# Thermoluminescence Study of Europium Doped Strontium Aluminates Phosphor $SrAl_2O_4$:Eu

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**Abstract:**

**Aims**: Present study includes synthesis and characterization of alkaline earth aluminates $SrAl_2O_4$ phosphor. TL property of $SrAl_2O_4$ has also been studiedwith Eu doping. **Material and Method**: Synthesis of phosphor were done by solid state reaction method.TL glow curves are recorded with different molar concentration of Eu (1, 2, 5, 7.5, 10, 12.5 and 15 molar%) for different γ-dose (50Gy, 150 Gy, 300Gy, 600Gy, 1000 Gy and 2000Gy) **Results:** Results of XRD characterization are matched with JCPDS card no. 34-0379, the highest intense peak is found at plane [-211] $SrAl_2O_4$ is observed with monoclinic structure with space group [$P2_1$].Two glow peak were found at temperature 175ºC and 275ºC at higher dose of irradiation for 1 molar% concentration of Eu doping. Intensity of TL were found to be increases linearly with dopant concentration of Eu and maximum value of intensity were found for 5 molar% concentration. **Conclusions**: TL response is linear up to 1000 Gy, hence these phosphor can be used for dosimteric purpose up to 1000 Gy. The kinetic parameter of TL peak were calculated, results indicate that TL peaks follow second order kinetics. Activation energy found to be increases with increase in γ-dose.Analysis of TL spectra of $SrAl_2O_4$:Eu has done and we found peaks at 530nm 575 nm and 630 nm respectively green, yellow and red in visible region.

**Keywords:** Dosimetry,phosphor, strontium aluminates, thermoluminescence, xrd.

## Introduction:

Thermoluminesce is a phenomenon in which photon were emitted from the material called phosphor during application of heat as a stimulating agent. Phosphors were basically a wide band gap material which were already irradiated with ionizing radiation such as UV, $\gamma$-ray ,X-ray,$\alpha/\beta$ particle[1]. Irradiation of phosphors with ionizing radiation results formation of electron-hole pairs. These free electrons get trapped at trapingcentre existing in the forbidden gap. To study TL phenomenon energy needs to supply to free the trapped electron, which is done by heating of phosphor. Released electron recombine with hole which leads to emission of light in the form of TL[2]. TL studies shows one or more peaks in glow curve. Each peak gives information about the details of trap distribution[3].Analysis of shape of glow curve and location of various peaks provide useful information of trap distributionwhich is mostly used for TL study and radiation dosimetry[4]. TL phenomenonare extensively used for radiation dose measurement[5]. Till now various phosphors have been developed and used for dosimetry purpose.

Alkaline earth aluminates phosphors are extensively studied phosphor and are known for their great brightness and long persistent glow[6-9]. There are large group of minerals which exhibit TL property. Alkaline earth aluminates also shows TL property and it belongs to group of menerals $MAl_2O_4$,(M=Sr, Ca, Fe, Mn). Alkaline earth aluminates are good luminescent material when they are doped with rare earth element; they also posses high TL intensity in visible region[10-11].

Various methods were investigated to synthesize $SrAl_2O_4$ Phosphor with rare earth doping. A solid state reaction method is mostly used to synthesize $SrAl_2O_4$ phosphor but other techniques such as combustion[12], Co-precipitataion[13] and sol gel[14-15] methods were found to be successful. $SrAl_2O_4$ phosphor prepared with rare earth doping by calcining appropriate mixture of $SrCO_3$, $Al_2O_3$, $Eu_2O_3$ and $B_2O_3$ in a reducing atmosphere at 1300ºC for 1 hour shows green emission of photon after UV exposure. Consequent discovery at that time initiated search for different and better luminescent material such as alkaline earth aluminates. $SrAl_2O_4$:Eu phosphor prepared by combustion method shows two peak at 206ºC and 345ºC after irradiation 15kGy of γ-rays[16]. $SrAl_2O_4$ phosphor doped with Eu and Dy prepared by reflux methodat 900ºC for 16 hours shows TL peak at 194ºC irradiated with 10kGy of Strontum-90 β-source[17]. Strontium aluminates have found suitable for application in radiation detection and radiation dosimetry[18]. $SrAl_2O_4$ phosphor with doping of rare earth Eu and Dy synthesized by solid state reaction method at 1300ºC shows UV emission and posses good TL response after excitation[19.] In the present investigation, we have prepared alkaline earth aluminates phosphor $SrAl_2O_4$ with Eu dopants by solid state reaction method. We have also investigated the $SrAl_2O_4$:Eu with XRD and TL measurement to understand the effect of γ-radiation in sample.

## Materials and Methods:

We have synthesized microcrystalline powder with strontium carbonate ($SrCO_3$), aluminium oxide ($Al_2O_3$) and europium oxide ($Eu_2O_3$) as starting materials and boric acid as a fuel. For preparing $SrAl_2O_4$:Eu phosphors, the mixture was kept in an alumina crucible with a cover and sintered at 1000 °C for 2 hour in adigitally controlled electronic furnace in open air. After cooling to room temperature, phosphor were taken out from furnace and ground. Finally, the pre-sintered samples were ground and sintered again at 1350 °C for 5 hour in a weak reducing atmosphere.

XRD studies are carried out with XRD Diffractometer D8 Discover using Cu Kα (1.54 Å) X-ray. XRD studies are made at room temperature and 2θ varied from 10º to 80º. TL response of $SrAl_2O_4$ was studied from temperature to 350ºC. To observe the effect of Eu concentration on phosphor, $SrAl_2O_4$ were doped with different molar concentration of Eu (1, 2, 5, 10, 7.5, 12.5 and 15 molar%) and TL glow curves were recorded for different γ-dose (50Gy, 150 Gy, 300Gy, 600Gy, 1000 Gy and 2000Gy) with TL reader at constant heating rate of 5°C per second. Two control samples were also kept, which were not irradiated throughout the procedure and used for background radiation correction. Effect of Eu doping on $SrAl_2O_4$ phosphor and TL spectra were also recorded.

**Result and Discussion:**

The X-ray diffraction pattern of prepared $SrAl_2O_4$ phosphor is shown in figure-1.

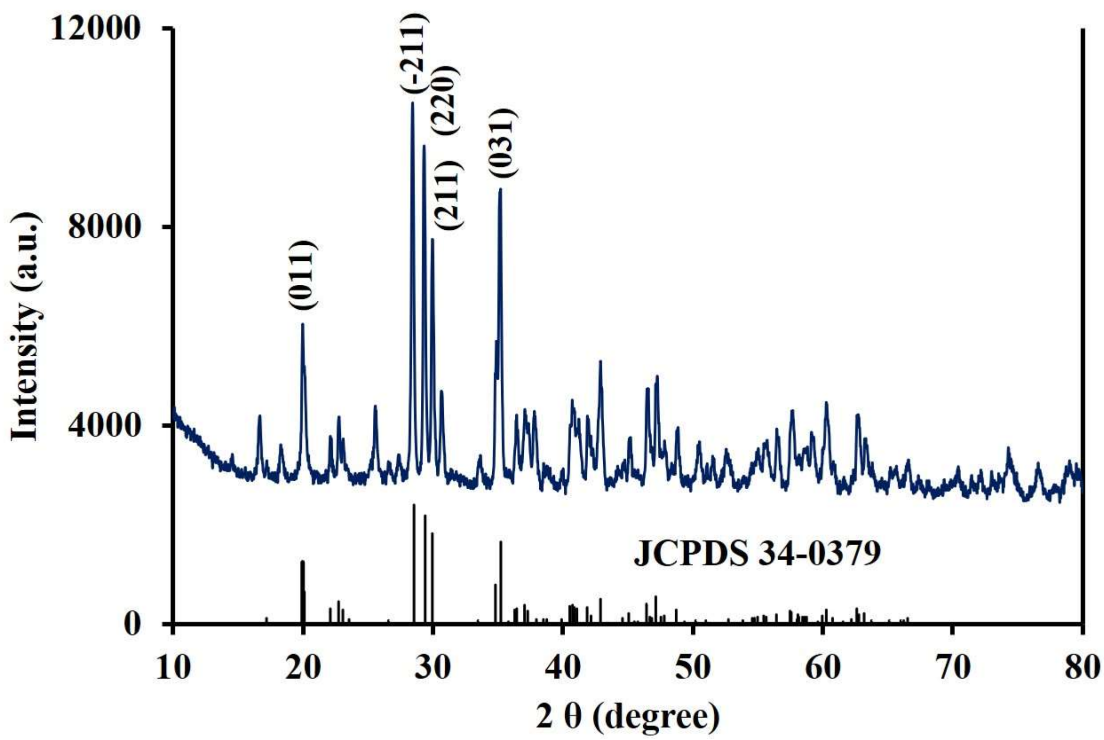


Figure 1: XRD diffraction pattern- $SrAl_2O_4$:Eu

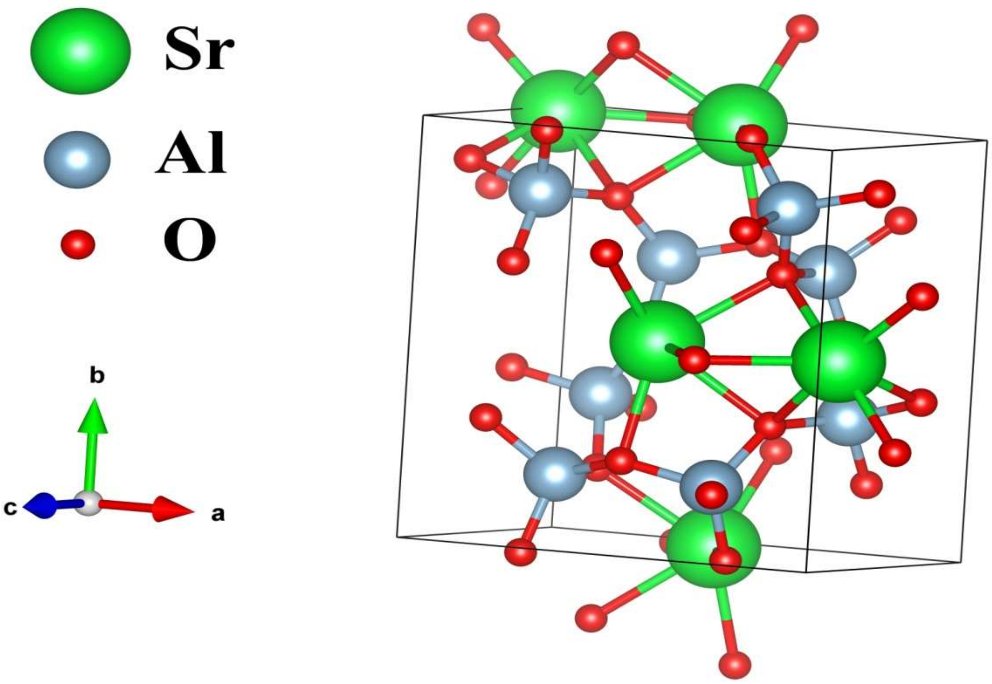


Figure 2: The crystal structure- $SrAl_2O_4$:Eu

The crystal structure of $SrAl_2O_4$:Eu is monoclinic as shown in figure-2. XRD pattern is recorded by XRD diffractometer D8 discover using Cu Kα X-ray(1.54 Å). XRD pattern shows the synthesis of $SrAl_2O_4$. The results are well matched with JCPDS card 34-0379, the highest intense peak is found at plane [-211]. The $SrAl_2O_4$ is observed with monoclinic structure with space group [$P2_1$] and lattice parameter found to be about (a=8.442Å, b=8.822Å, c=5.160Å). Average particle size of phosphor estimated by Scherrer`s formula.

$$c.s. = 0.9\lambda/\beta \mathrm{Cos}\theta \qquad ... (1)$$

where λ iswavelength of X-ray diffraction source, β –full width of peak at half of its maximum value, and θ is angle of diffraction. Crystalline size for all major peaks calculated and found average around 81nm. Doping of Eu in $SrAl_2O_4$ does not change the XRD pattern and no other extra peak is observed. Doped Eu ions does not have any significant influence on structure of crystalline phosphor because of nearly same ionic radii of $Eu^{2+}$(0.112nm) and $Sr^{2+}$(0.114nm)[20], their substitution does not resultsany significant distortion in the lattice parameter.

To study TL behaviour ofprepared $SrAl_2O_4$ phosphor, TL glow curve is recorded with different molar concentration of Eu (1, 2, 5, 7.5, 10, 12.5 and 15 molar%) for different γ-dose (50Gy, 150 Gy, 300Gy, 600Gy, 1000 Gy and 2000Gy). TL glow curve for different molar% of Eu doped $SrAl_2O_4$ with different γ-dose of exposure is shown in figure-3 to figure-9.

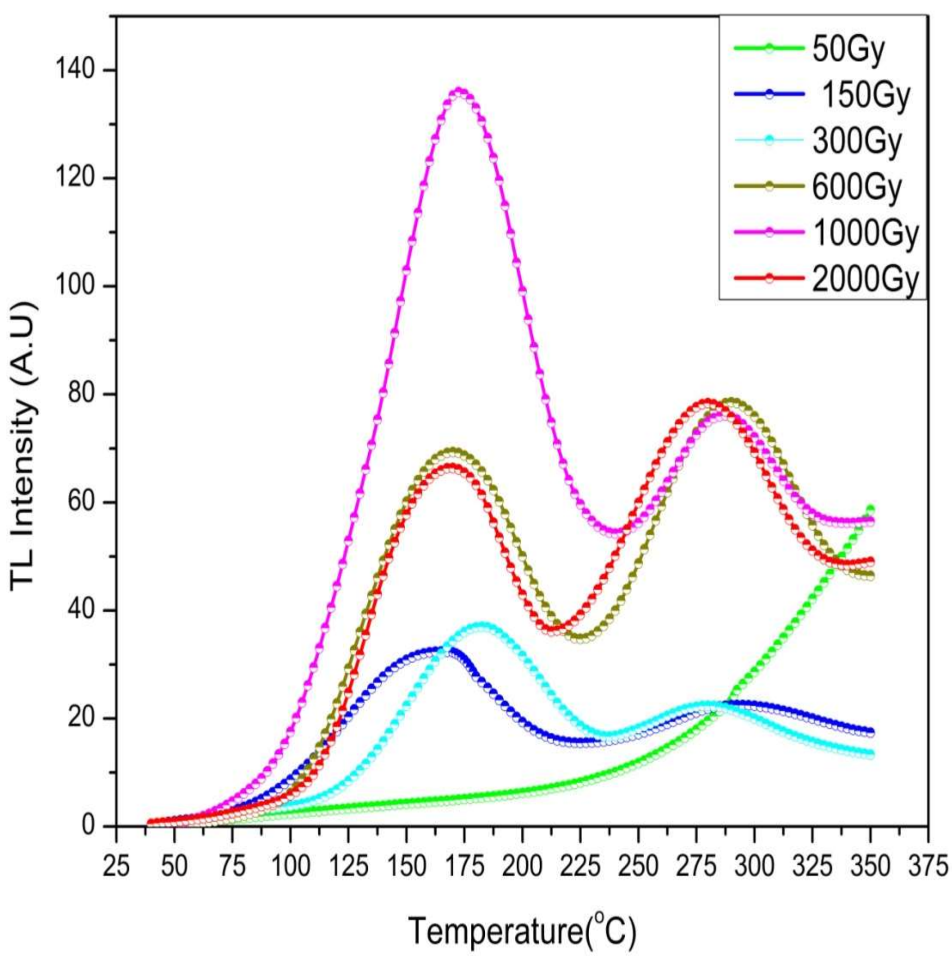


Figure 3: TL glow curve - $SrAl_2O_4$:Eu(1%) exposed with various γ-dose.

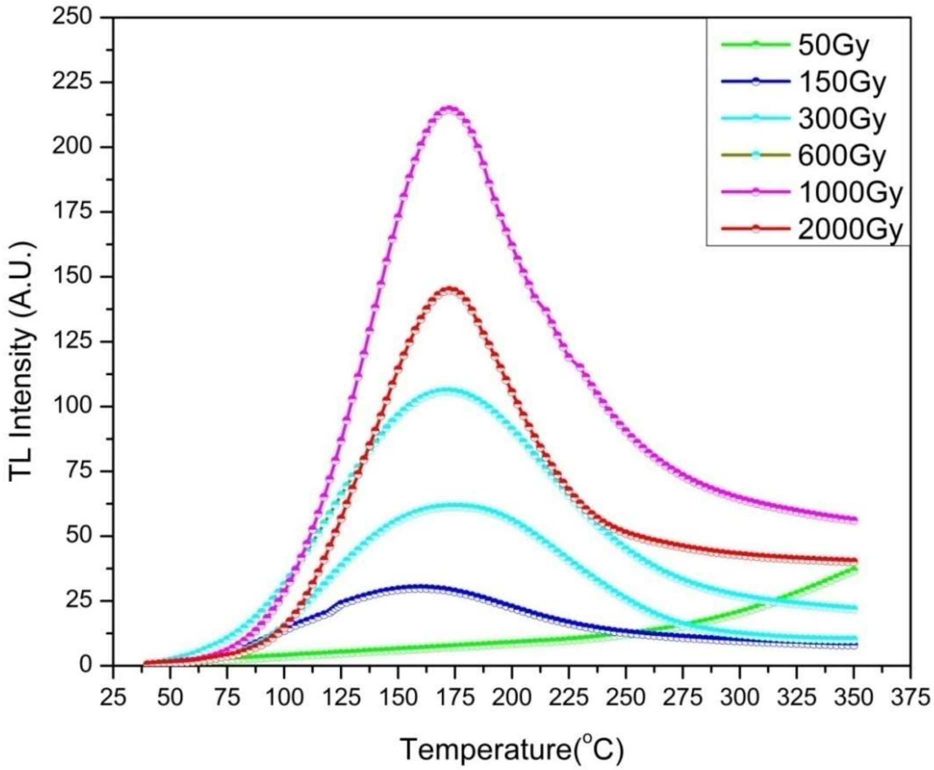


Figure 4: TL glow curve - $SrAl_2O_4$:Eu(2%) exposed with various γ-dose.

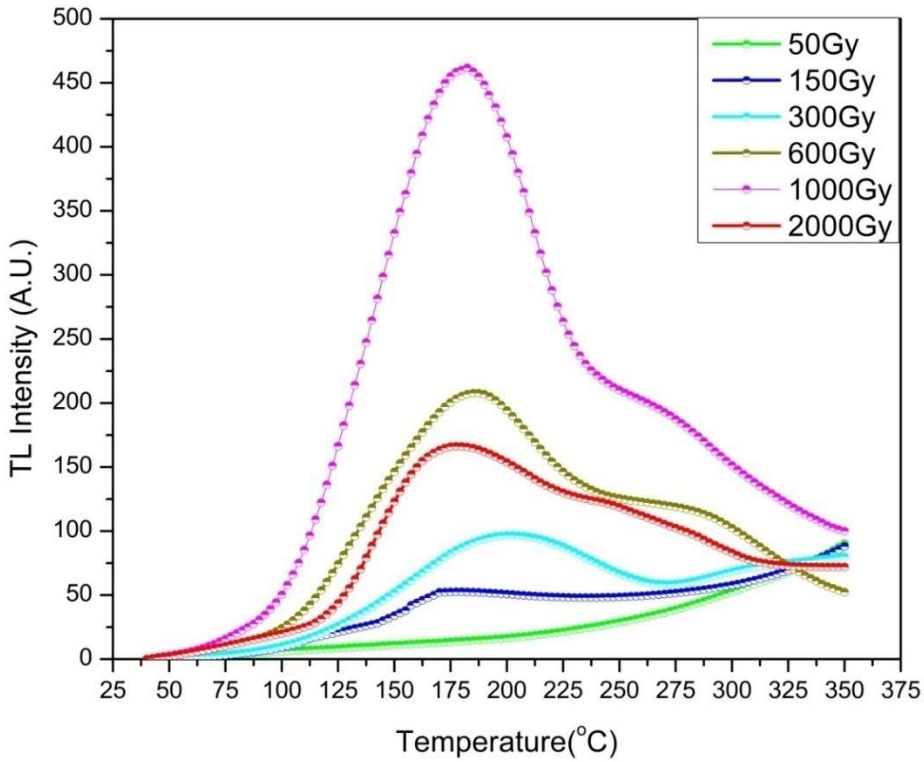


Figure 5: TL glow curve - $SrAl_2O_4$:Eu(5%) exposed with various γ-dose

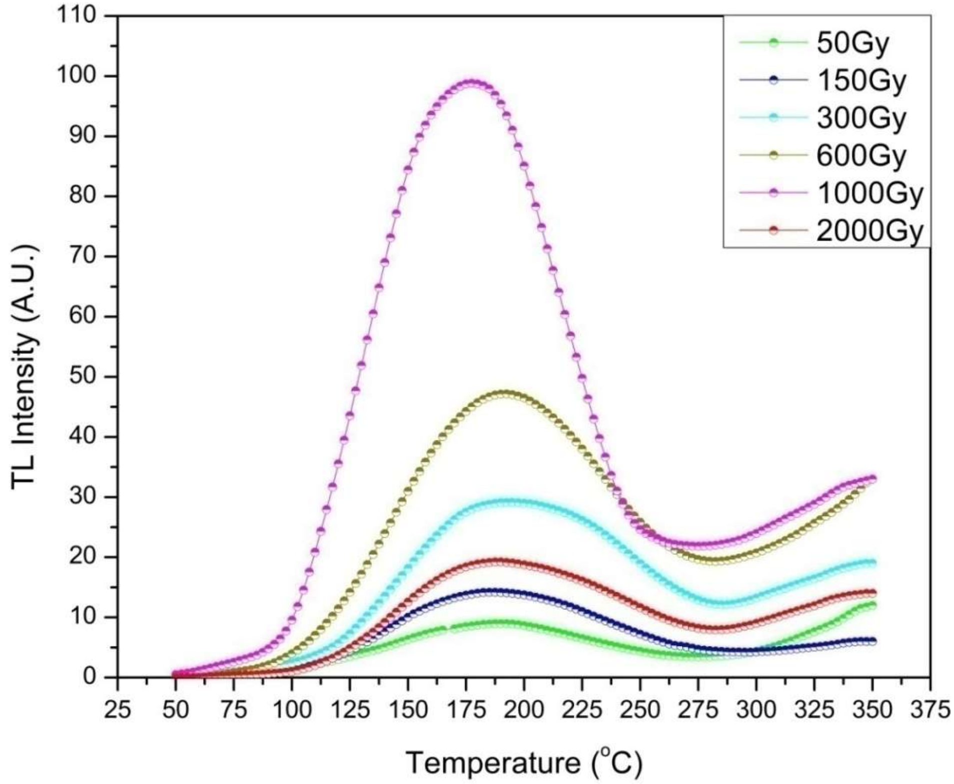


Figure 6:TL glow curve - $SrAl_2O_4$:Eu(7.5%) exposed with various γ-dose

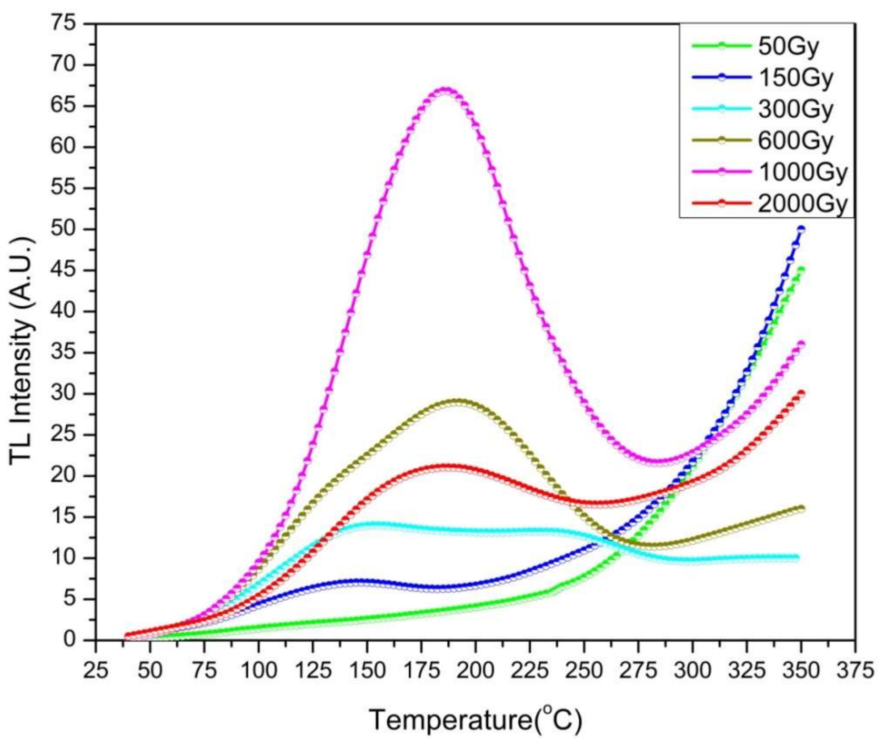


Figure 7: TL glow curve - $SrAl_2O_4$:Eu(10%) exposed with various γ-dose

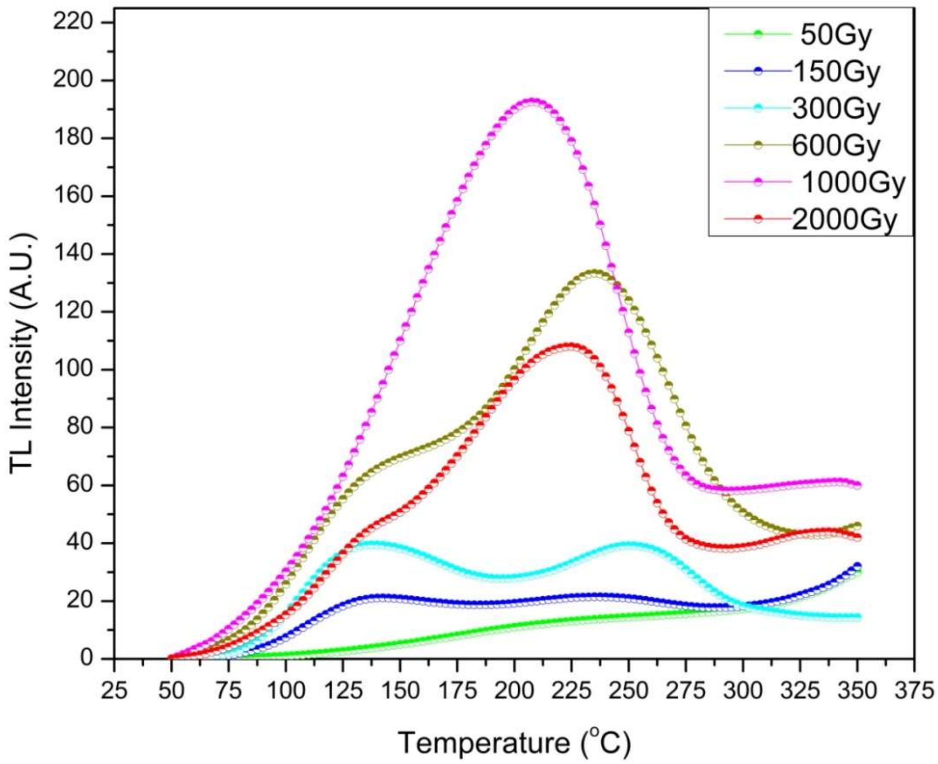


Figure 8: TL glow curve - $SrAl_2O_4$:Eu(12.5%) exposed with various γ-dose

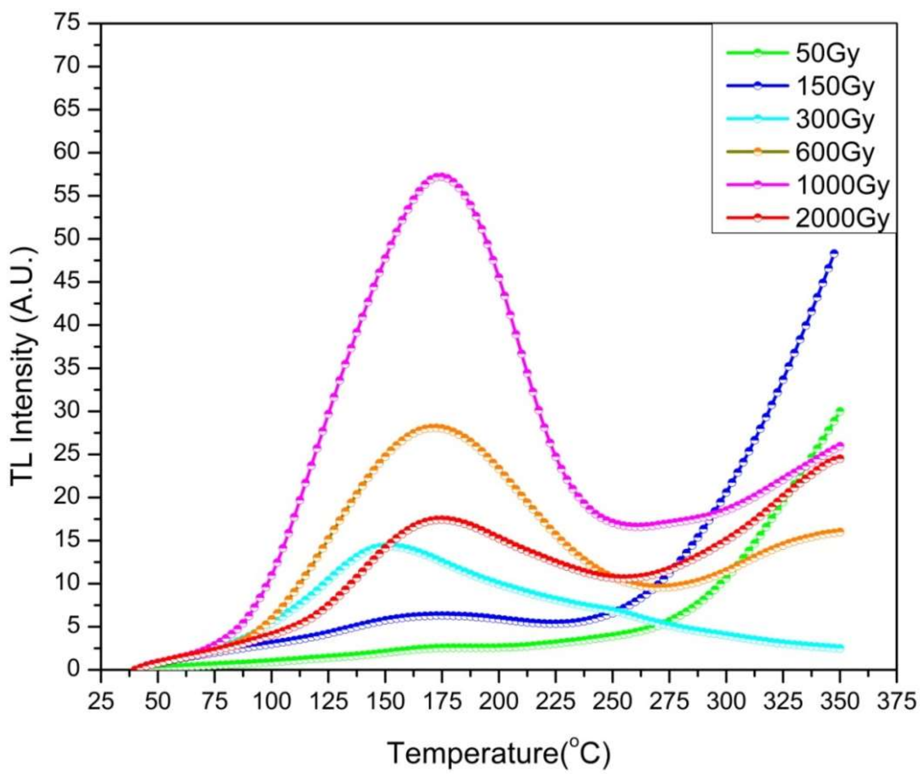


Figure9: TL glow curve - $SrAl_2O_4$: Eu(15%) exposed with various γ-dose.

The TL Glow curve consists of two peaks around temperature 175ºC and 270ºC for 1molar% concentration of Eu. Doping of rare earth elements creates discrete energy states within the forbidden gap of phosphor material which increases TL output. TL glow curve is similar for all concentration of Eu doping. When intensity of first peak increases,the second peak appears like shoulder and further increase in intensity of first peak, the second peak merges with first one and we find a slight shift in position of first peak towards second peak. Peak around 350ºC does not depend on dopant concentration and amount of dose, such peak is termed as spurious glow. Possibility of this glow may be due to the charge which may be unintentionally transferred from deep traps to dosimetric traps during irridation or may be due to trapping of charge in the trap as a mechanical effect (friction or grinding). Electrostatic charge or self dose is also considered for spurious glow.

To study the effect of Eu concentration, glow curves are deconvoluted and change of intensity of peak were observed. First peak increases linearly with γ-dose up to 1000Gy. Figure-10 shows the doping effect of Eu concentration on first peak of $SrAl_2O_4$:Eu irradiated at 1000 Gy of γ-dose of exposure.Intensity of TL were found to be increases linearly with dopant concentration of Eu and maximum value of intensity were found for 5 molar% concentration, then further decreases due to quenching[21]. Concentration quenching process is complicated in Eu doped $SrAl_2O_4$ phosphor because Eu substitute $Sr^{2+}$ ion. $Sr^{2+}$ ions are having two different sites with coordination no. 6 and 8, $Sr_1$& $Sr_2$. When Sr ions are substituted by Eu ions, there are $Eu_1$ and $Eu_2$ luminescence centre. As the concentration increases, distance between luminescence centre decreases, and luminescence intensity decreases when transfer of energy between centre starts. Distance between $Eu_1$-$Eu_2$ is shorter than $Eu_1$-$Eu_1$ or $Eu_2$-$Eu_2$, therefore increase in Eu concentration transition due to $Eu_1$ is quenched by transfer of excitation energy from $Eu_1$ to $Eu_2$.

Further increasing the concentration transfer of excitation energy from $Eu_2$ to $Eu_2$ adjacent to non luminescence centre take place. These are two possible mechanism for two peak in TL intensity at 5 and 12.5 molar% concentration of Eu.

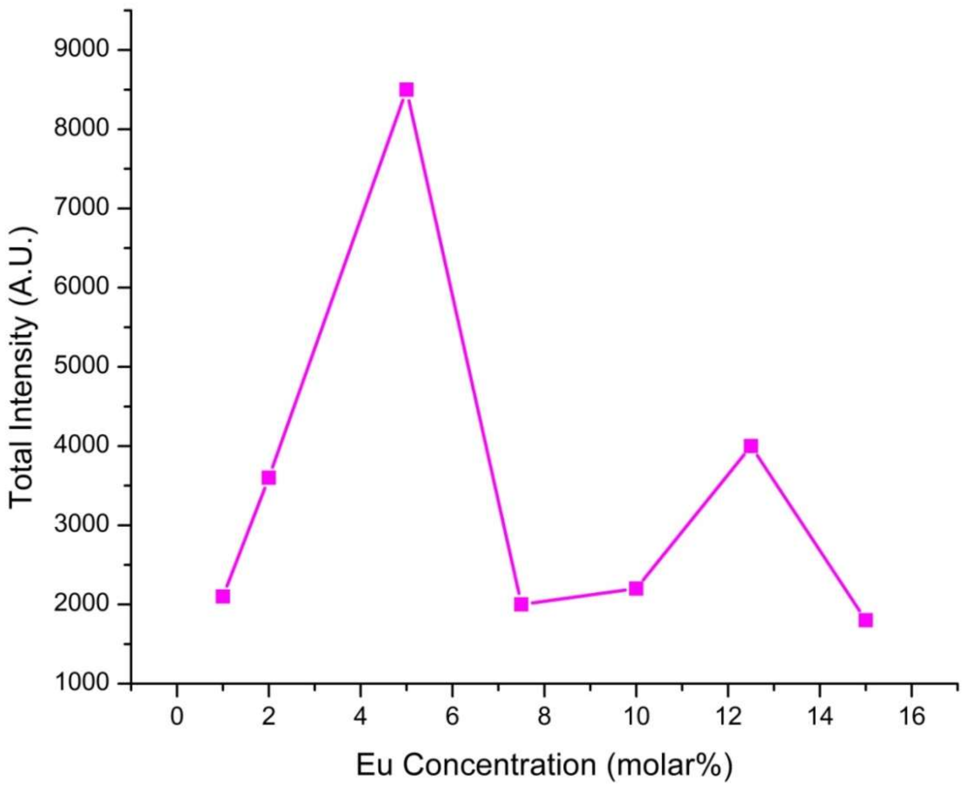


Figure 10:Total TL Intensity vs Eu Concentration in $SrAl_2O_4$ irradiated with 1000 Gy of γ-dose.

We observe the TL intensity is maximum at 5molar% concentration of Eu irradiated 1000Gy of γ-dose, hence TL kinetic parameter is calculated for the same. We consider first two peak for calculation of TL kinetic parameter.TL parameter is determined by Chen`s method. In this method geometrical shape of peak is used to determine the kinetic parameter of phosphor[22]. Let the temperature corresponding to maximum TL intensity is $T_m$ and $T_1$ is the temperature corresponding to half intensity with low temperature side of peak with $\tau(=T_m-T_1)$ is the half width, similarly $T_2$ is the temperature coresponding to half intensity with high temperature side of peak with $\delta(=T_2-T_m)$ is half width and total half width$\omega(=T_2-T_1)$,

Then frequency factor is defined as

$$\mu=\delta/\omega \ldots(2)$$

Activation energy is given as

$$E_\alpha=c_\alpha(kT^2_m/\alpha)-b_\alpha(2kT_m) \ldots(3)$$

Where, $c_\alpha$ and $b_\alpha$ are constant of Chen`s equation.

Frequency factor is given as

$$s = \frac{\beta E}{kT^2_m} \exp\left(\frac{E}{kT_m}\right)\left[1+(b-1)\frac{2kT_m}{E}\right]^{-1} \ldots(4)$$

Where $\beta$ is heating rate and k is boltzman constant. Kinetic parameter is calculated by Chen`s method and shown in table-1.

Table -1 Kinetics parameter by Chen`s method for Peak 1

| Dose | $\mu$ | $E_\tau$ (in eV) | $E_\delta$( in eV) | $E_\omega$ (in eV) | $S(s^{-1})$ |
|---|---|---|---|---|---|
| 50 Gy | 0.52 | 0.28 | 0.39 | 0.34 | $3.16\text{x}10^2$ |
| 150 Gy | 0.52 | 0.44 | 0.52 | 0.48 | $1.80\text{x}10^4$ |
| 300 Gy | 0.51 | 0.49 | 0.58 | 0.54 | $4.66\text{x}10^4$ |
| 600 Gy | 0.49 | 0.48 | 0.57 | 0.53 | $6.15\text{x}10^4$ |
| 1000 Gy | 0.51 | 0.64 | 0.71 | 0.68 | $6.03\text{x}10^6$ |
| 2000Gy | 0.52 | 0.66 | 0.72 | 0.69 | $8.76\text{x}10^6$ |

TL characterstic of a material is defined by parameter like kinetic order, trap depth and frequency factor. The Symmetry factor $\mu$ determines the order of kinetics for phosphor[23-24]. It is observed that first order kinetics does not shows any shift in the location of TL intensity for different doses while other glow peak maximum intensity tends to shift toward higher temperature. Activation energy increases with increase in γ-dose which may be due to excitation of charge carrier from deeper levels.

TL spectra is recorded with optical filters for $SrAl_2O_4$:Eu (5 molar%) at 1000Gy of dose exposure (figure-11).

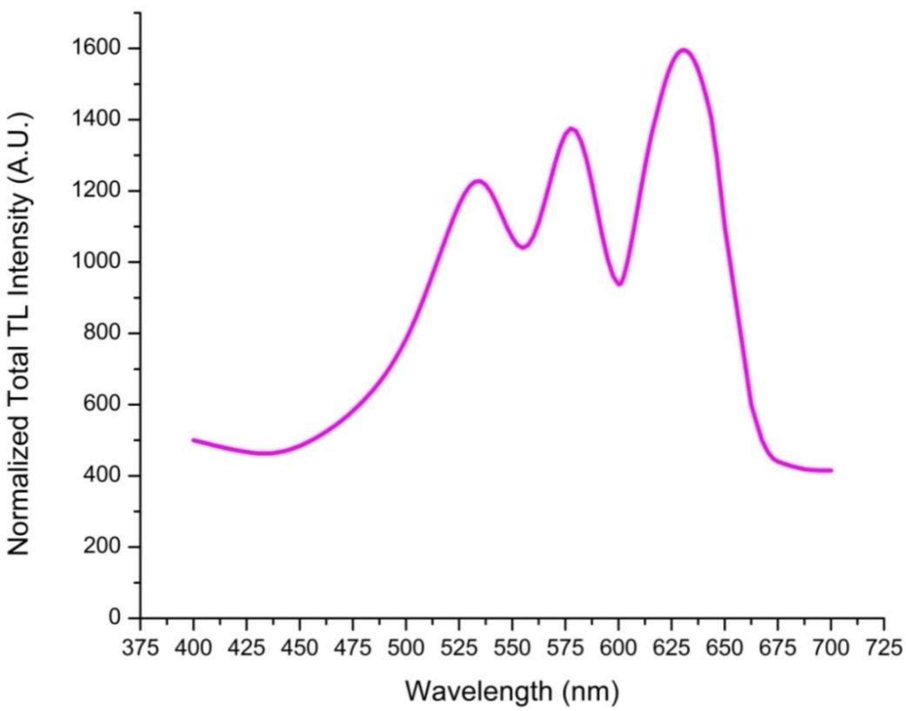


Figure 11: TL spectra of $Sr_{0.95}Al_2O_4:Eu_{0.05}$ irradiated with 1000Gy of γ-dose.

TL spectra shows peaks at 530 nm, 575 nm, and 630 nm[25]The peak at 575 nm and 630nm is correspond to $^5D_0$-$^7F_0$ and $^5D_0$-$^7F_2$ transition of $Eu^{3+}$ and the peak 530 nm is correspondto $4f^65d^1$-$4f^7$ transition of $Eu^{2+}$.

## Conclusion

The present study gives the basic understanding of TL properties ofEu doped alkaline earth aluminates. $SrAl_2O_4$ is chosen for study, as this phosphor is a best host for rare earth dopants,and comparably more thermal and chemically stable. Samples are prepared through solid state reaction method. Samples preparedthrough this methods are:$SrAl_2O_4$ ($Sr_{1-x}Al_2O_4:Eu_x$with x=0.01, 0.025, 0.05, 0.075, 0.1, 0.125, 0.15). Samples are characterized by X-ray diffractometer, which confirms the formation of monoclinic $SrAl_2O_4$. Diffraction pattern results are well matched with JCPDS card no. 34-0379 with lattice parameter a=8.442 Å, b=8.822Å, c=5.160 Å space group [$P2_1$]. The particle size is estimated using Scherrer formula and found to be 81nm. XRD pattern do not show any considerable change in structure due to rare earth doping. The results indicate that the doped Eu ions does not have any significant influence on structure of crystalline phosphor because of nearly same ionic radii of $Eu^{2+}$(0.112nm) and $Sr^{2+}$(0.114nm). TL glow curve shows two peaks around 175ºC and 275ºC for 1 molar% concentration of Eu.Initially positive correlation have been observed between TL intensity and Eu doping concentration. The maximum TL intensity were found for 5molar% concentration. Above this concentration quenching is observed. Further the concentration of Eu increases in $SrAl_2O_4$, another peak at 12.5molar% concentrationis found which may be due to presence of Eu in two different sitesof $Sr^{2+}$. We do not found significant change in TL intensity at low doses, hence higher dose of radiation is given to phosphor. Glow curve peak around 175ºC increases linearly with γ-dose up to 1000Gy and it is considered as a dosimetric peak. Hence phosphor can be used for dosimetric purpose in this linearity region, except at very low dose where TL responce is not significant. Kinetic parameter is calculated by Chen`s method, which suggest that both the peak follows the second order kinetics. TL spectra shows peaks corresponding to transition $4f^65d^1$-$4f^7$ of $Eu^{2+}$(530nm), $^5D_0$-$^7F_0$ of $Eu^{3+}$(575 nm) and $^5D_0$-$^7F_2$ of $Eu^{3+}$(630nm). This paper includes comprehensive study of TL measurement, TL spectra and effect of molar concentration of Eu on $SrAl_2O_4$ phosphor.

## Acknowledgement

I would like to thanks **Dr. Vivek Choudhary** (Dean Pt. J.N.M. Medical College, Raipur) for encouragement and assistance for the study. I would like to thanks all the staff of Departmentof Physics, Shri Rawatpura Sarkar University, Raipur for supporting throughout the study.

## Conflict of Interest

The authors declare no conflict of interest.

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