



## Blue emission of $\text{Eu}^{2+}$ -doped translucent alumina

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### ABSTRACT

Inorganic scintillators are very important in medical and industrial measuring systems in the detection and measurement of ionizing radiation. In addition to  $\text{Ce}^{3+}$ , a widely used dopant ion in oxide scintillators, divalent Europium ( $\text{Eu}^{2+}$ ) has shown promise as a high-luminescence, fast-response luminescence center useful in the detection of ionizing radiation. In this research, aluminum oxide ( $\text{Al}_2\text{O}_3$ ) was studied as a host material for the divalent europium ion. Polycrystalline samples of  $\text{Eu}^{2+}$ -doped translucent  $\text{Al}_2\text{O}_3$  were fabricated, and room temperature luminescence behavior was observed.  $\text{Al}_2\text{O}_3$  ceramics doped with 0.1 at%  $\text{Eu}^{2+}$  were fabricated with a relative density of 99.75% theoretical density and in-line transmittance of 22% at a wavelength of 800 nm. The ceramics were processed by a gel-casting method, followed by sintering under high vacuum. The gelling agent, a copolymer of isobutylene and maleic anhydride, is marketed under the commercial name ISOBAM, and has the advantage of simultaneously acting as both a gelling agent and as a dispersant. The microstructure and composition of the vacuum-sintered  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  were characterized by Scanning Electric Microscopy (SEM), Transmission Electron Microscopy (TEM), and Energy-dispersive X-ray spectroscopy (EDS). The phase composition was determined by X-ray diffraction measurements (XRD) combined with Rietveld analysis. The photoluminescence behavior of the  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  was characterized using UV light as the excitation source, which emitted blue emission at 440 nm. The radio-luminescence of  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  was investigated by illumination with X-ray radiation, showing three emission bands at 376 nm, 575 nm and 698 nm. Multiple level traps at different depths were detected in the  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  by employing thermoluminescence measurements.

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### 1. Introduction

In radiation detection, inorganic scintillators play an important role in all medical diagnostic imaging modalities that use X-rays or  $\gamma$ -rays, as well as in many industrial measurement systems [1,2]. The criterion of a promising scintillator includes high luminosity (high brightness) and a fast response of the scintillator to radiation exposure. Recently, the application of the  $\text{Ce}^{3+}$  emission center within different matrices has attracted much attention due to its useful 5d–4f transition [3], very fast decay time (38 ns) [4], and the largest radioactive transition probability in the rare-earth ions [5]. With increasing research into the rare-earth elements,  $\text{Eu}^{2+}$  is a promising choice as a emission center, as it possesses a highly efficient and relatively fast 5d–4f luminescence.

The electronic transitions of the divalent Europium ( $4f^7$ )  $\text{Eu}^{2+}$  ion have many potential applications in optical applications, such

as in phosphors [6], lasers [7], and scintillators for detecting ionizing radiation [8] due to its function as an efficient luminescence center. High luminosity and fast decay time are mainly decided by the host matrix and specific emission center. Recently,  $\text{Eu}^{2+}$  has been explored as a dopant in various materials, such as  $\text{SrI}_2$  [9],  $\text{CsBa}_2\text{Br}_5$  [10],  $\text{BaFI}$  [11],  $\text{Ba}_2\text{CsI}_5$  [12],  $\text{LiCaAlF}_6$  and  $\text{LiSrAlF}_6$  [13], and high light output and acceptable scintillation decay time being reported. However, the application of halide-based materials as scintillators suffers from major disadvantages, stemming from their sensitivity to moisture and low mechanical strength. Oxide ceramics, on the other hand, hold the advantages of high strength and chemical stability, high transparency, and the relative ease of doping with rare-earth elements as luminescence centers, and as such are ideal candidates for the new generation of scintillation materials. Different compounds of aluminum oxide have been studied as host matrices, including  $\text{Eu}$ -doped Garnet ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), which has been shown to have promising scintillation behavior [14].  $\alpha\text{-Al}_2\text{O}_3$  was the material studied here, which commonly sees application as a optical host crystal, and is a promising candidate

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for new generation emissive optical materials, which makes use of isolated impurities incorporated into ceramic matrices.

There are multiple methods to achieve the reduction of  $\text{Eu}^{3+}$  to form  $\text{Eu}^{2+}$  in solid samples, including reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  by laser induction [15], pulsed-laser deposition [16], wet chemistry methods to precipitate the desired valency of the ion [17], and annealing under reducing atmospheres [18,19]. Recently, researchers have reported with the assumption that the presence of  $\text{Al}^{3+}$  is a key factor in the reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  [14]. In the processing of  $\text{Eu}:\text{Al}_2\text{O}_3$ , the valence state of the Eu ion is strongly affected by oxygen partial pressure. It has been observed that at low oxygen partial pressures ( $\sim 10^{-3}$  Pa), the desired divalent ( $2+$ ) oxidation state of the Eu ion becomes the stable valence state, while  $\text{Eu}^{3+}$  is reduced [20].

In this study,  $\text{Eu}^{2+}$ -doped translucent  $\text{Al}_2\text{O}_3$  was prepared by gel-casting and high vacuum ( $10^{-3}$ – $10^{-5}$  Pa) sintering.  $\text{Eu}_2\text{O}_3$  was doped into  $\text{Al}_2\text{O}_3$ , and then subsequently reduced to form luminescent  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  with a blue emission at 440 nm and radio-luminescence emissions located at 376 nm, 575 nm and 698 nm.

## 2. Experimental section

### 2.1. Materials

All chemicals used in this study were reagent-grade quality materials supplied by commercial vendors.  $\text{Eu}_2\text{O}_3$  (99.99%, Sigma, USA) was used as the source for  $\text{Eu}^{2+}$ . High-purity  $\alpha$ - $\text{Al}_2\text{O}_3$  powder ( $> 99\%$ ) (CR-10, Baikowski, Annecy, France,  $D_{50}=0.45$   $\mu\text{m}$ ) was used as the matrix material. ISOBAM (Kuraray Co., Osaka, Japan) was used as spontaneous gelling agent and dispersant, the use of which has been detailed in similar applications by other authors [21–26], with de-ionized water as the solvent.

### 2.2. $\text{Eu}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ slurry fabrication and gelcasting process

A homogeneous slurry with a solids loading of 38 vol% was obtained by ball milling  $\text{Eu}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and ISOBAM together with de-ionized water for 5 h with  $\text{ZrO}_2$  grinding media. Bubble removal was performed before casting using a custom-made vacuum degassing system with an ultimate pressure less than 10 Pa, while the slurry was simultaneously stirred at 250 r/min. The resultant slurry was cast into plastic molds with diameters ranging from 4 to 9 cm; sizes similar to that used in the procedures of other authors [22–24]. Using this process, green bodies of  $\text{Al}_2\text{O}_3$  intimately mixed with different concentrations of  $\text{Eu}_2\text{O}_3$  were formed. The compositions were designed for the end ceramics to have compositions with dopant levels of 0 at%, 0.1 at%, 0.2 at%, and 0.5 at%  $\text{Eu}^{2+}$ .

### 2.3. De-binding and sintering

After gelling and demolding, the green bodies were dried in air for 24 h at room temperature with no applied heat or humidity control. Organics and water were removed by pre-sintering at 973–1273 K in air with dwell times ranging from 3 to 5 h and heating rates of 3–10 K/min. The final ceramics were obtained by high vacuum sintering at 2073–2173 K for 5 h at a heating rate of 3–10 K/min.

### 2.4. Characterization

The microstructures of the vacuum-sintered  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  were characterized by SEM (FEI Quanta 200, USA) and TEM (JEOL2100F, Japan). Chemical composition was measured using EDS (JEOL2100F, Japan). Phase composition of the ceramics was measured by X-ray

diffraction (XRD) (Bruker D2 Phaser, Germany) equipped with Cu radiation ( $\lambda=0.154$  nm) in the range of  $10$ – $75^\circ 2\theta$ . Unit cell parameters were determined from analysis of the XRD measurements using Rietveld analysis performed with TOPAS pattern fitting software. The in-line transmittance in the UV–vis region (Perkin Elmer Lambda 1050, USA) of the sintered doped  $\text{Al}_2\text{O}_3$  bodies was measured to be 22% at a wavelength of 800 nm. The relative densities of the sintered bodies were measured using Archimedes' principle density measurements, with the following average results: dry green body: 49.50% of theoretical density; pre-sintered green body: 76.80%, vacuum sintered ceramic: 99.75%. Photoluminescence (PL) spectra were obtained using a fluorescence spectrophotometer (JobinYvon Fluorolog-3spectrofluorometer, Horiba, USA) with a Xenon lamp as the excitation source. The luminescence decay curve was recorded using a pulsed Nd:YAG laser source at 266 nm (Spectron Laser System SL802G, Rugby, UK) with a pulse energy of approximately 5 mJ, at a frequency of 10 Hz, with a pulse duration of 5 ns. The radio-luminescence spectra of the  $\text{Eu}:\text{Al}_2\text{O}_3$  were recorded at room temperature (Acton Spectropro 2150i, CMX003 X-ray generator (35 kV, 0.1 mA)). Thermoluminescence behavior was characterized in the temperature range of 10–550 K, using Advanced Research Systems DE-202 for cooling and heating and CMX003 X-ray as the energy source.

## 3. Results and discussion

### 3.1. Microstructure

Fig. 1 shows the microstructure of pure  $\text{Al}_2\text{O}_3$  (Fig. 1(a)) and 0.1 at%  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  (Fig. 1(b)) after vacuum sintering. It can be readily observed that the 0.1 at%  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  sample has a larger average grain size than the pure  $\text{Al}_2\text{O}_3$  sample, which may indicate that europium facilitates grain growth in  $\text{Al}_2\text{O}_3$  during vacuum sintering, similar to the phenomenon observed in  $\text{Eu}:\text{Y}_2\text{O}_3$  [27]. Fig. 2 shows a surface microstructure (Fig. 2(a) and (c)) and grain size distribution (Fig. 2(b) and (d)) of vacuum-sintered  $\text{Eu}:\text{Al}_2\text{O}_3$  and undoped  $\text{Al}_2\text{O}_3$  fitted to a polynomial curve in the range of 20–105  $\mu\text{m}$ . The grains stack closely together with only a few isolated pores apparent, confirming that the samples are high density. The average grain size of vacuum-sintered  $\text{Eu}:\text{Al}_2\text{O}_3$  is approximately 63  $\mu\text{m}$ , as determined from a statistical and mean value grain size calculation using software (Nano Measurer, Version 1.2, Fudan University, Shanghai, China) shown in Fig. 2(b), which is larger than that of vacuum-sintered undoped  $\text{Al}_2\text{O}_3$  shown in Fig. 2(d). An impurity phase was observed in a cross-section of the  $\text{Eu}^{2+}:\text{Al}_2\text{O}_3$  ceramic, as shown in the TEM images in Fig. 3. The elemental composition of the impurity phase measured by EDS is shown in Fig. 4. Strong peaks from Eu were detected, indicating that the impurities are Eu-rich clusters. The segregation of undissolved europium may come from the large difference in ionic radii of  $\text{Eu}^{2+}$  (120 pm) relative to  $\text{Al}^{3+}$  (67.5 pm), causing a solubility limit of  $\text{Eu}^{3+}$  in  $\text{Al}_2\text{O}_3$  to be reached, causing precipitation of Eu at the grain boundaries. The Eu-rich segregates can be observed entangled together with  $\text{Al}_2\text{O}_3$  grains and appear to grow along or through the grain boundaries of the  $\text{Al}_2\text{O}_3$ . The segregation of europium at  $\text{Al}_2\text{O}_3$  grain boundaries has been observed and reported by other authors [28,29].

### 3.2. Phase identification

The phase composition and lattice parameters of the translucent  $\text{Al}_2\text{O}_3$  with and without Eu doping were determined by analysis of XRD measurements performed at room temperature, as shown in Fig. 5. Phase identification was performed using Diffrac EVA XRD data analysis software. It can be clearly observed that

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