

# A preliminary study of Thermoluminescence of beta-irradiated $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ , $\text{Dy}^{3+}$ phosphors

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**Abstract.**  $\text{Eu}^{2+}$  doped and  $\text{Dy}^{3+}$  co-doped strontium aluminate ( $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ ) phosphors were synthesized by the solution - combustion technique at 500 °C using urea as a reducer, a widely known method for preparing nano sized phosphors.  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{CH}_4\text{N}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Dy}(\text{NO}_3)_3$  were used as raw materials for the preparation of the  $\text{SrAl}_2\text{O}_4$  (RE: Eu, Dy) precursor. The thermoluminescence (TL) properties of beta ( $\beta$ ) irradiated  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  have been studied. The electron-trapping properties in terms of TL glow curves are discussed in detail. The TL intensity was recorded for different beta doses at different heating rates. The influence of repeated measurements on the same sample on peak temperature and TL intensity was also investigated. Different kinetic parameters like activation energy and frequency factor are calculated for different TL glow curves. We have also calculated the trap depth with the variable heating method.

## 1. Introduction

When an insulator, a semiconductor or a phosphor with deep traps is exposed to ionizing radiation for a while at rather low temperatures, it absorbs energy from the radiation and the (deep trap) defects become excited. When the temperature of the material is raised, it shows an increased after-glow called thermally stimulated luminescence (TSL) due to the recombination of electrons thermally reactivated from the deep traps where the energy is converted to luminescence and released in the form of visible light. This phenomenon is known as thermoluminescence (TL) [1]. The heat only acts as a stimulant whereas the ionizing radiation plays the role of an exciting agent. During the process of irradiating a material with  $\alpha$ -rays,  $\beta$ -rays, UV-rays,  $\chi$ -rays, or  $\gamma$ -rays, part of the irradiation energy is used to transfer electrons to traps [2]. Some of these trapped electrons locate themselves at a depth (E) below the conduction band. The trap levels or centers play a significant role in energy storage for persistent photoluminescent and thermoluminescent phosphors. This radiation energy stored in the form of trapped electrons is released by raising the temperature of the material and the released energy is converted to luminescence. This trapping process followed by the release of the stored energy in thermoluminescent materials is widely applied in radiology such as in ionizing radiation dosimeters. All phosphorescent materials may have a minimum threshold temperature for release of previously stored energy; but many have a minimum triggering temperature below normal temperatures and are not normally thought of as thermoluminescent materials [3]. Cooling a TL material and reheating it

does not make it emit light. It should first be exposed to radiation and then heated for it to emit light again. The storage capacity of a TL material makes it, in principle, suitable for dosimetric applications [4]. Materials that exhibit TSL include glasses, ceramics, plastics and some organic solids.

In order to obtain information about the luminescence process of phosphors and to apply them in various fields, knowledge of defects or traps and their location in the band gap of these materials is very important. TL measurement is a very important and convenient method of investigating and providing information concerning the nature of traps and trapping levels in crystals. The glow curve which is a representation of the temperature dependence of the emission intensity is a good means to measure the trap depth (i.e., the activation energy of traps) [5]. During TL measurements the irradiating source is cut off and the thermally stimulated luminescence recorded while gradually increasing the temperature. Various parameters of the trapping process such as activation energy ( $E_T$ ), amount of trap ( $n$ ), trapping rate, etc, are then deduced by analysing the shape and position of the obtained TL glow curve [6]. When a TL glow curve having several overlapping peaks is obtained, deconvolution is carried out in order to isolate one of the glow peaks from the others to enable the calculation of these parameters. The term "peak shape method" is reserved in the TL literature for such methods, although there are other methods for finding  $E_T$  which are also based on the glow-peak shape (i.e. curve fitting methods) [7, 8]. The work by Chen [9] is a reference point in the derivation of the peak shape methods.

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  has been studied by many researchers for its use as luminescent material. Nevertheless, there are few reports dealing with its use as a TL material. In this study we report on preliminary results on the TL behaviour of the as-prepared  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  synthesised by solution-combustion method at an initiating temperature of 500 °C to find out its suitability in various TL applications. In particular this study is concerned with the dosimetric analysis of the  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  TL glow curves such as the dose response. Also kinetic analyses were carried out using variable heating rate method to study the energy levels and the discrete trapping and recombination centres within the phosphor material.

## 2. Experimental

### 2.1. Synthesis

The  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  phosphor was synthesized using the solution - combustion method. The starting raw materials used in the experiment included various proportions of analytical pure grade Sr ( $\text{NO}_3$ )<sub>2</sub>, Al( $\text{NO}_3$ )<sub>3</sub>.9H<sub>2</sub>O, Eu( $\text{NO}_3$ )<sub>3</sub>.5H<sub>2</sub>O, Dy( $\text{NO}_3$ )<sub>3</sub>, and urea (CO(NH<sub>2</sub>)<sub>2</sub>). The raw materials were weighed according to the chemical composition of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ , dissolved in 10 ml of de-ionized water and thoroughly mixed using a magnetic stirrer for 15 minutes without heating to obtain a uniform saturated aqueous solution.

The solutions were then poured into China crucibles and placed one at a time in a muffle furnace pre-heated to 500 °C. The mixture ignited and a fast, self-sustaining combustion reaction took place. At first, the solution boiled losing all the water in the form of steam followed by decomposition letting off large amounts of gases (oxides of carbon, nitrogen and ammonia). The mixture then frothed and swelled enormously forming foam, then spontaneous ignition and smouldering occurred which gradually led to an explosion which ruptured the foam with a flame that glowed to incandescence. The product of combustion was a voluminous white  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  foam. The foam was taken out of the muffle furnace, cooled then milled resulting in a dry, and usually crystalline, fine white oxide powders. The whole combustion process took about 5 minutes. The powders were stored in transparent glass sample bottles for characterization.

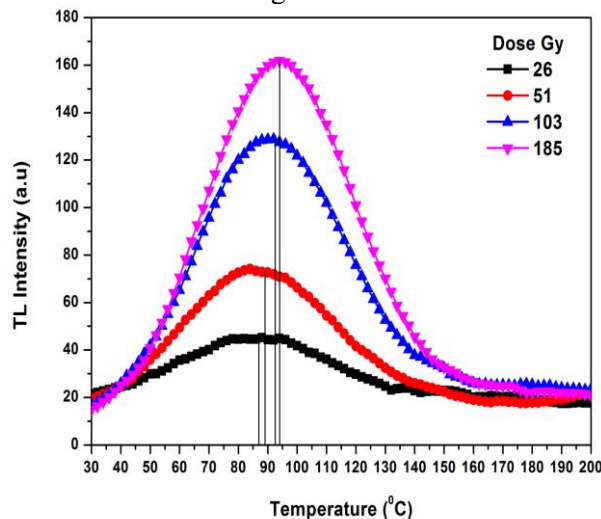
## 2.2. Characterization

TL measurements were made on the  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  phosphor. The samples were prepared into discs of 5 mm in diameter and 1 mm thick. A  $\beta$ -source based on the  $^{90}\text{Sr}$  isotope was used for TL excitation prior to heating. The radiation dose rate at the location of the samples was 10.75 Gy per minute. TL measurements were taken in a nitrogen atmosphere using a Risø model TL/OSL-DA-20 Luminescence Reader. The TL was detected by an Electron Tubes Ltd model 9235QB photomultiplier through a BG-39 band-pass filter (transmission band 340–620 nm FWHM). Samples were heated from 30 to 200 °C at various heating rates and after various radiation doses.

## 3. Results and Discussions

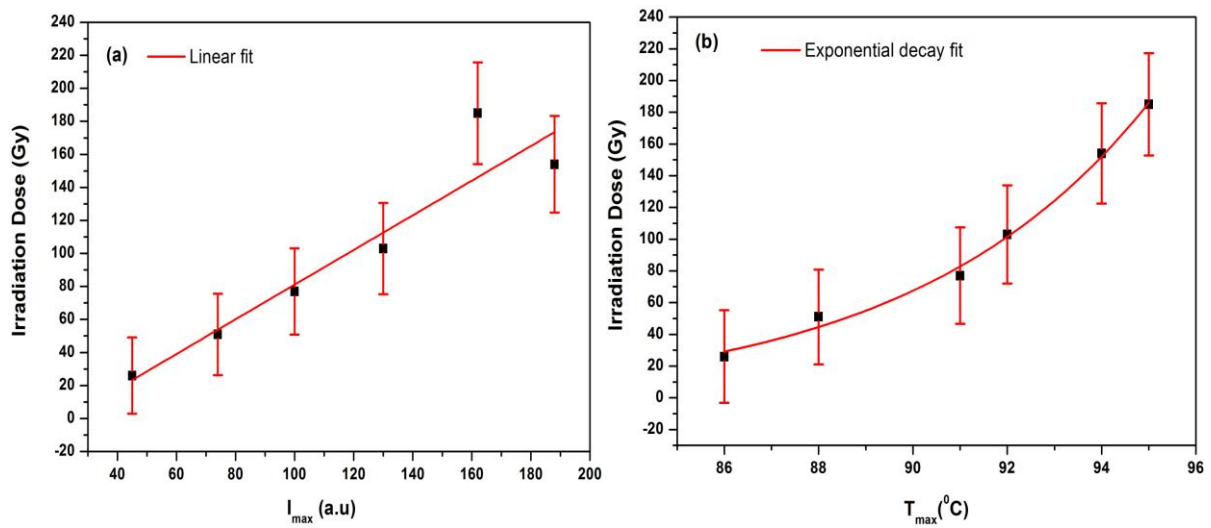
### 3.1. Dose response

To check the dose dependence effect on the peak positions, the samples were irradiated with doses from 26 to 185 Gy and the TL measured at a constant linear heating rate of 5 °C s<sup>-1</sup>. Figure 1 shows the effect of dose variation on TL intensity with different irradiation doses. The position of the peak temperature,  $T_{max}$ , is observed to shift towards higher temperatures from 86–95 °C while the TL intensity increased with increased radiation dosage levels.



**Figure 1.** TL glow curves of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  phosphor showing effect of irradiation doses on TL intensity.

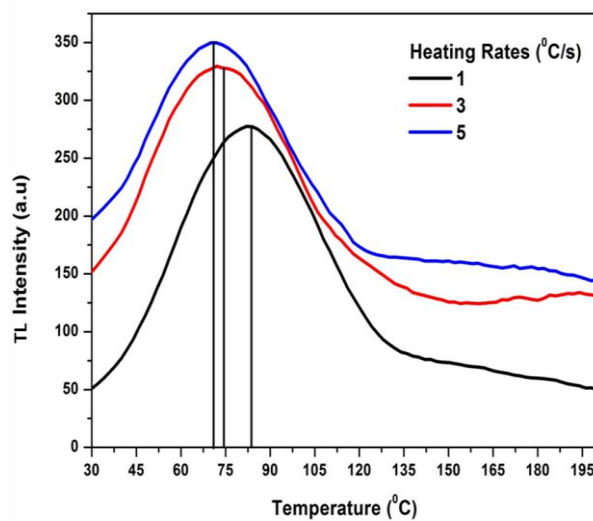
From figure 2 (a) it can clearly be seen that the peak intensities increase linearly with a slope of 1.0 with higher doses. The glow curve intensity ( $I$ ) during heating has been found to be proportional to the concentration  $n_0$  of the trapped charge carriers [10]. The increase in TL intensity with increase of absorbed radiation dose can be attributed to the increase in the number of electrons in the excited state, and hence recombination, with increasing radiation dose. In TL theory [8], the peak temperatures ( $T_{max}$ ) of glow peaks are expected to be influenced only by changes in the heating rate, but the contrary is seen in figure 2(b) which shows an exponential dependence. This might also be attributed to the population of the trap centers and luminescence centers. The higher concentration of defects that generate non-radiative states within the band gap could be responsible for decrease in the  $T_{max}$  rate of change which tends to saturation with increased doses. More measurements, however, are needed at other doses to make a final conclusion.



**Figure 2** Effect of irradiation doses on (a)  $I_{max}$  and (b)  $T_{max}$  peaks of the TL glow curve of the SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> phosphor.

### 3.2. Variable heating rates

This method was used to determine the kinetic parameters in this investigation. The behaviour of the glow curve was monitored as the heating rate increased from 1 °C/s<sup>-1</sup> to 5 °C/s<sup>-1</sup>. The glow curves of figure 3(a) shows the effect of these heating rates. The peak temperatures ( $T_{max}$ ) of the glow curves are seen to shift to the higher temperature side from 72 to 82 °C with increased heating rate. This shift of  $T_{max}$  is associated with a deeper trap depth [11]. Glow curve peaks at higher temperature are as a result of deeper traps which have higher activation energy  $E_T$ . Hence, larger heat energy is required to free charge carriers from the deep traps.

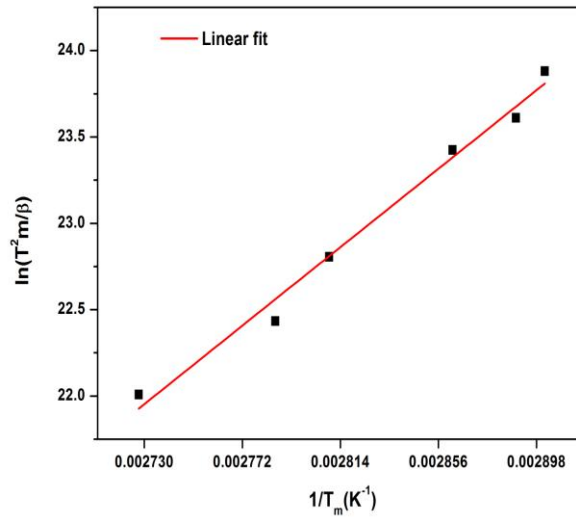


**Figure 3.** Effect of heating rate on TL intensity and Temperature of SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> phosphor.

The trap depths were calculated by the Hoogenstraaten method, which relates the TL peak temperature and heating rate [12]. The depth of each trap was determined using the following equation:

$$\ln\left(\frac{T_m^2}{\beta}\right) = \left(\frac{E}{k}\right) \frac{1}{T_m} + \ln\left(\frac{E}{sk}\right) \quad (1)$$

where  $\beta$  is the heating rate,  $T_m$  is the peak temperature ( $T_{max}$ ) of the glow curve,  $E$  is the trap depth,  $k$  is the Boltzmann constant, and  $s$  is a frequency factor or “escape frequency” of the trapped charge carriers. A plot of  $\ln\left(\frac{T_m^2}{\beta}\right)$  versus  $\frac{1}{T_m}$  gives a linear relation with slope  $\left(\frac{E}{k}\right)$  as shown in figure 4. The solid line through the data points gives the line of best fit for equation (1). Hence it is possible to obtain the trap depth or thermal activation energy ( $E_T$ ) from the slope of the straight line. In this investigation, the frequency factor ( $s$ ) is found to be  $5 \times 10^6 \text{ s}^{-1}$  and the trap depth due to  $\text{Dy}^{3+}$  ion substitution is  $0.89 \pm 0.01 \text{ eV}$ , which agrees with the theoretical value reported and shows a positive correlation between the trapping depth and the 4f-5d transition energy of  $\text{Dy}^{3+}$  [12,13,14]. The mechanism of electron trapping by rare earth ions can be explained using the model by Dorenbo [12]. The  $\text{Eu}^{2+}$  ( $4f^7$ ) and  $\text{Dy}^{2+}$  ground energy states are 3.2 eV and 0.9 eV respectively, below the bottom of the conduction band. On exposure to electrons of sufficient energy from  $\beta$ -irradiation, the electron from  $\text{Eu}^{2+}$  absorbs the radiation and gets optically excited moving from the ground state to the excited just below the conduction band. When the material is thermally activated through the TL process, the 5d electron is excited to the conduction band forming  $\text{Eu}^{3+}$ . The electron is then trapped by  $\text{Dy}^{3+}$  to form  $\text{Dy}^{2+}$  [16]. The energy difference between the lowest 5d state and the bottom of the conduction band is 0.017 eV [12].



**Figure 4.** A plot of  $\ln\left(\frac{T_m^2}{\beta}\right)$  versus  $\frac{1}{T_m}$

Dorenbo’s model [12] shows that the ground state of  $\text{Dy}^{2+}$  is located 0.9 eV below the bottom of the conduction band, which gives a value close to the trap depth of about 1 eV derived from TL studies by Yamamoto and Matsuzawa [17] and Nag and Kutty [18]. The trapped electron is thermally released

and recombines with  $\text{Eu}^{3+}$  yielding the 5d–4f emission of  $\text{Eu}^{2+}$ . Or in other words the  $\text{Eu}^{3+}$  ion releases a hole into the valence band reducing to the divalent  $\text{Eu}^{2+}$  state again becoming a source of electrons for the surrounding traps thus forming a cycle of continuous excitation. This explains the slow saturation and slow thermal release that brings about the persistent luminescence in phosphors.

#### 4. Conclusions

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$  phosphor was synthesized using the solution - combustion method. Samples were heated from 30 to 200 °C at various heating rates and irradiation doses. The total TL signal and glow curve peaks show increase with dose of the incident  $\beta$  - radiation and temperature ( $T_{max}$ ). The position of the peak temperature ( $T_{max}$ ) shifts towards higher temperatures with increased radiation dosage levels. At higher doses the rate of change of peak temperature ( $T_{max}$ ) seem to reduce, which could be due to higher concentration of defects that generate non-radiative states within the band gap. The peak TL intensity ( $I_{max}$ ) of the glow curves decreased while the peak temperatures ( $T_{max}$ ) are seen to shift to the higher temperature side with increase in heating rate. This might be attributed to the filling of the trap centers. For higher peak temperatures the trap depths are deep. The calculated value of activation energy was  $0.89 \pm 0.01$  eV.

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