

## Synthesis and Luminescence Characterization of Eu Activated Al<sub>2</sub>O<sub>3</sub> Phosphor

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*Synthesis and luminescence (photoluminescence, thermoluminescence and mechanoluminescence) characterization of Eu activated Al<sub>2</sub>O<sub>3</sub> phosphors prepared by combustion technique are reported in this paper. X-ray diffraction (XRD) patterns of the samples were recorded to confirm the formation of the sample. The photoluminescence (PL), thermoluminescence (TL) and mechanoluminescence (ML) properties of the  $\gamma$ -ray irradiated samples were studied. ML was excited impulsively by dropping a piston on the sample. In the PL emission, the sample having 0.25 mol% concentration of dopant shows emissions around 593 and 618 nm due to transition of Eu<sup>3+</sup> ion. In the TL glow curve two peaks one around 180°C and another 280°C were observed for the samples having 0.05 mol% and 0.25mol% of dopant concentration. However, the sample having 0.1mol% of dopant concentration showed a band. In ML glow curves two peaks were observed. ML intensity varied with dopant concentration. Optimum ML was observed for the sample having 0.1mol% of Eu. ML intensity increased with increasing impact velocity of the piston. It is suggested that recombination of the trapped charge carriers are responsible for ML and TL in this system.*

**Keywords:** phosphors, mechanoluminescence, thermoluminescence, photoluminescence, X-ray diffraction

### 1.1 Introduction

Recently much attention has been paid to the development of advanced rare earth (RE) activated phosphor materials because they are widely used in a variety of application such as flat panel displays Hg free lamps and X-ray imaging systems [1]. Mechanoluminescence (ML) is the phenomenon of light emission induced by a mechanical stress such as compression, torsion or friction of solids [2]. The use of ML paint enabled to accurately detect the crack tip even on a micro-scale not by detecting the crack opening displacement but by identifying the light emission that accompanies the crack tip stress field. The ML technique is much simpler, cheaper and more suited to the detection of fast crack than the conventional techniques such as Laser photo-elasticity, Laser ultrasound, Raman spectroscopy, electrical resistance techniques etc. which involves complicated instrumentation [3].

It is known that host materials and intentionally added impurity play an important role in luminescence process, usually fluorides are attractive host materials at the efficiency of up-conversion is quite high due to their low phonon energies[4]. Compared to fluorides, oxides have attractive properties such as high chemical stability and ease of synthesis [5]. It is also well known

that the quality of luminescent material is largely influenced by the synthesis technique. In recent years the combustion method has displayed unique advantages of lower synthesis temperature, such as shorter synthesis time and controlled size of the particles [6].

Aluminum oxide is a material of technological importance, because it offers a large transparent window for UV to near infrared, low permeability to alkali impurity, excellent mechanical properties and good chemical stability therefore, it is a good candidate to be used as a host material of the rare earth ions [7]. Aluminum oxide has a number of advantages as a thermoluminescence phosphor. It is abundantly available, chemically very inert and being a ceramic material, high temperature stable glow peaks can be expected which may find application in surveying radiation levels in heated environments [8].

In literature there are reports available for the photoluminescence (PL) properties of rare earth ions doped in  $\text{Al}_2\text{O}_3$  host matrix. Rakov et al [9] studied PL properties of  $\text{Eu}^{3+}$  doped  $\text{Al}_2\text{O}_3$  phosphors. Rai et al [10] studied the photoluminescence (PL), thermoluminescence (TL) and Mechanoluminescence (ML) properties of  $\text{Al}_2\text{O}_3:\text{Tb}^{3+}$  phosphor. Rani et al [11] studied the structural and optical properties of  $\text{Cr}^{3+}$  doped  $\text{Al}_2\text{O}_3$  nanoparticles. S. Kumar et al [12] studied the photoluminescence (PL) and optical properties of  $\text{Dy}^{3+}$  doped  $\alpha\text{-Al}_2\text{O}_3$  phosphor. The survey of literature show that no systematic investigations have been made on the luminescence (specially ML) of  $\gamma$ -ray-irradiated  $\text{Al}_2\text{O}_3:\text{Eu}$  phosphors. Hence in present investigation  $\text{Al}_2\text{O}_3:\text{Eu}$  phosphors were prepared by low temperature solution combustion synthesis (SCS) ( $\sim 500^\circ\text{C}$ ) and its photoluminescence (PL), thermoluminescence (TL) and mechanoluminescence (ML) properties were studied.

## 1.2 Materials and Methods

All the phosphor samples were prepared by the combustion technique as reported by Mackittrick [13] using hydrazine as a fuel. The starting materials taken were  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  compounds of ultra high purity (99.9%). All of them acquired from Alfa Aesar Lancaster, USA. Hydrazine was used as a reductive non-carbonaceous fuel that prevents carbon contamination. The sintering process is not required for this method. The reducing atmosphere created during combustion is enough to change the ionization state of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  ion [14]. A flow chart for the preparation of Eu doped  $\text{Al}_2\text{O}_3$  phosphor was described in figure 1. The crystalline structure and particle morphology of the resulting samples were investigated by X-ray diffraction analysis (XRD model D8 Advance Bruker AXS) using Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Data have been collected by step scanning  $2\theta$  from  $20^\circ$  to  $70^\circ$  and 9.6 sec swept time at each step at room temperature. In order to study the surface morphology of phosphor prepared by combustion synthesis, scanning electron microscope (model LEO 0435VP) has been carried out. Above Characterization were performed at Institute Instrumentation Centre, IIT Roorkee, Utranchal, India. PL was recorded using fluorescence spectrophotometer (Shimadzu RF-5301 XPC) and emission was recorded using a spectral slit width of 1.5 nm. Gamma irradiation was carried out using a  $^{60}\text{Co}$  source having exposure rate 0.930kGy/h. The TL was recorded using TL reader (Nucleonix TL 1009I). The ML was monitored by using a photomultiplier tube (RCA-931A) connected to digital storage oscilloscope (Scientific SM-340). ML was excited by dropping a piston (mass-0.7 kg) on to the sample from different heights. The impact velocity of the piston was calculated using formula  $v = \sqrt{2gh}$ .

## 1.3 Results and Discussion

Figure 2 shows the XRD pattern of  $\text{Al}_2\text{O}_3:\text{Eu}$  phosphor. The small amount of doped rare earth ions has virtually no effect on phase structures. The observed pattern was found to match with standard JCPDs [15] data of the compound  $\text{Al}_2\text{O}_3$  (JCPDs file no. 00-01-1243).

Figure 3 shows the surface morphologies of the powder sample. The microstructure of the sample reflects the inherent nature of the combustion process. The non uniform and irregular shapes of the particles as shown can be attributed to the non-uniform distribution of temperature and mass flow in the combustion flame.

Figure 4 shows the PL excitation (wavelength 345 nm) and emission spectrum of the  $\text{Al}_2\text{O}_3:\text{Eu}$  phosphors. In the PL emission curve of the samples having 0.05 mol% Eu, a peak around 424 nm is observed due to splinting of  $\text{Eu}^{2+}$  ions. In the PL emission spectrum of the sample having 0.1 mol% of Eu, an intense emission of  $\text{Eu}^{2+}$  ion around 448 nm in the blue region of the spectrum is observed. Sample having 0.25 mol% concentration of dopant shows emissions around 593 and 618 nm due to transition of  $\text{Eu}^{3+}$  ion. Unlike other rare earth impurity Eu exists in lattice as  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ionic states. The emissions from 360-440 nm in Eu doped phosphors are due to  $4f^65d \rightarrow 4f^7$  transition of  $\text{Eu}^{2+}$  ions [16]. The emission around 590 nm and 615 nm in Eu doped phosphors are due to  $^5D_0 \rightarrow ^7F_1$  and  $^5D_0 \rightarrow ^7F_2$  transition of  $\text{Eu}^{3+}$  ions [17]. The emission of  $\text{Eu}^{2+}$  is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electromagnetic spectrum. This is because the  $5d \leftrightarrow 4f$  transition is associated with the change in electric dipole and the 5d excited state is affected by crystal field effects [18].

Figure 5 shows TL glow curves of  $\text{Al}_2\text{O}_3$  phosphors. Two distinct peaks were observed in TL glow curve of samples having low concentration of dopant (0.05 mol %), due to two types luminescence centre are form. It is also observed that the TL intensity of both the peaks increase with concentration, shift and merged for 0.1 mol% of Eu. With the increasing concentration of Eu ions only one TL peak is observed due to low energy traps are shifted at higher energy level due to the pair formation of impurity at higher level concentration of impurity i.e. 0.1 mol% of Eu.

The TL glow curves of  $\text{Al}_2\text{O}_3:\text{Eu}$  phosphors are interesting. Initially for low concentration of dopant (i.e. 0.05 mol % of Eu), two peaks are observed at  $192.3^\circ\text{C}$  and  $266.6^\circ\text{C}$ . Both the TL peaks shifts and increase with concentration and merged for the sample having 0.1 mol % of Eu. On further increase in concentration of dopant, the broader peak again splits in to two distinct TL peaks, this splinting of TL peaks due to the symmetry of impurity is changes in the host lattice at again higher concentration.

Figure 6 shows time dependence of ML intensity of gamma irradiated  $\text{Al}_2\text{O}_3:\text{Eu}$  phosphors. Two distinct peaks are observed and the ML intensity increases with dopant concentration of Eu ions, attains an optimum value for a 0.1 mol % of  $\text{Eu}^{2+}$  then decreases with further increase in concentration of dopant. ML is defect related phenomenon, associated with a trap involved process, in which electrons (or holes) well in the trap for some time and then recombine with the luminescence center either by travelling in the conduction band (or valence band) or by electron (or holes) tunneling. As for ML materials, in particular, the recombination process is facilitated by the assistance of dislocation in the crystal [19]. In present investigation the probability of dislocation is very low because of the particle size of the crystal; probably, piezo-electrification during the impact is responsible for the de-trapping of the trapped charge carriers [20]. The occurrence of the second peak which occurs in the post deformation region may be due to the captures of carriers by the shallow traps lying away from the newly created surfaces where the electric field near the surface is not so effective [21].

Figure 7 shows the ML intensity when load of mass 0.7 kg was dropped from different heights on the sample. ML intensity increases with increase in height. More traps are released due to the load applied from more height on the phosphors; these traps are recombined with the luminescence centers and emit light.

Figure 8 shows the gamma dose dependence on TL intensity (area below curve) Fig. 8 shows the dependence of total TL intensity (area below curve) of  $\text{Al}_2\text{O}_3:\text{Eu}$  phosphors on  $\gamma$  - dose given to the sample. TL intensity increases linearly in the dose range 0.465-1.86 kGy. With increasing gamma doses given to the sample, number of hole trap centers increases and hence TL intensity increases with gamma dose. Since the number of hole trapping centers are limited in the sample, TL intensity seems to be saturated for higher gamma doses.

## 1.4 Conclusion

The polycrystalline  $\text{Al}_2\text{O}_3:\text{Eu}$  (0.05, 0.1, 0.25 mol %) phosphors were successfully synthesize by combustion technique at an initiating temperature of  $300^\circ\text{C}$  and its luminescence properties were investigated. This new synthesis condition allows rare earth ions to incorporate easily into the  $\text{Al}_2\text{O}_3$  lattice; in spite of large size difference between rare earth ions and the aluminum cations in the  $\text{Al}_2\text{O}_3$

structures. The luminescence (ML, PL and TL) efficiency is optimum for 0.1 mol % of  $\text{Eu}^{2+}$  ions. Gamma dose dependence of TL was studied. It was found that TL intensity increases linearly in the range 0.465-1.86 kGy. The enhancement of TL intensity with  $\gamma$  - irradiation suggest that the  $\text{Al}_2\text{O}_3:\text{Eu}$  is a suitable candidate for TL dosimetry.

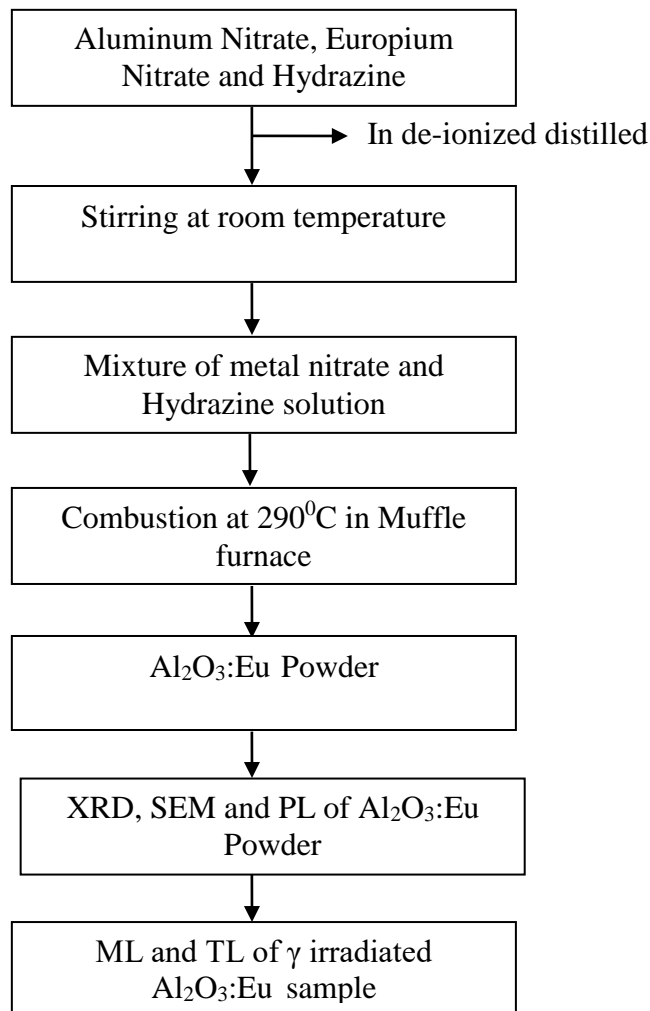
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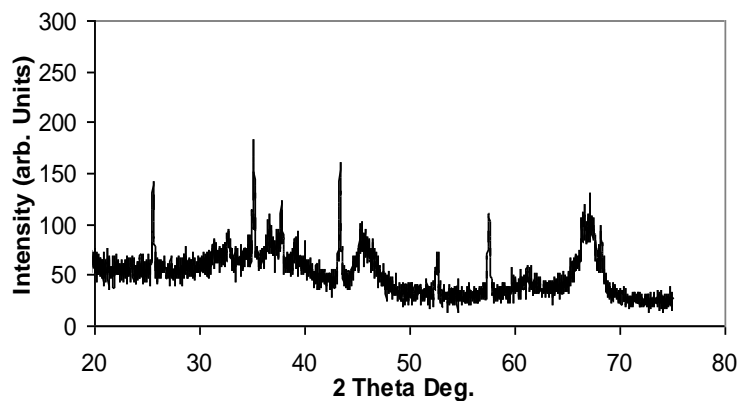
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### FIGURES WITH FIGURE CAPTIONS



**Fig.1 Flow chart of preparation and characterization of Al<sub>2</sub>O<sub>3</sub>:Eu phosphors**



**Fig. 2 XRD pattern of Al<sub>2</sub>O<sub>3</sub> : Eu (0.1 mol %) phosphors**

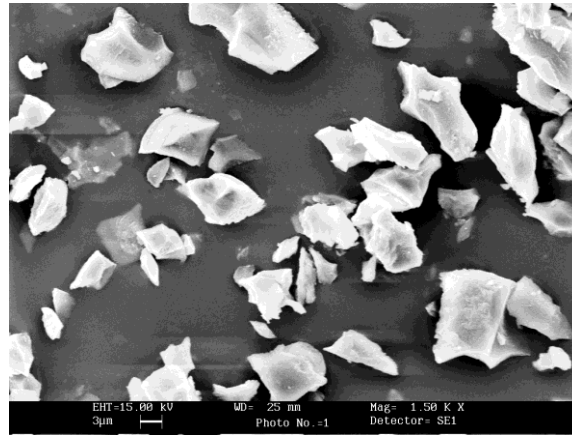


Fig.3 SEM photograph of Al<sub>2</sub>O<sub>3</sub>:Eu (0.1mol %) phosphors

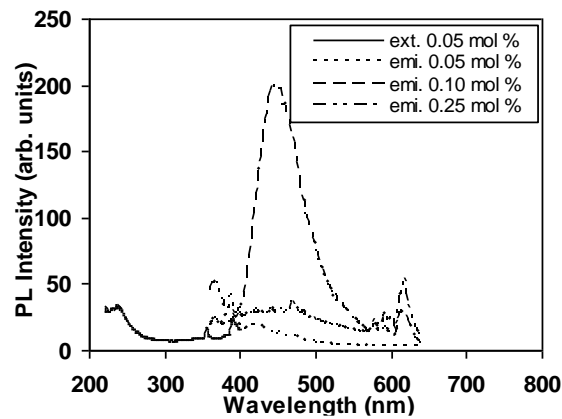


Fig. 4 (a) Excitation and (b) emission PL Spectra of Al<sub>2</sub>O<sub>3</sub>: Eu phosphors having different concentration of Eu

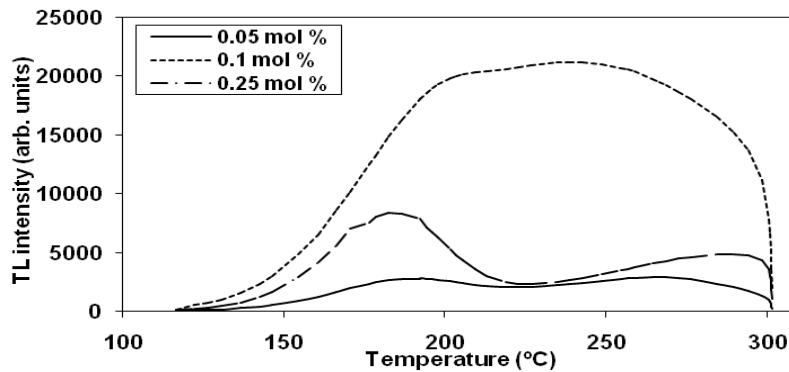


Fig.5 TL glow curve of Al<sub>2</sub>O<sub>3</sub>: Eu phosphors

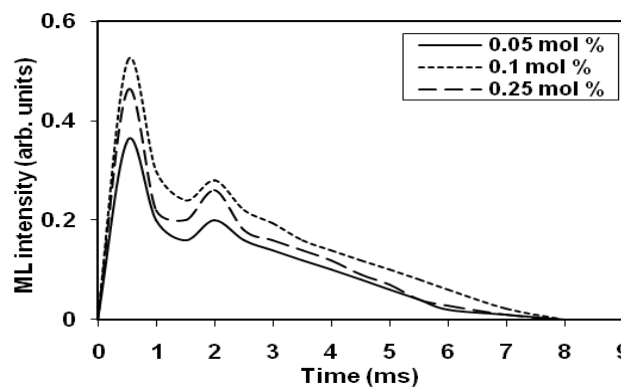
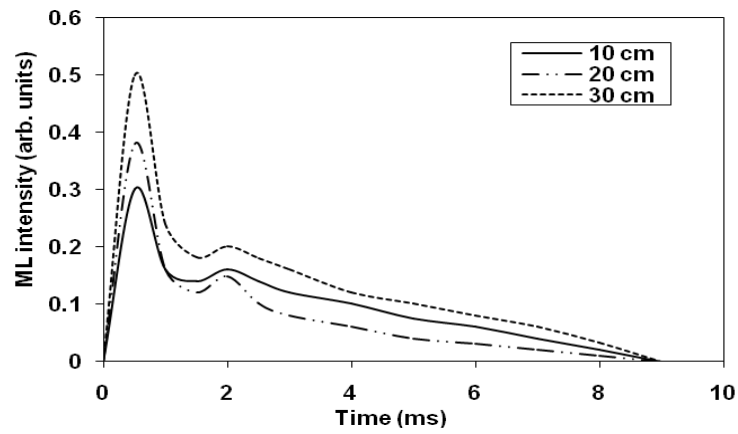
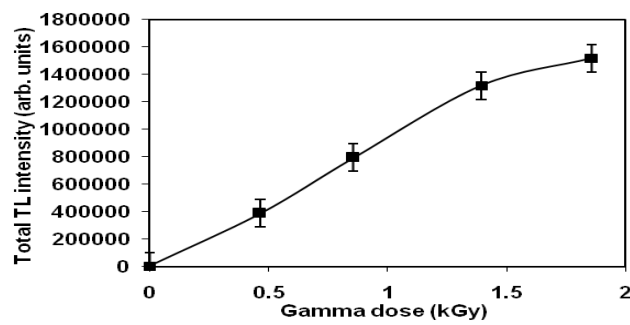


Fig.6 Time dependence on ML intensity of  $\gamma$  irradiated Al<sub>2</sub>O<sub>3</sub>: Eu (0.1mol %) phosphor





**Fig. 7** Height dependence on ML intensity of  $\gamma$  irradiated (0.934 kGy, 0.7 kg)  $\text{Al}_2\text{O}_3:\text{Eu}$  (0.1mol %)



**Fig. 8** Effect of  $\gamma$  dose on TL Intensity of  $\text{Al}_2\text{O}_3:\text{Eu}$  (0.1mol %) phosphor