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On the sulphony radicals in $\text{CaSO}_4:\text{Dy, Na}$ thermoluminescent phosphor: electron paramagnetic resonance studies

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Abstract. The defect centres formed in the thermoluminescent phosphor $\text{CaSO}_4:\text{Dy}$ on additionally doping with Na^+ (as a charge compensator) have been studied using the technique of electron paramagnetic resonance. The Na^+ ion at the Ca^{2+} site is found to stabilize the observed SO_4^- radical. The distortion of the SO_4^- tetrahedron is not significant and is of a different nature from that previously reported. An important feature of the new SO_4^- centre is that it is characterized by an axial g -tensor with $g_{\perp} > g_{\parallel}$. The addition of Na^+ to $\text{CaSO}_4:\text{Dy}$ increases the concentration of this defect centre. On the other hand, the addition of dysprosium is found to enhance the formation and stabilization of the observed SO_3^- centre in CaSO_4 . The paramagnetic and thermal properties of these defect centres are discussed in relation to the observed thermoluminescence in $\text{CaSO}_4:\text{Dy, Na}$.

1. Introduction

It is well established that calcium sulphate phosphors can show efficient thermoluminescence (TL) in the presence of certain suitable dopants, particularly rare earths (REs), in the lattice (Draai and Blasse 1974, Nambi *et al* 1974). This enhanced TL sensitivity and the ease of preparation have made RE-doped calcium sulphate phosphors attractive in TL radiation dosimetry. One of the most important of these ions is dysprosium (Dy) as it has the highest efficiency in activating TL in $\text{CaSO}_4:\text{Dy}$.

The processes of TL are related to defect centres which are created in $\text{CaSO}_4:\text{Dy}$ and valency reduction of Dy ions due to radiation. During heating, holes are released from the defect centres. These holes recombine with the electrons of the reduced Dy ions, oxidizing them back to the trivalent state and leaving them in the excited state. On relaxation to their ground state, TL is emitted. The identification and characterization of defect centres which are formed during irradiation are essential steps in understanding the mechanism of TL. Electron paramagnetic resonance (EPR) provides a convenient and sensitive technique for such a study.

In an EPR study of pure CaSO_4 single crystals, Danby *et al* (1982) showed that x-irradiation at 290 K produces two main paramagnetic SO_4^- defects which are observable only below 215 K. These two centres are found to be related to the TL glow peaks at 395 and 465 K. On the other hand, Morgan and Stoebe (1986, 1990) have carried out extensive investigations to understand the TL mechanisms in $\text{CaSO}_4:\text{Dy}$ using EPR and optical absorption techniques. Through the application of EPR, they have observed 18 different paramagnetic centres. Of all the radical ions produced, the SO_4^- ion appears to play an important role throughout the temperature range of TL. Morgan and Stoebe find several variations of the SO_4^- defect centre which are stabilized by a nearest-neighbour Ca vacancy. The presence of Dy impurities, which increases the concentration of Ca vacancies because of charge neutrality requirements, enhances both the concentration of SO_4^- centres and the intensity of the major TL peaks near 493 and 623 K. Some investigators (Pawar 1978, Chandra *et al* 1987) have tried to prevent the formation of Ca vacancies by codoping $\text{CaSO}_4:\text{Dy}$ with Na^+ (the ionic radii of Ca^{2+} and Na^+ are 0.99 Å and 0.97 Å, respectively). From an application point of view it is pertinent to mention that the natural Li^+ and $^6\text{Li}^+$ (ionic radius, about 0.68 Å) were initially used as monovalent codopants to increase the thermal neutron response of CaSO_4 thermoluminescent phosphors in order to use them for measurements of mixed fields of neutrons and γ -rays (Ayyangar *et al* 1974, Ikeya *et al* 1971).

In the present investigation, we have studied the defect centres formed in $\text{CaSO}_4:\text{Dy}$ phosphor on additionally doping with a monovalent cation, namely Na^+ , using the EPR technique.

2. Experimental details

The method described by Yamashita *et al* (1971) was utilized to prepare batches of $\text{CaSO}_4:\text{Dy}$ (0.1 mol%) and $\text{CaSO}_4:\text{Dy,Na}$. The batches of $\text{CaSO}_4:\text{Dy,Na}$ were prepared by varying the concentration of Na while the Dy concentration remained the same. The concentrations in the CaSO_4 matrix are given here in mole per cent of the added dopant. The maximum error due to weighing is estimated to be $\pm 0.44\%$ (1σ). The phosphors were pre-irradiation annealed at 873 K for 1 h. For ^{60}Co irradiations a γ cell (dose rate = 30 Gy min^{-1}) calibrated with a Fricke chemical dosimetry system was used. A muffle furnace whose temperature variation was controlled to within $\pm 3 \text{ K}$ was utilized to anneal the samples.

EPR experiments were carried out on a Varian E-112 E-line Century series EPR 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 the defect centres. These were carried out *in situ* in the EPR cavity using the Varian variable-temperature accessory. Each treatment consisted of heating for 1 min after which the sample was allowed to cool to 293 K.

3. Results and discussion

3.1. SO_4^- centre

Figure 1 shows the EPR spectra of $\text{CaSO}_4:\text{Dy}$ doped with various amounts of monovalent cation Na^+ . The spectrum can be divided into two groups of lines.

The first group of lines is intense and is in the vicinity of free-electron resonance. The second group of lines appears in the low-field region and is recorded with a gain setting of the receiver which is ten times higher. The spectrum is characteristic of a centre exhibiting an axially symmetric g -tensor with the principal values $g_{\parallel} = 2.0060$ and $g_{\perp} = 2.0113$. These lines are assigned to the SO_4^- radical (Huzimura 1979).

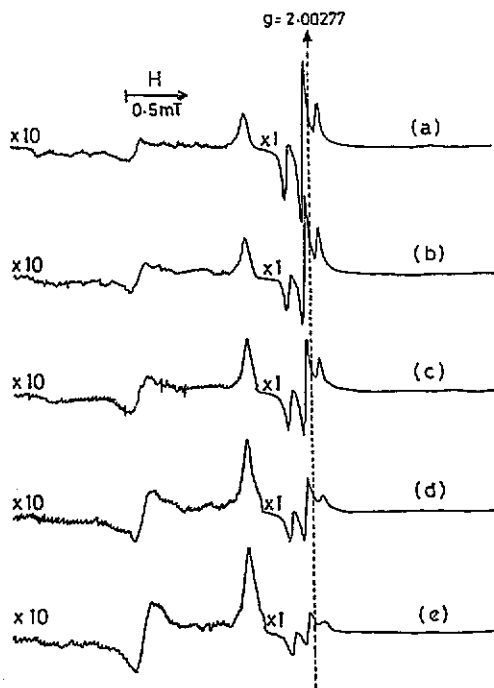


Figure 1. The EPR spectra of $\text{CaSO}_4\text{:Dy}$ with different doping concentrations of Na^+ ions: curve (a), $\text{CaSO}_4\text{:Dy}$ (0.1 mol%); curve (b), $\text{CaSO}_4\text{:Dy}$ (0.1 mol%), Na (0.02 mol%); curve (c), $\text{CaSO}_4\text{:Dy}$ (0.1 mol%), Na (0.05 mol%); curve (d), $\text{CaSO}_4\text{:Dy}$ (0.1 mol%), Na (0.2 mol%); curve (e), $\text{CaSO}_4\text{:Dy}$ (0.1 mol%), Na (0.5 mol%).

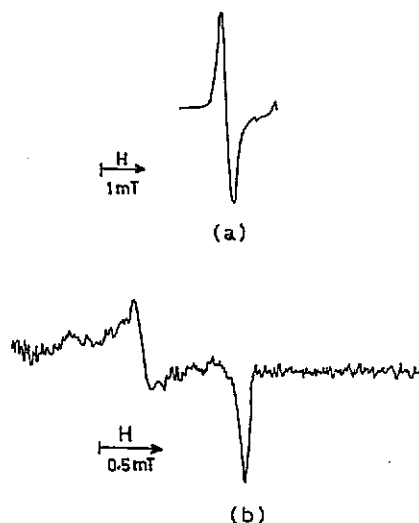


Figure 2. The EPR spectra of the SO_4^- radical in pure CaSO_4 powder (curve (a)) (Huzimura 1979) and $\text{CaSO}_4\text{:Dy}$ (0.1 mol%), Na (0.2 mol%) (curve (b)) (present study).

Table 1 gives the g -values of some of the SO_4^- centres reported in the literature. In a previous study of pure CaSO_4 , Huzimura (1979) has observed that the concentration of SO_4^- radicals increases with increasing Na doping. The g -tensor is, however, different from the present case and is nearly isotropic (table 1). Figure 2 shows a comparison of the SO_4^- radical spectrum obtained in the present study with that reported by Huzimura. The two signals are distinctly different and indicate that we are observing a different kind of SO_4^- radical. The yield of the radical is found to increase with increased Na doping. Figure 3, curve a, shows the dependence of the EPR signal intensity on the Na^+ ion concentration. The radical is found to decay with time and this behaviour is shown in figure 4, curve a.

A stable charge distribution of the SO_4^- radical is possible if the SO_4^- centres are preferentially forming near Ca^{2+} vacancies. The excess negative charge present at

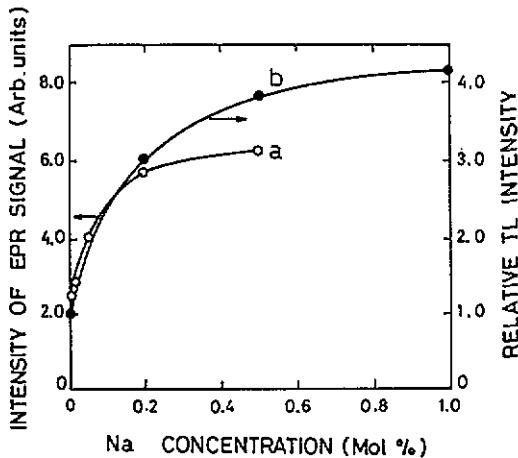


Figure 3. The dependences of the EPR signal intensity of the SO_4^- radical (curve a) and the corresponding relative TL intensity for 404 K peak (curve b) on the Na concentration in $\text{CaSO}_4:\text{Dy}$, Na systems.

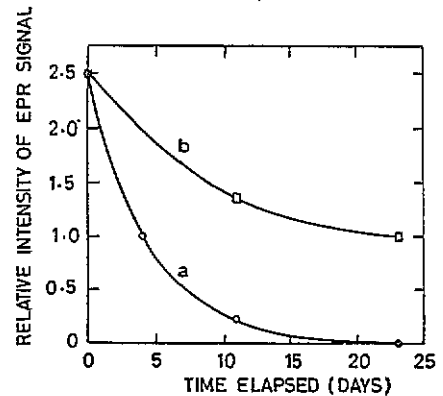


Figure 4. The relative variation in the intensities of the EPR signals, with time in days, due to the SO_4^- radical in $\text{CaSO}_4:\text{Dy}$ (0.1 mol%), Na (0.5 mol%) (curve a) and the SO_3^- radical in $\text{CaSO}_4:\text{Dy}$ (0.1 mol%), Na (0.2 mol%) (curve b).

Table 1. Principal g -values reported for radiation-induced SO_4^- radicals in CaSO_4 and doped CaSO_4 lattices.

Material	Temperature (K)	g -values	Reference
CaSO_4	300	$g_{\parallel} = 2.011 \approx g_{\perp} = 2.012$	Huzimura (1979)
$\text{CaSO}_4:\text{Tm}$	300	2.011, 2.022, 2.005	Huzimura et al (1980)
$\text{CaSO}_4:\text{Tm}$	300	2.004, 2.012, 2.023	Huzimura and Atarashi (1982)
$\text{CaSO}_4:\text{Tm}$	300	2.009, 2.020	Huzimura and Atarashi (1982)
$\text{CaSO}_4:\text{Dy}$	120	2.0006, 2.0091, 2.0395	Danby et al (1982)
$\text{CaSO}_4:\text{Sm}$	77	$g_{\parallel} = 2.0288, g_{\perp} = 2.0101$	Sheshagiri et al (1988)
$\text{CaSO}_4:\text{Sm}$	300	$g_{\parallel} = 2.0263, g_{\perp} = 2.0144$	Sheshagiri et al (1988)
$\text{CaSO}_4:^{241}\text{Am}$	77	$g_{\parallel} = 2.0370, g_{\perp} = 2.0060$	Natarajan et al (1988)
$\text{CaSO}_4:^{241}\text{Am}$	300	$g_{\parallel} = 2.0260, g_{\perp} = 2.0106$	Natarajan et al (1988)
$\text{CaSO}_4:\text{Dy}$	77	2.0022, 2.0081, 2.0386	Morgan and Stoebe (1990)
$\text{CaSO}_4:\text{Dy, Na}$	300	$g_{\parallel} = 2.0060, g_{\perp} = 2.0113$	This study

such a vacancy is partially cancelled by the generation of positive holes on the SO_4^- centre. This situation is possibly occurring in the SO_4^- radicals studied by Danby et al (1982) and Morgan and Stoebe (1990). A more stable configuration would be a situation wherein two-hole centres are formed at the SO_4^{2-} ion. In that case, the generation of two holes on oxygen ions completely cancels the excess negative charge at the Ca^{2+} vacancy. Morgan and Stoebe (1990), indeed, have observed such two-hole centres in their single-crystal study of the $\text{CaSO}_4:\text{Dy}$ system. In the present case, the SO_4^- radical appears to be stabilized by the Na^+ ion occupying a Ca^{2+} site. [Na^+ in V_{Ca}] has an excess negative charge. This is neutralized because of the hole on the SO_4^- radical. Apparently, there is not much distortion of the SO_4^- tetrahedron

compared with the $[\text{V}_{\text{Ca}}-\text{SO}_4^-]$ case, where the positive hole is not able to neutralize completely the negative charge at the V_{Ca} site. As the distortion is relatively small, the SO_4^- centre does not exhibit a rhombic g -tensor. In fact, it shows an axial g -tensor. In the present study, it is observed that $g_{\perp} > g_{\parallel}$ in contrast with the earlier cases of an axially symmetric SO_4^- radical (table 1).

The electronic structure of the SO_4^- radical has been discussed by Bishop *et al* (1966) and Samoilovich *et al* (1968) on the basis of semiempirical molecular orbital calculations assuming tetrahedral T_d symmetry for this kind of AB_4 type of molecule. The molecular orbitals are classified according to the group symmetry. These studies yielded the following electronic configuration for the 31-valence-electron SO_4^- ion:

$$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^5, {}^2T_1.$$

This configuration is in accord with the x-ray photoelectron and x-ray emission spectroscopy of SO_4^- ions in Li_2SO_4 (Kosuch *et al* 1980). More accurate *ab-initio* SCF MO calculations by Johansen (1974) also yield the same configuration for the SO_4^- ion.

Thus, the SO_4^- radical is expected to have a 2T_1 ground state with the unpaired electron confined to the ligand atoms. Consequently, only a small hyperfine interaction with the nucleus of the central atom is anticipated, which could be due to the polarization mechanism or possibly due to dipolar interactions.

Table 2. Principal g -values reported for radiation-induced SO_3^- (I, II, III) centres in pure and doped CaSO_4 lattices.

Material	Temperature (K)	g -value	Reference
CaSO_4	300	2.0048, 2.0038, 2.0029 (I)	Huzimura (1979)
CaSO_4	300	2.0050, 2.0035, 2.0018 (II)	Huzimura (1979)
$\text{CaSO}_4:\text{Tm}$	300	2.0011, 2.0021, 2.0061 (I)	Huzimura <i>et al</i> (1980)
$\text{CaSO}_4:\text{Tm}$	300	2.0037 (II)	Huzimura <i>et al</i> (1980)
$\text{CaSO}_4:\text{Tm}$	300	2.0010, 2.0020, 2.0060 (I)	Huzimura and Atarashi (1982)
$\text{CaSO}_4:\text{Tm}$	300	2.0020, 2.0030, 2.0040 (II)	Huzimura and Atarashi (1982)
$\text{CaSO}_4:\text{Tm}$	300	2.0006, 2.0010 (III)	Huzimura and Atarashi (1982)
$\text{CaSO}_4:^{241}\text{Am}$	300	2.0030 (I)	Sheshagiri <i>et al</i> (1988)
$\text{CaSO}_4:^{241}\text{Am}$	77	2.0034 (II)	Sheshagiri <i>et al</i> (1988)
$\text{CaSO}_4:\text{Dy, Na}$	300	2.0035, 2.0030, 2.0025	This study

As mentioned earlier, in the present case the SO_4^- centre appears to be stabilized by an Na^+ ion occupying a Ca^{2+} site. There is more efficient compensation of the excess negative charge present at the $\text{V}_{\text{Ca}}[\text{Na}^+]$ site due to the hole on the SO_4^- ion. Consequently, there is likely to be less reduction in the symmetry of the SO_4^- tetrahedron from T_d symmetry. Although C_{3v} and C_{2v} point groups may be considered as possible effective symmetries, the former is assumed, based on present EPR results which show an axial g -tensor.

Figure 5 shows the orbital energy diagram for the SO_4^- ion and also the changes on going from T_d to C_{3v} symmetry (Atkins and Symons 1967). We have, however, considered two possibilities for the C_{3v} symmetry case depending upon the extent of distortion. These are shown as $C_{3v}(a)$ and $C_{3v}(b)$ in figure 5. For simplicity, only relevant orbitals are shown and excitations for the g -shifts are also indicated.

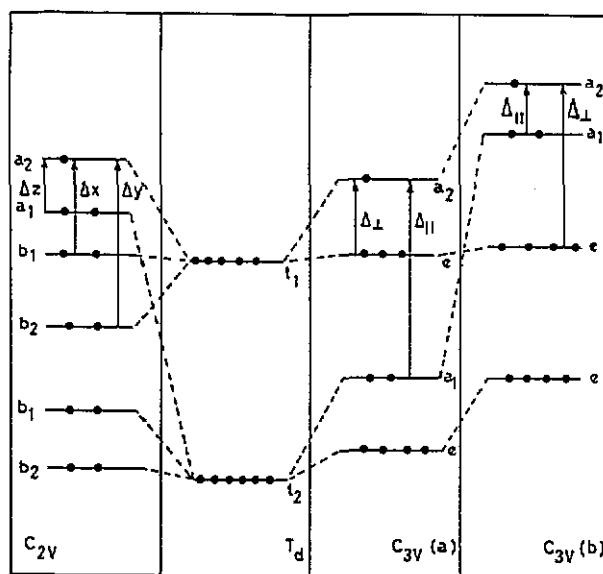


Figure 5. The proposed orbital level scheme for the SO_4^- ion showing the correlation between the T_d , C_{3v} and C_{2v} symmetries. $C_{3v}(a)$ refers to a small reduction in symmetry from T_d while $C_{3v}(b)$ corresponds to a relatively larger distortion from T_d symmetry. The relevant excitations for the g -shifts are indicated.

The g -shifts for the SO_4^- ion in C_{3v} symmetry are qualitatively understood as follows. The perpendicular value g_{\perp} arises from the excitation

$$\dots(e)^4(a_1)^2(e)^3(a_2)^2, {}^2E \leftarrow \dots(e)^4(a_1)^2(e)^4(a_2)^1, {}^2A_2$$

and the parallel value g_{\parallel} from the excitation

$$\dots(e)^4(a_1)^1(e)^4(a_2)^2, {}^2A_1 \leftarrow \dots(e)^4(a_1)^2(e)^4(a_2)^1, {}^2A_2.$$

From the energies assigned to the various orbitals in the orbital energy diagram (figure 5), it is seen that the closest e level lies beneath and close to the a_2 level (figure 5, $C_{3v}(a)$). Consequently, the perpendicular g -value (g_{\perp}) should be much larger than the free-spin value. On the other hand, the a_1 level is quite a way below the a_2 level and the parallel g -value is expected to be closer to the free-spin value. From this analysis, it appears that the SO_4^- radical will have a spectrum characterized by a small hyperfine interaction with the central nucleus and a g -tensor which exhibits axial symmetry with g_{\perp} greater than g_{\parallel} . The present experimental observations are in accordance with these expectations. As the major isotope ^{32}S is non-magnetic, and because ^{33}S is of very low abundance, it has not been possible to observe the above-mentioned hyperfine interaction with the ^{33}S nucleus.

For the case of an SO_4^- radical stabilized by a Ca^{2+} vacancy, the distortion from T_d symmetry is likely to be larger than the above as the excess negative charge present at such a vacancy is only partially cancelled by the hole on the radical. It is assumed that the radical still has a C_{3v} symmetry for simplicity. The changes in the energies of the relevant orbitals are shown in figure 5, $C_{3v}(b)$. The unpaired electron

still occupies the a_2 orbital and the ^{33}S hyperfine interaction is expected to be small. Thus, as the ground state is A_2 , the relevant excited states are A_1 and E for g_{\parallel} and g_{\perp} shifts, respectively. From the orbital level scheme (figure 5), it is seen that the a_1 level is close to the a_2 level in contrast with the case of a SO_4^- radical stabilized by a $V_{\text{Ca}}(\text{Na}^+)$ vacancy. Hence g_{\parallel} is expected to be large compared with the free-spin value as there is an appreciable admixture of the excited states by spin-orbit coupling. On the other hand, the g_{\perp} -value is expected to be close to the free-spin value as the e level lies much below the a_2 level. The experimentally observed values reported in the literature for the SO_4^- radical exhibiting an axially symmetric g-tensor are in reasonable agreement with this expectation (table 1). It is seen that $g_{\parallel} > g_{\perp}$, in marked contrast with the case of an SO_4^- radical stabilized by an Na^+ ion ($g_{\parallel} < g_{\perp}$). This change in the sign of $g_{\parallel} - g_{\perp}$ arises because of changes in the energies of orbitals owing to the relatively greater degree of distortion of the SO_4^- ion from T_d symmetry.

Although C_{3v} symmetry is assumed in the above discussion, there is always the possibility that the symmetry is reduced to C_{2v} in the case when the distortion becomes large. Figure 5 also shows the changes in the orbital energies for C_{2v} symmetry. It should be noted that the degeneracy of e levels (C_{3v} symmetry) will be lifted in C_{2v} symmetry. The unpaired electron is again in the a_2 level and the relevant excited states are B_1 , B_2 and A_1 for g_x , g_y and g_z shifts, respectively. The a_1 level is closest to the a_2 level and consequently the g_z shift will be the largest and this principal value will be larger than the free-spin value. On the other hand, the g_y -value will be much closer to the free-spin value and the g_x -value will be slightly higher than the free-spin value. The SO_4^- radical with C_{2v} symmetry exhibits a rhombic g-tensor and all the g shifts are likely to be positive. These expectations are well borne out by the experimental observations of Danby *et al* (1982) and Morgan and Stoebe (1990).

For an SO_4^- radical with C_{2v} symmetry, an axially symmetric g-tensor will be observed if the radical undergoes rotation about a unique axis. As the distortion is relatively large, g_{\parallel} is likely to be larger than g_{\perp} . This behaviour is observed for the SO_4^- radical in $\text{CaSO}_4:\text{Sm}$ (Sheshagiri *et al* 1988) and also in $\text{CaSO}_4:^{241}\text{Am}$ (Natarajan *et al* 1988), where the radical is found to be undergoing thermally activated molecular motion.

A step annealing technique was used to measure the stability of the SO_4^- centre. The sample was returned to room temperature and the signal intensity recorded after each step. The thermal decay of the EPR signal of SO_4^- is shown in figure 6. These measurements show that the SO_4^- radical may be removed by step annealing the sample to around 393 K. Hence, the 404 K TL peak observed in $\text{CaSO}_4:\text{Dy}, \text{Na}$ may be caused by the holes released from this $\text{SO}_4^- - V_{\text{Ca}}(\text{Na}^+)$ defect complex. In the $\text{CaSO}_4:\text{Dy}$ phosphor, Chandra *et al* (1987) have shown that the addition of a monovalent cation Na^+ enhances the low-temperature peak at about 404 K. Figure 3, curve b, shows the effect of Na concentration on the TL intensity of the 404 K peak. They ascribe this enhancement as possibly due to a better transfer efficiency of charge carriers to 404 K traps during irradiation. On the other hand, it could also arise from the increased availability of luminescent centres (Dy^{3+}) owing to better charge compensation achieved with the addition of monovalent cations. Thus the results presented in figure 3 show the possible existence of a correlation between the 404 K TL peak and the $\text{SO}_4^- - V_{\text{Ca}}(\text{Na}^+)$ defect complex. These results are in accordance with the thermal behaviour of this defect centre (figure 6).

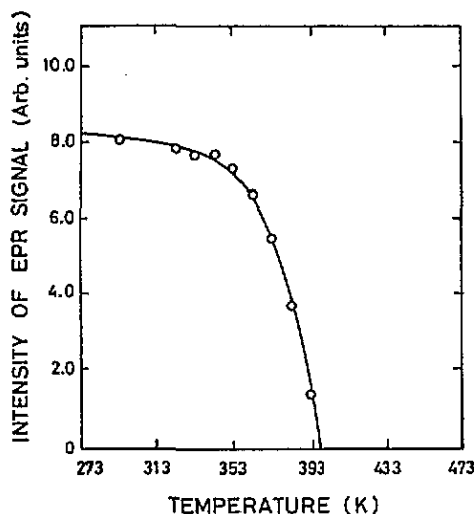


Figure 6. The thermal stability of the SO_4^- radical in $\text{CaSO}_4:\text{Dy}$ (0.1 mol%), Na (0.2 mol%).

3.2. SO_3^- centre

The EPR spectrum of $\text{CaSO}_4:\text{Dy}$ is also characterized by strong lines in the vicinity of $g = 2.0023$ (figure 1). The intensity of these lines is much higher than that of the lines corresponding to the SO_4^- radical mentioned above. On the assumption that these lines arise from a single radical, the principal g -values are $g_1 = 2.0035$, $g_2 = 2.0030$ and $g_3 = 2.0025$. Table 2 shows the principal g -values reported in the literature for radiation-induced SO_3^- centres in pure and doped CaSO_4 lattices, including those obtained in the present work. The g -factor of SO_3^- has been reported to be nearly isotropic (e.g. 2.0039 for $(\text{NH}_4)_2\text{SO}_4$ (Bailey and Cuesta-Barro 1975) and 2.0036 for $\text{K}_2\text{CH}_2(\text{SO}_3)_2$ (Chantry *et al* 1962)). As the average g -value is nearly 2.0036, the above EPR lines are ascribed to the SO_3^- radical.

The intensity of the SO_3^- lines in $\text{CaSO}_4:\text{Dy}$ has been found to decrease on doping with Na^+ ions, as shown in figure 7. It has also been observed that the yield of this radical centre is rather low in pure CaSO_4 as well as in $\text{CaSO}_4:\text{Na}$ (0.1 mol%) and $\text{CaSO}_4:\text{Dy}$ (0.1 mol%), Na (0.1 mol%). These results are shown in figure 8. By the addition of Na^+ to pure CaSO_4 , initially there is a slight increase in the SO_3^- concentration as a result of charge compensation. However, by the addition of Dy^{3+} , the SO_3^- radical concentration increases by a larger factor.

Figure 9 shows the dependence of the SO_3^- radical intensity on the Dy concentration for $\text{CaSO}_4:\text{Dy}$. The EPR signal intensity peaks at a concentration of 0.05 mol%, beyond which the intensity steadily decreases. This is similar to the activator-concentration-dependent quenching observed in the TL of $\text{CaSO}_4:\text{Dy}$ (Nambi *et al* 1974).

The formation of the SO_3^- radical involves the scission of O^- from SO_4^{2-} , i.e. $\text{SO}_4^{2-} \xrightarrow{\text{irradiation}} \text{SO}_3^- + \text{O}^-$. The presence of Dy in CaSO_4 appears to favour the formation and stabilization of the SO_3^- radical. However, the exact role of Dy is yet to be understood.

It may be mentioned that, in the study by Huzimura *et al* (1980), SO_3^- radical formation and decay were little affected by the presence of the rare-earth ion Tm in the CaSO_4 lattice, in contrast with the present case of Dy.

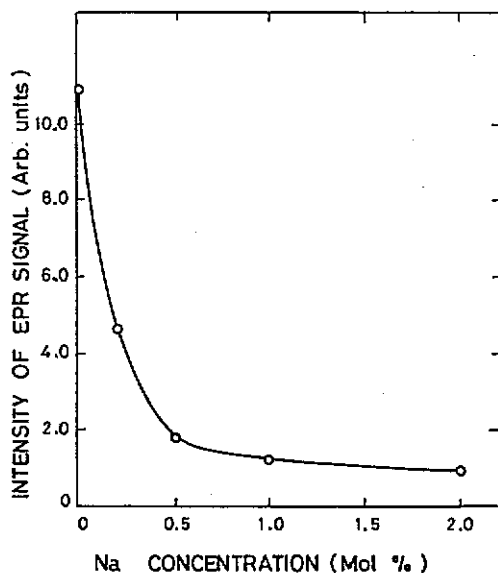


Figure 7. The dependence of the EPR signal intensity of the SO_3^- radical on the Na concentration in the $\text{CaSO}_4:\text{Dy}$, Na system.

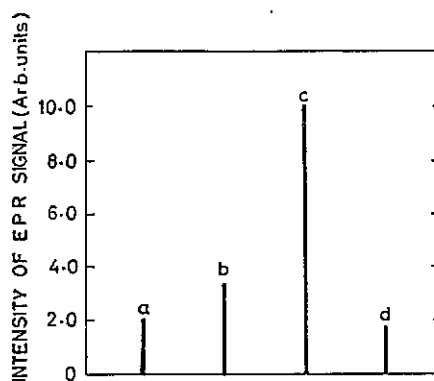


Figure 8. The EPR signal intensity of the SO_3^- radical for various samples: line a, pure CaSO_4 ; line b, $\text{CaSO}_4:\text{Na}$ (0.1 mol%); line c, $\text{CaSO}_4:\text{Dy}$ (0.1 mol%); line d, $\text{CaSO}_4:\text{Dy}$ (0.1 mol%), Na (0.1 mol%).

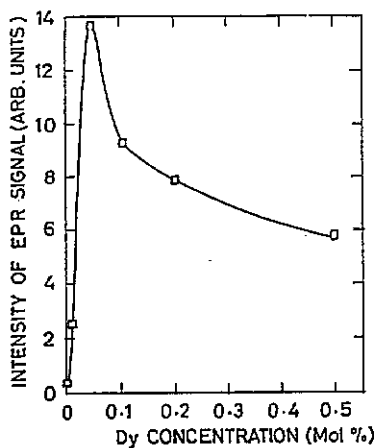


Figure 9. The dependence of the intensity of the EPR signal of the SO_3^- radical in $\text{CaSO}_4:\text{Dy}$ on the Dy concentration.

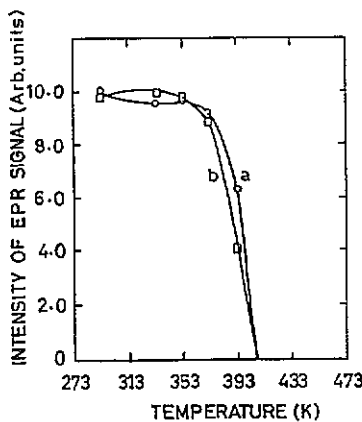


Figure 10. The thermal stability of the SO_3^- radical in $\text{CaSO}_4:\text{Dy}$ (0.1 mol%), Na (0.2 mol%) (curve a) and $\text{CaSO}_4:\text{Dy}$ (0.1 mol%) (curve b).

Step annealing measurements show that SO_3^- radicals decay in the temperature range 383–403 K. Figure 10 shows the thermal stability of the SO_3^- radical in $\text{CaSO}_4:\text{Dy}$ (0.1 mol%) and $\text{CaSO}_4:\text{Dy}$ (0.1 mol%), Na (0.2 mol%). A similar decay with temperature was observed for $\text{CaSO}_4:\text{Tm}$ by Huzimura *et al* (1980). While Na^+

codoping seems to decrease the formation of the SO_3^- centre, it does not appear to affect its thermal decay characteristics. It is surprising that the decay occurs in the same temperature range as for the SO_4^- centre (figure 6) which is observed to influence the TL emission at 404 K. Further investigations are needed to verify whether SO_3^- centres play any role in the TL emission in the temperature range indicated above.

4. Conclusions

Based on the results and discussions presented above, the following conclusions may be highlighted.

(1) For $\text{CaSO}_4:\text{Dy, Na}$, the TL emission between 380 and 404 K seems to be well correlated with the Na codopant which increases the formation and stabilization of the SO_4^- centre.

(2) The SO_4^- centre mentioned above seems to have a different configuration from that reported in the literature so far. The configuration observed at present refers to a tetrahedron not significantly distorted by $V_{\text{Ca}}(\text{Na}^+)$ and it is characterized by an axial g-tensor with $g_{\perp} > g_{\parallel}$.

(3) An SO_3^- centre correlated with the Dy dopant has been identified which is affected by the Na codopant. However, no TL role could be specifically assigned to this centre.

This work illustrates, once again, the complexity of the $\text{CaSO}_4:\text{Dy}$ phosphor by way of the TL mechanisms involved (Srivastava and Supe 1983) and the new observations which surface with each study and the manifestations of different kinds of defect centres.

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