

Thermally stimulated luminescence studies of undoped, Cu and Mn doped BaSO₄ compounds

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Thermally stimulated luminescence (TSL) of undoped and doped BaSO₄ with activators such as Cu and Mn has been investigated. The polycrystalline samples of undoped and doped BaSO₄ are prepared by melting method. The formation of BaSO₄ compound is confirmed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) studies. Comparison of TL intensity of the most intensive glow peak of Cu doped BaSO₄ compound with that of undoped BaSO₄ shows that addition of Cu impurity in BaSO₄ compound enhances the TL intensity by about 9 times. However, the addition of Mn impurity to undoped BaSO₄ increases the TL intensity by about three times when compared with that of undoped BaSO₄. Among the studied samples namely undoped, Cu and Mn doped BaSO₄; Cu-doped BaSO₄ has been found to be the most sensitive.

Keywords: Thermally stimulated luminescence, XRD, FTIR

1 Introduction

BaSO₄ is one of the most sensitive TL materials used in TL dosimetry¹. BaSO₄ doped with Cu and Mn showed high TL sensitivity and the TL response is considerably more stable². It is used as TLD for personal and environmental radiation monitoring due to its high sensitivity, stability, low cost and easy method of preparation. Also the main peaks of glow curves of undoped BaSO₄, BaSO₄: Cu and BaSO₄: Mn are expected to come at about 200°C. In this paper, undoped and doped (with Cu and Mn) BaSO₄ phosphor powders with mean particle size 10 to 20 µm have been prepared by recrystallization method, aiming at achieving high luminance. The structure and formation of the prepared samples have been studied by XRD and FTIR. The TSL studies of undoped and Cu and Mn doped BaSO₄ compounds are presented. The doping of impurities such as Cu and Mn in the host lattice plays important role in the thermally stimulated luminescence process. It has been observed in present studies that addition of Cu and Mn impurity enhances the TL intensity in alkali and alkaline earth borates^{3,4}.

2 Experimental Details

Pure and doped BaSO₄ were prepared by recrystallization method⁵. Pure BaSO₄ samples have been prepared by mixing BaCO₃ (99%, s.d. Fine-Chem LTD., Mumbai) and conc. H₂SO₄ (90%, universal Laboratories) in stoichiometric ratio and the mixture was heated at 650-700°C for 30 min. Then

the samples were cooled to room temperature by natural cooling. Finally the prepared samples were ground and sieved to obtain 100 to 200 mesh powders. Doped BaSO₄ samples were prepared in a similar manner by taking the starting materials in stoichiometric ratio and adding 0.5 wt% of CuCl₂ (98%, LOBA CHEMIE, Bombay) or MnCl₂ (99.5%, S.d. fine-Chem Ltd., Boisar) in the mixture. The preparation of the samples was done in the Department of Applied Physics, ISMU-Dhanbad, India.

The characterization of the prepared BaSO₄ samples was carried out by X-ray diffraction and FTIR studies. X-Ray diffractogram of these compounds were taken in the Department of Instrumentation Science, Jadavpur University, Kolkata, India, at the room temperature in a wide range of Bragg angle 2θ (15° ≤ 2θ ≤ 100°) using Rigaku X-Ray diffractometer (Miniflex, Japan) at a scanning rate of 1.00 degree per min.

The FTIR spectrum (KBr pellet) in the region 400 to 4000 cm⁻¹ was recorded in the Chemistry Department, ISMU, Dhanbad on FTIR-2000, (Perkin Elmer, Switzerland) Spectrometer. All samples were heated to 400° C for 5 min and then quenched to RT before X-irradiating them. The powder samples were irradiated by X-rays obtain from Cu target of Machlett tube operated at 20 kV and 15 mA. The TSL studies were made by using personal computer based thermoluminescence analyzer system (type 1007) supplied by Nucleonix Systems Private Ltd.,

Hydrabad, India. The glow curves were recorded by heating the samples at a uniform rate of 4 K/s with the help of temperature controller (type 574) and the luminescence emission was detected by a photomultiplier tube (type 9924 B). The photo-current from PM 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.

3 Results and Discussion

3.1 XRD results

The X-ray diffraction of pure BaSO₄ is taken at room temperature as shown in the Fig. 1. The sharp and single peaks of the XRD pattern suggested the formation of single-phase new compound. From the 2θ values of the diffraction lines, the interplaner spacing d of the peaks was calculated. The first peak of XRD for the prepared BaSO₄ arises at ($2\theta=$) 21.020 degree. The diffraction lines were indexed and unit cell configuration was identified using a computer program package Powdmult. Out of those a suitable orthorhombic unit cell was selected for which $\Sigma\Delta d$ ($=d_{\text{obs}}-d_{\text{cal}}$) was found to be minimum⁶. The lattice parameters of the unit cell of prepared BaSO₄ were $a = 8.848 \text{ \AA}$, $b = 5.441 \text{ \AA}$ and $c = 7.132 \text{ \AA}$. The comparison of observed and calculated d -values (\AA) of some reflections of BaSO₄ samples at room temperature are given in Table 1. A good agreement between the observed and calculated d -values (Table 1) suggests the suitability of the crystal structures and unit cell parameters. It is worth

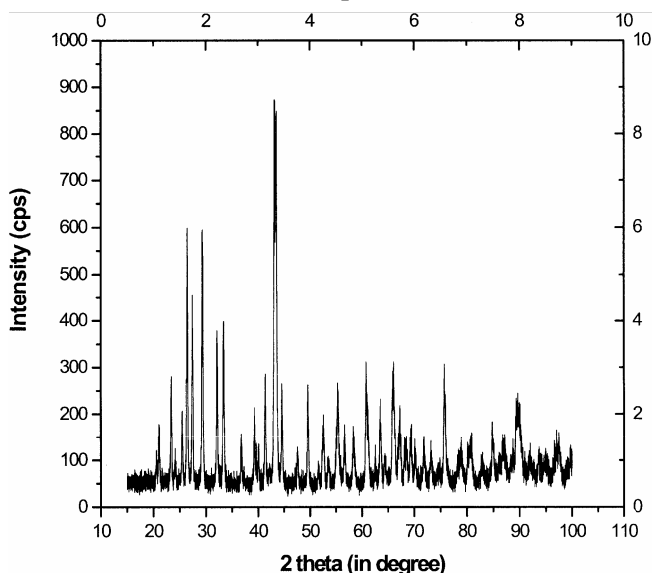


Fig. 1 — XRD pattern of BaSO₄ sample at room temperature

mentioning that the ($h k l$) values of most prominent peaks for BaSO₄ are (102), (211), (202) and (312).

3.2 FTIR results

Sulphates contain the SO₄²⁻ structural unit. The FTIR structure of pure BaSO₄ as observed experimentally are shown in the Fig. 2. Normally, sulphate contains two S=O and two S-O bonds. Actually, the four S-O bonds are equivalent. The sulphur-oxygen stretches⁷ of inorganic sulphates are found from 1140 to 1080 cm⁻¹. In present results of FTIR spectrum of prepared BaSO₄ (Fig. 2), the sulphur-oxygen stretch is found at 1177.31 cm⁻¹. Like any other bonds, sulphate bonds can bend giving rise to one or two bands normally in between

Table 1 — Comparison of observed and calculated d -values (\AA) of some reflections of BaSO₄ sample at room temperature

h	k	l	$2\theta(\text{degree})$	d_{obs}	d_{cal}	I/I_0*100
2	0	1	23.350	3.75946	3.8065	23
1	0	2	26.430	3.30748	3.3694	64
2	1	1	29.320	3.09296	3.0435	63
2	0	2	32.110	2.77636	2.7851	39
1	0	3	39.270	2.29590	2.2922	18
0	1	3	41.370	2.17847	2.1806	29
3	1	2	43.170	2.09713	2.0938	100
3	2	2	49.590	1.85090	1.8367	27
2	2	3	55.390	1.65943	1.6573	25
5	1	2	60.810	1.52188	1.5219	30
3	3	2	65.980	1.41761	1.4146	24
4	2	3	67.290	1.39154	1.3902	17
5	0	4	75.750	1.25601	1.2546	28
3	4	3	89.370	1.09609	1.0953	19

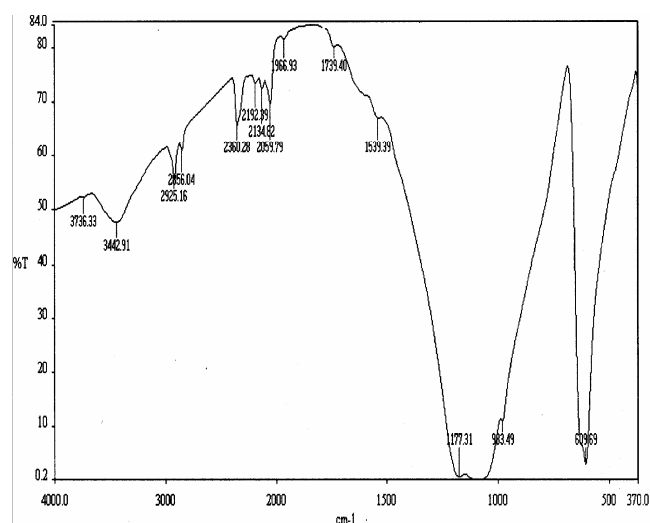


Fig. 2 — FTIR spectra of BaSO₄ sample at room temperature

680 to 610 cm^{-1} ranges⁷. These bands are seen in spectrum of BaSO₄ (Fig. 2) near about 610 cm^{-1} . It is worth noting 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 combination bands of the lower wave number S-O stretching and bending vibrations.

3.3 TSL results

The TSL glow curves of BaSO₄ powder samples were recorded by X-ray irradiating at RT for 5, 10, 15 and 20 min as shown in the Fig. 3. The samples of RT, X-ray irradiated BaSO₄ exhibit three glow peaks at temperatures 130, 200 and 245°C of which 130°C glow peak is the strongest. Moreover the intensities of the glow peaks are found to increase with the increase of X-ray dose. The TSL glow curves of Cu doped BaSO₄ powder samples were recorded by X-irradiating at RT for 5, 7, 10 and 15 min as shown in the Fig. 4. The TSL glow curves of RT, X-irradiated Cu-doped BaSO₄ exhibit two glow peaks at 160 and 230°C of which the intensity of 230°C glow peak is maximum. In this case also the intensities of glow peaks are found to increase with

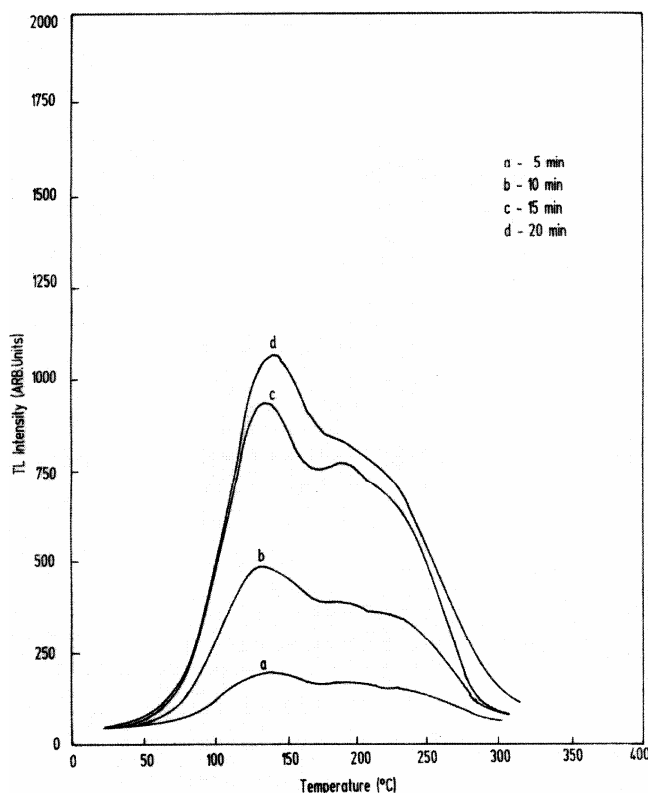


Fig. 3 — TSL Glow curves of BaSO₄ sample for different times of X-irradiation

the increase of X-ray dose. The TSL glow curves of Mn doped BaSO₄ powder sample were recorded by X-ray irradiating at room temperature for 5, 10, 15 and 20 min, as shown in Fig. 5. It exhibits two peaks at 150 and 225°C of which the glow peak at 150°C is

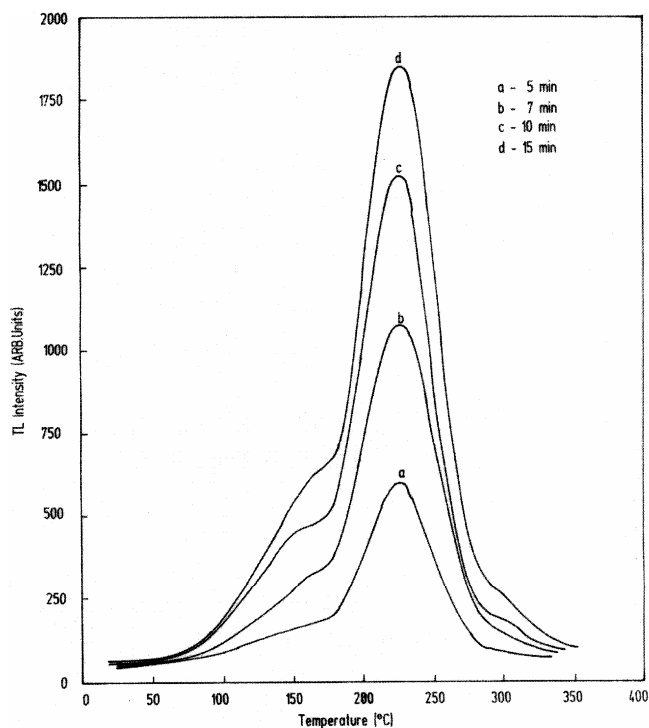


Fig. 4 — TSL Glow curves of BaSO₄:Cu sample for different times of X-irradiation

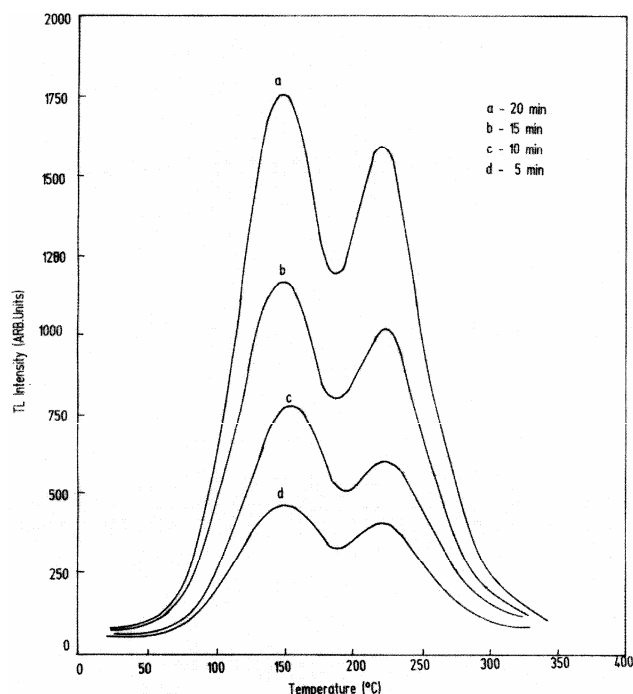


Fig. 5 — TSL Glow curves of BaSO₄:Mn sample for different times of X-irradiation

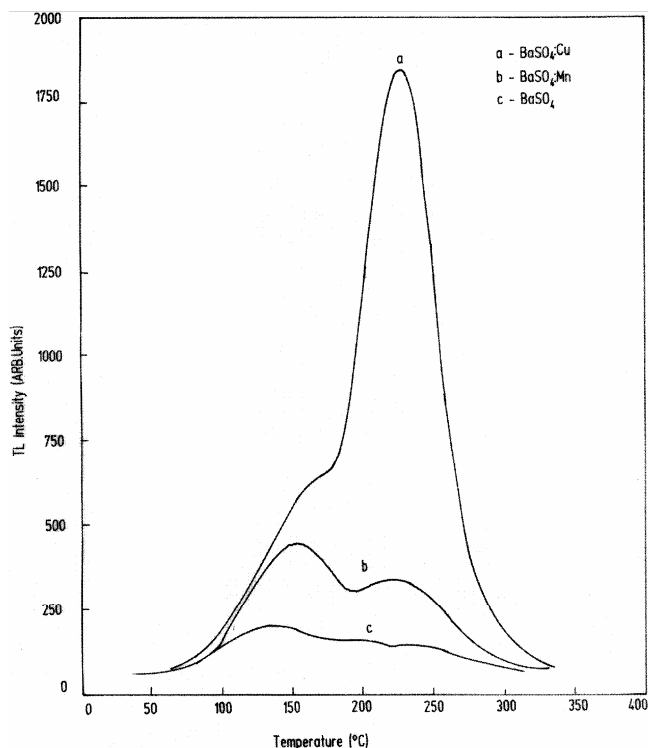


Fig. 6 — Comparative TSL glow curves of undoped, Cu and Mn doped BaSO₄ samples

more intense than 225°C glow peak. It is observed, in this case also, that the glow peaks grow in intensities with the increase of X-ray dose. Comparison of intensity of glow peak (Fig. 6) in Cu doped BaSO₄

compound shows that addition of Cu impurity to undoped BaSO₄ compound enhances the TL intensity by about 9 times and that (Fig. 6) in Mn doped BaSO₄ compound enhances the TL intensity by about 3 times.

4 Conclusions

XRD studies confirm that compound BaSO₄ have orthorhombic structure at room temperature. FTIR studies of pure BaSO₄ performed at room temperature shows that the observed peaks are in good agreement with the standard values. Hence this confirms the formation of the BaSO₄ compound. The TL sensitivity of BaSO₄ phosphor is enhanced with the incorporation of Cu and Mn impurity. However, among the studied samples namely undoped, Cu and Mn doped BaSO₄; Cu-doped BaSO₄ is found to be the most sensitive.

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