Effect of thermal annealing on scintillation properties of Ce:Gd₂Y₁Ga_{2.7}Al_{2.3}O₁₂ under different atmosphere

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Abstract Cerium-doped 1% Ce:Gd₂Y₁Ga_{2.7}Al_{2.3}O₁₂ (-GYGAG) single crystal samples grown via Czochralski method were annealed under air, O₂ and N₂ atmospheres from 350 to 1400 °C. The X-ray excited luminescence spectra, energy spectra and UV as well as thermally stimulated luminescence (TSL) spectra were performed comparatively on “as-grown” and thermally annealed samples. It was found that the luminescence efficiency after annealing in air and O₂ was significantly enhanced compared to the non-annealed samples and this phenomenon was suggested to be caused by the existence of some oxygen vacancies in the Ce:GYGAG crystals. And the oxygen vacancies in the as-grown GYGAG crystals can be effectively eliminated by means of annealing in O₂ containing atmosphere without changing the luminescence mechanism. From the TSL curves before and after annealing, three traps within 77–650 K were found to be related to oxygen vacancies.

1 Introduction

Cerium and Praseodymium ion plays an important role in scintillation crystals as activators [1–4]. Ce³⁺ and Pr³⁺-doped Lu₃Al₅O₁₂ garnet crystals display a series of promising scintillation properties [5–8]. However, scintillation performance of doped LuAG is strongly degraded by traps lying below the bottom of conduction band, and

those shallow traps were proved to be related to the anti-site defects [9–11]. Interestingly, further studies on intrinsic defects occurring in the LuAG host [12, 13] motivated the search for new garnet-based scintillator materials. It has been reported that Ga³⁺ admixture to Ce:LuAG diminishes the trapping effects [14] due to the burying shallow traps into conduction band as a result of the lowering of the conduction band edge with Ga admixture [15]. In contrast to the effects of Ga³⁺, the admixture of Gd³⁺ into Ce:Y₃Al₅O₁₂ can increase the conduction band edge and lower the position of the Ce 5d₁ level [16, 17]. Thus, in the frame of so-called “band-gap engineering” and “5d-level positioning” strategies [18–20], a family of (Lu, Y, Gd)₃(Ga, Al)₅O₁₂ scintillators were developed, of which 1%Ce:Gd₃Ga₃Al₂O₁₂ crystal has high light yield up to 46,000 Ph/MeV [18] and 1%Ce:Gd₂Y₁Ga_{2.7}Al_{2.3}O₁₂ crystal demonstrates excellent properties with its light yield 65,000 Ph/MeV in our previous work [20].

Thermal annealing treatment is always applied to scintillators to improve their overall scintillation quality. Systematical annealing experiments of Ce:Lu₂Si₂O₇ crystals under different temperatures and different atmospheres were performed by Feng et al. [20], they found a strong increase of luminescence intensity of Ce:LPS annealed in air above 1400 °C, which was due to vacancies' filling by diffusing oxygen atoms. Drozdowski et al. [21–23] annealed Pr:LuAlO₃ and Pr:Lu₃Al₅O₁₂ crystals in hydrogen and air atmosphere, respectively, and a great yield enhancement was achieved in these crystals. And the positive influence of annealing in air at high temperatures are explained by the creation of an alternative fast radiative pathway through stable Ce⁴⁺ centers and diminishing concentration of oxygen vacancies [24].

However, little attention has been put on the effect of annealing at elevated temperatures on (Y, Gd)₃(Ga, Al)₅O₁₂

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scintillators, which present great light yield improvement compared to the LuAG crystals. In this work, the thermal annealing effects on Ce:Gd₂Y₁Ga_{2.7}Al_{2.3}O₁₂(GYGAG) crystals in different atmospheres were studied and the positive effects were explained. The scintillation properties before and after annealing were compared and discussed. The results of correlated Absorption spectra, X-ray excited Radioluminescence, Thermoluminescence (TSL) and UV-excitation and emission spectra measurements, performed on the “as-grown” and annealed samples, have been analyzed.

2 Materials and experiment

The CeO₂, Y₂O₃, Ga₂O₃, Gd₂O₃ and α -Al₂O₃ raw powders of 99.99% purity were used in this study as starting material. They were weighed according to the stoichiometric ratio of Gd₂Y₁Ga₃Al₂O₁₂:1% Ce and were calcinated at 1500 °C before crystal growth. The crystal was grown by the Czochralski method using iridium crucible, and a Ø1-inch boule one was attained. Details about the growth parameters were presented in [20]. The samples with dimensions of 5 × 5 × 1 and 10 × 10 × 2 mm³ were cut from the crystal ingot and polished carefully before annealing. The first annealing treatment was performed on two big samples in air at 350, 700, 1000, 1100, 1200, 1300 and 1400 °C, each for 6 h. The small 5 × 5 × 1 mm³ samples were annealed at 1200 °C in the following atmospheres: 100% N₂, Ar, O₂ and air. The heating and cooling rate in the annealing process was about 100 °C/h.

The measurement of X-ray excited luminescence (XEL) was performed by using a home-made equipment. Optical absorption spectra were measured at RT by using a Shimadzu UV-2501 PC spectrophotometer. The UV-excited emission spectra and fluorescence decays were recorded on the Perkin-Elmer LS50B and FLS-920 spectrofluorometer, respectively.

The thermal stimulated luminescence (TSL) curves of Ce:GYGAG crystals were determined with a FJ-427A1 thermal spectrometer with a linear heating rate of 1 K/s from 313 to 763 K and 0.15 K/s from 77 to 300 K. Prior to two dimensional TSL experiment, the samples were irradiated with X-ray for 90 s. Meanwhile, three dimensional TSL curves (the TSL as a function of both the temperature and the wavelength, shortened as 3D TSL) were measured at the as-grown and annealed samples. The samples were exposed to X-ray for 240 s prior to 3D TSL experiment.

3 Results and discussion

A sample of Ce:GYGAG with dimension of 10 × 10 × 2 mm³ was sequentially annealed in air at a series of temperature from 350 to 1400 °C for 6 h, the XEL

Fig. 1 X-ray excited radioluminescence spectra of as-grown and air-annealed Gd₂Y₁Ga₃Al₂O₁₂:1%Ce crystals. The inset shows the integrated intensity at each annealing temperature

spectra and their integrated intensities at different annealing temperature are shown in Fig. 1. It is clearly found that the scintillation efficiency could be enhanced after annealing and the biggest (around 260% as-grown) was attained at 1100 °C, but it significantly decreases after annealing at higher temperature (>1200 °C), and the same results was found under O₂ annealing. Such phenomenon is similar to the Lu_{0.8}Sc_{0.2}BO₃:Pr [25], which is attributed to the removal of the oxygen vacancies and the decrease of the scintillation efficiency after annealing at a higher temperature is caused by the oxidization of praseodymium ions. While the phenomenon is different from the other Ce³⁺-doped oxide scintillators [21, 26], whose scintillation efficiency is enhanced after annealing, but keep stable even at high temperature (1400 °C). To prove that O₂ containing atmosphere exerts critical effects on the scintillation efficiency of the crystals after annealing, another sample was annealed in nitrogen atmosphere, as shown in Fig. 2. Contrast to the annealing process in air, the scintillation efficiency of the crystal decreased after annealing in nitrogen atmosphere. It is interesting that the scintillation efficiency does not keep consistent, but fluctuates at different annealing temperature. The same phenomenon is found in argon annealing atmosphere. As the instrument was calibrated each time before testing, it seems that annealing temperature has some impacts on the scintillation efficiency regardless of the ambient atmosphere, although the mechanism is unclear. The ¹³⁷Cs pulse height spectrum of Ce:GYGAG crystals before and after annealing at 1200 and 1400 °C in air and nitrogen atmosphere are presented in Fig. 3. In the air atmosphere, one observes the biggest photoelectron yield at 1200 °C, while the photoelectron yields both decrease at 1200 and 1400 °C after annealing in nitrogen compared to the as-grown. This

Fig. 2 X-ray excited radioluminescence spectra of as-grown and nitrogen-annealed Gd₂Y₁Ga₃Al₂O₁₂:1%Ce crystals. The inset shows the integrated intensity at each annealing temperature

Fig. 3 ¹³⁷Cs Pulse height spectra of Ce:GYGAG sample annealed under air and nitrogen (the inset) in comparison to the as-grown

phenomenon is consistent with the results of the X-ray excited radioluminescence spectra. As mentioned above, it is proposed that the removal of oxygen vacancies plays a dominant role in the air-annealing process (lower than 1200 °C). On the other hand, the decrease of the XEL intensity after 1200 °C can be tentatively explained by the Ce³⁺ oxidation to stable Ce⁴⁺. In the O₂ contained atmosphere, the possible remedy of oxygen vacancies can be described as follow:

The other indirect evidence of the oxidation process and the remedy of oxygen vacancies after high temperature air-annealing will be presented in the following paragraph.

Optical absorption spectra of as-grown and air-annealed Gd₂Y₁Ga₃Al₂O₁₂:1%Ce crystals are plotted in Fig. 4. Thermal etching would occur when the sample was annealed at 1400 °C (the pictures in Fig. 4), so after annealing, the samples' surfaces

Fig. 4 Optical absorption spectra of as-grown and air-annealed Gd₂Y₁Ga₃Al₂O₁₂:1%Ce crystals

were polished before each test. Three peaks as in [27] can be observed: the 4f-5d_{1,2} transitions of Ce³⁺ center at 342 and 438 nm, the Gd³⁺ 4f-4f transition ⁸S_{7/2}-⁶I_{3/2} at 274 nm. Compared with the as-grown sample, the intensity of 342 and 438 nm peak of the annealed ones decrease slightly. The possible explanation is the accumulation of Ce⁴⁺ while annealing, which leads to the reduction of the stable Ce³⁺ and accordingly the decrease of 4f-5d_{1,2} transitions intensity. Such phenomenon is consistent with the divalent cation Mg²⁺ and Ca²⁺ co-doped LuAG:Ce [28] and LYSO:Ce [29]. Here we can also find the increasing intensity of broadband absorption 200–350 nm after air-annealing, and the band can be attributed to the Ce⁴⁺-O²⁻ charge transfer(CT) absorption [28–31]. On the other hand, the Ce⁴⁺-O²⁻ charge transfer(CT) absorption band in our experiment does not show the same features with that given in the literature, it may be due to that the samples co-doped with divalent ions lead to more amount of stable Ce⁴⁺, thus more stronger absorption around 260 nm in the Ca²⁺, Mg²⁺, B²⁺ co-doped hosts [21, 28, 29].

To get better knowledge of the depth of deep traps in the sample, the Thermally Stimulated Luminescence (TSL) curves of GYGAG:Ce before and after annealing in air for 6 h at 1200 °C are shown in Fig. 5. The general form of TSL intensity *I*, as a function of temperature *T*, can be described by the following equation [32]:

$$I(T) = sn_0 \exp\left(-\frac{E_t}{\kappa_B T}\right) \times \left[\frac{(l-1)s}{\beta} \int_{T_0}^T \exp\left(-\frac{E_t}{\kappa_B T'}\right) dT' + 1 \right]^{-1/(l-1)} \quad (2)$$

In the above equation, *n*₀ is the concentration of trapped charges at *t* = 0, *E_t* the energy level of the trap, *κ_B* the

Fig. 5 Glow curves of the Ce:GYGAG crystal: the as-grown and air-annealing at 1200 °C, recorded at a heating rate of 1 K/s following a 90 s X-ray irradiation

Boltzmann constant, l the kinetic order, s the frequency factor, and β is the heating rate. Because Eq. (2) cannot be directly used to fit the experimental data, a modified one (3) [21] was adopted in our fitting process,

$$I(T) = sn_0 \exp\left(-\frac{E_t}{\kappa_B T}\right) \times \left[\frac{(l-1)s}{\beta} \times T \times \exp\left(-\frac{E_t}{\kappa_B T}\right) \left[\left(\frac{\kappa_B T}{E_t}\right) - 2\left(\frac{\kappa_B T}{E_t}\right)^2 + 6\left(\frac{\kappa_B T}{E_t}\right)^3 + 1\right]^{-l/(l-1)}\right] \quad (3)$$

According to Eq. (3), all the TSL data were fitted using ORIGIN 8 software. After several trials to fit the experimental curves we found that the most optimum fitting model consists of four peaks for TSL curves at around 350, 398, 422 and 496 K, which are labeled as 1#, 2#, 3# and 4# respectively, as shown in Fig. 5. The calculated TSL parameters are listed in Table 1. The slight shifts of the peaks after air-annealing are believed to be caused by non-ideal heat transfer between the samples and the heating plate [33]. Theoretically, when the crystal sample is annealed under air at high temperature, the oxygen in air would diffuse into the crystal lattice and fill the oxygen vacancies, so that there should be great decrease even disappearance in intensity of one or more peaks. After air-

Fig. 6 Glow curves of air-annealed Ce:GYGAG compared to the non-annealed, recorded at a heating rate of 0.15 K/s following a 10 min X-ray irradiation

annealing at 1200 °C, the intensity of 3# and 4# peaks decrease a lot, thus both of them are considered oxygen-vacancy-related traps.

Glow curves of 1%Ce:GYGAG before and after annealing are presented in Fig. 6, revealing the existence of several shallow traps. One can easily notice that there are two main traps at very low temperature, i.e., 1# (103 K) and 2# (114 K), but the curves cannot be appropriately fitted with Eq. (3), so it is very difficult to determine an exact number of traps and accurate values of their depths and frequency factors. On the other hand, it can be clearly seen that the peak 2# declines a lot after air-annealing at 1200 °C whilst it keeps the same after N₂-annealing. The possible explanation for this is that shallow trap 2# is related to oxygen vacancies. Figure 7 shows the 3D TSL curves and their corresponding contour plots of the Ce:GYGAG crystal (a) before and (b) after air-annealing at 1200 °C. The two contours show the sample's luminescent wavelength ranging both between 500 and 700 nm (characteristic of Ce³⁺ 5d-4f transition) before and after annealing. Figure 8 shows that the photoluminescence spectra of the Ce:GYGAG sample before and after air-

Table 1 TSL parameters of Ce:GYGAG crystals before and after air-annealing at 1200 °C, derived from Eq. (3) curve fit ($T_{\max}$ —temperature, at which the glow curve peaks; E —trap depth; s —frequency factor in s⁻¹; n_0 —concentration of trapped charges; l —the kinetic order)

Sample	Peak labels	$T_{\max}$ (K)	E (eV)	s/s^{-1}	n_0/m^{-3}	l
As-grown	1#	355	0.79	6.6×10^{10}	792.94	2
	2#	400	0.98	6.91×10^{11}	907.07	1.99
	3#	424	1.03	5.75×10^{11}	3542.66	1.50
	4#	497	1.32	7.76×10^{12}	205.52	2
After air-annealing at 1200 °C	1#	347	0.78	1.48×10^{11}	918	2
	2#	396	0.70	2.19×10^8	942.89	1.7
	3#	420	0.97	1.41×10^{11}	2613.48	1.39
	4#	489	1.09	4.68×10^{10}	96.91	1.7

Fig. 7 The 3D TSL curves of Ce:GYGAG crystal: **a** before annealing, **a1** the 3D TSL curve before annealing and **a2** the corresponding contour of **a1**; and **b** after annealing, **b1** the 3D TSL curve after annealing and **b2** the corresponding contour of **b1**

Fig. 8 Excitation (a) and emission (b) spectra of the Ce:GYGAG sample before and after air-annealing process at different temperature

annealing process at various temperature and it can be found that the excitation and emission peaks do not shift after the annealing process. From the data in the Figs. 7 and 8, we conclude that the Ce³⁺ ions are the recombination centers for the detrapped charge carriers, which is applicable for the traps corresponding to TSL peaks 1[#], 2[#], 3[#] and 4[#].

4 Conclusions

The results presented in this paper indicate that thermal annealing, mostly in 100% air and O₂ (below 1200 °C), can be successfully utilized to improve the scintillation performance of 1%Ce:GYGAG by increasing its scintillation efficiency. However, the luminescence efficiency of the

crystal will decline after air-annealing above 1200 °C due to the dominant role of the oxidation of Ce^{3+} to Ce^{4+} . It is proposed that the enhanced scintillation efficiency of the as-grown 1%Ce:GYGAG after air-annealing is caused by the removal of oxygen vacancies inevitably present in the as-grown crystals. There are three traps, a shallow and two deeper ones monitored by TSL, which are related to the oxygen vacancies. Deeper study of the influence of these traps on the scintillation mechanism and characteristics (e.g., light yield, energy resolution, decay time) are definitely needed. With the removed drawbacks mentioned above the, Ce:GYGAG scintillator would join the group of the brightest oxide scintillators known today.

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