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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 for a set of Ce-doped aluminum garnet and perovskite single crystals. Positive effects consisting mainly in increase of light yield and decrease of afterglow were found to varying extent in all the materials. It is explained by the positive role of created stable Ce^{4+} center in scintillation mechanism and by decrease of deep trap concentration based on oxygen vacancies.

1. Introduction

Research and development in the field of scintillation materials has 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 1990s it was recognized that the presence of stable tetravalent Ce^{4+} ions in $YAlO_3$(YAP):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 detail in the study of Lu_2SiO_5(LSO):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 (A=Sr, Ba) even much earlier [11]. Recently, high scintillation light yield has been reported in the Ce^{4+}-containing LYSO:Ce,Ca [12] and a new model of the Ce^{4+} involvement in scintillation mechanism of orthosilicate scintillators has been proposed in Refs. [13,14] consisting in (i) an immediate capture of electron from the conduction band by a stable Ce^{4+} center and (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 Ref. [13] the existence of stable Ce^{4+} centers was proved also by the XANES (X-ray absorption near-edge spectroscopy) technique. In aluminum garnets the Ca-codoping of $Y_3Al_5O_{12}$(YAG):Ce crystal resulted in complete disappearance of characteristic Ce^{3+} 4f–5d^1 absorption band; nevertheless in cathodoluminescence spectra the typical Ce^{3+} emission did dominate [15]. In the Mg-codoped $Lu_3Al_5O_{12}$:Ce (LuAG:Ce) optical ceramics

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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 a 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–$5d^1$ 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 a little decrease in light yield was observed. Finally, the Ca^{2+} [19,20] and Mg^{2+} [21] codoping has been applied in recently discovered ultraefficient $Gd_3Ga_3Al_2O_{12}$: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 Ref. [20] a clear correlation between the absorption increase below approximately 360 nm and increased concentration of stable Ce^{4+} centers was provided using a 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 Ce^{3+}/Ce^{4+} centers ratio may appear as a new tool in optimizing the scintillation performance in some modern oxide-based scintillators. This work 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 further the influence of stable Ce^{4+} center on the luminescence and scintillation mechanism in cerium doped complex oxide scintillators is discussed.

2. Experimental

The 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 a micropulling down technique from an iridium crucible and studied earlier in Ref. [17]. Polished plates 1 mm thick and up to 1 cm^2 in area were prepared for the experiments. The same experiments were applied to the as grown and air annealed (1300 °C, 12 h) samples cut from neighboring positions in the parent crystal boule.

Optical absorption was measured by a Shimadzu 3101PC spectrometer, luminescence spectra and decays and spectrally unresolved thermoluminescence were measured by a 5000M model spectrofluorometer, Horiba Jobin Yvon and light yield (LY) was measured by the dedicated home-made set-up equipped with a hybrid photomultiplier (HPMT) detection, for further technical details see Refs. [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 ± 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 approximately 340 nm shown as the difference spectrum IA in Fig. 1. It is qualitatively the same as that observed in Ref. [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 Refs. [16,17]. Possible signal saturation due to Ce^{3+} luminescence is noted around the maximum of 4f–$5d^1$ 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 Ref. [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 the 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], in LuAG host.

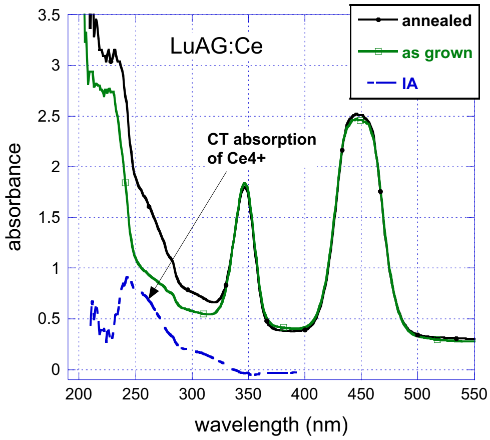

Fig. 1. Absorption spectra of the Cz-grown LuAG:Ce single crystal samples "as grown" and "air annealed". Their difference spectrum IA shows the annealing-induced absorption ascribed to CT transition of Ce^{4+}.

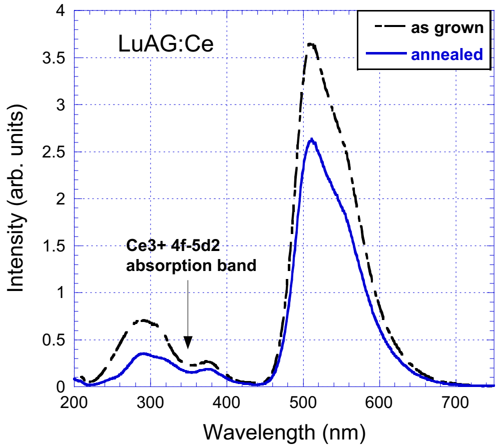

Fig. 2. Radioluminescence spectra of Cz-grown LuAG:Ce single crystal samples (excitation X-ray, 40 kV, 15 mA).

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 Ref. [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 an annealing procedure (see Table 1). In case of light yield, however

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