Ce:YAG ceramics: the influence of the synthesis technology features on the luminescent and the optical properties

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**Abstract.** In this paper, we report on the dependence of the luminescent and the optical properties on the synthesis conditions of the transparent 0.1 at.% Ce:YAG and 1 at.% Ce:YAG ceramics. The ceramics were produced from the nanopowders with a diameter of about 10–15 nm by means of the laser method. The fundamental difference between the two described methods is in the synthesis of the main phase YAG: directly during the vacuum sintering (1 – the first method) and before the vacuum sintering (2 – the second method). For this purpose, the transparent samples (Ø10×2 mm) with the optical transmittance ranging from 58 to 82% at the wavelength of 600 nm were obtained. The first method was proven to be the most preferable in terms of the exact dosage of the dopant which gives the samples the best scintillation characteristics. In a point of fact atom of cerium can potentially leave the material at any or at a certain stage of the ceramics synthesis, reducing the total concentration of Ce$^{3+}$ in YAG.

1. **Introduction**

The most of the scintillation materials used in the detectors of the ionizing radiation are used for the single-crystal form. It is well known that the growth of the scintillation crystals with the high melting temperature is a labor-intensive and expensive process. One of the perspective approaches to it is the replacement of the monocrystals with the ceramic materials [1].

The important factors influencing the scintillation properties are the high optical quality of material, the high effective atomic number, the low scintillation decay time, the uniformity of the activator ions’ distribution in the crystal lattice. The ceramic technology holds out the high-transparent and the large-size garnet materials production opportunity at the lower temperatures and the homogeneous distribution or the gradient-controlled activator ions distribution [2, 3]. In this paper, we are mainly presenting the dependence between the research results on the optical and the luminescent properties of one of the known scintillation ceramic materials, namely, the aluminum-yttrium garnet $\text{Y}_3\text{Al}_5\text{O}_{12}$ activated by Ce$^{3+}$ ($\text{Ce}^{3+}$:YAG) with the Ce$^{3+}$ dopant concentration of 0.1 and 1 at.% on the synthesis technology features. We assume that the ceramics synthesis is the main link to a simultaneous achievement of the high-doping level and the uniformity of the activator ions distribution in the crystal lattice.
2. Experimental

We used the submicron commercial powders with >99.99% purity. The ceramic general flow chart is presented in Table 1. The samples of the transparent Ce\textsuperscript{3+}:YAG ceramics were fabricated from our own production-received nanopowders Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, 1 at.% Ce\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} with the diameter of about 10–15 nm by means of the laser method [4]. The nanopowders were produced in the metastable phases. For their transformation in the main phases, the nanopowders Al\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3}, 1 at. % Ce\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} were annealed at 1200 and 900 °C for 3 hours in the atmospheric muffle electric furnaces with the silicon-carbide heaters, respectively. The nanopowders Al\textsubscript{2}O\textsubscript{3}, Y\textsubscript{2}O\textsubscript{3}, 1 at.% Ce\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} were in the required stoichiometric proportion ((Ce + Y):Al = 3:5) for the synthesis of Ce\textsuperscript{3+}: YAG with the necessary concentration (0.1 and 1 at. %) of cerium. The mix of the nanopowders was mixed on a bead mill with an inclined axis in a plastic bottle for 48 hours using the YSZ balls. The mass ratio of the nanopowder: balls: ethanol was 1:4:8. Tetrathyloxilane (TEOS, (C\textsubscript{2}H\textsubscript{5}O\textsubscript{4})Si) of 0.5 wt.% (0.14 wt.% SiO\textsubscript{2}) was used as a sintering aid in all samples. After that, the mix was vaporated in the rotational vacuum evaporator and was annealed at 600 °C for 3 hours to remove the alcohol fragments.

The received powders were molded into compacts (disks Ø14×4 mm) at 200 MPa in a metal mold to a density of 40–50% from the theoretical density of YAG (4.55 g/cm\textsuperscript{3}) by means of the cold uniaxially press (CUP) method. The compacts were annealed in the atmosphere at 800 °C for 3 hours to remove the organic impurity. The compacts were sintered in a high-temperature vacuum furnace with graphite heaters under 5×10\textsuperscript{-5} mbar vacuum and at 1700–1780 °C for 20 hours. After the vacuum sintering, the samples obtained the black color because of the oxygen deficiency in YAG structure. The samples were annealed in the atmosphere at 1300 °C for 5 hours to complete the oxygen deficiency.

### Table 1. Ceramic general flow chart.

| First method | Second method |
|--------------|---------------|
| Raw materials of yttrium oxide, cerium oxide and aluminum oxide with purity >99.99% | |
| Produce of nanopowder Al\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3}, 1 at.% Ce\textsuperscript{3+}:Y\textsubscript{2}O\textsubscript{3} (10–15 nm) [4] | |
| Annealing of nanopowder (1200 and 900 °C/3 h) | |
| Mixing of nanopowder (Y+ Ce):(Al) = 3:5 (48 h) in ethyl alcohol (C\textsubscript{2}H\textsubscript{5}OH) | |
| Addition 0.5 wt.% TEOS, (C\textsubscript{2}H\textsubscript{5}O\textsubscript{4})Si (0.14 wt.% SiO\textsubscript{2}) | |
| Mix evaporation | |
| Annealing (600 °C/3 h) | Briquetting (20%) |
| - | |
| Passing (200 mesh) | Powders’ mix transformation into YAG |
| - | (1200 °C/3 h) |
| - | Milling of bricket (C\textsubscript{2}H\textsubscript{5}OH) |
| - | Mix evaporation |
| - | |
| Annealing (600 °C/3 h) | |
| Cold uniaxially press (200 MPa) | |
| Annealing (800 °C/3 h) | |
| Vacuum sintering (1700 °C ~ 20 h) | (1780 °C ~ 20 h) |
| Annealing 1300 °C/5 h | |
| Optical polishing | |

During this procedure, the samples were synthesized in two different methods. The fundamental difference between these methods is in the synthesis of the main phase of the aluminum-yttrium garnet: directly during the vacuum sintering (1 – the first method) and before the vacuum sintering (2 – the second method). In the first method, the powders’ mix after annealing have passed through a
200 mesh screen additionally and then were annealed (samples No.2406 – 1 at.% Ce, No.2421 – 0.1 at.% Ce), or were not annealed (samples No.2405 – 1 at.% Ce, No.2420 – 0.1 at.% Ce) in the air atmosphere at 600 °C for 3 hours to remove the organic impurity. At the same time, the temperature of the vacuum sintering was 1700 °C for 20 hours. In the second method, even before the vacuum sintering (samples No.1851 – 1 at.% Ce, No.1854 – 0.1 at.% Ce), and after the annealing the powders’ mix was transformed into YAG in briquettes with the density of 20 % from the theoretical density at 1200 °C for 3 hours in the atmospheric furnaces. Further, the briquettes were crushed and ball milled similarly to the procedure of mixing powders. At the same time, the temperature of the vacuum sintering was 1780 °C for 20 hours. After that, the ceramics were polished. The methods, in which we received optical ceramics earlier [5] underlie the synthesis of these ceramics.

The specific surface area of powders (BET analysis) was determined by the automated gas adsorption analyzer (TriStar 3000, Micromeritics Instrument Corporation, USA). The structures of the sintered ceramics were determined by an X-ray diffraction (XRD) on the copper radiation (Cu Kα1,2 λ=1.542Å) with the graphite monochromator on a secondary beam (D8 Discover GADDS, Bruker AXS, Germany). The processing of the XRD results was carried out via the full-height analysis program named TOPAS 3. The surface morphology was studied with the optical microscope (BX51TRF-5, Olympus Corp., Japan). The optical transmittance and the absorption spectra of the obtained Ce3+:YAG ceramics samples were measured using a UV-2450 (Shimadzu, Japan) optical dual-beam spectrophotometer (200–900 nm). The X-ray luminescence (XRL) spectra were measured using a monochromator MDR-23 equipped by an X-ray source of URS-1,0 (40 kV, 10 mA, W-anode) and Hamamatsu R928 and FEU-106 photomultipliers (experimental physics department, UrFU, Russia).

3. Results and discussion

The results of the implementation of the above-stated procedures by means of the solid-state reaction method, 6 samples (Ø10×2 mm) with the Ce3+ dopant concentration of 0.1 and 1 at.% are fabricated (figure 1).

As it was already mentioned in this paper, the fundamental difference between the two methods is in the synthesis of the main phase of the aluminum-yttrium garnet from the yttrium and aluminum oxides powders: directly during the vacuum sintering (1 – the first method) and before the vacuum sintering (2 – the second method). This difference is visible on an X-ray phase pattern (XRD) of the compacts: the first method – figure 2a, the second method – figure 2b.
The compact (the first method) was annealed at 800 °C for 10 hours. According to the technology, the removal of the organic chemistry annealing for 3 hours has been carried out, but for the precise fixation of the reactions lack between the yttrium and aluminum oxides the time has been increased to 10 hours. The research has shown that there are no reactions between the oxides (figure 2a). Herewith, XRD shows the existence of the cubic phase $Y_2O_3$ (60 wt.%) and the crystallites average sizes (OKR) = 43(5) nm, the existence of aluminum oxide various phases: rhombohedral corundum (10 wt.%) and OKR = 48(10) nm, monoclinic $\theta$-phase $Al_2O_3$ (20 wt.%) and OKR = 22(2) nm, cubic $\gamma$-phase $Al_2O_3$ (10 wt.%) and OKR = 29(3) nm. The existence of a large number of various aluminum oxide phases is caused by the pre-annealing of the nanopowder and the compact.

The compact (the second method) was also annealed at 800 °C for 10 hours. In XRD evidence (figure 2b) it contains the next phases: the orthorhombic perovskite phase $YAlO_3$ (65 wt.%) and OKR = 90(20) nm, the rhombohedral corundum (17 wt.%) and OKR = 70(10) nm, the cubic garnet $Y_3Al_5O_{12}$ (14 wt.%) and OKR = 78(6) nm, the cubic $Y_2O_3$ (4 wt.%) and OKR = 54(6) nm, the unidentified crystal phase (<1 wt.%). Most probably, the unidentified crystal phase is one of aluminum oxide modifications. As we can see from XRD (figure 2b), the parent compact has been received from the reacted oxide powders which have formed a phase cubic garnet $Y_3Al_5O_{12}$ required for orthorhombic perovskite phase $YAlO_3$ and the non-reacted parent material: the yttrium and the aluminum oxides. Besides, we also observe crystallites size (OKR) increase and phase transformations natural to heat treatment.

As a result of both ways, after vacuum sintering, 100% YAG phase ceramics are fabricated that is confirmed by XRD (figure 2c, 2d).

One of the important ceramics synthesis stages is the powder molding stage, therefore, the nanopowders compaction considerably differing from the same pressure molding (in this case is 200 MPa) is also notable. So, for example, in the first method, the density of a compact was about
2.02 g/cm³ (44.4% of YAG density), for the second method – 2.18 g/cm³ (47.9% of YAG density). The powders in the second case (second method) were coarser after the calcination and the milling compared to the initial nanopowders in the first method. The nanopowders compaction problem still exists and is under study [6, 7]: there is less size particle so much the worse they consolidate. The density of the initial powder particles affects the final characteristics of the optical ceramics.

Besides, the final dispersion of particles on the choice of the corresponding YAG synthesis temperature was also considered. In the first method, the temperature of 1700 °C has been chosen, as the smaller powder was used, and respectively, the more active in terms of sintering because of the more developed particles surfaces. For the second method, the temperature of 1780 °C has been chosen, as the coarser powder was used. The powder was coarsened even after the milling because of the powder agglomeration and the phase transformations. On BET evidence powders analysis for the first method (before the CUP stage), the surface area yttrium oxide is 17.92 m²/g, aluminum oxide is 57.5 m²/g. On BET evidence powders analysis for the second method (before a CUP stage) surface area is 11.7 m²/g. Data of the powders BET analysis is agreed with XRD crystallites average sizes (OKR) fore-quoted (figure 2a, 2b) where OKR of materials phases in a compact much greater than the parent nanopowders OKR sizes.

For a microstructure research, the ceramic’s side plane was polished and then was subjected to a thermos-etching in the air at a temperature of 1350 °C for 5 hours. The research has shown that the ceramics average grain sizes do not depend on the method of fabricating. There is a dependence between the samples and the various concentration of ions Ce³⁺ (figure 3). The average grain size decreases from 24–27 µm (0.1 at.% Ce) up to 17 µm (1 at.% Ce). The grain size decrease, most likely, is related to a higher dopant Ce³⁺ concentration, which inhibits the grain growth because of the various cerium Ce³⁺ ionic radiuses in comparison with the yttrium Y³⁺ ionic radius.

Figure 3. The photographs of the polished Ce³⁺: YAG ceramics samples surfaces:
the first method: 0.1 at. % Ce (a), 1 at. % Ce (b);
the second method: 0.1 at. % Ce (c), 1 at. % Ce (d).
The optical absorption and transmission spectra of the investigated samples are shown in figure 4a and 4b, respectively. The spectra demonstrate the noticeable absorption bands with the maxima at 228, 260, 304, 338, and 457 nm, associated with 4f→5d transitions in Ce$^{3+}$ ions.

![Figure 4. The optical absorption (a) and transmittance (b) spectra of ceramic Ce:YAG samples.](image)

As can be seen from the optical absorption spectra (figure 4a), the intensity of the above absorption bands of the samples synthesized in the framework of one method essentially depends on the concentration of the dopant. However, it is also seen that the intensity of the absorption bands in the samples with the same concentration of charged dopant and synthesized by different methods, is different (for example, spectra for samples No.2420, 2421 (first method) and No.1854 (second method), figure 4a). As a result of this analysis of the optical absorption spectra, it can be concluded that the samples synthesized by means of the second method contain a smaller amount of Ce$^{3+}$ ions. Based on this, the first method can be considered as the most preferable in terms of the exact dosage of the dopant.

The optical transmission spectra (figure 4b) reveal that the transmittance of the ceramics samples at a 600 nm wavelength was 58 to 82%. We also noted that the transmission coefficient in the 500–900 nm region (figure 4b), which determines the optical quality of the samples, directly correlates to the concentration of the Ce$^{3+}$ ions in YAG lattice. The low value of the cerium ions concentration corresponds to the high optical quality of the samples. We assume that one of the reasons for this effect can be the influence of the grain size on the optical properties of the ceramic samples. As mentioned above, with increasing Ce$^{3+}$ concentration the average grain size in the sample is decreased. With a smaller grain size, the additional light-scattering centers have appeared leading to a degradation of the optical quality of the samples. We believe that an increase in the vacuum sintering time should lead to an increase in the grain size, which causes an increase in the ceramics transparency with a higher concentration of the Ce$^{3+}$ dopant.

The following effect should also be noticed. The samples with the identical dopant concentrations synthesized with the first method (samples No.2420, No.2421 (0.1% Ce) and No.2405, No.2406 (1% Ce)) have a different transmission coefficient at 500–900 nm wavelength region (see figure 4b). The grain sizes in the pairs of samples mentioned above are the same. The difference in pairs of the samples lies in the presence or absence of the additional annealing having passed through a 200 mesh screen during the synthesis (see table 1). We believe that the samples that have not undergone the additional annealing contain more pores and defects caused by the contamination of the organic impurity in the initial powder.

The XRL spectra of the samples were measured in the range of 200–800 nm (figure 5). It is evident from the figure that all the samples exhibit an intense luminescence with a band maximum at the 525–538 nm region corresponding to the radiative d→f transitions ($^2D\rightarrow^2F_{5/2}$ and $^2D\rightarrow^2F_{7/2}$) in the Ce$^{3+}$ ions. On the normalized XRL spectra (figure 5b), it is demonstrated that the increase in the concentration of
the dopant in the samples leads to the maximum shift of the luminescence spectrum from 525 to 538 nm. In the 240–460 nm region, a luminescence band associated with the decay of the self-trapped excitons (STE) in the YAG host [8]. The complex shape of the STE band is due to the presence of the absorption bands from Ce$^{3+}$ in this region. In addition, the luminescence bands of the uncontrolled rare earth ions Gd$^{3+}$ and Tb$^{3+}$ (figure 5) are observed in the XRL spectra. The presence of such contamination in negligible quantities does not affect the main luminescence band of Ce$^{3+}$ ions.

The investigated samples with the highest luminescence intensity (figure 5a) are samples synthesized in the framework in the first method with 1% of Ce (No.2405 and No.2406). Among the samples with a cerium concentration of 0.1%, the sample with highest intensity is No.2420. It is interesting to note that this sample has a worse optical quality than similar samples with 0.1% of Ce. However, in this case, a decrease in the optical quality of the sample compensated by an increase in the concentration of the dopant. For a more accurate estimation of the relative content of Ce$^{3+}$ in YAG ceramics, the attention should be drawn to the luminescence band of the STE. The intensity of the STE band in this case indirectly indicates the relative concentration of the cerium ions in YAG (inset in figure 5b). The higher is the concentration of cerium ions in YAG, the lower is the intensity of the emission band of the STE. The intensity of the emission band of the STE for sample No.2420 is lower than that of samples No.2421 and 1854, which means that the concentration of Ce$^{3+}$ ions in it is greater.

As a result of the similar STE band intensity analysis in the XRL spectra, considering at the same time the results of the optical absorption and the spectra transmission analysis (as mentioned above), we may conclude that the content of the Ce$^{3+}$ ions in YAG lattice in the second method of the ceramics synthesis is less.

4. Conclusions

We have fabricated the samples of the 0.1 at.% Ce:YAG and 1 at.% Ce:YAG sized Ø10×2 mm ceramics generated from the nanopowders with the diameter of about 10–15 nm by means of two different methods. The fundamental difference between the two methods is in the synthesis of the main phase of the aluminum-yttrium garnet: directly during the vacuum sintering process (1 – the first method), and before the vacuum sintering (2 – the second method). The result of the research carried by means of the XRD method has revealed that during the synthesis of the samples at the temperature of 800 °C no reactions between the initial oxides have been detected. Upon the increase in the temperature of the synthesis to 1200 °C, the samples contained 14% YAG and 66% YAP. The temperatures of 1700 °C (in the first method) and 1780 °C (in the second method) caused the formation of the single-phase compositions of YAG.
It has been demonstrated that the increase in the concentration of the dopant from 0.1 at.% Ce$^{3+}$ to 1 at.% Ce$^{3+}$ in the samples synthesized by means of these two methods has caused the average grain size to reduce from 24–27 µm to 17 µm, which in turn, is one of the reasons for the decrease in the transparency of the ceramics’ samples in the wavelength ranged 500–600 nm from 82 to 58%. During the synthesis of the main phase of the aluminum-yttrium garnet in ceramics directly during the sintering of the samples, the absence of the intermediate annealing phase after the passing (200 mesh) of the powder before pressing (CUP) leads to a decrease in the transparency of the finished ceramics.

The luminescent-optical measurements have shown that the brightest glow among the synthesized ceramics was obtained by the samples synthesized by means of the first method at a 1% Ce. The shift of the maximum XRL spectrum from 525 to 538 nm with the increase of the dopant concentration from 0.1 at.% Ce$^{3+}$ to 1 at.% Ce$^{3+}$ has been detected. In the XRL spectra synthesized samples the dependence of the variation intensity effect of the STE luminescence band on the concentration of the Ce$^{3+}$ ions in YAG has been discovered, which allows to estimate the relative concentration of the Ce$^{3+}$ ions in YAG with more certainty than by means of the spectra of the absorption and transmission. It has been demonstrated that the samples synthesized in the second method contain fewer amounts of Ce$^{3+}$ ions than those synthesized in the first method, whereas the initial dopant concentration in the ready-made samples is the same.

The above allows us to conclude that:

Firstly, the given comparison of the two methods to the synthesis of the Ce:YAG ceramics, the atom of cerium Ce can be not only in the condition of Ce$^{3+}$ but can potentially leave the material at any or a specific stage of the ceramics synthesis reducing the final concentration of Ce$^{3+}$ in YAG;

Secondly, the first method of the synthesis (the synthesis of the main phase of the aluminum-yttrium garnet directly during the vacuum sintering) is the most preferable in terms of the exact dosage of the dopant and from the point of view of simplicity, time and energy consumption and, consequently, the cost-efficiency the of optical scintillation ceramics production technology based on YAG.

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