# Effect of Annealing Temperature on Thermoluminescence of Rare Earth Doped $CaSO_4$

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***Abstract* –Nanoparticles of rare earth doped $CaSO_4$ with size around 28 nm were prepared for high temperature radiation dosimetry applications, via Wet Precipitation Method. Samples were characterised by XRD, UV-Vis and TL techniques. Phosphors annealed at different temperatures were exposed to 6MeV and 15MeV energy photon beam and the TL responses were recorded. Samples annealed at 900º C for 2 hours gave maximum TL response. The peak emission temperature observed for the prepared phosphors was 356 º C which is very high compared with the standard phosphor $CaSO_4$: Dy which is around 240ºC. The XRD pattern showed orthorhombic structure.**

***Keywords: Thermoluminescence, Dosimeter***

## I. INTRODUCTION

Thermoluminescence has applications in Archaeology, Geology, Biology, Forensic Science, Space Science etc and its most striking application is in Radiation Dosimetry [1]. The development of thermoluminescent dosimeters using $CaSO_4$ has a very long history due to its high sensitivity, simple structure, and good chemical and thermal stability. A large number of variants have been proposed from time to time. Rare earth doped $CaSO_4$ are excellent thermoluminescent phosphors and $CaSO_4$: Dy and $CaSO_4$: Tm are important among them due to high sensitivity and very low fading when stored under standard environmental conditions. They are very useful in monitoring radiation levels from various sources [2, 3, 4]. Co doping in very small quantities plays an important role in the luminescence efficiency of the phosphor. It may enhance or subside, the thermoluminescence efficiency depending on the host dopant lattice matching. Attempts to improve the thermoluminescence characteristics of $CaSO_4$: Dy and $CaSO_4$: Tm, are sustained till date. The present work reports a new phosphor with a very high TL peak temperature. The phosphor is prepared by co-doping $CaSO_4$: Dy with suitable co-dopant. [3, 4]. The phosphor can be used for high temperature TL applications.

## II EXPERIMENTAL

Wet precipitation method was used for phosphor synthesis [8, 9]. All reactants were of analytical grade,

Merck. The wet precipitation of $CaSO_4$ occurs through the chemical reaction.

$$Ca(NO_3)_2 + (NH_4)_2SO_4 \longrightarrow CaSO_4$$

$Dy_2O_3$ and Sodium Meta Silicate (SMS) were used as dopants. Samples were prepared by varying dopant concentrations.

0.1M solutions of Ca $(NO_3)_2$ and $(NH_4)_2SO_4$ were prepared. Dopant solutions were added and the solutions were mixed under constant stirring using a magnetic stirrer and kept undisturbed for 24 hours. The precipitate was collected, washed with double distilled water and dried. The sample was calcinated at 500°C for 3 hours. The resultant phosphor was finely powdered, annealed at temperatures 700°C, 800°C and 900°C for two hours. The samples so obtained were subjected to different studies.

## III. RESULTS AND DISCUSSION

### *A. X-Ray Diffraction*

The X-ray diffraction studies were carried out using a Cu-$K_a$ target on Bruker AXS D8 Advance X ray Diffractometer. Fig 1 shows the X-ray Diffraction pattern of the phosphor. The pattern matches with JCPDS File number **37-1496** that of CaSO4. The phosphor is having orthorhombic structure with Bmmb (63) space group. The lattice parameters calculated were in good agreement with the standards reported.

| Lattice parameters reported | Lattice parameters calculated |
|---|---|
| a = 6.993A° | a = 6.985 A° |
| b= 7.001 A° | b = 6.987 A° |
| c = 6.241A° | c = 6.234 A° |

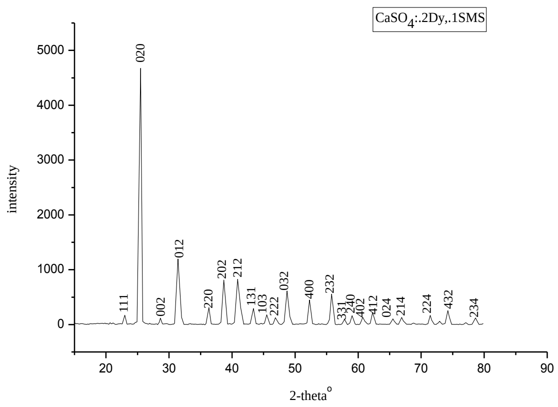


Fig 1: XRD pattern of the synthesized phosphor

The particle size was also calculated using Scherer's formula,

$$d = 0.9\lambda/\beta\cos\theta$$

assuming the particles are stress free [5, 6, 9]. The average grain size of the phosphor is approximately 28 nm.

*B. Thermoluminescence Study*

*1)TL Variation with Annealing Temperature*

The TL glow curve of the phosphors annealed at temperatures 700°C, 800°C and 900°C were recorded using a TL analyzer TL1007 NUCLEONIX at a heating rate of 10°C/sec after subjecting the phosphor to 6MeV and 15 MeV X-ray photon beam. Samples with two different dopant concentrations were prepared. $CaSO_4$:0.2Dy, 0.1SMS ($S_1$) and $CaSO_4$:0.3Dy, 0.1SMS ($S_2$). Figure 2 shows the TL glow curve of sample $S_1$ annealed at different temperatures and exposed to 6MeV photons.

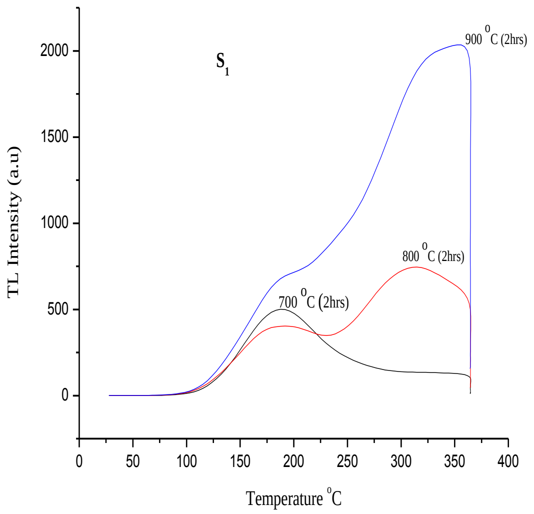


Fig 2: TL glow curve of sample $S_1$ (6MeV)

As annealing temperature increases, the temperature of emission shifts from $187^0$C to $356^0$C. The intensity of emission also increases. This implicates an increase in trap depth as well as effective trap filling. The phosphor annealed at $900^0$C gave maximum TL response. The very high emission temperature indicates the effectiveness of this phosphor to be used in high temperature radiation dosimetry applications. Fig: 3 shows the TL response for sample $S_2$ annealed at different temperatures and exposed to 6MeV. As in the case of sample $S_1$, the peak emission temperature is $356^0$C whereas the intensity of emission increases. This may be due to the increase in doping concentration of Dy.

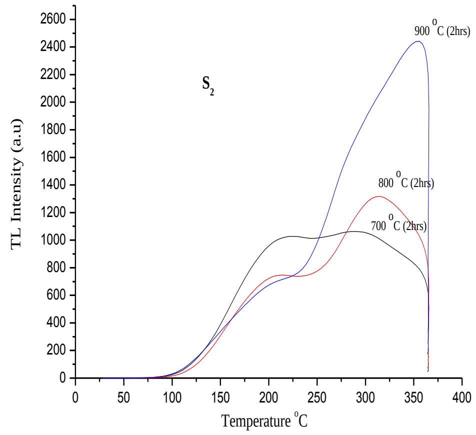


Fig 3: TL response for phosphor $S_2$ (6MeV)

The TL peak temperature of both $S_1$ and $S_2$ is very high compared with the standard phosphor $CaSO_4$: Dy used for dosimetric applications, which is around $240^0$C and intensity of emission is low. Low emission intensity may be due to the quenching effect of sodium ions present in the phosphor. Co- doping with SMS incerases the trap depth but gave less effective trap filling compared to standard. The main advantage of the emission peak at $356^0$ is its applications in high temperature radiation dosimetry [7, 8].

The energy dependence of a dosimeter decides its suitability in medical dosimetry. The phosphors $S_1$ and $S_2$ were subjected to photon radiation of 15 MeV energy and the TL responses were recorded. Fig: 4 show the TL response for sample $S_1$ and $S_2$ at energy 15MeV. From the figure it is clear that the glow curve intensity decreases in comparison with the phosphor irradiated at energy 6MeV. The peak emission temperature also shifted to the low temperature side. Interaction of X-radiation at 6MeV energy with the phosphor is predominantly photoelectric than the radiation at energy 15 MeV. The probability for a photoelectric phenomenon to occur is inversely proportional to the cube of radiation energy [8].

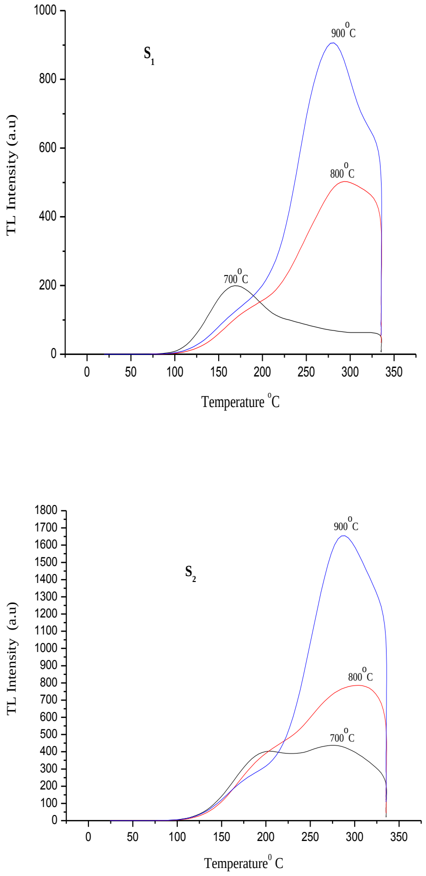


Fig 4: TL responses for $S_1$ and $S_2$ (15 MeV energy)

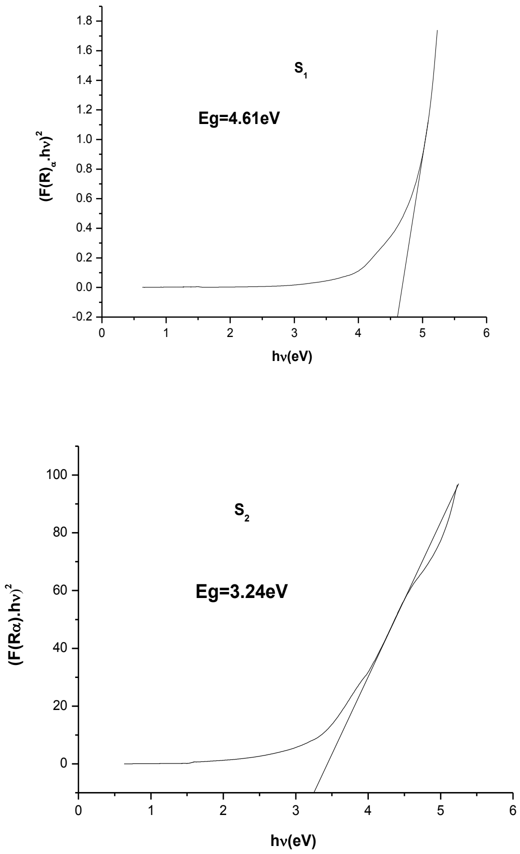


Fig:5 Kubelka-Munk plot for S1 and S2
The band gap for $S_1$ is $E_g$=4.61eV and for $S_2$ is $E_g$=3.24eV.

*B) UV-Visible Analysis*

The sample obtained after heat treatment was subjected to UV-VISIBLE analysis using Varian, Cary 5000 Spectrophotometer over a spectral range of 237nm to 1963nm. The Kubelka–Munk transformation of the measured reflectance can be given by the following equation;

$$K= (1-R)^2/2R=F(R)$$

where K is reflectence transformed according to Kubelka-Munk, R is the reflectancy (%) and F(R) is the Kubelka – Munk function. The band gap $E_g$ and the absorption coefficient α are related as

$$\alpha h\nu = A(h\nu-E_g)^{1/2}$$

If the compound scatters in perfectly diffuse manner, K becomes equal to 2α. So by using the equation

$$(F(R)\ h\nu)^2=A\ (h\nu-E_g)$$

band gap energy of the phosphor can be calculated by plotting $(F(R)\ h\nu)^2$ versus hν. X intercept of the linear region of the plot will give the band gap energy of the prepared phosphor [6, 10]. Figure 5 shows the Kubelka-Munk plot for samples $S_1$ and $S_2$ annealed at $900^0$C.

## IV. CONCLUSIONS

The samples were synthesized successfully. The prepared samples $CaSO_4$:0.2Dy,0.1SMS($S_1$) and $CaSO_4$:0.3Dy,0.1SMS ($S_2$) gave a very high TL emission temperature which makes it applicable in high temperature radiation dosimetry. The energy dependence on TL phenomena was also studied. Co-doping resulted in a huge shift in peak emission temperature from 240˚C to 356˚C compared with the standard phosphor used for dosimetry applications. Other properties like surface morphology, reusability, dose dependence, fading etc are to be investigated further.

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