The role of cerium variable charge state in the luminescence and scintillation mechanism in complex oxide scintillators : the effect of air annealing

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Abstract

The influence of annealing in air at elevated temperatures on the absorption, luminescence and scintillation characteristics was studied at the set of the Ce-doped aluminum garnet and perovskite single crystals. Positive effect consisting mainly in increase of light yield and decrease of afterglow was found in varying extent at all the materials. It is explained by the positive role of created stable Ce⁴⁺ center in scintillation mechanism and by decrease of deep trap concentration based on oxygen vacancies.

Keywords: scintillator, Ce⁴⁺, aluminum garnets, perovskites, air annealing

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1. Introduction

Research and development in the field of scintillation materials became very active in last two decades due to a number of applications in high energy physics, medical imaging, high-tech industry and most recently also homeland security areas [1-5] which require novel material concepts of scintillators providing increased performance in one or more critical parameters depending on particular application demands. Usage of aliovalent codopants [6], bandgap engineering [7] and solid solution concept [8] are some of the recipes which led to high performance commercially successful materials.

Due to its allowed 4f-5d transition favorably placed in the near UV-visible spectral range the trivalent Ce^{3+} dopant is one of the most frequently used emission centers in the search for new single crystal scintillators which is also applied in most of the commercially successful ones in last two decades. In the study of aluminum perovskite single crystals in early 1990's it was recognized that the presence of stable tetravalent Ce^{4+} ions in $\text{YAlO}_3(\text{YAP})\text{:Ce}$ decreases the scintillation performance due to related induced absorption bands overlapping with the scintillation spectrum of YAP:Ce in near UV [9]. The charge transfer absorption of Ce^{4+} has been described in more details in the study of $\text{Lu}_2\text{SiO}_5(\text{LSO})\text{:Ce}$ crystals [10] as a broad band peaking around 276 nm with the low energy tail down to 350 nm. Similar spectral features have been revealed in diffuse reflectance spectra of powders of Ce^{4+} -doped A_2ZrO_4 ($\text{A}=\text{Sr}, \text{Ba}$) even much earlier [11]. Recently, high scintillation light yield has been reported in the Ce^{4+} -containing LYSO:Ce,Ca [12] and new model of the Ce^{4+} involvement in scintillation mechanism of orthosilicate scintillators has been proposed in [13,14] consisting in (i) an immediate capture of electron from the conduction band by a stable Ce^{4+} center, (ii) radiative de-excitation of such a temporary Ce^{3+} which in the following final step (iii) captures a hole from the valence band to complete the cycle returning into stable Ce^{4+} charge state. In [13] the existence of stable Ce^{4+} centers was proved also by XANES (x-ray absorption near-edge spectroscopy) technique. In aluminum garnets the Ca-codoping of $\text{Y}_3\text{Al}_5\text{O}_{12}(\text{YAG})\text{:Ce}$ crystal resulted in complete disappearance of characteristic Ce^{3+} 4f-5d¹ absorption band, nevertheless in cathodoluminescence spectra the typical Ce^{3+} emission did dominate [15]. In the Mg-codoped $\text{Lu}_3\text{Al}_5\text{O}_{12}\text{:Ce}$ (LuAG:Ce) optical ceramics where the absorption spectra show that stable Ce^{4+} ions were induced by such a codoping, very high light yield has been measured recently [16] indicating again rather positive role of stable Ce^{4+} center in scintillation mechanism of aluminum garnets. This concept was further developed in single crystals of LuAG:Ce codoped by Mg^{2+} in a broad concentration range [17]: at the highest codopant concentrations comparable with that of Ce^{3+} only the Ce^{4+} center is present in the material as characteristic 4f-5d¹ absorption band of Ce^{3+} is practically lacking. The scintillation response lacks any slower components well known from LuAG:Ce single crystals [18] due to the delayed radiative recombination process, radiation hardness increases, reabsorption losses decrease, and only little decrease in light yield were observed. Finally, the Ca^{2+} [19,20] and Mg^{2+} [21] codoping has been applied in recently discovered ultraefficient $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}\text{:Ce}$ multicomponent garnet scintillator [22], in which mainly the acceleration of scintillation response was found while light yield

was rather decreasing, especially in the former codopant case. In [20] clear correlation between the absorption increase below approx. 360 nm and increased concentration of stable Ce^{4+} centers was provided using XANES method as well. Beneficial influence of annealing in air at elevated temperatures on light yield values has been recently reported for several Ce and Pr doped aluminum garnets [23].

It follows from the above mentioned recent results that tuning of stable $\text{Ce}^{3+}/\text{Ce}^{4+}$ centers ratio may appear as a new tool in optimizing the scintillation performance in some modern oxide-based scintillators. This paper demonstrates the stabilization of Ce^{4+} center induced by annealing in the oxidizing atmosphere (air) in Ce-doped aluminum garnet and perovskite single crystal scintillators and discuss further the influence of stable Ce^{4+} center on the luminescence and scintillation mechanism in Cerium doped complex oxide scintillators.

2. Experimental

Czochralski (Cz) method was used to prepare single crystals of Ce-doped YAG, LuAG and YAP grown from molybdenum crucibles under reductive atmosphere in CRYTUR company, while the Mg-codoped (100 ppm) LuAG:Ce crystal was grown by micropulling down technique from iridium crucible and studied earlier in [17]. Polished plates 1 mm thick, up to 1 cm² area were prepared for the experiments. The same experiments were applied to the as grown and air annealed (1300 °C, 12 hours) samples cut from neighbour positions in the parent crystal boule.

Optical absorption was measured at Shimadzu 3101PC spectrometer, luminescence spectra and decays and spectrally unresolved thermoluminescence were measured at 5000M model spectrofluorometer Horiba Jobin Yvon and light yield (LY) was measured at the dedicated home-made set-up equipped with hybrid photomultiplier (HPMT) detection, for further technical details see [17, 24]. Calibrated spectral sensitivity of the HPMT photocathode ensures even in the green part of the spectra an error of LY value less than $\pm 5\%$.

3. Experimental results

3.1 Ce-doped LuAG

In Fig. 1 the absorption spectra of the “as grown” and “annealed” samples are provided. Annealing in air at such elevated temperature induced an additional absorption below approx. 340 nm shown as the difference spectrum IA in Fig. 1. It is qualitatively the same as that observed in [17] due to Mg^{2+} codoping and can be ascribed to the stable Ce^{4+} center, namely to its charge transfer (CT) absorption transition as in [16,17]. Possible signal saturation due to Ce^{3+} luminescence is noted around the maximum of 4f-5d¹ absorption band within 435-455 nm. We note here that due to the nature of CT absorption process its onset value is similar in oxides and it was in fact shown for the Ce-doped orthosilicate and LuAG hosts (see Fig. 1 in [17] and related discussion there). Furthermore, these CT absorption transitions

are completely analogous in case of Yb^{3+} and Ce^{4+} centers where the former was widely studied in literature [25, 26]. It is worth noting that the approximate energy difference between the ground state position of Yb^{2+} and Ce^{3+} centers (ending states of CT transitions) in an oxide host is about 1.8 eV [27] which perfectly fits the experimental values of CT absorption onsets occurring at about 240 nm [26] and 350 nm [16,17], respectively, in LuAG host.

Fig. 1 Absorption spectra of the Cz-grown LuAG:Ce single crystal samples “as grown” and “air annealed”. Their difference spectrum IA shows the annealing-induced absorption ascribed to CT transition of Ce^{4+} .

In Fig. 2 radioluminescence spectra of the same couple of samples as in Fig. 1 are given. Interestingly, air annealing decreases the intensity of luminescence both in the Ce^{3+} (510 nm) and host (290-300 nm) emission bands which was observed also in [16]. The relative intensity of the latter band decreases even more in the annealed sample which might be due to re-absorption effect given by the additional Ce^{4+} -related CT absorption. Photoluminescence decay time of the Ce^{3+} emission is not affected by annealing procedure, see Table 1.

In case of light yield, however, its value increases by about 25% in the annealed sample, see Table 1, which evidences the acceleration of scintillation response.

Fig. 2 Radioluminescence spectra of Cz-grown LuAG:Ce single crystal samples (excitation X-ray, 40 kV, 15 mA).

In Fig. 3 the afterglow characteristics are shown. Apparently, the annealed sample shows approx. four times lower level of afterglow signal compared to the “as grown” one which is consistent with the light yield increase in Table 1. Also in this measurement the higher intensity of radioluminescence signal (X-ray ON) is confirmed for the “as grown” sample consistently with Fig. 2.

Fig. 3 Spectrally unresolved afterglow time profile after the X-ray cut-off (X-ray ON 40 kV, 15 mA).

Thermoluminescence (TSL) glow curve was also measured to evidence the influence of annealing process on the electron traps. After initial baking at 500 °C in air to empty traps the sample was mounted at cold finger of Optistat cryostat, Oxford Instrument. After cooling down it was irradiated at 77 K for 15 minutes by X-ray (40 kV, 15 mA) and then linearly heated with 5 K/min speed and the light output was continuously monitored. Measurement was made in spectrally unresolved mode (monochromator grating

in reflection mode). Glow curves of both samples are in Fig. 4. Apparently, annealed sample shows greatly reduced intensity of TSL signal in all the peaks noted in Fig. 4. It is worth noting that their position matches very well those measured earlier at LuAG:Ce samples of the same origin [28, 29], but the extent of their reduction in the annealed sample is clearly smaller in the first two peaks at the lowest temperatures (145 K and 168 K). Tentatively, one can explain the effect at the first two peaks as due to the introduction of competing fast radiative recombination pathway through the stable Ce^{4+} centers, while for the peaks at higher temperatures the combined effect of stable Ce^{4+} and diminished oxygen vacancy concentration [30] can reduce the peak intensities even more.

Fig. 4 Thermoluminescence glow curves measured after X-ray irradiation at 77 K (40 kV, 15 mA, 15 min) in spectrally unresolved mode (heating rate 5K/min).

3.2 Mg-codoped LuAG:Ce

As mentioned above, this sample was prepared by the micropulling down technique in Sendai laboratories and studied “as grown” in [17]. The same treatment and experiments were applied here to reveal the effect of air annealing on the Mg codoped LuAG:Ce (Mg concentration was 100 at. ppm in the melt). Generally, the effect was much lower, if any, in comparison with the samples in Section 3.1. Derived from the absorption spectra in Fig. 5 the concentration of stable Ce^{4+} centers practically did not change. Photoluminescence decay time of Ce^{3+} center is also not noticeably affected by the annealing procedure, see Table 1.

Fig. 5 Absorption spectra of as grown and air annealed LuAG:Ce,Mg sample prepared by micropulling down technique.

Radioluminescence intensity measured in the same way as in Fig. 2 has also shown hardly any difference between the as grown and annealed samples and only small increase of light yield was obtained in the latter one, see Table 1.

3.3 Ce-doped YAG

In the case of YAG:Ce sample prepared by the same technology as LuAG:Ce one described in Section 3.1 the same trends are observed in all the characteristics which have been measured. Annealing in air induces the presence of stable Ce^{4+} centers evidenced in absorption spectra. Radioluminescence intensity also decreases in the annealed sample, but comparatively less. Photoluminescence decay of Ce^{3+} is not affected by annealing. On the contrary, light yield increase after annealing is 34% and the light yield value exceeds 30 000 phot/MeV, see Table 1, which is among the highest values ever measured in this material. Similarly, positive effect in the afterglow is stronger compared to LuAG:Ce, see Fig. 6: in few hundreds of milliseconds after X-ray cut-off the signal intensity drops four orders of magnitude and approaches that of BGO reference sample which is known by extremely low level of afterglow among all scintillator materials.

Fig. 6 Spectrally unresolved afterglow time profile after the X-ray cut-off (X-ray ON 40 kV, 15 mA).

Table 1 Photoluminescence decay times of Ce^{3+} center and light yield values (1 μs shaping time, ^{137}Cs 662 keV photon excitation) for all the samples.

Compound/status		PL decay time (ns)	Light yield (ph/MeV)
LuAG:Ce	as grown	58.9	16770
	Annealed	59.7	21170
LuAG:Ce, Mg100	as grown	59.5	22160
	Annealed	60.1	23980
YAG:Ce	as grown	65.7	22570
	Annealed	65.3	30260
YAP:Ce	as grown	17.8	9770
	Annealed	15.9	10740

3.4 Ce-doped YAP

As mentioned in Introduction, the presence of Ce^{4+} center in YAP:Ce was found harmful for scintillation performance two decades ago [9]. The reason was that the induced absorption overlapped with the Ce^{3+} emission peaking around 360 nm in YAP host. In fig. 7 the annealing-induced absorption indeed overlaps with radioluminescence spectrum of YAP:Ce.

Fig. 7 Absorption and radioluminescence (RL, exc=X-ray, 40 kV, 15 mA) spectra of YAP:Ce samples.

Such overlap will inevitably lead to re-absorption losses, but the light yield does show even a small increase in the annealed sample, Table 1. At the same time, the photoluminescence decay in the annealed sample shows only a little sign of acceleration which would be the evidence of nonradiative energy transfer towards the CT absorption band of Ce^{4+} . The decay time value from single exponential approximation of the decay curve in fig. 8 is of 15.9 ns which is about 10% shorter with respect to 17.8 ns measured at the as grown sample.

Fig. 8 Photoluminescence decay of the Ce^{3+} center in annealed YAP:Ce sample. Exc = 310 nm, em = 360 nm. Solid line is convolution of instrumental response and function $I(t)$ in the figure.

4. Discussion and Conclusions

The effect of annealing in air at elevated temperature of 1300 °C was studied in Ce-doped LuAG, YAG and YAP single crystals grown in reductive (oxygen-free) atmosphere. In case of LuAG:Ce, also the Mg-

codoped sample from an earlier study [17] was included for comparison. In the LuAG, YAG and YAP group of crystals the air annealing clearly converted some part of stable Ce^{3+} centers into Ce^{4+} ones which is evidenced by characteristic charge transfer absorption of the latter center in near UV spectral region with the onset around 340-380 nm. In the garnet samples such an annealing process shows generally positive effect: light yield was increased by 25 – 35%, afterglow decreased several times and in LuAG:Ce also the measured thermoluminescence characteristics point to substantial diminishing of electron trap influence in the transfer stage of scintillation mechanism which is achieved by the introduction of competing fast radiative recombination pathway through the stable Ce^{4+} centers and decrease of oxygen vacancy concentration. Despite of spectral overlap of charge transfer absorption of Ce^{4+} and emission of Ce^{3+} in YAP host, the light yield does show a small increase and rather small effect of depleting nonradiative energy transfer from $5d^1$ excited state of Ce^{3+} towards charge transfer absorption center was found in the photoluminescence decay measurement. Thus, for thin samples such an annealing might be plausible even for YAP:Ce optimization.

In the Mg-codoped LuAG:Ce a considerable part of cerium ion was converted into $4+$ charge state due to the divalent codopant already in the as grown sample which is the most probable reason for its little sensitivity to this kind of annealing process and relative stability of all the characteristics measured.

Positive effect of annealing in air on the scintillation response consists not only in the creation of an alternative fast radiative recombination pathway through stable Ce^{4+} centers [13,14,16,17], but also in diminishing concentration of oxygen vacancies [30] arising in the growth process due to the oxygen-free (oxygen-poor) atmosphere, which give rise to deep electron traps.

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