightness. Ceramic samples with a ratio of Al/Ga equal to 3/2 have their luminescence brightness lower than samples with 5/0. Further decrease in the ratio leads to a sharp loss of brightness by 2−3 times for the samples with a ratio of 2/3, and by another 2 times for the samples with a ratio of 1/4. The luminescence brightness of samples with full replacement of aluminum by gallium is close to the limit value for the measurement. Samples with equal Al/Ga ratio from one series and from different series may have as high as 15% difference in their brightness.

Fig. 4, *b* shows results of luminescence brightness studies for the same ceramic samples of various series with different Al/Ga ratios excited by the laser chip radiation at 337 nm. In general, the trend of brightness dependence on the Al/Ga ratio is kept unchanged. And as is the case with the excitation at 450 nm, the luminescence brightness is higher in samples with higher Al/Ga ratio. However, significant quantitative differences in the behavior are observed. With decrease in Al/Ga ratio down to 2/3, the PL efficiency excited by the radiation at 450 nm decreases by 2−3 times, and when the ratio decreases down to 1/4, the decrease in efficiency is 4−6 times. In the case of excitation at 337 nm, the PL efficiency decreases by not more than 2 and 3 times, respectively.

4. Conclusion

It is shown that samples of ceramics with dimensions of up to $30 \times 20 \times 5$ mm can be produced by direct exposure of the feed that is a mix of Y_2O_3, Al_2O_3, Ga_2O_3 oxides with addition of Ce_2O_3 in a stoichiometric ratio as an activator to an electron beam with an energy of 1.4 MeV and a power density of 18−25 kW/cm^2.

The luminescence of produced samples is excited by radiation in the range of 350 and 450 nm, the PL bands are located in the range of 510−540 nm, depending on the sample composition. With decrease in Al/Ga ratio in the feed composition from 5/0 to 4/1, the PL intensity of synthesized samples increases, and with further decrease in the ratio it drops. The main behavior patterns of the luminescence (spectra, the dependence on the Al/Ga ratio) are similar to those that are known for luminophores synthesized by conventional methods.

Thus, the radiation synthesis with its high speed and throughput without the use of any auxiliary and process facilitating agents is possible to synthesize cerium-doped YAGG : Ce ceramics.

We have studied the brightness that characterize the efficiency of excitation energy transformation to luminescence. It is shown that samples with Al/Ga ratio from 5/0 to 4/1 in their composition, when excited at 450 nm, have a PL efficiency as high as 50% of that measured in commercially available luminophores. An increase in this value can be expected through optimization of compositions and quality of the initial raw materials. As can be seen from the presented results of the study, there is a scattering of the transformation efficiencies in samples with the same ratios of ingredients. The highest scattering is observed in samples with Al/Ga ratios if 2/3 and 3/2, i.e. close to equality of Al and Ga ions. It is clear that this ratio case is the most difficult for the provision of lattice formation within the short time of synthesis.

Interesting is the difference between transformation efficiency dependencies on Al/Ga ratio measured under excitation at 337 and 450 nm. Two excitation bands at $\lambda_{mac} = 460$ and 340 nm are caused by $4F_{5/2} \rightarrow 5D_0$, $5D_1$ transitions, the wide luminescence band at $\lambda_{mac} = 520$ and 580 nm is caused by $5D_0 \rightarrow 4F_{5/2}$, $4F_{7/2}$ transitions in Ce ions [7,9]. It is known that modification (codoping) has an effect on the electron structure of luminescence centers [10,11], which is manifested in a change in excitation and luminescence spectra shapes. A difference is detected in behavior patterns of PL intensity dependence on the Al/Ga ratio under excitation at 337 and 450 nm. The cause of this phenomenon is not clear.

Conflict of interest

The authors declare that they have no conflict of interest.

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