



Comparative investigation of transparent polycrystalline ceramic and single crystal $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ scintillators: Microstructural and thermoluminescence analyses

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ABSTRACT

$\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (LuAG:Ce) single crystal and polycrystalline ceramic were investigated on their microstructural characteristics and luminescent and scintillating properties towards the identification of possible causes for the lower scintillation performance of the polycrystalline ceramic. Emphasis was placed on the thermoluminescence (TL) response. Radioluminescence results indicated a (11x) higher content of defects in the single crystal than in the polycrystalline ceramic. Lower optical transparency, higher self-absorption, and a higher degree of structural disorder localized in the grain boundaries of the polycrystalline ceramic were observed. TL results showed six glow peaks in the single crystal and four glow peaks in the polycrystalline ceramic within the 50–400 °C temperature range, all with first-order kinetics TL mechanism. Trap depths at similar peak temperatures were ~1.2–1.5 times deeper in the single crystal. In terms of scintillation response related to a $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) crystal within the 31–662 keV gamma-ray energy range, the single crystal was about 2x brighter than the polycrystalline ceramic.

1. Introduction

Scintillators are sensors used for the detection and measurement of ionizing radiation and find application in numerous strategic fields, including national security, medical imaging, oil exploration, environmental monitoring, as well as in science and technology. Among the many possible forms for scintillators, polycrystalline ceramic scintillators are receiving increasing attention due to a number of advantages over single crystals, including faster and lower cost fabrication methods, higher homogeneity of the dopant, greater shape control, and easier fabrication of materials with high melting temperatures. Despite the aforementioned advantages, scintillation performance of polycrystalline ceramics is commonly inferior to single crystals. Thermoluminescence (TL) measurements of scintillators are regularly executed toward probing the material in terms of traps that can capture charge carriers and thus reduce scintillation yield. However, currently, there is a knowledge gap relating fabrication and post-fabrication processing conditions and content of defects in polycrystalline ceramics. Within this context, limited investigation of the effects of sintering conditions on the content

of open-volume defects and thermoluminescence (TL) output of selected materials was executed [1–3], while reduction of TL signal concurrent to luminescence and scintillation enhancement by post-fabrication thermal treatment of a transparent polycrystalline ceramic was reported [4].

$\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ (LuAG:Ce) is an attractive material not only due to its high density and fast decay time, but also because it remains an effective scintillator at temperatures as high as ca. 500 °C, either as single crystal or as polycrystalline ceramic [5]. Moreover, it was shown that fabrication of polycrystalline ceramics with luminosity similar to that of single crystals is possible [6]. Fig. 1 illustrates the evolution of the luminosity of LuAG:Ce polycrystalline ceramics since its first fabrication in 2005 [6–15]. Interestingly, a LuAG:Ce single crystal and polycrystalline ceramics prepared in different ways were compared and a higher concentration of Lu_{Al} anti-site defects in the single crystal was reported [12]. The polycrystalline ceramic with lower light yield had no TL signal below 300 K, suggesting the absence of Lu_{Al} anti-site defects [12]. Also, the effects of sintering conditions on the LuAG microstructure and on the $\text{Pr}^{3+} 4f \leftrightarrow 5d$ transition were investigated in detail [3]. In this work, a comparative investigation between LuAG:Ce transparent polycrystalline

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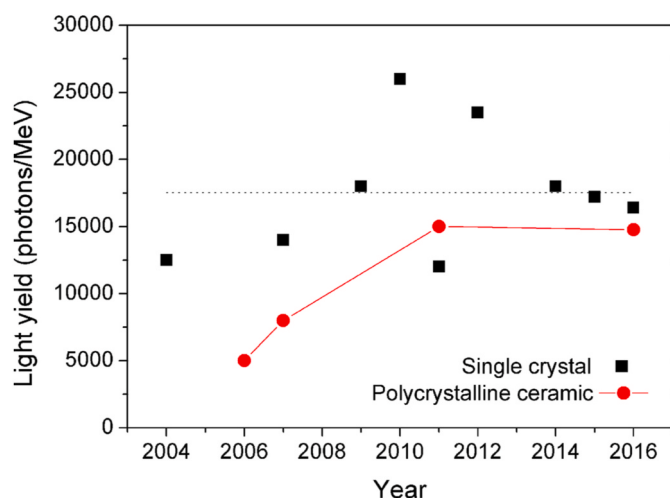


Fig. 1. Evolution of the light yield of polycrystalline ceramics (red circles) and single crystals (black squares) based on a literature survey [6–15].

ceramic and single crystal scintillators was executed towards the identification of factors that limit the scintillation performance of polycrystalline ceramic scintillators. Emphasis was placed on TL investigation of LuAG:Ce that yielded the identification of recombination centers and the determination of the order of kinetics of the TL process, together with the determination of all trap depths. It is hoped this work will help the development of other garnet scintillators.

2. Experimental procedure

The LuAG:Ce single crystal was grown by the Czochralski method using an 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 of oxygen ($\sim 0.25\%$) continuously monitored by a residual gas analyzer [16]. A polished single crystal with dimensions of $3.9 \times 3.9 \times 3.9 \text{ mm}^3$ was used in this work. The transparent ceramic was fabricated by high temperature vacuum sintering with a nominal composition $\text{Lu}_{2.985}\text{Ce}_{0.015}\text{Al}_5\text{O}_{12}$ (i.e., nominal Ce concentration = 0.075 at.% of the whole chemical formula, or 0.5% substituting for Lu). Precursor powders were prepared by co-precipitation using high purity (99.99%) starting materials and tetraethyl orthosilicate (TEOS) as a sintering additive. Powders were calcined and uniaxially pressed at $\sim 10 \text{ MPa}$, and the pellet was heated at 400°C , cold isostatically pressed, and sintered at 1800°C for 10 h. A polished transparent ceramic with a 13.5 mm diameter and a 2.9 mm thickness was used in this work. By means of optical absorption and energy dispersive X-ray spectroscopy (EDX) measurements, the concentration of Ce in the samples was estimated to be $\sim 0.04 \text{ at.}\%$ for the single crystal and $\sim 0.06 \text{ at.}\%$ for the polycrystalline ceramic.

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.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR) measurements were executed in single reflection mode within the 400–4000 cm^{-1} range with 1 cm^{-1} resolution using a Thermo-Scientific Nicolet 6700 FT-IR spectrometer equipped with a diamond crystal plate.

Photoluminescence emission (PL) and excitation (PLE) spectra were obtained using a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer equipped with double monochromators for both excitation and emission, and a 450 W Xe lamp as the excitation source.

Fluorescence lifetime measurements were executed with an Edinburgh Instruments FLS-1000 spectrofluorometer using picosecond

pulsed LEDs EPLED-365 emitting at 362.8 nm (11.8 nm full width at half maximum (FWHM) bandwidth, 884.0 ps pulse width at 10 MHz). A 4 nm bandwidth was used for detection with the monitoring wavelength at 520 nm, while EPLED repetition rate was fixed at 2 MHz.

Radioluminescence (RL) measurements were executed at room temperature using a custom-designed Freiberg Instruments Lexsyg Research spectrofluorometer equipped with a Varian Medical Systems VF-50J X-ray tube with a tungsten target. The X-ray source was coupled with an ionization chamber for continuous irradiation intensity monitoring and was operated at 40 kV and 1 mA. The 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 a cooled (-80°C) Andor Technology DU920P-BU Newton CCD camera (spectral resolution was ca. 0.5 nm/pixel).

TL spectroscopy was executed with a Freiberg Instruments Lexsyg Research spectrofluorometer with the configuration above, and TL emission spectra were obtained at several different temperatures. Measurement sequence consisted of: 1) temperature ramp up to 450°C at 5°C/s followed by annealing at 450°C for 300 s to clean all traps and cooling down to 50°C , 2) X-ray irradiation (40 kV, 0.01 mA) at room temperature (RT), and 3) TL readout at 0.25°C/s up to 450°C with 4 s integration time.

TL measurements were executed in the 50–400 $^\circ\text{C}$ 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) for different amounts of time, from 30 s to 300 s. For RL and TL measurements, small platelets were cut from the original samples due to space limitations of the instruments sample holder. TL results were corrected by suitable linear best fits of the integral RL response as a function of temperature [5]. In this work, all glow curves are presented after this correction, and glow curve analysis was also executed on the corrected TL results. Computerized glow curve fitting was executed with the GlowFit software that uses the least squares Levenberg-Marquardt minimization algorithm and is based on the (first-order kinetics) Randall-Wilkins model [17]. In the case of measurements for the heating rate method, a Lexsyg Research spectrofluorometer equipped with a Hamamatsu H7360-2 photomultiplier tube was used. TL measurements consisted of the following procedure: 1) temperature ramp up to 450°C at 5°C/s followed by annealing at 450°C for 300 s to clean all traps and cooling down to RT, 2) X-ray irradiation (40 kV, 0.01 mA) for 1 s at RT, and 3) TL readout at selected heating rate up to 450°C with 1 s integration time. Steps 1 to 3 were repeated for each heating rate used: 0.1°C/s , 0.2°C/s , 0.5°C/s , and 1°C/s .

Light yield relative to a $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) single crystal used as reference was determined by means of differential pulse height distribution measurements using a Hamamatsu R6095 bialkali photocathode photomultiplier tube operated at 1000 V and 2 μs shaping time inside a light-proof box. Various gamma-ray sources were used spanning energies from ca. 31–662 keV: ^{137}Cs , ^{241}Am , ^{57}Co , ^{133}Ba , and ^{22}Na (511 keV gamma-ray from electron-positron annihilation). The relative light yield was determined by taking the ratio of the sample photopeak position to the BGO photopeak position for each gamma-ray energy using the same gain. Samples were not wrapped in Teflon tape.

3. Results and discussion

The results of optical transmission measurements of the polycrystalline ceramic and the single crystal are presented in Fig. 2. Both samples exhibited high optical transparency down to about 500 nm with transmission of the polycrystalline ceramic being lower (transmittance = 72%) than that of the single crystal (transmittance = 82%). To put these values in perspective, the theoretical optical transmission of LuAG was estimated to be 83.3% [18]. The reduced transmittance of the polycrystalline ceramic was most likely due to residual porosity after

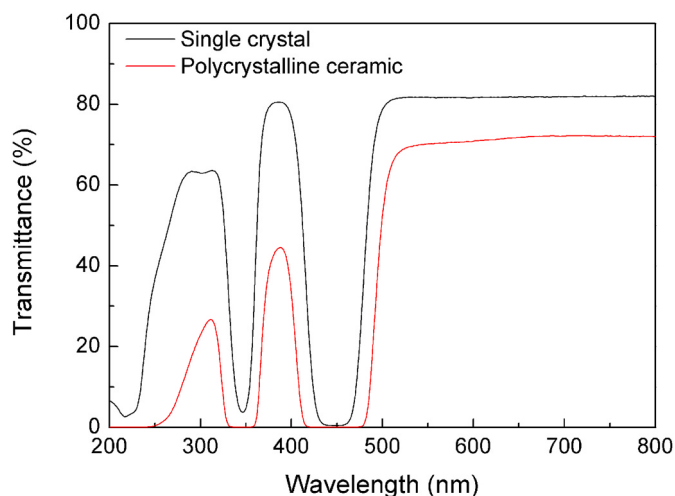


Fig. 2. Optical transmittance of single crystal (black line) and polycrystalline ceramic (red line).

sintering, in agreement with the identification of residual nanoscopic porosity by means of positron annihilation spectroscopy measurements of several oxide polycrystalline ceramics either sintered at high temperatures or sintered and hot isostatically pressed [1,2]. At lower wavelengths, both samples presented absorption bands centered at about 449 and 349 nm (2.76 and 3.55 eV, respectively) that were ascribed to the $Ce^{3+} 4f \rightarrow 5d_1$ and $5d_2$ transitions, respectively [12]. Saturation could be seen for the 449 nm band for both samples, and for the 349 nm band for the polycrystalline ceramic. The cutoff wavelength for the single crystal was lower than for the polycrystalline ceramic indicating higher ultraviolet transparency.

Infrared spectroscopy was used to investigate structural disorder in the polycrystalline ceramic by means of ATR FTIR measurements. Fig. 3 presents the spectra of the polycrystalline ceramic and single crystal normalized to the most intense peak at $\sim 700\text{ cm}^{-1}$. The ideal structure of LuAG:Ce is composed of octahedral and tetrahedral sites occupied by Al, and dodecahedral sites occupied by Lu and Ce. The vibrational modes observed in the spectra in Fig. 3 were correlated to the vibrations of these structural units. The absorption band at 410 cm^{-1} was ascribed to the translational mode of the octahedral cations, the band at 445 cm^{-1} to the symmetric bend of the AlO_4 tetrahedra, the bands within $\sim 470\text{--}600\text{ cm}^{-1}$ to the asymmetric bends of the tetrahedra, and the

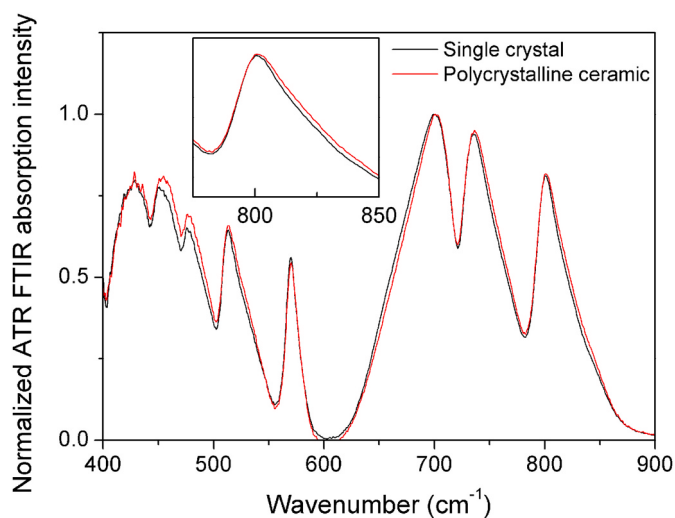


Fig. 3. Normalized ATR FTIR results of single crystal (black line) and polycrystalline ceramic (red line).

bands within $600\text{--}900\text{ cm}^{-1}$ to the asymmetric stretching modes of the tetrahedra [19,20]. Broadening was observed in the majority of the bands of the polycrystalline ceramic, with the FWHM of its bands being $4\text{--}5\text{ cm}^{-1}$ wider than for the single crystal, as illustrated in the inset of Fig. 3. These results indicated concurrent distortion of all three types of structural units. This was understood by the shared nature of oxygen ions in the garnet structure, with each oxygen ion being bonded to two dodecahedra, one octahedron, and one tetrahedron, wherein tetrahedra and octahedra share edges with the dodecahedra [21]. It is well-known for the garnet structure that an increase in the volume of the unit cell is related to a decrease of the frequency of the vibrational modes [21,22], but no systematic shift of the bands of the polycrystalline ceramic was observed in relation to those of the single crystal. The ATR FTIR measurements probed a large number of grains and grain boundaries, but the results were dominated by the absorption of the grains due to the considerably larger volume of the grains compared with the volume of the grain boundaries. Consequently, these results showed the atomic network within the grains to be neither under compressive nor under tensile stress. The broadening of the absorption bands was, therefore, ascribed to variations of the interionic distances restricted to within the grain boundaries. This was interpreted as indicative of disorder being localized to grain boundaries.

PLE spectra monitored at 2.43 eV (510 nm) and PL spectra excited at 3.53 eV (351 nm) of the single crystal and polycrystalline ceramic are presented in Fig. 4a and b, respectively. The excitation bands matched the position of the absorption bands observed in the optical transmission spectra (Fig. 2) and were ascribed to the $4f \rightarrow 5d_{1,2}$ electronic transitions of Ce^{3+} . The fine structure superimposed to the excitation band between 2.6 and 2.9 eV has been ascribed to the Xe lamp used as the excitation source [23]. The FWHM of the PLE bands was $\sim 1.3\times$ broader for the polycrystalline ceramic than for the single crystal due to inhomogeneous broadening. These results showed some level of structural disorder in the close neighborhood of Ce^{3+} ions. The resulting enhanced self-absorption in the polycrystalline ceramic was found to be $\sim 1.8\times$ higher than in the single crystal based on the ratio of the intersection area between the PL and PLE spectra within $2.4\text{--}2.8\text{ eV}$ divided by the total area of the PL spectrum. The intersection of the PL and PLE spectra

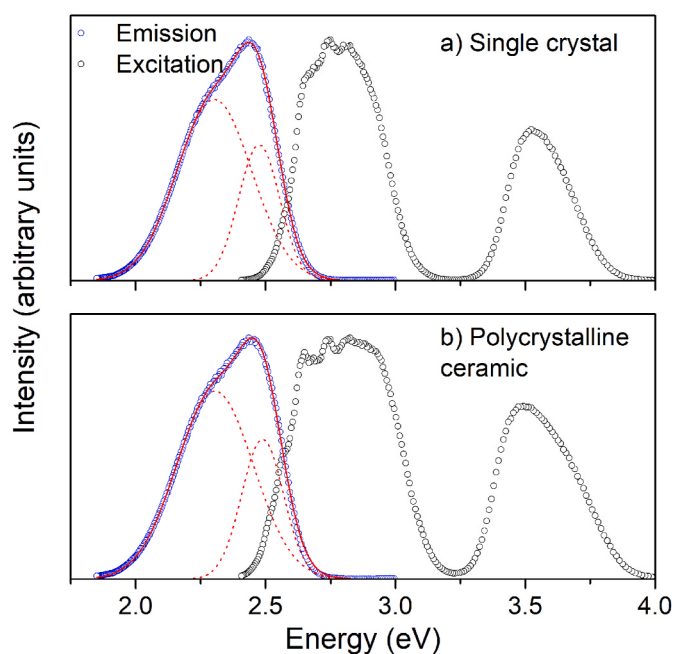


Fig. 4. PL spectrum excited at 3.53 eV (blue circles) and PLE spectrum monitored at 2.43 eV (black circles) of a) single crystal and b) polycrystalline ceramic. Red dotted lines correspond to Gaussian bands, and continuous red line to best fit.

was around 2.6 eV for both the polycrystalline ceramic and the single crystal, in agreement with previous results [24].

PL spectra were composed of a broad band centered at around 2.43 eV. This band was fitted with two Gaussian bands centered at 2.30 and 2.49 eV (dotted red lines, Fig. 4a and b). These bands were ascribed to the $5d_1 \rightarrow 4f$ ($^2F_{5/2}$, $^2F_{7/2}$) transitions, with the ground state split into two levels due to spin-orbit coupling. The same split of ~ 0.18 eV was observed in both samples, in agreement with results reported in the literature [25,26], as expected by the highly localized nature of the spin-orbit interaction not being affected by the local environment of the Ce^{3+} ions. No difference in position and FWHM of the Gaussian bands was observed between the single crystal and the polycrystalline ceramic.

RL spectra presented an intense band peaked at ~ 2.43 eV that was ascribed to the emission of Ce^{3+} (Fig. 5a for the single crystal; Fig. 5b for the polycrystalline ceramic). The results of the spectral fitting with two Gaussian bands (green lines) were similar to the results of the spectral fitting of the PL spectra and are not discussed further. RL measurements also revealed weaker emission above ~ 3 eV ascribed to defects. However, the shape of the ‘defect’ emission is misleading. The absorption bands of Ce^{3+} ions centered at 2.76 and 3.55 eV form two ‘peaks’ in the RL spectra (Fig. 5c and d). These ‘peaks’, however, do not correspond to individual defect bands but were the result of the partial absorption of the emission band of Lu_{Al} antisite defects by Ce^{3+} ions [27]. This is confirmed in Fig. 6 where the optical transmission and RL spectra of polycrystalline ceramic and single crystal are superimposed. According to previous investigations of $LuAG:(Ce)$ summarized in Table 1, emission bands centered at 3.10 and 3.15 eV were ascribed to a F^+ -type defect [28,29], while emission at 2.99 eV was related to the presence of oxygen vacancies [30]. Emission at 3.25 and 3.45 eV were attributed to Ce^{3+} occupying an Al^{3+} site (Ce_{Al}), and at ~ 3.18 eV to Ce_{Al} perturbed by a defect in a nearby Lu site [31]. Emission bands within 4.13–4.28 eV were attributed to the emission of excitons localized around Lu_{Al} antisite defects [32–34]. Moreover, a broad emission band within ~ 2.75 – 5.25 eV superimposed to the bands above was ascribed to the luminescence of Lu_{Al} antisite defects [27,29,32,34]. According to the literature survey above, the presence of F^+ -type, Ce_{Al} , perturbed Ce_{Al} , and Lu_{Al} defects

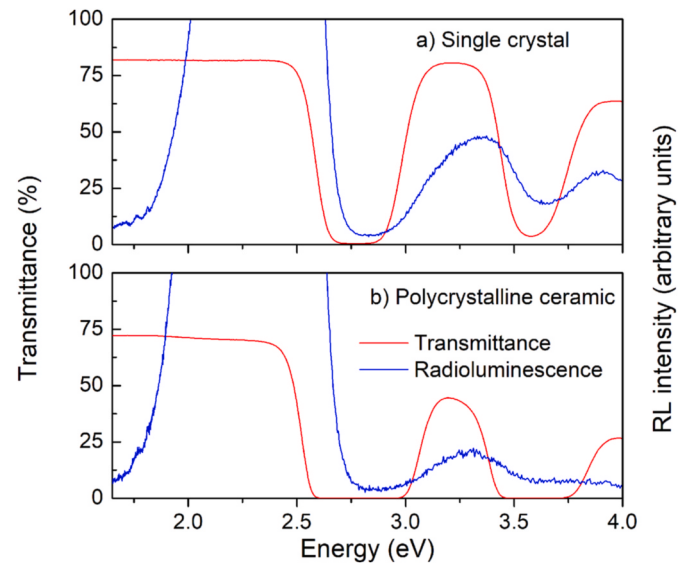


Fig. 6. Superposition of transmittance (red) and RL (blue) spectra of a) single crystal and b) polycrystalline ceramic.

Table 1

Summary of luminescence from $LuAG:(Ce)$.

Emission (eV)	Origin	References
2.30, 2.49	$Ce^{3+} 5d_1 \rightarrow 4f$ ($^2F_{5/2}$, $^2F_{7/2}$)	[24–26]
2.99, 3.10, 3.15	F^+ -type center/Oxygen vacancy	[28–30]
3.18	Perturbed Ce_{Al}	[31]
3.25, 3.45	Ce_{Al}	[31]
4.13, 4.28	Exciton localized at Lu_{Al}	[32–34]

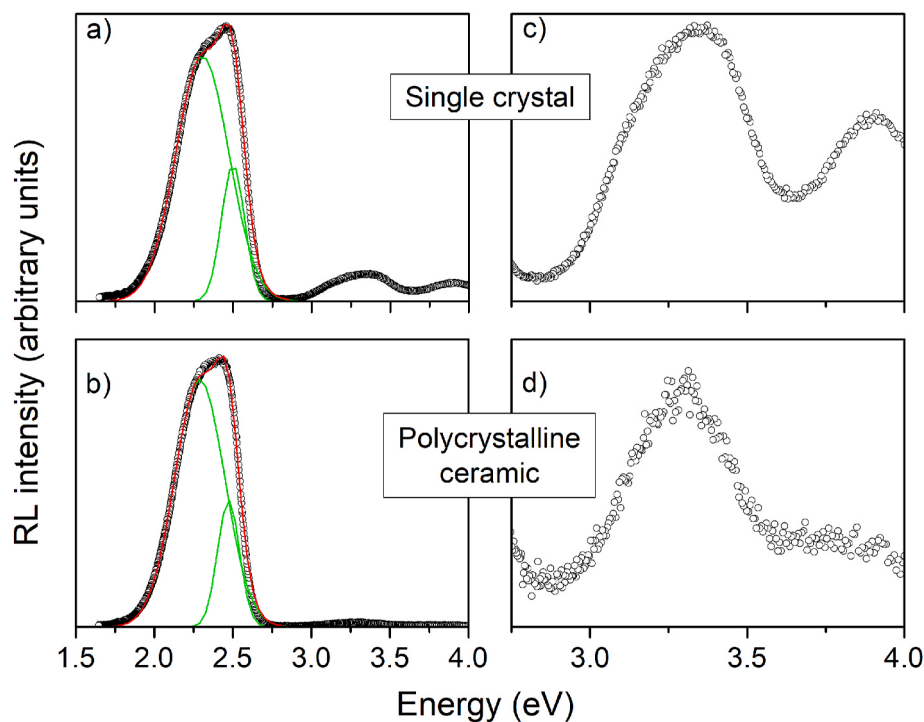


Fig. 5. RL spectra of a) single crystal, b) polycrystalline ceramic, c) highlight of single crystal defects emission and d) highlight of polycrystalline ceramic defects emission.

was compatible with our results. While it was not possible to identify the presence of specific defects, RL results were used to quantify the relative concentration of luminescent defects in the two samples by assuming the intensity of the RL band to be proportional to the concentration of the defects. Due to the difficulties of making absolute intensity measurements, the total intensity of the emissions related to defects (2.85–4.0 eV) was normalized to the intensity of the Ce^{3+} band (1.65–2.85 eV) in the respective spectrum and also by the Ce concentration of the sample. This analysis showed the relative intensity of the defects-related band to be 11x larger in the case of the single crystal than in the polycrystalline ceramic. A more precise comparison of the relative concentration of defects in the two samples should have taken into account the effect of the Ce concentration on the RL output. However, the available data on RL intensity as a function of the Ce content in the range of interest is inconclusive [35] and hindered further analysis.

In order to obtain complementary data on the defects-related emission, additional PL and PLE measurements were executed. PLE measurements monitored at 2.95 eV and PL measurements excited at 3.53 eV are shown in Fig. 7a and b for the single crystal and polycrystalline ceramic, respectively. The PLE spectra were composed of three distinct bands at 3.43, 4.13, and 4.62 eV, and the PL spectra had a broad band peaked at 3.12 eV with a shoulder at 2.97 eV. Babin et al. [28] reported on the emission of a F^+ -type center at 3.15 eV with three corresponding excitation bands at 3.4, 5.3, and 6.1 eV. Based on these results, emission at 3.12 eV together with the excitation band at 3.43 eV were ascribed to a F^+ -type center, while the 2.97 eV band was ascribed to an unknown defect related to oxygen vacancies, in agreement with results reported for Czochralski-grown LuAG:Ce single crystals [30]. PL measurements excited at 4.13 and 4.62 eV (Fig. 8) yielded similar spectra as those excited at 3.53 eV (Fig. 7) with the noticeable difference that excitation at 4.13 eV yielded very weak Ce^{3+} emission below about 2.6 eV. The excitation band at 4.62 eV was found in good agreement with an unidentified excitation band at ~ 4.65 eV observed in an undoped Czochralski-grown LuAG single crystal annealed in H_2 atmosphere [30]. To the best of our knowledge, the excitation band at 4.13 eV has not been previously reported in the literature.

Lifetime measurement (open circles) and best-fit (lines) results are presented in Fig. 9 for a) single crystal, and b) polycrystalline ceramic. A single exponential function yielded accurate representation of the results, yielding lifetimes of 55 ns and 62 ns for the single crystal and polycrystalline ceramic, respectively, in good agreement with the literature [8,12,13,24–26,36].

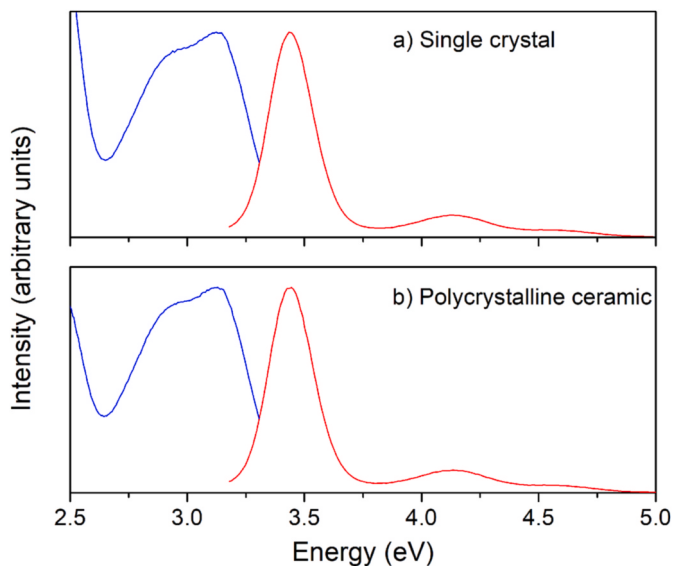


Fig. 7. PL spectra excited at 3.53 eV (blue) and PLE spectra monitored at 2.95 eV (red) of a) single crystal and b) polycrystalline ceramic.

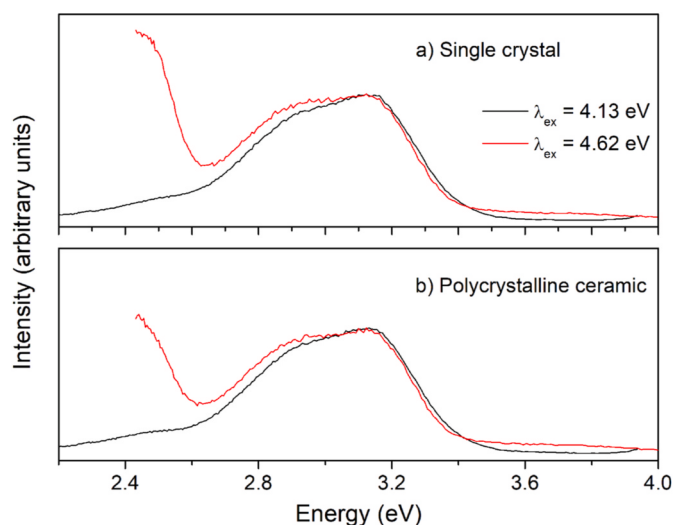


Fig. 8. PL spectra excited at 4.13 eV (black) and 4.62 eV (red) of a) single crystal and b) polycrystalline ceramic.

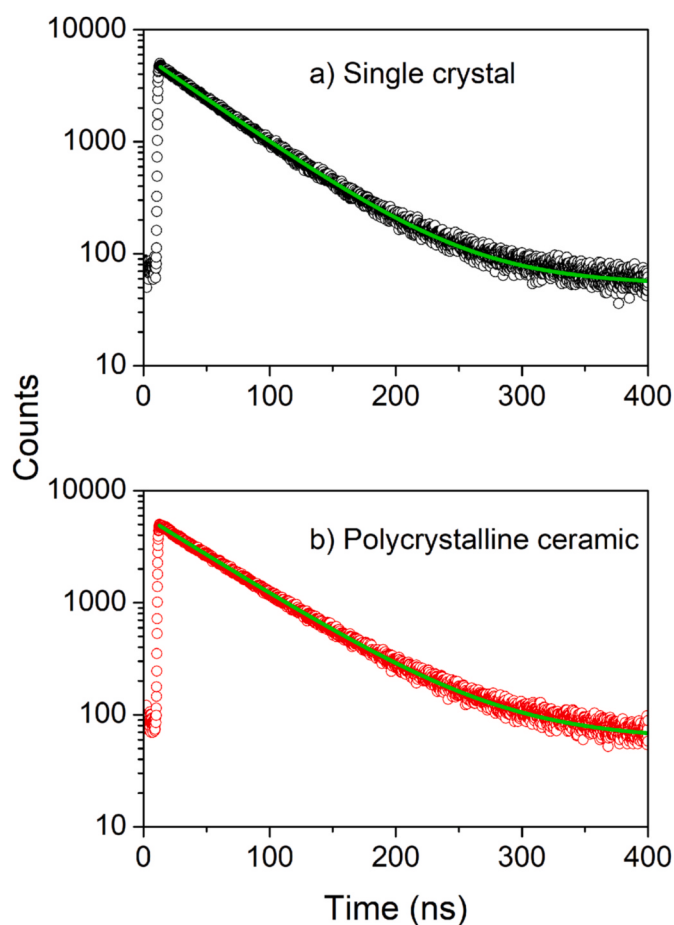


Fig. 9. Lifetime decay curves (open circles) and single exponential best fit (continuous lines) of a) single crystal and b) polycrystalline ceramic.

TL measurements of LuAG:Ce bulk single crystals grown by the micro-pulling and Czochralski methods as well as of LuAG:Ce single-crystalline films prepared by the liquid phase epitaxy (LPE) method have been reported previously [30,37–42]. On the other hand, to the best of our knowledge, this was the first in-depth TL investigation of a LuAG:Ce transparent polycrystalline ceramic. Table 2 summarizes a

Table 2

Summary of glow peak positions (left most column, in °C) of LuAG:Ce polycrystalline ceramics and single crystals fabricated by different methods, as indicated. When reasonable, glow peak positions were grouped within temperature ranges ≤ 19 °C. NA indicates “not analyzed” because the temperature was out of the range reported in the referred work.

Reference:	29	35	36	37	38	39	40	This work	This work	15
Fabrication Method:	Czochralski	Czochralski	Czochralski	μ pulling	μ pulling	LPE	LPE	Czochralski	Ceramic	Ceramic
Temperature (°C) 45–50		•	•	•	•					
79–88		•	•		•			•	•	•
100–110	•					•		•	•	
127–130		•	•				•			
150–160				•	•	•		•		
210–218	•					•				
230–234				•	•			•		
265–284		•	•	•	•			•	•	•
319–325	•					•	•			
339–350		•	•		•					•
368–375				•		•				
391–400			•			•		•		
420–421		•						NA	NA	NA
475	•		NA			NA	NA	NA	NA	NA

survey of all the glow peaks reported in the literature [15,30,37–42], including this work, wherein glow peak positions (T_m) were grouped within reasonable temperature ranges ≤ 19 °C. It is noted that only in this work glow curves were analyzed with different methods, while in all other cases the number of peaks was extracted by visual analysis of the glow curves. Further, many of the glow peaks reported in the literature were considerably broad, especially in the case of samples prepared by the LPE method, allowing for the presence of weaker glow peaks to go undetected by visual analysis. In fact, in this work, the presence of the glow peak at 100–105 °C was only revealed by glow curve fitting, as discussed below. In addition to the uncertainty of extracting the peak position directly from the graphs from Refs. [15,37,38,41], it is also noted that the discrepancy related to the presence or absence of the 45–50 °C glow peak could be possibly attributed to the limitations of the experimental setup used in different laboratories. Another possible source of discrepancy in the peak position of results reported from the LPE studies is the heating rate, not reported in Refs. [41,42] (all other results were obtained with a 1 °C/s heating rate). Analysis of Table 2 showed that more glow peaks were consistently reported for samples prepared by the micropulling and Czochralski fabrication methods [30, 37–40] than for the polycrystalline ceramic (this work and ref. 15), and all the glow peaks observed in the polycrystalline ceramic were also consistently observed in samples prepared by the Czochralski method [this work and refs. 30, 37, 38]. However, not all the same glow peaks were observed in all samples, not even for the same fabrication method, and not a single glow peak was common to all fabrication methods. Results by Douissard et al. [41] showed the number of glow peaks and the peaks position were not affected by the Ce content, at least within 5–10 mol%. Overall, these results suggest the presence/absence of glow peaks to be sensitive to fabrication conditions commonly overlooked like low level impurities.

In the above reports, results were discussed in terms of the glow peak position only, without further analysis of the TL behavior. In this work, the nature of the recombination center(s) was determined through TL spectroscopy measurements, and the order of kinetics of the TL mechanism was determined. The glow curves were further analyzed using several methods: the heating rate (β) method, glow curve fitting, and through an analysis involving the shape of the glow curve, as discussed below. Figs. 10 and 11 present the results of TL spectroscopy measurements, i.e., TL emission spectra obtained at different temperatures for the single crystal and polycrystalline ceramic, respectively. In each case, spectra were grouped and ascribed to a glow peak (refer to Tables 3 and 4 for peak identification) according to the temperature and the behavior of the emission intensity. Typically, the observation of an increase in intensity followed by a decrease for increasing temperatures correlated to a glow peak, as can be seen in the individual plots. The weak signal

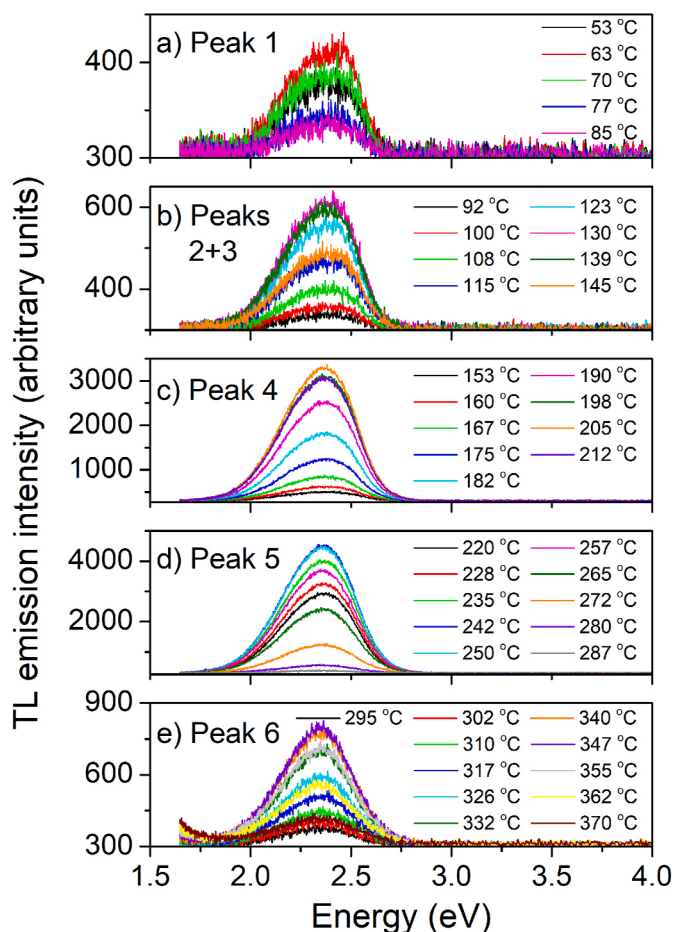


Fig. 10. TL spectroscopy results of LuAG:Ce single crystal obtained at different temperatures. TL emission spectra were grouped according to their temperatures and intensity behavior. Refer to Table 3 for glow peak identification.

observed at the highest temperatures ($> \sim 330$ °C) at low energies ($< \sim 1.75$ eV) was due to blackbody radiation of the instrument (Figs. 10e and 11c). These results unequivocally showed for the first time that besides the availability of variety of luminescent defects (cf. Fig. 5), Ce^{3+} was the sole recombination center involved in the TL process both for the single crystal and the polycrystalline ceramic.

Representative results of mass-normalized TL measurements are

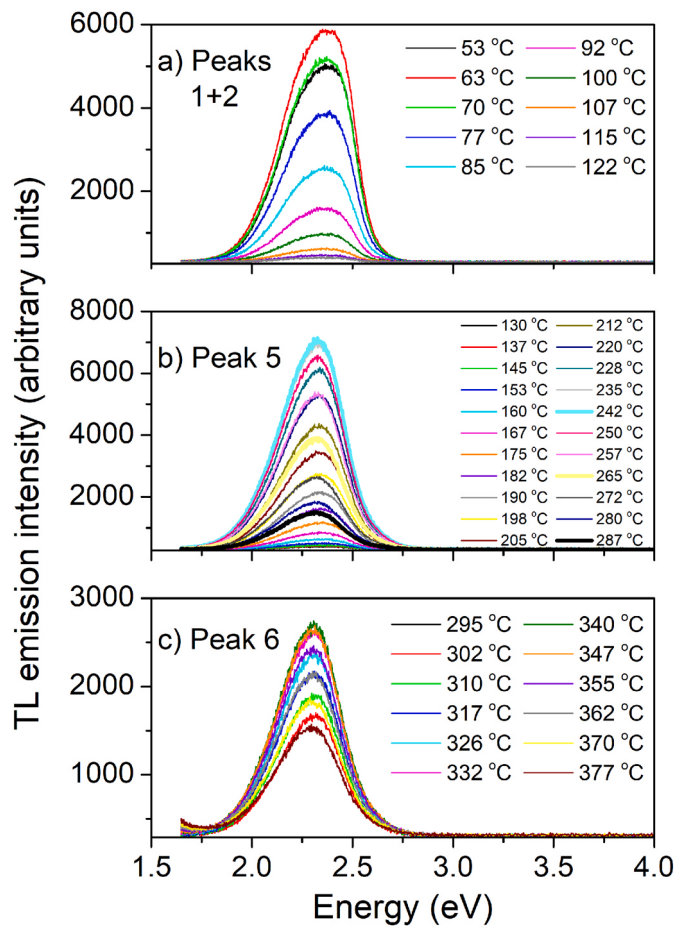


Fig. 11. TL spectroscopy results of LuAG:Ce polycrystalline ceramic obtained at different temperatures. TL emission spectra were grouped according to their temperatures and intensity behavior. Refer to Table 4 for glow peak identification.

shown in Fig. 12 for the single crystal (black circles) and polycrystalline ceramic (red circles). Integrated mass-normalized TL intensity yielded $TL_{\text{Ceramic}} \sim 1.6 \times TL_{\text{Crystal}}$, that is close to the polycrystalline ceramic to single crystal Ce concentration ratio = 1.5, suggesting an overall same integral TL output for both the single crystal and polycrystalline ceramic. The glow curves were dominated by the emission within ~ 180 – 340 °C, together with glow peaks within *ca.* 50–120 °C and 340–400 °C, with the single crystal having an additional glow peak at ~ 160 °C. The order of kinetics of each glow peak was investigated employing X-ray irradiation with different durations, from 30 to 300 s, together with the monitoring of the glow peak position. These results are shown in Fig. 13 and in Tables 3 and 4 and revealed all glow peaks to have first-order kinetics due to the lack of a systematic shift of the peak

position for increasing irradiation doses. The results of the heating rate method are shown in Figs. 14 and 15 for the single crystal and polycrystalline ceramic, respectively. Since the heating rate method is sensitive to the glow peaks position, this approach yielded five trap depth values for the single crystal and two for the polycrystalline ceramic because peak 2 could not be discerned by visual inspection. The trap depths obtained through this method are listed at the bottom of Tables 3 and 4. It is noted that the peak position used for the entries of the heating rate method results in Tables 3 and 4 corresponded to the peak position of the glow curve envelope for $\beta = 1$ °C/s, while Tables 3 and 4 were organized based on the peak positions extracted from the curve fitting analysis. Overall, the trap depth energy increased for higher peak temperatures, and for peaks 1 and 5 that matched in temperature the trap depth values of the single crystal and the polycrystalline ceramic were similar within ~ 0.1 eV.

In order to evaluate if the observed glow peaks corresponded to a single trap, the FWHM of each glow peak was estimated using McKeever and Chen's expression $E_{\text{McC}} = 2.52k_B T_m^2 / \text{FWHM} - 2k_B T_m$ [43,44], where k_B is Boltzmann's constant, and FWHM is the full-width at half-maximum of each glow peak, and making E_{McC} equal to the trap depth value determined by the heating rate method (cf. Tables 3 and 4). The FWHM values obtained through this expression were equal or larger than the experimental FWHM values of peaks 1, 3, 4 and 5 of the single crystal and peak 1 of the polycrystalline ceramic (noting that peak 2 could not be discerned by visual inspection, and peak 6 could not be analyzed since its FWHM could not be determined). Further analysis was executed by computerized glow curve fitting using GlowFit software. The results of glow curve fitting are summarized in terms of the peak position and trap depth of each glow peak in Tables 3 and 4 for all irradiation times, and Fig. 12 illustrates the best fit results for the 120 s irradiation (continuous lines) for both the single crystal and the polycrystalline ceramic. Interestingly, best fit revealed the glow peak around 85 °C to be composed of two partially superimposed glow peaks (peaks 1 and 2), while the glow peak at 284 °C (peak 5) of the polycrystalline ceramic could be fit as a single glow peak contrary to the conclusion based on the FWHM analysis discussed above. Glow curve fitting also confirmed the absence of glow peak at 160 °C for the polycrystalline ceramic. The highest temperature glow peak of the polycrystalline ceramic (peak 6) could not be fitted because its peak was beyond the operational range of the TL reader. In these tables, the trap depth was also calculated using McKeever and Chen's expression with data extracted from the fitting of each glow peak as input. It is noted that glow peak superposition leads to a higher degree of uncertainty in the determination of T_m , directly affecting the analysis based on McKeever and Chen's expression. This analysis could not be done for the highest temperature glow peak (peak 6) because the FWHM could not be determined. The tables also present the average values of T_m , E , and E_{McC} for each sample. The analyses based on McKeever and Chen's expression and on glow curve fitting mutually supported each other, while the relatively higher discrepancy of the energy values obtained by the heating method was tentatively attributed to the effect of temperature

Table 3

Summary of the analysis of glow curves of LuAG:Ce single crystal using GlowFit software for different irradiation times. “?” indicates values that could not be calculated. Results obtained by the heating rate (β) method are presented at the bottom of the Table. The T_m values reported for the β method correspond to $\beta = 1$ °C/s.

Irradiation time (s)	Peak 1			Peak 2			Peak 3			Peak 4			Peak 5			Peak 6		
	T_m (°C)	E (eV)	E_{McC} (eV)	T_m (°C)	E (eV)	E_{McC} (eV)	T_m (°C)	E (eV)	E_{McC} (eV)	T_m (°C)	E (eV)	E_{McC} (eV)	T_m (°C)	E (eV)	E_{McC} (eV)	T_m (°C)	E (eV)	E_{McC} (eV)
30	84	1.04	1.06	100	0.99	0.95	163	1.13	1.14	237	1.44	1.45	282	1.27	1.28	391	1.75	?
120	83	1.01	1.02	100	1.03	1.04	159	1.10	1.11	233	1.45	1.46	280	1.24	1.24	390	1.73	?
300	83	1.02	1.03	101	1.06	1.08	159	1.08	1.09	233	1.48	1.49	280	1.30	1.31	393	1.52	?
Average	83	1.02	1.04	100	1.03	1.02	160	1.10	1.11	234	1.45	1.47	281	1.27	1.28	391	1.67	?
β method																		
T_m (°C)	88			–			161			244			284			388		
E (eV)	0.70			–			0.82			0.96			1.3			1.5		

Table 4

Summary of the analysis of glow curves of LuAG:Ce polycrystalline ceramic using GlowFit software for different irradiation times. “?” indicates values that could not be calculated; “-” indicates the glow peak was absent. Results obtained by the heating rate (β) method are presented at the bottom of the Table. The T_m values reported for the β method correspond to $\beta = 1^\circ\text{C/s}$.

Irradiation time (s)	Peak 1			Peak 2			Peak 3			Peak 4			Peak 5			Peak 6		
	T_m ($^\circ\text{C}$)	E (eV)	E_{McC} (eV)	T_m ($^\circ\text{C}$)	E (eV)	E_{McC} (eV)	T_m ($^\circ\text{C}$)	E (eV)	E_{McC} (eV)	T_m ($^\circ\text{C}$)	E (eV)	E_{McC} (eV)	T_m ($^\circ\text{C}$)	E (eV)	E_{McC} (eV)	T_m ($^\circ\text{C}$)	E (eV)	E_{McC} (eV)
30	87	0.87	0.87	104	0.69	0.68	-	-	-	-	-	-	284	0.88	0.89	>400	?	?
120	89	0.88	0.89	107	0.67	0.69	-	-	-	-	-	-	285	0.90	0.88	>400	?	?
300	88	0.88	0.89	104	0.70	0.70	-	-	-	-	-	-	282	0.93	0.92	>400	?	?
Average	88	0.88	0.88	105	0.69	0.69	-	-	-	-	-	-	284	0.90	0.90	>400	?	?
β method																		
T_m ($^\circ\text{C}$)	83			-			-			-			272			-		
E (eV)	0.81			-			-			-			1.2			-		

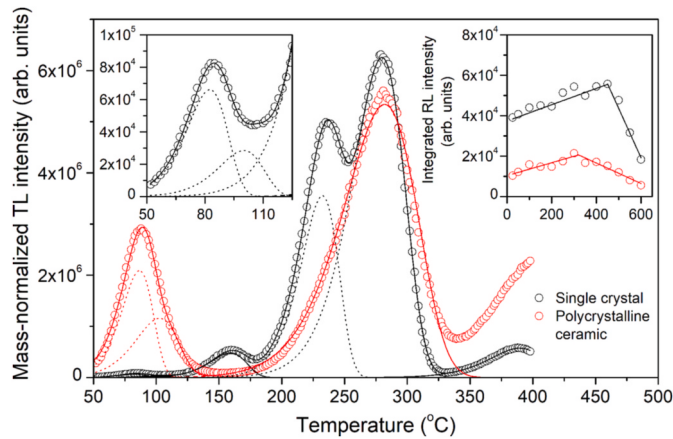


Fig. 12. Mass-normalized TL spectra (open circles) of single crystal (black) and polycrystalline ceramic (red) obtained after 120 s X-ray irradiation, together with glow curve best fitting results obtained with GlowFit software. Individual glow peaks are shown as dotted lines. Left inset: highlight of 50–125 $^\circ\text{C}$ region of single crystal glow curve. Right inset: integral RL intensity and linear best fits as a function of temperature. See text for details.

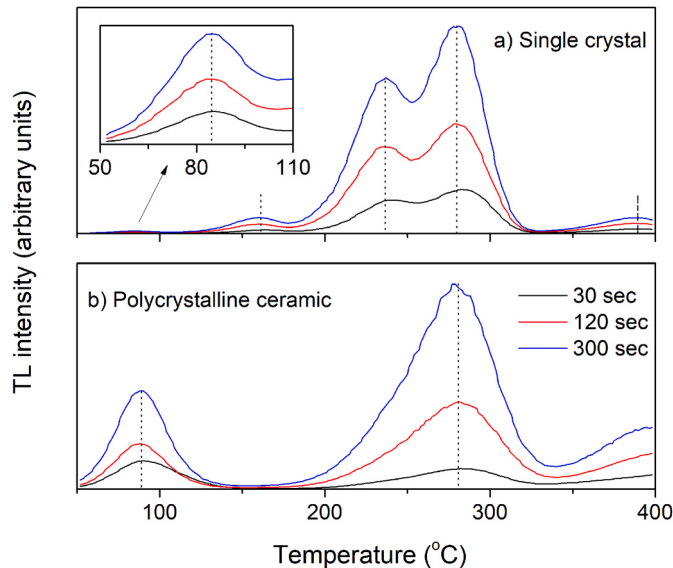


Fig. 13. TL glow curves obtained after X-ray irradiation for different times from 30 to 300 s of a) single crystal and b) polycrystalline ceramic.

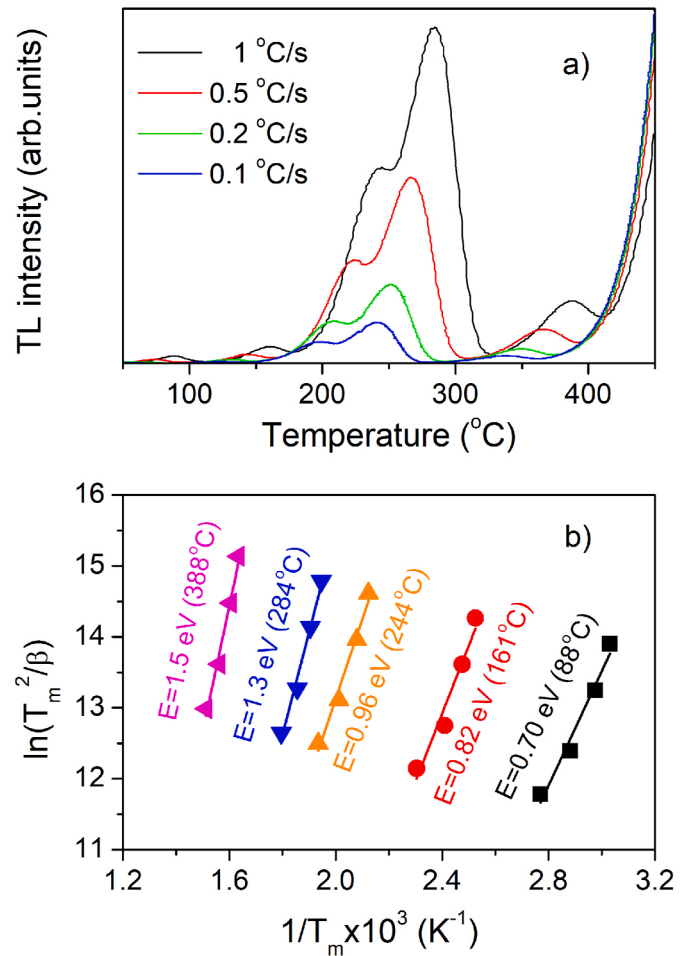


Fig. 14. a) TL glow curves obtained with different heating rates and b) results of the heating rate method of the single crystal.

lag, as discussed in detail in Ref. [45]. The lack of systematic variation of the position of peaks 1 and 2 as a function of the irradiation time, as determined by the fitting results (cf. Tables 3 and 4), supported the assumption that all glow peaks have first-order kinetics TL mechanism. Within a temperature range of about 10 $^\circ\text{C}$ (79–88 $^\circ\text{C}$, and 100–110 $^\circ\text{C}$), both glow peaks had been reported before, though not in the same sample [15,30,37,38,40,41]. The results for the trap depth obtained by the curve fitting and McKeever and Chen’s expression agreed well, similarly to the findings of a TL analysis of YPO_4 doped with rare earths [44]. In order to compare single crystal against polycrystalline ceramic scintillators, it was assumed that glow peaks at similar peak temperatures were originated from the same type of trap. Comparison of the trap

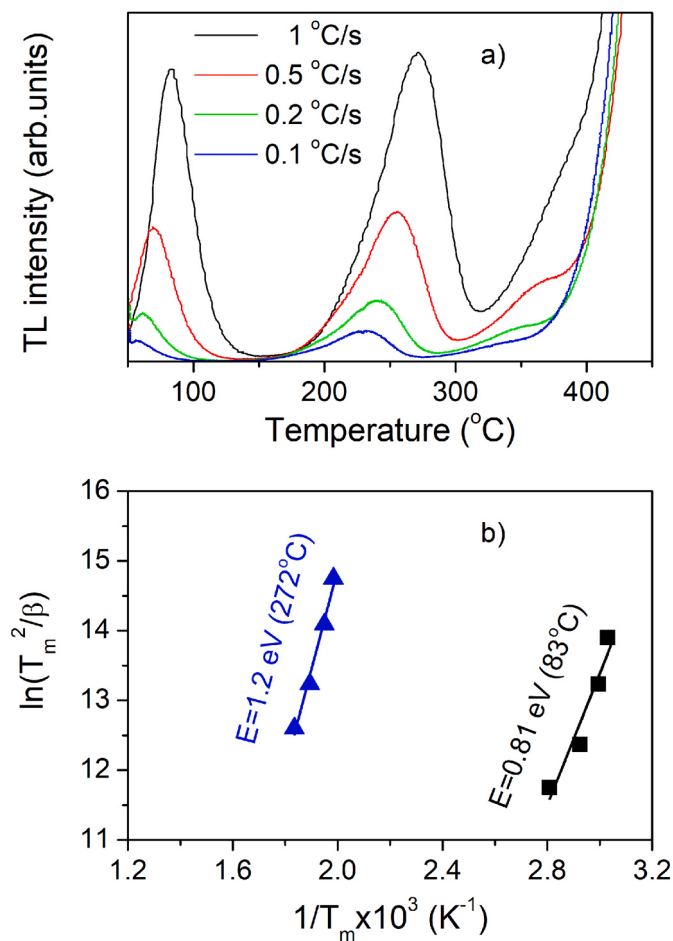


Fig. 15. a) TL glow curves obtained with different heating rates and b) results of the heating rate method of the polycrystalline ceramic.

depth values revealed trap depths in the single crystal to be ca. 1.2x to 1.5x deeper than in the polycrystalline ceramic.

The luminosity relative to a BGO single crystal used as reference was evaluated by means of differential pulse height distribution measurements using several gamma-ray sources. Results were normalized to the BGO luminosity for each gamma-ray energy, where the absolute luminosity of BGO can be found in Ref. [46]. These measurements are illustrated in Fig. 16 for ^{22}Na where the photopeak was fit with a Gaussian band (continuous green line). The relative light yield of the polycrystalline ceramic (red circles) and single crystal (black squares) as a function of different gamma-ray energies is shown in Fig. 17. Light output of the single crystal was within 13–35% higher than that of BGO, depending on the gamma-ray energy, and about two times higher than that of the polycrystalline ceramic. These differences could be at least partially accounted for the lower optical transparency and enhanced self-absorption combined with the detrimental effects to the scintillation performance of using a sintering aid in the fabrication of the polycrystalline ceramic [47]. Energy resolution determined at 662 keV for the polycrystalline ceramic was 19%, in agreement with a previous report [48], and slightly better than for the single crystal whose energy resolution was 22%.

4. Conclusions

In this work, a comparison between LuAG:Ce polycrystalline ceramic and single crystal scintillators was executed in terms of their structural, luminescent, and scintillation properties. Results showed lower optical transparency and a higher degree of structural disorder in the

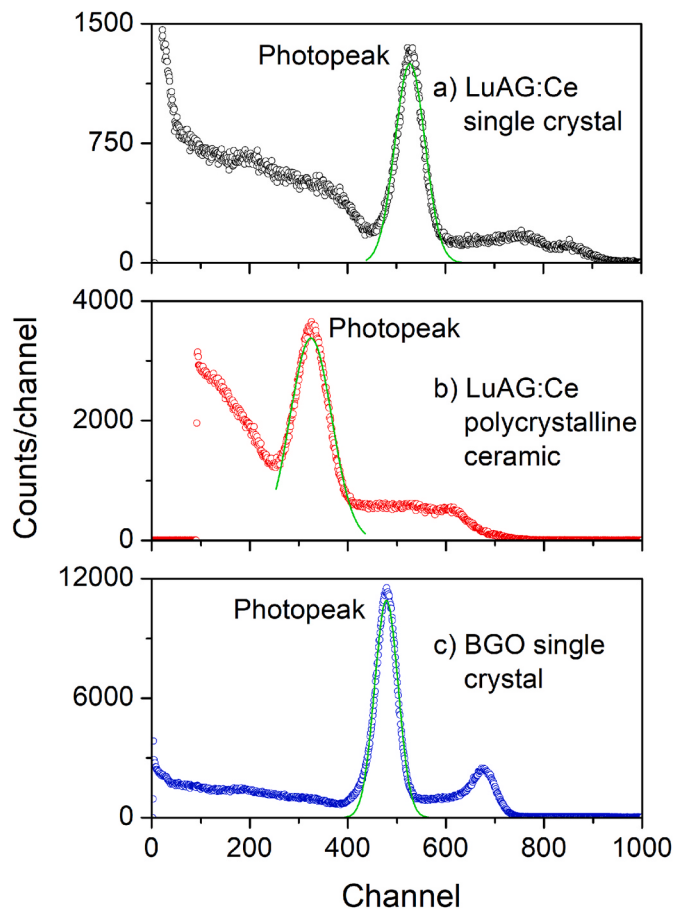


Fig. 16. Differential height distribution measurements using ^{22}Na source: a) LuAG:Ce single crystal, b) LuAG:Ce polycrystalline ceramic and c) BGO single crystal. Green lines correspond to Gaussian band best fit of the 511 keV photopeak.

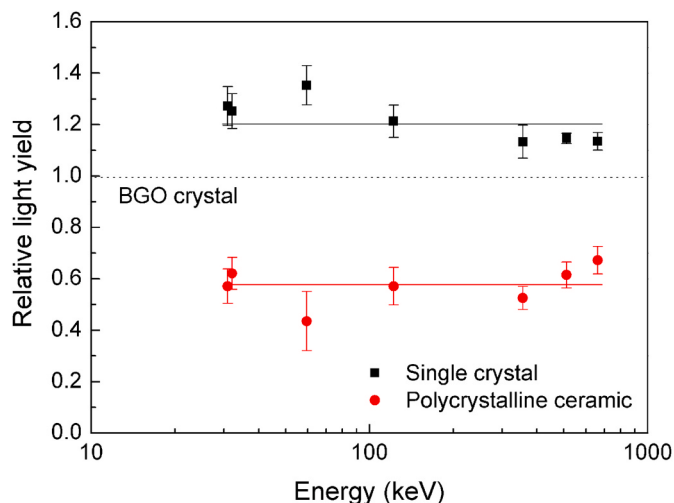


Fig. 17. Relative light yield of LuAG:Ce single crystal (black squares) and polycrystalline ceramic (red circles) normalized to the luminosity of a BGO single crystal concomitant to making BGO luminosity individually equal to 1 for each gamma-ray energy (dotted line).

polycrystalline ceramic. Structural disorder was manifested in terms of broadening of the optical absorption, PLE bands, and infrared absorption bands. RL and PL/PLE measurements indicated the presence of

defects, including F^+ -type centers and possibly oxygen vacancies, Ce_{Al} , perturbed Ce_{Al} and Lu_{Al} antisite defects. RL results indicated a much higher (11x) content of defects in the single crystal than in the polycrystalline ceramic. A literature review of the TL of LuAG:Ce revealed an overall lack of consistency between the different reports. Within the 50–400 °C range, this work revealed the presence of six glow peaks in the single crystal and four glow peaks in the polycrystalline ceramic, all with first-order kinetics. It was determined that Ce^{3+} was the sole recombination center in the TL process. Further, trap depths at similar peak temperatures were ~1.2–1.5 times deeper in the single crystal. In terms of scintillation performance, the polycrystalline ceramic showed lower relative luminosity compared to the single crystal. The reasons for this behavior included lower optical transparency and enhanced self-absorption due to structural disorder.

Credit author statement

A.A. Trofimov: Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization; T.A. DeVol: Formal analysis, Investigation, Resources, Writing - Review & Editing; L.G. Jacobsohn: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

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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