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# Radioluminescence of Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce single crystal and transparent polycrystalline ceramic at high temperatures



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### ABSTRACT

The radioluminescence (RL) of a Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce (LuAG:Ce) single crystal and a transparent polycrystalline ceramic was investigated at high temperatures, up to 600 °C. Two bands were observed, one within 1.8–2.8 eV attributed to Ce<sup>3+</sup>, and another within 2.8–4.5 eV attributed to the collective behavior of different types of defects. The integrated RL intensity of the Ce<sup>3+</sup> band normalized to the respective value at RT increased by a factor of 1.4x from room temperature (RT) up to 450 °C for the single crystal, and by a factor of 1.9x up to 300 °C for the polycrystalline ceramic. Comparison between the integrated RL intensity and glow curves suggested the radiative recombination of electrons thermally released from traps to account for the increase in RL intensity. Beyond these respective temperatures, integrated RL intensity decreased linearly with a rate ~1.4x higher for the single crystal. At about 500/530 °C the normalized integrated RL intensity was the same as at RT for the polycrystalline ceramic and the single crystal, respectively, showing that LuAG:Ce scintillators can be effectively used over a broad range of temperatures.

## 1. Introduction

The luminescence of  $Ce^{3+}$  involves the  $5d \rightarrow 4f$  parity allowed transition that has a large transition probability and thus a fast decay time of tens of nanoseconds. Spin-orbit coupling splits the 4f ground state into two levels,  ${}^{2}F_{5/2}$  and  ${}^{2}F_{7/2}$ , separated by about 0.25 eV. The 5d ( ${}^{2}D_{3/2}$ ) level is split in up to five components by the crystal field depending on the crystallographic symmetry of the  $Ce^{3+}$  ion, and since this level lacks shielding from other Ce electrons it is strongly electron-phonon coupled with the structure. Electron-phonon coupling leads to a strong influence of the nature of the host on the luminescence of  $Ce^{3+}$ . Indeed,  $Ce^{3+}$  emission has been observed over a broad spectral range, from *ca.* 290–700 nm [1]. In garnets,  $Ce^{3+}$  is surrounded by eight oxygen ions forming a dodecahedron that presents a distorted cubic symmetry. The splitting of the 5d level depends on the characteristics of these bonds, with higher distortion of the cubic symmetry around the  $Ce^{3+}$  ions leading to higher splitting of the 5d level [2].

Among the garnets, the high-temperature luminescence of  $Ce^{3+}$  in  $Y_3Al_5O_{12}$  (YAG) has received considerable attention due to its loss of efficiency, chromatic change, and lifetime degradation during the operation of light emitting diodes (LEDs) [2–8]. In general, the luminescence response of garnets at high temperatures is of current technological relevance [9], and in addition to that, oil logging during

geophysical exploration requires the operation of scintillators at high temperatures [10–12]. While the luminescence and scintillation of Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Pr (LuAG:Pr) and several Ce-doped scintillators have been investigated at high temperatures, the luminescence of LuAG:Ce at higher temperatures has received relatively lower attention [6,13]. Moreover, it is presently important to establish a benchmark against the performance of single crystal and polycrystalline ceramic scintillators. Within this context, the radioluminescence (RL) performance of a Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce (LuAG:Ce) single crystal and a transparent polycrystalline ceramic was comparatively evaluated under X-ray excitation at high temperatures, from room temperature (RT) up to 600 °C.

## 2. Experimental procedures

The LuAG:Ce single crystal was grown by the Czochralski method using a 60 mm diameter, 60 mm tall iridium crucible that was inductively heated by an 8 kHz power supply.  $Lu_2O_3$ ,  $Al_2O_3$ , and  $CeO_2$ starting materials were at least 99.99% pure and the flowing atmosphere was nitrogen mixed with a small amount (~0.25%) of oxygen continuously monitored by a residual gas analyzer [14].

The transparent polycrystalline ceramic was fabricated by high temperature vacuum sintering with nominal composition  $Lu_{2.985}Ce_{0.015}Al_5O_{12}$  (*i.e.*, nominal Ce concentration substituting for

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Lu = 0.5%; nominal 0.075 at.% of the whole chemical formula). Precursor powders were prepared by the co-precipitation method using high purity (99.99%) starting materials and 0.5% tetraethyl orthosilicate (TEOS) as a sintering additive. Powders were calcined and uniaxially pressed at ~10 MPa, and the pellet was heated at 400 °C, cold isostatically pressed, and sintered at 1800 °C for 10 h. The concentration of Ce in the samples was estimated to be ~0.04 at.% and ~0.06 at. % for the single crystal and polycrystalline ceramic, respectively, by means of optical absorption and energy dispersive X-ray spectroscopy (EDX) measurements. For RL and thermoluminescence (TL) measurements, small platelets were cut from the original samples due to space limitations of the instruments sample holder.

Optical transmission was measured in the 200–800 nm range using a PerkinElmer Lambda 950 UV/Vis/NIR spectrometer. Spectra were not corrected by the thickness of the samples.

RL measurements were executed from RT up to 600 °C using a customer-designed Freiberg Instruments Lexsyg Research spectrofluorometer equipped with a Varian Medical Systems VF-50J X-ray tube with a tungsten target coupled with an ionization chamber for irradiation dose monitoring. Light emitted by the sample was collected by a lens and converged into an optical fiber connected to an Andor Technology Shamrock 163 spectrograph coupled to an Andor Technology DU920P-BU Newton CCD camera. RL measurements were executed under continuous X-ray irradiation (40 kV and 1 mA) according to the following procedure. The sample was heated at 2.5 °C/s and stabilized at the temperature of interest for 5 s when the RL measurement was executed with an integration time of 1 s. After this measurement the sample was heated up to the next temperature of interest, 25 or 50 °C higher than the previous temperature, and the measurement procedure repeated. Spectra from 1.65 eV (750 nm) to 4.5 eV (275 nm) were obtained at each temperature. Two sets of measurements with different temperature steps and ranges were obtained for each sample; results were not corrected for the spectral sensitivity of the system.

TL measurements were executed in the 50–400 °C range using a Thermo Scientific Harshaw thermoluminescence dosimeter (TLD) reader model 3500 with a heating rate of 1 °C/s. Before each measurement, samples were annealed at 400 °C for 1 or 5 min to deplete all traps followed by X-ray irradiation using a Rigaku Ultima IV X-ray diffractometer (Cu target, 40 kV, 40 mA) from 30 to 300 s. TL results were corrected by the samples masses.

### 3. Results and discussion

The optical transmission spectra of the polycrystalline ceramic and the single crystal are presented in Fig. 1. Both samples exhibited high optical transparency up to about 2.5 eV. The transmission of the polycrystalline ceramic was lower (~70%) than that of the single crystal (~80%) most likely due to residual porosity after sintering. The two major absorption bands centered around 3.54 eV and 2.76 eV were attributed to the Ce<sup>3+</sup>  $4f \rightarrow 5d_1$  and  $5d_2$  transitions, respectively.

Selected RL spectra as a function of temperature are presented in Figs. 2 and 3 for the single crystal, and in Figs. 4 and 5 for the transparent polycrystalline ceramic. Two emission bands were observed. The most intense band within 1.8–2.8 eV (Figs. 2 and 4) was attributed to the emission  $Ce^{3+}$ , while the emission band within 2.8–4.5 eV (Figs. 3 and 5) was attributed to the collective behavior of different types of defects. For comparison, at RT, the peak intensity of  $Ce^{3+}$  emission was 13x higher than the peak intensity of the defects band in the case of the single crystal, while 75x higher in the case of the polycrystalline ceramic. These results together with the fact that the Ce concentration was ~1.5 times higher in the polycrystalline ceramic than in the single crystal suggested the single crystal to have a considerably higher concentration of defects than the polycrystalline ceramic. The  $Ce^{3+}$  band changed in intensity, shape, peak position and width as the temperature increased (cf. Figs. 2 and 4). From RT to about 100 °C, the intensity



Fig. 1. Optical transmission of single crystal and polycrystalline ceramic.



Fig. 2. Lower energy range RL spectra of the single crystal as a function of temperature.



Fig. 3. Higher energy range RL spectra of the single crystal as a function of temperature.



Fig. 4. Lower energy range RL spectra of the transparent polycrystalline ceramic as a function of temperature.



Fig. 5. Higher energy range RL spectra of the transparent polycrystalline ceramic as a function of temperature.

increased and the presence of the two overlapping bands originated from electronic transitions from the 5d excited state to the spin orbit coupling split ground state were observed. As the temperature increased further, the emission intensity increased up to 300 °C for the polycrystalline ceramic and up to about 400-450 °C for the single crystal concomitant to a band peak shift to lower energies and band shape change towards a more symmetrical one. Increasing reabsorption for higher temperatures was ascribed for the red shift and change in shape. The increase of RL intensity for temperatures above RT was attributed to the progressive release of electrons from a variety of traps known to exist in LuAG:Ce [15-17]. A similar increase of RL intensity for higher temperatures was previously observed in YAG:Ce [18]. The decrease of the emission energy for higher temperatures had already been reported for LuAG:Ce in a complementary temperature range, from -223 °C to RT [13], and also in other Ce-doped garnet and garnet-type materials [4,7,9]. Moreover, the onset for thermal quenching in LuAG:Ce single crystal had been previously reported to be ~427 °C [6], in good agreement with the present results. Further increase of the temperature up to 600 °C was followed by a decrease in intensity and further shifting of the peak position towards lower energies. At 500 °C and higher temperatures, the contribution of blackbody radiation from the instrument to the spectra could be observed as a tail rapidly increasing for energies below  $\sim 2 \text{ eV}$ .



**Fig. 6.** Normalized integrated RL intensity as a function of temperature for the single crystal (blue solid squares and blue solid triangles) and the polycrystalline ceramic (red solid circles and red solid diamonds; red open circles are based on data from Ref. [13]). Red and blue dotted lines are linear best fits. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

The behavior of the normalized integrated RL intensity of the Ce<sup>3+</sup> band as a function of the temperature is shown in Fig. 6, together with low temperature data, from -223 °C to RT, of a LuAG:Ce polycrystalline ceramic extracted from Ref. [13] (red open circles). Two sets of results are presented for each sample, revealing the reproducibility of the measurements. Each set of measurements was normalized to the respective value at RT. As a consequence, no direct comparison between the sets of results should be attempted; only intensity ratios within a given set of results can be compared with intensity ratios of another set of results. An overall increase of the integrated RL intensity was observed (dotted lines are linear best fits of both sets of measurements of each sample). The normalized integrated RL intensity increased by a factor of ~1.4x from RT up to 450 °C for the single crystal, and by a factor of  $\sim 1.9x$  up to 300 °C for the polycrystalline ceramic. Beyond these temperatures, respectively, the normalized integrated RL intensity decreased linearly (dotted lines are linear best fits of both sets of measurements of each sample) with the single crystal presenting a decrease rate ~1.4x faster than the polycrystalline ceramic. Moreover, the normalized integrated RL intensity of the polycrystalline ceramic and of the single crystal was equivalent to the value at RT at around 500 and 530 °C, respectively, as determined by data interpolation. These results showed LuAG:Ce scintillators can be effectively used over a broad range of temperatures.

Previous work on YAG:Ce suggested a correlation between the increase of RL intensity with the release of electrons from traps for higher temperatures [18]. Fig. 7 compares the integrated RL intensity with the glow curve of the polycrystalline ceramic (Fig. 7a) and of the single crystal (Fig. 7b), with both curves presenting peaks at reasonably the same temperatures. The similarities between the shape of the integrated RL intensity with that of the glow curve support the idea that electrons released from traps contribute to RL through radiative recombination at Ce<sup>3+</sup> sites. Indeed, TL results obtained within a broad range of irradiation times, from 30 to 300 s, revealed the kinetics of the recombination mechanism to be of first order, *i.e.*, electron re-trapping was negligible.

In addition to the  $Ce^{3+}$  band, a weaker band was observed at higher energies (Figs. 3 and 5). According to previous investigations of LuAG(:Ce), emission bands centered at 3.10 and 3.15 eV were assigned to a F<sup>+</sup>-type defect [19,20], while emission at 2.99 eV was related to



**Fig. 7.** Comparison between the two sets of measurements of the integrated RL intensity with the glow curve of the: a) polycrystalline ceramic, and b) single crystal.

the presence of oxygen vacancies [17], *i.e.*, a F<sup>+</sup>-type defect. Emission at 3.25 and 3.45 eV were attributed to Ce occupying an Al site (Ce<sub>Al</sub>), and at ~3.18 eV to Ce<sub>Al</sub> perturbed by a defect in a nearby Lu site [21]. Moreover, a broad emission band within ~2.75–5.25 eV superimposed to the bands above was attributed to the luminescence of Lu<sub>Al</sub> antisite defects [20,22]. However, RL emission above ~2.8 eV was affected by the temperature-dependent absorption of Ce<sup>3+</sup> ions that presents absorption bands centered at 2.76 and 3.54 eV. The spectral super-imposition of the Ce<sup>3+</sup> absorption bands and the defects emission bands hindered reliable spectral analysis. However, based on the published results discussed above, the presence of F<sup>+</sup>-type, Ce<sub>Al</sub>, perturbed Ce<sub>Al</sub>, and Lu<sub>Al</sub> was deemed compatible with the present RL results. Moreover, it was possible to determine the defects total thermal quenching temperature to be about 175 °C for the single crystal and about 300 °C for the polycrystalline ceramic.

#### 4. Conclusions

An investigation of high temperature RL emission of a LuAG:Ce single crystal and a transparent polycrystalline ceramic under X-ray excitation was executed up to 600 °C. From RT,  $Ce^{3+}$  emission increased 1.4x up to 450 °C for the single crystal and 1.9x up to 300 °C for the polycrystalline ceramic. Comparison between RL and TL results supported the idea that radiative recombination at  $Ce^{3+}$  sites of electrons thermally released from traps was responsible to the increase in RL intensity. Importantly, it was estimated by data interpolation that at about 500 and 530 °C for the polycrystalline ceramic and the single crystal, respectively, the integrated RL intensity of both samples was equivalent to the respective intensity value at RT showing LuAG:Ce to

be an effective scintillator over a broad range of temperatures.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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