

Laser sintering of persistent luminescent $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}\text{Dy}^{3+}$ ceramics



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ABSTRACT

Described herein is the use of a laser sintering technique to produce persistent luminescence $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}\text{Dy}^{3+}$ ceramics exhibiting enhanced translucency in the visible/near infrared spectral range. In this technique, a CO_2 laser was used as the main heating source for sintering with no atmospheric control. The ceramics sintered at a power density of 1.2 W/mm^2 yielded single monoclinic CaAl_2O_4 phase, homogeneous grain size distributions and transmittance up to 45% in the range of 400 nm–900 nm. Upon conventional sintering in air, the ceramics exhibited the characteristic blue emission from the Eu^{2+} ions corresponding to the $5d \rightarrow 4f$ transition at 440 nm, and weak emission from Eu^{3+} ions between 550 nm and 700 nm, corresponding to the ${}^5D_0 \rightarrow {}^7F_J$ transitions.

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1. Introduction

Persistent luminescence is a phenomenon where a material emits light, usually in the visible range, for hours after the excitation source has been switched off [1]. The persistent luminescence decay time is defined as the duration from the moment of switching off the excitation source to the moment when the emission light intensity is reduced to 0.32 mCd/m^2 (i.e., 100 times the perception limit of the human eye) [2,3]. Materials that exhibit persistent luminescence have attracted attention due to their potential for use in electronic displays, high-energy detectors, digital radiography, optical memories and for image storage [4,5]. In recent years, calcium aluminate based materials have found new applications in the field of advanced ceramics as optical ceramics, catalyst support, flame detectors, dental cements and structural ceramics [6]. When doped with Eu and Dy ions, calcium aluminate presents persistent luminescence visible to the naked eye for up to 10 h originated from Eu^{2+} ions [4]. The blue emission of $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ (CAED) is observed only when the synthesis is performed in a reducing atmosphere that promotes the reduction of Eu^{3+} to Eu^{2+} [7–10].

It is well known that there is a strong relationship between the

physical properties of ceramic materials and their processing conditions. Recently, the laser sintering technique has been presented as an alternative unconventional technique [11–19] wherein a CO_2 laser is used as the principal heating source. The main advantages of this method are rapid processing times, the potential for using high heating and cooling rates (about $2000 \text{ }^\circ\text{C/min}$) without crucibles thereby reducing the risk of contamination, and the potential for sintering materials with high melting points. This technique has been successfully used to obtain dense ceramics for diverse applications, including, for example translucent $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ scintillators [11,12], SrAl_2O_4 persistent luminescent materials [13], refractory ceramics like Y_2O_3 [14] and YAG [15], and electronic ceramics with useful dielectric properties [16–19]. In this work, the use of laser sintering as an alternative technique to produce translucent CAED ceramics with persistent luminescent properties is investigated and reported.

2. Experimental procedures

Calcium aluminate powders doped with europium and dysprosium ($\text{Ca}_{0.985}\text{Eu}_{0.01}\text{Dy}_{0.005}\text{Al}_2\text{O}_4$ – CAED1_05, and $\text{Ca}_{0.998}\text{Eu}_{0.001}\text{Dy}_{0.001}\text{Al}_2\text{O}_4$ – CAED_01) were synthesized using a modified polymeric precursor method as described in Refs. [13,20]. The precursor materials utilized were $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (99%, Aldrich), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (99%, Aldrich), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.5%, Aldrich) and

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$\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.5%, Aldrich). Powders were calcined at 600 °C for 5 h in air, mixed with a binder solution of polyvinyl alcohol (concentration of 0.1 g/ml), and uniaxially compacted into disks of 4 mm diameter and 1.2 mm thickness using a pressure of 120 MPa.

Laser sintering was performed using a CO_2 laser (GEM-100L—Coherent) in continuous-wave mode as the main heating source. The compacted pellets were put on a base made of calcium aluminate, while the laser beam (diameter of 6.7 ± 0.3 mm) was directed and held at the center of the pellet throughout the sintering process. The chemical composition of the base and the laser beam diameter are essential to reduce the heat exchange between the pellet and environment thus minimizing temperature gradients. After a preheating stage at 200 °C, using a hot plate, the laser power density was increased at a linear heating rate of 0.01 W/mm²s up to 0.28 W/mm² and held at this value for 20 s. This initial power ramping stage was used to decrease the thermal gradient in the sample, thus inhibiting crack formation. Afterwards, the power density was raised again at a linear rate of 0.06 W/mm²s up to 3.10 ± 0.08 W/mm² and held at this value for 120 s. The laser power was then turned off and the sample left to cool in air. This process was repeated on the other face of the pellet. Using these conditions, the total CAED laser-sintering time was 10 min, which is remarkably fast in comparison to conventional sintering using an electric furnace that can last for several hours. It is important to mention that the whole process of synthesis and sintering was carried out in air.

X-ray diffraction (XRD) was performed using a Rigaku diffractometer RINT 2000/PC with Cu K_α radiation over a 2θ range between 10° and 60° in continuous scan mode with steps of 0.021°. The morphological characteristics of the as-sintered samples were analyzed using a Hitachi S3400-N Scanning Electron Microscope (SEM) in backscattered electron (BSE) mode. The local chemical composition was determined by means of energy-dispersive X-ray spectroscopy (EDS) measurements. Photoluminescence (PL) and persistent luminescent decay measurements were performed at room temperature using a Fluorolog 3 Horiba spectrofluorometer with a Xenon lamp of 450 W as the excitation source. The transmittance measurements were made using a halogen lamp, an integrating sphere and an Ocean Optics HR2000 spectrometer coupled with optical fibers. Persistent luminescent decay curve was calibrated to the absolute luminance (mCd/m²) by using a radiance meter (ILT 1700) coupled with a contact luminance probe (ILT - SPD025Y). These measurements were done in accordance with DIN 67510-1. X-ray absorption near edge (XANES) data were collected at the Eu L_{III}-edge (6977 eV) at room temperature, in the XAFS2 beam line of the Brazilian Synchrotron Light Laboratory (LNLS).

3. Results and discussion

Fig. 1 shows the XRD of the conventionally and laser sintered ceramics together with ICSD 70-0134 standard. The results show that both samples presented a single monoclinic CaAl_2O_4 phase. According to the literature [21], the stabilization of the monoclinic phase is essential to achieve good persistent luminescence properties.

Fig. 2 provides an SEM image (BSE mode) of the surface of the laser-sintered CAED1_05 ceramic. The ceramics exhibit a homogeneous grain size distribution and were fairly well sintered based on the apparent low porosity. Furthermore, brightness differences were observed between the grain and grain boundary regions at the surface of the samples, indicating the presence of denser ions (likely Eu and Dy) [13]. This evidence is confirmed by EDS elemental linescan and mapping analyses. An increase in lanthanide concentration was observed to be associated with a decrease in calcium concentration at the grain boundary regions. The crystal

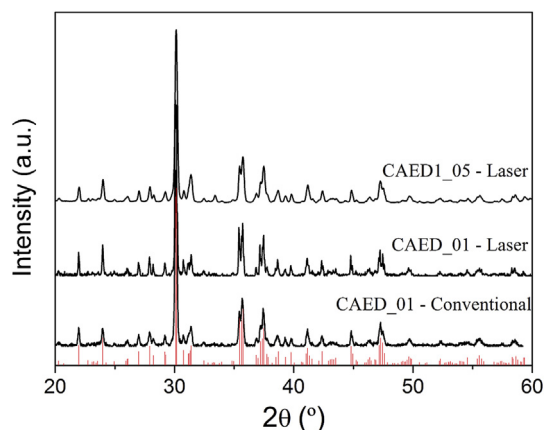


Fig. 1. XRD patterns of the conventionally (1250 °C for 2 h), and laser ($P_{\text{max}} = 3.10 \pm 0.08$ W/mm² for 30 s) sintered ceramics. The peaks were indexed according to Inorganic Crystal Structure Database (ICSD) number PDF-70-0134 for CaAl_2O_4 .

structure of CaAl_2O_4 is monoclinic space group $\text{P}2_1/\text{n}$ (No. 14), the no. of chemical formulas in the unit cell (Z) = 12 [22]. The structure consists of channels comprised of rings formed by six corner-sharing AlO_4 tetrahedra and Ca^{2+} cations situated within the channels occupying three different sites. Two of them (Ca1 and Ca2) are six- and one (Ca3) is nine-coordinated. According to Vegard's law [23], a complete solid solubility is expected when the difference between the radii of the participating ions is smaller than about 15%. For Eu^{2+} , the difference decreases from 16% (coordination number, CN: 6) to 5% (CN: 9) with increasing coordination number [24,25]. For Eu^{3+} and Dy^{3+} , this difference remain at about 6% and 9% (CN: 9), respectively, but, in this case, a charge compensation by interstitial oxygen (O_i') is necessary [26]. Besides, during the laser-sintering process, the samples are subjected to very high heating and cooling rates that influenced the dynamics and mass diffusion mechanisms [27], altogether facilitating Eu^{3+} and Dy^{3+} segregation at the grain boundaries. Similar microstructure was observed by Smet et al. [28] after using electron-beam annealing method to reduce europium in $\text{CaAl}_2\text{O}_4\text{:Eu,Nd}$. Similarly to laser sintering, e-beam annealing causes fast heating and cooling rates and, as a consequence, dopant segregation at grain boundary was also observed [28]. Nevertheless, e-beam annealing was efficient to reduce europium ions and the samples presented long and intense persistent luminescence. However, e-beam annealing is usually performed in vacuum ($\sim 10^{-6}$ mbar) while laser sintering is performed in air making the method presented here easier to apply in large scale and less time consuming (10 min for each sample). In the sample with lower dopant concentration (CAED_01), while segregation at grain boundary was not observed (results not show), these results are inconclusive since 0.002 mol% of dopants (Eu + Dy) is too low to be quantified by EDS. Despite compositional heterogeneity, the laser-sintered samples exhibited persistent luminescence properties, as it will be described later in this work.

In Fig. 3, the emission and excitation PL spectra of the laser-sintered samples are presented. When excited at 335 nm (wavelength of maximum excitation), the emission spectra present a broad emission band, centered at 440 nm, corresponding to the $5d \rightarrow 4f$ transition of Eu^{2+} in the CaAl_2O_4 matrix [8,10,28]. On the other hand, under excitation at 280 nm, the emission from Eu^{3+} ($^3\text{D}_0 \rightarrow ^7\text{F}_j$ transitions) can be observed [29]. Since the calcined powder and conventionally sintered ceramic did not present any Eu^{2+} luminescence, these results demonstrate that laser sintering is effective in promoting the partial reduction of Eu^{3+} to Eu^{2+} without

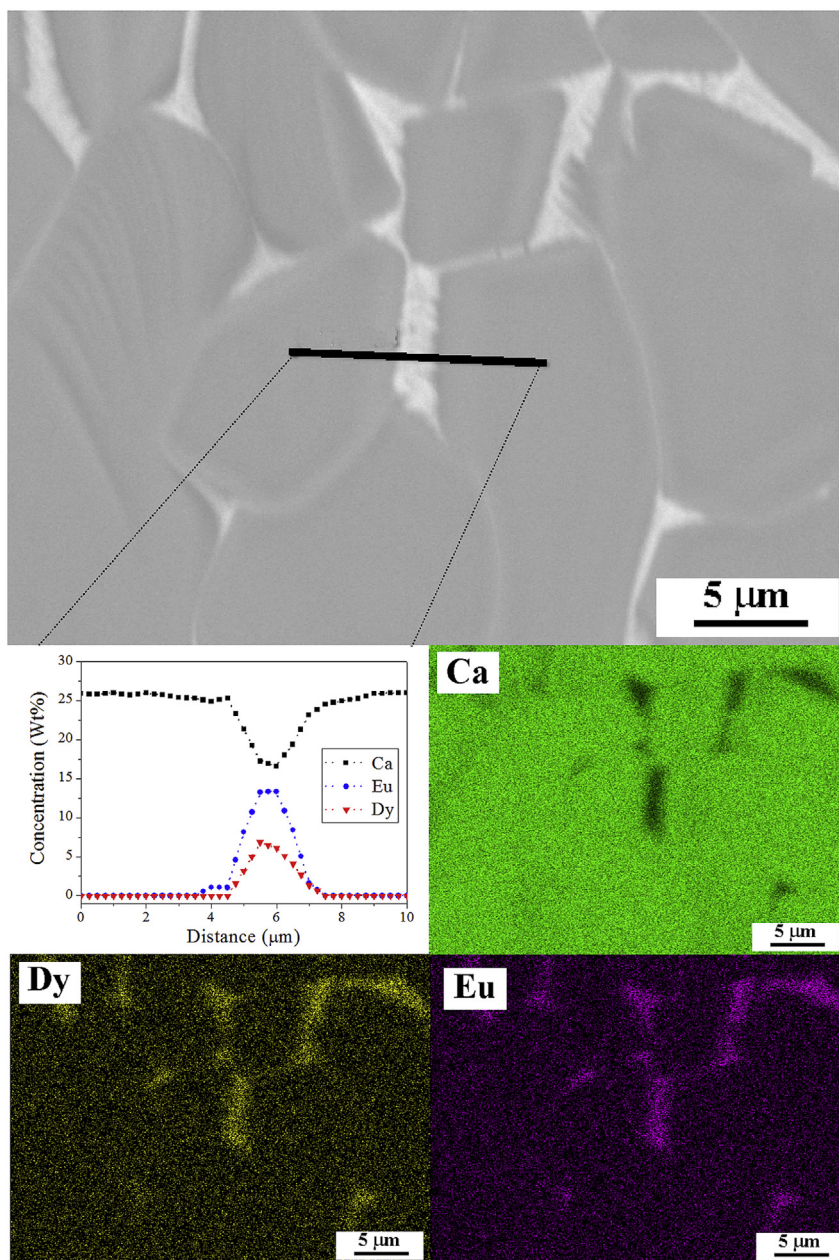


Fig. 2. SEM image of the surface of the as-sintered CAED1_05 ceramics using BSE mode (top). EDS linescan taken across the grain boundary and elemental mapping images (below) in which the brighter regions at the grain boundaries indicate higher Eu and Dy concentrations.

the need for a reducing atmosphere.

Fig. 4 shows the persistent luminescence decay curve of the laser-sintered ceramics after irradiation at 335 nm for 4 min. The samples exhibited persistent luminescence for more than 12 h even though they were sintered in air. The literature notes that [4] persistent luminescence for CAED can last for more than 10 h. However, annealing in reducing atmosphere typically is required. The inset in Fig. 4 also shows a photograph of the laser-sintered ceramic after irradiation by an ultraviolet lamp, where the bright blue light produced by Eu^{2+} is observed [4]. The images were taken in a darkroom using a digital camera immediately and 5 min after the optical excitation ceased.

Fig. 5 shows the optical transmittance of the laser-sintered ceramics. The ceramics were polished to the thickness of 0.5 mm and exhibited transmittance of about 45% (CAED1_05) and 30%

(CAED_01) over the range from 400 to 900 nm. This is a noteworthy result since the conventionally sintered sample (not show here), was fully opaque. This is an important feature since powder and opaque ceramics can only be efficiently excited at their surfaces due to the strong scattering of the excitation light [14,30]. Translucency in persistent luminescence ceramics are of relevance since it allows for the whole volume of the sample to be excited and to store charge, thus increasing luminescence output and possibly extending the range of applications [30,31]. The inset to Fig. 5 shows the polished laser-sintered sample (CAED1_05) in which it is possible to read through the translucent ceramic. It is important to note that although the CO_2 laser beam had a Gaussian profile during sintering, there was no difference in transparency between the center and the edges of the ceramic body. The samples also presented white color and no blackening, as reported by Avci et al. [32]. Avci

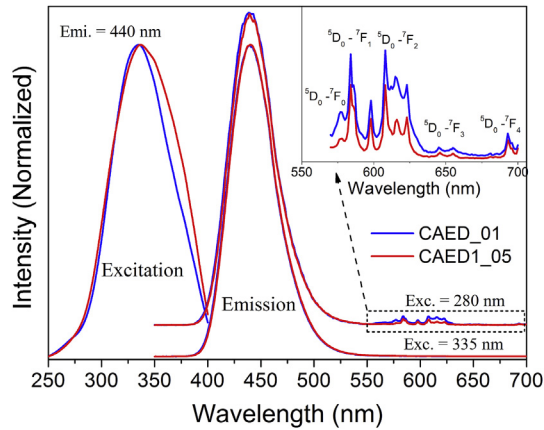


Fig. 3. PL spectra of laser-sintered ceramics measured at room temperature. The PL emission spectra were measured with excitation at 280 nm and at 365 nm, and the excitation spectra monitored at 440 nm. Emission spectra excited at 280 nm were vertically shifted to improve visual clarity. The inset highlights the emission from Eu^{3+} ions (${}^6\text{D}_0 \rightarrow {}^7\text{F}_j$ transitions).

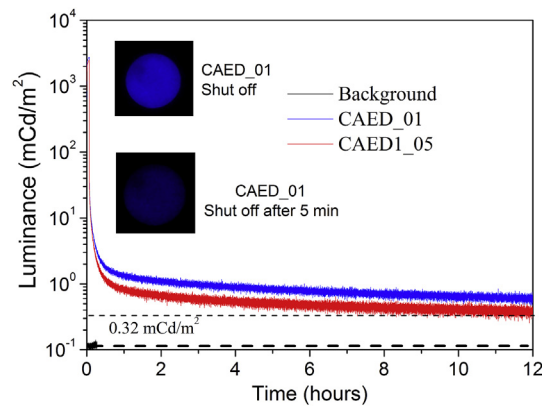


Fig. 4. Persistent luminescence decay curve (luminescence) after 335 nm irradiation for 4 min. The detection limit of the system is shown as heavy black dashed line. Images taken immediately after and 5 min after ceasing the UV excitation are also shown.

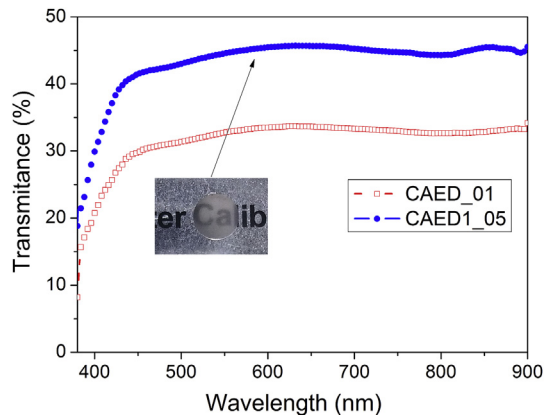
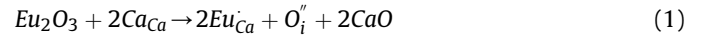


Fig. 5. Transmittance spectra of CAED laser-sintered ceramics (0.5 mm). The inset shows a photograph of the CAED1_05 sample in which it is possible to read through the translucent ceramic.

et al. [32] produced $\text{CaAl}_2\text{O}_4:\text{Eu},\text{Nd}$ powders under H_2/N_2 atmosphere to reduce Eu^{3+} . According to the authors, the powder blackening resulted in a reduction of the luminescent emission

intensity and avoiding this blackening could be essential to obtaining better luminescent properties. Therefore, these results also suggest that laser-sintering is an effective method to obtain dense ceramics with reduced light scattering, no blackening, and that exhibit persistent luminescence for more than 12 h.

Fig. 6 provides the X-ray absorption spectra in the XANES region of the laser-sintered samples and of Eu_2O_3 and EuS as standards for Eu^{3+} and Eu^{2+} , respectively, measured around the Eu L_{III} -edge [32]. In order to identify the valence of the Eu ion and obtain more precise information about the ratio between the two Eu valences, the spectra were normalized by the maximum absorption value. The low signal-to-noise ratio of the CAED_01 spectrum is due to the low Eu concentration (0.1 mol%). The results show that both Eu valences are detected in the samples, characterized by a shoulder around 6974 eV for the Eu^{2+} ion and a peak at 6983 eV for the Eu^{3+} ion. It is important to note that even though the samples were sintered in air, laser sintering allowed for the stabilization of the Eu^{2+} . Rezende et al. [26,33] suggested the substitution of Eu^{3+} at the Sr^{2+} site ($\text{Eu}_{\text{Sr}}^{\bullet}$) or at the Ba^{2+} site ($\text{Eu}_{\text{Ba}}^{\bullet}$) in $\text{SrAl}_2\text{O}_4:\text{Eu}$ and $\text{BaAl}_2\text{O}_4:\text{Eu}$ respectively, together with an oxygen interstitial to keep electrical neutrality. The formation of these defects is described in eq. (1) using the Kröger-Vink notation [26]. During the heating at high temperatures, (neutral) oxygen is lost in gaseous form altogether with the neutralization of $\text{Eu}_{\text{Ca}}^{\bullet}$ through the capture of an electron in order to maintain charge neutrality, i.e., through the formation of $\text{Eu}_{\text{Ca}}^{\times}$ (Eu^{2+}) (eq. (2)). According to Rezende et al. [33,34], eq. (2) is reversible when the samples are cooling in an oxidizing atmosphere, like air. In our case, the stabilization of the $\text{Eu}_{\text{Ca}}^{\times}$ (Eu^{2+}) was attributed to the very high cooling rate (quenching effect) of about $2000\text{ }^{\circ}\text{C}/\text{min}$ [13,16] that did not allow the full oxidation of Eu^{2+} into Eu^{3+} . Therefore, it is possible to found both Eu^{3+} and Eu^{2+} in the laser sintered samples.



Additionally, the relative intensity of the peaks in the XANES spectra is related to the Eu concentration in the host material. It can be seen that the low concentration sample (CAED_01) had proportionally more Eu^{2+} than the high concentration sample (CAED1_05). The dependence of the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio on the total Eu concentration is not fully understood, and is being reported for the first time in this work. Further, it is seen that the intensity of the Eu^{2+} peak is smaller than that of the Eu^{3+} , thus indicating that

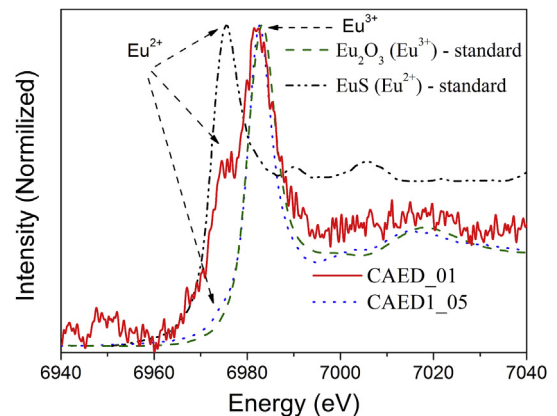


Fig. 6. XANES spectra of CAED laser-sintered ceramics together with Eu_2O_3 (Eu^{3+}) and EuS (Eu^{2+}) standards measured around the Eu L_{III} -edge.

there is less Eu^{2+} than Eu^{3+} in the laser-sintered samples. However, even with a limited fraction of Eu^{2+} , the PL emission spectra (Fig. 3) are dominated by Eu^{2+} , remarkably for an excitation wavelength which preferentially excites Eu^{3+} . Similar behavior was also observed by Avci et al. [32] when studying the influence of the temperature on the Eu valence in $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Nd}^{3+}$ under annealing in reducing N_2/H_2 atmosphere. We believe that through the optimization of the sintering conditions it should be possible to obtain ceramics with higher amounts of Eu^{2+} and therefore with enhanced persistent luminescence output.

4. Conclusions

To the best of our knowledge, persistent luminescent $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}\text{Dy}^{3+}$ translucent ceramics with transparencies up to 45% within 400–900 nm were successfully fabricated for the first time. Besides segregation of Dy and Eu ions in the grain boundaries, intense blue emission band centered at 440 nm and characteristic of the $5d \rightarrow 4f$ transition from Eu^{2+} was observed. The laser-sintered ceramics exhibited persistent luminescence decay that was visible to the human naked eye for longer than 12 h. These samples also exhibited the $4f \rightarrow 4f$ Eu^{3+} (${}^5D_0 \rightarrow {}^7F_J$) transitions indicating that the laser sintering was not perfectly effective in reducing all of the Eu^{3+} ions to Eu^{2+} . The presence of both Eu valences was confirmed by XANES results, with the low concentration sample (CAED_01) presenting proportionally more Eu^{2+} than the high concentration sample (CAED1_05). This behavior will be the aim of future studies. Finally, the persistent luminescence observed in these samples can be attributed to the crystallization of only the monoclinic phase, partial reduction of the Eu, and translucency of the samples obtained by laser sintering process without the need of reducing atmospheres.

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