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# Characterization and TSL dosimetric properties of Mn doped $BaSO_4$ phosphor prepared by recrystallisation method

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ABSTRACT

Mn doped $BaSO_4$ powders were prepared by recrystallisation method and the formation of the compound was confirmed by X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR) and scanning electron microscopic (SEM) studies. The thermally stimulated luminescence (TSL) studies of Mn doped $BaSO_4$ sample (doping concentration is 0.5 mol%) showed glow curve having two glow peaks at 147 and 225 °C after heating at a constant heating rate of 4 °C/s. Comparison of TL intensity of the most intensive glow peak of Mn doped $BaSO_4$ compound with that of undoped $BaSO_4$ shows that the addition of Mn impurity in $BaSO_4$ compound enhances the thermoluminescence (TL) intensity by about 3 times. The trap parameters associated with the glow peaks in X-irradiated $BaSO_4$:Mn sample were obtained by glow curve shape method. The thermoluminescence dose response, reproducibility and fading of the $BaSO_4$:Mn phosphor were also studied.

## 1. Introduction

Daniel et al. first applied the thermoluminescence (TL) phenomenon on dosimetry purpose in 1953 [1], since then the TSL dosimetry has taken a decisive lead both in individual and environmental radiation monitoring over photography, radio photo luminescence (RPL), thermally stimulated exoelectron emission (TSEE), thermally stimulated current (TSC) etc. This can be attributed to various factors, the most important being reliability, sensitivity and ease of production or economic commercial availability [2]. Thermoluminescent materials are widely used in day-to-day life. Their best-known applications are dosimetry of ionizing radiation, CTV screen phosphors, scintillators, X-ray storage and screens intensifying phosphors, laser materials etc. [3–5].

For dosimetric purposes, a thermoluminescent phosphor is expected to show the following features: a relatively simple glow curve, with the temperature of the main peak at about 200 °C; high efficiency of light emission and low threshold dose; high resistance against environmental factors such as humidity, solvents, light; low fading and good linearity of the TL signal in the specific useful range of radiation dose. The high equivalent absorption coefficient is also one of the most important properties for the thermoluminescent materials in the field of personnel and environmental dosimetry.

The thermoluminescence studies of $BaSO_4$ compounds are of interest because of their high equivalent absorption coefficient ($Z_{eff} = 45$), low cost and easy handling process and therefore it is particularly suited for applications in radiation dosimetry as well as for detecting very small exposures of low energy X-rays [6]. The first preparation of $BaSO_4$, doped by Dy, was reported in 1974 [7]. Then, a second preparation was carried out in the years 1984 [8] and 1986 [9], and used to study hadronic and electromagnetic cascade showers. Also $BaSO_4$ doped with suitable impurities (e.g. Dy, Eu, P) can find an application as an X-ray storage phosphor due to its high TL sensitivity coupled with high effective atomic number [6]. Many workers have investigated the TL properties of $BaSO_4$ by using Eu as a dopant. Dixon and Ekstrand [7] have developed $BaSO_4$:Eu following the recrystallisation technique developed by Yamashita et al. [10]. Its TL sensitivity was comparable to that of $CaSO_4$:Dy. However its glow peak occurred at a relatively low temperature of 443 K. It faded by 13% over a 30-day storage period at room temperature (RT). A minimum measurable dose of 50 μGy was reported. In a later investigation Nagpal and Varadharajan claimed that the BaSO4:Eu developed by them was 1.25 times more sensitive than $CaSO_4$:Dy [11]. However, they reported a minimum measurable dose of about

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500 μGy in view of spurious signal from unirradiated phosphor. Atone et al. made BaSO4:Eu by co-precipitation method and firing the precipitate at 973 K in air [12]. The TL peaked around 450 K but its sensitivity to gamma rays was found to be 3.5 times less than that of $CaSO_4$:Dy. Also the application of highly sensitive phosphors on the basis of rare earth doped sulfates of alkaline earth elements is restricted by a number of factors, of which anomalous fading is one. Hence in order to prepare a sensitive dosimetric material, the choice of the impurity is one of the most important factors. It has been observed in our studies that the doping of Mn impurity in the host lattice (alkali and alkaline earth borates) plays important role in the thermally stimulated luminescence process and enhances the TL sensitivity [13,14]. So keeping these in view, TSL studies of $BaSO_4$ are carried out by incorporating Mn impurity in the host lattice.

## 2. Experimental details

The sample of Mn doped $BaSO_4$ was prepared by recrystallisation method [2,3,15]. The Mn doped $BaSO_4$ sample has been prepared by mixing $BaCO_3$ (99%, s.d. Fine-Chem LTD., Mumbai) and conc. $H_2SO_4$ (90%, Universal Laboratories) in stoichiometric ratio, adding of $MnCl_2$ (98%, LOBA CHEMIE, Bombay) in required proportions in the mixture. The mixture was heated at 650–700 °C in a quartz crucible for 30 min in normal atmosphere. Then the sample was cooled to room temperature by natural cooling. Finally the prepared sample was ground and sieved to obtain fine mesh powders. Conc. $H_2SO_4$ is highly toxic and through skin contact with the acid will lead to serious skin burns and its chronic exposure may cause the lung damage and possibly cancer. Necessary precautions were taken by adding conc. $H_2SO_4$ slowly and carefully and using lab coat, gloves, mask etc. The characterization of the prepared $BaSO_4$:Mn sample was carried out by X-ray diffraction, SEM and FTIR studies. X-ray diffractogram of this compound was taken at the room temperature in a wide range of Bragg angle $2\theta$ ($15^\circ \leq 2\theta \leq 100^\circ$) using Rigaku X-ray diffractometer (Miniflex, Japan) at a scanning rate of 1.00°/min. The morphology of the powder phosphor was observed on a FEI, QUANTA-300 Scanning Electron Microscope. The sample was gold coated using a sputter coater Polaron SC7610 system. FTIR spectra of the samples were recorded on FTIR-2000 (PerkinElmer, Switzerland Spectrometer) with KBr pellet technique from 4000 to 400 $cm^{-1}$.

$BaSO_4$:Mn sample was heated to 400 °C for 5 min and then quenched to RT before X-irradiating them. The powder sample was irradiated by X-rays obtained from Cu target of Machlett tube operated at 20 kV and 15 mA. The HVL value of the X-ray beam used in the present experiment is 0.4 mm Al and the effective photon energy of the X-ray beam is 48 eV. The radiation dose (also known as total ionizing dose, TID) is a measure of the energy deposited in a medium by ionizing radiation. It is equal to the energy deposited per unit mass of medium, and so has the unit J/kg, which is given the special name Gray (Gy). Also the intensity or dose of the radiation emitted from the source of the X-ray beam diminishes with the square of its distance from the source. The radiation dose rate in our experimental studies is 50 mGy/min at the distance of 5 cm. The TSL studies were made by using personal computer-based thermoluminescence analyzer system (type 1007) supplied by Nucleonix Systems Private Ltd., Hyderabad, India. The glow curves were recorded by heating the sample at a uniform rate of 4 K/s with the help of temperature controller (type 574) and the luminescence emissions were detected by a photo-multiplier tube (type 9924 B). The photo-current from tube is amplified by a DC amplifier, which is interfaced to a personal computer. The TSL output is finally recorded by a printer connected to the personal computer. Furthermore, to reduce the signal spurious and to enhance the thermal contact between the heater and sample, we used slow heating rate (4 °C/s) and 'glue'. Silicone grease is used in the latter application.

## 3. Results and discussion

### 3.1. XRD results

Fig. 1 shows the XRD pattern of $BaSO_4$:Mn phosphor at room temperature. The sharp and single peaks of the XRD pattern suggested the formation of single-phase new compound. The XRD pattern of $BaSO_4$:Mn belongs to orthorhombic space group *Pmna*53 and its lattice parameters were $a = 8.85$, $b = 5.44$, $c = 7.13$ with $\alpha = \beta = \gamma = 90^\circ$. The XRD pattern of Mn doped $BaSO_4$ samples was in good agreement with the reported data of barium sulfate having JCPDS card no: 00-001-1229 [16]. The ($h\,k\,l$) values of each peak for Mn doped $BaSO_4$ compound are given in the XRD pattern as shown in Fig. 1.

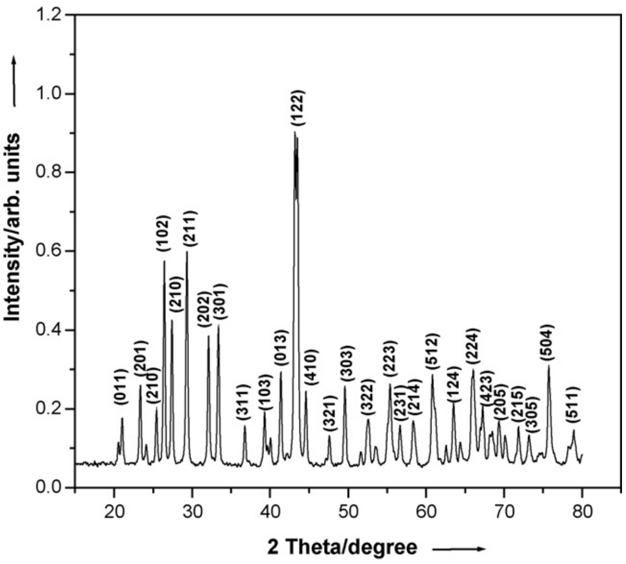

**Fig. 1.** XRD pattern of $BaSO_4$:Mn sample at room temperature.

### 3.2. FTIR results

Sulfates contain the $SO_4{}^{-2}$ structural unit. The 'FTIR' structure of Mn doped $BaSO_4$ as observed experimentally is shown in Fig. 2. Normally, sulfate contains two S=O and two S–O bonds. Actually, the four S–O bonds are equivalent. The sulfur–oxygen stretches of inorganic sulfates are found from 1140 to 1080 $cm^{-1}$ [17]. In our results of FTIR spectrum of prepared $BaSO_4$ (Fig. 2) the sulfur–oxygen stretch is found at 1116 $cm^{-1}$. Like any other bonds, sulfate bonds can bend giving rise to one or two bands normally in between 680 and 610 $cm^{-1}$ range. These bands are seen in spectrum of $BaSO_4$:Mn (Fig. 2) near about 630 $cm^{-1}$. It is worth noticing that the bending bands are sharper than the stretching bands. This is commonly observed in inorganic infrared spectra. The unmarked groups of peaks near 2000 $cm^{-1}$ (Fig. 2) are overtones and characteristic bands around 3000 and 1600 $cm^{-1}$ are ascribed to atmospheric water vapor since KBr readily absorbs moisture in the air, and these undesirable peaks in every spectra we obtained can be seen, and this indicates that the prepared sample consists of a certain amount of moisture. Fortunately, these undesirable peaks do not affect the identification of substance

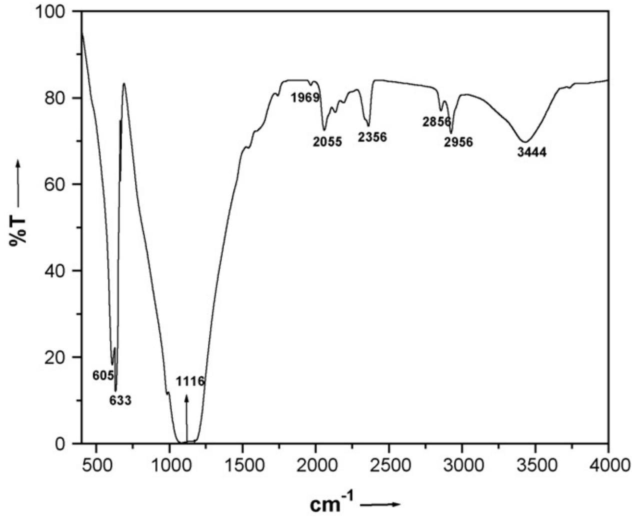

**Fig. 2.** FTIR spectra of $BaSO_4$:Mn sample at room temperature.

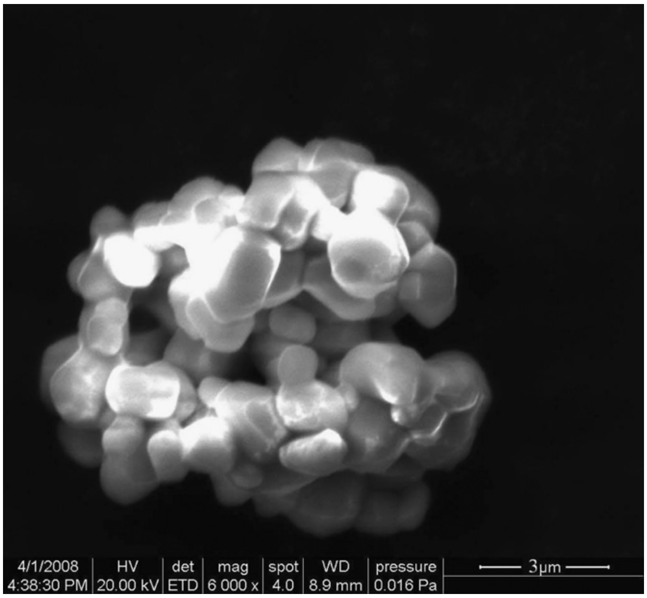

**Fig. 3.** SEM photograph of $BaSO_4$:Mn sample at room temperature.

involved in this experiment due to different absorption positions of water and the possible product. The combination bands of the lower wave number S–O stretching and bending vibrations.

### 3.3. SEM

The microstructure of the as-prepared Mn doped $BaSO_4$ powder sample is studied by SEM and is shown in Fig. 3. The SEM photograph shows single morphology with different particle size. The particles can be categorized into two types: one that shows particles with particle size (∼) 0.5–1.0 μm and the other shows the slightly bigger particles with size about 1.5–2.0 μm. The microstructure displayed granular structure with particle sizes in the range of 0.5–2.0 μm and this non-uniform particle size is caused due to the non-uniform distribution of temperature and mass flow during the synthesis. Luminescence efficiencies are related to the phosphor crystallite size with the optimum size being in the 0.5–10 μm range [18]. Smaller crystals are less efficient because of lower bulk emission intensity. Also, tighter packing of the smaller particles will increase the probability that the emitted light will get lost (attenuated) within the screen. Larger crystals cause difficulties in coating the phosphor particles into smooth, thin screens. This powder sample can easily be termed as ‘ultra fine phosphor’ because particle size is less than 10 μm [18]. Moreover the particles have some angular edges and the smaller particles looks like regular hexagon.

### 3.4. TSL studies

#### 3.4.1. Dose threshold

The lowest level of detection, known as the minimum detectable dose (M.D.D) or dose threshold, was calculated from the following relation:

$$D_{\mathrm{th}} = 2.26\sigma S$$

where ‘$\sigma$’ is the standard deviation of the background reading value of unirradiated samples in units of nC and ‘$S$’ represents the conversion factor (=2.30) in units of mGy/nC. It was found that the M.D.D. is 25 μGy.

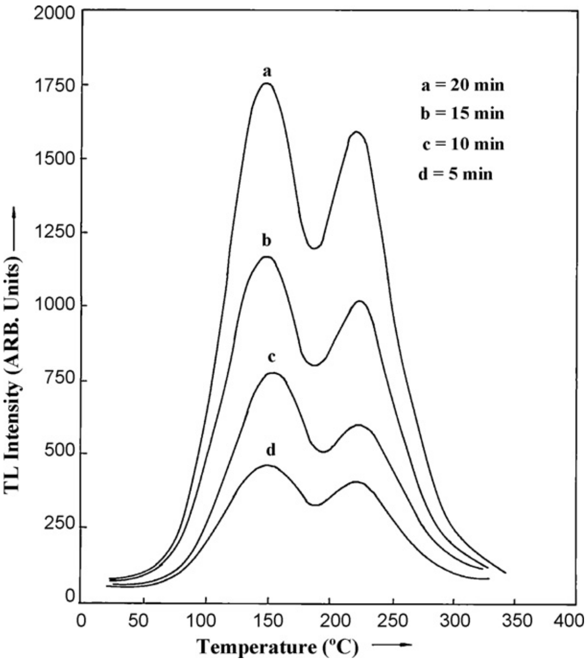

**Fig. 4.** TSL glow curves of $BaSO_4$:Mn sample for different times of X-irradiation at RT.

#### 3.4.2. TSL glow curves

The TL measurements were performed with the size fraction of 1.5–2.0 μm obtained by sieving. During this study, glow curves of Mn doped $BaSO_4$ sample were recorded for different times of X-irradiation. The TSL glow curves of $BaSO_4$:Mn powder sample were recorded after X-irradiating at room temperature for 5, 10, 15 and 20 min with corresponding doses are ranging from 250 to 1000 mGy (Fig. 4). The room temperature X-irradiated $BaSO_4$:Mn sample exhibits two glow peaks at temperatures 147 and 225 °C, the intensity of the 147 °C glow peak being stronger. Moreover the intensities of the glow peaks were found to increase with the increase of X-ray dose. These TSL glow curves show two glow peaks (Fig. 5) indicating that two different sets of traps are being activated within the particular temperature range each with its own value of activation energy ($E$) and frequency factor ($s$). Moreover, with increasing X-ray dose the growth in the TL intensity of the high temperature peak is more distinct than that of the low temperature peak.

Generally, TL emissions will occur because of recombination: (a) of a released hole with a trapped electron on a special ion which works as a luminescent centre; or (b) the same as (a) except the roles of hole and electron are exchanged; or (c) both electron and hole are released and recombine at a suitable emitting centre, or at least the energy emitted by the recombination is transferred to the centre.

We shall now discuss a simple but revealing model to explain the above described temperature dependent luminescence signals, with the aim to understand the basic factors which influence TL emission in materials such as $BaSO_4$:Mn. The model (and the definition of the various parameters) is shown schematically in Fig. 6. In this model we assume that optical excitation generates free carriers in the $BaSO_4$:Mn barriers that surround the quantum well. We also assume that the defect level ($E_t$), of total density $n_0$, is near the conduction band of $BaSO_4$:Mn. In this simplified model, it is considered that at the end of the excitation, $n_0$ (in $m^{-3}$) electrons are accumulated in the trap and at least the same concentration of holes in the quantum well. At a temperature $T$ (in K), the rate of release of trapped electrons is proportional to Boltzmann function

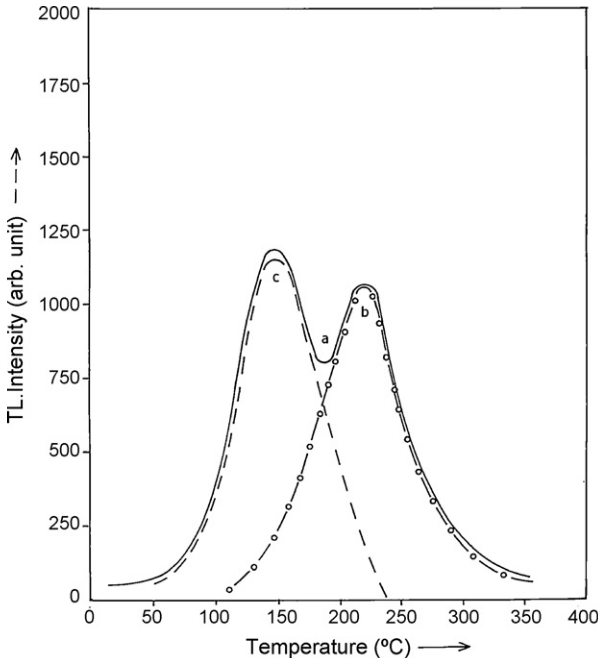

**Fig. 5.** Isolation of 147 °C glow peak of $BaSO_4$:Mn sample: (a) TSL glow curve of $BaSO_4$:Mn sample for 15 min. X-irradiation (—), (b) normalized TSL glow curve obtained after heating the $BaSO_4$:Mn sample up to 150 °C (—○—) and (c) isolated peak obtained after subtracting curve 'b' from curve 'a' (— —).

$\exp(-E_t/kT)$, where $E_t$ is the activation energy (in eV) of the trap and $k$ is Boltzmann's constant (in eV/K) and as the temperature increases this function grows rapidly. During thermal excitation, electrons captured into the defect state can be excited out of the trap or can relax from the trap. The number of electrons released per unit time is also proportional to the total concentration of trapped electrons. Once an electron is in the conduction band, it immediately recombines with hole in the quantum well which yields an emitted photon. The experimentally observed luminescence is the result of the recombination between the electrons and holes in the quantum well. Moreover the released carriers may also be retrapped before they recombine, in this way giving rise to a delay in the luminescence emissions and a spreading out of emission over a wide range of temperature and this is called the second order process. In the second order process the probability of retrapping is very high and it is given as $\sigma_{rt} = s\exp(-E_t/kT)$, where $s$ (in $s^{-1}$) is a constant. However in the first order process the recombination probability ($\sigma_t$) of detrapped charge carrier with their counterpart has a constant value with time but in the case of second order process the light emission is delayed due to retrapping of charge carriers and it might be expected that the second order curve will display more luminescence during the second half of the peak than the first order curve the second order glow curves are nearly symmetrical. But it is seen that the first order glow curve rises steadily to the peak and then falls rapidly to zero as the temperature rises or in other words the first order glow curves are not symmetrical. Now it has been seen from Figs. 4 and 5 that the main glow curve of $BaSO_4$:Mn ($T_m$ = 147 °C) is almost symmetrical and broad and we can assume that this glow curve is may be due to second order mechanism.

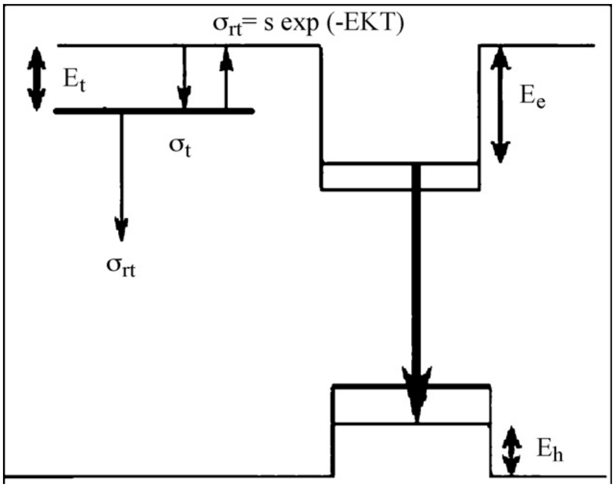

**Fig. 6.** Schematic illustration of model used in analyzing luminescence mechanism.

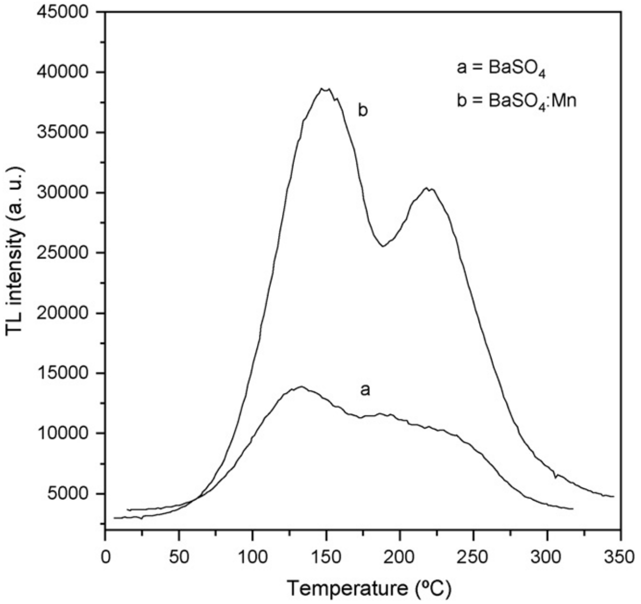

**Fig. 7.** Comparative TSL glow curves of undoped and Mn doped $BaSO_4$ samples for 10 min X-irradiation.

The increase in the intensities of the glow curves with the increase of irradiation dose can be understood by the fact that more and more traps responsible for these glow peaks are getting filled with increasing irradiation dose and subsequently these traps release their charge carriers on thermal stimulation to finally recombine with their counterparts, thus giving rise to different glow peaks.

A comparison of intensities of the glow peaks (Fig. 7) shows that the addition of Mn impurity to the undoped $BaSO_4$ compound enhances the TL intensity by 3 times.

In general, the undoped sample, whose emission can be related to intrinsic defects or to some unwanted impurity in the starting powder, exhibits a poor TL efficiency than the doped samples. In such cases, TSL response is found to be insufficient for reliable studies in the low dose range measurements. On the other hand, as expected, the TL signal steadily increased after incorporation of metal impurities such as Mn impurity, which is well known as very efficient activator in many materials. Moreover, the glow curve shapes of undoped samples can be changed after the doping of impurities. If the glow curve structure of undoped sample is changed after the doping, it indicates that there are interactions between intrinsic defects and doped impurities. In our results as expected, the TSL sensitivity was found to increase appreciably after incorporation of Mn-ions. Also in our results, the glow curve shape of $BaSO_4$ is highly changed after the doping. This result indicates that there are strong interactions between intrinsic defects and the Mn dopant.

### 3.4.3. *Trapping parameters*

Trap parameters such as order of kinetics ($b$), activation energy ($E$) and frequency factor ($s$) were calculated for the 147 and 225 °C glow peaks of $BaSO_4$:Mn phosphor using the glow curve shape (Chen's) method.

*3.4.3.1. Glow curve shape method.* The method based on the shape of glow curve proposed by Chen [19] was used to calculate the trapping parameters. To determine these parameters the following shape parameters were determined: the total half intensity width ($\omega = T_2 - T_1$), the high temperature half width ($\delta = T_2 - T_m$), the low temperature half width ($\tau = T_m - T_1$), where $T_m$ is the peak temperature and $T_1$ and $T_2$ are temperature on either side of $T_m$ corresponding to half peak intensity.

In order to calculate the trapping parameters associated with the 147 and 225 °C glow peaks, by the glow curve shape method the peak on the low temperature side with respect to the prominent peak is first to be removed by thermal cleaning technique. To do this the sample was X-irradiated for 15 min (the corresponding X-ray dose is 750 mGy) and heated up to 150 °C and then rapidly cooled to room temperature. Now the TSL glow curve was recorded which exhibited one isolated peak at 225 °C as shown in Fig. 5b. This glow curve was normalized with respect to the composite glow curve for 15 min as shown in Fig. 5. Then the single glow curve of peak temperature 147 °C was obtained by subtracting the glow curve of peak temperature 225 °C (Fig. 5b) from the whole glow curve which is shown in Fig. 5c. The inset of Fig. 6 shows the isolated glow curve of peak temperature 147 °C.

*3.4.3.1.1. Order of kinetics.* Order of kinetics ($b$) was determined by calculating the symmetry factor ($\mu_g$) of the glow peak from the known values of shape parameters [20]:

$$\mu_g = \frac{\delta}{\omega} = \frac{T_2 - T_m}{T_2 - T_1} \tag{1}$$

The shape factor ($\mu_g$) for the 147 °C glow peak of $BaSO_4$:Mn was found to be 0.52. That means second order of TL has performed, and retrapping of the excitation occurs resulting and taken into account. But the shape factor ($\mu_g$) for the 225 °C glow peak of $BaSO_4$:Mn was found to be 0.42, which indicates that the probability of retrapping is negligible.

Furthermore Balarin has proposed the following parameter:

$$\gamma = \frac{\delta}{\tau} = \frac{T_2 - T_m}{T_m - T_1} \tag{2}$$

This parameter ranges from 0.7 to 0.8 for a first order kinetics and from 1.05 to 1.20 for a second order kinetics [21]. This parameter ($\gamma$) for the 147 °C glow peak of $BaSO_4$:Mn was found to be 1.08 which suggests that this peak obeys second order kinetics. The Balarin parameter ($\gamma$) for the 225 °C glow peak of $BaSO_4$:Mn was found to be 0.72 which suggest that this peak obeys first order kinetics.

In general, the first order kinetics implies that the process of retrapping is negligible and the trap should be situated very close to the luminescence centre. In addition to this, the characteristics of the second order TL peak are that it is wider and it is more symmetric than the first order peak. This can be understood from a consideration of the fact that in a second order reaction, significant concentrations of released electrons are retrapped before they recombine, in this way giving rise to a delay in the luminescence emissions and a spreading out of emission over a wide range of temperature.

*3.4.3.1.2. Activation energy.* Activation energy ($E$) was calculated by using the Chen's equations for second order glow peaks which gives the trap depth in terms of $\tau, \delta, \omega$. A general formula for $E$ was given by

$$E = \frac{c_\gamma k T_m^2}{\gamma} - b_\gamma 2kT_m \tag{3}$$

where $\gamma$ is $\tau$, $\delta$ or $\omega$. The constants $c_\gamma$ and $b_\gamma$ for the three equations ($\tau$, $\delta$ and $\omega$) and for first order kinetics are $C_\tau = 1.51$, $b_\tau = 1.58$, $C_\delta = 0.976$, $b_\delta = 0$, $C_\omega = 2.52$, $b_\omega = 1.0$ and for second order kinetics are $C_\tau = 1.81$, $b_\tau = 2.0$, $C_\delta = 1.71$, $b_\delta = 0$, $C_\omega = 3.54$, $b_\omega = 1.0$.

The activation energy for the 147 °C glow peak of $BaSO_4$:Mn when calculated by Eq. (3) using low temperature half width, high temperature half width and full width of the peak at its half height was found to be $0.56 \pm 0.006$, $0.61 \pm 0.006$ and $0.59 \pm 0.006$ eV giving mean value of activation energy $0.59 \pm 0.006$ eV.

The activation energy for the 225 °C glow peak of $BaSO_4$:Mn when calculated by Eq. (3) using low temperature half width, high temperature half width and full width of the peak at its half height were found to be $0.60 \pm 0.006$, $0.65 \pm 0.006$, and $0.63 \pm 0.006$ eV giving mean value of activation energy $0.63 \pm 0.006$ eV.

*3.4.3.1.3. Frequency factor.* Once the order of kinetics and activation energy were determined, the frequency factor ($s$), which expresses the frequency with which the electrons strike the sides of the potential well of the trap and the reflection coefficient was calculated using the equation given by Chen and Winer [22]:

$$\frac{qE}{kT_m^2} = s\left[1 + (b-1)\frac{2kT_m}{E}\right] \exp\left(-\frac{E}{kT_m}\right) \tag{4}$$

where $q$ is the heating rate.

The frequency factor ($s$) for the 147 °C glow peaks of $BaSO_4$:Mn when calculated by using Eq. (4) was found to be $0.7 \times 10^6$, $2.9 \times 10^6$ and $1.7 \times 10^6\ s^{-1}$ respectively giving mean value of frequency factor $1.77 \times 10^6\ s^{-1}$.

The frequency factor ($s$) for the 225 °C glow peaks of $BaSO_4$:Mn when calculated by using Eq. (4) were found to be $1.2 \times 10^5$, $5.2 \times 10^5$ and $2.8 \times 10^5\ s^{-1}$ respectively giving mean value of frequency factor $3.1 \times 10^5\ s^{-1}$.

The as calculated trapping parameters for the glow peaks of $BaSO_4$:Mn when calculated by using Chen's glow curve shape method are given in Table 1.

### 3.4.4. *Reproducibility*

The reusability is another desirable property for a dosimetric phosphor. If the sensitivity of the sample does not change after several cycles of exposure and readouts, then it is considered to be good as a dosimetric phosphor. The $BaSO_4$:Mn (0.5 mol%) was also tested for its reusability. The sample was irradiated at 750 mGy of X-rays and the TL glow curves were recorded from room temperature to 400 °C. It was then quickly cooled to room temperature and exposed to X-ray source again to accumulate the same dose. The glow curve was again recorded for the second time; several such cycles of exposures and glow curve recordings were performed and are shown in Fig. 8. No significant change in the TL intensity of

**Table 1**
Trap depth and frequency factors of the TL glow peak for $BaSO_4$:Mn.

| Peak temperature $T_m$ in K | Parameters | $\tau$ | $\delta$ | $\omega$ | Mean value |
|---|---|---|---|---|---|
| 420 | $E$ (eV) | $0.56 \pm 0.006$ | $0.61 \pm 0.006$ | $0.59 \pm 0.006$ | $0.59 \pm 0.006$ |
| | $s$ ($s^{-1}$) | $0.7 \times 10^6$ | $2.9 \times 10^6$ | $1.7 \times 10^6$ | $1.77 \times 10^6$ |
| 498 | $E$ (eV) | $0.60 \pm 0.005$ | $0.65 \pm 0.005$ | $0.63 \pm 0.005$ | $0.63 \pm 0.005$ |
| | $s$ ($s^{-1}$) | $1.2 \times 10^5$ | $5.2 \times 10^5$ | $2.8 \times 10^5$ | $3.1 \times 10^5$ |

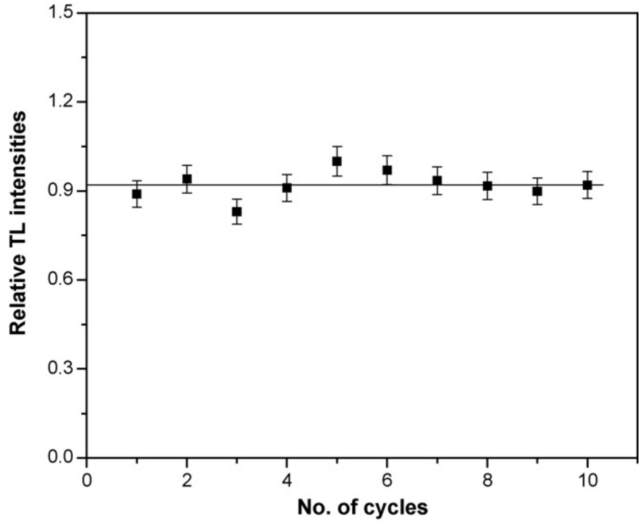

**Fig. 8.** Reproducibility of the 420 K glow peak of $BaSO_4$:Mn sample through 10 repeated cycles of annealing-irradiation-readout.

both the 147 and 225 °C peaks was observed. Excellent reusability is thus seen in the present sample and mainly for the dosimetric peak under consideration at 147 °C.

### 3.4.5. *TL fading*

For samples to be useful in dosimetry the TL should be stable and should not fade upon storage after exposure. In order to check the decay of TL intensity with time of $BaSO_4$:Mn phosphors, the sample after X-irradiation was kept in dark for different periods of time and then TSL glow curves were recorded. Figs. 9 and 10 show the relative TL response of 147 and 225 °C glow peaks as a function of storage time. It is observed that 147 and 225 °C glow peaks of $BaSO_4$:Mn phosphors show a fading of 41% and 37% respectively in a post-irradiation interval of 7 days. It is worth mentioning that research workers Rodrıguez et al. studied the TL properties of YAG crystal and observed 65% fading after 194 h of storage. They commented that 35% remnant TL signal can be considered for dosimetric applications [23]. Also according to Murthy and co-workers 41% remnant TL signal of $Sr_3Al_2O_6$:$Tb^{3+}$ phosphor after 30 days is good enough to be considered for dosimetric applications [24]. In view of these observations, it is proposed that 59% remnant TL signal of 147 °C glow peak and 63% remnant TL signal 225 °C glow peak of $BaSO_4$:Mn phosphor after 7 days of storage is high enough for this sample to be considered as a TL dosimeter. Moreover the glow peak temperatures with different storage time remain constant, suggest that the broad peaks are not made up of two or more overlapping peaks.

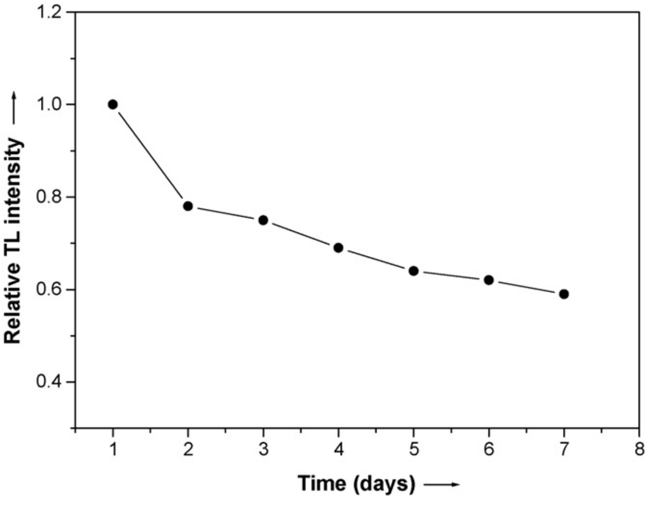

**Fig. 9.** Relative TSL response for 420 K glow peak of $BaSO_4$:Mn as a function of the elapsed time from irradiation.

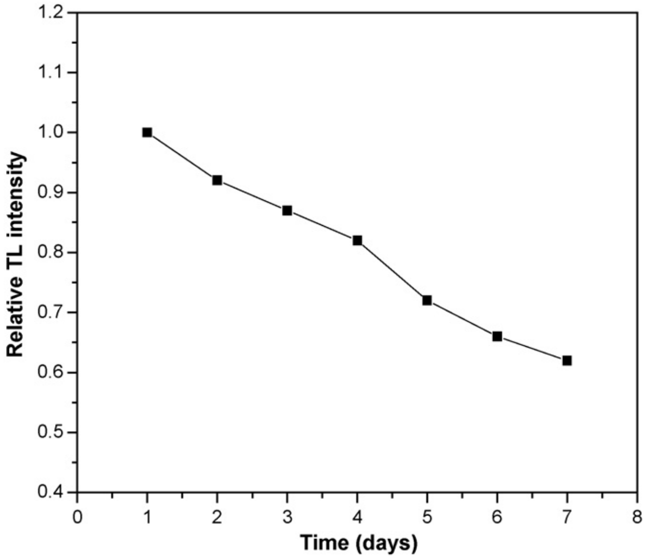

**Fig. 10.** Relative TSL response for 498 K glow peak of $BaSO_4$:Mn for 420 K glow peak as a function of the elapsed time from irradiation.

It is worth mentioning that peaks appearing at a significantly higher temperature than the excitation temperature (or, rather, the storage temperature), are expected to be stable for long periods of time. Peaks appearing rather close to the storage temperature are susceptible to thermal fading. In our experiment also it is observed that the 225 °C glow peak is more stable and it shows less fading relative to the 147 °C glow peak of Mn doped $BaSO_4$ phosphor.

### 3.4.6. *TL dose response*

The relationship between dose and the TL response, integrated over the whole glow curve, of the phosphor was studied in the pro-

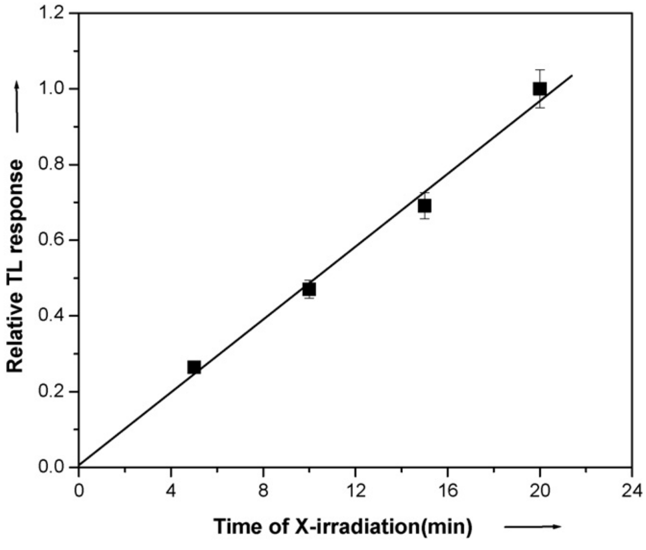

**Fig. 11.** Relative TSL response of $BaSO_4$:Mn sample for 420 K glow peak as a function of X-irradiation time.

tection dose ranging from 250 to 1000 mGy of X-irradiation. The relative TL intensity was plotted as a function of X-ray irradiation time for the $BaSO_4$:Mn sample in Fig. 11. The TL-dose dependence curve for the most intensive glow peak of $BaSO_4$:Mn phosphor ($T_m = 420\,K$) was observed to be almost linear in the studied range of irradiation time. The linearity of the TL response of this sample as a function of absorbed dose up to 1 Gy suggests that it will be a good material for low dose measurements. Particularly, if one considers the possible areas of use of this phosphor, it will be very suitable for detecting very small exposures of low energy X-rays.

## 4. Conclusions

The $BaSO_4$ phosphor activated by Mn was synthesized by the recrystallisation method at high temperature. The TL sensitivity of pure $BaSO_4$ phosphor is enhanced with the incorporation of Mn impurity. From the experimental results it is evident that the glow curves of $BaSO_4$:Mn phosphor consisted of well defined dosimetric peaks. $BaSO_4$:Mn has also been found to have good linearity in the protection dose ranging from 250 mGy to 1 Gy, excellent reproducibility and low fading. In addition, in the absorbed dose range from 250 mGy to 1 Gy, the structure of the TL glow curves of BaSO4:Mn phosphor is almost independent of radiation dose. Moreover, it can be prepared very easily and thus can be used in the radiation dosimetry.

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