Luminescence and Scintillation Properties of $\text{Lu}_3\text{Al}_5\text{O}_{12}$ Nanoceramics Sintered by SPS Method

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Abstract

Ce-doped lutetium aluminum garnet $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG) nanoceramics were fabricated at 1600 °C and 1700 °C by spark-plasma sintering (SPS) method from nano-powders prepared by radiation synthesis. Both undoped and Ce-doped LuAG ceramic samples were also prepared from the nano-powders at 1700 °C with significantly increased pre-heating rate. The backscattered electron images revealed large amount of pores in all the Ce-doped samples causing their significant opacity. On the other hand, very large grains and no pores were revealed in the undoped sample, which was the only transparent one. The radioluminescence measurements revealed superior overall scintillation efficiency of the samples sintered

at the temperature 1700 °C, and their defect emission in the UV region was ascribed to oxygen-vacancy-related defects such as F^+ centers. The photoluminescence decay of the defect emission was characterized by an extremely fast decay time of a few nanoseconds. Influence of sintering procedure and subsequent annealing on the luminescence and scintillation properties is discussed.

Keywords: Lutetium-aluminium-garnet; spark-plasma-sintering; nanoceramics; scintillator; Ce-doping

1. Introduction

Scintillation materials based on inorganic single crystals have been employed in the ionizing radiation detection and related applications for several decades [1]. They can be utilized in high-energy physics, environmental monitoring, geological survey, medical imaging, security scanning, astronomy and others. Increasing demands on their performance trigger a continuous search for new materials. Crystal growth of such materials is often difficult due to various reasons, such as substantially high melting temperature and resulting enhanced requirements for the crystal growth equipment or applied growth techniques. Sintered ceramic materials might facilitate the search for new materials and their development reducing the cost of the detection element. In most of the materials, lower sintering temperature (compared to the temperature of the crystal growth from the melt) may influence the formation and nature of the defects. Therefore, different luminescence and scintillation properties might be observed. Defects created at the grain boundaries might negatively affect the scintillation process. Also, segregation at grain boundaries and resulting concentration quenching might in some cases deteriorate the performance of the ceramic scintillation and luminescent materials compared to that of crystals [2].

Scintillation materials based on synthetic garnets have been extensively studied for almost 40 years. The garnet-based materials such as YAG ($Y_3Al_5O_{12}$), contain so-called anti-site defects (AD), which means that Y^{3+} ions can occupy, besides their regular dodecahedral position, also an octahedral Al^{3+} site [3]. Similar behavior can be expected for the Ce-doped lutetium-aluminium garnet scintillator $Lu_3Al_5O_{12}:Ce$ (LuAG:Ce). Considering smaller ionic radius of Lu^{3+} , it could be easier to substitute Lu^{3+} for Al^{3+} and the

probability of the AD formation in LuAG would be higher than that in YAG. Occurrence of the anti-site defects in Ce-doped LuAG was proved by various experimental techniques and atomistic simulations, see [4] and references therein.

Anti-site defects give rise to shallow electron traps, which slow down the transport of electrons towards the Ce^{3+} luminescence center during the scintillation process [5]. This obviously leads to occurrence of slow components in the scintillation decay and significant light yield deterioration. As these defects are isoelectronic (i.e. not charged), it is very difficult to suppress their formation by traditional defect engineering methods, such as introduction of excessive charge by aliovalent ion codoping. This worked for example for suppression of positively-charged oxygen vacancies by Zr^{4+} codoping in Ce-doped yttrium-aluminium perovskite (YAP:Ce) scintillators [6]. It is obvious that suppression of anti-site defects in bulk crystals is a challenging task and a completely different approach is needed. Interestingly, it has been found recently that the electron-trapping ability of an AD can be greatly suppressed by Ga^{3+} admixture into the Al-sublattice [7] and new garnet-based scintillation materials with superior performance were developed [8].

These anti-site defects are created due to the very high temperatures required for the growth of garnet single crystals from the melt. Therefore, the formation of such defects is much less probable during the solid state sintering performed at substantially lower temperatures and the related defects and unwanted phenomena are expected to disappear. This was indeed observed already in 2007 by Mihokova et al. [9], when the absence of AD in Ce-doped yttrium-aluminium-garnet (YAG:Ce) optical ceramics was confirmed by correlated radioluminescence and thermoluminescence experiments. The absence of thermoluminescence glow peaks at low temperatures, absence of the defect-related emission at 300 nm in radioluminescence spectrum and absence of sub-microsecond scintillation decay components were the major pieces of evidence confirming the very low amount or absence of ADs in the ceramic. In the mentioned study the samples were prepared by vacuum sintering [10]. The same conclusions were made in the case of other vacuum-sintered LuAG:Ce samples as well [11]; however, new slow components of

microsecond and longer time scale were observed. They were ascribed to new deep traps present only in the ceramic materials.

The spark plasma sintering (SPS) is another alternative sintering technique. It allows preparation fully dense and fine-grained transparent ceramics at relatively low temperatures in a short period of time (see [12] and references therein). An attempt to sinter and study the LuAG ceramic bodies sintered by SPS was made recently [13]. The undoped LuAG bodies were successfully sintered and their transparency, morphology and mechanical properties were studied. It was also found that higher sintering temperatures around 1600-1700°C are more suitable for sample preparation, as favorable properties such as better densification, hardness and higher transparency were achieved. On the other hand, there is a question how other defects and various phenomena related to the grain boundaries will affect the scintillating material performance.

This was a significant impulse for further attempts to sinter the Ce-doped material and study its scintillation properties [14]. Absence of the above mentioned AD-related submicrosecond slow components was highly probable but on the other hand, the influence of other defects needed to be studied for the SPS-sintered LuAG:Ce scintillators.

Since the samples are prepared under reducing conditions (vacuum, carbon die and punches), defects related to oxygen vacancies would be certainly present. Improvement of transmittance after annealing in air especially in the ultraviolet and visible ranges was observed in [13] and can be due to elimination of the defects related to oxygen vacancies.

It is possible to use conventional powders to prepare the ceramics; however, it was found that nanopowders have very large surfaces facilitating the mass transfer and thermal surface processes, which makes nanopowders excellent starting materials for SPS sintering [15, 16]. Recent development of a unique photo-induced radiation synthesis of oxide nanopowders [17] provides an interesting alternative source of starting materials.

In this work we study the morphology and both scintillation and luminescence properties of SPS-sintered LuAG:Ce ceramic samples prepared from nanopowders synthesized by the novel photo-induced radiation

synthesis. We also compare the luminescence and scintillation properties of the ceramic samples before and after annealing in air and discuss possible influences and the role of defects related to oxygen vacancies.

2. Experimental details

The nanopowders used in this work were prepared by UV-light-induced precipitation of solid precursor from solutions of lutetium nitrate, aluminium nitrate and ammonium formate (all chemicals of >99.995 % purity) and subsequent calcination at 1200 °C, producing pure LuAG without any phase impurities. The nanoparticle size was relatively uniform (30-50 nm) and the Ce concentration was around 0.2 mol. %. For details regarding the photo-induced synthesis see [17].

The LuAG:Ce nanoceramic bodies were prepared by the Syntex-Lab SPS apparatus as follows: 1 g of the powder was introduced into a carbon die with an inner hole diameter of 10 mm and closed with two carbon punches. The samples were sintered in vacuum. In the apparatus, a mechanical pressure of 10 MPa was applied and the temperature was increased to 1000 °C in 30 minutes and kept for 5 minutes. Then the temperature was raised in 10 minutes to the sintering temperature, which was 1600 or 1700 °C and an increase of the pressure to 100 MPa followed immediately. The samples were kept at these conditions for 45 minutes and then the power was switched off leaving the apparatus to cool down. No sintering aids were added.

The samples will be further denoted as NN with the sintering temperature given after the abbreviation.

Other Ce-doped and undoped nanopowder samples were prepared the same way as described above, just a rapid pre-heating to 1000 °C was performed only in 4 minutes. The sintering temperature was 1700 °C for both of them. These samples prepared under the rapid pre-heating will be further denoted as RP1700 for the Ce-doped one and RP1700undop for the undoped one.

After the preparation and characterization, all the samples were annealed in a furnace at 1200 °C for 12 h in air. These samples are denoted by a letter “A” at the end of the corresponding acronym. Selected

experiments were performed for the annealed samples as well. The sample acronyms with their composition and fabrication parameters are summarized in table 1.

The surface morphology of the sintered bodies was investigated using backscattered electron (BSE) imaging performed with Hitachi S3400N scanning electron microscope.

The radioluminescence (RL) spectra under X-ray excitation were measured using the modified Horiba Jobin-Yvon 5000M spectrofluorometer coupled with Seifert X-ray generator (Mo anode, operated at 40 kV and 15 mA). The spectra were corrected for experimental distortions using a correction curve. All the measurements were performed at room temperature.

The photoluminescence decay time was measured using the same apparatus by the single-photon counting method under excitation with nanosecond hydrogen pulsed flashlamp or pulsed LED sources (NanoLED, Horiba Jobin-Yvon). The decay curves were fitted by the sum of exponential functions using the deconvolution procedure with the instrumental response to obtain true decay times.

The scintillation decay under soft X-ray (SXR) excitation was performed using nanosecond pulsed excitation source consisting of Ar plasma produced by short laser pulses (7 ns) in a gas puff target. The emitted radiation was filtered using a twin Ti filter of 0.4 μm thickness which resulted in a quasi-monochromatic radiation with an energy of 430 eV. The light emitted from the sample further passed through a monochromator (Jobin Yvon H20, France) and was detected by a photomultiplier (Hamamatsu R7056, Japan). The signal was amplified by a trans-impedance amplifier (Analog Devices AD847, USA) and digitized by an oscilloscope (Agilent Infiniium DSO7104, USA). For further details see [18]. The resulting curves were also corrected for the instrumental response using a deconvolution procedure.

3. Results and discussion

The sintered nanoceramic bodies NN1600 and NN1700 are shown in the Figure 1 together with their sintering temperatures. Both of them were slightly translucent and of dark-green color. The high quality

commercial LuAG:Ce reference single-crystal with the Ce concentration of 0.42 mol. % provided by the Crytur Company, Czech Republic, is shown for comparison.

The photographs of the RP1700 and RP1700undop samples prepared using a rapid pre-heating are shown in Figure 2. The appearance of the Ce-doped RP1700 sample (Figure 2b) does not seem to be different from the Ce-doped samples in the Figure 1. On the other hand, the RP1700undop sample (Figure 2a) was highly transparent with very few carbon inclusions. Since the ceramic bodies from both undoped and Ce-doped starting nanopowders were prepared under identical conditions, we can infer that there may be an influence of the Ce doping on the sintering process. There might also be some difference in the nanopowder starting materials for the Ce-doped and undoped samples. The samples prepared in [13], which did not contain any Ce, were mostly transparent as well, however the grain size in the samples sintered at 1700 °C was roughly one order of magnitude smaller than in the RP1700undop sample studied in this work. This would point to already mentioned improved mass transfer and enhanced surface processes in the nanopowders, at least in the undoped ones.

The comparison of BSE images for the NN1700 sample with different magnification is shown in Figure 3. Large amount of pores was observed in the center of the sample, as shown in the Figure 3a. The morphology of the NN1600 sample was almost identical (not shown here). The pores are responsible for the opacity of these Ce-doped samples. However, a difference in morphology was observed for the NN1700 sample at its edges, as displayed in Figure 3b and zoomed in the Figure 3c. A compact area with no pores and large grains was observed, which means that higher sintering temperature already slightly stimulates the grain growth, which was also observed in [13].

The BSE images for the RP1700 and RP1700undop samples are compared in Figure 4. Very large grains with very few pores can be observed in the RP1700undop sample (Figure 4a), while no grains at all can be distinguished in the Ce-doped RP1700 one (Figure 4b), which also contains a considerable amount of pores causing its opacity. This phenomenon tentatively ascribed to Ce-doping needs further investigation.

The comparison of the radioluminescence spectra for the LuAG:Ce samples NN1600 and NN1700 is shown in Figure 5a together with the spectrum of the $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) reference single crystal scintillator and the LuAG:Ce single crystal (SC). The spectra of the ceramic samples are dominated by Ce^{3+} 5d-4f emission peaking around 500 nm. The intensity of this emission in the NN1700 sample is almost 4 times higher than the emission peak intensity of the BGO and almost as high as that of the LuAG:Ce SC, while that of the NN1600 is considerably smaller. The intensity of Ce^{3+} -related emission peak increases with the increasing temperature of sintering. This can hardly be explained by an oxidation of Ce^{3+} to the tetravalent Ce^{4+} , as was done in [19], due to strictly reducing conditions in the SPS process. It can be explained by a different light collection efficiency for structured or polycrystalline materials in the luminescence measurements. It has been often observed that ceramic scintillators, though not transparent, have significantly higher light yield than their single-crystal counterparts, as was observed for example in [20]. The light collection for the NN1700 sample can be most probably influenced by the compact areas where grain growth took place and no pores are present, which would explain its higher radioluminescence intensity. The spectrum of the NN1700 sample also shows some weak broad-band defect emission at 260 and 400 nm, while only a small trace of such an emission can be observed in the NN1600 (see the inset of the Figure 5a). Both these peaks probably originate from the complex defects related to oxygen vacancies created during SPS sintering under reducing conditions (carbon die, vacuum) or it can also be related to the defects present at the grain boundaries. It is necessary to emphasize that the RL spectrum has a minimum at around 345 nm, which exactly corresponds to the Ce^{3+} 4f-5d₂ absorption transition in LuAG. It is possible that the defect luminescence can be modified in this region. Similar phenomenon was observed for example in [21] for Ce-doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) ceramics prepared by vacuum hot pressing. The two defect bands reported in [21] were found at different positions at 310 and 380 nm. The former was ascribed to a defect emission associated with defect emission of the bulk lattice inside the grain and the latter to defect emission related to grain boundaries. The defect emission in the LuAG:Ce single crystal around 280 nm can be ascribed to the self-trapped exciton associated with the AD, while a weak shoulder at 340 nm can be due to electron-hole recombination at the AD [22]. It is important

to note that the intensity of the defect emission in the NN1700 ceramic sample is much lower than that in the single crystal.

Similar comparison is shown in Figure 5b, where the RL emission spectra of the RP1700 and RP1700undop samples are compared with RL spectra of BGO reference crystal and LuAG:Ce single crystal. We can see that the intensity of the Ce^{3+} emission peak in the RP1700 sample is even slightly higher than that of the single crystal. We should also consider that the Ce concentration in the single crystal was 0.42 mol. %, whereas in all the other samples it was 0.2 mol. %. The defect emission in the ultraviolet region seems different from that of the NN1700 sample. The prominent emission peak around 311 nm is ascribed to the ${}^6\text{P}_{7/2}$ - ${}^8\text{S}_{7/2}$ transition of the Gd^{3+} impurity, which is however further obscured by another defect emission, most probably of the same origin (oxygen vacancies) as for the NN1700 sample. The Gd^{3+} emission peak is also poorly resolved due to wide slits used for this measurement. Worse spectral resolution can be also responsible for absence of the dip related to the Ce^{3+} 4f-5d₂ transition. However, slight depression in the curve can be still observed around 345 nm.

The radioluminescence spectrum of the RP1700undop sample consists only of the defect emission band and Gd^{3+} impurity. It has almost exactly the same shape as the UV part of the RP1700 RL spectrum; just its intensity is higher, probably due to the absence of competition for the excitation energy with the Ce^{3+} doping ions. The defect emission in both RP1700 and RP1700undop samples seems to be complex and probably composed of more components, as was observed for example in [23] for undoped YAG ceramics. The broad defect band in [23] is shifted to longer wavelengths probably due to different host and different method of sintering and starting powder morphology.

The photoluminescence spectra for the LuAG:Ce NN1600 and NN1700 samples under 193 nm excitation (to the defect states shaping the absorption edge) are shown in the Figure 6. Their features resemble those of the RL emission in the Figure 5a. The spectra are composed of the Ce^{3+} 5d-4f peak at 514 nm and two defect-related peaks at 260 and 400 nm. The intensity of the latter emission increases with increasing

temperature of sintering. Considering the reducing conditions in the SPS process, this again supports the idea that it is connected to the defects related to oxygen vacancies. Similar consideration might also be valid for the defect related to the 260 nm peak, but further investigation is necessary.

The decay curve of the Ce^{3+} 5d-4f emission under the direct 4f-5d₁ excitation at 452 nm is shown in Figure 7a for the NN1700 sample. This curve was fitted by a single-exponential function characterized by a decay time of 54 ns, a value close to values reported in the literature for the LuAG:Ce bulk material [11]. Figure 7b shows the photoluminescence decay curve of the Ce^{3+} 5d-4f emission for the same sample under 193 nm excitation, which corresponds to the transition to the defect states shaping the absorption edge and simulates the last stage of the scintillation process. In this case, the dominant decay time is slightly prolonged to 64 ns and another slow component is present. As we can exclude the presence of the ADs, this component is related to other complex defects created in ceramics during sintering. Further treatment of the samples such as annealing in air might improve the scintillation characteristics, as will be shown later.

The corresponding decay curves for the 270 and 403 nm emissions under excitation at 193 nm for the NN1700 sample are shown in Figure 8a and 8b, respectively. The curves for both emission peaks correspond to a very short decay characterized by a sub-nanosecond decay times. For the 403 nm peak a 3 ns component is also observed. For precise decay time determination, an apparatus with much higher sub-nanosecond time resolution is required. There can also be a possible influence of scattered excitation light in the case of the 270 nm emission decay and its 2nd order for the 403 nm emission decay. The 270 nm emission peak can be assigned to some kind of excitonic emission. Closely spaced excitonic levels with very short decay times are expected in garnet crystals [5]. Thus, similarly as in [21], the short wavelength defect emission at 270 nm can be related to the bulk matrix inside the grains. The 403 nm peak decay curve resembles to that reported in [24] so this peak was ascribed to an emission of an F^+ center or related defect [24]. Very similar results were obtained for the NN1600 sample. Taking into account the results in

[21], it might be that these defect can be also present at the grain boundaries at increased concentrations with respect to the bulk lattice inside the grain.

Figure 9 shows the photoluminescence emission spectrum of the RP1700 sample under the 205 nm excitation (into the defect states shaping the absorption edge). It clearly resembles the spectra of both the NN1600 and NN1700 samples in Figure 6 and also consists of the Ce^{3+} 5d-4f emission around 510 nm and two defect-related peaks at around 270 and 410 nm. Their relative intensities are smaller than those in the NN1700 sample, which might indicate a slightly limited defect creation during the rapid pre-heating. Little differences in the peak positions might also point to their slightly different nature. The Gd^{3+} impurity emission is not observed under 205 nm excitation. It might be that some other defects shaping the defect luminescence in figure 5b can be excited at shorter wavelengths below 200 nm, as was observed for example in [21,23]. This can be valid for the other (NN1600, NN1700) samples. Regarding the decay times, the results were similar to those for the NN1600 and NN1700 with values of 55 ns for the Ce^{3+} emission and very short decay times for the 270 and 410 nm peaks (not shown here).

Unlike for the RP1700 sample, the photoluminescence spectra of the RP1700undop sample are surprisingly different from the RL one. They are quite complicated and contain several broad bands at 320, 460 and 600 nm. The first two can be excited under 200 nm and the third one under 325 nm. The decay curves related to those emissions are complicated and in microsecond time scale (not shown here). Complex defect emission consisting of peaks with similar positions of the maxima (340 nm, 460 nm) was reported for undoped YAG ceramics in [23]. The possibility of energy transfer between some of the related defects was suggested. Similar can be possible for the RP1700undop sample considering the emission and excitation wavelengths of particular emission peaks mentioned just above. This may explain the complicated course of some of the decay curves.

3.1. Effects of annealing in air

After performing the above experiments, the samples were annealed at 1200 °C in the air for 12 hours. The color of the samples got lighter and slightly yellowish, most probably due to burning out some carbon inclusions. The radioluminescence spectra of the annealed NN1600A and NN1700A samples are compared together in the Figure 10a with the spectra for BGO and LuAG:Ce SC. The radioluminescence intensities of both samples significantly increased. The intensity of the Ce^{3+} 5d-4f transition in the NN1700A sample is 7 times as high as that of the BGO and significantly outperforms the single crystal. The Ce^{3+} emission intensity in the NN1600A sample also increased significantly, though it is still 2 times smaller than that of NN1700A. It was expected that the annealing in air would remove the defects related to the oxygen vacancies and their luminescence would disappear. However, the emission peaks at 280 and 380 nm are present; see the inset of the Figure 10a. If we compare their positions with those in the Figure 5a (non-annealed samples), we can see that their positions are slightly different, which can be a sign of some modification of the defects. Their intensities are also smaller with respect to those for the non-annealed samples (Figure 5a) pointing to the fact that the concentration of defects was decreased by annealing.

Slightly different effect of annealing was observed in the samples prepared with the rapid preheating, see Figure 10b. The intensity of the Ce^{3+} emission decreased after annealing for the RP1700A sample and is significantly lower than that of the SC. The defect emission in both RP1700A and RP1700undopA has also decreased by about a factor of 2. The Gd^{3+} impurity luminescence at 313 nm is clearly resolved in both spectra. The broad structured band around 700 nm observed in the spectrum for the RP1700undopA sample was ascribed to the Cr^{3+} impurity. The decrease of the defect emission can obviously be related to removal of the oxygen vacancies by annealing, which is again not completed. As shown by absorption measurements in [21] for Ce-doped YAG ceramics, annealing introduced new defects in the material, which were responsible for luminescence quenching. However, creation of additional defects was not proved by absorption measurements of the RP1700undop and RP1700undopA samples, which were the

only samples where absorption measurement was possible (not shown here). The decrease of the Ce^{3+} emission with annealing cannot be explained from the available results and further research is necessary.

The photoluminescence spectra of the NN1600A, NN1700A and RP1700A LuAG:Ce ceramic samples under 193 nm excitation are shown in the Figure 11. We can again observe some defect luminescence for all the samples between 200 and 300 nm. In the RP1700A sample there is a well resolved peak around 280 nm in this region while in the other two samples the PL signal increases towards shorter wavelengths. Again, no Gd^{3+} impurity emission is observed. Another well resolved peak is observed around 385 nm in all the samples. In RP1700A it is the weakest. Its decay kinetics is shown for the NN1700A sample in the Figure 12. The decay is so fast that the experimental data copy the instrumental response and no fit could be made. Similar results were observed for other samples. This luminescence can be again related to an F^+ center or it can be of an excitonic origin [5]. It may also be that second order of the scattered light also influences the measurement making the decay time faster than reported in [5] or [24]. When compared to the Figure 8b which shows the result of the same experiment performed on the same sample before annealing, we can see that the 3 ns component disappeared. This confirms modification or disappearance of the defects related to oxygen vacancies. It is worth mentioning that the spectrum for the RP1700undopA sample under 193 nm excitation was completely different and the 380 nm peak was missing. Some sharp peaks related most probably to some rare-earth impurities (Tm^{3+} , Tb^{3+}) were present together with the structured band from the Cr^{3+} impurity (not shown here).

The SXR-excited scintillation decay curves for the NN1600A, NN1700A and RP1700A are depicted in the Figures 13a, 13b and 13c, respectively. Please note the log-log scale. All decays are very complicated and 5 exponentials were needed to satisfactorily fit the experimental data. Presence of very fast components with a few nanosecond decay time in all three curves indicates that the fast defect-related emission discussed above takes place in the scintillation process in all the Ce-doped samples and again confirms the presence of the defects even after annealing. The differences from the values discussed above are caused most probably by different way of excitation by SXR and rather complicated fitting

procedure. The component with decay time around 50 ns found in the NN1700A and RP1700A samples can be undoubtedly ascribed to Ce^{3+} . In the NN1600A sample only a 33 ns component was found. The whole decay curve for this sample is apparently shorter all over the scale, which might be caused by some quenching process. This can also be reflected in the lower radioluminescence intensity of the NN1600A sample. Longer components with decay time between hundreds of ns and to tens of μs were observed in all the samples and are related to delayed charge carrier transport towards the luminescence centers due to their capture by defects.

4. Conclusions

LuAG:Ce ceramic samples were prepared by SPS method from nanopowders at different sintering temperatures (1600 °C, 1700 °C). Very small pores and compact areas with large grains were observed for sample sintered at 1700 °C indicating a pronounced grain growth in some areas. The overall scintillation efficiency of the ceramic sintered at 1700 °C was as high as that of the single crystal, while the defect luminescence intensity under X-ray excitation was lower and of different origin than that of the single crystal. In the single crystal this emission is ascribed to the self-trapped exciton associated with the anti-site defect and an electron-hole recombination at the same defect. The defect bands observed at 270 and 400 nm in the prepared ceramic sample sintered at 1700°C were ascribed to an unknown defect related to oxygen vacancies and F^+ centers (charged oxygen vacancies), respectively. The photoluminescence decay time upon excitation into the Ce^{3+} 4f-5d₁ band at 452 nm resulted in the Ce^{3+} 5d-4f emission with a decay time of about 54 ns for both samples. However, under the nearly band-to-band excitation at 193 nm, the decay was as slow as 64 ns and also with a longer, sub-microsecond decay component. This was again observed for both samples. The decay time of the 400 nm defect band related to F^+ center was extremely fast with a decay time of a few nanoseconds.

Two additional samples (Ce-doped and undoped) were sintered at 1700 °C with rapid pre-heating. The Ce-doped sample showed even slightly higher radioluminescence intensity than a LuAG:Ce single crystal. It follows from the photoluminescence spectra of the defect luminescence that the pre-heating stage does not play an important role in the creation of complex defects related to oxygen vacancies. Neither grains nor compact areas were resolved on the surface, only many small pores were found.

The undoped sample was the only transparent sample with no sign of opacity due to significant grain growth. It might be that the absence of Ce can also play some role in the sintering process, but some differences in starting materials might as well be responsible for facilitating the grain growth.

Annealing in air for 12 h at 1200 °C significantly improved the radioluminescence intensity related to the Ce^{3+} 5d-4f emission peak for the samples prepared at 1600 °C and 1700 °C but did not completely remove the defect emission related to oxygen vacancies. Similar behavior was observed in the Ce-doped sample prepared with rapid preheating, but the intensity of the Ce^{3+} -related radioluminescence peak decreased with respect to the sample prepared with slower preheating.

It is highly probable that the radioluminescence intensities for the ceramic samples were influenced by the structure of the sample that improved the light collection efficiency during measurements.

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Figure 1. LuAG:Ce ceramic bodies sintered at different temperatures from different starting materials.

Figure 2. Appearance of the undoped LuAG RP1700undop (a) and LuAG:Ce RP1700 (b) samples sintered at 1700 °C from nanopowder with a rapid pre-heating.

Figure 3. BSE images of the LuAG:Ce sample (NN1700) sintered from nanopowder at 1700°C.

Figure 4. BSE images of the undoped LuAG RP1700undop (a) and LuAG:Ce RP1700 (b) samples sintered at 1700 °C from nanopowder with a rapid pre-heating.

Figure 5. a) X-ray-excited radioluminescence spectra of the LuAG:Ce ceramic samples NN1600, and NN1700 compared with the BGO standard sample and LuAG:Ce single crystal. The inset shows the part of the spectrum of the NN1600 sample, b) X-ray-excited radioluminescence spectra for the undoped LuAG and LuAG:Ce (RP1700undop, RP1700) samples sintered at 1700 °C from nanopowder with a rapid pre-heating, compared with that of the BGO standard scintillator and LuAG:Ce single crystal.

Figure 6. Photoluminescence spectra for the LuAG:Ce NN1600 and NN1700 samples under 193 nm excitation.

Figure 7. a) Photoluminescence decay curve of the Ce^{3+} emission (505 nm) under 452 nm excitation (4f-5d transition) and b) photoluminescence decay curve of the Ce^{3+} emission (505 nm) under 193 nm excitation of the sample sintered from nanopowder at 1700 °C (NN1700).

Figure 8. Photoluminescence decay curves of the defect emission at: a) 270 nm, b) 403 nm under 193 nm excitation of the sample sintered from nanopowder at 1700 °C (NN1700).

Figure 9. Photoluminescence spectrum for LuAG:Ce RP1700 sample sintered at 1700 °C from nanopowder with a rapid pre-heating.

Figure 10. a) X-ray-excited radioluminescence spectra of the annealed LuAG:Ce ceramic samples NN1600A, and NN1700A compared with the BGO standard sample and LuAG:Ce single crystal. The inset shows magnification of the spectra in the UV region. b) X-ray-excited radioluminescence spectra for the annealed undoped LuAG and LuAG:Ce (RP1700undop, RP1700) samples sintered at 1700 °C from nanopowder with a rapid pre-heating, compared with that of the BGO standard scintillator and LuAG:Ce single crystal.

Figure 11. Photoluminescence emission spectra for the 193 nm excitation for the NN1600A, NN1700A and RP1700A samples.

Figure 12. Photoluminescence decay of the 385 nm peak under 193 nm excitation for the NN1700A sample.

Figure 13. SXR-excited scintillation decay curves for a) NN1600A, b) NN1700A, c) RP1700A LuAG:Ce samples.

Table 1.

Sample	Ce concentration (mol %)	Preheating time to 1000°C (min)	Sintering temperature (°C)	annealing
NN1600	0.2	30	1600	Not performed
NN1700	0.2	30	1700	Not performed
RP1700undop	0	4	1700	Not performed
RP1700	0.2	4	1700	Not performed
NN1600A	0.2	30	1600	1200°C 12h in air
NN1700A	0.2	30	1700	1200°C 12h in air
RP1700undopA	0	4	1700	1200°C 12h in air
RP1700A	0.2	4	1700	1200°C 12h in air

Figure1

Figure2

Figure3

Figure4

Figure5a

Figure5b

Figure6

Figure7a

Figure7b

Figure8a

Figure8b

Figure9

Figure10a

Figure10b

Figure11

Figure12

Figure13a

Figure13b

Figure13c