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Luminescence and ESR Studies of CaS:Dy Phosphor

Vijay Singh¹, ZHU Jun-Jie(朱俊杰)²**, T. K. Gundu Rao³, Manoj Tiwari³, PAN Hong-Cheng(潘宏程)¹

¹Department of Chemistry, Key Laboratory of Analytical Chemistry for Life Science, Nanjing University, Nanjing 210093
²Regional Sophisticated Instrumentation Centre, IIT, Powai, Mumbai-400 076, India
³Department of Post Graduate, Studies and Research in Physics, Bhoj College, Kotra, Bhopal-462 003, India

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CaS phosphor activated with Dy ions is prepared by the solid-state diffusion method. The phosphor is characterized by x-ray powder diffraction, thermogravimetric analysis and photoluminescence. Defect centres formed in CaS:Dy are studied using the technique of electron spin resonance. The thermoluminescence glow curve shows peaks at around 117°C and 345°C. Irradiated CaS:Dy exhibits ESR lines due to defect centres. The thermal annealing behaviour of one of the defect centres appears to correlate with the TL peaks at 117°C and 345°C. This centre is characterized by an isotropic g-value of 2.0035 and is assigned to an F⁺ centre.

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Alkaline-earth sulfide phosphor materials are of great importance in the field of radiation detection, lamp industry and in digital radiography as storage phosphors.¹⁻⁶ In particular, CaS doped with rare earth has recently attracted attention of investigators because of their potential as phosphors for device applications such as multi-colour thin film electroluminescence.⁷⁻⁹ Luminescence of Dy³⁺ has attracted much attention because of its white light emission. Many kinds of host materials have been studied.¹⁰⁻¹² Dy³⁺ doped phosphors are useful in dosimetry of ionizing radiation using thermoluminescence. CaSO₄:Dy, CaF₂:Dy, MgB₂O₇:Dy etc. are some of the phosphors¹³ used in personnel monitoring using thermoluminescence dosimetry. It has been known that ESR is a very useful method for studying the physical properties of luminescence centres and luminescence mechanism. The ESR results might provide some useful information related to the luminescence properties. It is established on the basis of thermoluminescence (TL) and electron spin resonance (ESR) studies that defect centres are related to the process of TL in phosphor. It has been observed that the release of holes/electrons from defect centres at characteristic traps initiate luminescence process in these materials. The purpose of this work is to investigate the correlations between the ESR and thermoluminescence in CaS:Dy phosphor.

Herein, we have studied the Dy (0.1 mol%) doped CaS phosphor. The product was characterized by using techniques such as powder x-ray diffraction (XRD), Thermogravimetric analysis (TGA), photoluminescence (PL), thermoluminescence (TL) and electron spin resonance (ESR). It has been established on the basis of thermoluminescence and electron spin resonance studies that defect centres are related to the process of TL in phosphors. It has been observed that the release of holes/electrons from defect centres at characteristic traps initiate luminescence process in these materials. In the present investigation, we have studied the defect centres formed in the CaS:Dy system using the technique of electron spin resonance and thermoluminescence.

Sample preparation: Calcium sulfide phosphor was obtained using solid-state reaction between activator (Dysprosium, 0.1 mol%) and calcium sulphate using Na₂SO₄ as flux and fired at 1000°C in a muffle furnace for 2h. AR grade carbon was used as a reducing agent during its synthesis. After heat treatment, the resultant powder was pulverized in dry atmosphere and stored, keeping in view the extreme purity as the main consideration in preparation. The details of phosphor preparation are the same as reported in earlier papers.¹⁴⁻¹⁶

XRD, TGA, PL, TL and ESR Measurements: Powder XRD pattern was performed on a Philips X'pert x-ray diffractometer with graphite monochromatized Cu Kα radiation (λ = 0.15418nm) and nickel filter at a scanning step of 0.03°, continue time 10 s, in the 2θ range from 10° to 80°. Thermogravimetric analysis (TGA) was carried out on a Labsys TG-DSC16 system. The experiment was conducted in nitrogen atmosphere at a heating rate of 20°C/min. PL experiments were carried out on a Shimadzu RF-5401 PC spectrophotometer. Thermoluminescence glow curves were recorded with the usual setup consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (931B), dc ampli-

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** Email: jzhuj@nju.edu.cn
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fier and a millivolt recorder. ESR measurements were carried out on a Varian E-112 E-line Century series X-band ESR spectrometer. 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 ESR cavity using the Varian variable temperature accessory.

Figure 1 shows the x-ray diffraction pattern of as-prepared CaS:Dy phosphor. It shows that the products are well crystallized in a cubic structure, and no detectable trace of impurity. From left to right, the peaks are (110), (200), (220), (222), (311), (400) and (420), respectively. The XRD pattern matched perfectly with the JCPDS (77-2011). Sulfide could be obtained by varying different parameters such as firing temperature, duration of firing, reducing agent and ambient atmosphere. Thermal analyses such as DTA, TGA, and DTG etc. are used to determine the optimum values of the above parameters. The TGA analysis of CaS:Dy prepared by reducing CaSO4 with pure carbon was obtained. From the investigation it could be concluded that reduction process started from 420 °C and attained a maximum at 600°C and ended at around 850°C, and it is similar to the previously report of sulfide prepared by the carbon reduction process.[17] The emission spectrum of Dy3+ falls mainly in two narrow bands in the visible region arising from 4F9/2 → 6H15/2 (470-500 nm) and 4F9/2 → 6H13/2 (570 nm) transitions. The relative intensities of the two bands depend on the local symmetry.[18] When the ratio of the blue or green emission is appropriate, one can obtain white emission using Dy3+. The excitation spectra of CaS:Dy shown by curve a in Fig.2 shows two prominent peaks at 280 nm and 350 nm. In the emission spectra of CaS:Dy shown by curve b in Fig.2, two peaks are observed, one at 486 nm due to 4F9/2 → 6H15/2 transition and the second at 575 nm due to 4F9/2 → 6H13/2 transition of Dy3+ ion. We observe that the Dy3+ ion in host has comparatively longer time in its trivalent state (4F9/2 level), and it is an important sensitizer in energy transfer process. Therefore these ions can be useful in lasers, and solar energy concentrations, etc.

The TL glow curve observed in CaS:Dy is shown in Fig.3. The glow curve consists of two peaks at 117°C and 345°C. Undoped CaS and CaS:Dy exhibited strong signals due to the presence of impurity Mn2+ ions. However, the ESR lines observed after irradiation lie close to free-electron resonance (g = 2.0023) and are relatively independent of interference from Mn2+ lines. The ESR spectrum observed immediately after irradiation at room temperature is shown in Fig.4(a). This spectrum consists of lines from at least two defect centres (revealed by thermal annealing experiments). The dominant spectrum is seen clearly without any interference from other centres after thermal annealing at 370°C. This spectrum is shown in Fig.4(d) and arises from a species (centre I) characterized by a rhombic g-tensor with principal values g1 = 2.0108, g2 = 2.0049 and g3 = 2.0022. This species is yet to be identified.

![Fig. 1. X-ray diffraction pattern of polycrystalline CaS:Dy (0.1 mol%) phosphor.](image1)

![Fig. 2. Photoluminescence spectra of CaS:Dy: (a) emission spectra of CaS:Dy (λexc = 350 nm), (b) excitation spectra of CaS:Dy (λem = 486 nm).](image2)

![Fig. 3. TL glow curve of CaS:Dy phosphor.](image3)
The thermal annealing behaviour of centre I is shown in Fig. 6. It is seen that the intensity of the ESR lines associated with this centre reduces in the temperature range 170–340°C. However, the actual decay of the centre takes place at high temperatures with the ESR line intensity decreasing rapidly beyond 400°C. No specific TL role could be assigned to this centre.

![Graph showing ESR spectra](image)

**Fig. 4.** Room temperature ESR spectra of irradiated CaS:Dy phosphor, i.e. spectrum immediately after irradiation (a), and spectra recorded after thermal annealing at 160°C (b), 240°C (c) and 340°C (d).

![Graph showing thermal annealing behaviour](image)

**Fig. 5.** Thermal annealing behaviour of F+ centres in CaS:Dy phosphor.

Apart from centre I, an additional line (centre II) has been observed after irradiation close and to the left of the TCNE marker \((g = 2.0028)\). This is shown in Fig 4(a). The centre associated with this line has a principal \(g\)-value 2.0035 and a linewidth of 1.5 Gauss. However, the intrinsic line width of these centres is small and is observed in the cases where the neighbouring nuclei have zero magnetic moments. The similar appearance was also reported for the F+ centres observed in CaO and MgO lattices.\(^{[19,20]}\) The line width of the ESR line in MgO is only 0.5 Gauss and in CaO, it is less than 0.5 Gauss. In the present case of CaS, the neighbouring cations (Ca) of the centres have no nuclear magnetic moments, and as a result the centre exhibits small line width. A likely trapping centre which can be formed in a system such as CaS:Dy is the F+ centre (an electron trapped at an anion vacancy). This centre was first observed by Hutchison (1949)\(^{[21]}\) in neutron irradiated LiF. In LiF, a single broad line (linewidth \(\approx 100\) Gauss) with a \(g\)-factor 2.008 was observed. A similar centre has been observed in other systems, notably in alkali halides after x-ray or gamma irradiation. The main characteristic features of such centres are: (1) a small \(g\)-shift, which may be positive or negative, (2) a large linewidth and (3) saturation properties characteristic of an inhomogeneously broadened ESR line. The large linewidth arises from an unresolved hyperfine structure.

![Graph showing thermal annealing behaviour of centre I](image)

**Fig. 6.** Thermal annealing behaviour of centre I in the CaS:Dy system.

The F+ centre consists of an electron occupying an anionic vacancy formed by removal of a negative ion from the lattice. Hyperfine interactions with the nearest-neighbouring cations account for most of the linewidths. Defect centre II formed in the present system is characterized by a small \(g\)-shift, and the linewidth however is relatively small. The centre also does not exhibit any resolved hyperfine structure. On the basis of these observations and considerations of the characteristic features of the defect centres likely to be formed in a system such as CaS:Dy, centre II is tentatively assigned to an F+ centre. It is to be mentioned that an intense signal at \(g = 2.0032\) observed...
in x-ray irradiated CaS at room temperature has been attributed to the F$^+$ centre.[22]

The stability of centre II was measured using the step-annelling technique. The thermal annealing behaviour of the F$^+$ centre (Fig. 5) shows three temperature regions where there is a reduction in intensity of the corresponding ESR line. The first region from 90°C to around 160°C is likely to arise from recombination of charges, released from unknown traps, at F$^+$ centre sites. This region appears to be associated with the observed TL peak at 117°C. Subsequently, there is a reduction in intensity from 180°C to around 300°C and this also arises from recombination of charges, released from unknown traps, at F$^+$ centre sites. The third annealing region above 320°C is related to the decay of the F$^+$ centre and is likely to correlate with the TL peak at 345°C. It appears from these observations that the two TL peaks in the CaS:Dy system are related to the F$^+$ centre.

In conclusion, due to the $^4$F$_{9/2}$ → $^6$H$_{13/2}$ transition and the $^4$F$_{9/2}$ → $^6$H$_{15/2}$ transition of Dy$^{3+}$ ion in CaS:Dy, phosphor may be useful in several optoelectronic devices. The TL glow curve of CaS:Dy indicates two peaks at 117°C and 345°C. A dominant paramagnetic centre with principal $g$-values $g_1 = 2.0108, g_2 = 2.0049$ and $g_3 = 2.0022$ has been observed in the irradiated phosphor. No specific correlation could be observed between this centre and the TL peaks. A second centre with an isotropic $g$-value 2.0035 was observed in the irradiated phosphor. This species has been assigned to F$^+$ centre and appears to correlate with the TL glow peaks at 117°C and 345°C.

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References

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