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Thermoluminescence Properties and Trap Parameters Determination of $CaSO_4$:Dy,P,Si Phosphor under X-Ray Excitation.

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ABSTRACT

Detailed thermoluminescence analysis were done on $CaSO_4$:Dy,P,Si phosphor under X-ray excitation. Method of preparation was conventional solid state synthesis. Powder X-ray diffraction pattern of the phosphor was taken to ascertain phase conformation. TL properties of the phosphor were recorded after subjecting it to X-rays for a time period of 60seconds. The most striking observation from the TL analysis is a peak emission temperature at 360^0C with a very good intensity of emission. The dosimetric peak emission temperature is very high compared to any other commercially available standard dosimeters being used at present. Kinetic analysis of the experimental TL glow curve has been carried out using glowcurve deconvolutionmethod to determine the trapping parameters which is a pre requisite to study the dosimetric properties of any phosphor.

Keywords: Thermoluminescence, Trapping parameters, Glow curve deconvolution.

I. INTRODUCTION

Thermoluminescence is the light emission during heating of a sample that has been previously subjected to high energy radiation. Defects and traps in the host lattice can be effectively studied using TL since it involves radiative recombination of thermally released holes or electrons from their traps[1,2]. The main objective of TL experiments is to extract data from glow curves to calculate the values for various parameters associated with the luminescence processes which include activation energy(E), frequency factor(s) and order of kinectics(b)[3]. TL intensity depends strongly on the material, impurities used, lattice defects, dose and type of ionising radiation. The applications of TL include radiation dosimetry, forensic sciences, radiation protection, geology and archeology. Among various TL phosphors, $CaSO_4$:Dy is the most important and widely used one. Lots of works were already done on $CaSO_4$:Dy with various co-dopants and the studies are still on due to its high sensitivity and low fading characteristics. Phosphorous is found to be a very good co-dopant in $CaSO_4$:Dy with good TL characteristics [4,5].

Here the development of a high temperature TL phosphor with Si as a second co-dopant in $CaSO_4$:Dy,P, prepared through solid state synthesis method is reported.

II. EXPERIMENTAL

2.1. Preparation

The phosphor powder samples of $CaSO_4$: Dy,P,Si(0.1mol%,0.1mol%,0.1mol%) were prepared through solid state synthesis[6]. Reactants used for preparation were $CaCO_3$, $(NH_4)_2SO_4$, $Si(OOCCH_3)_4$, Dy_2O_3 and $(NH_4)_2HPO_4$. Acetone was used as the wetting medium during the synthesis. It is non-reacting with the starting materials and ensures the uniform mixing. The reactants were taken and mixed thoroughly in a motorised agate along with dopants for 1 hour. The reaction governing the process is

$$CaCO_3 + (NH_4)_2SO_4 \longrightarrow CaSO_4 + (NH_4)_2CO_3 \qquad (1)$$

The residue was transferred in to an alumina crucible and given a primary calcination at 500^0C for 3 hours and then allowed for a slow cooling. The resultant phosphor powder was subjected to annealing at various temperatures in the range 700^0Cto 1200^0C and the TL properties were analysed under X-ray excitations.

2.2 Characterization

The room temperature PXRD pattern of the phosphor was taken from a Bruker Axis D8 Advance Diffractometer with Cu-K_α radiation to confirm phase formation. The thermal stability of the phosphor was analysed using TGA spectrum obtained from Perkin Elmer STA6000 TG Analyzer, in nitrogen atmosphere at a flow rate of 20ml/min and at a heating rate of 10°C/min. The surface morphology of the phosphor was studied using Jeol 6390 LV model Scanning Electron Microscope. All the TL measurements were performed using a TL1007- NUCLEONIX Analyser. For X-irradiation, beam generated at a maximum energy of 30 KeVfrom a Radon make source of Half Value Thickness (HVT) 0.5mm of Aluminium was used. X-rays from a therapeutic source of 6MeV energy was also used for TL analysis. TL glow curves were recorded at a constant heating rate, $\beta=10^0$C/s and its TL intensity is measured in terms of the peak height of the glow peak.5mg samples were used for each TL measurement. Computerised Glow Curve Deconvolution (GCD) were done on experimental glow curve of the phosphorirradiated with 30 KeV energetic X-rays.

III. RESULTS AND DISCUSSION

3.1 X-ray diffraction studies

Fig.1 shows the X-ray diffraction pattern of prepared $CaSO_4$:Dy,P,Si(0.1mol%, 0.1mol%, 0.1mol%) phosphor. The pattern matches with the standard $CaSO_4$ as per ICDD File No 72-0916.The phosphor possesses orthorhombic structure with Amma(63) space group. The calculated lattice parameters are in good agreement with the reported standards.The lattice parameters are mentioned in table 2.

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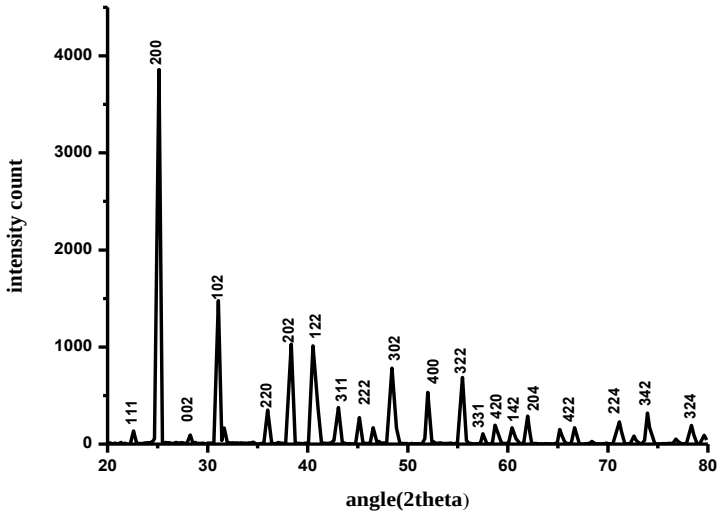

Fig.1 X-ray diffraction pattern of $CaSO_4$:Dy,Si,P (0.1mol%, 0.1mol%, 0.1mol%) phosphor.

Table1:Lattice parameters obtained from PXRD pattern.

Lattice	a(Å)	b(Å)	c(Å)
ICDD file no 72-0916	7.006	6.998	6.245
$CaSO_4$:Dy,Si(0.1mol%,0.1mol%)	7.04	7.006	6.276
$CaSO_4$:Dy,P,Si(0.1mol%,0.1mol% ,0.1mol%)	7.082	7.000	6.298

The XRD pattern of the prepared $CaSO_4$:Dy,Si, P shows a lower shift in 2θ value than the standard JCPDS data. Lattice shows expansion.The expansion or contraction of the lattice is usually the net result of the contribution due to oxidation states of host and dopants, size of dopants and the number of dopants. Here the lattice expansion is a result of the number of dopants used in phosphor preparation. A comparison of the cell volume comparisons of different lattices are given in table 1.

Table 2Comparison of cell volumes obtained from PXRD pattern

Lattice	Cell volume ($Å^3$)
$CaSO_4$	308.18
$CaSO_4$:Dy(0.1mol%)	309.05
$CaSO_4$:Dy,Si(0.1mol%,0.1mol%)	309.59
$CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%)	312.23

3.2Thermal stability

The thermal stability of the $CaSO_4$:Dy,Si(0.1mol%,0.1mol%) phosphor upto 1000^0Cwas studied by recording the Thermogravimetry (TG) curve with mass variation against temperature.Since TGA was done on annealed sample, no water loss is seen in the curve. The material appeared to be stable over the entire temperature scan. The slight mass reduction may be due to the drying of the sample during the course of time[7].

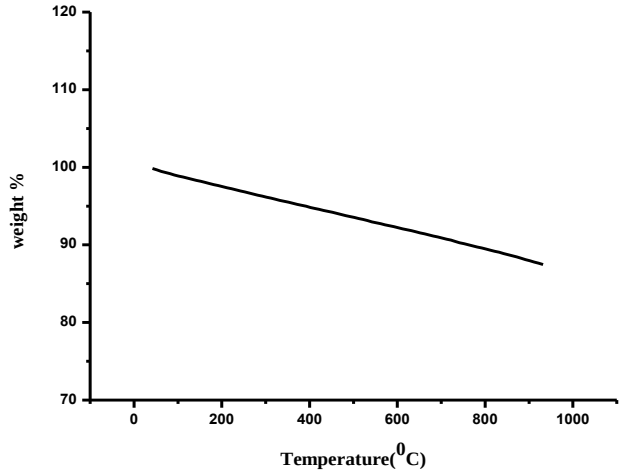

Fig. 2. TGA curve of $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%) phosphor

3.3 Surface Morphology: SEM

Particles with well-defined edges and having cuboidal shape with size in the micrometre range are seen. Size varies from single to a few micrometres. Particle size in micrometre range is a desirable characteristic of a phosphor for thermoluminescence to occur[7]. SEM micrograph for the phosphor $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%) is given in fig.3.

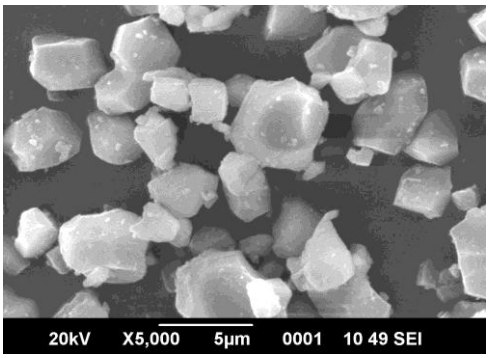

Fig.3 SEM micrograph of phosphor $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%)

3.4Thermoluminescence studies

3.4.1 TL studies under therapeutic X-ray excitation.

Phosphors annealed at different temperatures from 700^0C to 1200^0C were irradiated with 6MeV therapeutic X-rays and the TL glow curves were recorded. Annealing at 1000^0C gave maximum TL response. The glow curve is given in fig.4. The phosphor shows a peak emission temperature at 363^0C with a fairly good intensity of

emission. It also shows a shoulder peak at 180^0C with a very low intensity. The main peak is about 12 times intense than the shoulder peak.

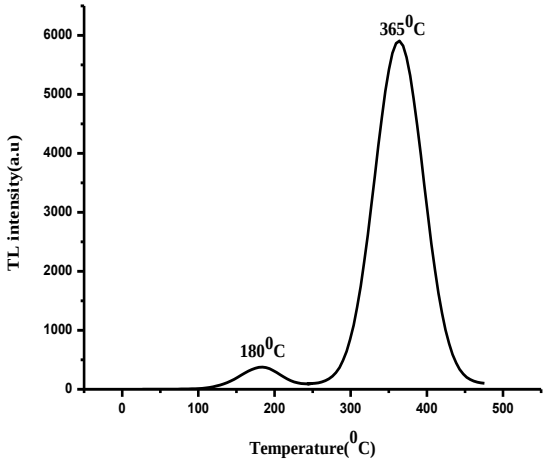

Fig.4 TL response of$CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%)phosphor irradiated with 6MeV therapeutic X-rays

3.4.2 TL studies underlow energyX-ray excitation.

Phosphors annealed at different temperatures were irradiated with 30keV X-rays and the TL responses were measured. As the high energy therapeutic X-rays, phosphor annealed at 1000^0C gave maximum TL response with a peak emission temperature at 360^0C with a shoulder peak at 170^0C, but with a very high intensity of emission. The glow curve of phosphor $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%) irradiated with 30keV X-rays is given in fig. 5.

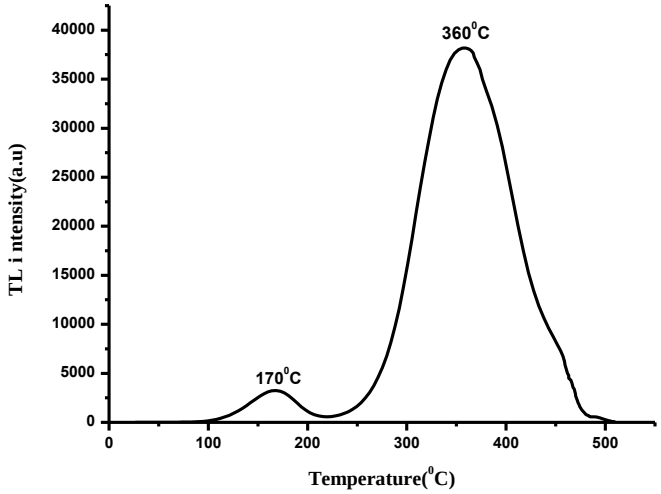

Fig.5 Glow curve of $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%) phosphor annealed at 1000°C and under 30keV X-ray excitation.

The energy dependence of a dosimeter decides its suitability in medical dosimetry applications.Excitations with 6MeV therapeutic X-rays and 30keV X-rays gave almost same peak emission temperature but with a different TL emission intensity. TL response for 30keV X-rays was almost 11 times intense than that for 6MeV therapeutic X-rays. Interaction of X-radiation at 30keV energy with the phosphor is predominantly photoelectric than the radiation at energy 6MeV. The probability for a photoelectric phenomenon to occur is inversely proportional to the cube of radiation energy.

3.4.2 Kinetic parameters

The kinetic parameters of the experimental glow curve for 30keV energetic X-rays were calculated using Glow Curve Deconvolution (GCD) method for general order kinetics suggested by Kiti's et al., given by [8]

$$I(T) = I_m b^{b/b-1} exp\left\{\frac{E}{kT}\frac{T-T_m}{T_m}\right\} \times \left[(b-1)(1-\Delta)\left(\frac{T^2}{T_m^2}\right) \times exp\left\{\frac{E}{kT}\frac{T-T_m}{T_m}\right\} + Z_m\right]^{-b/b-1} \quad (2)$$

where*I(T)* is the TL intensity at temperature T(K), I_m the maximum peak intensity, b order of kinetics, E activation energy(eV) and k the Boltzmann's constant.

$$\Delta = {2kT}/{E} \text{and} Z_m = 1 + (b-1)\Delta_m$$

Fig.6 shows the deconvolution of the glow peak of $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%). The kinetic parameters are given in table 3.The goodness of fit is calculated from the Figure Of Merit (FOM) given by

$$FOM = \frac{\Sigma|TL_{experimental} - TL_{fit}|}{\Sigma TL_{fit}} \quad (3)$$

and the FOM was calculated to be 0.51 which confirms a good agreement between theoretical and experimental glow curve [3].

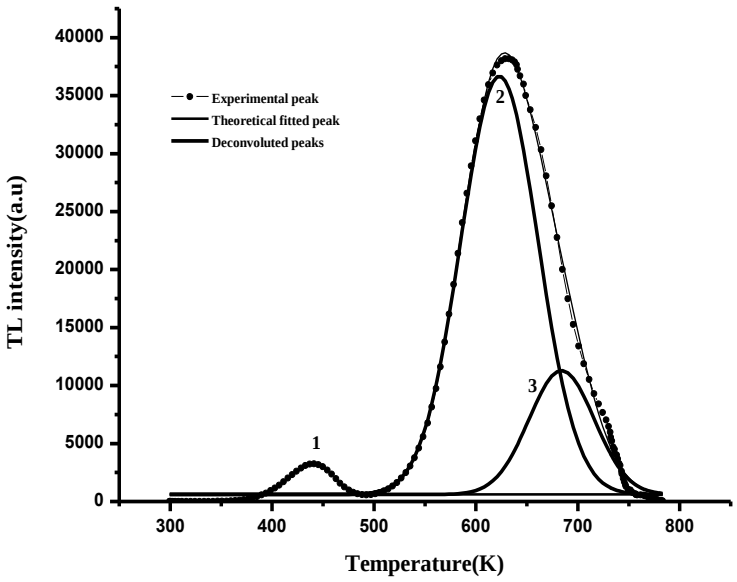

Fig.6 Glow curve deconvolution for $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%) phosphor exposed to 30keV energetic X-ray

Table 3. Kinetic parameters of $CaSO_4$:Dy,P,Si(0.1mol%,0.1mol%,0.1mol%), β=10°C/s

Peak number	T_{max}(K)	Order of kinetics(b)	Activation energy	Frequency factor
E(eV)	$S(s^{-1})$			
1	440	1.6	0.70	4.7×10^6
2	623	1.8	1.12	3.0×10^6
3	685	1.9	1.60	3.3×10^7

IV. CONCLUSIONS

The TL properties of Si co-doped $CaSO_4$:Dy,P phosphor prepared via conventional solid state synthesis is discussed. Phosphors were irradiated with 30keV X-rays and 6MeV therapeutic X-rays.TL response for 30keV X-rays was almost 11 times intense than that for 6MeV therapeutic X-rays.Interaction of X-radiation at 30keV energy with the phosphor is predominantly photoelectric than the radiation at energy 6MeV.The kinetic parameters are calculated using glow curve deconvolution method.

V. ACKNOWLEDGMENT

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