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Electron spin resonance, thermoluminescence and fluorescence studies on BaSO₄:Eu and BaSO₄:Eu, P thermoluminescent phosphors

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Received 9 November 1994, in final form 21 March 1995

Abstract. The paramagnetic radicals formed in the TL phosphors BaSO₄:Eu and BaSO₄:Eu, P have been studied using the technique of ESR. Two radicals, assigned to SO₂⁻, were observed at room temperature. One of them exhibits a hyperfine interaction with a nearby cation. Step annealing measurements suggest a connection between these radicals and the TL glow peaks at 170 and 215 °C. Co-doping BaSO₄:Eu with phosphorus enhanced its TL efficiency. ESR and fluorescence emission measurements indicate that the enhancement results from an increased intake of divalent europium into the lattice.

1. Introduction

With a view to replacing conventional x-ray films and screens, many high- Z_{eff} phosphors are being developed for their potential use as x-ray imaging devices. Ba₅SiO₄Br₆:Eu (Meijerink *et al* 1989) and BaFBr:Eu (Gurvich *et al* 1990, von Seggern *et al* 1988, Takahashi *et al* 1984) are examples of high- Z phosphor-based photostimulable screens used for the assessment of the spatial dose distribution of high-energy photons in an irradiated human body. Okamoto *et al* (1986) have reported the development of sensitive BaSO₄:Eu TL phosphor-based screens for the study of hadronic and electromagnetic cascade showers in ultra-high-energy interactions. The TL sensitivity of BaSO₄:Eu Teflon discs has been reported (Azorin *et al* 1991, Bhatt *et al* 1991) to be higher than that of similar CaSO₄:Dy-embedded Teflon discs for ⁶⁰Co γ -rays. We have now developed a more sensitive phosphor, namely BaSO₄:Eu, P which could be used as an x-ray storage phosphor and also for personal and environmental radiation dosimetry.

The TL process in BaSO₄:Eu is related to the defect centres created by γ -irradiation. On the basis of ESR measurements, Krystek (1980) has reported $V_{\text{Ba}}\text{-SO}_4^-$ (where V_{Ba} is the Ba²⁺ vacancy), SO₂⁻ (trapped hole centres), and F, F⁺, α_2^{3+} (electron traps) as the radiation-induced defects in BaSO₄ single crystals. From their results they have concluded that the release of holes initiates the luminescence process in the material. The release of holes from the defect centres has also been found to be responsible for the TL phenomenon in CaSO₄:Dy and CaSO₄:Dy, Na systems (Morgan and Stoebe 1990, Gundu Rao *et al* 1993).

Yamashita *et al* (1985) prepared BaSO₄:Eu by the coprecipitation technique followed by sintering at 1000 °C for 1 h in an N₂ gas atmosphere. They observed that Eu enters BaSO₄ as Eu²⁺. They proposed Eu²⁺ ↔ Eu⁺ conversion as an integral part of the TL process. Luthra and Gupta (1974), on the other hand, proposed that trapping and recombination centres are characteristic of the host lattice. The energy of recombination is transferred to the Eu²⁺ ion and thus the TL emission is in the form of characteristic Eu²⁺ emission. Recently Atone *et al* (1993) have reported the preparation of BaSO₄:Eu by coprecipitation followed by thermal treatment at either 400 °C or 700 °C. Thus they were able to incorporate Eu into the BaSO₄ lattice predominantly in Eu³⁺ or Eu²⁺ form. However, the TL sensitivities of these samples were $\frac{1}{16}$ and $\frac{1}{3.5}$ respectively of that of CaSO₄:Dy TLD phosphor. Atone *et al* (1993) have also reported that Eu³⁺ ↔ Eu²⁺ or Eu²⁺ ↔ Eu⁺ conversion is not an integral part of γ -induced TL. Thus, it is essential to identify and characterize the defect centres formed due to irradiation in order to understand the mechanism of the TL process. ESR provides a convenient and sensitive technique for such a study.

On additionally doping with phosphorus, we have found that the TL efficiency of the BaSO₄:Eu phosphor is enhanced more than five times. In the present study, we have combined ESR, TL and fluorescence data to obtain information about the identification and decay of various defect centres and also to look for a possible reason for the enhanced TL efficiency of the BaSO₄:Eu, P system.

2. Experimental details

Barium sulphate doped with europium (Eu²⁺) and co-doped with phosphorus (P⁵⁺) were prepared by two different methods, namely recrystallization and coprecipitation. The procedure adopted by Yamashita (1974) and Dixon and Ekstrand (1974) was utilized for preparing samples by the recrystallization method. In the coprecipitation method, BaCl₂ · 2H₂O, (NH₄)₂HPO₄ and Eu₂O₃ were used as the basic ingredients. BaSO₄:Eu and BaSO₄:Eu, P were prepared by dissolving BaCl₂ · 2H₂O (Analar grade) and (NH₄)₂HPO₄ (in the case of BaSO₄:Eu, P) in deionized water and Eu₂O₃ in dilute sulphuric acid. When the two solutions were mixed together, the BaSO₄:Eu and BaSO₄:Eu, P were coprecipitated. The liquid on the top of the precipitates was removed. The precipitates were allowed to settle down by keeping the solution undisturbed. The precipitates were then washed several times with distilled water until the water in the beaker became neutral. After the precipitates were dried on a hot plate, the precipitates were divided into several parts for treating them at different temperatures (from 400 to 900 °C) for 1 h. Various samples of BaSO₄:Eu were prepared by varying the concentration of europium from 0.05 to 0.5 mol%; 0.2 mol% gave the optimum sensitivity. Samples of BaSO₄:Eu, P were prepared by taking that concentration of dopant (0.5 mol% Eu) which was higher than that yielding maximum TL sensitivity in BaSO₄:Eu and varying the phosphorus concentration. The phosphorus concentration was varied from 0.05 to 0.5 mol%. As the main TL peak occurred at a relatively low temperature of 160 °C for BaSO₄:Eu and BaSO₄:Eu, P prepared by the method of Yamashita (1974), samples prepared by the coprecipitation process were used in the following experiments. For ⁶⁰C irradiations, a γ cell (dose rate, 54 Gy min⁻¹) calibrated with a Fricke chemical dosimetry system and telecobalt therapy machine were used.

The powder samples were pre-irradiation annealed at 400 °C for 1 h and given a test γ dose. ESR and fluorescence of these samples were measured. 50 mg samples each of BaSO₄:Eu and BaSO₄:Eu, P phosphors were separately given a test γ dose of 1 Gy. The TL

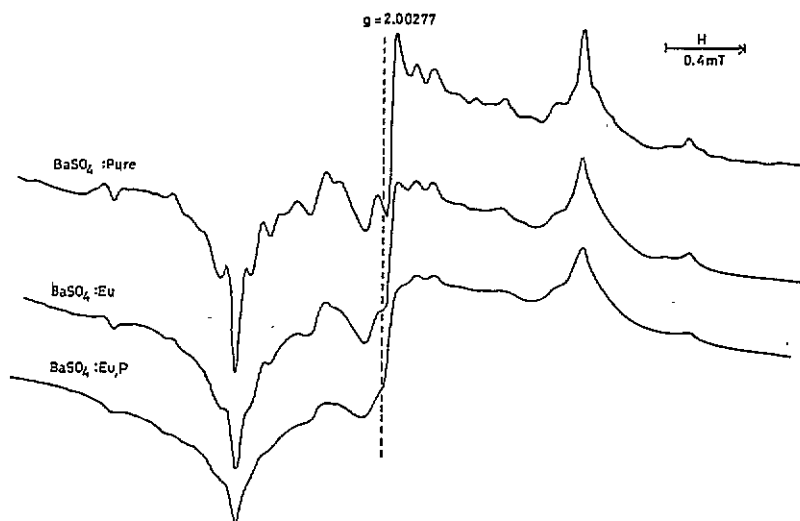


Figure 1. ESR spectra of BaSO_4 (pure), $\text{BaSO}_4:\text{Eu}$ (0.5 mol%) and $\text{BaSO}_4:\text{Eu}, \text{P}$ (0.5 mol%, 0.2 mol%) recorded at room temperature.

glow curves were recorded on an x-y recorder using a locally made TLD reader described elsewhere (Bhatt *et al* 1988).

ESR experiments were carried out on a Varian E-112 E-line Century series ESR spectrometer which utilizes 100 KHz field modulation. TCNE ($g = 2.00277$) was used as a standard for g -factor measurements. Step heat treatments were performed to follow the decay and evolution of defect centres. These were carried out *in situ* in the ESR cavity using the Varian variable-temperature accessory. Each treatment consisted of heating for 2 min after which the sample was allowed to cool to 25 °C.

Fluorescence for various samples was studied on a Hitachi F-4000 fluorescence spectrometer. The same amount of sample was used every time. Emission and excitation spectra were recorded with a spectral width of 1.5 nm.

3. Results

Figure 1 shows the ESR spectrum of $\text{BaSO}_4:\text{Eu}$, $\text{BaSO}_4:\text{Eu}, \text{P}$ and pure BaSO_4 recorded at 25 °C after irradiation with 5 kGy of ^{60}Co rays at 25 °C. The scan range has been selected to record only the lines in the vicinity of free-electron resonance. There is, however, an overlap from Eu^{2+} lines in the ESR spectra of $\text{BaSO}_4:\text{Eu}$ and $\text{BaSO}_4:\text{Eu}, \text{P}$. Also the radical lines are broadened in europium-doped systems, in contrast to pure BaSO_4 systems, probably due to the presence of Eu^{2+} paramagnetic ions in the lattice. The ESR spectra arising from a low dose of γ irradiation in pure BaSO_4 and $\text{BaSO}_4:\text{Eu}, \text{P}$ systems are shown in figure 2. It is observed that a higher irradiation dose results in increased concentrations of radicals and no new defect centres are observed at higher doses. It is seen from figure 1 that similar spectra are observed for the three systems. The spectrum may be divided into two groups of lines. These groups are shown in figure 3. The first group (figure 3(b)) appears intense and is centred around the free-electron resonance. The spectrum is characteristic of a centre exhibiting a rhombic g -tensor with the principal g -values 2.0074, 2.0025 and 1.9965. This centre is assigned to an SO_2^- radical and henceforth is referred to as $\text{SO}_2^-(\text{A})$ (see section 4).

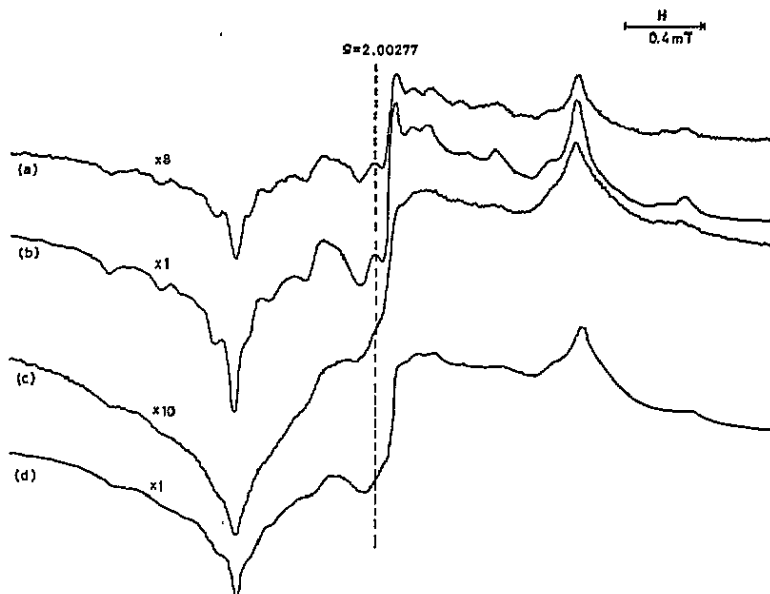


Figure 2. ESR spectra of $\text{BaSO}_4:\text{Eu,P}$ (0.5 mol%, 0.2 mol%) and pure BaSO_4 at room temperature: curve (a), pure BaSO_4 at 50 Gy irradiation; curve (b), pure BaSO_4 at 5 kGy irradiation; curve (c), $\text{BaSO}_4:\text{Eu,P}$ (0.5 mol%, 0.2 mol%) at 200 Gy irradiation; curve (d), $\text{BaSO}_4:\text{Eu,P}$ (0.5 mol%, 0.2 mol%) at 5 kGy irradiation. For recording the ESR spectra (a) and (b), the receiver gain has been increased by factors of 8 and 10, respectively.

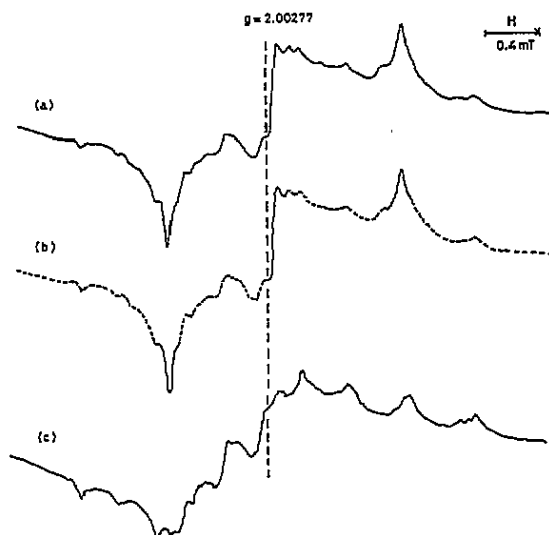


Figure 3. ESR spectra of $\text{BaSO}_4:\text{Eu}$ (0.5 mol%) at room temperature. Spectrum (a) is decomposed into spectra (b) and (c).

Figure 3(c) shows a second group of ESR lines which seems to arise from a single radical. The spectrum may be understood in terms of a radical with rhombic g -tensor where the unpaired electron interacts with a nearby cation with a nuclear spin of $I = 3/2$.

The principal g -values are found to be 2.0089, 2.0040 and 1.9976. As barium (¹³⁵Ba and ¹³⁷Ba) has a nuclear spin of $\frac{3}{2}$, each of the ESR lines will be split into four lines due to hyperfine interaction. However, the observed spectrum cannot be understood in terms of barium hyperfine interaction as the dominant central lines due to ¹³⁸Ba ($I = 0$ and abundance = 71.83%) were not observed in the composite spectrum. Thus, the nearby cation hyperfine interaction could be explained (Hofstaetter 1995) due to the presence of traces of Na⁺ or K⁺ ions (each with a nuclear spin of $\frac{3}{2}$; abundance of ²³Na and ³⁹K are 100% and 93.1%, respectively) in the BaSO₄ host lattice. The possible presence of traces of Na⁺ or K⁺ in BaSO₄ host cannot be ruled out as a contaminant. The observed principal hyperfine couplings are 7.8, 7.6 and 13.2 MHz. These values indicate that the hyperfine interaction is very nearly dipolar in character. Hence the hyperfine couplings are decomposed into an isotropic coupling constant A_{iso} and an anisotropic coupling constant τ by assuming the maximum coupling value to be positive and the other two values negative. The isotropic coupling constant A_{iso} is found to be -0.48 MHz and the anisotropic values are -7.3 , -7.0 and 13.7 MHz. This radical is also assigned to SO₂⁻, referred to as SO₂⁻(B) (see section 4).

The presence of europium in the barium sulphate lattice or codoping with phosphorus does not cause any significant change in the intensity of the radical.

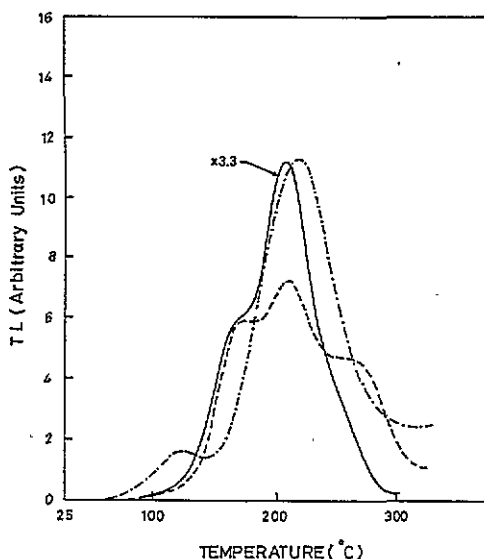


Figure 4. TL glow curves of BaSO₄:Eu,P (—), BaSO₄:Eu (----) and CaSO₄:Dy (— · —).

Figure 4 shows the TL glow curves for CaSO₄:Dy, BaSO₄:Eu and BaSO₄:Eu,P TL phosphors. It is seen that for BaSO₄:Eu and BaSO₄:Eu,P the main TL peak occurs at 215 °C with the 170 and 280 °C TL peaks appearing as shoulders on either side. Codoping of 0.2 mol% phosphorus in BaSO₄:Eu (0.5 mol%) is found to give the optimum TL sensitivity and desired glow peak structure. It is also seen (figure 4) that for BaSO₄:Eu,P the high-temperature (280 °C) peak is reduced to a small hump. Phosphorus concentrations greater than 0.2 mol% in BaSO₄:Eu resulted in a shift of the main dosimetry peak (215 °C) to lower temperatures. The observed γ TL sensitivities of BaSO₄:Eu (0.5 mol%) and BaSO₄:Eu,P

(0.5 mol%, 0.2 mol%) are compared in table 1 with $\text{CaSO}_4\text{:Dy}$ (0.05 mol%), the well known highly sensitive TL phosphor used in radiation dosimetry. It is seen that codoping of $\text{BaSO}_4\text{:Eu}$ (0.5 mol%) with 0.2 mol% phosphorus increases its TL sensitivity by 5.6 times. The TL sensitivity of $\text{BaSO}_4\text{:Eu,P}$ (0.5 mol%, 0.2 mol%) is about 2.95 times that of $\text{CaSO}_4\text{:Dy}$ (0.05 mol%). It may be mentioned that Van der Voort and Blasse (1990) have observed that phosphorus codoping results in an enhanced luminescence efficiency for $\text{CaSO}_4\text{:Eu}$. Figure 5 shows the TL glow curves for $\text{BaSO}_4\text{:Eu,P}$ at γ doses of 0.5 kGy and 5 kGy, respectively. It can be seen that the glow curve structures are nearly the same in the two cases. This indicates that no new TL active peak centres are formed at these irradiation doses.

Table 1. γ sensitivity of $\text{BaSO}_4\text{:Eu,P}$ prepared by coprecipitation.

Phosphor	TL sensitivity (215 °C) (peak height)
BaSO_4 (pure)	0.01
$\text{CaSO}_4\text{:Dy}$ (0.05 mol%)	1.00
$\text{BaSO}_4\text{:Eu}$ (0.5 mol%)	0.55
$\text{BaSO}_4\text{:Eu,P}$ (0.5 mol%, 0.2 mol%)	2.94

Table 2. Relative concentration of $\text{SO}_2^-(\text{A})$ and $\text{SO}_2^-(\text{B})$ radicals in BaSO_4 (pure), $\text{BaSO}_4\text{:Eu}$ and $\text{BaSO}_4\text{:Eu,P}$ samples.

Phosphor	Relative concentration of radicals after γ irradiation ^a	
	$\text{SO}_2^-(\text{A})$	$\text{SO}_2^-(\text{B})$
BaSO_4 (pure)	7.00	4.90
$\text{BaSO}_4\text{:Eu}$	6.22	4.90
$\text{BaSO}_4\text{:Eu,P}$	5.48	4.03

^a The intensities of these radicals was nearly zero in unirradiated samples.

A step annealing technique was used to measure the stability of the SO_2^- centres. The sample was returned to room temperature and the signal intensity recorded after each step. Figure 6 shows the behaviour of the ESR spectrum of the $\text{SO}_2^-(\text{A})$ radical with temperature. The presence of europium in the barium sulphate lattice or codoping with phosphorus does not cause any change in the intensity of the radical (table 2). The thermal decay of the ESR signal of $\text{SO}_2^-(\text{A})$ is shown in figure 7. These measurements show that the $\text{SO}_2^-(\text{A})$ radical may be removed by step annealing the sample to around 170 °C.

Figure 8 shows the behaviour of the ESR spectrum of the $\text{SO}_2^-(\text{B})$ radical with temperature. Figure 9 shows the thermal decay of the ESR signal of the $\text{SO}_2^-(\text{B})$ radical. It is seen that the radical decays at around 220 °C and thus relates well to the main 215 °C TL peak observed in the $\text{BaSO}_4\text{:Eu}$ system.

A broad band in the vicinity of 380 nm, characteristic of Eu^{2+} , is observed in the emission spectra of europium-doped BaSO_4 and hence it is concluded that europium is incorporated into the BaSO_4 lattice in its divalent state. Our ESR experiments show that there is no appreciable change in the intensity of the Eu^{2+} signal after γ irradiation. It is, therefore, likely that irradiation does not cause any change in the divalent state of europium

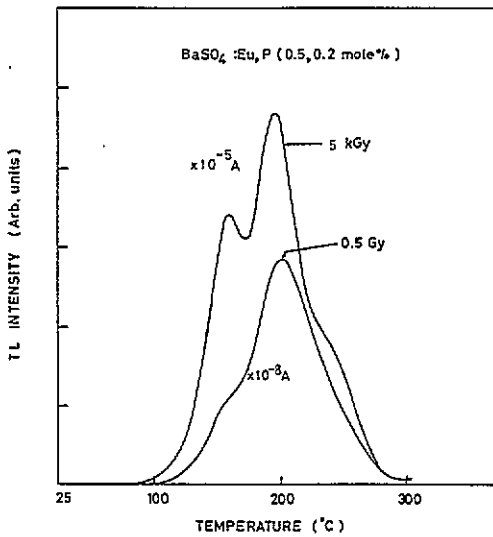


Figure 5. TL glow curve of $\text{BaSO}_4:\text{Eu}, \text{P}$ after test γ doses of 0.5 Gy and 5 kGy. The notations 10^{-8} A and 10^{-5} A on the glow curves are the current ranges of the d.c. amplifier unit.

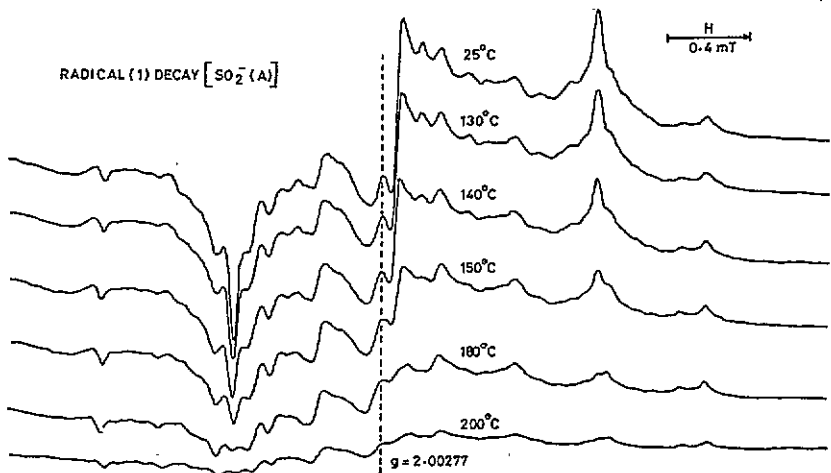


Figure 6. Effect of post-irradiation annealing treatment on the ESR spectrum of the $\text{SO}_2^-(\text{A})$ radical in the BaSO_4 lattice with increasing temperature.

ion. The TL emission spectra of $\text{BaSO}_4:\text{Eu}$ and $\text{BaSO}_4:\text{Eu}, \text{P}$ are characteristic of the Eu^{2+} ion, and hence Eu^{2+} acts as the activator in these lattices.

Figure 10 shows the relative growth of ESR and fluorescence signal intensities with annealing temperature. One-to-one correspondence in the growth of these signals indicate enhanced incorporation of Eu^{2+} in the BaSO_4 lattice at elevated temperatures with an optimum intensity at around 900°C .

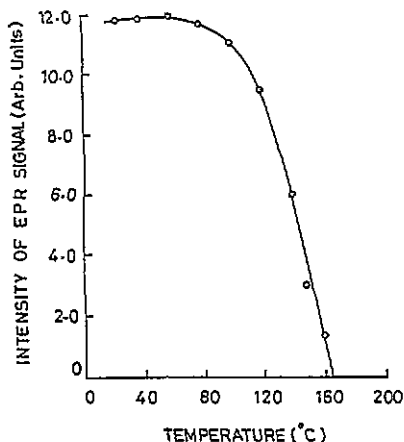


Figure 7. Stability of the ESR signal of the $\text{SO}_2^-(\text{A})$ radical in the BaSO_4 lattice with increasing temperature.

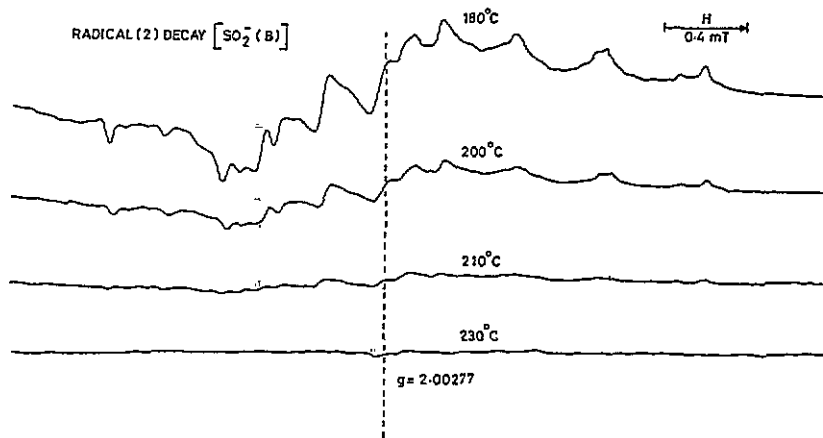


Figure 8. Effect of post-irradiation annealing treatment on the ESR spectrum of the $\text{SO}_2^-(\text{B})$ radical in the BaSO_4 lattice with increasing temperature.

4. Discussion

The SO_2^- radical is formed in the present system from the parent SO_4^{2-} ion. SO_2^- is a 19-electron radical with a bent structure. It is likely to have C_{2v} symmetry with the following electronic structure:

$$(1a_1)^2(1b_2)^2(2a_1)^2(2b_2)^2(3a_1)^2(1b_1)^2(1a_2)^2(3b_2)^2(4a_1)^2(2b_1)^1, {}^2B_1. \quad (1)$$

The ground state is B_1 and mixes mainly with the occupied states. Hence, the principal values of the g -tensor are expected to show a positive deviation from the free-electron value. The ground state is expected to be constituted by out-of-plane p orbitals with a little admixture of d orbitals (Atkins and Symons 1967). If the d orbitals are neglected, the g -shift for the direction perpendicular to the plane of the radical is almost zero as the p orbitals which constitute $2b_1$ molecular have a zero component of angular momentum about this axis, and the principal g -value corresponding to this direction should be close to the free-electron g -value. As the g -shift corresponding to the two-fold symmetry axis of

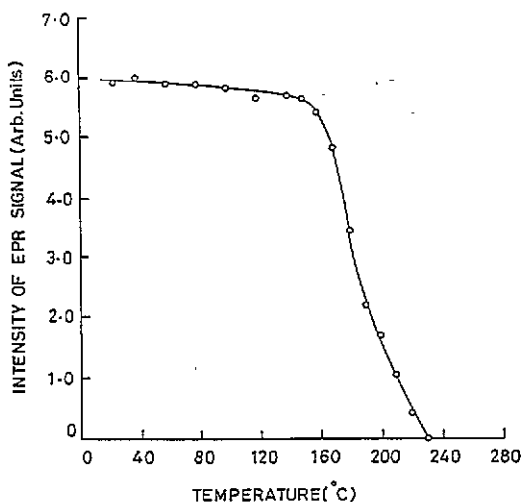


Figure 9. Stability of the ESR signal of the SO_2^- (B) radical in the BaSO_4 lattice with increasing temperature.

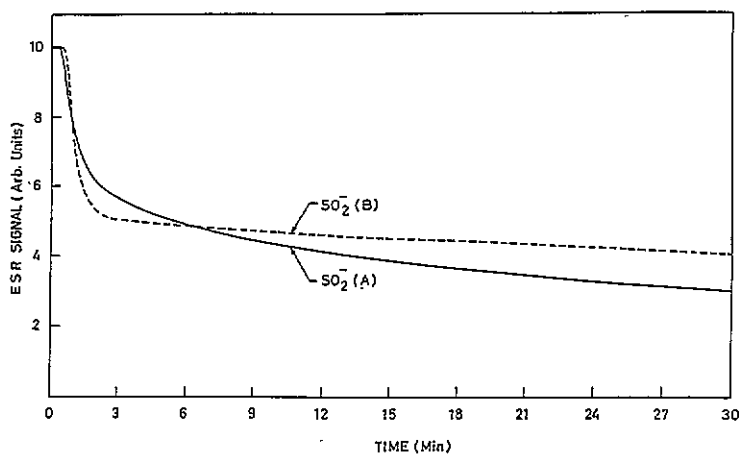


Figure 10. Relative stabilities of the SO_2^- (A) and SO_2^- (B) radicals in the BaSO_4 lattice during an isothermal anneal at 120°C .

the radical arises from mixing of a B_2 state with the ground B_1 state and as this state is relatively close lying, this admixture will produce a small positive shift. The third principal g -value arises from mixing of the A_1 state and leads to a large positive g -shift due to close proximity of the A_1 state to the ground state. The observed g -values for the radical assigned to SO_2^- are in reasonable agreement with these expectations. We have optimized the geometry of the SO_2^- radical using the gradient optimization method. The S-O bond is found to be 1.54 \AA whilst the O-S-O angle is found to be 108° . The molecular orbital occupied by the unpaired electron is calculated using the MNDO method (Dewar and Thiel 1977) to be

$$\phi(2b_1) = c_1 S(3s) + c_2 S(3p_2) + (b_1/\sqrt{2}) O(2p_{x_1} + 2p_{x_2}) \quad (2)$$

where $c_1 = 0.71$, $c_2 = 0.12$ and $b_1 = 0.69$.

Thus the unpaired electron is predominantly in the out-of-plane p orbitals with the main portion of the unpaired electron density confined to the central sulphur atom. As the major isotope ^{32}S is non-magnetic, the ESR lines due to $^{33}\text{SO}_2^-$ radicals will be of very low intensity and difficult to observe in the present study concerned with powder samples.

Several SO_2^- radicals, each with a distinct reorientation, can be formed from the parent SO_4^{2-} ion. The observed barium interaction for only one of the SO_2^- radicals can be understood on the basis that this radical is formed in such a way that the out-of-plane p orbitals which constitute the molecular orbital occupied by the unpaired electron are directed towards a nearby cation.

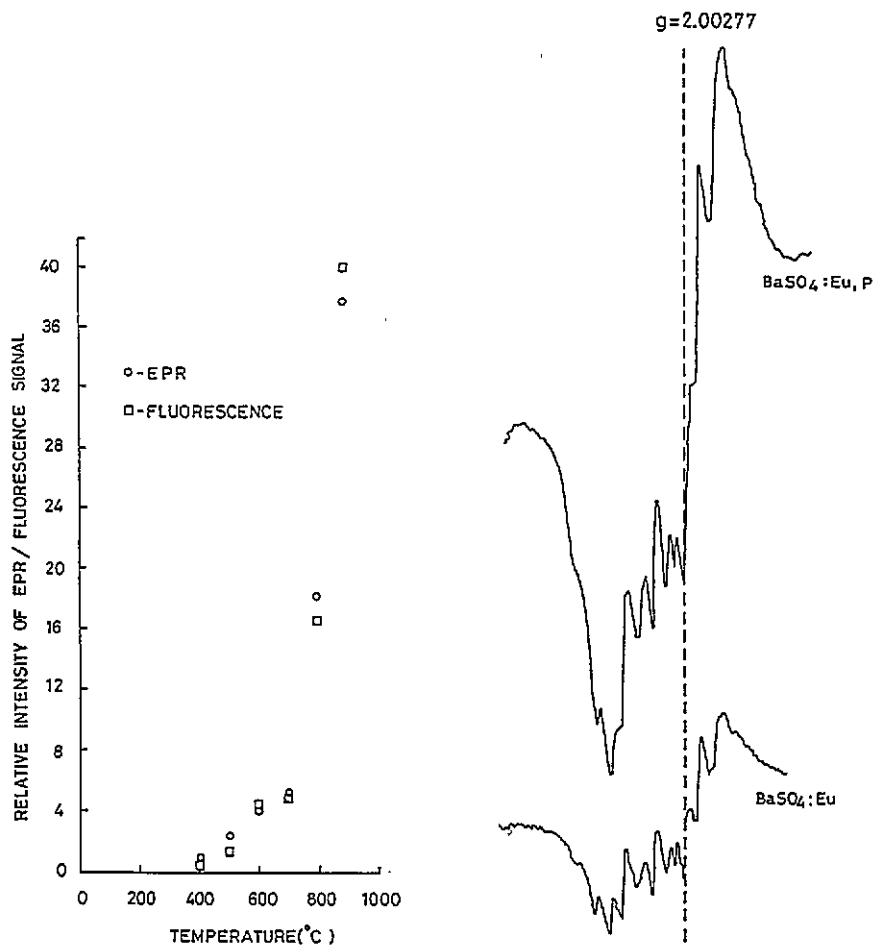


Figure 11. Relative growth of the ESR (O) and fluorescence (□) signal intensities with annealing temperature for $\text{BaSO}_4:\text{Eu}$.

Figure 12. Relative ESR spectra of the Eu^{2+} ion in $\text{BaSO}_4:\text{Eu,P}$ and $\text{BaSO}_4:\text{Eu}$.

Our MNDO results show that the negative charge of the SO_2^- radical is localized equally on the oxygen atoms. The observed hyperfine interaction of the SO_2^- (B) radical points to the presence of a nearby cation. The cation represents an effective positive charge. This

proximity of positive charge is likely to give more stability to the $\text{SO}_2^-(\text{B})$ radical than to the $\text{SO}_2^-(\text{A})$. This conjecture is well supported by the isothermal decay experiments. Figure 11 shows the results of these experiments carried out at 120°C . It is seen that the $\text{SO}_2^-(\text{B})$ radical is more stable than the $\text{SO}_2^-(\text{A})$ radical. The observed decay of the $\text{SO}_2^-(\text{B})$ radical has only a single component contribution. On the other hand, decay of the $\text{SO}_2^-(\text{A})$ radical also has a small contribution from $\text{SO}_2^-(\text{B})$ due to overlap of ESR lines of the two radicals (figure 3) and should be considered as two components contributing to the decay.

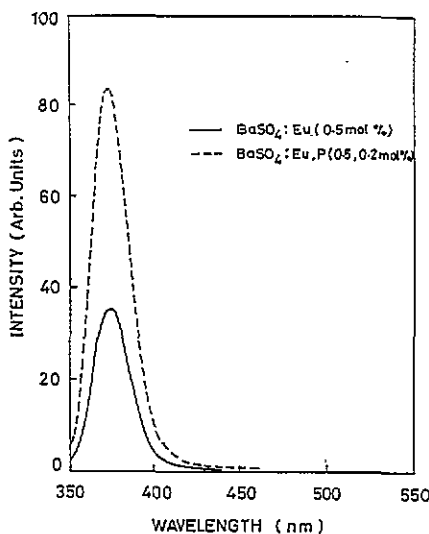


Figure 13. Intensity of fluorescence emission for $\text{BaSO}_4:\text{Eu}$ (0.5 mol%) (—) and $\text{BaSO}_4:\text{Eu,P}$ (0.5 mol%, 0.2 mol%) (---) phosphors.

We have observed that, on codoping of $\text{BaSO}_4:\text{Eu}$ (0.5 mol%) with phosphorus (0.2 mol%), the TL efficiency of $\text{BaSO}_4:\text{Eu}$ can be increased by about 5.6 times. The question is whether this increase is due to an increase in the yield of the radicals responsible for TL peaks or due to an increase in luminescence centres. The present experiments show that there is no appreciable enhancement in the concentration of radicals. On the other hand, the Eu^{2+} concentration is found to increase by about 3 times on codoping with phosphorus. Figure 12 shows a part of the Eu^{2+} ESR spectra near the free-electron resonance for both $\text{BaSO}_4:\text{Eu}$ and $\text{BaSO}_4:\text{Eu,P}$. As can be seen in this figure, there is a clear enhancement of Eu^{2+} ions in the $\text{BaSO}_4:\text{Eu,P}$ system. We have confirmed this finding by fluorescence experiments. Figure 13 shows the fluorescence emission from the Eu^{2+} ion, which again shows a threefold increase in the Eu^{2+} concentration in the phosphorus codoped system. Thus the barium sulphate lattice appears to favour more incorporation of europium into the lattice with phosphorus codoping. This accounts for only a part of the increased TL efficiency of the $\text{BaSO}_4:\text{Eu,P}$ phosphor. The remaining contribution to the TL efficiency seems to be related to the presence of cation vacancies in the BaSO_4 lattice. Studies by Krystek (1980) have shown that the BaSO_4 lattice inherently contains cation vacancies. If the vacancy is situated near a europium ion in the lattice, this ion can undergo a large relaxation, giving rise to a low efficiency due to direct feeding of the ground state. Verwey *et al* (1988) have observed such radiationless processes for the Eu^{3+} ion in glasses. The presence of P^{5+} , which acts as a charge compensator, decreases the cation vacancy

concentration. This leads to a reduction in high radiationless relaxation rate and results in the observed enhancement of TL emission.

Our results indicate that there is more incorporation of europium ions into BaSO₄ in the presence of a charge compensator P⁵⁺. The effects of charge compensators on the rare-earth RE ions in model systems with high symmetries have been studied by several workers (Hughes and Pells 1974, Miller and Wright 1979, Hammers *et al* 1982, Porter and Wright 1982, Gayen and Hamilton 1983, Tissue and Wright 1987). These studies were concerned with luminescence spectra of RE ions and show a pronounced effect of charge compensators on the symmetry of the RE ion in the lattice. In this context, the following points may be noted concerning the charge compensator P⁵⁺ in the barium sulphate lattice. The increased negative charge of the anion [PO₄]³⁻ is likely to induce an added attraction with a nearest-neighbour cation. This results in a lowering of the potential minima at the cation site. The overall effect is the presence of a small sublattice of lowered-energy cations. The europium ion now sees a more energetically favourable lattice wherein it can replace a Ba²⁺ ion. However, it must be pointed out that there is no direct experimental evidence in the present work, which points to an energetically favourable location for the europium ion in barium sulphate lattice.

5. Conclusions

Based on the present results, the following conclusions may be highlighted.

(1) TL emission near 170 °C is well correlated with a defect centre assigned to an SO₂⁻(A) radical.

(2) The SO₂⁻(B) radical exhibiting a cation hyperfine interaction is associated with the main TL peak at 215 °C.

(3) On codoping of BaSO₄:Eu (0.5 mol%) with phosphorus (0.2 mol%), the TL efficiency of BaSO₄:Eu can be increased by about 5.6 times. However, its γ -sensitivity is about 3 times that of the well known high-sensitivity CaSO₄:Dy.

(4) The increased TL efficiency of the phosphor is linked to the presence of the charge compensator P⁵⁺. The enhancement of the efficiency is brought about by two effects: firstly vacancies, which result in high radiationless relaxation rate, are decreased by the charge compensator; secondly, more europium ions are incorporated into the BaSO₄ lattice.

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