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## **Hydrazine Assisted Self Combustion Synthesis of CaAl<sub>2</sub>O<sub>4</sub>:Eu Phosphor And Its Mechanoluminescence Characterization.**

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### **Abstract**

Europium doped monoclinic CaAl<sub>2</sub>O<sub>4</sub> phosphors were obtained at low temperatures (500°C) by the process of combustion of corresponding metal nitrate–hydrazine mixtures, over a time of 5 min. The product was investigated by X-ray powder diffraction. Mechanoluminescence (ML) emission spectra were taken to investigate the luminescence centres. Two ML spectra were observed at around 455nm and 606nm. The ML intensity initially increased with time attained an optimum value for a particular time then decreased and finally disappeared. It is found that ML intensity of the phosphor depends on temperature and also the phosphor strongly depends on gamma ray dose given to it. The fading of the phosphor is quite low therefore it may be advantageously used for high temperature dosimetry applications.

**Keywords:** CaAl<sub>2</sub>O<sub>4</sub>: Eu; combustion synthesis (SHS); Mechanoluminescence.

### **1.Introduction**

Phosphorescent phosphors have great potential in several applications for devices and luminous paints and have been widely studied.

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Eu<sup>2+</sup> doped alkaline earth aluminates, MA<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup> (M= Ba,Ca,Sr,) phosphors with a strong photoluminescence in the blue-green visible range have been studied by many researchers [1, 2]. Eu<sup>2+</sup> activated phosphors MA<sub>2</sub>O<sub>4</sub> and MA<sub>12</sub>O<sub>19</sub> (M = Sr, Ba, Ca, Mg) are well known since the studies by Blasse and Brill [3] in the 1960s. Their research led to the conclusion that these are phosphorescent materials with high quantum efficiency in the visible region. Recently, Aitasalo et al. have reported the sol-gel preparation, structure and luminescence of Eu<sup>2+</sup> doped CaAl<sub>2</sub>O<sub>4</sub> materials. They have observed the broad band UV excited luminescence of Eu<sup>2+</sup> ions in hexagonal CaAl<sub>2</sub>O<sub>4</sub>: Eu at the blue region ( $k_{max} = 448$  nm) due to transitions from the 4f<sup>6</sup>5d<sup>1</sup> to the 4f<sup>7</sup> configuration of the Eu<sup>2+</sup> ion [4]. The synthesis of metal aluminates usually involves the solid-state reaction of the corresponding metal carbonate with Al<sub>2</sub>O<sub>3</sub> at high temperatures and for long time [5]. These materials have important industrial applications with a long persistence luminescence.

Less attention have been paid towards the combustion method and ML study of CaAl<sub>2</sub>O<sub>4</sub>. Combustion synthesis has been emerged as an important technique for the synthesis of advanced materials because it is simple, fast, and energetically economic and yields high purity and homogeneous products.

Mechanoluminescence (ML) is the phenomenon of light emission induced by elastic deformation, plastic deformation and fracture of special class of solids. For a long time the interest in ML has been academic in nature, with the majority of works either reporting new ML materials, detailing methods for quantitative generating and measuring ML, recording ML spectra and suggesting mechanisms underlying the deformation- and fracture-induced excitation processes [6–8].

In this article, a survey of the synthesis, characterization namely ML spectra, XRD, SEM and mechanoluminescence(ML) properties of Eu doped CaAl<sub>2</sub>O<sub>4</sub> sample is discussed.

As the metal ions of AB<sub>2</sub>O<sub>4</sub> are changed, the ionic ratios (A<sup>2+</sup>/B<sup>3+</sup>) change and the symmetry of unit cell may change. The ideal spinel crystallizes in the cubic space group *Fd3- m* with 8 tetrahedral *a* sites and 16 octahedral *d* sites. The usual anions are oxygens and are located on the 32 *e* sites arranged in cubic close packed layers. The unit cell contains eight molecules of AB<sub>2</sub>O<sub>4</sub>. In the normal spinel structure, all the divalent cations are located on tetrahedral *a* sites, while all trivalent cations are located exclusively on octahedral *d* sites.

## 2. Experiment

All the phosphor samples were prepared by the combustion technique using hydrazine as a fuel. The starting materials taken were Ca (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O, Eu(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O compounds of ultra high purity (99.9%). Hydrazine was used as a reductive non-carbonaceous fuel that prevents carbon contamination. Stoichiometric amount of all material were taken in a glass beaker and dissolved in distilled water. The beaker was kept in a furnace set at 300°C. The reaction is self-propagating and is able to sustain this high temperature long enough. The entire combustion process was over in about 5 min. This technique can produce a homogeneous product in a short amount of time without the use of an expensive high-temperature furnace.

Formations of the samples were confirmed by XRD pattern recorded by X-ray diffractometer (PW-1710). The gamma-ray-irradiation was carried out using <sup>60</sup>Co source. ML was excited impulsively by dropping a load on

the sample placed on a Lucite plate with different impact velocities. The luminescence was monitored by a 931A photomultiplier tube positioned below the Lucite plate and connected to storage oscilloscope (SM-340). All ML measurements were carried out after gamma irradiation. In order to study the surface morphology of phosphor prepared by combustion synthesis, scanning electron microscope (model Hitachi S-3400N) has been carried out. Different optical filters were used for the measurement of ML spectra.

### 3. Result and Discussion

#### 3.1 XRD Study

The below figure 1 represents the pictorial image of XRD pattern of  $\text{CaAl}_2\text{O}_4$  which is well matched with the JCPDS card No. 83-2025 of  $\text{CaAl}_2\text{O}_4$ . Other forms of calcium aluminates are not detected.

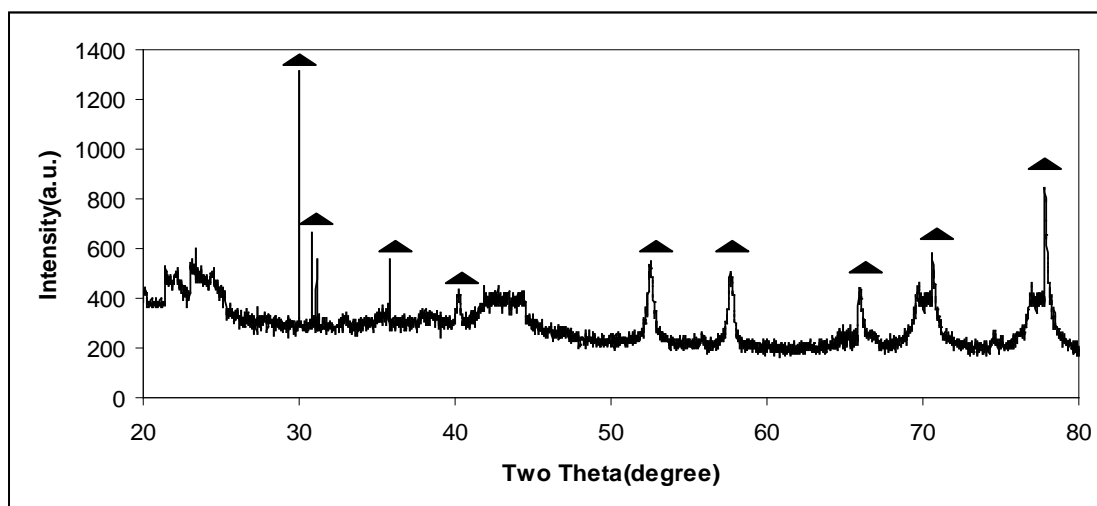


FIG.1 XRD pattern of  $\text{CaAl}_2\text{O}_4$ : Eu.

#### 3.2 SEM characterization

An SEM study was carried out to investigate the surface morphology and crystallite sizes of the synthesized phosphor powder. The synthesis was carried out at  $500^\circ\text{C}$  by a combustion reaction. This shows that the combustion reactions of the mixtures took place well. The typical morphological image represented in Fig. 2 show representative SEM micrographs taken for  $\text{CaAl}_2\text{O}_4$  phosphor materials. The surface of the powder shows a lot of voids and pores, which may be formed by the evolved gases during combustion.

#### 3.3 ML Spectra

In order to find the luminescence centres responsible for ML emission, we have recorded ML spectrum. The ML emission spectra, corresponding to excitation of Eu at 455 nm as well as 606 nm, are depicted in Fig 3. Intense and broad excitation peak of  $\text{Eu}^{2+}$  is found in the UV spectra region, and is associated with  $4f \rightarrow 5d$  electronic transitions. The emission peak observed at 455nm is due to the transition of  $\text{Eu}^{2+}$  from excited state of  $4f^6 5d^1$

configuration to the ground state  $^8S_{7/2}$  of  $4f^7$  configuration. However in the emission spectra, we also observed one peak in the 606 nm regions, attributable to  $^5d_0 \rightarrow ^7f_1$  transition of  $\text{Eu}^{3+}$  ions (Fig 3). Also Palilla et al. and Aitasalo et al. have reported the peaks at 440 nm for Eu doped monoclinic  $\text{CaAl}_2\text{O}_4$  and at 448 nm for hexagonal  $\text{CaAl}_2\text{O}_4: \text{Eu}^{2+}$  synthesized using sol-gel technique respectively [9].

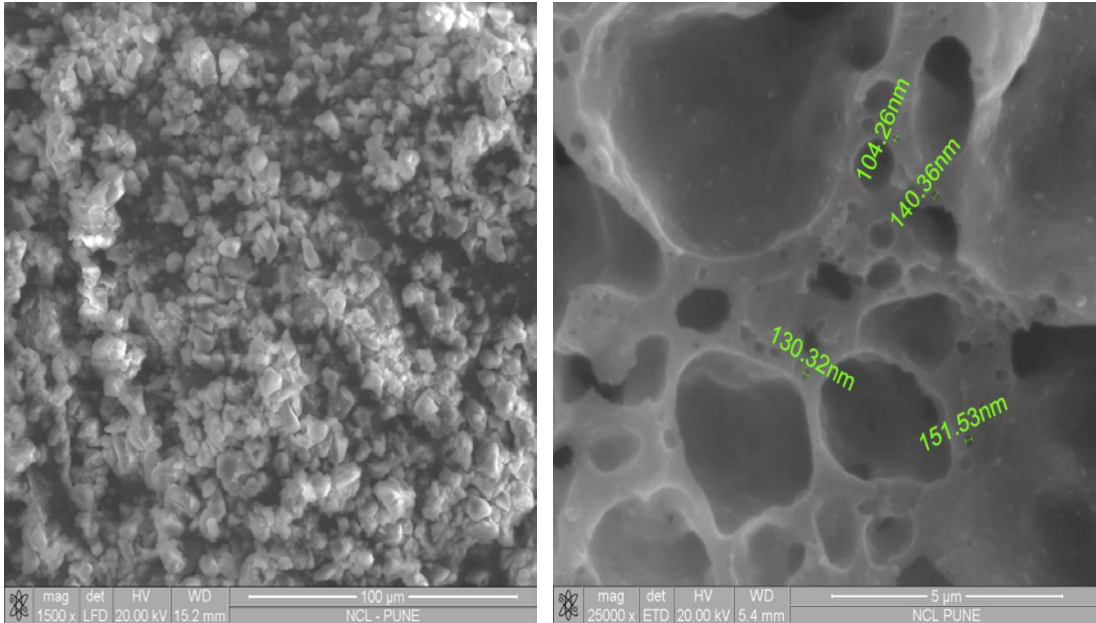
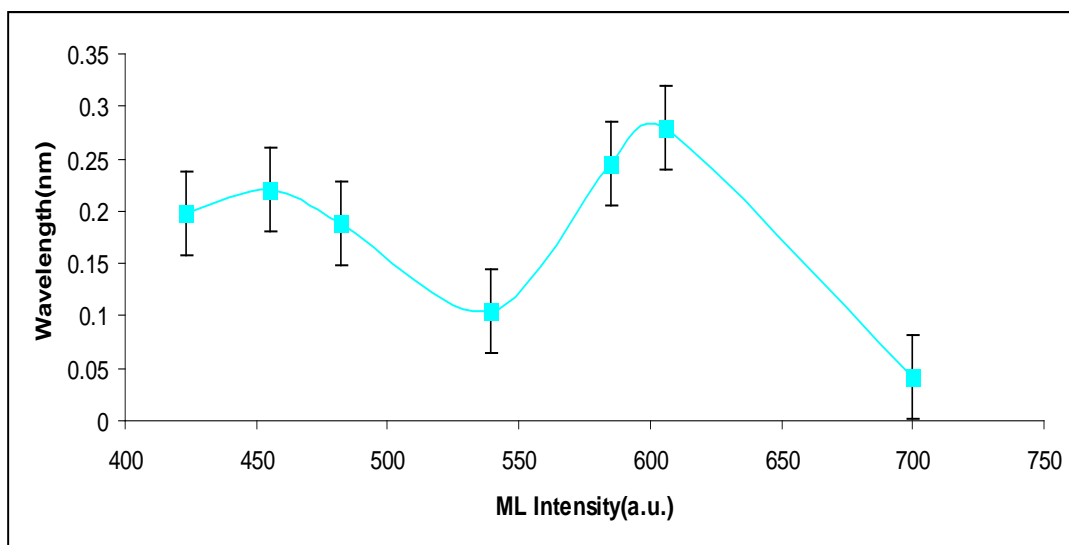


FIG 2(a)

FIG 2 (b)

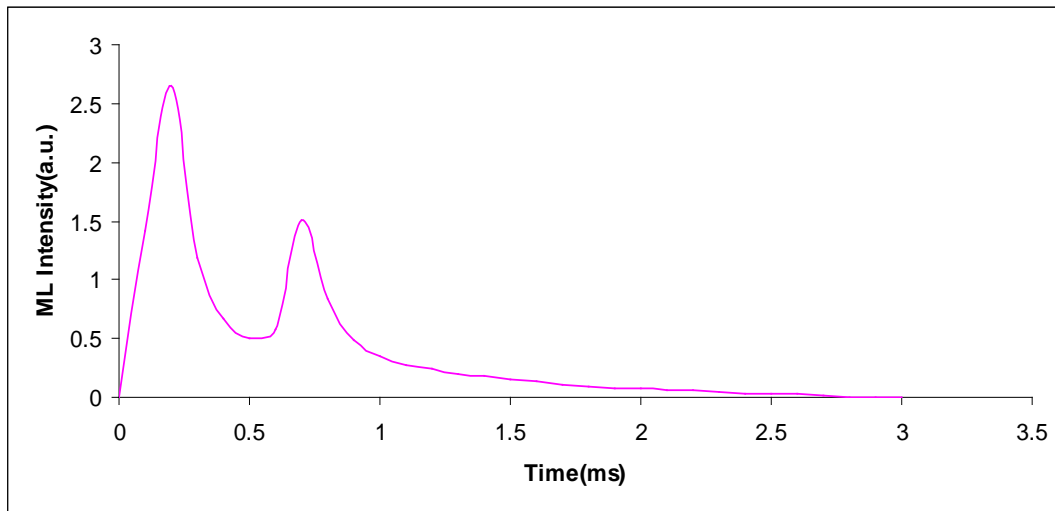
**Fig. 2(a) (b) SEM images of  $\text{CaAl}_2\text{O}_4: \text{Eu}$  phosphor.**



**Fig. 3 ML emission spectra of CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphor.**

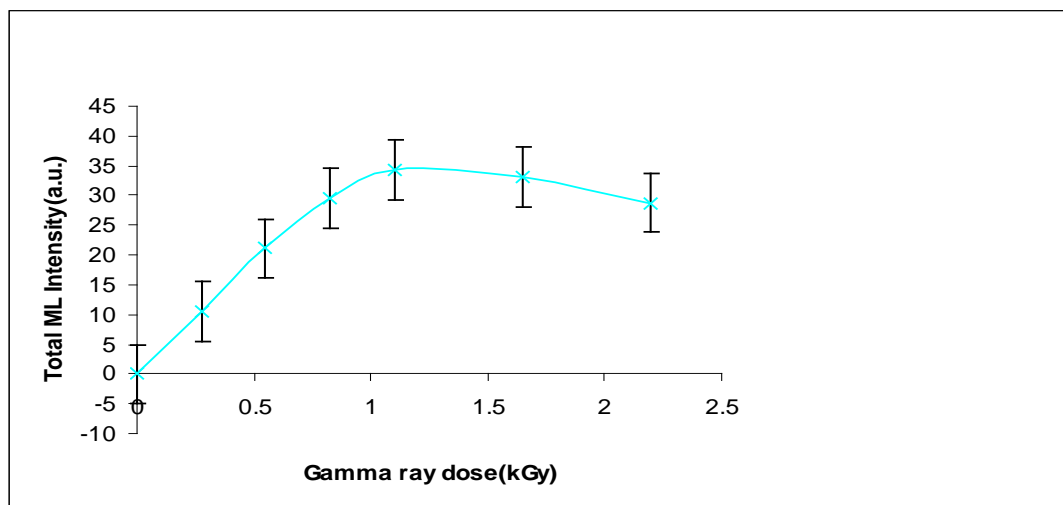
**3.4 ML Characterization**

Figure 4 shows the ML intensity versus time curve of gamma ray irradiated CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphors. Two distinct peaks were observed when ML was excited by dropping a load of mass 0.7 kg on to the sample. ML intensity increases linearly with increasing the impact velocity of the piston dropped on to the sample. ML intensity initially increased with time attained an optimum value for a particular time then decreased again increases to a value then decreases and finally disappeared for all the samples.



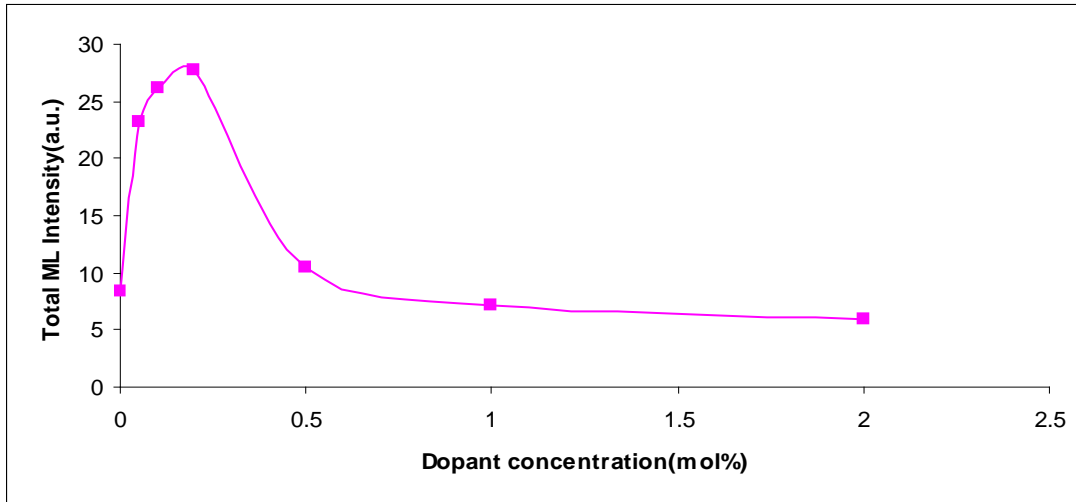
**Fig. 4 ML intensity versus time curve of gamma ray irradiated CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphor**

Figure 5 shows the dependence of ML intensity on  $\gamma$ -ray dose of CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphors. ML intensity increased almost linearly with  $\gamma$ -ray doses given to the samples.



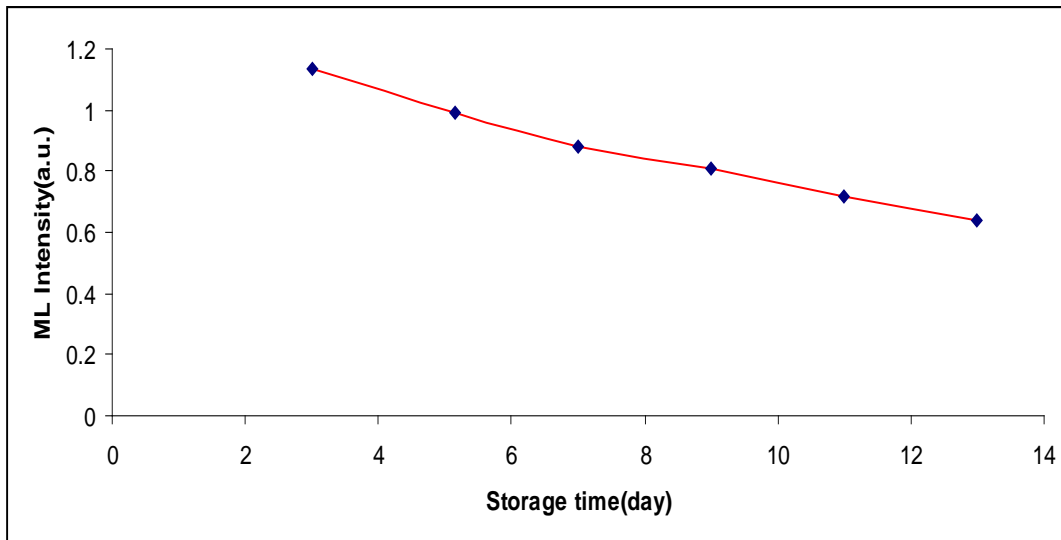
**FIG.5 Dependence of total ML intensity on gamma ray dose given to CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphor.**

Figure 6 shows the total ML intensity as a function of the dopant concentrations. It is clear that in all the samples, ML intensity initially increased with increasing the dopant concentration attained an optimum value for a particular concentration of dopant then concentration quenching occur. Optimum ML is found for 0.2 mol% dopant.



**Fig.6 Total ML intensity as a function of the dopant concentration of gamma ray irradiated CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphor.**

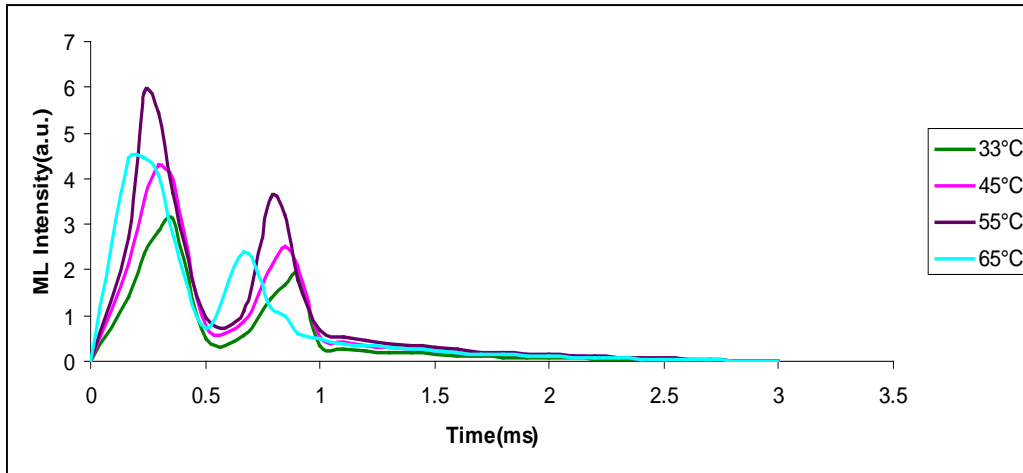
Figure 7 shows low fading of CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphor within 15 days of its irradiation with gamma ray dose. Figure shows only 25-30% fading within observed time.



**Fig.7 Fading of gamma ray irradiated CaAl<sub>2</sub>O<sub>4</sub>: Eu (0.2 mol %) phosphor**

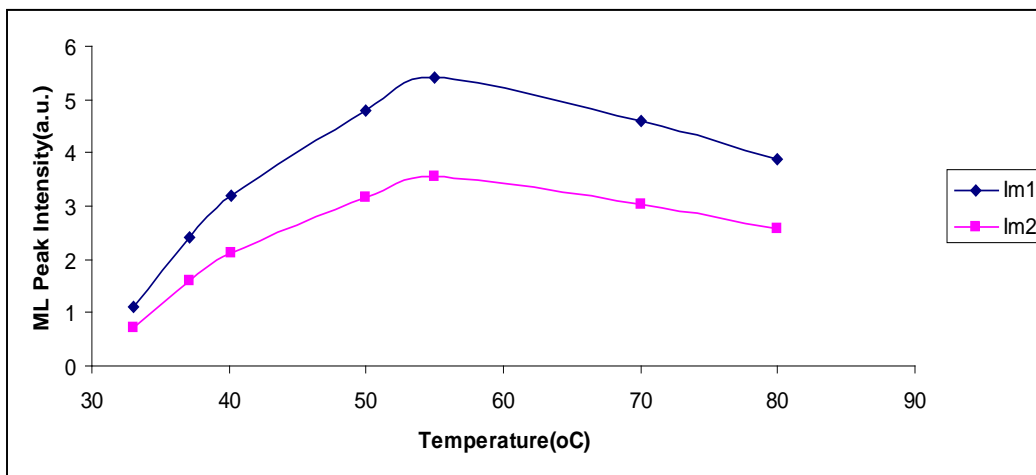
Figure 8 shows time dependence of the ML intensity of gamma ray irradiated CaAl<sub>2</sub>O<sub>4</sub> phosphor for different temperature. The ML intensity initially increase with time attain a maximum value then decreases, again

increases and then decreases and finally disappear for all the sample but with the increase of temperature of the surroundings, the ML peak intensity increases up to a certain temperature then decreases with further increase in temperature. It is also observed that the peak of ML intensity shifted towards shorter time with the increase of temperature.



**FIG.8 Time dependence of the ML intensity of gamma ray irradiated  $\text{CaAl}_2\text{O}_4$  phosphor for different temperature.**

Figure 9 shows the effect of temperature on the peak ML intensity of gamma ray irradiated  $\text{CaAl}_2\text{O}_4$  phosphor for different temperature. The Peak intensity  $I_{m1}$  and  $I_{m2}$  corresponding to first and second ML peak which initially increases with temperature attain a maximum value at  $55^\circ\text{C}$  then decreases with further increase in temperature.



**FIG.9 The effect of temperature on the peak ML intensity of gamma ray irradiated  $\text{CaAl}_2\text{O}_4$  phosphor for different temperature.**

The origin of light emission are not due to the charges on the fracturing surfaces and piezoelectricity as the particle size is very small observed in XRD and  $\text{CaAl}_2\text{O}_4$  has a centrosymmetric structure (Fd3m). Therefore it

is suggested that ML of  $\text{CaAl}_2\text{O}_4:\text{Eu}$  is strongly related to the movement of dislocations and the recombination of activated electrons and holes.

The movement of dislocations excites carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centres (Eu). In  $\text{CaAl}_2\text{O}_4$ , the most probable centres which can be observed are the V centres (a hole trapped at a cation vacancy) and F centres (an electron trapped at an anion vacancy). It is known that the cation disorder and non-stoichiometric of aluminates like  $\text{CaAl}_2\text{O}_4$  provide a large number of lattice defects, which may serve as trapping centres. The Eu ion can easily enter the lattice, in place of  $\text{Ca}^{2+}$  ion, as the ionic radius of  $\text{Eu}^{3+}$  (0.094 nm) is close to the ionic radius of  $\text{Ca}^{2+}$  ion (0.094 nm). Since ML glow curve shows the characteristic emission of Eu. This energy may be transferred non-radiatively to Eu ions causing their excitation and subsequent de-excitation of excited Eu ions. Density of defect centres increases with increasing gamma ray dose given to the sample that is why total ML intensity (i.e. area below curve) increases with increasing gamma ray dose.

#### 4. Conclusion

A novel  $\text{CaAl}_2\text{O}_4:\text{Eu}$  Phosphor was successfully synthesized by Combustion Synthesis. Combustion synthesis was proved to offer the advantage of producing high purity, crystalline calcium aluminate powder using minimal experimental equipment and inexpensive starting materials in a relatively short time. The combustion process described here has several advantages over the other methods in terms of simplicity, cost effectiveness, energy saving, purity and homogeneity. The present work on Eu doped monoclinic  $\text{CaAl}_2\text{O}_4$  sample prepared via a combustion method indicates that Eu ions are present in divalent and trivalent oxidation state as seen from its ML emission Spectra. Temperature dependence of the ML curve shows that ML is highly influenced by the surrounding's temperature. Since ML emission in this system is induced by the gamma ray and ML increases with gamma ray dose, it may use as mechanoluminescence dosimetry. Therefore  $\text{CaAl}_2\text{O}_4:\text{Eu}$  may be used as a good ML phosphor. This fundamental work might be important in developing new luminescent devices applicable for ML sensors.

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