LUMINESCENCE EFFICIENCY OF CERIUM-DOPED YTTRIUM ALUMINUM GARNET CERAMICS FORMED BY RADIATION ASSISTED SYNTHESIS

The variety of applications of yttrium-aluminum garnet (YAG)-based luminescent materials and the morphology necessary for these purposes required the development of many technologies for their synthesis. All synthesis technologies used are complex. The structural phase of yttrium-aluminum garnet is formed with any technology, at temperatures exceeding 1.500 °C. The starting materials for the synthesis are metal oxides of aluminum, yttrium and other oxides for activation and modification. It seems possible to use hard radiation to form a new phase. Radiation synthesis of ceramics is realized in less than 1 s, without the use of any additives and influences.

The synthesis was carried out at the electron accelerator of the Institute of Nuclear Physics (Novosibirsk). In this work, we studied the spectral-kinetic and quantitative characteristics of luminescence for the first time obtained by the method of radiation synthesis of ceramic samples of yttrium-aluminum garnet doped with cerium with statistical processing of their values. The dependences of the reproducibility of the spectral characteristics of the luminescence of the samples on the preliminary preparation of the charge for synthesis have been investigated. Several cycles of luminophore brightness studies have been performed.

It is shown that the obtained ceramics based on yttrium-aluminum garnet doped with cerium possesses the required spectral-kinetic properties, and the efficiency of conversion of the chip radiation into luminescence is achieved, which is comparable to that available in commercial phosphors. The maximum measured values of the position of the bands are from 553.5 to 559.6 nm. Brightness values range from 4.720 to 1.960 cd/m^2.

It was found that the main reason for the scatter in the characteristics of the luminescent properties of ceramics of yttrium-aluminum garnet, activated by cerium obtained by radiation assisted synthesis is the high rate of synthesis and, especially, the high rate of cooling of the samples

Keywords: white LEDs (light-emitting diode), yttrium-aluminum garnet, phosphors, luminescence, synthesis in the radiation field

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1. Introduction

Ceramics is a promising material for use in various fields of technology, including optics. Optical ceramics, unlike single crystals, are mechanically isotropic and more durable, ceramic grains are disoriented, so their properties are isotropic. Their lattice direction always changes: there is no flat solder, double refraction. Optical ceramics is a promising material for use as scintillators, phosphors [1]. The properties of ceramics are isotropic; ceramics can be made of any shape. Therefore, ceramics has advantages over commonly used single crystal materials. There are different approaches to creating optical ceramics, depending on the composition, but they have common features.

Multicomponent oxide materials are promising materials for use as phosphors, scintillators, active laser media, and photonic elements. The expansion of the range of such materials for various applications is constrained by the possibility of their synthesis with desired properties using available methods.

Phosphors based on metal oxides are widely used for LED lighting technology. By converting the radiation of efficient chips based on InGaN with the help of such phosphors, it was possible to obtain LEDs with a luminous efficacy exceeding that of all existing light sources. Therefore, by now, "white" light-emitting diodes (LEDs) have already become dominant among light sources for lighting.

The most effective powders for use as phosphors, at present, are powders from microcrystals of yttrium-aluminum garnet, activated with cerium: YAG:Ce. Transparent YAG:Ce ceramics can be used as active laser media to convert the chip radiation into visible radiation in high-power LEDs.

LEDs with YAG:Ce X-ray phosphor already provide a luminous efficacy of 160 lm/W. This is far from the maximum achievable value, which is mainly determined by the phosphor and can have values up to $230-250$ lm/W. The disadvantage of modern LEDs with YAG:Ce luminophores is the difficulty in ensuring good color rendering: the color rendering index is usually 70. Synthesis of YAG:Ce ceramics and phosphors is complicated. The melting points of the metal oxides from which the phosphor is obtained are in the range of 2.050 °C (Al_2O_3) – 2.460 °C (Y_2O_3). Of the existing synthesis methods, the most widespread method is solid-phase synthesis, which is considered optimal at the present time. New methods are being developed and existing methods are being improved. It seems promising to determine the possibility of synthesizing YAG:Ce ceramics in the field of hard radiation, when the efficiency of solid-phase reactions will be stimulated by radiation in addition to thermal radiation. This can make it possible to form ceramics at relatively low temperatures, speed up the process, and improve the quality of the resulting material.

2. Literature review and problem statement

YAG-based materials are widely used as active media for lasers [2], phosphors for converting chip radiation in LEDs [3], scintillators for recording hard ultraviolet [4], X-ray radiation [5]. Luminescent materials based on YAG are used in the form of crystals, ceramics, powders, films. The variety of applications and the morphology necessary for these purposes required the development of many technologies for their synthesis.

The most common method for producing YAG luminophores is solid-phase synthesis from mixtures of metal oxide powders, described for different compositions in [6–8]. The synthesis is carried out in 2 stages. At the first stage, the stoichiometrically selected composition of the Y_2O_3–Al_2O_3 mixture is heated to temperatures of 900–1,200 °C. At these temperatures, sintering of the components occurs. To increase the efficiency of the reaction between the particles of Y_2O_3–Al_2O_3 oxides, sintering is usually carried out in the liquid phase, for example, in the medium of molten barium fluoride. Intermediate phases are obtained: perovskite – $YAlO_3$ (YAP), monoclinic $Y_4Al_2O_9$ (YAM), corundum – Al_2O_3, a little of the required YAG phase in a sintered ceramic sample. Such a sample can be easily crushed to the desired consistency, which is done in ball mills. After this, the second stage of the synthesis begins. At this stage, the resulting fine powder is heated to high temperatures in the range of 1,500–1,700 °C. At these temperatures, the components introduced to accelerate the reactions are

removed (for example, barium fluoride), the intermediate phases are transformed into the final YAG phase. The synthesis is carried out from substances with melting points over 2.000 °C. In order to avoid the evaporation of the most low-melting compounds, the initial powders are sintered into ceramics at temperatures of 1.500–1.700 °C, then repeated long-term annealing is carried out at temperatures of about 1.700 °C, to obtain the dominant YAG phase. Control over the processes in such extreme conditions is difficult. The reproducibility of the synthesis results is insufficient. There are problems with homogeneity of the obtained phosphor particles in composition, structure, and size. It is difficult to ensure uniform mixing of submicron precursor particles; it is difficult by grinding ceramics to obtain luminophore particles of equal size. Therefore, the improvement of synthesis methods continues.

Among the promising methods under development is the sol-gel method [9], which can be used to obtain powders with the required grain sizes. The sol-gel method includes the following main stages: solution preparation – the formation of a sol-gel, washing, drying, heat treatment. In this method, the formation of a highly dispersed material in the form of a mixture of initial reagents is achieved by creating a sol – a colloidal solution of the initial reagents. In order to carry out the processes of hydrolysis and polycondensation, water is introduced into the reaction medium. The starting materials are mixed with an aqueous solution, the powders are dissolved, and a sol is formed as a result of hydrolysis. A sol is a dispersed system with a liquid dispersion medium and a solid nanodispersed phase. When the sol is dried, the process of polycondensation and hydrolysis takes place, followed by a transition into a gel, that is, into a system with increased viscosity, without free water. After the formation of the gel, drying and annealing are sequentially carried out at a temperature not exceeding 1,200 °C. These methods lead to the formation of not only the required YAG phase before annealing, but also the transition phases of perovskite – $YAlO_3$ (YAP), monoclinic $Y_4Al_2O_9$ (YAM), and corundum – Al_2O_3. During the synthesis by the sol-gel method, powders of fine fractions are obtained. The main disadvantage of this method is that in addition to the main yttrium-aluminum garnet phase, residual phases of synthesis reactions, residues of the initial and intermediate synthesis products remain in the phosphor.

Self-igniting synthesis (SIS) methods [10] seem to be very attractive, since the synthesis process takes little time. The "combustion" method is used to produce powders with submicron particle sizes. Yttrium and aluminum nitric acid solutions are used as starting materials for YAG production. Then the required amount of fuel is added to the initial mixture of solutions. As fuel, organic compounds such as carbamide (CH_4N_2O), aminoacetic acid ($C_2H_5NO_2$) or carbohydrazide (CH_6N_4O) can be used. The mixture is placed in a crucible, the crucible in an oven. When heated to a temperature of 500 °C, ignition occurs. The energy released during the chemical exothermic reaction between nitrates and fuel contributes to the rapid heating of the system to high temperatures (>1.600 °C) and maintaining these high temperatures without an external heating source. The synthesis is carried out as follows. The initial mixture of water, nitrates and fuel decomposes, dehydrates and ignites in 3–5 minutes. The resulting product is a voluminous foamy product, the volume of which increases 4–5 times in comparison with the original. After the combustion reaction,

the resulting powders are ground in a mortar, placed in a crucible and calcined at different temperatures. It was shown that the garnet phase crystallizes directly from the interacting initial mixtures without the formation of intermediate phases. Compared to other processes, the products obtained by the combustion process are generally more homogeneous. The disadvantages of this method are as follows. Combustion processes are poorly controlled; during combustion, additional products are formed from the compositions introduced for the implementation of combustion, and strong agglomerates of particles are formed.

Chemical deposition methods involve the co-deposition of ceramic components from solution in the form of insoluble salts. Precipitating agents and chemicals are added to the water, as a result of the reaction between the substance and the solution, salts are precipitated. After filtration, the precipitated sediments are subjected to heat treatment. In [11], $Y(NO_3)_36H_2O$ and $Al(NO_3)_39H_2O$ were dissolved in deionized water with a molar ratio of 3:5, obtaining a mixed solution in which the concentration of Y and Al was 0.5 M. the level of 0.05 at %. The precipitating agent was added to the mixed solution at a rate of approximately 30 ml/min controlled by a peristaltic pump at various speeds of rotation of the electromagnetic stirrer. The suspension was kept for 48 hours, filtered, then washed with distilled water and alcohol to obtain a precipitate. The precursors were obtained after drying the precipitate at 90 °C for 46 hours in a dryer. The obtained precursors were sieved through a sieve and then calcined in air at various temperatures from 900 to 1,300 °C to obtain pure YAG:Ce nanopowders. The disadvantages of the coprecipitation method are the difficulties in the purification of luminophores from residual and intermediate products used in the synthesis, the need for an additional stage of high-temperature annealing, which is necessary to obtain oxides. However, this method produces powders with a grain size of at least a hundred nanometers; obtaining particles of a smaller size is not possible.

Laser sintering has recently been proposed as a new type of heat treatment and molding technology. Laser sintering not only creates complex and precise three-dimensional parts, but also provides compactness through high-temperature reactions in a short time, that is, an order of magnitude less compared to traditional processes. In [12], the study focused on the production of YAG:Ce by mixing precursor powders with an inorganic polymer to form granules by uniaxial pressing followed by sintering with a CO_2 laser at different powers. Ceramic based on yttrium-aluminum garnet doped with cerium (YAG:Ce) was prepared by sintering with CO_2 laser radiation with different power. Precursor materials for aluminum oxide, yttrium, and $Ce(NO_3)_3H_6O$ were used without purification. The starting materials were ground in a ball mill in 40 ml of ethanol for 20 hours in a stoichiometric ratio of 2.89:5:0.055 (Y:Al:Ce). The ball mills used in this study were pure alumina. After grinding, the raw materials were dried in an oven at 90 °C for 6 hours and transferred to an alumina solution for grinding. After mixing, the raw materials were dried at 90 °C for 6 hours and milled for 10 minutes. The mixture is molded into granules with a diameter of 10 mm. For uniaxial pressing 35 kg/cm^2 for 10 min. After preparing the granules, a CO_2 laser is used for sintering at various powers from 15 to 40 W. Then they were sintered in a traditional furnace at 1.500 °C for 12 and 24 hours in air. In [12], the possibility of synthesis by laser

radiation was shown, but in comparison with the radio method, the synthesis rate is not high.

The above brief review of the main methods for the synthesis of YAG:Ce luminophores shows that all existing methods are complex. Synthesis processes are difficult to control. Annealing always requires a high temperature. In the synthesis process, auxiliary materials are used to facilitate the conversion of starting materials to phosphor. Then all these materials and excess products obtained with their participation must be removed from the final product. Most of the synthesis methods used are still implemented only in laboratory conditions; technology scaling (transition from laboratory to industrial scale) is a separate problem.

It seems possible to use hard radiation to stimulate the reactions of mutual exchange of elements for the formation of a new phase. In [13], the possibility of radiation synthesis of luminescent ceramics based on MgF_2 was shown. A mixture of MgF_2 powders with an activator in the form of WO_3 powder under the action of a high-energy electron flow from an ELV 6 accelerator in 1 s was transformed into a ceramic with properties characteristic of a LiF:W scintillator [14]. The works showed the possibility of radiation synthesis of luminescent ceramics based on MgF_2:W [15], YAG [16]. Under the action of a powerful flow of electrons from the charge, ceramics with properties characteristic of YAG phosphors were formed. Thus, the possibility of radiation synthesis of luminescent materials with high melting points was demonstrated. Radiation synthesis of ceramics is realized in less than 1 s, without the use of any additives and influences. It is shown that the obtained ceramics based on YAG:Ce have spectral-kinetic properties characteristic of industrial phosphors. The radiation method of synthesizing a new one, according to this process of forming ceramics, has not been studied. Additional synthesis operations are required in the radiation field, depending on external factors and synthesis schedule. This work is aimed at improving the method of radiation synthesis of YAG:Ce ceramics, determining the dependence of the luminescent properties of ceramics on the technological procedures of the synthesis process.

3. The aim and objectives of the study

The aim of the study is to investigate the luminescence efficiency of YAG:Ce ceramics obtained by radiation synthesis.

To achieve the aim, the following objectives were set:
– to prepare a charge and synthesize ceramics;
– to study the morphology of the obtained samples;
– to measure the photoluminescence of the obtained samples;
– to measure the brightness of radiation for the synthesized samples.

4. Materials and methods

For the synthesis of ceramics based on yttrium-aluminum garnet (YAG), a charge of stoichiometric composition corresponding to the formula $Y_3Al_5O_{12}$ was prepared. This composition is obtained from the following weight ratio of the initial powders Y_2O_3 and Al_2O_3. The mixture should contain 57 wt. % Y_2O_3 and 43 % Al_2O_3. Weighing was

carried out with an accuracy of 1 %. As is known, with any method of YAG synthesis, materials have a large number of antidefects: Al cations occupy the places of Y nodes and vice versa. Concentrations of antidefects reach and may even exceed 10 %. Therefore, the discrepancy in the degree of stoichiometry in the initial charge up to 1 % does not affect the actual crystal structure obtained. An activator in the form of cerium oxide (Ce_2O_3) in an amount of 2 % was added to the prepared mixture of Y_2O_3 and Al_2O_3 powders. It is assumed that cerium ions activators enter the lattice by replacing yttrium ions. It is known that in all used technologies of YAG synthesis, an activator is added in an amount from 0.02 to 2 %. The choice of the activator concentration of 2 % is explained by the following. Previous studies [17, 18] have shown that 2 % Ce is the optimal concentration for YAG ceramics. The formation of radiation synthesis technology is at the very beginning. The processes of ceramic synthesis using radiation are fundamentally different from those occurring in other technologies. In all the technologies used, synthesis is carried out or is finally accomplished by stimulating diffusion processes with heat at high temperatures. It is not known what conditions determine the dissociation of cerium oxide and the entry of cerium ions into the lattice. Powders of oxides of the HC brand were used for synthesis. Yttrium oxides were obtained from two different sources of supply and differed in their granulometric composition (hereinafter referred to as Y_2O_3 (1) and Y_2O_3 (2). For the synthesis, powders of UV grade oxides were used. Yttrium oxides were obtained from two different sources and differed in particle size distribution: 500 nm and 2 µm. The prepared mixture was then mixed in a stirrer with blades and a changing inclination of the vessel in which the mixing took place. The bulk density of the resulting mixture was 1.05...1.25 g/cm^3, depending on the background of the initial powders. Some of the resulting mixtures were compacted: the mixture was mixed with alcohol, mixed thoroughly, poured into a crucible and left to dry. After compaction, the bulk density increased to 2.1 g/cm^3. Ceramics were synthesized from previously fragmented synthesized samples, the density of which was 2.1 g/cm^3.

The prepared mixture was poured into a massive copper crucible with dimensions of 120×50×40 mm and leveled with an even layer.

Ceramics were synthesized using the ELV-6 accelerator of the INP SB RAS (Novosibirsk). The electron accelerator provides the possibility of generating an electron flow with an energy of 1.4 MeV, with a power of up to 80 kW in stationary mode. The beam power could be varied by changing the emitter current.

The ELV-6 accelerator is equipped with a device for the output of a powerful beam of high-energy electrons into the atmosphere through a system of holes in the diaphragms. The electron beam is removed from the accelerator chamber with a high vacuum into a medium with atmospheric pressure through a differential vacuum pumping system consisting of three stages. In each stage, the vacuum decreases by about two orders of magnitude. The electron beam at the exit of the chamber has a diameter of about 2 mm and expands as it moves away.

The synthesis was carried out by direct action on the charge of an electron flux with an energy of 1.4 MeV and a power density of 18–25 kW/cm^2 of the ELV-6 accelerator. The flow was scanned in a perpendicular direction along the surface of the crucible. The crucible moved relative to the scanning beam at a speed of 1 cm/s. The mass thickness of an electron penetration beam with an energy of 1.4 MeV into the yttrium-aluminum garnet (YAG) is 0.78 g/cm^2.

To determine the reproducibility of the properties of the obtained ceramic samples, we studied the luminescence characteristics of YAG:Ce ceramic samples synthesized in the field of powerful electron fluxes on a Solar CM2203 (Belarus) spectrophotometer. In order to assess the efficiency of conversion of excitation radiation into luminescence, several cycles of brightness studies were performed using a brightness meter.

Luminescence spectra were measured when excited with λ_{em}=450 nm. For measurement, ceramic samples were crushed mechanically. The need for crushing ceramics is due to the fact that the structure of the samples is complex: a solid outer surface and a porous structure inside. By crushing the sample, it was possible to average the radiative characteristics of the sample. The resulting powder was placed in cuvettes-washers for measuring luminescence spectra.

5. Results of studies of the luminescent characteristics of the obtained samples

5. 1. Preparation of a charge for synthesis

For synthesis, the crucible with the charge was placed on a massive metal table under the beam of the accelerator output window. The position of the crucible in height and position relative to the accelerator window were set with an accuracy of at least 1 mm. This achieved the desired density and distribution of the electron flux over the surface of the crucible and its constancy during scanning. In our experiments, the electron flux in the plane of the charge surface had a Gaussian distribution relative to the beam axis with a diameter of 10 mm at the half-height of its intensity. The exposure time of the electron flow to the entire surface of the crucible with the charge was 10 seconds.

After the irradiation was completed, after 10 minutes, the crucible with the prepared ceramic sample was replaced with a new one. Then the crucible with the sample was cooled on a cold metal plate, the sample was removed from the crucible.

When scanning, ceramics are synthesized in the crucible. Drop-shaped samples and plates of irregular shape and sizes up to 80×40×50 mm are formed. The type of samples in the crucible after exposure to the electron flux depended on the type of charge and on the background of the raw materials used for synthesis. In each experiment, a series of samples was formed in the crucible. The number, shapes and location of samples in crucibles vary in different experiments. The number of samples of different shapes could reach 15–20 pieces. There is no well-defined pattern of distribution of the formed samples over the crucible area. We can only say with confidence that there are smaller samples at the very end of the crucible, where the beam scanning process ends. Fig. 1 shows photographs of ceramic fragments obtained in a series of successive synthesis experiments. The number in the photo means the serial number established by the authors in the journal with a description of the initial compositions for synthesis. Measurements were carried out repeatedly for each sample, for a series of samples obtained in one experiment, for different series listed in Table 1.

Fig. 1. Photos of fragments of the studied ceramic samples

Table 1

Designations and descriptions of the obtained and
investigated series of ceramic samples

No.	Beam power, kW	Description
50	23	Compacted in a crucible, p=2.1 g/cm^3
51	23	Compacted in a crucible, p=2.1 g/cm^3
52	23	From crushed previously synthesized ceramics, Compacted in a crucible, p=2.6 g/cm^3
53	23	Compacted in a crucible, then transferred to another crucible, p=2.1 g/cm^3
54	23	Compacted in a crucible, then transferred to another crucible, p=2.1 g/cm^3
55	23	Compacted in a crucible, p=2.1 g/cm^3 with Y_2O_3 (1)
56	23	Uncompacted with Y_2O_3 (1), p=1.15 g/cm^3
57	23	Uncompacted with Y_2O_3 (1), p=1.15 g/cm^3
58	23	Uncompacted with Y_2O_3 (2), p=1.05 g/cm^3
59	18	Uncompacted with Y_2O_3 (2), p=1.05 g/cm^3
60	15	Uncompacted with Y_2O_3 (2), p=1.05 g/cm^3
80	40	Uncompacted with Y_2O_3 (2), p=1.05 g/cm^3

Table 1, for series samples 50, 51, 52, 53, 55, 56, 57, 58, 60 and 80, shows information about the initial charge compositions, the degree of compaction to achieve different bulk densities, irradiation modes differing in scanning speed, Y_2O_3 background, and to assess reproducibility.

5. 2. Morphology of the obtained samples

The morphology of the samples was studied using a Hitachi TM3030 (Japan) scanning electron microscope (SEM). Examples of SEM images at the yttrium-aluminum garnet cleavage site are shown in Fig. 2.

In the SEM images, it can be seen that the ceramic samples are soldered together particles with dimensions of ~10...50 microns. Most of the particles have the form of a melt. There are particles with a well-defined cut, which indicates the formation of microcrystals.

Analysis of the results of studying the morphology of synthesized ceramic samples showed that compacting the charge before synthesis allows obtaining samples with lower porosity. Samples 50, 51, 52, 55 made of compacted charge are dense plates with a thickness of up to 4 mm. Samples 57, 58, 60, 80 made of uncompacted charge have the form of complex shaped bubbles with a hard shell and empty inside, up to 8 mm thick. The shape of the samples does not depend on the background of Y_2O_3 used for synthesis. The dependence of the type of samples on the preliminary compaction indicates that the interparticle space of the charge contains

a large amount of air, which is involved in the formation of the sample shape. As follows from the above results, the synthesis of ceramics is realized in the range of used radiation flux power densities from 23 to 15 kW/cm^2. It should also be noted that the synthesis is also realized at a radiation flux power density of 40 kW/cm^2 at a crucible displacement velocity relative to the scanning electron beam of 2.5 cm/s. Under such irradiation conditions, the absorbed dose at each point of the surface is equal to that obtained when exposed to a flow of about 15 kW/cm^2 at a crucible displacement velocity relative to the scanning electron beam of 1.0 cm/s.
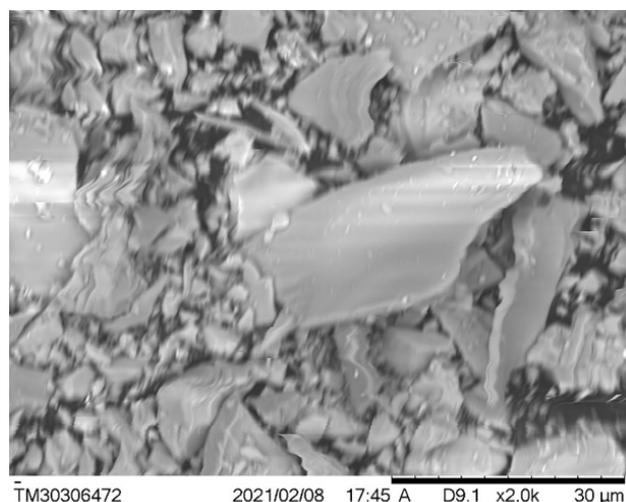
a
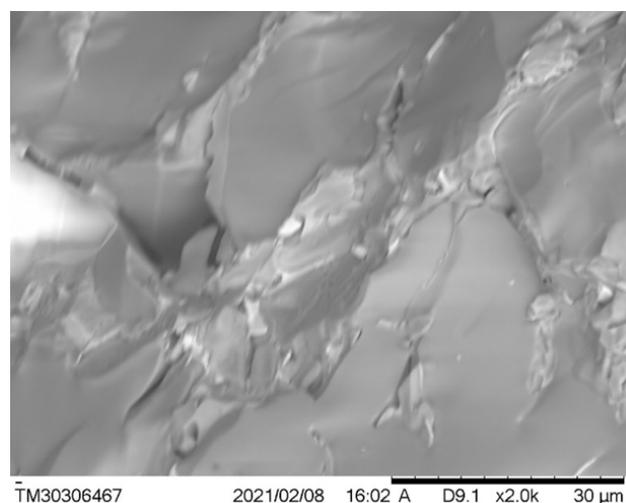
b

Fig. 2. Typical SEM images at the site of the split of ceramic
samples synthesized in the radiation field:
a — YAG:Ce; b — YAGG:Ce

5. 3. Investigation of photoluminescence of synthesized samples

To determine the spectral characteristics, the luminescence spectra were measured. Fig. 3 shows examples of measurement results of luminescence spectra of samples of series 50 and 80. The last digit in the notation in the figure means the number of the sample obtained in this series, that is, in one experiment, in one crucible. In all the studied samples of all series, when excited by the radiation of the chip at

450 nm, a luminescence band in the region of 560 nm was observed. Measurements of all samples of different series were carried out, the measurement errors of the position of λ m and the half-width of the bands in the region of 560 nm were determined. The measurement results are shown in Table 2.
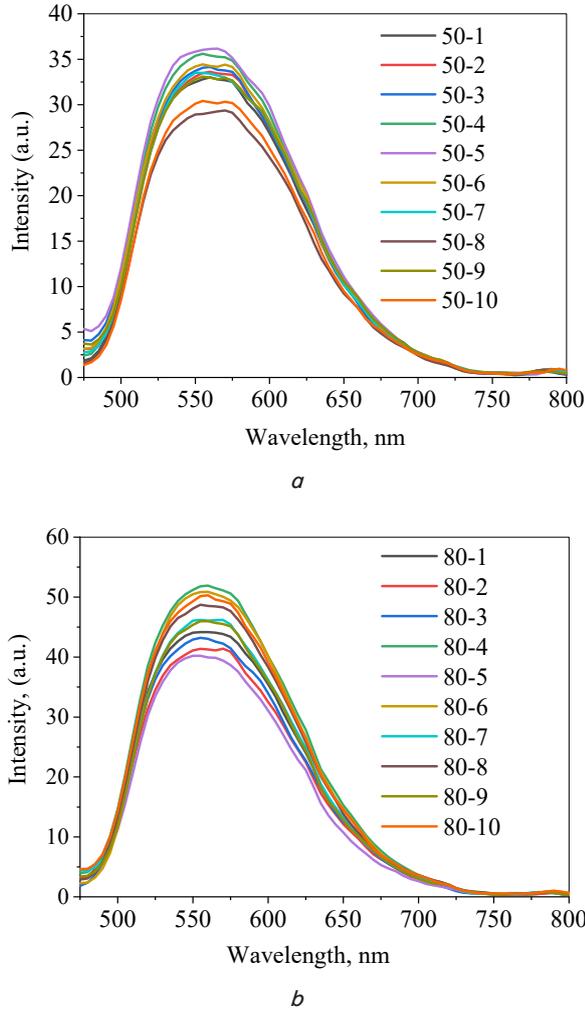

a

b

Fig. 3. Luminescence spectra of YAG:Ce ceramics samples:
a − 50; *b* − 80

Table 2

Average values of positions and half-widths of luminescence bands

Name of the sample	λ_m, nm	ΔE, eV
50	557±2.5	0.473±0.005
51	558±3	0.480±0.006
52	555±2	0.461±0.004
53	556±0.8	0.457±0.005
55	557±2	0.436±0.03
56	555.8±2.0	0.457±0.01
57	556±2	0.459±0.007
58	561±2	0.462±0.004
60	562±5	0.457±0.012
80	556±2	0.459±0.01

The given values of the characteristics of the luminescence bands correspond well to those known for crystals, ceramics, phosphors based on YAG:Ce [19−23]. In general,

it can be seen that the spread of the measured values of the characteristics of the bands in the samples of the series from the pre-compacted charge (50, 51, 53 and 55) is less than from the uncompacted ones (56, 57, 58, 60, 80). We emphasize that this difference, or the tendency to differ, is small. Thus, the spread of the values of the characteristics of the bands in samples of different degrees of compaction is less than in samples of the same series. Consequently, there is some factor in the formation of ceramics, which determines the spread to a greater extent. Such a factor may be the high rate of synthesis and relaxation of the ceramic structure during cooling.

5. 4. Photometry of the obtained samples

Luminescence spectra are a qualitative characteristic of a phosphor. The quantitative characteristic of a phosphor is the energy output, which determines the efficiency of converting the energy of exciting radiation into luminescence. Quantitative measurements of optical radiation fluxes and, accordingly, luminescence fluxes are complex. To determine the energy output, spherical photometers (integrating spheres) are commonly used. Measurements with their help require careful preparation, measurement accuracy is low. It seems promising to determine the relative energy yield by measuring the brightness described in [24]. Brightness is a measure of the amount of light radiation from a unit area in a single solid angle. This value is measured with high accuracy by simple devices – brightness meters. Comparing the luminescence brightness of the test phosphor during excitation with the brightness of a similar industrial phosphor with the same radiation spectrum makes it possible to evaluate the conversion efficiency with high accuracy and speed.

When the luminescence spectra of the test and reference phosphors are equal, the relative conversion efficiency η is directly proportional to the ratio of their fluxes Φ (1):

$$\eta_{rel} = \frac{\eta_{ts}}{\eta_r} = \frac{\Phi_{ts}}{\Phi_r}. \tag{1}$$

In turn, the luminescence flux is directly related to the luminosity and, for an equally bright surface, the brightness (2):

$$\Phi = 2\pi * L * S. \tag{2}$$

Therefore, with an equal surface area of the emitter, which is provided by the optical system of the chroma meter, we can assume that (3)

$$\eta_{rel} = \frac{L_{ts}}{L_r}. \tag{3}$$

The brightness was measured using a CS-200 (Japan) brightness meter. The sources of excitation were 450 nm chips. An LC17 light filter was placed in front of the light guide of the brightness meter in order to get rid of the scattered radiation of the chip. In the measurements, the angle of view was 1 or 0.2 degrees, which made it possible to measure the brightness of an object with a diameter of 5 and 2 mm. Before the brightness measurements, the brightness of the ambient light background was determined. Usually, the background brightness did not exceed 1 % of the luminophore brightness when measured at an angle of 1 degree.

For measurements, ceramic samples were ground into powder. All powders of the studied samples and standards were poured into the cuvettes in an even layer and placed on

a work table, which could be displaced by a micrometer screw relative to the entrance window of the light guide. This made it possible to measure a series of phosphors at once without changing the relative placement of the stand elements. The excitation source was placed on a stand in front of the table, its position relative to the cuvette with a phosphor and the power modes did not change. The developed stand allows for operational measurements of the relative efficiency of the phosphor. The accuracy of brightness measurements is 2–3 %.

We have carried out studies of the relative efficiency of converting exciting radiation (chip with λ=450 nm) into luminescence of ceramic samples synthesized in the radiation field. Commercial phosphors SDL 4000 (NPO Platan, Russia) and YAG-02 (Grand Lux Optoelectronics Co. Ltd, China) were selected as exemplary standards, relative to which the brightness of the studied samples was measured. YAG:Ce phosphors SDL 4000 and YAG-02 are produced and used in large quantities in the production of white LEDs. It is known that their luminescent properties are well controlled and have not changed for several years.

The results of the brightness measurements are presented in Table 3 and in Fig. 4. There are also the results of measuring the luminosities of the SDL 4000 and YAG-02 phosphors. Brightness measurements were carried out repeatedly for each sample and a series of samples obtained in one experiment. The table shows the average values of the measurements.

A visual representation of the brightness of phosphors obtained by the radiation method relative to industrial ones can be made from the diagrams shown in Fig. 4.

Fig. 4, *a* shows the results of a study of the dependence of the averaged values of the brightness of each series of phosphor samples upon excitation by the LED radiation at 450 nm on the degree of compaction and the results of measurements of commercial phosphors.
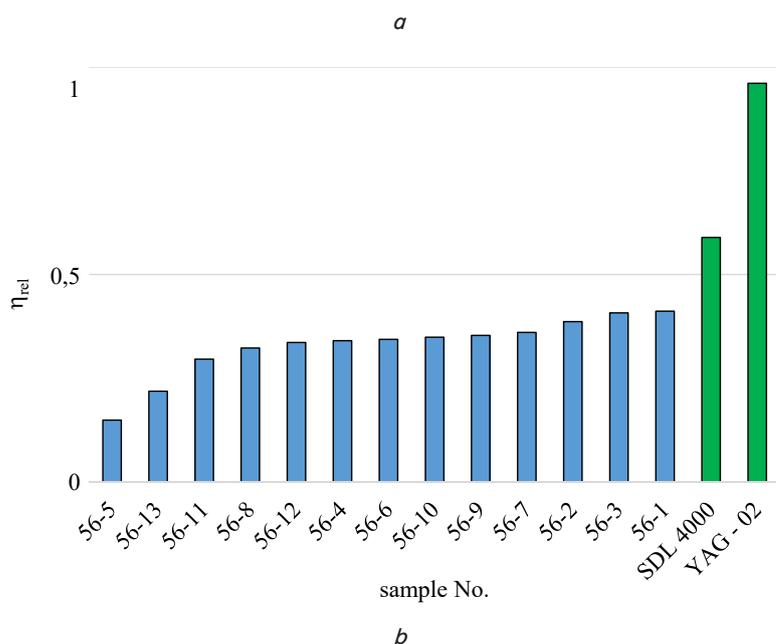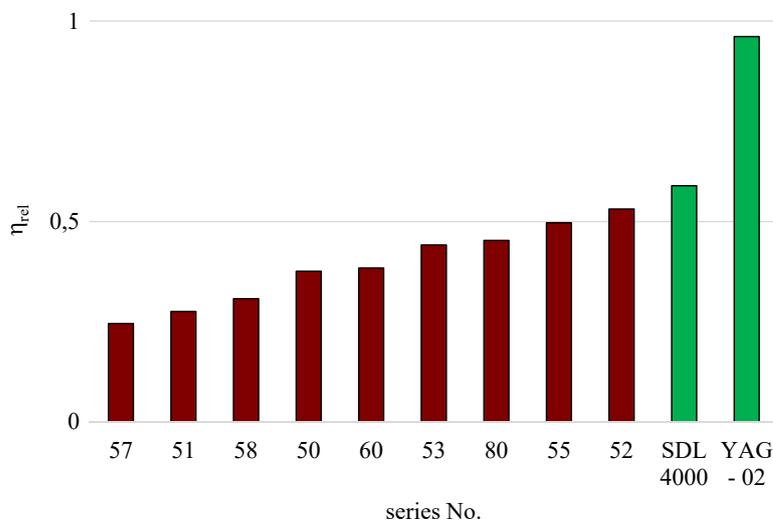

Fig. 4. Relative efficiency of conversion of the η_{rel} radiation: *a* — of the chip by phosphors from different series; *b* — individual samples from the same series

Fig. 4, *b* shows the results of a study of the dependence of the brightness of the 56 series samples under excitation by the LED radiation at 450 nm.

As follows from the presented results, the brightness of the synthesized samples, and, accordingly, the energy efficiency of converting LED radiation into luminescence is 0.35–0.6 relative to YAG-02 and 0.6–0.9 SDL 4000. There is a spread of luminescence brightness values of the same series samples. However, for most samples it is insignificant (Fig. 4, *b*).

6. Discussion of the results of studies of the luminescent characteristics of the obtained samples

As follows from the presented results (chapter 5. 3), the luminescence spectra of YAG:Ce ceramic samples obtained by radiation synthesis do not depend on the degree of preliminary compaction. However, the ratio of the dense and porous parts of the sample depends on the degree of compac-

Table 3

Luminosity of phosphors obtained by radiation synthesis and SDL 4000 and YAG-02

Sample	Brightness, cd/m²
57	1,960
51	2,200
58	2,460
50	3,010
60	3,070
53	3,530
80	3,620
55	3,970
52	4,250
SDL 4000	4,720
YAG-02	7,690

tion. Therefore, the need for compaction is determined only by the goals of achieving the required functional properties for the use of the material. For the manufacture of phosphor, which is obtained by crushing samples, there is no need for preliminary compaction of the charge. For the manufacture of luminescent plates, samples synthesized from a compacted sheet should be used.

The presented results of the study allow us to draw the following conclusions. Compaction of the charge before synthesis definitely leads to a change in morphology. The samples obtained from the pre-compacted charge are denser, with fewer pores. The compaction effect is especially pronounced for sample 52, which was obtained from previously crushed ceramics. The morphology of the obtained samples does not depend on the background of YAG:Ce used for the synthesis of yttrium oxide (chapter 5. 3).

The spectral characteristics of luminescence depend little on the degree of compaction of the charge for synthesis, the background of yttrium oxide (Table 2, Fig. 4). There is a noticeable shift in the positions of the band maxima up to 5 nm in the samples from the uncompacted charge relative to the samples from the compacted one. In the samples from the compacted charge, there is less spread of the positions of the band maxima, on average less than half-width. Consequently, the luminescence centers are embedded in the forming crystal lattice during the primary synthesis. However, preliminary compaction of the charge contributes to the formation of a more perfect crystal structure in the region of the glow center.

The radiation technology for the synthesis of luminescent ceramics based on refractory oxides was first implemented by the authors of this work [16]. The presented results of the work confirm that radiation synthesis of dielectric refractory materials can hold great promise. The method is simple, the synthesis technology, preliminary preparation and irradiation take little time, the synthesis volumes can be quite large at a low cost. Linear electron accelerators, convenient for radiation synthesis, have a high efficiency in excess of 80 %; the power of electron fluxes can exceed 500 kW [25]. The flows of accelerated electrons in magnitude, position and distribution in space are monitored and controlled using simple devices. The value of the electron energy can provide the required thickness of the processed layer of the substance. Therefore, the radiation fusion technology seems to be very attractive.

There is a lot of work to optimize the synthesis of ceramics: the dependence on the power density of the flow of high-energy electrons, the technology of preliminary prepa- ration of the charge, and its composition. It is necessary to carry out studies of physical and chemical processes in materials in the field of powerful radiation fluxes, their specificity, leading to such an effective formation of a new phase without any other effects, without introducing additional substances in order to facilitate synthesis. It is extremely important to carry out work aimed at determining the possibility of forming new phases from refractory dielectric materials of other remnants.

7. Conclusions

1. For the synthesis of ceramics based on YAG:Ce, a mixture was prepared with a charge composition: 55 wt% Y_2O_3, 43 wt % Al_2O_3, and 2 wt % Ce_2O_3. The synthesis was carried out at an electron energy of 1.4 MeV with a power density of 18–23 kW/cm^2. The formation of ceramics occurs in a time of no more than 1 s, without the use of any other substances that facilitate the synthesis. Under the experimental conditions, the productivity of ceramic synthesis was 0.5 g/s.

2. SEM studies have shown that ceramic samples are microcrystals soldered together with a size of ~10...50 microns.

3. The luminescence characteristics are in good agreement with those known for crystals, ceramics, and phosphors based on YAG:Ce. The results obtained show that the formation of the YAG structure of the lattice and the nearest environment of the activator in the lattice does not strongly depend on the bulk charge density. The reactions of synthesis of the new phase are likely to proceed in plasma from the products of radiolysis. However, a slight narrowing of the bands in the samples from the pre-compacted charge indicates that the compaction has some effect on the formation of the lattice structure.

4. The brightness of the synthesized samples and, accordingly, the energy efficiency of converting LED radiation into luminescence is 0.6–0.9 relative to the reference commercial phosphor (SDL4000).

Acknowledgments

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