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Optical absorption and luminescent processes in thermoluminescent $\text{CaSO}_4:\text{Dy}$

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Abstract. Optical absorption in irradiated and non-irradiated single crystals of CaSO_4 and $\text{CaSO}_4:\text{Dy}$ is studied. The intrinsic defect centres SO_4^- , SO_3^- , SO_2^- , O_3^- and O^- are identified in irradiated samples. However, these centres are generally observed only if stabilised by Dy impurity ions within the structure. Dy^{2+} absorption is also observed in irradiated doped samples. Luminescence via energy transfer to Dy ions is corroborated by this study. Areas where these results may be used to develop further understanding of the thermoluminescence process in $\text{CaSO}_4:\text{Dy}$ are discussed.

1. Introduction

Anhydrous calcium sulphate doped with rare earths is known to be a sensitive thermoluminescent (TL) dosimeter material with many applications [1, 2]. While the material is widely used, the TL mechanisms involved are complex and are still not well understood. The TL models generally involve one or more of the following [3–6]: trapping involving radicals such as SO_4^- , SO_3^- , and SO_2^- ; potential involvement of the rare-earth impurities in the trapping process; reduction of the rare-earth impurities to the divalent state during irradiation and re-oxidation to the trivalent state during heating; and luminescence via rare-earth transitions. In the current study, optical absorption is used to investigate these processes as part of a broader investigation of TL mechanisms in CaSO_4 .

The study of $\text{CaSO}_4:\text{Dy}$ using optical absorption has, in the past, been limited to the use of powder samples. Results have been reported of optical absorption measurements in CaSO_4 powder doped with rare-earth impurities Ce, Eu, Dy and Tm [7], made with reference to an unirradiated sample. This study noted a significant net background absorption that was attributed to packing differences in the samples. (High background absorption is one of the main problems encountered in using powder specimens for optical absorption.) It was concluded from the data obtained in [7] that characteristic RE^{2+} absorption bands were clearly superimposed on this background. Successive thermal treatments were found to bleach these absorption bands; however, no correlation was made between the bleaching and known TL glow peaks or transitions.

In a similar study of powdered $\text{CaSO}_4:\text{Dy}$ [6], optical absorption results indicated the presence of $\text{CaSO}_4:\text{Dy}$ bands due to Dy^{2+} transitions. However, it was concluded

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Table 1. Optical absorption bands of intrinsic defects in selected lattices.

Centre model	Optical absorption band (nm)	Temperature (K)	Material	Reference
SO ₄ ⁻	250	290	SrSO ₄	[9]
SO ₄ ⁻	370	300	BaSO ₄	[10]
SO ₄ ⁻	210	300	SrSO ₄	[8]
SO ₃ ⁻	270–300	77	SrSO ₄	[11]
SO ₃ ⁻	240	300	Na ₂ SO ₄	[12]
SO ₃ ⁻	575–600	300	BaSO ₄	[13]
SO ₃ ⁻	240, 270	300	KNH ₂ SO ₃	[14]
SO ₂ ⁻	300–400	290	SrSO ₄ , SrSO ₄	[11, 13]
SO ₂ ⁻	380	290	SrSO ₄	[8]
SO ₂ ⁻	330	290	Na ₂ SO ₄	[12]
O ₃ ⁻	475	290	Na ₂ SO ₄	[12]
O ₃ ⁻	440	290	AgClO ₃	[15]
O ₃ ⁻	435	290	Ba(ClO ₃) ₂ ·H ₂ O	[16]
O ⁻	620	290	SrSO ₄	[8]
O ⁻	620, 650	290	BaSO ₄	[13]

that only a small percentage (less than 1%) of the total Dy in CaSO₄ was reduced by irradiation; apparently this small amount of Dy²⁺ is sufficient to produce the TL response. The lack of any characteristic Dy²⁺ emission in the TL spectrum was suggested as being due to non-radiative multiphonon transitions which are favoured in the CaSO₄:Dy²⁺ system.

An optical absorption study of single crystals of SrSO₄, a material similar to CaSO₄, has also been undertaken [8]. Optical absorption peaks were reported between 175 and 1200 nm and various defect centres were assigned to the major absorption bands observed. The results of [8] and others giving absorption bands of oxy-sulphur radicals in lattices similar to CaSO₄ are summarised in table 1.

To extend our understanding of optical absorption processes and thermoluminescence in CaSO₄:Dy, single-crystal samples were grown for the present study. Procedures and results will now be presented.

2. Experimental procedure

The crystal growth method used was modified from that in [17]. Analytical reagent grade CaCO₃ and high purity (99.99% pure) Dy₂O₃ were dissolved in hot sulphuric acid, with dopant concentrations maintained at 0.01 mol%. This hot acid was then introduced into the growth vessel, and acid was allowed to evaporate from the vessel under controlled conditions. The overall system consists of a growth vessel, flowing dry nitrogen gas to remove acid fumes from the vessel, a condenser to remove a majority of the acid vapour from the N₂ carrier gas, and NaOH solution wash bottles to neutralise any remaining acid. The system is completely closed as far as the acid is concerned and by reusing the recovered acid for the next growth run, the system distils the acid, thereby increasing its purity in each successive run.

In the solution–evaporation growth technique, controlling the rate of evaporation is vital to the production of high-quality single crystals. In this system there are two methods by which to control evaporation rate: by regulating the flow of the dry nitrogen used to carry the acid fumes out of the growth vessel, and by regulation of the acid temperature. The optimum growth conditions were found to be at a N_2 flow rate of 750 ml min^{-1} with the acid temperature held at 250°C .

Both undoped and Dy-doped CaSO_4 were grown in this study. Inductively coupled plasma spectroscopy analysis was used to measure unintentional impurity concentrations above 1 ppm in as-grown samples. The major impurities were found to be Sr (22 ppm), Mg (9 ppm), Al (2 ppm), Ba (1 ppm), and Cu, Ti, Na, Zr, (trace).

X-ray diffraction studies of the $\text{CaSO}_4:\text{Dy}$ samples grown from acid solution all demonstrated the β - CaSO_4 anhydrite structure. This structure has orthorhombic symmetry, space group Bbmm, and lattice parameters: $a = 6.998$, $b = 7.006$ and $c = 6.245$ [18]. Orientation of the monocrystals was accomplished by analysis of Laue back-reflection patterns. Through the course of the crystal characterisation, three cleavage planes were identified as (100), (010) and (001).

Gamma-irradiation of the samples employed a 30000 Ci ^{60}Co source. This facility had an exposure rate of $1 \times 10^6 \text{ R per 24 h}$ during this work; exposure times were usually 24 h.

The TL measurements in this study were performed using a Harshaw Thermoluminescence Dosimeter (TLD) reader model 2000A coupled with a Harshaw model 2080 TL analyser. The heating rate was programmed at 1°C s^{-1} . All TL samples were ground to powder to insure good thermal conduction between the sample and heater.

3. Results and discussion

Calcium sulphate is a colourless crystal and non-irradiated samples generally do not absorb in the visible region of the spectrum. Optical absorption (OA) arising due to irradiation in $\text{CaSO}_4:\text{Dy}$ arises predominantly from two sources: (i) defect centres intrinsic to the CaSO_4 structure and (ii) oxidation of the rare-earth impurity ion to the 2+ valence state.

Intrinsic paramagnetic defects in CaSO_4 can have electronic transitions within the visible or near-visible region which can be detected with optical absorption. In fact, centres such as SO_4^- , SO_3^- , SO_2^- and O_3^- have been detected with OA in SrSO_4 , BaSO_4 and CdSO_4 [8]. As may be seen in table 1, the absorption bands of intrinsic defects in sulphate lattices range over the whole of the optical region. However, it has been concluded that in materials such as SrSO_4 and BaSO_4 minor and trace elements are in some way related to the colouring mechanisms, since pure specimens of these sulphate lattices, including CaSO_4 , do not become coloured through irradiation [19].

Room-temperature optical absorption spectra of non-irradiated and irradiated $\text{CaSO}_4:\text{Dy}$ are shown in figures 1 and 2. More highly resolved spectra showed no additional absorptions than these. As show in figure 1, $\text{CaSO}_4:\text{Dy}$ shows no strong absorption lines in the near-UV and visible regions prior to irradiation. The background rise in the UV absorption in figure 1 indicates the onset of phonon-assisted band-to-band transitions occurring in the material. This would indicate that CaSO_4 has a band gap in the range 7–8 eV. The band gap of CaSO_4 has been quoted as 10 eV [20]; however, this reference is unsubstantiated.

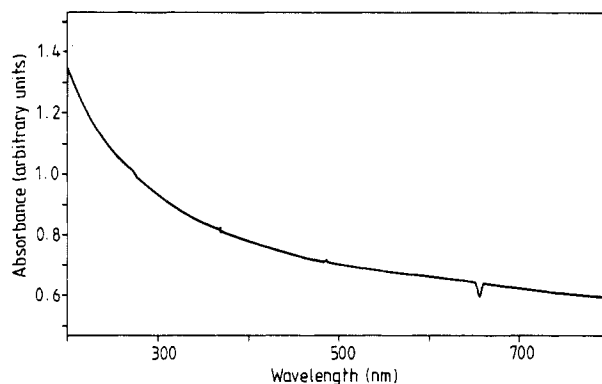


Figure 1. Typical optical absorption spectrum of annealed $\text{CaSO}_4:\text{Dy}$ single crystal.

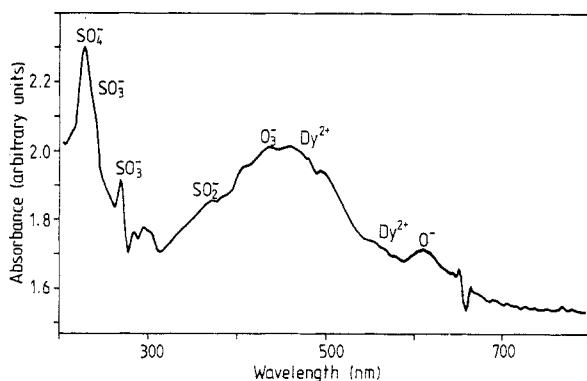


Figure 2. Typical optical absorption spectrum of γ -irradiated $\text{CaSO}_4:\text{Dy}$ single crystal.

The UV-optical absorption seen in irradiated $\text{CaSO}_4:\text{Dy}$ single crystals shows strong lines in the UV and wide bands in the visible (figure 2). The absorption band centred at 460 nm also shows some reproducible structure demonstrating a multi-peak nature. Unfortunately, optical absorption experiments at liquid nitrogen temperature did not improve the sharpness of these peaks in these materials. It should be noted that the absorption bands observed in these single crystals are a great improvement on those observed for powders, where only broad absorption bands are observed. The ability in this work to identify specific peaks allows the identification of complexes present in these samples; identification of the observed peaks is discussed below and is indicated on the figures.

3.1. Identification of optical absorption peaks

Identification of these absorption peaks entails a review of the possible radiation-related defects which can occur in $\text{CaSO}_4:\text{Dy}$, and an examination of the electronic structure of these defects, as they pertain to transitions in the optical and near-UV region. In this discussion, defects identified in a related electron spin resonance (ESR) study are used as a starting point for the interpretation of the optical absorption results. This ESR work,

which confirms the presence of SO₄⁻, SO₃⁻, SO₂⁻, O₃⁻ and O⁻ is discussed in detail elsewhere [21, 22].

The electronic energy levels of the sulphate ion SO₄⁻ have been calculated assuming tetrahedral T_d symmetry in [23] and Samoilovich [11]. SO₄⁻ ions in Li₂SO₄ were studied with x-ray photoelectron and x-ray emission spectroscopy [24]. This study yielded the following electronic configuration for this ion:

$$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^5.$$

This coincides with the calculation in [25]. According to the data in [24], the forbidden transition (2t₂) → (1t₁) corresponds to an absorption of 233 nm. The sulphate ion of Li₂SO₄ has slightly distorted tetrahedral local symmetry which approximates T_d [26]. In the CaSO₄ structure, the SO₄⁻ ion resides in a site with C_{2v} symmetry, which is expected to split the t₁ orbitals into a₂, b₁ and b₂ orbitals. It is likely that this would lift the forbidden nature of the above transition [27]. In the present study, the absorption peak occurring at 230 nm is attributed to the SO₄⁻ radical. This result is consistent with the values reported in table 1 for SO₄⁻ absorption in other materials.

The energy levels of the 25-electron sulphite radical, SO₃⁻, have been calculated [28, 29]. It was concluded in [29] that the most likely electronic configuration is

$$(1a_1)^2(1e)^4(2a_1)^2(2e)^4(3e)^4(3a_1)^2(1a_2)^2(4e)^4(4a_1)^1(5a_1)^0.$$

It has been found that the SO₃⁻ ion in materials such as K₂CH₂(SO₃)₂, NH₃⁺SO₃⁻, KNH₃SO₃ and K₂NH(SO₃)₂ consistently absorbs at 240 nm and 270 nm [14]. According to the energy levels in [29], the 240 nm absorption transition corresponds to the transition

$$\dots (3a_1)^2(1a_2)^2(4e)^4(4a_1)^1 \rightarrow \dots (3a_1)^1(1a_2)^2(4e)^4(4a_1)^2$$

which would absorb a 237 nm photon. This transition, however, is parity-forbidden and the next likely transition is (3e)³ → (4a₁)². The most likely transition for the 270 nm absorption band is

$$\dots (4a_1)^1(5a_1)^0(5e)^0 \rightarrow \dots (4a_1)^0(5a_1)^0(5e)^1$$

which corresponds to 260 nm in the energy levels of [29]. By the use of x-ray photoelectron spectroscopy of Na₂SO₃, it was found [24] that the transition

$$\dots (2e)^4(3e)^4(4e)^4(1a_2)^2(4a_1)^1 \rightarrow \dots (2e)^3 \dots (4a_1)^2$$

corresponded to absorption at 263 nm. For the data presented in figure 2, the shoulder at 240 nm and the peak at 270 nm are attributed to absorption by the SO₃⁻ radical in CaSO₄.

The ions SO₂⁻ and O₃⁻ are both 19-electron radicals with C_{2v} symmetry; ESR data [21, 22] indicate that it is likely that these two centres retain this symmetry in the CaSO₄ lattice. The molecular orbital energies for SO₂ were calculated and an electronic configuration of

$$(5a_1)^2(3b_2)^2(6a_1)^2(4b_2)^2(7a_1)^2(2b_1)^2(5b_2)^2(1a_2)^2(8a_1)^2(3b_1)^0$$

was found [30]. Assuming a similar structure for the SO₂⁻ ion, this would yield a 2B₁ ground state. The transition

$$\dots (8a_1)^2(3b_1)^1 \rightarrow \dots (8a_1)^1(3b_1)^2$$

has been as the most probable in the iso-electronic ion ClO₃⁻ [31]. According to [30],

this transition would correspond to a wavelength of ≈ 100 nm. From table 1, SO_2^- , in various sulphate lattices, has known absorption bands between 300 and 400 nm. The shoulder at 370 nm in figure 2 of the present work is attributed to the SO_2^- radical.

The ozonide ion O_3^- has been shown to absorb in the region 435–480 nm in various materials (see table 1). The electronic configuration was found [32] to be

$$\dots (1a_2)^2(2b_2)^2(3a_1)^2(2b_1)^1.$$

In KClO_3 , the transition $(1a_2)^2 \dots (2b_1)^1 \rightarrow (1a_2)^1 \dots (2b_1)^2$ corresponds to a wavelength of ≈ 440 nm [32]. In this region of figure 2, there is a broad absorption band centred at ≈ 450 nm which contains reproducible fine structure. The peak at 435 nm is believed to be due to O_3^- absorption.

In the literature, the absorption data for the negative oxygen ion, O^- , are somewhat confused. Absorption was found at 620 and 650 nm in both barites and celestites which was attributed to the O^- ion [14]. Absorption in irradiated KClO_3 and KClO_4 was studied and the optical absorption in these materials at wavelengths of 254, 300 and 386 nm was attributed to complexes of O^- with ClO_2^- and ClO_3^- [33]. It was concluded [33] that these bands occurred as a result of charge transfer between the ClO_3^- and ClO_4^- and the O^- defects. In the present study of CaSO_4 , there exist absorption bands that correspond to both of these previous studies: absorption at 612 nm could correspond to O^- as in SrSO_4 [8] and bands at 257, 303 and 410 nm may correspond to charge transfer between O^- and SO_2^- or SO_3^- (which are isoelectronic to ClO_2^- and ClO_3^- defects). However, without further studies of these transitions our assignments cannot be considered conclusive.

3.2. The role of Dy impurity

Numerous studies concerning the reduction of rare-earth (RE) impurity ions from the 3+ valence state to the 2+ state by ionising radiation in various matrices have been reported. The most conclusive studies involve optical absorption and fluorescence in $\text{CaF}_2:\text{RE}$ [34, 35]. Optical absorption of the Dy^{2+} ion in CaF_2 was reported [34], distinct absorption lines being observed near 470, 570 and 720 nm. Photoconductivity in $\text{CaF}_2:\text{Dy}^{2+}$ was studied and it was shown that this conductivity commences at a wavelength of ≈ 710 nm [36]. It was concluded [36] that this corresponds to the energy difference between the Dy^{2+} impurity level and the edge of the conduction band of CaF_2 . This value also corresponds to the absorption band at ≈ 720 nm observed in $\text{CaF}_2:\text{Dy}$ [34].

The single-crystal optical absorption spectrum of $\text{CaSO}_4:\text{Dy}$ shown in figure 2 compares well with that in [6], and with $\text{CaSO}_4:\text{Dy}$ powder spectra in [3]. Using these results, we attribute the peak at 460 nm and the shoulder near 560 nm to Dy^{2+} absorption. However, there is little conclusive evidence to support the claim in [3] that the absorption of $\text{CaSO}_4:\text{Dy}$ compares well with the absorption of irradiated $\text{CaF}_2:\text{Dy}$ observed in [34].

The UV absorption of an undoped sample of CaSO_4 after irradiation is shown in figure 3. A comparison of figures 2 and 3 shows that the OA of this material lacks almost all of the absorption bands that are observed in the doped material after irradiation. It was concluded that this lack of absorption was evidence that the Dy^{2+} in the material was responsible for the absorption bands in the Dy-doped material [6].

A broader explanation of the influence of the Dy impurity is that it acts to stabilise the radiation-induced defects and that it is these stabilised defects which cause the majority of the optical absorption. In the case of the undoped samples, the intrinsic

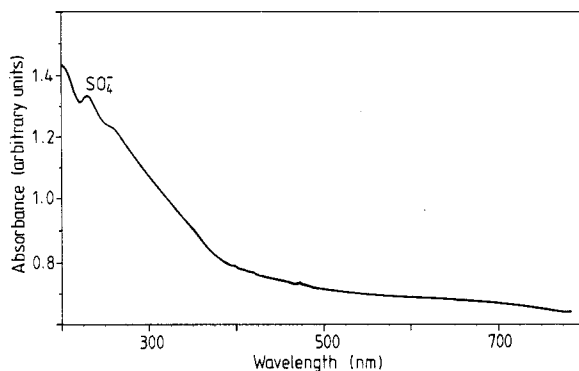


Figure 3. Typical optical absorption spectrum of γ -irradiated undoped CaSO_4 single crystal.

defects do not form or are unstable and decay rapidly and, consequently, no optical absorption is observed. This hypothesis is supported by the ESR results in [37] and by the OA spectra in figure 3, which shows only one absorption band, at 230 nm, which has been assigned to SO_4^- centres in the analysis above. In addition, the only defect centre detected in the same ESR study of undoped CaSO_4 [37] was that of an SO_4^- centre stabilised by a Ca vacancy. This indicates that centres such as SO_x^- , O_3^- and O^- , detected in this and other studies, are detectable because of the stabilising effects of impurity ions [8, 38].

3.3. The luminescent process

An important part of the TL model involves the luminescence process, in which recombination occurs accompanied or followed by energy transfer to the Dy, which is excited, and then re-emits the energy as TL. Studies [39–42] have demonstrated the functionality of this energy transfer mechanism involving rare-earth ions in the CaSO_4 lattice. These particular experiments were accomplished using VO_4^{3+} as the sensitising ion. The rare-earth ions that did not exhibit energy transfer were those that either (i) had no overlap between the VO_4^{3+} emission and the electronic transitions of the RE ion, or (ii) had non-radiative processes in competition with radiative processes.

Photostimulation studies have demonstrated that rare-earth impurity ions can be excited to emit fluorescence by light with a wavelength of approximately 340 nm. This is the same wavelength that is emitted in the TL of undoped CaSO_4 [43]. In doped $\text{CaSO}_4:\text{Sm}$ [44], evidence for reabsorption is seen in a band centred on 340 nm. This may indicate an energy transfer occurring between a recombination centre and the RE ions during TL in CaSO_4 . In undoped CaSO_4 , the 340 nm emission is not absorbed, but rather inefficiently emitted as TL [43]; this inefficiency is related to the absence of a rare-earth emission mechanism. In doped CaSO_4 , energy transfer is a viable mechanism for TL. In fact, it is observed that the RE ions that are capable of efficient energy transfer (Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} and Tm^{3+}) are the same RE ions that efficiently activate the TL process in CaSO_4 [3, 40].

The RE ions that do not efficiently activate the TL mechanism of CaSO_4 are: Ce^{3+} , Gd^{3+} , Ho^{3+} , Er^{3+} , Yb^{3+} and Lu^{3+} . Of these ions, Ho^{3+} and Er^{3+} are probably still receiving the energy from the recombination centre; however, non-radiative decay processes for these ions have been shown to be more likely and no TL is then observed

[40]. No energy transfer was observed for Gd^{3+} , Lu^{3+} and Ce^{3+} as there is no spectral overlap of these RE ions with VO_4^{3-} emission [40]. In TL, the emission from the recombination centre is near 335 nm [43], which is expected to overlap with all of the rare-earth ions with the exception of Ce^{3+} , Gd^{3+} , Yb^{3+} , and Lu^{3+} [45]. It is then observed that those RE ions which do not have spectral overlap with the undoped $CaSO_4$ emission also yield weak TL emission when used as a dopant in $CaSO_4$. In addition, the TL emission data in [3] show that the TL emission spectrum of these dopants gives substantial emission at wavelengths corresponding to undoped $CaSO_4$, indicating a lack of reabsorption. This means that energy transfer is not taking place in these samples and that the TL output suffers because of this deficiency. In contrast, $CaSO_4:Mn$, a known TL phosphor, shows no Mn fluorescence for any exciting wavelength within the range 200–800 nm, implying that the 335 nm emission from the $CaSO_4$ lattice is not transferred to Mn [44]. Moreover, $CaSO_4:Mn$ has a TL glow curve which does not resemble the glow curves of RE-doped $CaSO_4$. Thus it seems unlikely that an energy transfer mechanism is operative in the TL of $CaSO_4:Mn$.

4. Conclusions

While insufficient information is available from this study to identify a specific mechanism for TL in $CaSO_4:Dy$, these results demonstrate the importance of the SO_4^- , SO_3^- , SO_2^- , O_3^- and O^- radicals and Dy^{2+} impurities in the TL process. Irradiation produces optical absorption centres related to these species, but only when Dy^{2+} is present. Any model for TL trapping and recombination must be able to account for these observations.

The presence of the Dy^{2+} absorption lines in the optical absorption spectrum of $CaSO_4:Dy$ supports the idea that Dy^{3+} ions are reduced to Dy^{2+} during exposure to ionising radiation. The Dy^{2+} ions are reconverted to Dy^{3+} during subsequent heating, as these lines are not observed after TL readout.

The specific recombination centres involved in the TL of $CaSO_4:Dy$ have not been identified. However, it has been shown above that the emission from these recombination centres is most likely to be at 340 nm, and that this energy then excites the Dy ion, through an energy transfer mechanism, to emit the TL.

Acknowledgment

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