Thermally stimulated luminescence studies of undoped, Cu and Mn doped BaSO$_4$ compounds

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Thermally stimulated luminescence (TSL) of undoped and doped BaSO$_4$ with activators such as Cu and Mn has been investigated. The polycrystalline samples of undoped and doped BaSO$_4$ are prepared by melting method. The formation of BaSO$_4$ 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 BaSO$_4$ compound with that of undoped BaSO$_4$ shows that addition of Cu impurity in BaSO$_4$ compound enhances the TL intensity by about 9 times. However, the addition of Mn impurity to undoped BaSO$_4$ increases the TL intensity by about three times when compared with that of undoped BaSO$_4$. Among the studied samples namely undoped, Cu and Mn doped BaSO$_4$; Cu-doped BaSO$_4$ has been found to be the most sensitive.

Keywords: Thermally stimulated luminescence, XRD, FTIR

1 Introduction

BaSO$_4$ is one of the most sensitive TL materials used in TL dosimetry\(^1\). BaSO$_4$ doped with Cu and Mn showed high TL sensitivity and the TL response is considerably more stable\(^2\). 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 BaSO$_4$, BaSO$_4$: Cu and BaSO$_4$: Mn are expected to come at about 200°C. In this paper, undoped and doped (with Cu and Mn) BaSO$_4$ 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 BaSO$_4$ 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 BaSO$_4$ were prepared by recrystallization method\(^5\). Pure BaSO$_4$ samples have been prepared by mixing BaCO$_3$ (99%, s.d. Fine-Chem LTD., Mumbai) and conc. H$_2$SO$_4$ (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 BaSO$_4$ samples were prepared in a similar manner by taking the starting materials in stoichiometric ratio and adding 0.5 wt% of CuCl$_2$ (98%, LOBA CHEMIE, Bombay) or MnCl$_2$ (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 BaSO$_4$ 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 20 (15°≤ 20 ≤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.,
Hyderabad, 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 BaSO$_4$ 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 20 values of the diffraction lines, the interplanar spacing $d$ of the peaks was calculated. The first peak of XRD for the prepared BaSO$_4$ 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 $\Sigma \Delta d$ ($=d_{obs} - d_{cal}$) was found to be minimum. The lattice parameters of the unit cell of prepared BaSO$_4$ were $a = 8.848$ Å, $b = 5.441$ Å and $c = 7.132$ Å. The comparison of observed and calculated $d$-values (Å) of some reflections of BaSO$_4$ 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 mentioning that the $(h k l)$ values of most prominent peaks for BaSO$_4$ are (102), (211), (202) and (312).

3.2 FTIR results

Sulphates contain the SO$_4^{2-}$ structural unit. The FTIR structure of pure BaSO$_4$ 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 stretches of inorganic sulphates are found from 1140 to 1080 cm$^{-1}$. In present results of FTIR spectrum of prepared BaSO$_4$ (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.

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Fig. 1 — XRD pattern of BaSO$_4$ sample at room temperature

Fig. 2 — FTIR spectra of BaSO$_4$ sample at room temperature
680 to 610 cm\(^{-1}\) ranges. These bands are seen in spectrum of BaSO\(_4\) (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 BaSO\(_4\) 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 BaSO\(_4\) 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 BaSO\(_4\) 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 BaSO\(_4\) 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 the increase of X-ray dose. The TSL glow curves of Mn doped BaSO\(_4\) 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. 3 — TSL Glow curves of BaSO\(_4\) sample for different times of X-irradiation](image-url)

![Fig. 4 — TSL Glow curves of BaSO\(_4\):Cu sample for different times of X-irradiation](image-url)

![Fig. 5 — TSL Glow curves of BaSO\(_4\):Mn sample for different times of X-irradiation](image-url)
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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