



Changes in trap parameters in various mixed oxide garnets



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HIGHLIGHTS

- Thermally stimulated luminescence of mixed oxide garnet ceramics was studied.
- TSL of Cr-, Yb-related impurity defects was identified in many garnet compositions.
- Table of Cr-related trap positions in energy gap for mixed garnets was created.
- Cr-related trap was found at 0.4–1.4 eV below the CB, depending on garnet composition.

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ABSTRACT

Shallow and deep electronic traps in various mixed oxide garnet ceramics $(Y, Lu, Gd)_3(Al, Ga)_5O_{12}$ have been studied by thermally stimulated luminescence spectroscopy in the 80–550 K temperature range. It is shown that the substitution of Al ions by Ga and Y by Gd or Lu in YAG:Ce affects the properties of the traps. It is established that the studied ceramics contain residual impurities of chromium and ytterbium. On the base of the obtained and literature data, a table of the Cr-related trap position relative to the bottom of the conduction band in $RE_3(Ga_x, Al_{5-x})_5O_{12}:Ce$ garnets ($RE = Lu, Y, Gd$ and combinations thereof) has been constructed.

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1. Introduction

In the search for new efficient scintillators for medical and industrial applications, cerium-doped oxide garnets have been investigated extensively during recent years. $Y_3Al_5O_{12}:Ce$ (YAG:Ce) and $Lu_3Al_5O_{12}:Ce$ (LuAG:Ce) were shown to have relatively low light yields (<30000 ph/MeV [Moszynski et al., 1994]), whereas more than 60000 ph/MeV can be expected [Rodnyi et al., 1995]. Relatively high light yields, up to 60000 ph/MeV were found in mixed oxide garnets (e.g. (Y,Gd)-garnets [Kamada et al., 2011, Cherepy et al., 2014] and $Gd_3(Ga, Al)$ -garnets [Prusa et al., 2013, Zorenko et al., 2015]). However, many of the mixed oxide garnets as well as YAG:Ce and LuAG:Ce are characterized by a multi-exponential decay and a severe afterglow [Mihokova et al., 2013]. The afterglow is due to trapping of both electrons and holes.

Many investigations have been devoted to both intrinsic and extrinsic traps in garnets [Nikl et al., 2008 and references therein]. The presence of shallow defects related to anti-sites was shown with thermally stimulated luminescence (TSL) [Nikl et al., 2007] as well as with EPR [Laguta et al., 2007, Asatryan et al., 2014] techniques. Recently it was shown also that some of the deeper defects in YAG:Ce can be associated with impurities, in particular with lanthanide impurities [You et al., 2012] or some of the transition metals such as Cr^{3+} [Xu et al., 2011, Ueda et al., 2015].

In this paper we study TSL of mixed oxide garnets containing Cr and Yb impurities as they are expected to be present even in high purity starting materials (based on their chemical similarity with starting materials), aiming at identifying the related trap depths.

2. Experimental

All the $(Y, Lu, Gd)_3(Al, Ga)_5O_{12}:Ce$ 0.2 mol. % garnet ceramic samples in this study were prepared at the Philips Research Eindhoven facility by sintering of a mix of base oxides of 4 N-purity in air

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at around 1700 °C in the form of pills of 14 mm diameter and 0.7–1.4 mm thickness. The supplier lists of starting materials state that Cr and Yb as impurities are present in total in amounts less than 2 and 5 ppm respectively. On the basis of the X-ray diffraction patterns it was concluded that all the samples consists of a single garnet phase. The list of samples studied is shown in Table 1.

The thermally stimulated luminescence (TSL) curves were obtained in the 80–550 K temperature range after irradiation with X-rays (Tube parameters were 55 kV acceleration voltage and 10 mA current) detected with PMT R6357 that is sensitive in the range of 200–900 nm. The irradiation took place during 5 min; the samples were positioned 3 cm away from the tube. The waiting time on between irradiating the samples and the start of the measurements was 10 min, all of the TSL curves shown in the present work were recorded with $\beta = 15$ K/min heating rate. Black-body emission was subtracted from the TSL curve. The curves were also corrected for thermal quenching of the luminescence, measured with a UC-920 Edinburg Instruments spectrofluorimeter under excitation with light with wavelength 450 nm in the range RT–550 K. The operating range of the spectrometer's emission arm was 470–800 nm, the resolution was set at 2 nm. The equipment was calibrated to correct for the wavelength dependent transmission of the monochromators and the spectral sensitivity of the PMT.

3. Experimental results

Firstly, we wanted to see if there will be an impact from variations in cation stoichiometry of a garnet composition on their TSL curve structure. One can expect formation of intrinsic defects to be greatly influenced by the type of non-stoichiometry imposed upon e.g. YAG:Ce garnet either by excess of Y_2O_3 or Al_2O_3 starting oxides [Kuklja, 2000] during synthesis. As opposed to that, impurity-related TSL peaks are not expected to be influenced significantly by slight cation stoichiometry changes.

TSL curves of YAG:Ce samples with several different stoichiometries are shown in Fig. 1, the curves are normalized to the TSL peak at 397 K. One can see that indeed samples with varying cation concentration ratios show a very different TSL peak structure at 100–300 K: for YAG:Ce with excess of Y^{3+} ions (Fig. 1, curve 1) the TSL peak at 180 K can be seen much clearer as compared to two other samples (curves 2 and 3), in which TSL peaks at 200 and 230 K also have significant intensity. The samples with intended exact stoichiometry formula and with excess of Al look very similar (Fig. 1, curve 2 and 3 respectively), it is highly probable that the intended exact-stoichiometry sample had a (unintended) slight excess of Al too. As opposed to that, the shape of the TSL curves above RT (Fig. 1) in all the samples is very similar and seems not to be influenced by stoichiometry at all.

Generally, the low-temperature TSL peaks are attributed to anti-site defects [Nikl et al., 2005, Zorenko et al., 2005], or other structural defects [Varney and Selim, 2014]. It was also shown that some of the peaks above RT in YAG:Ce can be related to Cr (384 K, 9 K/min [Ueda et al., 2015]), Yb (468 K, 120 K/min [You et al., 2012]) or Eu (618 K, 300 K/min [Milliken et al., 2012]) impurities. From this

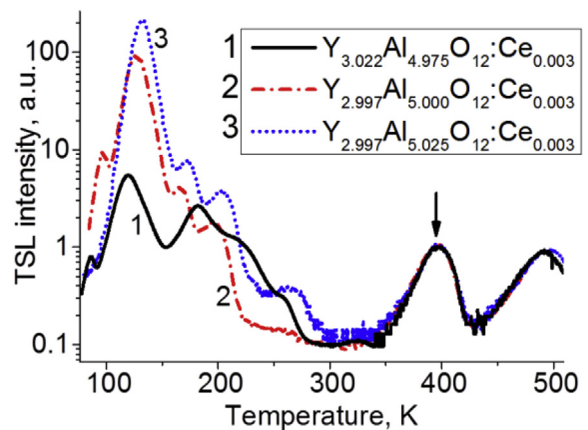


Fig. 1. TSL curves of YAG:Ce ceramic, with various stoichiometry of cations. $\beta = 15$ K/min.

literature data and experimental results in Fig. 1 the tentative conclusion is drawn that TSL peaks that are not influenced by stoichiometry of the garnets can be associated with impurities.

For perovskites [Vedda et al., 2009] it was proposed that defect complexes of O^- or oxygen vacancies spatially correlated to a RE-impurity can be the ones capturing the carriers and generating TSL process. Moreover, for YAGG:Ce,Cr [Ueda et al., 2015], the authors have concluded that $Cr^{3+/2+}$ ions on octahedral sites are responsible for storage of electrons and creation of the TSL peak. We do not have yet enough experimental data to make a final conclusion on the carrier capture mechanism and the defects involved, therefore in this work we will simply refer to TSL peaks associated with impurities as “Cr- or Yb-related peaks”.

As the next step we checked the influence of changes in garnet composition on the TSL peak structure, like substitution of Al ions by Ga and substitution of Y by Gd or Lu in YAG:Ce. Our main focus was at TSL around and above RT.

The dependences of TSL curves on Ga addition into YAGG:Ce or LuAGG:Ce crystals and polycrystals were investigated very thoroughly by the authors in [Fasoli et al., 2011, Ueda et al., 2015]. For all these compositions a shift to lower temperatures of all the TSL peaks with increasing Ga content was observed. It was also found [Xu et al., 2011] that co-doping with 0.05 mol. % Cr greatly enhances one of the TSL peaks in YAGG:Ce. With further TSL investigations for $Y(Al_{5-x}Ga_x)G:Ce$, $x = 0-5$ authors of [Ueda et al., 2015] have traced this peak from 384 K for YAG:Ce down to 161 K for YGG:Ce, measured with $\beta = 10$ K/min heating rate.

A very similar approach of tracing Cr-related TSL peak was conducted in our work (not shown for brevity), for YAG:Ce the peak was found at 397 K (see e.g. Fig. 1), $\beta = 15$ K/min and for $Y(Al_1Ga_4)G:Ce$ at 238 K, $\beta = 15$ K/min. The discrepancy in the TSL peak maximums between our results and the results of [Ueda et al., 2015] work is attributed to a small difference in the heating rates in the TSL measurements.

Table 1

The description of multicomponent garnet ceramic samples under study.

Composition	Changes in Ga/Al, x	Changes in RE/Gd, y	Abbreviation
$Y_3(Ga_xAl_{5-x})O_{12}:Ce$	$x = 0,1,2,3,4$		YAGG:Ce
$Gd_3(Ga_xAl_{5-x})O_{12}:Ce$	$x = 2,3$		GdAGG:Ce
$Lu_3(Ga_xAl_{5-x})O_{12}:Ce$	$x = 0,2,3$		LuAGG:Ce
$Lu_1Gd_2(Ga_xAl_{5-x})O_{12}:Ce$	$x = 1,2,4$		LuGdAGG:Ce
$Y_{3-y}Gd_yAl_5O_{12}:Ce$		$y = 0.15,0.45,0.75,1.2$	YGdAG:Ce
$Lu_yGd_{3-y}(Ga_3Al_2)O_{12}:Ce$		$y = 0,0,3,3$	LuGdAGG:Ce

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