Evaluation of trapping parameters of europium doped tristrontium dialuminium oxide phosphor by different thermoluminescent analysis methods

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Abstract: In the present work, we have synthesized Europium (Eu) doped Tristrontium Dialuminium Oxide (Sr$_3$Al$_2$O$_6$:Eu) phosphor by solid state reaction method in air atmosphere. The thermoluminescence (TL) properties of the synthesized phosphor are investigated and presented. Theoretical analysis of glow curves of Sr$_3$Al$_2$O$_6$:Eu was done by computerized glow curve deconvolution (GCD) method, and the trapping parameters of the synthesized phosphor, such as activation energy, frequency factor, order of kinetics, etc. are discussed and explained. These trapping parameters are determined by different methods, such as Chen’s peak shape method, initial rise method, and Ilich method. The synthesized phosphor is found to be a good candidate for dosimetric applications.

1. Introduction

Sr$_3$Al$_2$O$_6$:Eu is one of the well-known materials, which is used in WLEDs [1], transparent polycrystalline ceramic [2], anti-counterfeiting devices [3], stretching/strain sensors [3], etc. It shows red light emission owing to the presence of rare-earth doped Eu$^{3+}$ ions in host Sr$_3$Al$_2$O$_6$ phosphor [4,5]. Akiyama and coworkers [6, 7] reported that Eu$^{2+}$ ions activated Sr$_3$Al$_2$O$_6$ emitted green light as it was prepared in the reducing atmosphere. Sharma et al. [8] found that up to 1mol% the photoluminescence (PL) intensity is found to be maximum. Its red emission made this phosphor useful in luminous paints for highways, airport, and warning signs [8]. For the production of a large amount of phosphors solid state reaction is used [9]. The emission colour in Eu doped Sr$_3$Al$_2$O$_6$ phosphor is decided by the Eu$^{2+}$ and Eu$^{3+}$ is depends on the preparation of this phosphor in normal air or reducing atmosphere [3]. The shallow and deep traps level decides the time of afterglow of the phosphor [10]. To know the trap level (activation energy) of the phosphor, the thermoluminescence (TL) analysis method is used. TL is also known as thermally stimulated luminescence, is a relatively complex process and widely used in radiation dosimetry since it involves a trap, a luminescent centre, and the transfer (during warm up) of an electron or a hole from the trap to the luminescent centre [11]. TL is a type of delayed phosphorescence, where the photon energy is released when a material is heated after subjecting it to ionizing radiations. For a better understanding of transition of charge carriers from trap levels in Sr$_3$Al$_2$O$_6$:Eu phosphor, it is essential to study the TL parameters by which a suitable model for TL may be predicted. The present paper reports the TL of Sr$_3$Al$_2$O$_6$:Eu phosphor and calculate the trapping
parameters such as order of kinetics, activation energy and frequency factor by using peak shape method, initial rise method and Ilich method.

2. Experimental
For the synthesis of Sr₃Al₂O₆:Eu³⁺ (8mol%) phosphor, the solid-state reaction method was employed [12, 13]. SrCO₃, Al₂O₃ and Eu₂O₃ were used as the raw materials in the present investigation. All precursor materials were weighed as per their stoichiometric ratios. The materials are mixed by using mortar and pestle and add appropriate amount of ethanol as a dispersing agent. Then, the mixture was carefully transferred to an alumina crucible and sintered at 1400 °C for 4 h in air. At room temperature the sample was ground for later use. The phase structure of Sr₃Al₂O₆:Eu phosphor is identified using PANalytical 3 kW X’pert Powder - Multifunctional X-ray Diffractrometer using Cu Kα radiations (λ =0.15406 nm) in the 2θ range from 10° to 80°. The thermoluminescence glow curve was recorded on a Nucleonics TLD reader (Model: 1009I). The heating rate in TL experiment was kept at 5°C/s.

3. Results and Discussions
Figure 1 shows the photograph of Sr₃Al₂O₆:Eu phosphor showing red glow under UV exposure.

![Figure 1. Photograph of red glow from Sr₃Al₂O₆:Eu phosphor under UV exposure.](image1)

![Figure 2. XRD patterns of Sr₃Al₂O₆:Eu phosphor.](image2)
The cubic phase of Sr$_3$Al$_2$O$_6$:Eu phosphor is confirmed by the XRD patterns as shown in figure 2 [12,13]. These diffractograms match well with COD card no. 96-901-5879. The average size of the crystallites in Sr$_3$Al$_2$O$_6$:Eu phosphor is calculated using Debye-Scherrer formula $D = \frac{K \lambda}{\beta \cos \theta}$, where $K$ is a constant, $\lambda$ the wavelength of X-rays, $\beta$ - the full width at half maxima (FWHM) and $\theta$ is the Bragg’s angle and it is found to be 66.5 nm.

The TL glow curve (under 5 min UV exposure) exhibits a single emission peak of Sr$_3$Al$_2$O$_6$:Eu phosphor as shown in figure 3. The TL peak is found to be broad and the area covered under it suggests that it contains multiple numbers of TL trap depths.

![TL glow curve deconvolution peaks of Sr$_3$Al$_2$O$_6$:Eu phosphor.](image)

But, sometimes the TL glow curves are complex and consists of a number of main peaks and some satellite peaks. The process used to separate complex glow curves and to get information about the traps from this glow-curve is known as deconvolution.

### 3.1 Chen’s peak shape method

Chen’s peak shape method is a very popular method for analyzing TL parameters. This depends on the shape and size of the TL glow curve and is useful to detect a number of energy levels formed due to defects and their positions in the forbidden energy-gap of the host materials. This method is based on the equations developed by Chen to determine trapping parameters given below [14]:

$$ E_\alpha = c_\alpha \left( \frac{kT_M^2}{\alpha} \right) - b_\alpha \left( 2kT_M \right) $$

where $\alpha$ is $\tau$, $\delta$, or $\omega$. The values of $c_\alpha$ and $b_\alpha$ are summarized as below:

$$ c_\tau = 1.510 + 3.0(\mu - 0.42) b_\tau = 1.58 + 4.2(\mu - 0.42) $$

$$ c_\delta = 0.976 + 7.3(\mu - 0.42) b_\delta = 0 $$

$$ c_\omega = 2.52 + 10.2(\mu - 0.42) b_\omega = 1 $$

The value of geometrical factor $\mu$ can be calculated using formula given below:

$$ \mu = \frac{T_2 - T_M}{T_2 - T_1} $$

where $T_m$ is the temperature corresponding to peak TL intensity, $T_1$ and $T_2$ are temperatures at half the maximum TL intensity. For first order kinetics, $\mu = 0.42$ and for second order kinetics, $\mu = 0.52$ [14].
According to order of kinetics, the values of activation energy and frequency factor using Chen’s \( \tau \)-equation, Chen’s \( \delta \)-equation and Chen’s \( \omega \)-equation can be calculated [14] where \( \tau = T_m - T_1 \), \( \delta = T_2 - T_m \), and \( \omega = T_2 - T_1 \).

Figure 4 (a-c) shows the TL glow curve of Sr\(_3\)Al\(_2\)O\(_6\):Eu\(^{3+}\) phosphor used for peak shape method. The order of kinetics, activation energy and frequency factor were calculated by using Chen’s peak shape method and the corresponding values are enlisted Table 1.

![Figure 4](image)

**Figure 4.** (a-c) TL glow curves of Sr\(_3\)Al\(_2\)O\(_6\):Eu phosphor used for peak shape method.

**Table 1.** Trapping parameters of Sr\(_3\)Al\(_2\)O\(_6\):Eu phosphor calculated by Chen’s peak shape method.

| Sample Name | Peak Number | Geometrical factor (µ) | Order of kinetics (b) | Method of calculation |
|-------------|-------------|------------------------|-----------------------|-----------------------|
|             |             |                        |                       | Chen’s \( \tau \) equation | Chen’s \( \delta \) equation | Chen’s \( \omega \) equation |
|             |             |                        |                       | Activation energy (eV) | Frequency factor (s) | Activation energy (eV) | Frequency factor (s) | Activation energy (eV) | Frequency factor (s) |
| Sr\(_3\)Al\(_2\)O\(_6\):Eu | Peak 1      | 0.45                   | 1.67                   | 0.75                  | 8.4x10\(^9\)          | 0.79                | 1.99x10\(^{11}\)     | 0.77                | 1.11x10\(^{11}\)   |
|             | Peak 2      | 0.50                   | 1.92                   | 0.82                  | 7.93x10\(^9\)         | 0.85                | 1.70x10\(^{11}\)     | 0.84                | 1.36x10\(^{11}\)   |
|             | Peak 3      | 0.54                   | 2.08                   | 0.70                  | 3.3x10\(^8\)          | 0.71                | 3.56x10\(^8\)        | 0.71                | 3.96x10\(^8\)      |

3.2 Initial rise method

The evaluation of trapping parameters through an initial rise method was first reported by Garlick and Gibson in 1948 [15]. In this method, the initial rise part of the TL glow curve was used to determine the trapping parameters. The graph is plotted between log of TL intensity versus 1/kT, where k is the Boltzmann constant and T is the temperature and the slope of the graph gives the activation energy [16]. The initial rise method is applied only when the TL glow curve is well separated by another one. The advantage of this method is, it is applied on any order of kinetics and does not require any knowledge of frequency factor. TL glow curve of Sr\(_3\)Al\(_2\)O\(_6\):Eu\(^{3+}\) phosphor used for initial rise method shown in figures 5 (a), (b) and (c) and their analysis by initial rise method shown in figures 5 (d), (e) and (f).
Figure 5. (a-c) TL glow curves of Sr$_3$Al$_2$O$_6$:Eu phosphor by initial rise method, (d-f) TL glow curve analysis of Sr$_3$Al$_2$O$_6$:Eu phosphor by initial rise method.

3.3 Ilich method

For the calculation of activation energy from TL glow curve, Ilich method is employed, which is independent of the order of kinetics. In this method, the activation energy is calculated by using critical temperature $T_c$ and the starting temperature $T_0$ [11]. Thus, the activation energy is expressed as:

$$E = k \frac{T_c^2}{T_c - T_0}$$  \hspace{1cm} (6)

The trapping parameters of Sr$_3$Al$_2$O$_6$:Eu phosphor by using Ilich method are shown in figure 6.
Figure 6. Peaks obtained after the deconvolution of TL glow curves for $\text{Sr}_3\text{Al}_2\text{O}_6$:Eu phosphor (analysis of trapping parameters done using Ilich method).

Table 2. Trapping parameters of $\text{Sr}_3\text{Al}_2\text{O}_6$:Eu phosphor calculated by Initial rise and Ilich methods.

| S. No. | Sample Name | Peak Number | Peak Position (K) | Activation energy (eV) |
|--------|-------------|-------------|-------------------|-----------------------|
|        |             |             |                   | Initial rise method   | Ilich Method         |
| 1      | $\text{Sr}_3\text{Al}_2\text{O}_6$:Eu | Peak 1     | 352               | 0.88                  | 0.74                 |
|        |             | Peak 2     | 381               | 0.85                  | 0.75                 |
|        |             | Peak 3     | 417               | 0.75                  | 0.73                 |

4. Conclusions
In the present investigation $\text{Sr}_3\text{Al}_2\text{O}_6$:Eu phosphor was prepared by solid state reaction method. The TL glow curve is found single and broad. The activation energy calculated by peak shape method is found in the range from 0.70 to 0.85 eV, through initial rise method it is found to range from 0.75 to 0.88 eV and by Ilich method the values lie between 0.73 and 0.75 eV. All the results suggest that the synthesized phosphor is a good candidate for dosimetric applications.

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