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Deep trapping states in cerium doped $(Lu,Y,Gd)_3(Ga,Al)_5O_{12}$ single crystal scintillators

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HIGHLIGHTS

- Deep trapping states of multicomponent garnets are monitored by the TSL technique.
- Analysis of TSL glow peaks by the initial rise technique is performed.
- $Gd_3Ga_3Al_2O_{12}$ is the host with the lowest trap concentration and afterglow.

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ABSTRACT

We study deep trapping states in Ce^{3+}-doped garnet crystals with the composition $(Lu,Y,Gd)_3(Ga,Al)_5O_{12}$, recently shown as having remarkably high light yield. We use thermally stimulated luminescence (TSL) technique above room temperature and determine the composition $Gd_3Ga_3Al_2O_{12}$ as the host showing the lowest concentration of traps. This host consistently manifests very low afterglow comparable to that of the standard BGO crystal. We also perform TSL glow peak analysis based on the initial rise technique to evaluate trap depth and other characteristics associated with TSL peaks.

1. Introduction

Oxides materials based on the garnet structure are promising candidates for scintillator hosts, due to well-mastered technology originally developed for other applications, their optical transparency, and easy doping by rare-earth elements. The Ce-doped $Lu_3Al_5O_{12}$ (LuAG) single crystal was shown to be a perspective scintillating material (Nikl et al., 2000) with a relatively high density (6.7 g/cm^3), fast scintillation response (60–80 ns) of the Ce^{3+} emission peaking around 500–550 nm, and light yield as much as 25,000 photons/MeV reported for heavily Ce-doped LuAG grown by the Bridgman method (Dujardin et al., 2010). Scintillation performance of LuAG:Ce is degraded by the presence of shallow traps (Nikl et al., 2007) whose effect can be suppressed by modifications of the band gap resulting from Ga admixture into the LuAG structure (Fasoli et al., 2011). However, too high concentration of Ga can lead to a quenching of the Ce^{3+} luminescence due to a proximity of the Ce $5d_1$ excited state and the bottom of the conduction band (Ogino et al., 2009). On the other hand it is also known (Wu et al., 2007) that an admixture of large La or Gd cations into the YAG structure induces larger crystalline field that favorably down-shifts 5d states of the Ce^{3+} ion within the host band gap.

Recently, remarkably high light yield was reported for tailored compositions of Ce-doped $(Lu,Gd)_3(Ga,Al)_5O_{12}$ single crystals grown by micro-pulling down technique (Kamada et al., 2011a,b). The result was achieved thanks to combination of band gap engineering and strategies for favorable $5d_1$ Ce^{3+} level positioning by admixing Ga and Gd into the LuAG structure. The luminescence and scintillation mechanisms of those crystals were addressed in Nikl et al. (submitted for publication).

In this work we study the set of Ce-doped $(Lu,Y,Gd)_3(Ga,Al)_5O_{12}$ single crystals grown by Czochralski technique. We use the thermally stimulated luminescence (TSL) technique to monitor the deep trapping states in these materials. TSL glow curves above room temperature feature several distinguished TSL peaks. We correlate TSL signal below 100 °C with the measured afterglow

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signal. We also use the initial rise method to determine the characteristics of traps associated with corresponding TSL peaks. In particular, we evaluate trap depths, frequency factors and room temperature lifetimes of those traps.

2. Samples and experimental details

The set of Ce-doped $(Lu,Y,Gd)_3(Ga,Al)_5O_{12}$ single crystals was grown by Czochralski (Cz) technique. Concentration of Ce was 1%, except for $Gd_3Ga_3Al_2O_{12}$ host where 1% and 2% Ce-doped crystals were prepared. Plates with dimensions about 5 × 5 × 1 mm were polished to an optical grade.

TSL measurements in air were performed by Harshaw Model 3500 Manual TLD Reader with a heating rate of 1 °C/s. Samples were irradiated at RT with the ^{60}Co source with the dose rate 64.3 Gy/h and received the dose 2.1 Gy. The duration between irradiation and the TSL run was 2 min and kept constant. For each sample two to three successive measurements of the standard TSL glow curve were performed to check the reproducibility of the results. TSL glow curves were monitored in the spectral range 400–650 nm.

Photoluminescence (PL) emission spectra in the temperature range 270–500 K and the spectral range 200–800 nm were performed by a custom made 5000M Horiba Jobin Yvon spectrofluorometer. Excitation was realized by deuterium steady state lamp. An Oxford Instruments liquid nitrogen bath optical cryostat allowed the temperature regulation from about 270 to 500 K. Afterglow measurement was performed by the same apparatus in the spectrally unresolved mode. Excitation was realized by an X-ray tube operated at 40 kV.

3. Experimental results and discussion

The TSL glow curves of Ce-doped $(Lu,Y,Gd)_3(Ga,Al)_5O_{12}$ crystals after irradiation at room temperature (RT) are displayed in Fig. 1. They feature 3 to 4 distinguished peaks at about 65,115 and 170–180 °C up to about 250 °C. Above this temperature all samples feature a broad TSL structure. TSL peaks and consequently also corresponding traps seem similar in all multicomponent garnet crystals. In samples with the same concentration of Ce^{3+} (1%) the highest TSL signal is observed for the garnet sample with no Gd. Substitution of Gd for the rare-earth ion (Lu or Y) lowers the TSL signal, i.e. reduces the number of traps. Samples with Y have lower TSL compared to those with Lu. The lowest TSL signal was observed for $Gd_3Ga_3Al_2O_{12}$ (GGAG) host crystal.

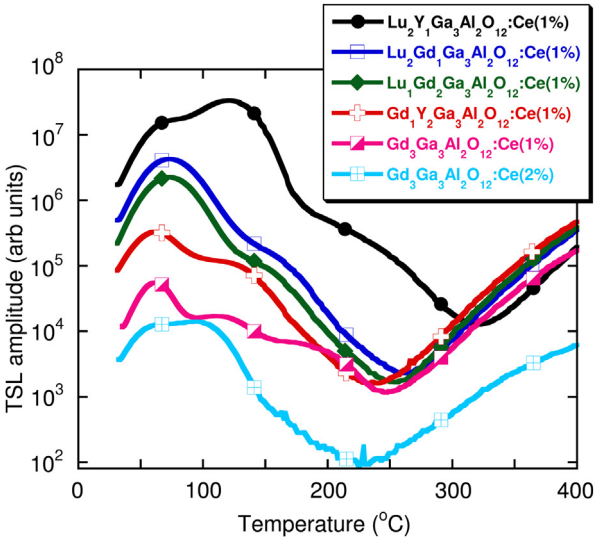

Fig. 1. TSL glow curves of $(Lu,Y,Gd)_3(Ga,Al)_5O_{12}$:Ce after γ-irradiation at RT.

To evaluate the depths of traps associated with glow peaks above room temperature we applied the *initial rise* technique (McKeever, 1985). We performed analysis of well-resolved peaks in three selected samples (see Table 1). For each peak we performed two to three partial cleaning measurements with different temperatures T_{stop}. However, as manifested by the temperature dependence of integrated PL intensity (example for GGAG sample in the inset of Fig. 2), the Ce^{3+} recombination center is quenched above RT. Consequently, before analysis, the glow curves need to be corrected for this temperature quenching of recombination center. Correction curve (solid line in the inset of Fig. 2) was obtained from the fit of PL intensity data.

The initial part of the glow peak can be approximated by an exponential function (McKeever, 1985)

$$Amp(T) = b + W \times \exp(-E/kT), \quad (1)$$

where b is a constant, E is the trap depth, w is a preexponential factor, k is the Boltzmann constant and T is the absolute temperature. Numerical analysis of the data was performed by fitting the function (1) to the data obtained after partial cleaning of the glow curve and correction for the temperature quenching of recombination center.

Example of Arrhenius plot of data and fits corresponding to selected temperatures T_{stop} for GGAG sample are displayed in Fig. 2 with T_{stop} indicated in the figure. Corresponding trap depths resulting from fits are listed in Table 1. For GAGG sample that well manifests all three analyzed TSL peaks we measured the dependence of the TSL signal on the administered radiation dose. Changing the dose by two orders of magnitude we did not observe any shift of the TSL peak positions (see Fig. 3). Therefore one may assume that the traps corresponding to TSL peaks follow the first order recombination kinetics. As a result, we calculated associated frequency factors using the formula relating the frequency factor s, the heating rate β (1 K/s) and the temperature maximum of the TSL peak T_m (McKeever, 1985):

$$\beta E/kT_m^2 = s \times \exp(-E/kT_m). \quad (2)$$

The trap depth E is taken from the initial rise evaluation, in particular, for each trap we used average values indicated in Table 1.

The lifetime of the trap τ at the temperature T can be calculated as (McKeever, 1985):

$$\tau = s \times \exp(E/kT). \quad (3)$$

Table 1
Characteristic parameters of traps associated with TSL peaks in $Lu_2YGa_3Al_2O_{12}$ (LYGAG), $Lu_2GdGa_3Al_2O_{12}$ (LGGAG) and $Gd_3Ga_3Al_2O_{12}$ (GGAG). T_m, T_{stop}, E, E_{ave}, s and τ are the temperature of the TSL peak maximum, temperature of partial cleaning, trap depth, frequency factor and the TSL peak lifetime at RT, respectively.

T_m [°C]	T_{stop} [°C]	LYGAG E [eV]	LGGAG E [eV]	GGAG E [eV]	E_{ave} [eV]	s [s^{-}]	τ at RT [h]
64	45			0.92	0.88 ± 0.04	~10^{12}	~0.3
	50	0.87	0.88	0.89			
	55	0.84	0.89				
	60	0.85					
115	100			1.02	1.04 ± 0.02	~10^{12}	~10^2
	105	1.05		1.03			
	110	1.04					
180	165			1.12	1.13 ± 0.01	~10^{11}	~10^4
	170			1.14			