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A Study of Thermoluminescent Mechanism Involved in Natural Barite

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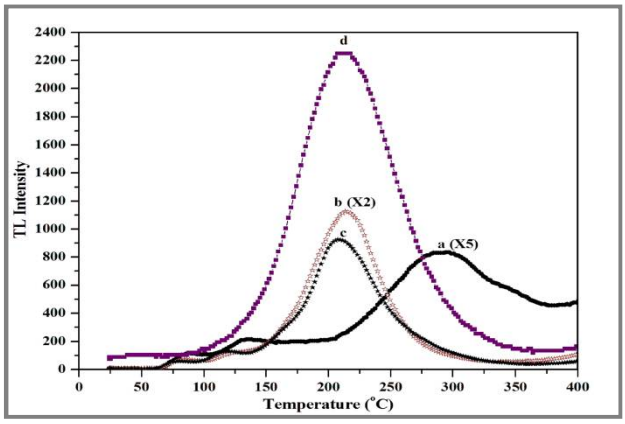
ABSTRACT

Thermoluminescence (TL) glow curves were recorded for barite sample collected from Mangampeta Mine, Cuddapah District, Andhra Pradesh. The sample was analyzed for impurity concentration using inductively coupled plasma mass spectroscopy. Thermoluminescence and photoluminescence (PL) emissions are centered at 370 and 385 nm, respectively. Electron spin resonance (ESR) study was carried out for radical identification. From the analysis of TL, PL and ESR studies the possible thermoluminescent mechanism involved in barite was studied.

Graphical Abstract



a) TL glow curves of natural barite samples NTL, b) TL of sample irradiated to 100 Gy, c) TL of sample annealed at 400°C with irradiation of 100 Gy, d) annealed at 800°C with 100 Gy irradiation (Heating rate=10°C/s)

Keywords: Molecular docking, Anti-cancer, Anti-depressant, Anti-bacterial, Binding affinities.

INTRODUCTION

Barite sample was collected from Mangampeta mine, Cuddapah district, Andhra Pradesh, India. The sample was stored in dark until TL measurements were carried out. The sample was crushed and ground carefully with a mortar and pestle and washed for 2 min with 1% HCl solution then

with distilled water to remove any organic material, and then dried on an even. Magnetic particles were removed using a suitable electromagnet [**1-5**].

The thermally stimulated luminescence (TL) measurements were done using a computerized TL reader, which was supplied by Nucleonix-TLD-96 reader India Pvt. Ltd. TL emission spectrum was recorded using a Nucleonix TL reader suitably modified for emission wavelength recording. Impurity concentration in barite sample was analyzed using inductively coupled plasma–Mass spectroscopy (ICP-MS). The ICP-MS spectrometer used for the transmission elemental analysis was Jobin Youn-24. The analysis of the rare earth elements for this study was done by Sciex Elan 250 model spectrometer. ESR spectra of unirradiated and irradiated samples were recorded by mean of an X-band spectrometer (varian model E109) with a 100 kHz magnetic field modulation at TE_{102} mode cavity [**6-10**].

MATERIALS AND METHODS

Barite sample was collected from Mangampeta mine, Cuddapah district, Andhra Pradesh, India. The sample was stored in dark until TL measurements were carried out. The sample was crushed and ground carefully with a mortar and pestle and washed for 2 min with 1% HCl solution then with distilled water to remove any organic material, and then dried on an even. Magnetic particles were removed using a suitable electromagnet.

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RESULTS AND DISCUSSION

TL glow curves: TL glow curves were recorded for the collected barite samples with different modes such as natural thermoluminescence (NTL), sample irradiated with a test dose of 100 Gy, and for a sample annealed at 400 and 800°C then irradiated with a test dose of 100 Gy. The glow curves obtained for all the samples show a similar structure with respect to shape, intensity and peak position. Representative glow curve characteristic of natural thermoluminescence, artificial thermoluminescence (100 Gy) and annealed (400 and 800°C) then irradiated (100 Gy) samples are illustrated in Figure 1.

The natural thermoluminescence (NTL) of the sample consists of two glow peaks appearing at 80 and 120°C and a high temperature peak at 295°C (Figure 1a). For the irradiated sample the peak at 215°C is a new peak induced by irradiation (Figure 1b). The 800°C annealed sample (Figure 1d) shows a single high sensitivity glow peak (215°C) with the complete removal of low temperature glow peaks (80 and 120°C). The appearance of the low temperature glow peaks in the previous cases may be due to the presence of certain defects in the lattice. However, in annealed samples, these defects are removed. Hence the low temperature peaks disappear in this case.

TL, PL emission and ICP-MS studies: Figures 2 and 3 show the TL and PL emission spectra of selected natural barite samples. The TL and PL emissions are centered at 370 and 385 nm, respectively. In general, the emission spectra of $BaSO_4$ in figures 2 and 3 show characteristics emission of individual impurities. But in natural samples, a possible way to identify the impurity

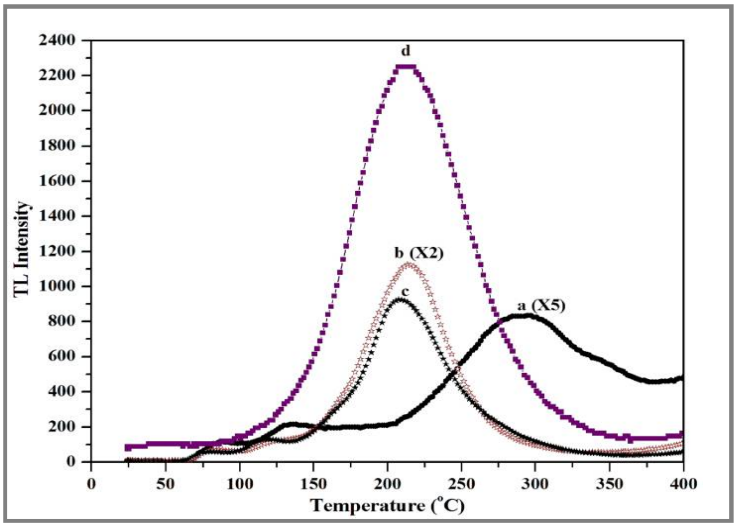

Figure 1. a) TL glow curves of natural barite samples NTL, b) TL of sample irradiated to 100 Gy, c) TL of sample annealed at 400°C with irradiation of 100, d) annealed at 800°C with 100 Gy irradiation (Heating rate = 10°C/s).

responsible for TL emission are i) by measuring the elemental concentrations of impurity ions in the natural samples ii) by comparing the PL and TL emission spectra of natural barite samples with those of synthetic $BaSO_4$ samples with the known doped impurities. Therefore, the trace elemental concentrations were measured through ICP-MS and their results are presented in Table 1.

Table 1. Impurity concentration in natural barite sample using inductively coupled plasma-mass spectroscopy (ICP-MS).

Impurity	Concentrations (ppm)	Impurity	Concentrations (ppm)
Ca	90	Ag	15
Mg	75	Eu	10
Sr	35	Sm	50
Mn	20	Tm	--
Pb	--	Dy	--
Cu	--	Ce	--
Cr	30	Tb	10
Al	15	--	--

The UV band observed at 370 nm on the TL emission spectrum (Figure 2) is a known emission involving energy levels of $4f^6$ 5d and $4f^7$ configuration of the Eu^{2+} ion [**11**]. According to Yamashita *et al.* [**12**], the TL emission spectrum of Eu^{2+} ions in the barium sulfate lattice shows up in the wavelength region of 375 nm.

Luminescence due to Eu is known in many minerals, including barite, where the presence of two different forms of this luminescence centre was established. The first one is connected with the direct isomorphic substitution of Eu^{2+} for Ba^{2+}. This gives an emission at 380 nm and the second one is connected with a substitution of Eu^{3+} for Ba^{2+} and subsequent reduction Eu^{3+} - Eu^{2+} effected by natural irradiation. This shows up as a PL band at 460 nm [**13**]. Yamashita *et al.* [**12**] observed the PL emission bands of all alkaline earth sulfate phosphors activated with Eu^{2+} ions in the locality of 380 nm. In the present case, the PL emission band is observed at 385 nm (Figure 3). By comparing the experimental results with relevant literature, the present investigation shows more possibility of substitution of Eu^{2+} ion for Ba^{2+} in the barite host lattice and is assumed to be responsible for the observed TL emission.

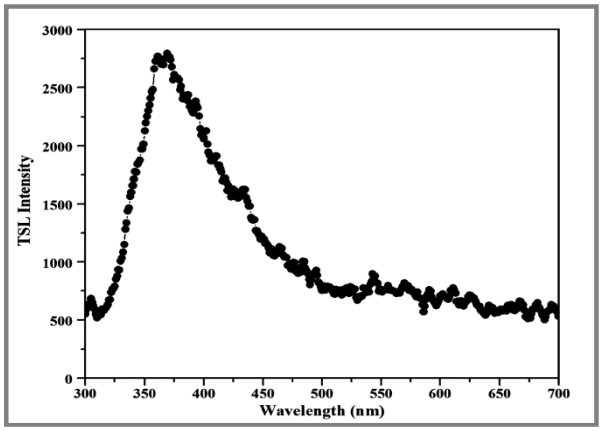

Figure 2. TL emission spectrum of barite sample.

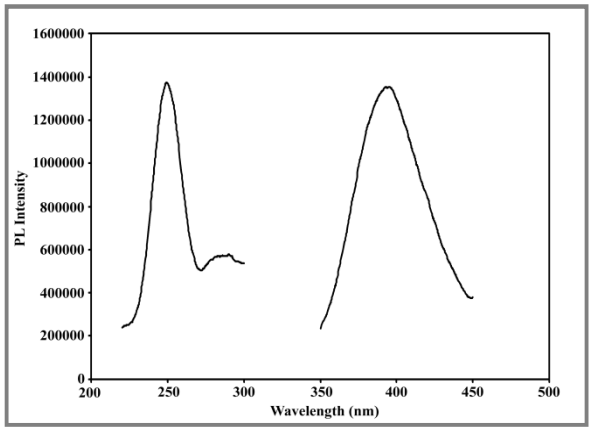

Figure 3. PL excitation and emission spectra of barite sample.

Identification of radicals: Figure 4a shows an ESR spectrum of a natural barite sample without irradiation, which has g factor values of 2.0225 and 2.0150. Figure 4b shows an ESR spectrum of irradiated barite sample (100 Gy ^{60}Co gamma dose), which shows a triplet signal with the g factor values of 2.0055, 2.0032 and 2.0021.

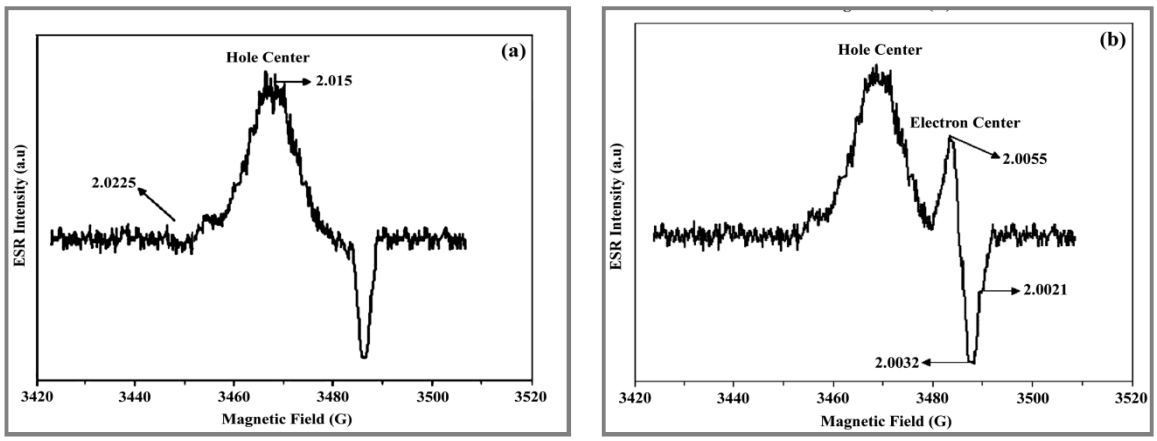

Figure 4. ESR spectra for a) unirradiated and b) gamma irradiated barite.

In the present study, the g-factor values obtained are compared with the available literature values and it can be concluded that the g values obtained from the collected samples could be related to the hole-type defect center and it corresponds to SO_4^- radical. The g values obtained from the irradiated sample's ESR spectrum reveals that it could be related to the electron type defect center and corresponds to SO_3^- radicals [**14, 15**]. The slight disagreement between the literature and observed g values may be due to the lattice environment of the radicals.

Mechanism: An empirical model for the TL process in natural black coloured barite has been demonstrated on the basis of analyzing the ESR, TL and PL results obtained and as well as the previously available literature [**16**].

After natural irradiation, electrons released from the parent sulfate radicals SO_4^{2-} and the released electrons are captured by the Eu^{3+} ions, reducing these to Eu^{2+} state. The sulfate ion reaches SO_4^- state and acts as the hole-trapping center which was confirmed through ESR studies in Figure 5.

$$\left.\begin{aligned} SO_4^{2-} &\rightarrow SO_4^- + e^- \\ Eu^{3+} + e^- &\rightarrow Eu^{2+} \end{aligned}\right\} \text{Natural irradiation}$$

During the irradiation process the already existing SO_4^- radicals in the barite lattice releases the electron-hole pairs and reaches the SO_3^- (electron trapping center) state and the released charge carriers are trapped in the corresponding trapping centers. On TL read out, the trapped charge carriers recombine and the recombination energy is released non-radioactively and absorbed by the nearest impurity ion (Eu^{2+}) which gets excited, and acts as a luminescence centre. When the luminescence centre returns to the ground state, the absorbed energy is released in the form of light *i.e.,* the characteristics emission of the impurity ion (Eu^{2+}). This is clearly illustrated in the Figure 5.

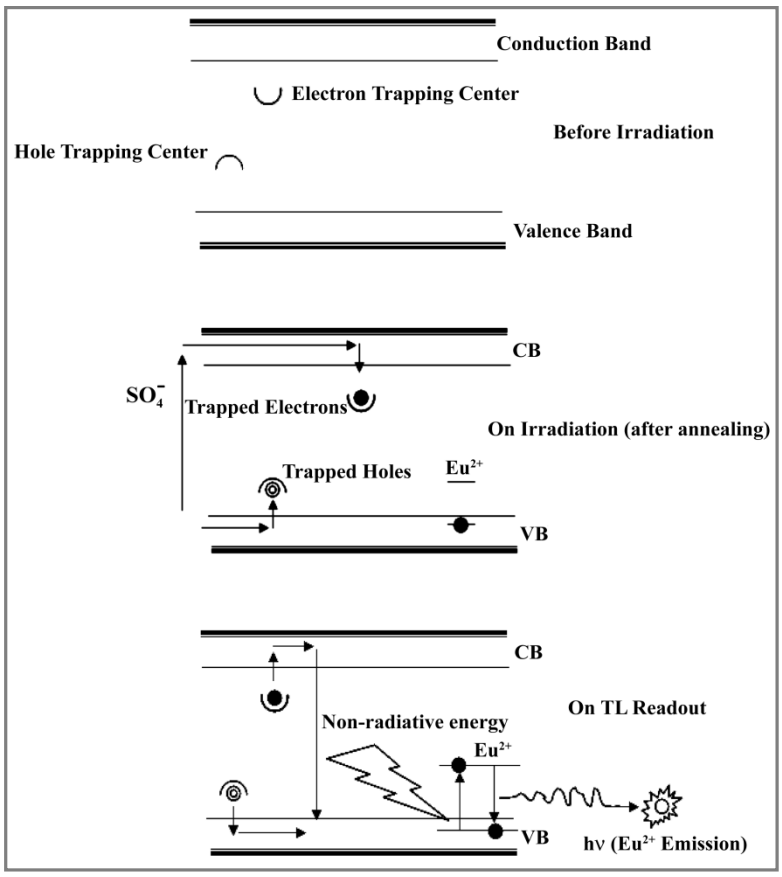

Figure 5. Schematic diagram of TL mechanism involved in natural barite.

APPLICATION

The studies are useful to study the possible thermoluminescent mechanism involved in barite.

CONCLUSION

TL glow curves of selected barite sample were recorded successfully. The NTL of the sample consists of two low temperature glow peaks appearing at 80 and 120°C and a high temperature peak at 295°C. On irradiating the sample at 100 Gy a new peak appears at 215°C. The sample annealed at 800°C shows a single highly sensitive glow peak at 215°C. An ESR study of a non-irradiated sample revealed the SO_4^- radicals. However, SO_3^- radicals were formed after irradiating the sample. Using ICP-MS analysis, the presence of impurity ions was identified. The TL and PL emissions are centered at 370 and 385 nm, respectively. The PL emission spectrum shows a direct isomorphic substitution of Eu^{2+} ion for Ba^{2+} ion because only one emission band is observed at 385 nm. The possible TL mechanism involved in the sample analyzed shows that the electron hole pairs are

released from sulfate radicals created on irradiation and are trapped in the corresponding trapping sites. On TL read out, the trapped charge carriers recombine and the recombination energy is released in the form of non-radioactive energy. This non-radioactive energy is absorbed by the nearest impurity Eu^{2+} ion exciting it to the excited level. The excited impurity ion acts as a thermoluminescence centre, giving its characteristics light emission. Further, the sample was used for TL dosimetric analyses.

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