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Characterization and thermoluminescence studies of $CaSO_4$:Tm,Si phosphor under X-ray excitation.

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Abstract : $CaSO_4$:Tmphosphorsco-doped with silica prepared through solid state synthesis were subjected to a detailed thermoluminescence analysis. Preliminary studies were done for the structural characterization of the phosphor material.PL spectra were recorded to understand the emission mechanism. TL characteristics of the phosphor were recorded under X-ray excitations. The most noticeable feature of the $CaSO_4$:Tm,Si phosphor is the peak emission temperature around 365°C with a fairly large intensity of emission. The dosimetric emission temperature is very high compared to that of the commercially available standard phosphor $CaSO_4$:Dy. The fading was found to be around 7% over a period of 2 months. The observed properties of the Si co-doped $CaSO_4$:Tm phosphor made it suitable for its use in various radiation dosimetry applications.
Keywords : Thermoluminescence, Environmental Radiation Dosimetry, Photoluminescence.

1.Introduction

At present thermoluminescence (TL)dosimetry phosphors are used for personal and environmental radiation dosimetry applications. Among them$CaSO_4$based phosphors are of great interest since its high sensitivity thermoluminescence dosimeters has a long history. A large number of variants have been proposed as they are very suitable to monitor environmental radiations from natural sources. These phosphors possess high sensitivity as well as low fading[1,2]. $CaSO_4$:Tm and $CaSO_4$:Dyare well known for years due to their performance characteristics as well as ease in preparation and makes them useful tools in environmental radiation dosimetry applications. Bernal et al. studied the TL properties of Eu doped $CaSO_4$ via a cheap, easy and environment friendly method as the synthesis route plays an important role in TL properties of the phosphor [2].The mechanoluminescence (ML) and thermoluminescence studies of $CaSO_4$:Dyunder γ-irradiations were proposed by Kher et al. to provide a better understanding of defect centres formed in the lattice [3]. Lakshmanan et al. proposed a high sensitive $CaSO_4$:Dyphosphor via co-precipitation technique resulted in a better glow curve structure, better linearity, uniform morphology and grain size for the phosphor [4]. $CaSO_4$:Tm is widely used for measuring very small doses [5,6]. It has taken a decisive lead in individual and environmental radiation monitoring among the existing phosphors because of its high performance standards [7]. Efforts are on to improve the thermoluminescence properties of these phosphors worldwide. Energy transfer mechanism from one dopant to another is sometimes used to enhance the sensitivity of a phosphor. Co-doping of $CaSO_4$:Dywith Bi was investigated by Bakshi et al. in an effort to improve the TL properties of the phosphor [8]. Schmidt et al. studied the effect of 23 co-dopants in $CaSO_4$:Dy and concluded that none of these co-dopants improved the sensitivity of $CaSO_4$:Dy[9]. Study of effective co-dopants such as P and Mo for $CaSO_4$:Dy and $CaSO_4$:Tm phosphors were

investigated by Atone et al. [10]. Ag is reported as a very good co-dopant in both $CaSO_4$:Dy and $CaSO_4$:Tm[1,11]. The peak emission temperature is shifted to 375°C in both the phosphors without much compromise in emission intensity. The combination of Dy and Ag as well as Tm and Ag worked well resulting in the enhancement in TL properties of both the phosphors $CaSO_4$:Dy and $CaSO_4$:Tm[1,11]. The selection of dopants for a particular host material mainly depends on the ionic radii of the dopants and the host. Many attempts have been made earlier in co-doping Si with $CaSO_4$:Dy and $CaSO_4$:Tm through various methods. None of the attempts gave satisfactory results. We have successfully co-doped Si with the above phosphors via solid state synthesis. Studies on $CaSO_4$:Tm co-doped with Si is reported here.

2. Experimental

2.1. Preparation

Solid state synthesis was used to prepare the phosphor $CaSO_4$:Tm,Si[12]. $CaCO_3$,$(NH_4)_2SO_4$, $Si(OOCCH_3)_4$ and $Tm_2O_3$of AR grade, Merck were used as the starting materials for phosphor preparation. The reaction governing the process is

$$\mathbf{CaCO_3 + (NH_4)_2SO_4 \longrightarrow CaSO_4 + (NH_4)_2CO_3} \quad (1)$$

All the reactants were taken in stoichiometric ratio along with dopants. The starting materials were added in to a motorised agate and mixed thoroughly for 1 hour. Acetone was used as the wetting medium. The resultant powder was given a primary calcination at 500^0C for 3 hours was then allowed for slow cooling. The residue $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) subjected to annealing at various temperatures in the range 600^0Cto 1200^0C was finely powdered and used for further structural and thermoluminescence characterization. $CaSO_4$:Tm and $CaSO_4$:Si were also prepared under identical conditions for comparison.

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 from TGA spectrum recorded with Perkin Elmer STA6000 TG Analyzer. The surface morphology of the phosphor was studied using Jeol 6390 LV model Scanning Electron Microscope. The particle size and shape of the phosphors was analysed using Joel/JEM 2100 model TEM. ICP-AES analysis was performed to confirm the presence of Si in $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor using Perkin Elmer OES-ICP, Model 5300DV. The sample was subjected to UV-Vis analysis using Varian, Cary 5000 Spectrophotometer over a spectral range of 237nm to 1963nm. The PL emission spectrum was recorded from Shimadzu Spectroflourophotometer. All the TL measurements were performed using a TL1007- NUCLEONIX Analyser. For X-irradiation, beam generated at energy of 30 KeV for a period of 60 seconds, from a Radon make source of Half Value Thickness (HVT) of 0.5mm of Aluminium was used. The samples used in all the above studies were prepared under identical conditions. This was done to avoid any change in the phosphor properties which may occur due to change of any condition under which the samples are prepared. 5mg samples were taken for each TL measurement. Peak height is taken as TL intensity in all the glow curves presented in this paper. The TL responses of the phosphors were compared with standard $CaSO_4$:Dy.

3. Results and discussion

3.1 X-ray diffraction studies

Fig.1 shows the X-ray diffraction pattern of the prepared $CaSO_4$:Tm,Si (0.1mol%,0.1mol%) phosphor. The pattern matches with International Classification of Diffraction Data (ICDD) File No 72-0916 of $CaSO_4$. It is observed that the highest intense peak corresponds to the (200) plane. It is seen that the phosphor possesses orthorhombic phase structure with Amma(63) space group. The calculated values of lattice parameters and unit cell volume are given table1.

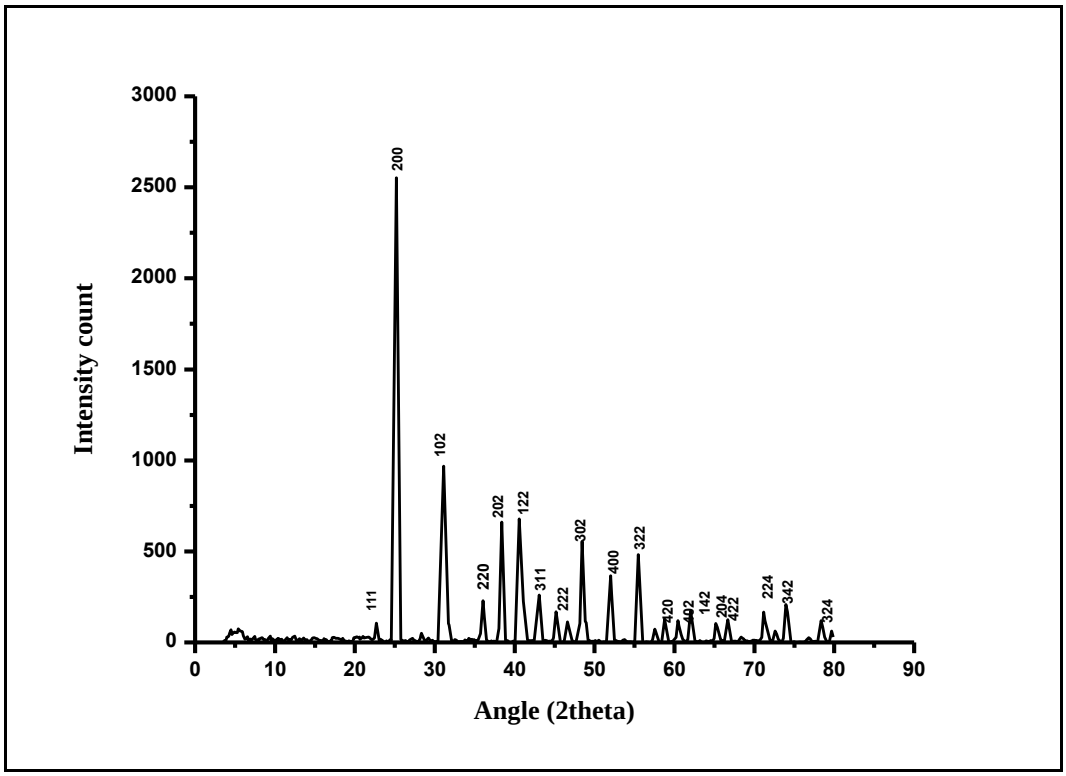


Fig.1 Powder XRD pattern of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor.

Table 1. Lattice parameters and cell volume obtained from PXRD pattern.

Lattice	a(Å)	b(Å)	c(Å)	cell volume($Å^3$)
ICDD file no 72-0916	7.006	6.998	6.245	308.18
$CaSO_4$:Tm,Si(0.1mol%,0.1mol%)	7.059	7.006	6.273	310.23

The XRD pattern for the prepared $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor showed a lower shift in 2θ value than the standard ICDD data, resulted in a very slight lattice expansion. The ionic radius for Ca^{2+}, $Tm^{3+}$and Si^{4-} is 0.99Å, 0.869Å and 0.4Å respectively. The radii of both the dopants are less than that of the host ion. It is reported earlier that if the ionic radius of dopant is less than that of the host, lattice contraction results [13] and if the ionic radius of dopant is greater than that of the host, lattice expansion results [14]. 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. Increased number of dopants as well as oxidation states of host and dopants might have contributed to lattice expansion in this case. A detailed study on this point is required to ascertain the exact reason for expansion and contraction of the lattice.

3.2Thermal stability

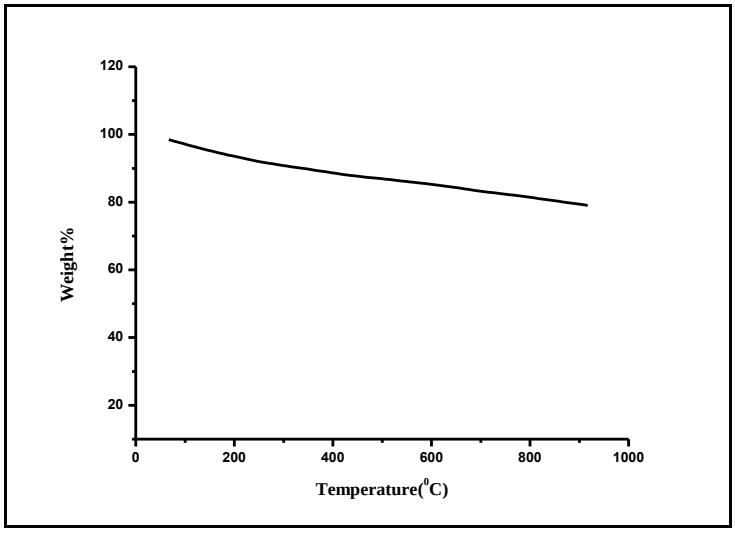


Fig.2 TGA curve for $CaSO_4$:Tm,Si(0.1mol%,0.1mol%).

TGA curve for $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor is shown in fig.2. Thermal stability of the phosphor was analysed using the Thermogravimetric curve. The phosphor was seen stable in the entire temperature range from 100°C to 1000°C. Annealed phosphor was used for thermogravimetric analysis. Hence no water loss was observed in the curve. Absence of endotherms indicates the thermal stability of the material, which is a major requirement for the material to be used in various dosimetry applications[15]. The TGA plot shows a very slight mass reduction which may be due to the drying of material during the course of time[15].

3.3Morphology and grain size: SEM, TEM

The SEM micrograph of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) is shown in fig.3. Particles of irregular shapes with different sizes in the micrometer range were seen. Small flakes formed a cluster to become a large particle and an organized packing was also observed. Particles size was found to be greater than that obtained from the powder XRD data. This may be due to the agglomeration of particles[15,16,17].

TEM analysis was performed to obtain the particle size and shape of the phosphor $CaSO_4$:Tm,Si(0.1mol%,0.1mol%). TEM images are shown in fig. 4(a) &4(b). Particles were of irregular shapes with well defined boundaries having size less than 2µm. The cluster formation and the reason for size change can be clearly understood from the TEM images. The observations from SEM and TEM were in good agreement with each other.

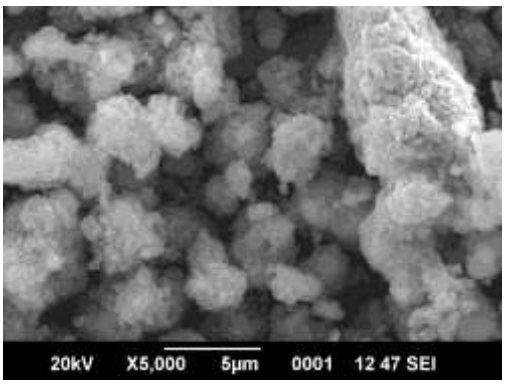
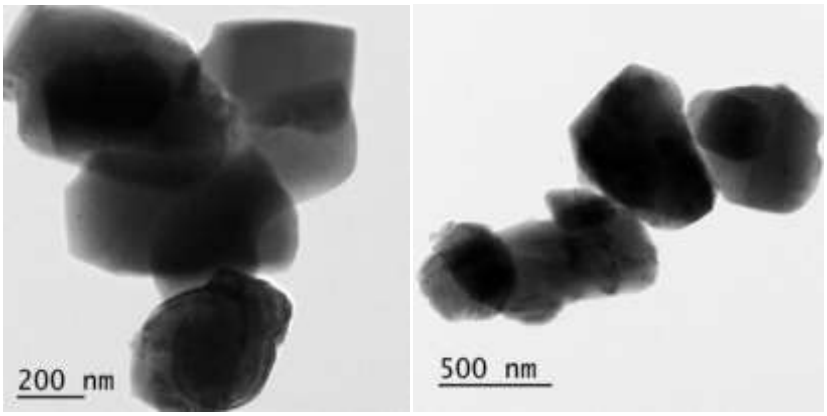


Fig.3. SEM micrograph of the phosphor $CaSO_4$:Tm,Si(0.1mol%,0.1mol%).



(a) (b)

Fig.4 (a) & (b) TEM images of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%).

3.4 Optical band gap: UV-Vis analysis

The diffuse reflectance spectrum of the powder sample was recorded and the optical band gap of the material was determined by using Kubelka-Munk function [18,19], the equation being

$$(F(R_\alpha)\, h\nu)^2 = A\,(h\nu - E_g) \qquad (2)$$

The Kubelka-Munk plot for the phosphor $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) is shown in fig.5. The optical band gap for $CaSO_4$:Tm,Si(0.1mol%, 0.1mol%) phosphor was found to be E_g= 5.17eV.

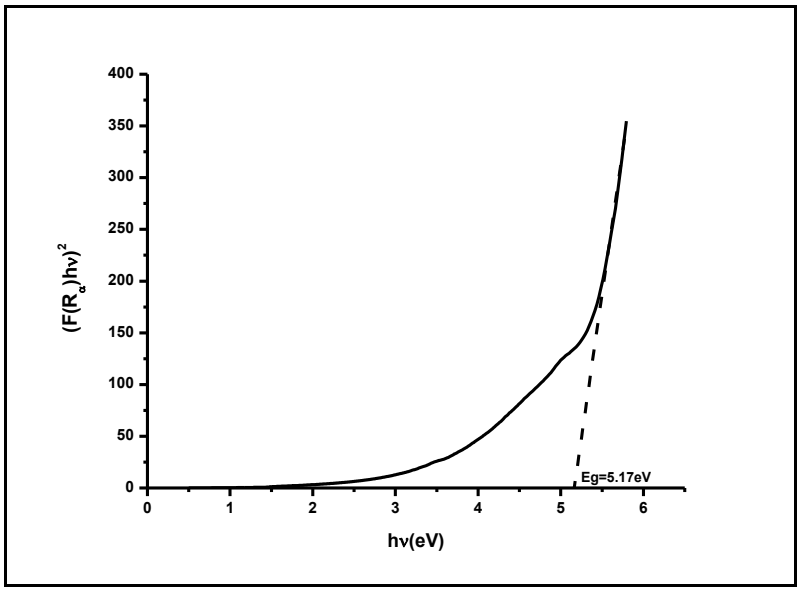


Fig.5 Kubelka-Munk plot for the reflectance spectra of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor.

3.5 ICP-AES analysis

ICP-AES analysis was done to confirm the presence of Si in $CaSO_4$:Tm,Si(0.1mol%, 0.1mol%) phosphor using Perkin Elmer OES-ICP, Model 5300DV. 0.1 g of sample powder was digested in conc: HNO_3-HCl-HF mixture and diluted to 50ml with de-ionized water and then analysed. The concentration of analyte element was determined from the calibration plot obtained by analysing standard solutions. The concentration of Si was found to be 49 ppm.

3.6 Photoluminescence studies

The PL emission spectra of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) taken at room temperature is given in fig.6. The characteristic emission of Tm^{3+} was obtained around 373nm, 463nm, 558nm and 649nm corresponds to transitions $^1I_6 \rightarrow {}^3F_4$, $^1D_2 \rightarrow {}^3F_4$, $^1D_2 \rightarrow {}^3H_5$ and $^1G_4 \rightarrow {}^3F_4$ respectively for an excitation wavelength of 339nm [10,14-20]. Earlier studies have shown characteristic emission of Tm^{3+} over a range from 356nm to 800nm for various transitions [17,20-26]. There was no change in the emission wavelength of Tm^{3+} with Si co-doping. This implies that Si present in the lattice does not act as luminescence centers in $CaSO_4$:Tm,Si(0.1mol%,0.1mol%). Si can act as a sensitizer which helps in incorporating more and more Tm^{3+} ions into the crystal lattice[27].

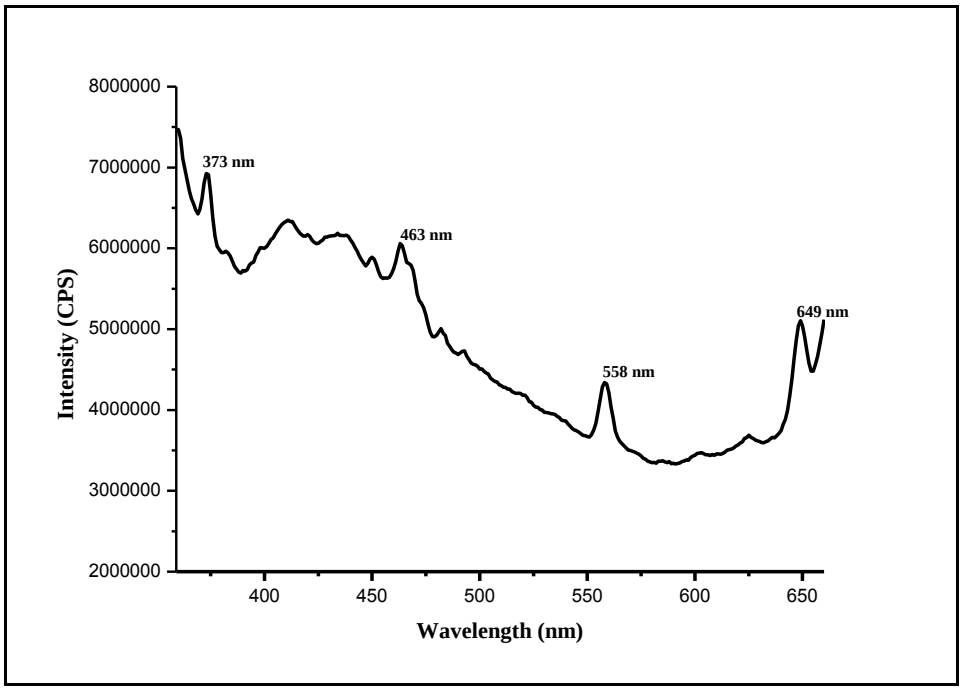


Fig.6 PL emission spectra of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%)(λ_{ex}=339 nm).

3.7 Thermoluminescence studies

3.7.1 TL studies under X-ray excitations

$CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor, annealed at different temperatures from 600^0C to 1200^0C were subjected to X-irradiation and TL measurements were performed at a heating rate of 10^0C/s. The phosphor gave maximum TL response for the sample annealed at 700^0C. The peak emission temperature of $CaSO_4$:Tmis shifted to 365°C from 220°C. The TL intensity of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) is seen to be one third of that of standard $CaSO_4$:Dy phosphor under X-ray excitations and identical TL measurement conditions while it is 1.8 times sensitive compared to prepared $CaSO_4$:Tm(0.1mol%) phosphor.

Fig.7 shows the glow curve of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) annealed at 700°C. A shoulder peak around 190° C is seen. The main peak at 365°C is about five times intense than that of shoulder peak which makes it applicable for various radiation dosimetry applications. The shoulder peak can be eliminated by suitable thermal cleaning processes. The variation in TL intensity with annealing temperature under X-ray excitation is shown in fig.8.

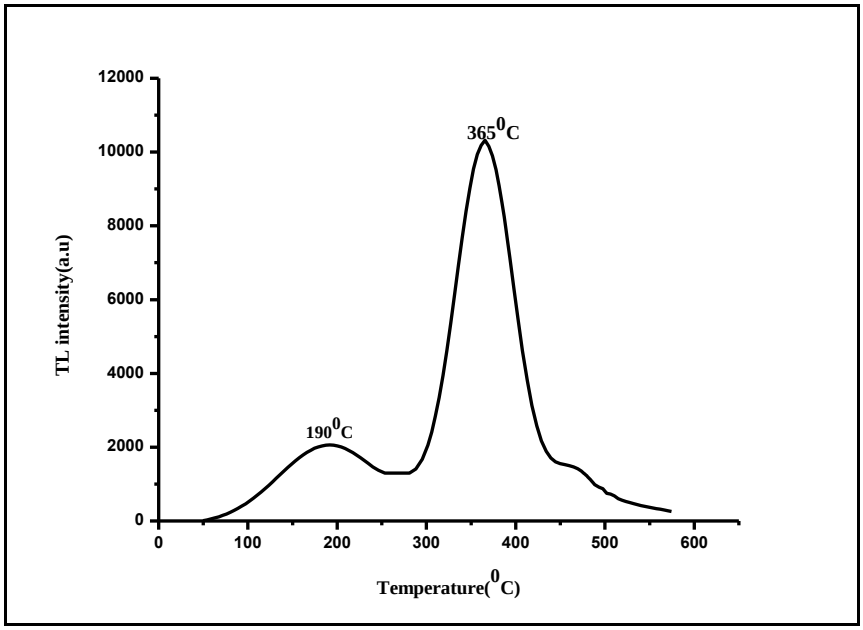


Fig.7 Glow curve of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) annealed at 700°C.

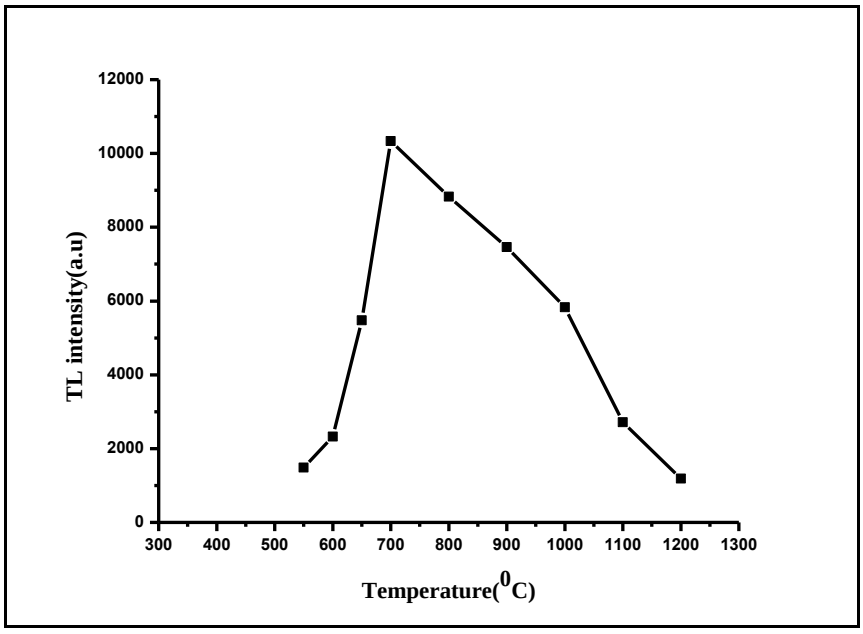


Fig.8 Variation of TL intensity with annealing temperature under X-ray excitation for $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor.

The peak emission temperature at 365°C is a characteristic property of Si ions present in the lattice of $CaSO_4$:Tm as a co-dopant. Fig. 9 shows the recorded TL glow curve of $CaSO_4$:Si phosphor for doping concentration 0.1mol% under 30keV X-ray excitations. Phosphor showed TL emission at 365°C, with a lower intensity of emission.

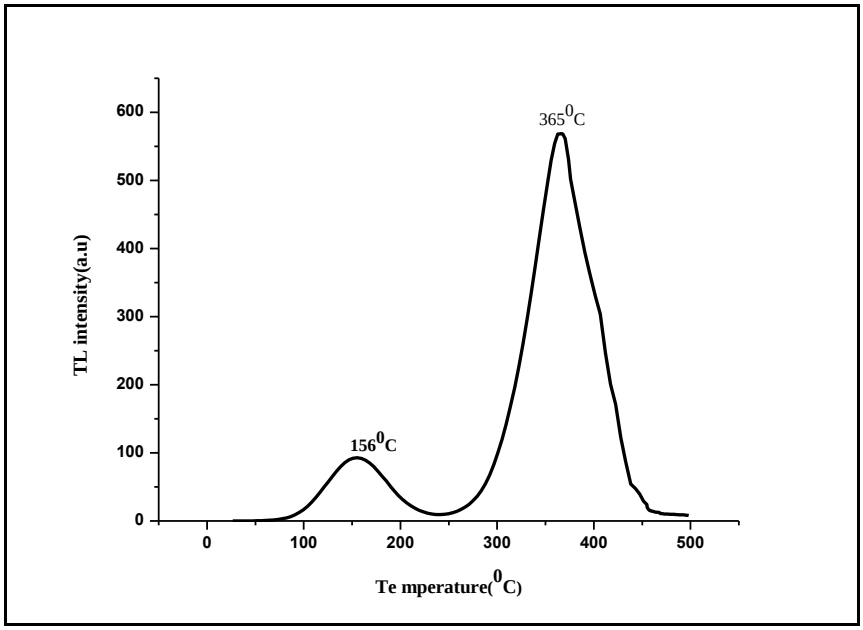


Fig.9 Glow curves of $CaSO_4$:Si(0.1 mol%) under X-ray irradiation.

The TL response of the phosphor $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) in comparison with commercially available standard phosphor $CaSO_4$:Dy is given in fig.10 and the comparison with previously reported phosphors along with standard phosphor is framed in table 2.

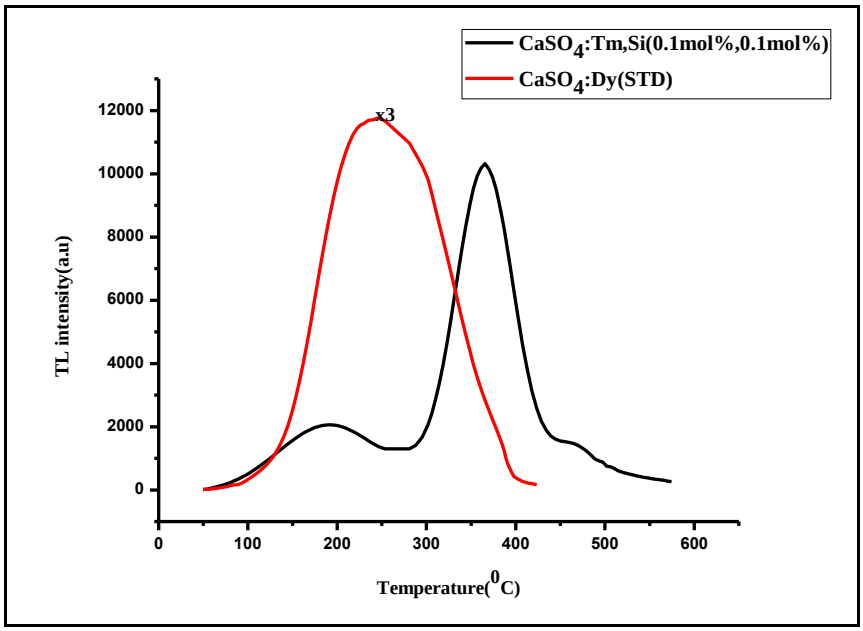


Fig. 10 TL response of the phosphor $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) compared with that of standard phodphor$CaSO_4$:Dy

Table 2. TL parameters of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) in comparison with standard $CaSO_4$:Dy, prepared $CaSO_4$:Tm(0.1mol%) and previously reported phosphors.

Phosphors	Peak Temperature °C	Relative TL Sensitivity compared to	
		$CaSO_4$:Dy	$CaSO_4$:Tm(0.1mol%)
* $CaSO_4$:Tm,Ag	375	-	-
*$CaSO_4$:Dy,Ag	375	-	-
$CaSO_4$:Dy(Standard)	250	1	6.2
$CaSO_4$:Tm(0.1mol%) (prepared)	220	0.16	1
$CaSO_4$:Tm,Si(0.1mol%,0.1mol%)	365	0.29	1.8
$CaSO_4$:Si(0.1mol%)	365	0.016	0.1

*previously reported [1,11]

3.7.2 Fading

Periodic TL measurements were done to study the fading of the phosphor $CaSO_4$:Tm,Si(0.1mol%,0.1mol%). Variation in TL intensity of the phosphor with storage time is shown in fig.11. The fading of the phosphor is 2% in two weeks, 3.89% in one month and around 7% in two months. These low fading properties is excellent considering the criteria for a phosphor in dosimetry applications that it should be less than 20% at any temperature upto 50°C [28]. Thus, as regards fading the sample stands on a higher pedestal [29].Though the intensity of emission is found to be less than that of commercially available standard $CaSO_4$:Dy TLD phosphor, the lower fading rate offer more chances to this phosphor to be used in different dosimetry applications other than clinical, especially environmental applications. It can be used with limited fading during a longer period of time, nearly three times compared to standard phosphors CaF_2:Dy and CaF_2:Mn [28,29].

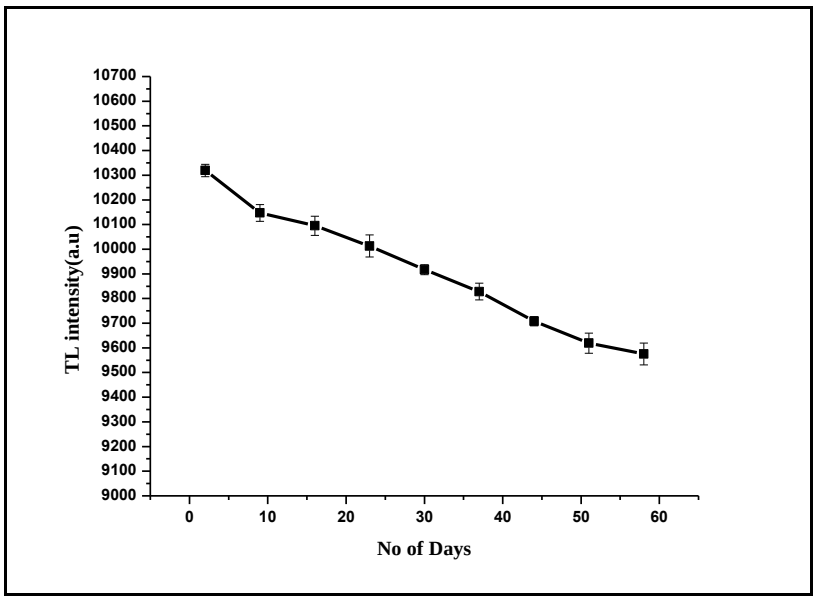


Fig.11 TL responses of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor in function of storage duration.

3.7.3 Reusability

The phosphor$CaSO_4$:Tm,Si(0.1mol%,0.1mol%) has been tested for its reusability by subjecting it to X-ray generated at 30keV. Thermal cleaning at 500°C for 1 hour was performed to eliminate the residual dose from the phosphor after each TL measurements. Annealing may change the defects created in the phosphor and thus its sensitivity. Five repeated cycles of annealing, irradiation and readouts were performed in the same material. The variation in TL intensities of the phosphor for different cycles of measurements is shown in fig.

12. Each data point is an average of three measurements. The standard deviation of the three measurements is given as the error in the measurements.

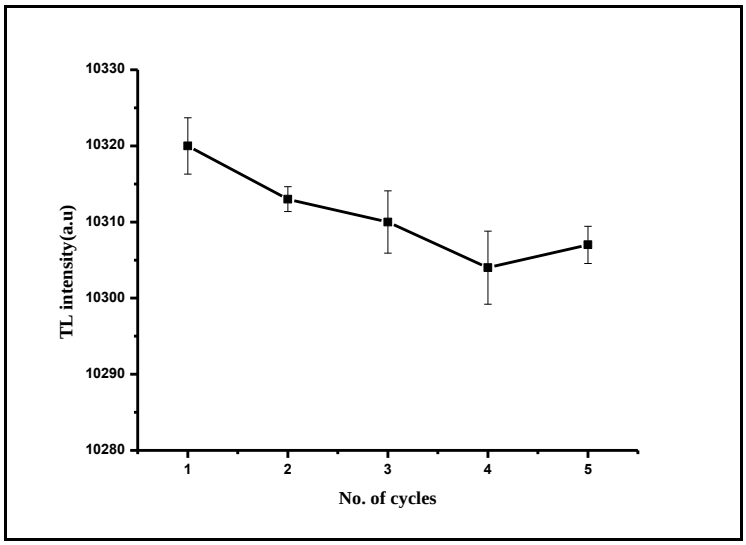


Fig.12.TL responses of $CaSO_4$:Tm,Si(0.1mol%,0.1mol%) phosphor after repeated cycles of use.

Conclusions

The TL properties of Si co-doped $CaSO_4$:Tm phosphor under X-ray excitations, prepared via conventional solid state method were studied. Phosphor annealed at 700°C gave maximum TL response. An increase of 145°C is observed in the peak emission temperature of $CaSO_4$:Tm on Si co-doping. The emission temperature was shifted from 220°C to 365°C. The TL response of the phosphor was compared with commercially available standard $CaSO_4$:Dy phosphor. The peak emission temperature is found to be very highfor the Si co-doped phosphor compared to standard $CaSO_4$:Dyphosphor which possesses a dosimetric emission around 250°C. The fading rate of this phosphor is around 7% which is very well acceptable for a phosphor to be used in different dosimetry applications, especially in environmental radiation dosimetry. The phosphor is found to be reusable which is an important property to be possessed by all dosimetric materials.

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