Effect of the sintering aids on optical and luminescence properties of Ce:YAG ceramics

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Abstract. This reports on experimental results of a synthesis of Ce:YAG ceramics with a thickness of 2 and 8 mm and Ce³⁺ concentrations of 0.1, 0.5, 2 at% and a study of their optical and scintillation characteristics with and without using of a SiO₂ sintering aid. It is shown that using of the sintering aid (0.14 wt% SiO₂) in this ceramics production method results in deterioration of optical and scintillation characteristics. An effect of Si⁴⁺ ions on luminescence properties of Ce:YAG ceramics is revealed. The maximum light output has been achieved in the ceramics without the sintering aid (21900 photon/MeV – 0.5% Ce:YAG, h=8 mm) compared with ceramics synthesized by us previously (20800 photon/MeV – 1% Ce:YAG, h=2 mm).

1. Introduction

The most scintillation materials used in ionization radiation detectors are applied in a monocristalline condition. It is well known that growing of single crystals with the high melting point is a painstaking and costly process. In some cases, an alternative to difficult-to-make crystal scintillation materials may be similar transparent ceramic materials with comparable light output, optical quality, and luminescence decay properties [1, 2]. Currently, new transparent ceramics are intensively searched for, and their synthesis methods are constantly improved.

An yttrium aluminium garnet scintillator Ce³⁺:Y₃Al₅O₁₂ (Ce:YAG) is well known among these materials. As of today, various methods for production of YAG-based scintillators, both monocristalline and optically transparent materials, are developed. One of Ce:YAG scintillation ceramics production methods is the solid-phase reaction method. The materials to be synthesized have high melting points (1930°C for YAG). Therefore, sintering aids, such as SiO₂, MgO [3,4], are usually added to reduce the synthesis temperature and accelerate the material sintering process [5]. However, at the present time it is demonstrated that these aids may have an effect on optical and luminescence characteristics of Ce:YAG [4,6], but this question is sufficiently underexplored. Furthermore, attempts to synthesize transparent ceramics with the thickness over 5 mm are mostly unsuccessful. These unsolved issues lead to significant restrictions in industrial application of ceramics.

In this paper, we attempt to determine the effect of sintering aids on optical and scintillation characteristics of Ce:YAG ceramics and to study a possibility to synthesize large ceramics with the thickness over 5 mm.
2. Experimental

2.1 Samples synthesis

The samples were synthesized by a method published in [7]. The samples of Ce$^{3+}$:YAG ceramics were synthesized from nanopowders Al$_2$O$_3$, Y$_2$O$_3$, 1 at%Ce$^{3+}$:Y$_2$O$_3$ with the diameter of about 10-15 nm; these powders were produced by the laser ablation method [8]. Commercial powders with the purity of >99.99% were taken as raw materials. Firstly, the initial substances were annealed in the air in the electric muffle furnaces with SiC heating elements for 3 hours at 1200°C and 900°C for Al$_2$O$_3$ and Y$_2$O$_3$, 1 at% Ce$^{3+}$:Y$_2$O$_3$, respectively, to remove metastable phases.

The ceramics samples were synthesized by different methods. Samples synthesis details and stages are shown in Table 1.

Synthesis of samples with sintering aids (samples 2587, 2421, 2427, 2409, 2520, 2519). The initial materials for samples were nanopowders Al$_2$O$_3$, Y$_2$O$_3$, 1 at% Ce$^{3+}$:Y$_2$O$_3$ (or 2 at% Ce$^{3+}$:YAG), which were mixed in the required stoichiometric ratio. The nanopowders were mixed for 48 hours in ethanol in a plastic container using an inclined-axis ball mill with yttria-stabilized zirconia (YSZ) balls. During mixing of the powders, 0.5 wt% TEOS (tetraethoxysilane (C$_2$H$_5$O)$_4$Si) was added as a sintering aid, which is equivalent to 0.14 wt% SiO$_2$. Then the mixture was vaporised in a rotary vacuum vaporizer and annealed in the atmosphere at 600 °C for 3 hours to remove alcohol residues. Additionally, the mixture of the initial powders for samples 2421, 2427, and 2409 was sieved using a 200 mesh sieve and annealed in the air at 600 °C for 3 hours to remove organic impurities.

Pressing of the powder mixtures for furnishing of the samples with the thickness of 2 mm was performed by the single-axis static pressing method under the pressure of 200 MPa in metal moulds with the effective diameter of 14 mm to the density equal to 40-50% of the full YAG density (4.55 g/cm$^3$). Compacts for furnishing of the samples with the thickness of 8 mm were initially pressed in metal moulds under the pressure of 16 MPa for compaction, and then isostatically pressed in a hydrostat under the pressure of 200 MPa in latex shells after vacuum treatment (2519 and 2524 samples). For removal of organic impurities, the ceramics were annealed in the air at 600-800 °C for 3 hours. The compacts were sintered in a high-vacuum electric furnace with graphite heating elements under 5·10$^{-5}$ mbar and at 1700 °C for 20 hours.

The samples without sintering aids (2524, 2525) were synthesized under an alternative procedure. The difference from the above mentioned procedures lay in that, before sintering, the powder mixture was compacted to the density equal to 20% of the full YAG density and annealed at 1200 °C for 3 hours in an atmospheric furnace to create YAG structures. Further, the samples were crushed and milled in the same way as for mixture making using an inclined-axis ball mill with yttria-stabilized zirconia (YSZ) balls. Then, after the pressing (see above) the samples were sintered in a vacuum furnace at 1780 °C for 20 hours. This sample synthesis procedure enabled to synthesize YAG beforehand in contrast to the procedures described above, where YAG was synthesized from the initial powders during the vacuum-sintering of the ceramics.

After the vacuum-sintering all samples were black due to oxygen deficiency in their structures. In order to replenish this deficiency the samples were annealed in the air atmosphere at 1300 °C for 15 hours. Then, the ceramics were ground and polished. The final dimensions of the ceramics were Ø10±2 and Ø 10×8 mm.

2.2 Equipment

The structures of the sintered ceramics were determined by X-ray diffraction (XRD) on copper radiation (CuK$_\alpha$, $\lambda$=1.542Å) with the graphite monochromator on a secondary beam (D8 Discover GADDS, Bruker AXS, Germany). Processing of results of XRD was executed in the program of the full-height analysis TOPAS 3.

The optical transmittance and absorption spectra of the obtained Ce$^{3+}$:YAG ceramics samples were measured using a UV-2450 (Shimadzu, Japan) optical dual-beam spectrophotometer (200-900 nm). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using a
Perkin Elmer LS55 spectrophotometer (NANOTECH Centre, Ural Federal University). 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 photo multipliers (experimental physics department, UrFU, Russia).

**Table 1. Ceramic general flow chart**

| Samples | 2421 | 2427 | 2520 | 2519 | 2525 | 2524 |
|---------|------|------|------|------|------|------|
| Own numbering | 2409 | 2519 | 2525 | 2524 |
| Ce$^{3+}$, at% | 0.1 | 0.5 | 0.5 | 0.5 | 0.5 | 2 |

| Shape | Cylinder |
|-------|----------|
| Diameter, mm | 10 |
| Height, mm | 2 | 2 | 8 | 2 | 8 |

| Stage | Synthesis conditions |
|-------|----------------------|
| 1. | Raw materials of yttrium oxide, cerium oxide and aluminum oxide with purity >99.99% |
| 2. | Nanopowders producing (Al$_2$O$_3$ and Y$_2$O$_3$, 1-2 at.% Ce$^{3+}$:Y$_2$O$_3$ (10-15 nm) [8]) |
| 3. | Nanopowders annealing (1200 and 900 °C/3 h) |
| 4. | Mixing (Y$_2$O$_3$+Ce:Y$_2$O$_3$):(Al$_2$O$_3$) = 3:5 (48 h) in ethyl alcohol (C$_2$H$_5$OH) |
| 5. | Addition 0.5 wt% TEOS (0.14 wt% SiO$_2$) |
| 6. | Mixture evaporation |
| 7. | Annealing (600 °C/3 h) |
| 8. | Sifting (200 mesh) |
| 9. | YAG synthesis (1200 °C/3 h) |
| 10. | Milling in C$_2$H$_5$OH |
| 11. | Mixture evaporation |
| 12. | Annealing (600 °C/3 h) |
| 13. | Uniaxial static pressing (200 MPa) |
| 14. | Uniaxial static pressing (16 MPa) |
| 15. | Cold isostatic pressing (200 MPa) |
| 16. | Cold isostatic pressing (200 MPa) |
| 17. | Vacuum sintering (1700 °C ~ 20 h) |
| 18. | Annealing (600-800 °C/3 h) |
| 19. | Annealing 1300 °C/15 h |
| 20. | Optical polishing |

3. **Results and Discussion**
The images of the several samples of synthesized ceramics are given on figure 1. Upon the synthesis results, it is found that using of sintering aids in the above-described synthesis procedure can lead to deterioration of optical characteristics in some cases. An example for this is Sample 2519, 8 mm thick, SiO$_2$ sintering aid. There has been observed a cluster of pores and second phases in a form of white...
opaque areas in this sample. However, sample 2520, 2 mm thick, synthesized in the same way with the same sintering aid, has shown the monophasic structure and high optical quality (Figure 1b). Sample 2524, 8 mm thick, synthesized without sintering aids, has also shown no additional phases. Furthermore, we had to extend the annealing period to 15 hours, i.e., 3 times longer than for the thinner samples (2 mm), in order to bleach the larger samples (to remove F-centres), which made total sense, since the thicknesses of the samples were also quite different (4 times), and the oxygen diffusion rate in the YAG lattice is constant.

There was made a microsection of Sample 2519 for phase composition analysis. According to XRD data the central part of the ceramics contain two crystalline phases: YAG – 97.46% and YAM (monoclinic yttrium aluminium oxide, $Y_4Al_2O_9$) – 2.54%. Presence of YAM phase in the ceramics indicates the shortage of aluminium, which could be attributed to the irregular shrinkage and YAG synthesis process rate due to presence of the sintering aid and to possible aluminium evaporation. The sample contains no additional phase in its periphery (YAG – 100%).

For the analysis of optical and luminescence properties we have taken only monophasic samples 2524, 2421, 2427 and 2409, differing from each other in presence/absence of the sintering aid SiO$_2$ and Ce$^{3+}$ dopant concentration.

The optical transmission and absorption spectra of the synthesized samples are given in figure 2. There are observed absorption bands in these spectra, which are typical for Ce$^{3+}$ ions in YAG with the maximums in the range of 450, 340, and 250 nm, corresponding to $4f\rightarrow5d$ transitions in Ce$^{3+}$. The optical transmission and absorption coefficients measured from the spectra are given in table 2. It is evident from the results that sample 2427 (0.5% Ce:YAG with the sintering aid SiO$_2$, figure 2a, table 2) has the best optical characteristics among the samples of the same thickness (2 mm). Notwithstanding the fact that the transmission coefficient of the sample with the thickness of 8 mm is the lowest among all the samples (57 %), in comparison with those of the samples with thickness of 2 mm, its absorption coefficient has the best value (see table 2). This fact allows for the conclusion that a sintering aid used for YAG synthesis acceleration and temperature reduction could degrade optical characteristics of YAG-based transparent ceramics. However, since the samples with and without SiO$_2$ aids were produced under different conditions, a significant effect of the synthesis conditions on the optical characteristics of the samples cannot be ruled out.

Variations observed in the absorption spectra should also be noticed (figure 2b). The spectra of the samples with the sintering aids show an absorption band on the area of 305 nm, which is not available in the absorption spectra of the samples without the sintering aids. Occurrence of this band is of unknown nature. Nevertheless, it might be safely assumed that this band occurs due to addition of the sintering aid SiO$_2$. 
Figure 2. Optical transmission (a) and absorption (b) spectra of Ce:YAG synthesized ceramic samples.

The XRL spectra of the synthesized samples are shown on figure 3. All the spectra contain an intensive luminescence band in the range of 525-540 nm, which corresponds to intracenter transitions $5d \rightarrow 4f$ in Ce$^{3+}$ ions in the YAG host. The wide band in the range of 250-450 nm can be associated with light emission by self-trapped excitons (STE) in the YAG. It should be noticed that the higher the concentration of Ce$^{3+}$ activator in the YAG is, the weaker the light emission of the STE band is. A series of narrow bands in this area could be attributed to luminescence of uncontrolled rare-earth impurities, Gd$^{3+}$ and Tb$^{3+}$. It may be stated that the XRL spectra of all the examined samples are similar to each other, irrespective to presence or absence of the sintering aids or to synthesis methods.
The shift of the maximum of the Ce\textsuperscript{3+} luminescence band (525-540 nm) is caused only by the activator concentration.

**Table 2. Optical and luminescence characteristics of the ceramics**

| Sample      | Thickness, mm | \( T \), % at 550 nm | \( \alpha \), cm\(^{-1} \) at 550 nm | Luminescence decay parameters |
|-------------|---------------|-----------------------|--------------------------------------|------------------------------|
|             |               |                       |                                      | Amp. of fast comp: \( \tau \) (ns) | Amp. of slow comp: \( \tau \) (ns) |
| 0.5\%Ce, 2524 | 8             | 57                    | 0.31                                 | 1; 90                        | 0.011; 773                  |
| 0.1\%, 2421   | 2             | 75                    | 0.62                                 | 1; 120                       | 0.073; 966                  |
| 0.5\%, 2427   | 2             | 81                    | 0.45                                 | 1; 104                       | 0.058; 667                  |
| 2\%, 2409     | 2             | 61                    | 1.08                                 | 1; 87                        | 0.018; 680                  |

For a more detailed study of effects of the sintering aids on the luminescence and optical properties of Ce:YAG ceramics the PL and PLE spectra were measured (figure 3b). There are observed luminescence excitation and Ce\textsuperscript{3+} light emission bands (transitions 4\( f \leftrightarrow 5d \)), typical for Ce:YAG, in the PL and PLE spectra. However, it is noteworthy that photoluminescence properties of Ce:YAG ceramics respond unexpectedly to variations in the activator concentration and presence/absence of the sintering aid SiO\textsubscript{2}. When the activator concentration increases from 0.1 to 2\% (samples with the sintering aid SiO\textsubscript{2} – 2421, 2427, and 2409), a significant broadening of the luminescence excitation band in the range of 450 nm (transition 4\( f \leftrightarrow 5d_1 \), figure 3b) is observed. This broadening is attributed to an occurrence of two additional shoulders with the maximums in the range of 410 and 510 nm. Interestingly, the most width of this band is observed in the PLE spectrum of sample 2524 with the thickness of 8 mm, 0.5\% Ce:YAG, without the sintering aid. The highest intensity is observed in the shoulders in the 450 nm band on sample 2524 in comparison with other samples synthesized without using of the sintering aid. The similar behaviour can be observed in the luminescence excitation band with the maximum in the range of 340 nm. It is evident that the broadening band assumes a sophisticated irregular shape (figure 3b).

It is also noteworthy that the short wave part of the PL spectrum for sample 2524 (figure 3b) is significantly shifted. It could be attributed to occurrence of an absorption shoulder in the range of 510 nm. The shift of the maximum in the PL spectra of samples 2421, 2427, and 2409 from 526 to 535 nm in case of Ce\textsuperscript{3+} concentration increase from 0.1 to 2\% could also be attributed to the intensity growth of the absorption band in a form of a shoulder with the maximum in the range of 510 nm.
(a)

(b)
Occurrence of additional shoulders in the excitation bands with the maximums in the range of 340 and 450 nm can be connected with changes in the symmetry of the impurity Ce$^{3+}$ luminescence center. When introduced into the YAG host, Ce$^{3+}$ ions replace Y$^{3+}$ ions. However, due to the difference in the
ion radius between Ce$^{3+}$ and Y$^{3+}$ ions in eightfold coordination (0.128 and 0.116 nm, respectively) a local distortion of YAG crystalline structure occurs, when Ce$^{3+}$ ions are embedded. As the concentration of Ce$^{3+}$ ions in YAG increases, a distortion degree also increases, which may lead to non-equivalent crystallographic positions of Ce$^{3+}$ ions, particularly, to occurrence of some groups of luminescence centers with different symmetries. Energy levels 5d$_{1}$ and 5d$_{2}$ of cerium are very sensitive to their local environment, and changes in environment configuration may lead to changes in their energy, which becomes obvious in the excitation spectra, when Ce$^{3+}$ concentration increases (figure 3b). Embedding of Si$^{4+}$ ions into the YAG structure enables to compensate distortion of CeO$_8$ polyhedra to the certain extent by the effect of their less ion radius. Si$^{4+}$ ions replace Al$^{3+}$ ions occupying fourfold and six-fold coordination in the YAG. In this case the ion radius of Si$^{4+}$ ions in any coordination is less than the radius of Al$^{3+}$ ions (fourfold coordination 0.040 and 0.053 nm, and sixfold coordination 0.054 and 0.067 nm, respectively). Without the sintering aid SiO$_2$ the compensation effect does not occur, and shoulders appear in the excitation spectrum in the bands with the maxima at 340 (4f→5d$_{2}$) and 450 nm (4f→5d$_{1}$) with the highest intensity among all the samples studied.

For study of dynamic luminescence characteristics of Ce:YAG ceramics there were measured luminescence decay curves in case of pulsed electron beam excitation. Measurement results are shown on figure 3 and in table 2. It is revealed that the increase of Ce$^{3+}$ ion concentration in the samples of transparent YAG-based ceramics leads to a significant shortening of luminescence decay kinetics (figure 3c). This effect was observed by us previously [2] and could be attributed to luminescence quenching in case of sufficiently high concentration of the activator in the host. It is interesting, however, that the best characteristics were shown in the sample synthesized without the sintering aid SiO$_2$ and with Ce$^{3+}$ concentration equal to 0.5% (figure 3c and table 2). Particularly, near-complete absence of the slow component is observed (table 2). Presence of the slow component in the luminescence of the samples with SiO$_2$ can be attributed to occurrence of shallow traps for charge carriers during replacement of Si$^{4+}$ ions with Al$^{3+}$ ions. Due to the difference in charge states between Si$^{4+}$ and Al$^{3+}$ ions an electron trap occurs on Si$^{4+}$ ions; this trap can catch an electron during the luminescence excitation and energy transmission processes. During the excited state relaxation periods the electron can leave the trap and recombine on the cerium luminescence center, resulting in occurrence of the slow component.

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In order to evaluate scintillation efficiency the amplitude luminescence spectrum was measured, when excited using a gamma-ray source with $^{137}$Cs (figure 3d, table 3). Comparing the measured characteristics with our previous results [2], we reveal that sample 2524 (0.5%Ce:YAG, 8 mm thick, synthesized without the sintering aid) has the best characteristics among all the examined samples.
Table 3. Scintillation characteristics of the ceramics

| Sample          | Dimensions, mm | Resolution in our exp., % | Decay time, ns | ALY, photon/MeV |
|-----------------|----------------|--------------------------|----------------|-----------------|
| 0.5%Ce, 2524    | Ø 10×8         | 20                       | 90             | 21900           |
| 1%Ce, 1851 [2]  | Ø 10×2         | 25                       | 99             | 20800           |
| CsI-Tl          | Ø 10×2         | 11.2                     | 1000           | 65000           |
| NaI-Tl          | Ø 10×18        | 9.3                      | 250            | 43000           |

Upon the results of the above-described performed measurements and published data [9] we managed to establish an energy diagram (figure 4), which illustrates energy transmission processes in Ce:YAG ceramics synthesized using the sintering aid SiO\(_2\) and without it. The luminescence excitation and decay processes may develop as follows. Depending on the excitation energy level, there can be observed either light emission by STE in connection with interband transfer of electrons O2p→Y4d, or light emission by impurity Ce\(^{3+}\) ions due to 4f→5d transitions in Ce\(^{3+}\) ions. Due to availability of an energy transmission channel and increased possibility of non-radiative relaxation by the effect of phonons in case of the increase of Ce\(^{3+}\) activator concentration, STE band luminescence intensity decreases. The effect of the sintering aid SiO\(_2\) on the energy dissipation processes in Ce:YAG is illustrated in a form of changed splitting of 5d\(_1\) and 5d\(_2\) levels and a shallow electron trap is occurred.

![Figure 4. Energy diagram of luminescence processes in Ce:YAG with and without SiO\(_2\)](image-url)

4. Conclusions
Scintillation Ce:YAG ceramics with the thicknesses of 2 and 8 mm and Ce\(^{3+}\) concentrations of 0.1, 0.5, 2 at% was synthesized by the solid-phase reaction method from nanopowders produced by the laser ablation method using the sintering aid SiO\(_2\) and without it and without hot isostatic pressing. It is shown that using of the sintering aid (0.14 wt\% SiO\(_2\)) in this synthesis method leads to degradation of optical and scintillation characteristics.
It is determined that the bleaching annealing duration for removal of F-centers in the ceramics for the samples with the thickness of 8 mm is 3 times longer than for those with the thickness of 2 mm. The absorption coefficient on the wavelength of 550 nm for the sample with 0.5% Ce:YAG (without the sintering aid) is the lowest (0.31 cm⁻¹) among all the ceramics being previously synthesized by us. It is revealed that the PLE spectrum of thin samples (2 mm thick) broadens with the growth of the concentration. The bands in the excitation spectrum of the sample with the thickness of 8 mm and 0.5% Ce have the maximum width.

The decay constant of the fast component in the sample with 0.5% Ce:YAG (8 mm thick) synthesized without the sintering aid is 90 ns, which corresponds to those (87 ns) in the ceramics with 2% Ce:YAG and 2 mm thickness, synthesized using the sintering aid (0.14 wt% SiO₂). The contribution of the slow component in the ceramic sample (8 mm thick) synthesized without the sintering aid is more than 5 times lower than in the sample (2 mm thick) synthesized using the sintering aid. The maximum light output has been achieved in the ceramics without the sintering aid (21900 photon/MeV – 0.5% Ce:YAG, h = 8 mm) compared with ceramics synthesized by us previously (20800 photon/MeV – 1% Ce:YAG, h = 2 mm).

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