

Cathodoluminescent and Photoluminescent Properties of Al₂O₃ Powders Doped with Eu

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Eu-doped Al₂O₃ powders were made by a coprecipitation technique using aluminum nitrate and europium chloride as precursors at annealing temperatures of 500, 700, and 900 °C. Room temperature cathodoluminescence and photoluminescence characteristics of Al₂O₃:Eu powders as a function of the dopant concentration and annealing temperature have been studied. The emissions from Eu-doped powders have the spectral characteristics typical of radiative transitions among the electronic energy levels associated with the 3⁺ ionized state of this ion. The X-ray diffraction patterns show a broad peak that tends to become narrower as the annealing temperature is raised. Energy dispersive spectroscopy indicates that the powders are oxygen-rich, which may indicate a low density or porous material. Finally, scanning electron microscopy images show a variety in the shape and size of the powder particles associated with the milling procedure implemented in order to obtain the powders.

1. Introduction

There is a considerable interest in the development of phosphors for applications in advanced display technologies including plasma, field emission, and electroluminescent displays. Some of the materials used for this kind of applications are rare-earth (RE) activated oxide phosphors such as Y₂O₃ [1], In₂O₃ [2], ZrO₂ [3], ZnO [4], Y₃Al₅O₁₂ [5], etc., activated with Eu, Tb, Ce, and other rare earths. These materials have excellent light output and color rendering capabilities. They have also been used in powder form for cathode ray tube (CRT) phosphors and other related applications such as fluorescent lamps, image intensifiers for X-ray screens, and X-ray phosphors for photostimulable storage screens, among others [6]. Factors associated with stability, ease of synthesis, and environmental safety often make them significantly superior to other phosphors such as sulfur-based materials that tend to degrade rapidly under the high current densities such as those needed for field emission display (FED) technology. Besides they do not contaminate the electron emitters in FEDs and are chemically inert to plasmas commonly used in plasma operated flat panel displays [7, 8]. Among oxide-based phosphors, aluminum oxide is an important material due to its application as a dielectric layer on different types of microelectronic devices [9] and as gate oxides in metal-oxide–semiconductor structures such as passivation layers or dielectric

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films in chemical sensors [10]. Because of this, the amount of information regarding the electrical properties of this material is considerable. On the other hand, Al₂O₃ can be an important component in electroluminescent devices, for instance it has been doped with V, Ti, Cr, Eu, Ce, Tb, Mn, etc. [11]. Nevertheless the research done in the area of luminescent properties, in particular the cathodoluminescent ones, is relatively scarce.

The present work reports, to our knowledge for the first time, the cathodoluminescence characteristics of Eu-doped aluminum oxide powders as well as the photoluminescence ones. The spectra and overall intensity of the light emission have been studied as a function of doping concentration and annealing temperatures. Both photoluminescence and cathodoluminescence spectra have several peaks that are associated with interlevel transitions between electronic energy levels of Eu³⁺ ions showing a dominant red light emission. X-ray diffraction patterns of these powders indicate that they are amorphous or have very poor crystallinity. Scanning electron microscopy images from these powders show that they are composed of particles with size and shapes determined by the milling procedure. The stoichiometry and presence of europium in the powders have been measured by energy dispersive spectroscopy.

2. Experimental Details

The Al₂O₃:Eu powders were prepared by a simple coprecipitation technique using aluminum nitrate and europium chloride mixed with ethanol. The mixture was heated at 250 °C for 30 min in air, after which the temperature was raised at 350 °C for 30 min more in order to evaporate the solvent and complete the synthesis. The dopant concentrations were 5, 10, 15, and 20 atom percent (at%). The powders obtained in this way were manually milled using an agate mortar and divided into three series. Each of them were then post-annealed at temperatures of 500, 700, and 900 °C, respectively, for 2 h. No further milling was performed with the resulting materials. Al₂O₃:Eu synthesized powders were pressed to obtain pellets 10 mm in diameter and 3 mm thick.

Cathodoluminescence (CL) measurements were performed with a commercial luminoscope, model ELM2 MCA, RELION Co. (electron source and beam controller). The emission was collected by means of an optical fiber connected to a commercial spectrofluorometer (Perkin Elmer LS50B) in its bioluminescence mode. The wavelength range analyzed was from 400 to 800 nm, the electron beam accelerating voltage used was 12 kV, and the beam current over a circular area of 5 mm in diameter approximately was 0.5 mA. The photoluminescence (PL) spectra were obtained with a spectrofluorometer in the wavelength range from 400–800 nm. 250 nm light was found to be suitable as excitation energy for the photoluminescence measurements. The spectra were measured using a 430 nm filter to block out the excitation signal. The final spectrum was a result of an average over three scans at 400 nm/min. A Siemens D-5000 X-ray diffractometer with a Cu target ($\lambda = 1.5406 \text{ \AA}$) was used to obtain the X-ray diffraction (XRD) patterns of the powders. The surface morphology of the powders was observed with a scanning electron microscope (JEOL JSM-6300) with 15 kV voltage and 5000x. The chemical composition of the powders was measured using energy dispersive spectroscopy (EDS) with a Leica Cambridge electron microscope Stereoscan 440, using a Link-Isis software and the ZAF method. The standard for the EDS measurements was the Multielement X-ray Reference Standard (Microspec, Serial 0034, Part. No. 8160-

53). The electron beam voltage and current were 20 kV and 1000 pA, respectively. Each data point was determined from the average of three measurements on different areas of a given sample.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns for $\text{Al}_2\text{O}_3:\text{Eu}$ powders prepared with 10% of Eu and post-annealed at 500, 700, and 900 °C for 2 h. These spectra show one broad peak centered around $2\theta = 30^\circ$ that becomes sharper when the annealing temperature is raised from 500–900 °C. It seems that some degree of molecular ordering is beginning to appear at 900 °C, although no complete crystallization is observed. The spectra obtained for 500 and 700 °C do not present any crystalline structure either.

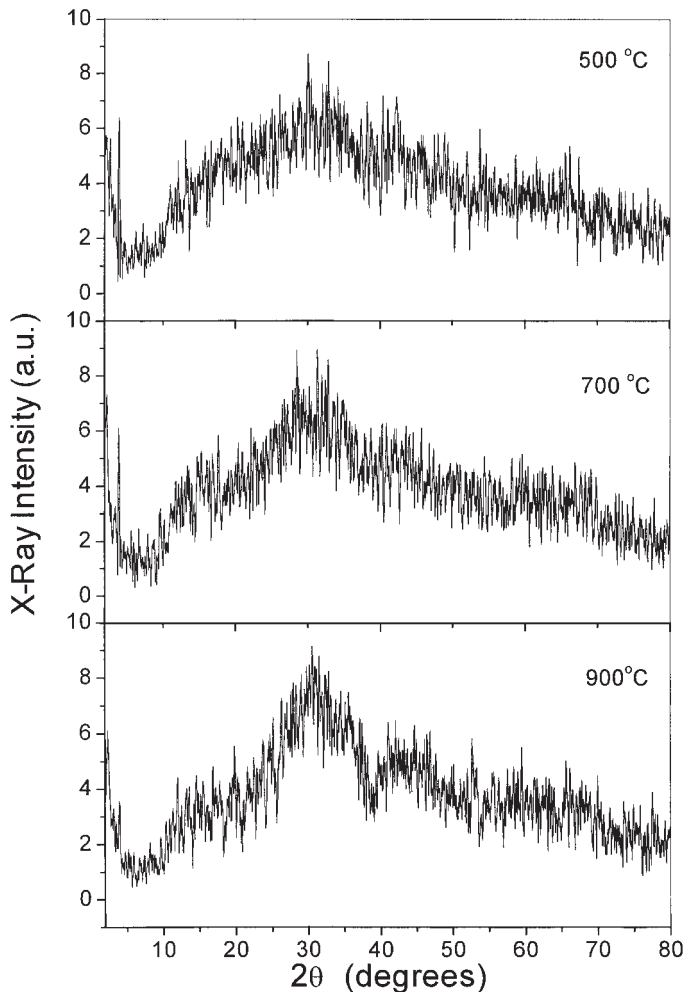


Fig. 1. X-ray diffraction patterns for europium-doped aluminum oxide powders with 10 at% Eu for annealing temperatures of 500, 700, and 900 °C

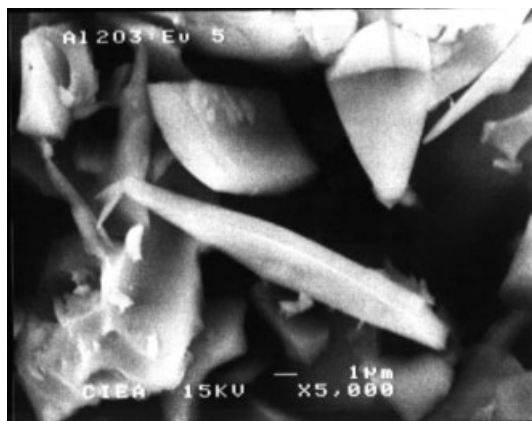


Fig. 2. Scanning electron microscopy image from a sample of Al₂O₃:Eu powder with 10 at% Eu for 700 °C annealing temperature

Figure 2 shows a representative SEM image from the Al₂O₃:Eu powders studied. There is a great variety of particle sizes and shapes. The particle sizes range from approximately 4 µm to tens of microns, and several shapes such as plates, needle-like, and irregular geometrical forms are

observed. These characteristics are common to all the samples studied regardless of annealing temperature or doping concentration. Therefore, it is assumed that they are determined by the manual milling procedure. Table 1 lists the relative chemical content of europium, aluminum, and oxygen present in the powders as measured by EDS for the different dopant concentrations and annealing temperatures used for the preparation of the powders. The amount of Eu detected by EDS is approximately 1/5 of the concentration of europium chloride in the starting mixture. There is also a hint of reduction of the europium content as the annealing temperatures are increasing, for each of the doping concentration studied. The presence of chlorine in these powders was not quantified, although there are reports that indicate the presence of chlorine in important amounts only at low temperatures (<400 °C) [12]. Moreover, we observe that the oxygen to aluminum ratio in atom percent is larger than the 3:2 expected value for stoichiometric Al₂O₃. The excess in oxygen could indicate a low density material which could favor the absorption of water.

The CL emission characteristics for the powders are illustrated in Fig. 3, where the spectrum for Eu-doped powders with 10% of Eu, annealed at 900 °C, is shown. The

Table 1

Atom percent of europium, aluminum, and oxygen content in the powders as determined by EDS for different doping concentrations in the start mixture and at different annealing temperatures

	Eu ³⁺ in start mixture				annealing temperature
	5 at%	10 at%	15 at%	20 at%	
oxygen	69.63 ± 0.62	68.15 ± 0.6	72.26 ± 0.26	73.52 ± 0.26	500 °C
aluminum	29.05 ± 0.52	29.66 ± 0.36	24.15 ± 0.17	22.27 ± 0.26	
europium	1.32 ± 0.1	2.19 ± 0.26	3.59 ± 0.1	4.21 ± 0.1	
oxygen	69.44 ± 0.85	72.77 ± 0.26	72.02 ± 0.7	74.47 ± 0.1	700 °C
aluminum	29.35 ± 0.85	25.22 ± 0.26	24.77 ± 0.3	21.52 ± 0.17	
europium	1.21 ± 0.1	2.01 ± 0.05	3.21 ± 0.4	4.01 ± 0.1	
oxygen	69.66 ± 0.95	73.17 ± 0.72	72.24 ± 1.57	74.48 ± 0.81	900 °C
aluminum	29.19 ± 0.87	25.24 ± 0.52	24.89 ± 1.3	21.53 ± 1.01	
europium	1.14 ± 0.1	1.59 ± 0.2	2.87 ± 0.26	3.99 ± 0.2	

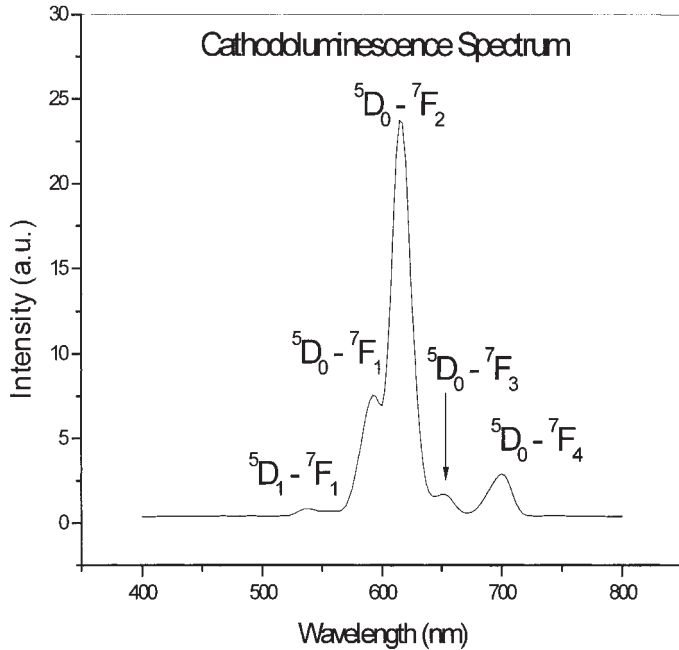


Fig. 3. Room temperature CL emission from aluminum oxide powders doped with Eu, for a sample with 10 at% Eu in the start mixture and 900 °C annealing temperature. The light emission from these powders shows the characteristic peaks associated with radiative transitions between the electron energy levels of Eu^{3+} ions

spectrum presents peaks centered at 540, 592.5, 615, 652.5, and 700 nm that are associated with interlevel transitions for the electronic energy levels of Eu^{3+} ions, in particular to those corresponding to transitions from ${}^5\text{D}_1$ to ${}^7\text{F}_1$, and from ${}^5\text{D}_0$ to ${}^7\text{F}_1$, ${}^7\text{F}_2$, ${}^7\text{F}_3$, and ${}^7\text{F}_4$, respectively [13, 14]. The strongest emission corresponds to the 615 nm red line associated with the ${}^5\text{D}_0$ to ${}^7\text{F}_2$ transition of the Eu^{3+} ion. The 592.5 nm orange line from the ${}^5\text{D}_0$ to ${}^7\text{F}_1$ transition is observed to be relatively weak, therefore the luminescence intensity is concentrated mainly in the forced electric dipole transition (615 nm) rather than in the magnetic dipole transition (592.5 nm) [6]. The luminescent characteristics of the Eu doped Al_2O_3 powders are mostly due to transitions that are generated within the atomic levels of the Eu^{3+} ion, yielding as a result sharp line emissions (f-f transitions) due to a shielding effect of the $4f^n$ valence electrons by the $5s^2p^6$ electron cloud.

The CL emission intensity for the 615 nm peak as a function of dopant concentration is shown in Fig. 4. It is observed that the luminescence intensity has an optimum at 10 at% mostly and a quenching process for higher concentrations. On the other hand, the CL emission does not reach saturation or quenching behavior at the annealing temperatures studied in this work.

The PL spectra are similar to CL spectra as shown in Fig. 5, presenting also the characteristic peaks that are associated with transitions between the levels ${}^5\text{D}_1$ to ${}^7\text{F}_1$ (545 nm), and from ${}^5\text{D}_0$ to ${}^7\text{F}_1$, ${}^7\text{F}_2$, ${}^7\text{F}_3$, and ${}^7\text{F}_4$ (590, 615, 650, and 700 nm, respectively) [13, 14] of the Eu^{3+} ion. Besides these peaks, there is a broad emission centered at 475 nm that is associated with instrumental artifact coming from the spectrofluorometer.

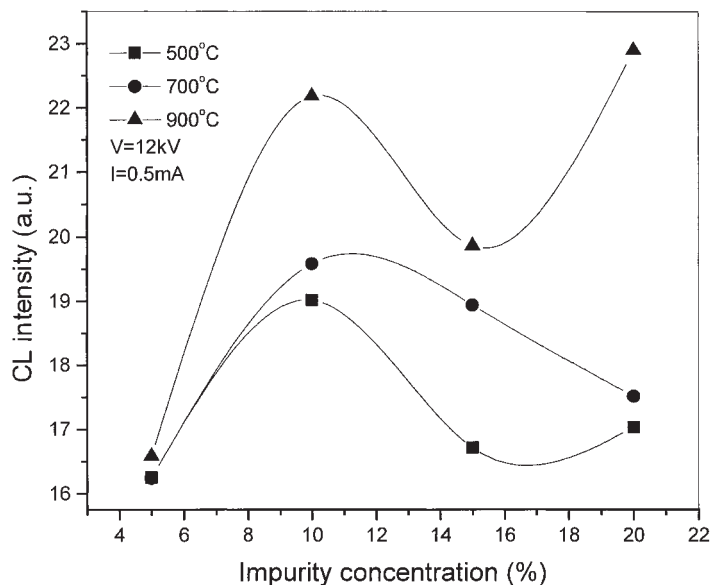


Fig. 4. Light emission (CL) for the main peak (615 nm) plotted as a function of doping concentration for different annealing temperatures. The CL intensity decays in general for concentrations above 10 at% and continues increasing as the annealing temperature is raised

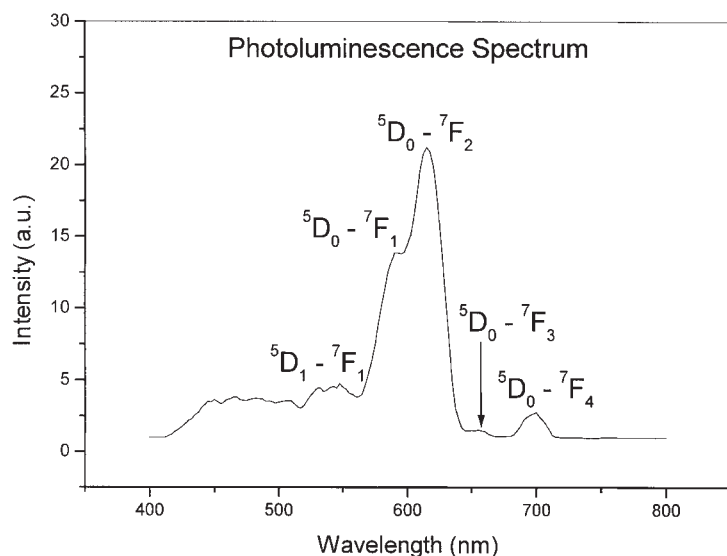


Fig. 5. Room temperature photoluminescence emission from aluminum oxide powders doped with Eu, for a sample with 10 at% Eu in the start mixture and 700 °C annealing temperature. The light emission from these powders shows the characteristic peaks associated with radiative transitions between the electron energy levels of Eu³⁺ ions

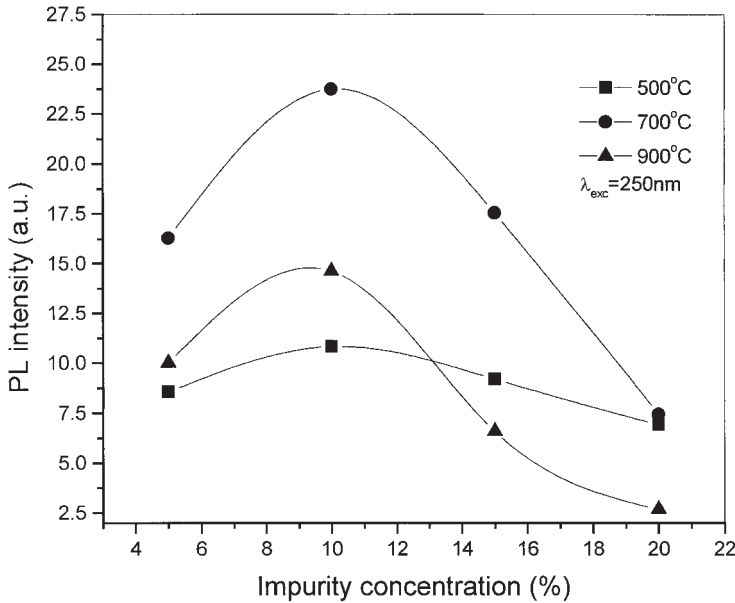


Fig. 6. Light emission (PL) for the main peak (615 nm) plotted as a function of Eu doping concentration for different annealing temperatures. The photoluminescence intensity decays for temperatures above 700 °C and for concentrations above 10 at%

Figure 6 shows the PL 615 nm peak intensity as a function of the powder doping concentration. We can observe that the optimum emission is reached at 10 at%, presenting a concentration quenching effect similar to that of CL. In contrast, the photoluminescence behavior with the annealing temperature shows an optimum at 700 °C and a quenching process for higher annealing temperatures that is not observed in CL.

It can be said about the behavior of the luminescent characteristics as a function of the doping concentration that even when the exact mechanism is still under study, the quenching effect could be associated with the interaction between the nearest Eu ions, as previously reported for other phosphors [6]. With respect to the PL emission as a function of the annealing temperature, the results listed in Table 1 suggest that the content of europium present in the powder annealed at 900 °C is less than that present in the powders annealed at lower temperatures. It is possible that a loss of europium as the annealing temperatures are increased is competing with the getting of more ordered material as suggested by the X-ray diffraction patterns shown in Fig. 1. On the other hand, the luminescence emission in the CL case does not reach a saturation quenching with the annealing temperature. This difference is not well understood at present, however it could be associated with the different nature of the excitation phenomena and penetration depth (for photons it is of the order of 0.5 microns, and about 1 micron for electrons). That is to say, while in PL one photon generates only one electron–hole pair, in the CL case, one energetic electron may generate more than one electron–hole pair, therefore the effect associated with the reduction of Eu as the annealing temperature is increased might not be as critical for CL as it is for PL [15]. Also in this case, the flux of electrons per second is estimated to be one order of magnitude higher than the flux of photons per second. Besides, a denser material obtained

at higher temperatures could enhance the energy transfer from the electrons into the powder and improve in this way the excitation process. However, there is still no clear explanation for this result and in order to get a better understanding of this process, further work is required.

4. Conclusions

Room temperature luminescent aluminum oxide powders doped with europium have been obtained by a simple and low-cost technique, namely coprecipitation, at three different annealing temperatures. The luminescent characteristics of these powders show that the Eu ion is incorporated as an atomic center into the host material. The peaks observed in CL and PL spectra are associated with interlevel transitions between electronic energy levels of Eu³⁺ ions, showing a dominant red light emission. Cathodoluminescence measurements are reported for the first time to our best knowledge. Scanning electron microscope images showed a powder morphology that is assumed to be determined by the manual milling procedure implemented in order to obtain the powders. Energy dispersive measurements showed that the powders are oxygen-rich. This could indicate a porous material which would give place to water absorption. Finally, X-ray diffraction patterns indicated that the powders are mostly amorphous, although this non-crystal state tends to be lightly reduced when the annealing temperature is raised. It seems that some degree of molecular ordering is taking place at 900 °C without reaching any crystallization of the powders.

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