

Mechanoluminescence & Thermoluminescence of SrAl₂O₄: Eu Nano-Phosphors

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Abstract: Eu doped strontium Aluminate phosphors were synthesized by combustion method using urea as a reducer at initiating temperature of 600°C. We have investigated the Fracto- Mechanoluminescence (ML) and Thermoluminescence (TL) of SrAl₂O₄: Eu. Two peaks have been found in time Vs ML intensity plot. The peak of ML intensity Vs time curve increases with increasing velocity of the piston. The total ML intensity (area below the curve) also increases with impact velocity and attains saturation at higher value of the impact velocity. We have also investigated that the ML intensity is completely recovered by irradiation with ultraviolet light. The TL intensity was recorded for different exposure time with UV light and it was observed that TL intensity is maximum for 15 minute exposure time. We have calculated the trap depth by different methods.

Keywords: Mechanoluminescence, Thermoluminescence, Combustion Synthesis, Strontium Aluminate.

INTRODUCTION

It has been a long history since people began to study the phosphorescent materials. However, conventional phosphorescent materials such as ZnS:Cu can hardly have bright light and long after glow time for the applications. The Eu²⁺-activated alkaline earth aluminates are an important class of phosphorescence materials because of their high quantum efficiency in visible region [1], long persistence of phosphorescence, good stability, color purity and good chemical, thermal and radiation resistance [2-6]. The potential benefit of rare earth ions as an activator has now well established in the field of luminescence. Different activators contribute significantly in tailoring the afterglow properties of phosphors from few seconds to many hours. In Eu the life time of 5d-4f transitions are about 3 orders of magnitude shorter than 4f-4f transition lifetime exhibited by other lanthanides and thus are of immense importance.

The synthesis of oxide phosphors has been achieved by a variety of routes: Solid-state reaction [7], sol-gel technique [8], micro-wave heating technique [9], hydroxide precipitation [10], an electric arc method [11] and combustion synthesis [12-14]. Combustion process is very simple, safe, energy saving and takes only a few minutes. The method makes use of the heat energy liberated by the redox exothermic reaction at a relative low igniting temperature between metal nitrates and urea as fuel. This method appears to hold promise for the preparation of complex oxide ceramics, such as aluminates [15-16]. The effect of different initiating temperature and mass of urea was reported [17] and it was found that the SrAl₂O₄:Eu²⁺ prepared at initiating temperature 600°C exists as a single phase monoclinic structure.

Mechanoluminescence (ML) is the phenomenon that a solid emits photons when it is fractured or deformed [18]. This phenomenon has been observed in many kinds of solids including ionic crystals, semiconductors, metals, glasses and organic crystals [19-20]. In polycrystalline Sr₃Al₂O₆:Eu, Dy intense ML was reported [21]. For SrAl₂O₄:Eu²⁺ it was demonstrated that ML is due to 4f⁷-4f⁶5d transition of Eu²⁺ [22]. ML from monoclinic structure SrAl₂O₄ was reported and it was found that only the α-SrAl₂O₄ phase produces strong ML [23]. These phenomenons are attracting considerable attention because they can be applied to sensing of structural damage and fracture. Although it was reported that SrAl₂O₄ doped with Eu²⁺ exhibits ML, the atomistic depiction about the effect of stress or strain on the rare-earth ion still remains unclear.

In this paper we measured ML and Thermoluminescence (TL) intensities of Eu-doped SrAl₂O₄ prepared by combustion synthesis at initiating temperature of 600°C. There is no strong statement on the ML phenomenon for Eu doped SrAl₂O₄ system prepared by combustion synthesis to the best of our knowledge.

EXPERIMENTAL

Analytical grade strontium nitrate Sr(NO₃)₂, aluminium nitrate Al(NO₃)₃·9H₂O, Europium oxide Eu₂O₃ and urea CO(NH₂)₂ were used as the starting materials. To prepare SrAl₂O₄:Eu phosphor, stoichiometric composition of the metal nitrates (oxidizers) and urea (fuel) were calculated using the total oxidizing and reducing valences of the components, which serve as the numerical coefficients so that the equivalence ratio is unity and the heat liberated during combustion is at a maximum. Then First of all Eu₂O₃ is converted into Eu(NO₃)₃ by mixing Eu₂O₃ into 2 ml of dil. HNO₃. Then weighed quantities of each nitrate and urea were mixed together and crushed into mortar for 1 hour to form a thick paste. The resulting paste is transferred to cru-

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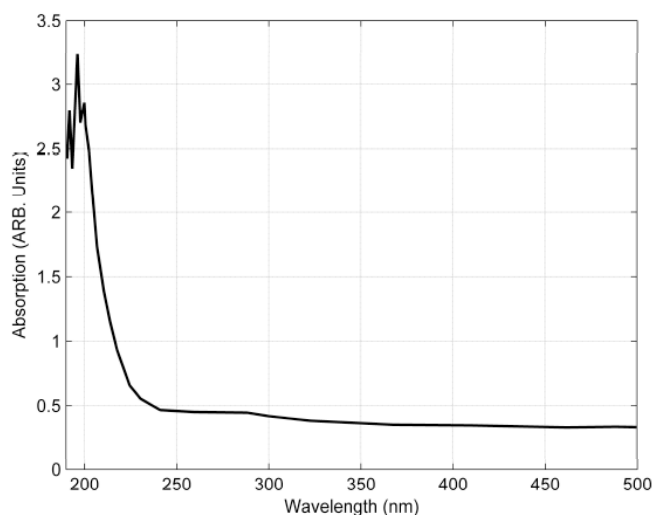


Fig. (1). Absorption spectra of SrAl₂O₄ having absorption edge at 240nm.

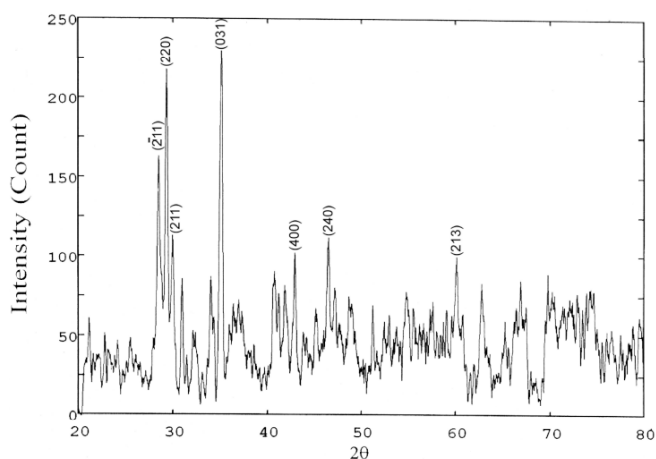


Fig. (2). X-ray diffraction pattern of SrAl₂O₄:Eu phosphor matched with JCPDS data file no. 34-0379.

cible and introduced into a vertical cylindrical muffle furnace maintained at 600°C. Initially the mixture boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases (oxides of carbon, nitrogen and ammonia). The process being highly exothermic continues and the spontaneous ignition occurs. The solution underwent smoldering combustion with enormous swelling, producing white foamy and voluminous ash. The flame temperature, as high as 1400 - 1600 °C, converts the vapor phase oxides into mixed aluminates. The flame persists for ~30 seconds. The crucible is then taken out of the furnace and the foamy product can easily be milled to obtain the precursor powder.

The ML was monitored by a homemade setup having RCA 931 photomultiplier tube positioned below the lucite plate and connected to a storage oscilloscope (Scientific 300 MHz, SM 340). Loads of different masses were dropped from fixed height. A routine TL setup (Nucleonix TL 10091) was used for recording TL glow. Absorption spectra was recorded using Shimadzu UV-1700 UV-Visible spectrophotometer.

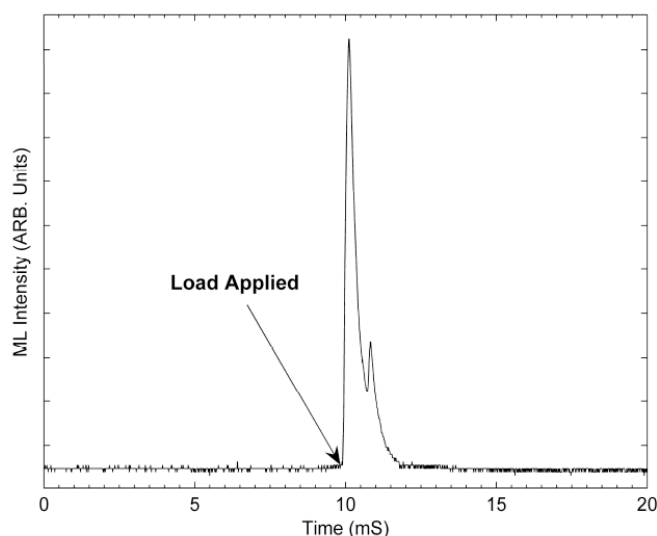


Fig. (3). Typical luminescence behavior of SrAl₂O₄ when load of 400gm was dropped from height 35cm.

Powder XRD data of the phosphor was collected on a Rigaku-D X-ray diffractor (40 kV, 35 mA) using Cu/K α radiation ($\lambda=1.5418$ Å).

RESULTS AND DISCUSSION

The study of optical absorption is important to understand the behavior of nano-crystals. A fundamental property is the band gap-the energy separation between the filled valence band and the empty conduction band. Optical excitation of electrons across the band gap is strongly allowed, producing an abrupt increase in absorption at the wavelength corresponding to the band gap energy. This feature in the optical spectrum is known as the optical absorption edge. Fig. (1) shows the optical absorption spectra of SrAl₂O₄:Eu in the range of 190nm-500nm. It can be seen that the spectra is featureless and no absorption occur for wavelength $\lambda>390$ nm(visible). The absorption edge is found at $\lambda = 240$ nm. The band gap was calculated corresponding to absorption edge (240nm). The band gap $E_{g, \text{(confinement)}}$ was found to be 5.18 eV.

According to the JCPDS card no. 34-0379 the x-ray diffraction patterns indicate that the crystal structure of SrAl₂O₄:Eu is mainly monoclinic (Fig. 2). The particle size was calculated using Scherrer technique. The diffraction intensity is maximum for (031) plane having $2\theta = 35.15^\circ$ and $\text{FWHM} = 6.8329 \times 10^{-3}$ radians. Taking $k=0.9$ the particle size was found to be 21.29 nm.

The characteristics of ML induced by the impact of a moving piston onto the asprepared phosphor was measured (Fig. 3). Two distinct peaks are observed in ML intensity vs. time curve. The presence of two peaks indicates some charge transfer process involved in ML process.

The luminescence intensity depends upon load applied. The experiment was carried out for different loads dropped from same height. The ML intensity increases with load applied Fig. (4).

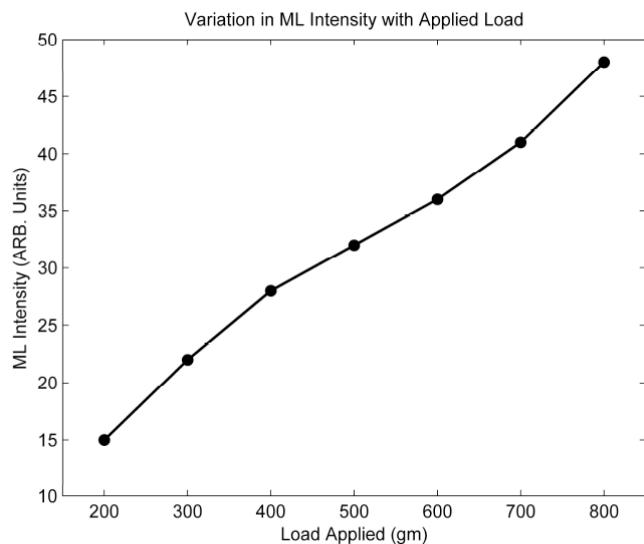


Fig. (4). Change in ML intensity with load applied.

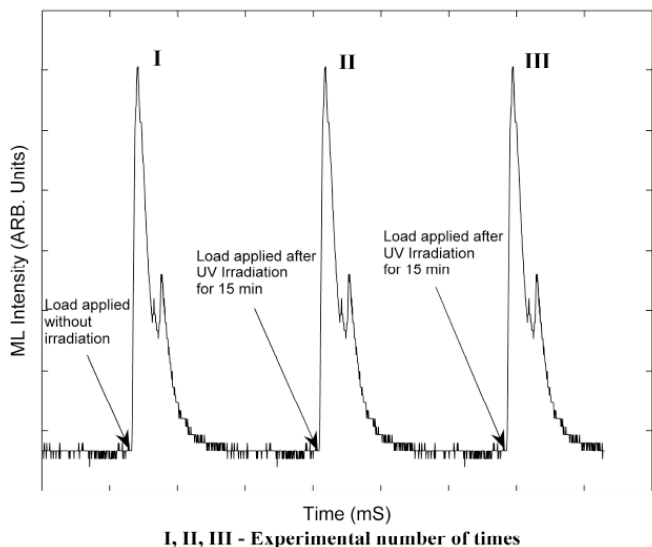


Fig. (5). Recovery phenomenon of ML intensity with UV irradiation.

The ML intensity decreases and ceases with repetitive application of load. After irradiation with UV light (365nm) for 15 minutes, when load is applied ML intensity is once again obtained, which is shown in Fig. (5).

Since the ML intensity is obtained when load is applied and it is completely recovered by UV irradiation, the origin of light emission is not the separation of the charges on the fracturing surfaces, which leads to the formation of an electric field and the liberation of exoelectrons [24, 25]. We think that the ML phenomenon of the Eu doped strontium aluminates are related to the movement of dislocations and the recombination of activated electrons and holes [26, 27]. The movement of dislocations excites carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centers, which is doped Eu^{2+} , give rise to the deformation luminescence [28]. It is suggested that ML is produced by the transition of Eu-ions between $4f^7$ & $4f^65d^1$.

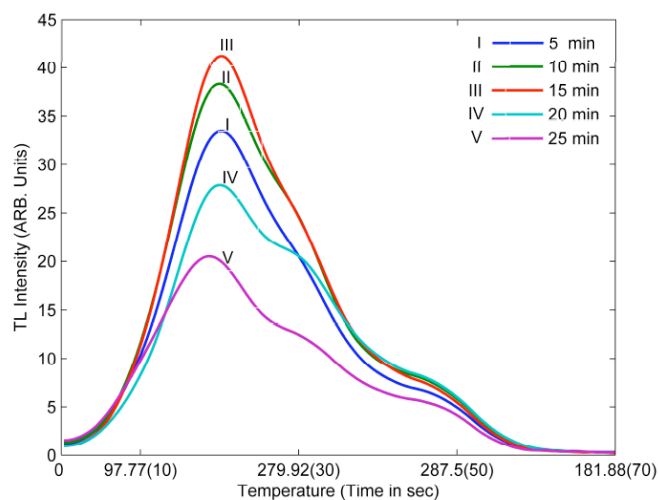


Fig. (6). TL intensity Vs Temperature plot for different time of irradiation.

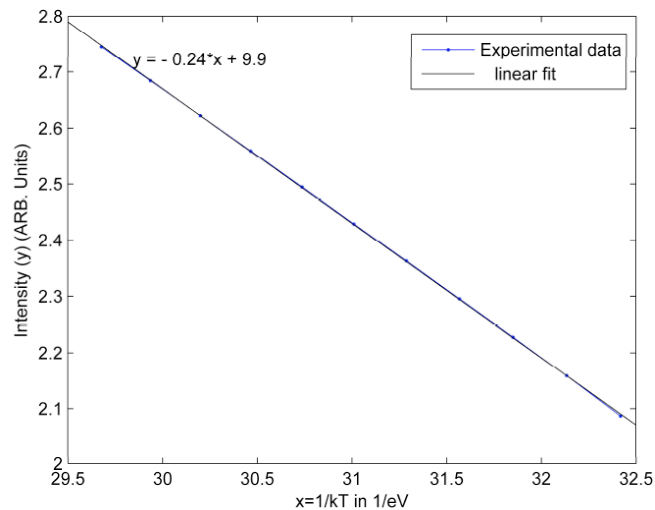


Fig. (7). Trap depth calculated with initial rise method, slope of the line = trap depth = 0.24 eV.

From the recovery phenomenon it is clear that SrAl_2O_4 has energy levels that trap excited electrons or holes.

The TL intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}$ was recorded after irradiation with UV light for different interval of time which has one peak at 196°C suggesting existence for trapping level. The TL intensity increases with increase in UV exposure time and it is maximum for irradiation time 15 min. Further increasing exposure time, TL intensity decreases. We suggest that quenching of colour centre may take place when sample is exposed to UV light for longer period and TL intensity decreases. The variation in TL intensity with irradiation time is shown in Fig. (6).

The trap depth was calculated using different methods. Fig. (7) shows the calculation of trap depth using initial rise method which came out to be 0.24 eV. The trap depth was also calculated using Chen's peak method and Glow-Curve fitting method giving trap depth 0.2522eV and 0.27eV respectively.

CONCLUSION

We have investigated the Mechanoluminescence and Thermoluminescence phenomena in the $\text{SrAl}_2\text{O}_4:\text{Eu}$ phosphor prepared with combustion synthesis, which is observed first to our knowledge. The ML intensity strongly depends upon the mass of the load applied. On repetitive application of the load ML intensity decreases which is recovered by irradiation the sample with UV light. We think that the movement of dislocation excites the carriers from the filled traps and the subsequent recombination of the electrons and holes in luminescence centers, give rise to the ML. The TL intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}$ depends upon the UV irradiation time and it was found to be maximum for 15 minute irradiation time.

ACKNOWLEDGEMENT

We are thankful to Dr. S. J. Dhoble for his valuable suggestions to prepare the sample.

CONFLICT OF INTEREST

None.

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Received: August 07, 2011

Revised: September 21, 2011

Accepted: October 04, 2011

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