

## Luminescent studies of impurity doped SrS phosphors

VIJAY SINGH\*, MANOJ TIWARI, T K GUNDU RAO<sup>†</sup> and S J DHOBLE<sup>‡</sup>

Department of Physics, Regional Institute of Education, Bhopal 462 013, India

<sup>†</sup>Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Mumbai 400 076, India

<sup>‡</sup>Department of Physics, Kamla Nehru College, Nagpur 440 009, India

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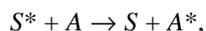
**Abstract.** SrS phosphors activated with Ce and Dy ions were prepared by solid-state diffusion method. Photoluminescent study was carried out on SrS : Ce, SrS : Dy and SrS : Dy, Ce. Thermoluminescence and electron spin resonance studies were also carried out on SrS : Dy phosphor. The thermoluminescence glow curve shows a peak at around 142°C. Irradiated SrS : Dy exhibits an ESR line due to a defect centre. Thermal annealing behaviour indicates that this centre correlates with the TL peak at 142°C. The centre is characterized by an isotropic  $g$ -value of 2.0039 and is assigned to a  $F^+$  centre.

**Keywords.** SrS phosphors; ESR; photoluminescence; thermoluminescence.

### 1. Introduction

Over the last few years, intensive research has been devoted to the realization of efficient luminescent materials. This is due to the versatility of their applications in the fields of fluorescent lamps, display devices, and detector systems, represented by X-ray screens and scintillators of phosphor masking. Considerable interest in the spectroscopic properties and energy transfer process in the last few years was caused by the problem of developing new luminescent materials.

Energy transfer between a sensitizer ion ( $S$ ) and an activator ion ( $A$ ) can be written as a chemical reaction



where asterisk indicates the excited state.

Alkaline earth sulphide phosphors have aroused much interest after the discovery of infrared stimulation and sensitized luminescence (Cabezas and Deshazer 1964; Daslot *et al* 1982), because of their potential as host materials for device applications, such as multicolour thin film electroluminescence (Davies *et al* 2001) and magneto-optical devices (Dubey *et al* 2002a,b). Lehmann and Ryan (1971, 1972) reported the results of a detailed and systematic investigation in CaS, concluding that it is an excellent host material for efficient cathode-ray tube phosphors when activated with rare earths. Metal sulphides, in particular, have found important use as phosphors. Zinc and cadmium sulphides were both commonly used in the past (Inaho and Hase 1999; Narisada and Kanaya 1999; Yoshioka and Ogawa 1999), but the toxic nature has lessened the use of Cd to all but a few unavoidable

applications. Therefore, non-toxic sulphides are most commonly used as a host lattice for phosphors. A number of reports have appeared describing spectroscopic properties of pure and activated sulphides and revealing applications of BaS, SrS and MgS in alloy semiconductors (Holloway and Jesion 1982), radiation dosimetry (Rao and Rao 1983) and fast high-resolution optically stimulated luminescence imaging (Gaslot *et al* 1982). Recently, ZnS phosphors prepared by Davies *et al* (2001) for cathode ray tube showed potential luminescence properties as compared to standard commercial materials.

Sulphides have proved to be potential candidates for the aforementioned applications. The present tendency of development of such materials is not especially oriented towards new phases but mostly towards a better knowledge and resulting optical properties of existing materials. Among the parameters which govern the luminescence efficiency, the method of preparation of these materials has been shown by experience to be the most significant and important.

Impurity doped sulphide is interesting for a large number of base materials. It was, therefore, decided to conduct photoluminescence, thermoluminescence and electron spin resonance studies of SrS with Ce and Dy as activators for determining the mechanism of luminescence and energy transfer process in the phosphors.

### 2. Experimental

#### 2.1 Sample preparation

Strontium sulphide phosphor was obtained using solid-state reaction with impurity (Ce and Dy) and strontium sulphate as starting materials and fired at 1000°C in a

\*Author for correspondence (vijayjiin@hotmail.com)

muffle furnace for 2 h. The reducing agent was AR grade carbon powder and  $\text{Na}_2\text{SO}_4$  as a flux used in synthesis. After heat treatment, the resultant powder was pulverized in a dry atmosphere and stored keeping in view the extreme purity as the main consideration in preparation. X-ray diffraction photograph technique was used to ensure proper crystallization of powder. The details of phosphor preparation are the same as reported in the earlier papers (Dubey *et al* 2002a,b, 2003).

## 2.2 TL, ESR and PL measurements

Thermoluminescence glow curves were recorded with the usual setup consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (931B), d.c. amplifier and a millivolt recorder. ESR measurements were carried out on a Varian E-112 E-line Century series X-band ESR spectrometer. Tetracycloethelene (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. Photoluminescence spectra were also recorded on FP-750 spectrofluorometer (Jasco, Japan) with red sensitive PM tube.

## 3. Results and discussion

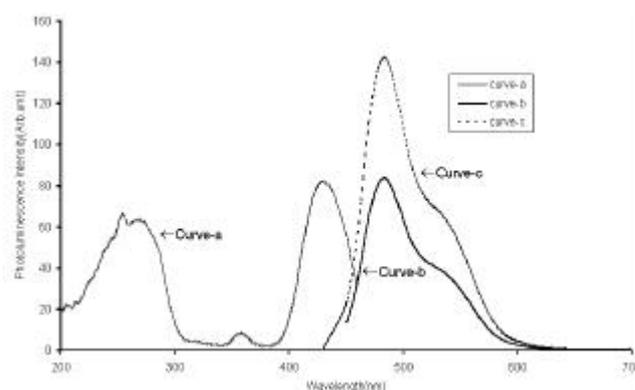
### 3.1 Photoluminescence spectra of $\text{SrS} : \text{Dy}^{3+}$

The importance of dysprosium ions as sensitizers in energy transfer process lie in the fact that they have a comparatively longer time in their trivalent state ( $^4F_{9/2}$  level). Therefore, these ions can be useful in lasers, solar energy concentrator etc. Cabezas and Deshazer (1964) observed radiative energy transfer between  $\text{Dy}^{3+}$  to  $\text{Tb}^{3+}$  and  $\text{Dy}^{3+}$  to  $\text{Nd}^{3+}$  in borosilicate glass. Van Uitert *et al* (1967) also studied the energy transfer from  $\text{Dy}^{3+}$  to  $\text{Tb}^{3+}$  and concluded that the transfer is non-radiative in tungstate. Joshi and Lohani (1981) and Joshi *et al* (2001) also reported the sensitization of  $\text{Ho}^{3+}$  ion by  $\text{Dy}^{3+}$  ion in zinc phosphate glass. The emission spectra of  $\text{SrS} : \text{Dy}$  shown in figure 1 (curve a) has two peaks which are observed at 485 nm due to  $^4F_{9/2} \rightarrow ^6H_{15/2}$  transition and 577 nm due to  $^4F_{9/2} \rightarrow ^6H_{13/2}$  transition of  $\text{Dy}^{3+}$  ion (excitation wavelength is 359 nm). The excitation spectra of  $\text{SrS} : \text{Dy}$  shown in figure 1 (curve b) shows multi-peaks in the range of 204–356 nm.

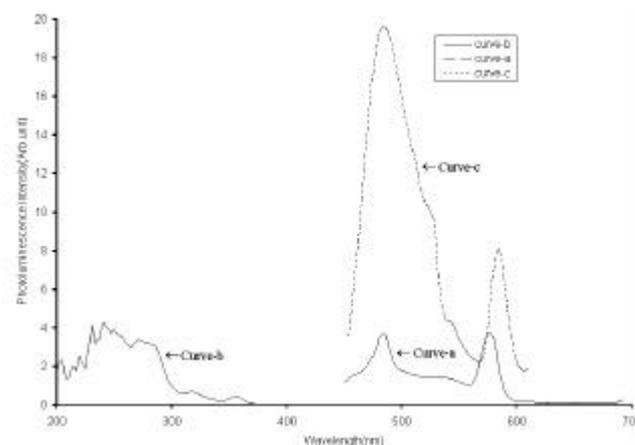
### 3.2 Photoluminescence spectra of $\text{SrS} : \text{Ce}^{3+}$

Sulphides activated with rare earths, particularly cerium, have been the subject of detailed spectroscopic studies because of their potential as efficient phosphor materials for cathode-ray tubes, electroluminescence panels and

fast high-resolution optically-stimulated luminescence imaging (Lehmann and Ryan 1972; Daslot *et al* 1982; Tanaka *et al* 1985). Ce-activated CaS is a well known fast-decaying green phosphor whose cathodoluminescence efficiency is more comparable to that of the best green ZnS-phosphors (Lehmann and Ryan 1972). Ce induces two emission bands at about 525 nm and 590 nm in MgS and 523 nm and 590 nm in CaS, respectively (Lehmann and Ryan 1971). Emission spectra of prepared  $\text{SrS} : \text{Ce}$  phosphor is shown in figure 2 (curve b) (excitation wavelength, 430 nm). Intense peak was observed at 485 nm and shoulder observed at 530 nm due to transition from the  $5d$  state of  $4f^2F_{7/2}$  state of the  $\text{Ce}^{3+}$  ion. Since the  $4f$  state is shielded from the influence of the surroundings, the crystal field causes only a small perturbation of the  $4f$  state, which is negligible in comparison with spin-orbit interaction. The energy separation between the  $^2F_{5/2}$  and  $^2F_{7/2}$  levels of the  $4f$  state in sulphides remains, therefore,



**Figure 1.** Photoluminescence spectra (curve a: excitation spectra of  $\text{SrS} : \text{Ce}$  (0.1 mole%) [ $I_{em} = 485$  nm]; curve b, emission spectra of  $\text{SrS} : \text{Ce}$  (0.1 mole%) [ $I_{ex} = 430$  nm]; curve c, emission spectra of  $\text{SrS} : \text{Ce}$  (0.1 mole%) [ $I_{ex} = 260$  nm]).



**Figure 2.** Photoluminescence spectra (curve a, emission spectra of  $\text{SrS} : \text{Dy}$  (0.1 mole%) [ $I_{ex} = 359$  nm]; curve b, excitation spectra of  $\text{SrS} : \text{Dy}$  (0.1 mole%) [ $I_{em} = 485$  nm]; curve c, emission spectra of  $\text{SrS} : \text{Dy}, \text{Ce}$  (0.1, 1.0 mole%) [ $I_{ex} = 260$  nm]).

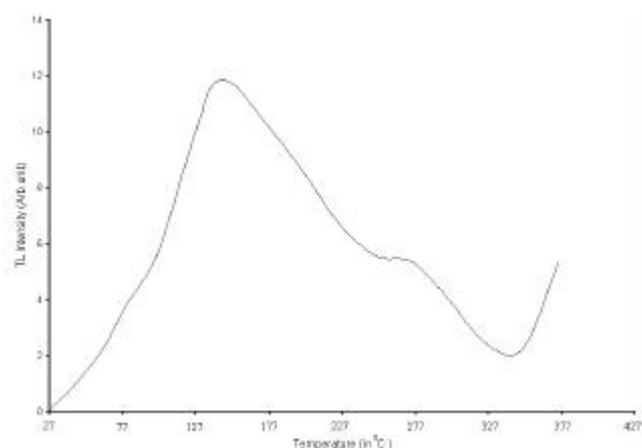
approximately the same as in the free ion. On the other hand, the  $5d$  state is sensitive to the crystal field and strongly couples with the lattice vibrations. The optical transition,  $5d \rightarrow 4F$  is, therefore, assisted by phonons and gives rise to broad emission bands as observed in figure 2. Figure 2 (curve a) shows the excitation peaks at 260 nm and 430 nm in SrS : Ce phosphor. When the SrS : Ce phosphor is excited by 260 nm wavelength, the emission peak is observed at 485 nm as in figure 2 (curve c). The intensity of 485 nm peak is increased by 1.75 times, as compared to 430 nm excitation of SrS : Ce. The increase in peak intensity is very useful for high-energy physics and medicine. The strong emission of  $Ce^{3+}$  ion in SrS phosphors may be used as a scintillator for the detection of gamma or X-rays.

### 3.3 Photoluminescence spectra of SrS : Ce, Dy

Figure 1 (curve c) shows the emission spectra of SrS : Ce, Dy phosphor (excitation wavelength, 260 nm). The peak intensity at 485 nm of  $Dy^{3+}$  ion is enhanced by five times due to  $Ce^{3+}$  ion used as a co-dopant. In SrS : Ce, Dy the intensity of  $Dy^{3+}$  ion increases due to energy transfer from one activator to another. The energy transfer process was observed in the SrS lattice, which is advisable in display device as well as in scintillation application.

### 3.4 TL measurements

Figure 3 shows a typical TL glow curve for SrS : Dy at a test gamma exposure of 225 Gy. It is seen that a prominent peak is observed at 142°C along with a shoulder at higher temperature side at around 275°C. The prominent TL peak at 142°C shows that the luminescence centres are formed during gamma irradiation of phosphors in SrS : Dy and they are released at 142°C temperature. The shoulder around 275°C shows another luminescence cen-

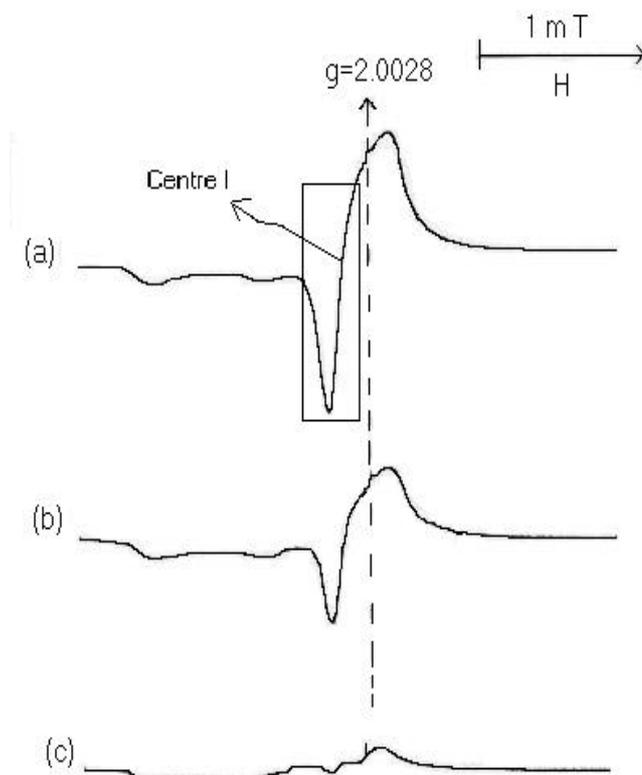


**Figure 3.** Typical TL glow curve of SrS : Dy (0.1 mole%) phosphors exposed to  $g$ -ray (225 Gy).

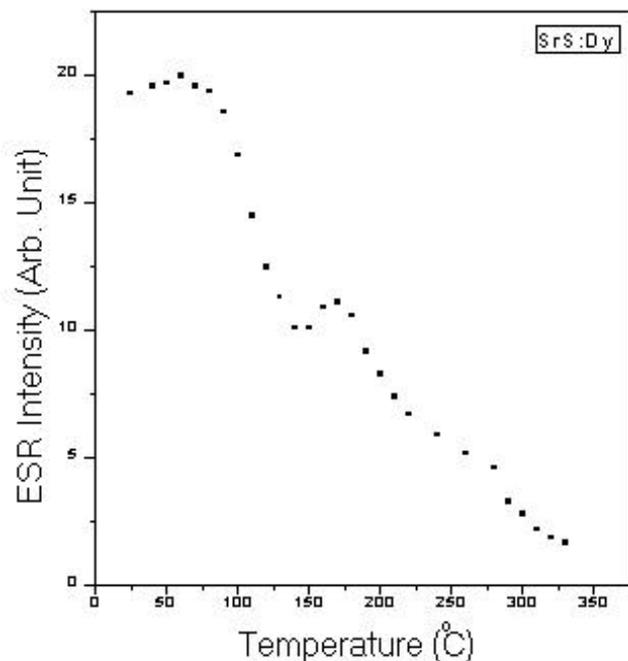
tre also generated in the phosphors at higher energy side, but its concentration is much less as compared to related luminescence centre of 142°C TL peak.

### 3.5 ESR measurements

Unirradiated sample exhibits a number of ESR lines possibly due to impurities. The room temperature ESR spectrum of gamma irradiated (dose: 30 kGy) SrS : Dy is shown in figure 4(a). The scan range has been selected to record only the lines in the vicinity of free-electron resonance. The ESR line close to the left of the TCNE ( $g = 2.0028$ ) marker is due to a defect centre (centre I). Centre I appears to exhibit a single ESR line with principal  $g$ -value of 2.0039 and a linewidth of 3 gauss. A likely trapping centre which can be formed in a system like SrS : Dy is the  $F^+$  centre (an electron trapped at an anion vacancy). This centre was first observed by Hutchison (1949) in neutron irradiated LiF. In LiF, a single broad line (linewidth,  $\sim 100$  gauss) with a  $g$ -factor of 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 a



**Figure 4.** ESR spectrum of gamma irradiated SrS : Dy system at room temperature. The spectrum recorded immediately after irradiation is shown in (a). The  $F^+$  centre line is indicated in (a). The spectra from samples annealed at 180°C and 300°C are shown in (b) and (c), respectively. The vertical line at  $g = 2.0028$  indicates the TCNE marker position.



**Figure 5.** Thermal annealing behaviour of  $F^+$  centre in SrS : Dy system. The indicated ESR intensities are measured from step annealing experiments. The sample was heated to a specific temperature and later the intensity was measured after allowing the sample to cool to room temperature.

centre are: (i) a small  $g$ -shift which may be positive or negative, (ii) a large linewidth and (iii) saturation properties characteristic of an inhomogeneously broadened ESR line. The large linewidth arises from an unresolved hyperfine structure.

The  $F^+$  centre consists of an electron occupying an anionic vacancy formed by the removal of a negative ion from the lattice. Hyperfine interactions with the nearest-neighbour cations account for most of the linewidth. Defect centre, I, 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 SrS : Dy, centre I is tentatively assigned to a  $F^+$  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 (Ghosh and Shanker 1979).

The stability of centre I was measured using the step-annealing technique. The thermal annealing behaviour of the  $F^+$  centre (figure 5) shows different temperature regions where there is a reduction in intensity of the corresponding ESR line. The first region from 80°C to around 150°C is likely to arise from recombination of charges, released from unknown traps, at  $F^+$  centre sites. This region appears to correlate with the observed TL peak at 142°C.

#### 4. Conclusions

Based on the results presented above, the following conclusions can be drawn.

(I) A defect centre formed in gamma irradiated SrS : Dy system has been tentatively assigned to a  $F^+$  centre.

(II) The TL peak at 142°C appears to correlate with the  $F^+$  centre.

(III) Due to  $^4F_{9/2} \rightarrow ^6H_{13/2}$  and  $^4F_{9/2} \rightarrow ^6H_{15/2}$  transitions of  $Dy^{3+}$  ion in SrS : Dy phosphors, SrS : Dy may be useful in several optoelectronic devices.

(IV) The study of SrS : Ce shows that the emission peak intensity is about 1.75 times when it is excited at 260 nm than that when excited at 430 nm. This may be due to strong emission of  $Ce^{3+}$  ion in SrS phosphor.

(V) The study of SrS : Ce, Dy shows that when SrS : Dy is co-doped with Ce its peak intensity at 485 nm due to  $Dy^{3+}$  ions increased by five times. Therefore, SrS : Ce, Dy may be used in display devices as well as in scintillation application.

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