High Temperature Thermoluminescence Emissions of $SrSO_4$ Nano Phosphors Doped with Eu and Mn

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***Abstract*— High temperature Thermoluminescence (TL) emissions of $SrSO_4$:Eu,Mn phosphor at 346^{0}C is reported here for the first time. The nanocrystalline phosphors were prepared by wet chemical precipitation method. The glow curve shows an intense peak at 346^{0}C, when the phosphor is subjected to X- irradiation. Co-doping with Mn enhances the trap depth and hence the TL emission temperature. Even though the luminescence intensity is found to be less, the phosphor becomes significant owing to its high temperature afterglow, which is one of the stringent requirements of a commercial thermoluminescent dosimeter (TLD). This phosphor appears to be fairly stable for TL measurements. Preliminary crystallographic and morphological studies of the phosphors were done using Powder X-ray Diffractogram and Scanning Electron Microscopy (SEM). The phosphor has a single phase orthorhombic structure and the crystallites are sized in nano range. The dopant compositions in the host matrix observed from the Energy Dispersive Spectra (EDS) were 0.18 atom% Eu and 0.13 atom% Mn. The single and well defined high temperature glow curve makes the phosphor suitable for high temperature radiation dosimetry applications.**

Keywords*— *Thermoluminescence, Radiation dosimetry.

I. INTRODUCTION

Thermoluminescent (TL) phosphors were proved to be highly sensitive radiation detectors and are widely used for radiation dosimetry applications. Thermal ejection of relatively stable electrons trapped by means of ionizing radiation with X-ray, gamma ray, alpha, e-beam or other fast particles leads to TL. Studies are on in the search of suitable host-dopant combinations due to the constant need for high sensitivity TL dosimetry phosphors for different applications [1]. Recently, nanostructured materials are on focus, because of their potential impact in many areas such as electronics, photonics, catalysis and sensing [2-4]. Among the various phosphors alkaline earth sulphates are of special interest due to their high TL sensitivity, stability and low cost [1]. TL properties of rare earth doped $CaSO_4$, $BaSO_4$, $SrSO_4$ and $MgSO_4$ with single as well as multiple dopants were studied recently. TL studies of Mn doped $SrSO_4$ compounds prepared via recrystallization method and irradiated by X-rays were done by J. Manam *etal*. [1]. Similarly, the TL performance of Eu doped $SrSO_4$ phosphors prepared through acid evaporation technique and irradiated with γ-rays were studied and reported by Q.Tang *etal*.[5] . Characteristics of the same host material prepared through a controlled chemical precipitation method by M. Kerikmäe *etal.* is also reported previously[6]. In many host lattices Mn is proved to be a best activator, when doped singly or codoped with rare earths [1,11,13]. Here the focus is on the TL properties of the $SrSO_4$:Eu nano phosphor co-activated with Mn. A much higher temperature TL emission is observed, when the phosphor is subjected to X-rays. An attempt is also made to estimate the activation energy corresponding to the trap from the geometry of the glow curve.

II. EXPERIMENTAL

$SrSO_4$:Eu,Mn nano phosphors were prepared by following the chemical precipitation technique described by Madhukumar *etal*.[7]. Analytical grade starting materials were used for the phosphor sample preparation. 0.5 mol% each of 99.995% pure Eu_2O_3 and MnO_2 were used for doping. After necessary washing, filtering and drying the precipitate was calcined at 400^{o}C for 1 hour to eliminate the traces of any other compounds or acids. Further, the calcined material was ground well and then annealed at 1050^{0}C in a programmable high temperature furnace for 3hours in air atmosphere, for the required crystalline phase formation.

Subsequently, various characterization studies were carried out. The crystalline properties were studied from the X-ray diffractogram taken from XPERT PRO Diffractometer using Cu K_α radiations of λ= 1.5406Å. SEM micrographs and EDS spectra obtained using JEOL 6390LV make Scanning Electron Microscope with EDS attachment were analysed. Thereafter, the thermoluminescence glow curve at a heating rate of 5^{0}C/s were recorded with a TL analyzer TL1007 NUCLEONIX. About 5 mg of the phosphor powder sample was used all the time for recording the TL readout, since the amount of phosphor sample influence the TL intensity. Pre-irradiations were made with Cu K_α X-rays generated at 20KV, 10mA from RADON make X-Ray unit before recording the TL.

III. RESULTS AND DISCUSSIONS

A. *Structure Analysis*

Fig.1 shows the typical X-ray diffraction pattern of the prepared $SrSO_4$:Eu,Mn nano phosphor. The spectrum shows orthorhombic lattice structure with Pnma 62 space group, in accordance with the JCPDS database of file number 00-001-0885. Observed and calculated *d*-values are in good agreement. The lattice parameters were found to be a=8.32Å, b=5.328 Å and c=6.80 Å, which are fairly in agreement with the parameters reported for the undoped host lattice, a= 8.36 Å, b= 5.36 Å, c=6.84Å. The slight deviation in the parameters may be presumably due to the interstitial incorporation of the Eu^{2+} and Mn^{2+} ions into the host lattice[1]. Effective crystallite size of the phosphors were calculated using the Scherer equation, assuming strain free line broadening of the diffraction peaks [2,8]. The estimated crystallite size from the line broadening of the highest intense peak corresponding to (240) plane was 32 nm, which confirms the nano nature of the phosphor. Estimated crystallite size from major peaks corresponding to other planes varies from 20nm to 70nm.

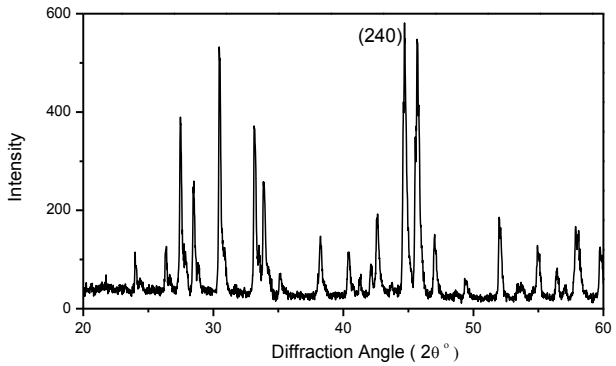
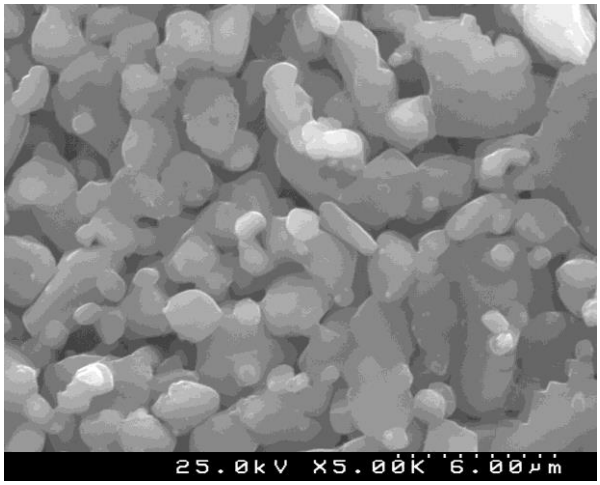


Fig.1. X-ray Diffractogram of $SrSO_4$:Eu,Mn nano phosphor

B. *Surface morphology and composition*

- From the SEM micrographs shown in fig.2, it is seen that the phosphor has a uniform distribution of particles of different morphologies. While, the spherically shaped small particles of almost uniform size are of 1µm diameter. Larger particles of irregular shape have an average dimension of 5x2 µm. The morphology mainly depend on the chemical conditions, temperature , mass flow etc. during synthesis[9]. The structural features of the material like crystallite size, particle morphology , particle size etc. will influence the luminescence efficiency [9,11,13].



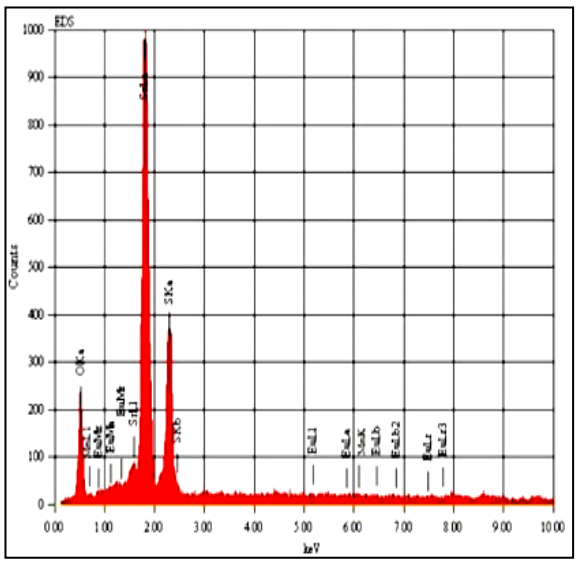
- Fig.2. SEM Micrographs of SrSO4:Eu,Mn phosphor

- The Energy Dispersive Spectral technique (EDS) was used to detect the chemical composition of the phosphor. Fig.3. shows the EDS spectra of the prepared $SrSO_4$:Eu,Mn nano phosphor.

- The spectra detect a composition of 0.18 at% of Eu and 0.13at% of Mn. The actual concentrations used for doping during synthesis were 0.5mol% of each dopants. No other significant impurities are found in the spectra.

TABLE 1. ELEMENTAL COMPOSITION

Element	Atom%
O	21.08
S	22.49
Sr	56.12
Eu	0.18
Mn	0.13



- Fig.3. Energy Dispersive Spectra of $SrSO_4$:Eu,Mn (0.18,0.13 at%) phosphor

C. *Thermoluminescence Studies*

The TL glow curves of the prepared phosphor powder samples were recorded at a heating rate of 5^0C/s after irradiating with Cu K_α X-ray beam generated at 20KV, 10mA from RADON make X-Ray unit at room temperature for 30 seconds. Fig.4 shows the recorded glow curve of the phosphor after background subtraction. It shows a single isolated peak at 346^0C. Previously, an X-ray storage emission at 277^0C was reported for $SrSO_4$:Eu phosphor prepared through a controlled chemical precipitation method by M. Kerikmäe *etal*.[6]. The glow curve indicates the suitability of the phosphor to detect very small exposures of low energy X-rays. But the intensity of emission is found to be less than that of $SrSO_4$:Eu phosphor. This can be attributed to the fact that codoping with Mn decreases the efficiency of trap filling, but enhances the trap depth. The general order kinetics can be applied to fit the glow curve. The trap depth (E) corresponding to 346^0C peak calculated using Peak Shape Method is found to be 1.59eV.

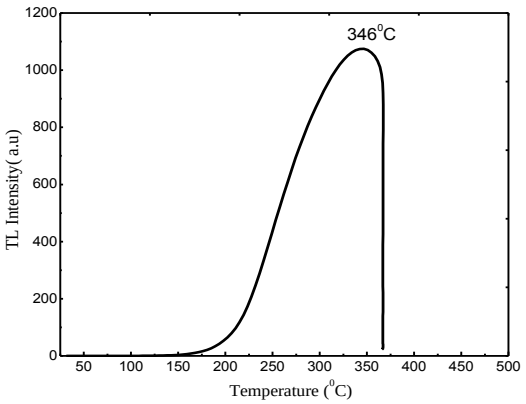


Fig.4. TL glow curve of X-irradiated $SrSO_4$:Eu,Mn nano phosphor. The emission peak is at 346°C.

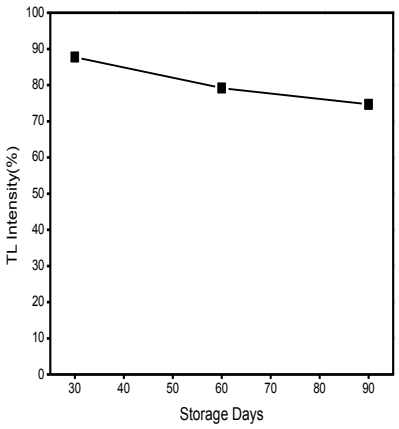


Fig. 5. Effect of storage on TL intensity of $SrSO_4$:Eu,Mn

Fig.5 shows the fading of TL intensity of $SrSO_4$:Eu,Mn with respect to storage days. While the fading is 12.23% after 30 days, it is only 25.35% after 90 days, indicating the stability of the phosphor. The percentage fading of the prepared nano phosphor is listed in table 2. Accepted convention is that the fading of a phosphor should be below 20% at ambient temperatures upto 50°C for dosimetric applications [14]. The well defined high temperature dosimetric peak of the $SrSO_4$:Eu,Mn phosphor together with its stability makes it a good candidate for TL measurements over a long period.

TABLE 2. FADING OF $SrSO_4$:Eu,Mn

Day	Fading (%)
30	12.23
60	20.82
90	25.35

IV. CONCLUSION

To summarise, $SrSO_4$:Eu,Mn nano phosphors were successively synthesized by wet chemical precipitation method. The study reveals that multiple doping with Eu and Mn in the $SrSO_4$ host lattice can produce excellent high temperature X-ray phosphor. The phosphor exhibits single and well defined dosimetric peak at 346^0C , much higher than that for $SrSO_4$:Eu phosphor for X-rays reported earlier. The fading is found to be comparatively low. Even though the TL sensitivity is decreased to some extent by the coactivtaion of Mn, because of the high dosimetric peak and low fading it can find potential applications in high temperature dosimetry over an extended period. The dependence on energy and dose of irradiation and reproducibility of the phosphor are to be investigated further.

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