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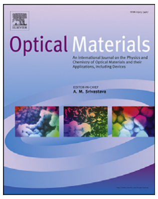

Laser sintering of persistent luminescent $CaAl_2O_4:Eu^{2+}Dy^{3+}$ ceramics

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ABSTRACT

Described herein is the use of a laser sintering technique to produce persistent luminescence $CaAl_2O_4:Eu^{2+}Dy^{3+}$ 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 → 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.

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 $CaAl_2O_4:Eu^{2+},Dy^{3+}$ (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 °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 $Bi_4Ge_3O_{12}$ 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 ($Ca_{0.985}Eu_{0.01}Dy_{0.005}Al_2O_4$ – CAED1_05, and $Ca_{0.998}Eu_{0.001}Dy_{0.001}Al_2O_4$ – CAED_01) were synthesized using a modified polymeric precursor method as described in Refs. [13,20]. The precursor materials utilized were $CaCl_2{\cdot}2H_2O$ (99%, Aldrich), $AlCl_3{\cdot}6H_2O$ (99%, Aldrich), $Eu(NO_3)_3{\cdot}6H_2O$ (99,5%, Aldrich) and

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$Dy(NO_3)_3 \cdot 5H_2O$ (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/mm^2s up to 0.28 W/mm^2 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/mm^2s up to 3.10 ± 0.08 W/mm^2 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/m^2) 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 structure of $CaAl_2O_4$ is monoclinic space group $P2_1/n$ (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 $CaAl_2O_4$: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 (~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.

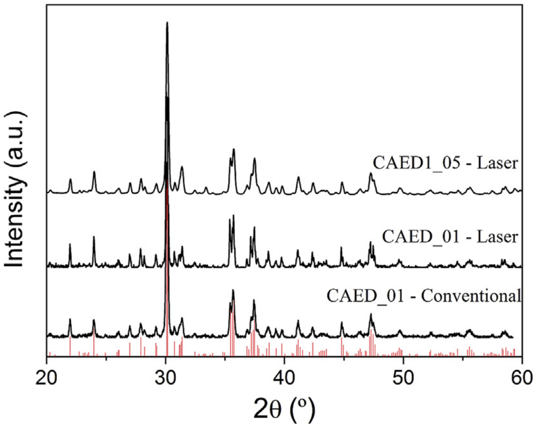

Fig. 1. XRD patterns of the conventionally (1250 °C for 2 h), and laser ($P_{max} = 3.10 \pm 0.08$ W/mm^2 for 30 s) sintered ceramics. The peaks were indexed according to Inorganic Crystal Structure Database (ICSD) number PDF-70-0134 for $CaAl_2O_4$.

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→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+} ($^5D_0 \rightarrow {}^7F_J$ 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

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