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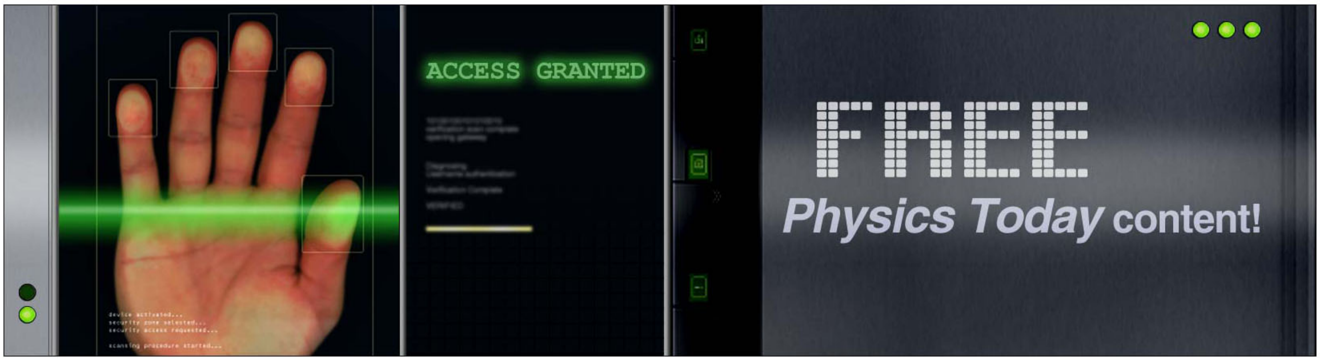

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Strong photoluminescence and cathodoluminescence due to $f-f$ transitions in Eu^{3+} doped Al_2O_3 powders prepared by direct combustion synthesis and thin films deposited by laser ablation

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In this letter, we report on fabrication and luminescent properties of phosphor powders and thin films of Eu^{3+} doped alumina Al_2O_3. The powders were fabricated by combustion synthesis process at a low temperature, 280 °C and showed strong photoluminescent and cathodoluminescent emissions. Powders of Eu^{3+} doped Al_2O_3 of concentration 1.0 mol % were deposited on quartz-glass substrates to form thin films by means of laser ablation. Under ultraviolet excitation and electron beam excitation, these samples containing microcrystalline structures showed strong luminescence due to $f-f$ transitions, and the dominant transition was the hypersensitive $^5D_0 \rightarrow {}^7F_2$ red emission of Eu^{3+}. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1592636]

Luminescence of rare-earth ions in different host matrices has been of great interest for researchers from both the scientific and technological communities. Much of this interest stems from the unique physical and chemical properties of the lanthanide oxides that make the materials useful in a variety of diverse applications, such as, laser materials, optical amplifiers, phosphors, and photocatalysts.[1–4]

Of the many rare-earth ions, Eu^{3+} ions have attracted significant attention because they have tremendous potential for applications in some optical fields, such as phosphors, electroluminescent devices, and optical amplifiers or lasers.[4–6] In addition, the luminescence of Eu^{3+} ions is particularly interesting because the emission corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition, centered near 612 nm, is one of the three fundamental colors (red, blue, and green).

Among the materials investigated to date, a few experiments have been performed on rare-earth ion doped aluminum oxide (Al_2O_3).[6–12] The Al_2O_3 crystal is a material with a significant technological importance because of the large optical transparency from ultraviolet to near-infrared, and because of its excellent mechanical properties and good chemical stability. Several structural modifications of Al_2O_3 are known and it seems α-Al_2O_3 is the only stable phase. These rare-earth doped Al_2O_3 materials have only been synthesized by techniques of sol-gel, ion beam implantation, and sonochemical preparation.[6–11]

In the present communication, we shall present a simple, low cost and yet highly effective method to prepare the rare-earth ion Eu^{3+} doped aluminum oxide (Al_2O_3). We used the technique of direct combustion synthesis to produce Eu^{3+} doped Al_2O_3 powders of various concentrations. By means of laser ablation, the powders were deposited on a quartz-glass substrate to form a thin film of a few hundreds nanometers in thickness. The material in both solid and powder forms has demonstrated strong photoluminescent and cathodoluminescent properties, which can be attributed to the $f-f$ transitions of Eu^{3+}.

The combustion synthesis method is an excellent technique for preparing micro/nanocrystalline materials due to its low cost, high yield, and good ability to achieve high purity in making single or multiphase complex oxide powders at the as-synthesized state.[13] Since the mixing of the reagents occurs at the molecular level and in solution, a high homogeneity and purity of the powders can be obtained because precursor impurities vaporize during the combustion. In the current project, the combustion synthesis process allows Eu^{3+} to incorporate into the Al_2O_3 lattice despite of the large size difference between Eu^{3+} (1.07 Å) and the Al^{3+} (0.54 Å).

Al_2O_3 powders doped with Eu^{3+} (1.0 mol %) were fabricated in the combustion synthesis process where europium nitrate $[Eu(NO_3)_3 \cdot 6H_2O]$, aluminum nitrate $[Al(NO_3)_3 \cdot 9H_2O]$ and hydrazine $(N_2H_4 \cdot H_2O)$ were used as a reductive noncarbonaceous fuel that prevents carbon contamination. The reaction is exothermic and occurred at ~280 °C (self-ignition temperature). The raw material was commercially available. The nitrates were first dissolved in de-ionized water and then the hydrazine was added in the solution. The solution was stirred for 20 min at room temperature. The resulting homogeneous solution was finally introduced into the reactor. The reactor was then tightly closed and a flux of 80 sccm of argon was established in order to create an inert atmosphere inside the reactor. The reaction was carried out at atmospheric pressure. Further details of this apparatus and procedures can be found elsewhere.[13] Through the synthesis process, the temperature as low as 280 °C was required to initiate the reaction. In the fabricated powders, europium ions are incorporated as the trivalent state.

Once the powders were prepared, we used the laser ablation to form thin films. Laser ablation targets were fabricated from powders of Al_2O_3 doped with Eu^{3+} (1.0 mol %). In order to obtain dense target, the Eu^{3+} doped Al_2O_3 pellet was sintered at 1200 °C for 6 h. We selected quartz glass for the substrate. The substrates were flat and previously degreased and cleaned by a standard cleaning process based on de-ionized water and hydrogen-peroxide solution. Laser ablation was performed by KrF-excimer laser radiation (248

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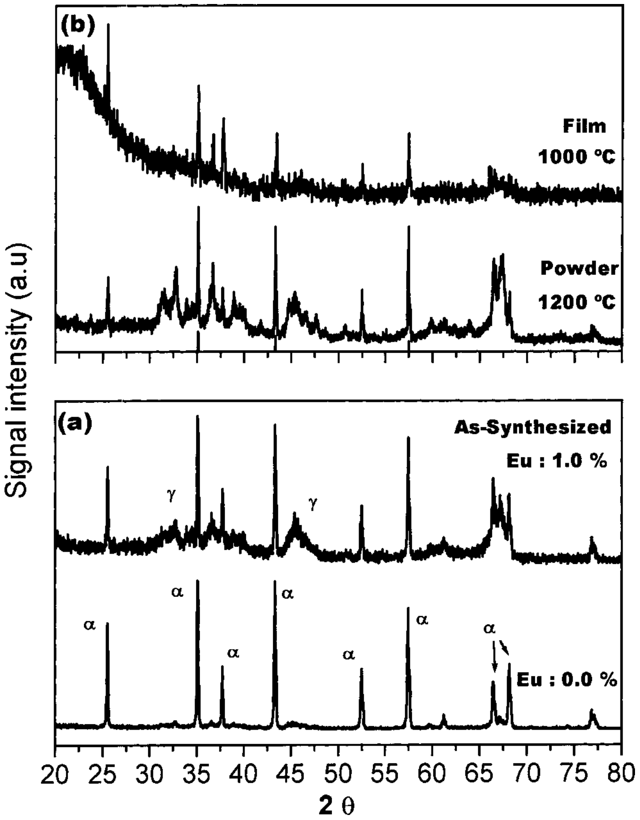

FIG. 1. XRD spectra of Eu^{3+} doped Al_2O_3: (a) as-synthesized powders doped with 0.0 and 1.0 mol % of Eu^{3+} obtained through combustion synthesis and (b) Eu^{3+} doped powders (1.0 mol %) heat treated at 1200 °C and Eu^{3+} doped Al_2O_3 thin film heat treated at 1000 °C.

nm wavelength, 25 ns pulse duration, repetition rate 10 Hz, 200 mJ pulse energy) by focusing the beam so that a fluence of 2 J/cm^2 can be located at the target. In order to obtain a homogenous ablation, the targets were rotated and the laser focus was moved across the target. The substrate-to-target distance was 2.0 cm. The sample was deposited using the pressure in the vacuum chamber 10^{-5} mbar. For a deposition time of 2 h, the film thickness was between 650 and 700 nm. After deposition, the films were annealed for 2 h at 1000 °C.

Before the luminescence measurements, the samples in the form of powders and thin films were examined with x-ray diffraction (XRD) for their structure and scanning electron microscopy (SEM) for surface topography.

The XRD patterns of the as-synthesized powders doped at 0.0, and 1.0 mol % of Eu^{3+}, obtained through combustion synthesis, are shown in Fig. 1(a). For this Eu^{3+} concentration, the diffraction patterns exhibit reflections characteristics of the α-Al_2O_3 and γ-Al_2O_3 lattice. It is evident from this figure that the presence of Eu ions inhibits the formation of the pure α phase in the as-synthesized state. Figure 1(b) shows an XRD pattern of the phosphor powder that was heated for 2 h in air at 1200 °C and an XRD pattern of the aluminum film that was heated at 1000 °C for 2 h. It is observed that for thermal treatment in the range of 1200 °C, the morphology of the powders does not change. In this case, Eu prevents the complete formation of the α-Al_2O_3 phase at this temperature because for undoped Al_2O_3 this phase transition commonly occurs below 1200 °C.[8] The positions of reflections for Eu^{3+} doped Al_2O_3 film are similar to those of powders, which indicates that the sample shows the α-Al_2O_3 and γ-Al_2O_3 lattice in its content.

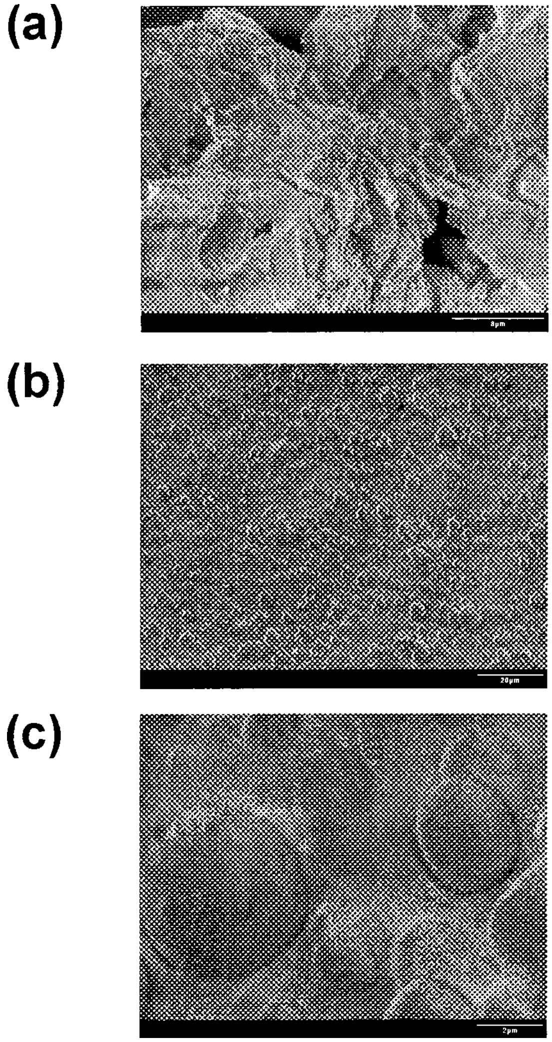

FIG. 2. Scanning electron micrograph of Eu^{3+} doped Al_2O_3 (a) precursor film and (b)–(c) Eu^{3+} doped Al_2O_3 thin film.

The SEM images of Eu^{3+} doped Al_2O_3 precursor film and of Eu^{3+} doped Al_2O_3 thin film were taken to provide detailed information about the surface morphology and the homogeneity of the deposited film. Figure 2(a) shows the SEM images of Eu^{3+} doped Al_2O_3 powders annealed at 1200 °C for 2 h. It is interesting to note the irregular shape of agglomerated particles in the photograph of these powders. Figures 2(b)–2(c) show the SEM images of the film. It can be seen from the images that the film is uniformly composed of very small particles with regular shapes.

The luminescence properties were investigated by measuring the photoluminescence (PL) spectra of as-synthesized and annealed powders and thin film samples. The PL spectra were recorded using a monochromator (Spex/Triax-180) and detected by a charge coupled device (CCD) camera. The light from a 450 W xenon lamp through the monochromator (Spex/Triax-180) was used for the optical excitation. The excitation spectra were measured by monitoring the peak intensity at 614 nm. The excitation and emission spectra of Eu^{3+} doped Al_2O_3 as-synthesized powders are shown in Fig. 3. The excitation spectrum, performed at room temperature,

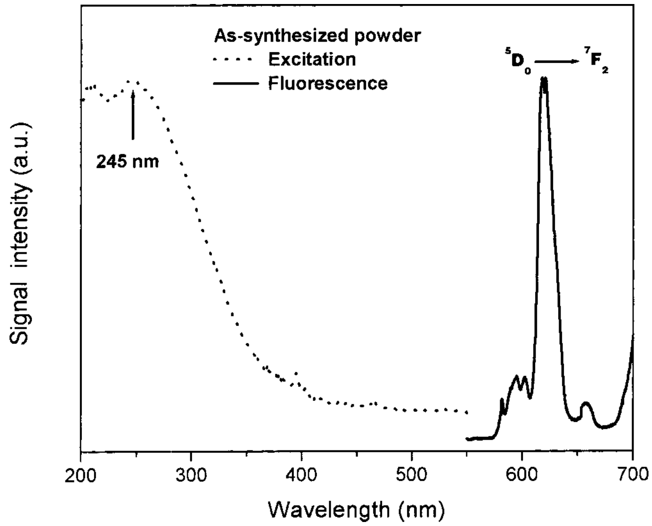

FIG. 3. PL excitation and emission spectra of as-synthesized powder samples of Eu^{3+} doped Al_2O_3 (1.0 mol %) measured at room temperature.

is observed in the UV region with a maximum at 245 nm. The strong peak emission was assigned to the transition $^5D_0 \rightarrow {^7F_2}$ of Eu^{3+}. The as-synthesized powders were excited at a wavelength of 245 nm. The PL emission lines of Eu^{3+} doped Al_2O_3 powders annealed at 1200 °C for 2 h and excited at a wavelength of 245 nm are shown in Fig. 4(a). The spectrum consists of a series of well resolved features at 593, 614, and 693 nm, which can be assigned to $^5D_0 \rightarrow {^7F_J}$, $J=1$, 2, 4, transitions, respectively. These emission lines represent actually the local environment of the Eu^{3+} ion. Among the $^5D_0 \rightarrow {^7F_J}$ transitions, the selection rule makes the $^5D_0 \rightarrow {^7F_1}$ and $^5D_0 \rightarrow {^7F_2}$ transitions of particular interest. The $^5D_0 \rightarrow {^7F_1}$ band at 598 nm is a magnetic dipole one and hardly varies with the crystal field strength around the Eu^{3+} ion. On the other hand, the hypersensitive transition $^5D_0 \rightarrow {^7F_2}$ at 614 nm is electric dipole allowed. Consequently, it depends on the local electric field and, hence, the local symmetry. Based on the earlier considerations it is clear that the $(^5D_0 \rightarrow {^7F_2})/(^5D_0 \rightarrow {^7F_1})$ intensity ratio, known also as the asymmetry ratio, gives a measure of the degree of distortion from the inversion symmetry of the local environment of the Eu^{3+} ion in the lattice. The asymmetry ratio of Eu^{3+} doped Al_2O_3 sample heat treated at 1200 °C is calculated and has a value of 4. A large value of the asymmetry ratio obtained for these samples is an indicative of strong electric fields of low symmetry at the Eu^{3+} ions. This result suggests that Eu^{3+} ions occupy low symmetry sites as theoretically inferred by Verdozzi *et al.*[12]

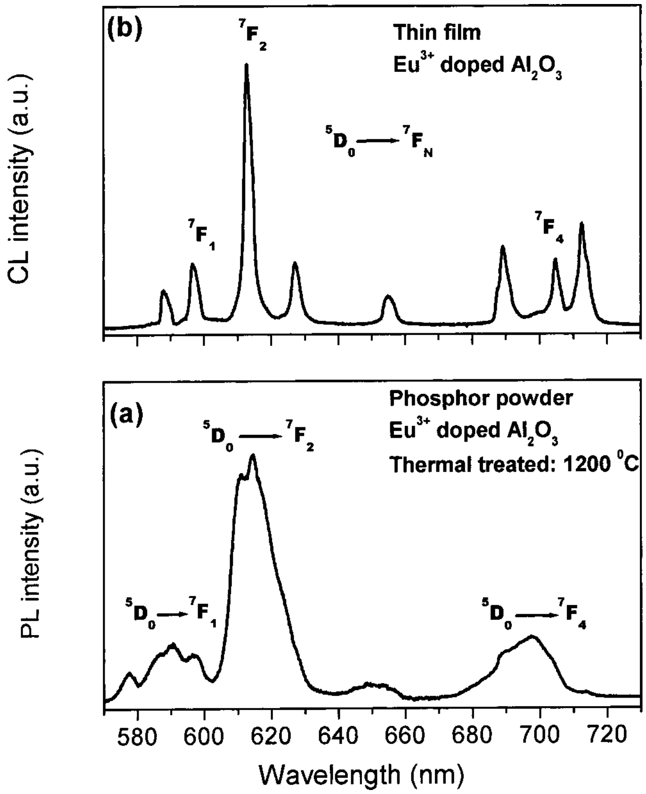

FIG. 4. PL and CL spectra, measured at room temperature, of (a) Eu^{3+} doped Al_2O_3 powders heated in air at 1200 °C for 2 h and (b) Eu^{3+} doped Al_2O_3 film heated in air at 1000 °C for 2 h. The excitation wavelength is 245 nm.

The cathodoluminescence (CL) emission spectra of the three samples were collected using a monochromator (Spex/Triax-180) through an optical fiber and detected by a CCD camera. Figure 4(b) shows the CL spectra, excited with a 5 keV electron, of Eu^{3+} doped Al_2O_3 thin film (1 mol %) prepared through ablation laser and annealed at 1000 °C for 2 h. The largest peak of emission, the red emission line around 614 nm, is assigned to the hypersensitive $^5D_0 \rightarrow {^7F_2}$ transition working using a forced electric dipole transition mechanism. This is a parity forbidden $f-f$ intraconfigurational transition. All samples presented an asymmetry ratio of 4, which indicates that the Eu^{3+} ions occupy a site with no inversion symmetry. Lack of inversion symmetry at the cationic site is quite favorable for observing the electric dipole transition as a forced transition due to the admixture of the odd parity states.

In summary, we have presented a simple and effective process to produce Eu^{3+} doped Al_2O_3 powders and thin films. The material may have strong fluorescence emission under light and electron excitation, and the emissions are due to the $f-f$ transitions, especially the $^5D_0 \rightarrow {^7F_2}$.

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