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Optical absorption and thermoluminescence of Dy³⁺-doped BaSO₄ γ irradiated at room temperature

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Abstract. The thermoluminescence (TL) of Dy³⁺-doped BaSO₄ γ irradiated at room temperature was studied in the temperature range 300–573 K. The TL glow curve of this phosphor material consists of four peaks at 407, 420, 442 and 487 K. The spectral character of the emission recorded during TL was found to be the same for all glow peaks and consists of several bands associated with the characteristic emission of Dy³⁺ ions due to transitions from the lowest excited state ⁴F_{9/2} to the ground-state multiplets ⁶H₇. Optical absorption measurements before and after irradiation, as well as after a TL run were also performed, in order to obtain better insight into the mechanism of TL production in this phosphor material. These measurements revealed that optical absorption in γ -irradiated BaSO₄:Dy³⁺ arises predominantly from two sources: firstly defect centres intrinsic to the barium sulphate structure, and secondly oxidation of the Dy³⁺ impurity ion to the 2+ valence state. A mechanism for TL based on a charge-transfer process between dysprosium ions and host-related hole centres is proposed. Some of the main dosimetric characteristics of this phosphor material are also reported.

1. Introduction

Numerous investigations dealing with the optical absorption, electron paramagnetic resonance (EPR) and thermoluminescence (TL) of γ - or x-irradiated calcium sulphate doped with rare-earth (RE) impurity ions have been performed during the last two decades (Nambi *et al* 1974, Huzimura *et al* 1980, Nambi and Bapat 1980, Las *et al* 1980, Danbi *et al* 1982, Bacci *et al* 1984, Sunta 1984, Teh-Chao *et al* 1984, Matthews and Stoebe 1982, Srivastava and Supe 1985, Morgan and Stoebe 1989). The interest in this phosphor material arises mainly because of its high sensitivity as a solid state dosimeter and the ease with which it can be economically prepared in the laboratory.

The influence of RE impurities in the TL of CaSO₄, γ irradiated at room temperature, has been studied by Nambi *et al* (1974) using different spectroscopic techniques. These workers found that the RE elements have little effect on the glow-curve peak temperatures and that the radicals such as SO₄⁻ and SO₃⁻, produced by ionizing radiation, form stable trapping sites of various activation energies which are responsible for the multipeak TL glow curves exhibited by the CaSO₄ phosphors. The TL emission spectra of the 16 RE-doped CaSO₄ systems investigated by Nambi *et al* consisted of the dipole-forbidden 4f → 4f transitions of the RE³⁺ impurity ion. Nambi *et al* also found that Dy³⁺ and Tm³⁺ are the most efficient activators of TL in CaSO₄ and follow the concentration quenching law.

To the knowledge of the present authors, three different models have been developed to account for TL production in RE-doped CaSO₄ to date. In the first model, electrons and holes

are trapped during irradiation at defect sites independent of the RE ion. During heating, the electrons and holes are detrapped and recombine. The recombination energy excites the RE^{3+} ions by means of a resonant energy transfer mechanism which gives rise to the observed $f \rightarrow f$ transitions of the RE ion. In the second model, some of the released electrons are trapped during irradiation by the RE^{3+} ions, reducing these to RE^{2+} . The released holes in turn are captured at the sulphate sites. During the TL process, mobile holes recombine with RE^{2+} to form excited states $RE^{2+} + h^+ \rightarrow (RE^{3+})^* \rightarrow (RE)^{3+} + (h\nu)_{TL}$. In the third model, the RE^{3+} ion acts as an electron trap with charge recombination at radical sites, resulting in energy transfer to RE ions which de-excite by luminescent emission. This model differs from the second model because the RE ion acts only as the luminescent centre and not as the centre of recombination which takes place at a radical. While Nambi and Bapat (1980) considered the second model as the most appropriate to account for experimental data in γ -irradiated $CaSO_4$ doped with Ce, Eu, Dy or Tm ions, Matthews and Stoebe (1982) found that the model most consistent with their data dealing with TL emission and optical absorption spectra of γ -irradiated Dy^{3+} -doped $CaSO_4$ was the third model.

To extend our understanding of the processes operating during TL in alkaline-earth sulphates doped with RE impurity ions, we analysed the optical absorption and TL of Dy^{3+} -doped $BaSO_4$ γ irradiated at room temperature, and the results obtained are presented in this paper. The objectives of this study are

- (a) to determine the TL emission spectrum as a function of temperature as the material is heated from room temperature to 573 K,
- (b) to analyse the dose dependence of the TL emission spectrum in the dose range 10^{-2} –10 Gy,
- (c) to understand the underlying TL mechanism and
- (d) to explore the possibility of using $BaSO_4:Dy^{3+}$ as a dosimetric material.

2. Experimental details

The single crystals of $BaSO_4:Dy(0.5 \text{ mol}\%)$ employed in the present investigation were grown in our laboratory following the solution–evaporation growth technique described by Morgan and Stoebe (1989). Crystallization was controlled by varying the temperature and the air flow rate. After an evaporation time of 12 h, using an air flow rate of 750 ml min^{-1} and with the acid temperature held at 558 K, high-quality single crystals were obtained. These crystals were washed repeatedly (ten times) with distilled water to remove all the remaining acid and dried at 570 K for 5 h before measurements were carried out.

Irradiations with ^{60}Co γ radiation were made with a Vickrad 200 unit of 6.15 TBq at a dose rate of 40 mGY S^{-1} .

The TL measurements were performed using a Harshaw 4000 TL analyser coupled with a PC to analyse the glow curves. The heating rate was programmed at 10 K S^{-1} from room temperature to 573 K. All readings were made in a N_2 atmosphere.

The basic electronic equipment for detecting the TL emission spectrum at a particular temperature was the same as described elsewhere (Camacho *et al* 1988, Rosete *et al* 1993). To record the spectrum, a 0.45 m Pacific grating monochromator possessing a scanning motor drive attachment and a Hamamatsu R943-03 photomultiplier tube were employed. The output of the phototube was processed by a Pacific photometer model 162 and then it was presented in a strip chart recorder.

Room-temperature optical absorption spectra were obtained in the wavelength region 190–900 nm with a Perkin–Elmer model λ -5 double-beam recording spectrophotometer.

Photoluminescence measurements were carried out using a Perkin-Elmer model 650-10S spectrofluorometer equipped with a 150 W Xe lamp and a red-sensitive detector.

3. Results and discussion

Before the irradiations were carried out, our Dy-doped BaSO_4 crystals were characterized using optical absorption and photoluminescence techniques. The crystals did not show any optical absorption band in the wavelength region 190–900 nm. The fluorescence spectrum obtained under UV excitation revealed the presence of three bands peaking at 475 nm, 573 nm and 655 nm which are the characteristic emissions of the Dy^{3+} ion due to the dipole-forbidden transitions ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$, ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{11/2}$, respectively (Fry *et al* 1968). These results gave evidence that Dy was present in our crystals in its trivalent state.

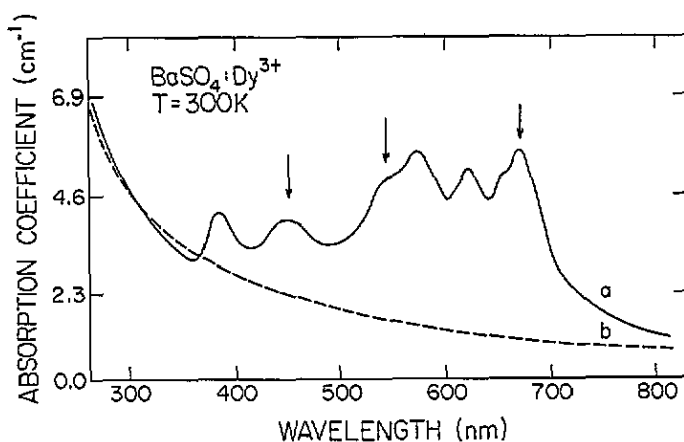


Figure 1. Room-temperature optical absorption spectra of γ -irradiated Dy-doped BaSO_4 (curve (a)) and unirradiated material (curve b).

Figure 1 portrays the room-temperature optical absorption spectrum of a crystal of Dy-doped BaSO_4 , γ irradiated at 300 K, for a dose of nearly 1 Gy. The absorption spectrum of the same crystal recorded before the irradiation was carried out is also given in figure 1 for comparison purposes. γ -irradiated material shows absorption bands at about 370, 450, 545, 576, 622, 650 and 670 nm. More highly resolved spectra have no additional absorptions to these.

Absorption in irradiated barium sulphate has been previously studied by several workers (Bakhtin *et al* 1973, Chaudhury *et al* 1984) and the optical absorption in this material at wavelengths of 370 nm, 575–600 nm and 620–650 nm was attributed to the intrinsic defect centres SO_4^- , SO_3^- and O^- , respectively. In the present study of Dy-doped BaSO_4 , absorption bands exist that correspond to both of these previous studies; absorptions at 622 and 650 nm could correspond to O^- , the band at 576 nm is believed to be due to SO_3^- absorption, and the band peaking at 370 nm may be attributed to absorption by the SO_4^- radical.

On the other hand, the wavelength peak positions 450, 545 and 670 nm of the absorption bands indicated by arrows in figure 1 are very similar to those at which the dipole-allowed

$4f^{10} \rightarrow 4f^9 5d$ transitions of the Dy^{2+} ion appear in the alkaline-earth fluorides and also in $CaSO_4$ (Nambi and Bapat 1980, Morgan and Stoebe 1989, Rubio 1991). This information may indicate that during irradiation of barium sulphate some of the Dy^{3+} ions act as electron traps to form Dy^{2+} .

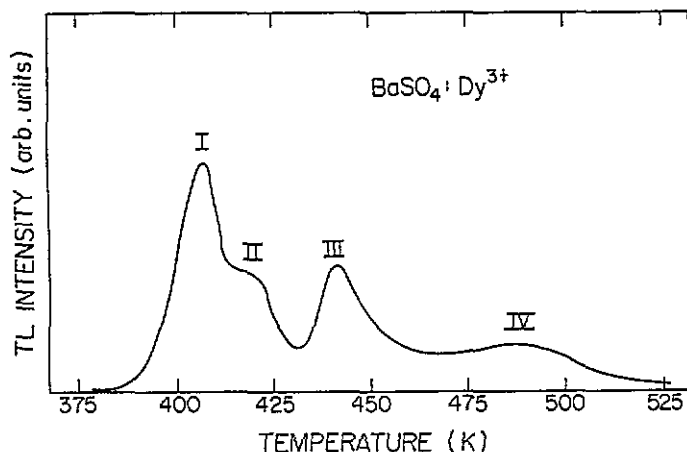


Figure 2. Typical TL glow curve of Dy-doped $BaSO_4$ irradiated with ^{60}Co γ radiation at 300 K.

A typical TL spectrum of Dy-doped $BaSO_4$, γ irradiated at room temperature, is portrayed in figure 2. The exposure level for the sample represented in this figure was about 1 Gy of ^{60}Co γ -rays. The glow curve exhibits a four-peak pattern. The four peaks appear at 407, 420, 442 and 487 K. A high γ -ray dose up to about 10 Gy did not reveal any significant changes in the shape of the glow curve, except a nominal increase in the overall intensity.

The TL emission spectra in the wavelength region 220–800 nm were taken at temperatures slightly below the corresponding glow peak temperatures. At least three scans were taken at each temperature to confirm the consistence of the spectral tracings obtained. The spectral character of the emission was found to be the same for all four peaks and it was independent of exposure up to 10 Gy. Figure 3 shows, as an example, the emission spectrum obtained for the case of the 407 K glow peak. The spectrum consists of three bands peaking at about 473, 573 and 660 nm. The wavelength peak positions of these emission bands are nearly identical with those appearing in the emission spectrum of Dy-doped $BaSO_4$ before irradiation. Therefore, they were ascribed to the characteristic emissions of the Dy^{3+} ion due to the transitions $^4F_{9/2} \rightarrow ^6H_{15/2}$ (473 nm), $^4F_{9/2} \rightarrow ^6H_{13/2}$ (573 nm) and $^4F_{9/2} \rightarrow ^6H_{11/2}$ (660 nm).

It was ascertained that, after the TL glow curve had been recorded, the absorption bands due to Dy^{2+} ions, as well as to the intrinsic defect centres SO_4^- , SO_3^- and O^- , disappeared and the absorption spectrum returned to the pre-irradiation stage. These facts indicated that the radiation-induced species were annihilated during the TL process.

It is known that a TL glow curve is characteristic of the various traps existing in a phosphor material which are thermally deactivated as the temperature is progressively increased. Hence, it is proposed that the radicals SO_4^- , SO_3^- and O^- , produced by γ irradiation, form stable trapping sites of various activation energies in the lattice of barium sulphate, which are responsible for the complex multipeak TL glow curve of this phosphor

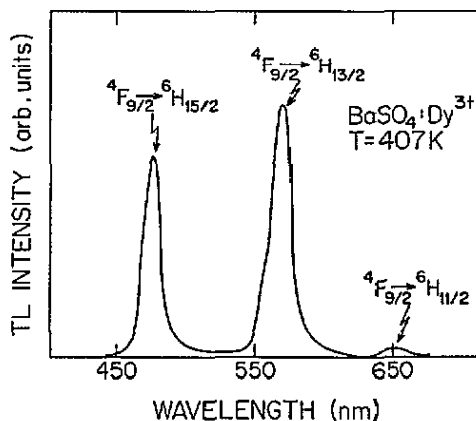


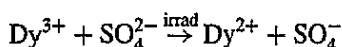
Figure 3. Spectral character of the thermally stimulated luminescence of the 407 K glow peak observed in our crystals of Dy-doped BaSO_4 γ irradiated at room temperature.

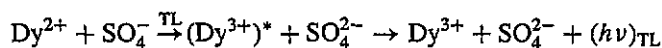
material. The trap value of the individual glow peaks calculated by the total curve-fitting method are given in table 1. Normally one does not expect a shallower trap (1.92 eV) to release holes at a higher temperature and a deeper trap (2.35 eV) to release holes at a lower temperature. The apparent anomaly in the value of the trap depth (1.92 eV) of the 487 K glow peak could be due to overlap of the glow peaks in this region. The lineshape in such cases naturally leads to lower values of trap depth on analysis. Even with a heating rate of 4 K min^{-1} we could not observe any significant evolution in the broad region, indicating that there may be a range of traps involved.

Table 1. Trap depth values of dysprosium-doped BaSO_4 .

| Peak temperature (K) | Order of kinetics | Trap depth (eV) |
|----------------------|-------------------|-----------------|
| 407 | I | 2.35 |
| 420 | I | 2.43 |
| 442 | II | 3.36 |
| 487 | I | 1.92 |

The model for TL production in Dy-doped BaSO_4 most consistent with the spectroscopic data described above is one in which, during exposure to ionizing radiation, some of the released electrons are captured by the Dy^{3+} ions, reducing these to Dy^{2+} . The released holes in turn are captured at the sulphate sites, forming trapped-hole centres of the type SO_4^- , SO_3^- , etc. Warming the irradiated sample causes these holes to become untrapped successively at different temperatures depending on their thermal stability. This gives rise to a series of glow peaks from near room temperature up to about 600 K. The emission of light takes place when the thermally released hole recombines with a Dy^{2+} ion, reconvertng the latter to Dy^{3+} in an excited condition. Its relaxation to the ground state produces the light emission which is characteristic of the Dy^{3+} ion. Thus, if we take SO_4^- as a representative hole centre, the mechanism of TL production in dysprosium-doped BaSO_4 can be written as





where the asterisk represents an excited state.

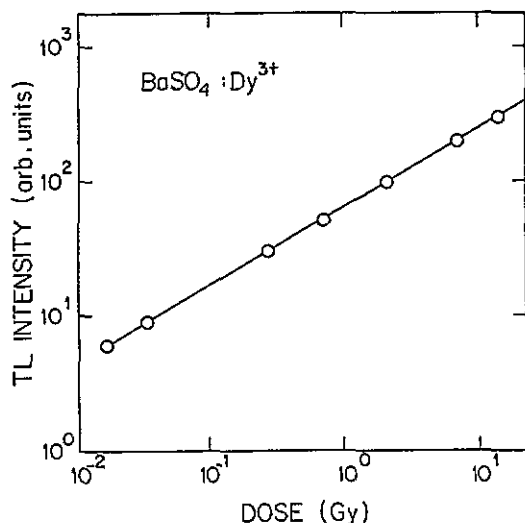


Figure 4. Thermoluminescent response of Dy-doped BaSO₄ as a function of ⁶⁰Co γ -radiation dose.

In order to explore the possibility of using the Dy-doped BaSO₄ phosphor material as a TL dosimeter, some of its main dosimetric characteristics were also analysed. In figure 4 we show the TL response of this material (area under the total TL emitted above 300 K) as a function of γ -irradiation dose on a logarithmic scale from 10⁻² to about 10 Gy. The data in this figure represent the average of at least three measurements obtained for different samples. The reproducibility of measurements was about 7%. Reference to figure 4 shows that quite a good linear dependence exists between the total output and γ -irradiation dose up to about 10 Gy. Above this value, the dependence deviates from the linear behaviour. Fading at room temperature was about 14% in a month. To make this determination the dose meters were irradiated at a dose of 1 Gy and then stored at 300 K in a covered black plastic box. After different storage periods of up to 30 d, all samples were read out and the different TL readings were compared with the readings carried out immediately after irradiation.

4. Summary

In summary, optical absorption, TL glow curves and TL emission spectra of room-temperature γ -irradiated Dy-doped BaSO₄ have been obtained in the present investigation. The TL glow curve consists of four peaks whose intensities increase with increasing exposure dose. The absorption due to the radiation-induced trapped hole centres SO₄⁻, SO₃⁻ and O⁻ has been identified. These centres have different activation energies and they are responsible for the multippeak TL glow curve of this phosphor material.

Our experimentally determined spectroscopic data give direct evidence of the reduction of the Dy^{3+} ions by γ irradiation and reoxidation of the doubly valent ions on subsequent heating with the simultaneous emission of the characteristic trivalent Dy fluorescence. The model that we are proposing for TL production in Dy-doped BaSO_4 is similar to that considered by Nambi *et al* (1974) to account for spectroscopic data obtained in γ -irradiated CaSO_4 doped with RE^{3+} impurity ions. Finally, our data suggest that $\text{BaSO}_4:\text{Dy}^{3+}$ may be employed as a useful solid state dosimeter. In order to establish firmly this possibility, experiments are now in progress in our laboratory with the aim of analysing some other dosimetric properties of this material such as threshold dose, neutron response, and sensitivity to daylight.

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