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Effect of dysprosium doping on the optical properties of SrS:Dy,Cl phosphor

E.I. Anila[a,*], M.K. Jayaraj[b]

[a] Department of Physics, Union Christian College, Aluva 683102, Kerala, India
[b] Optoelectronic Devices Laboratory, Department of Physics, Cochin University of Science and Technology, Kochi 682022, India

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ABSTRACT

The fundamental optical properties of dysprosium (Dy) doped strontium sulfide bulk samples for various dopant concentrations from 0.1 to 1.0 at.% were investigated by X-ray diffraction (XRD), electron paramagnetic resonance spectroscopy (EPR), room temperature photoluminescence (PL), photoluminescence excitation (PLE) and diffuse reflectance spectroscopy (DRS). Investigations by electron paramagnetic resonance yielded the state of Dy in the sample as Dy^{3+}. An additional ESR line due to F^+ center was observed. The PL emission spectrum consisted of several intense lines and a number of weaker ones which were identified as transitions between energy levels of Dy^{3+}. The optimum doping concentration for maximum intensity was found to be 0.25 at.%. Blue shift of the absorption edge energy and red shift of the PLE spectrum were observed with increasing doping concentration. The former is due to Burstein–Moss (BM) effect and the latter is attributed due to the presence of band tailing states.

1. Introduction

Alkaline earth sulfide phosphors have aroused much interest after the discovery of infrared stimulation and sensitized luminescence [1,2] because of their potential as host materials for device applications, such as multicolour thin film electroluminescence [3] and magneto optical devices [4,5]. Non-toxic sulfides are most commonly used as a host lattice for phosphors. Due to the wide variety of emission wavelength possible from 4f–4f transitions of rare earth ions in the visible spectrum, rare earth doped alkaline earth phosphors are widely being investigated [6]. The close match of the ionic radii of rare earth ions and cation of SrS host material, allow the rare earths to fully incorporate in these lattices. In the case of ZnS lattice it is difficult to fully incorporate the rare earth ions because of large difference in ionic radii. The electroluminescent emission spectra of the lanthanide luminescent impurity in SrS and ZnS show a difference in relative peak intensities [7,8]. This has been attributed to the differences in the branching ratio of the emitting level due to crystal field effects. SrS:Dy is a promising phosphor for yellow electroluminescence. Although considerable attention has been paid to the study of PL of SrS phosphors activated with dysprosium, not much quantitative data are available relating to the influence of concentration of Dy on the PL and band gap of SrS:Dy phosphors. In this paper, a detailed study on the dependence of doping concentration of Dy on the band gap and excitation energy of SrS host matrix is presented.

2. Experimental

SrS:Dy,Cl phosphor was prepared by solid state reaction of SrS (99.9%.Alfa Aesar) with $DyCl_3$ (99.99%,Indian Rare Earths Ltd.). The mixture was fired at 900 °C for 1 h in hydrogen sulfide atmosphere. This powder was pulverized in a dry atmosphere and stored, keeping in view of the extreme purity as the main consideration in the preparation. The crystal structure of the synthesized phosphors was studied using a Rigaku X-ray diffractometer with Cu Kα X-ray. The PL and PLE spectra were recorded with Jobin Yvon Fluoromax-3 Flourimeter. The optical band gaps of the samples were estimated from the diffuse reflectance spectra recorded with Jasco-V-570 UV–vis–NIR spectrophotometer. The nature of the luminescent impurity in the host was studied by recording the ESR spectra using VarianE-112 E-line Century series X-band ESR spectrometer. The electrical conductivity of the samples pelletized at a pressure of 2 tonnes was measured using a Keithley source measure unit (SMU 236). Silver paste was used as the electrode on either side of the pellets having a diameter of 1 cm.

3. Results and discussion

3.1. X-ray diffraction studies

The powder X-ray diffraction patterns of SrS:Dy,Cl fired at 900 °C for 1 h are shown in Fig. 1. XRD spectra of samples matched the JCPDS file no. 8-489 for cubic SrS without any traces of impurities. It shows that the small percentage of doping does not affect the crystal structure of the host material.

3.2. EPR measurements

EPR measurements were carried out on a VarianE-112 E-line Century series X-band EPR spectrometer at room temperature

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[*] Corresponding author. Tel.: +91 484 2609194; fax: +91 484 2607534.
E-mail addresses: anilaei@gmail.com, anila@cusat.ac.in (E.I. Anila), mkj@cusat.ac.in (M.K. Jayaraj).

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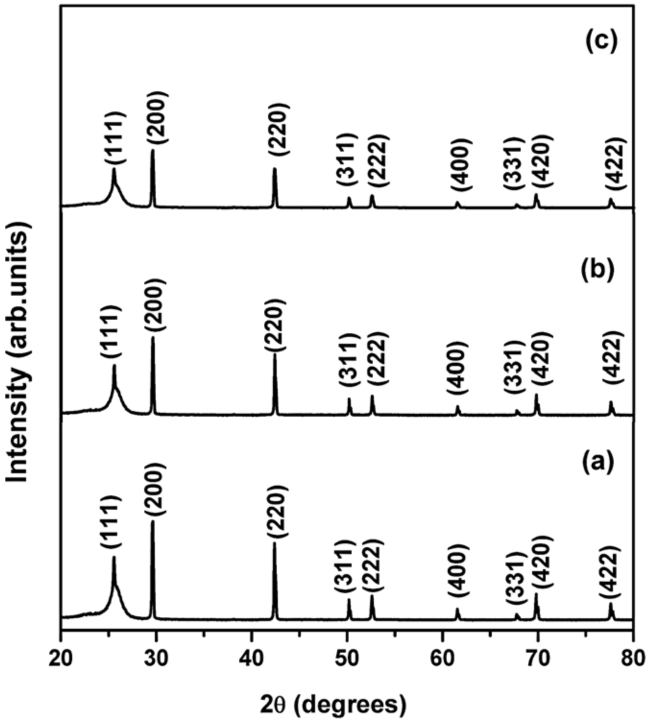

Fig. 1. XRD patterns of SrS:Dy,Cl phosphor for different doping concentrations: (a) 0.1 at.%, (b) 0.5 at.% and (c) 1 at.%.

for the concentrations of Dy varying from 0.1 to 1 at.%. Tetracycloethelene (TCNE, $g = 2.00277$) was used as a standard for g-factor measurements. EPR yielded site-selective information on Dy impurities in the SrS lattice. The spectrum of the powder samples showed a symmetric signal at a g value of 2.08 and another signal at a g value 2.00587 and line width 20 gauss close to the left of the TCNE marker. The line adjacent to the marker (Fig. 2) is due to the F$^+$ center [9,10] produced by sulfur vacancy. The symmetric signal with six lines is due to the hyperfine splitting of Dy^{3+} ($I = 5/2$). The relative intensity of the EPR signal corresponding to the Dy^{3+} ions increased with doping concentration. Dy^{3+} is introduced by doping DyCl$_3$ which is incorporated as Dy^{3+} on Sr sites. To maintain charge neutrality, defect complexes like $[\mathrm{Dy^{3+}}_{\mathrm{Sr}}\,\mathrm{V_{Sr}}]^-$ or $[\mathrm{Cl_S}^-\,\mathrm{V_{Sr}}]^-$ are possible. Chlorine ions can occupy sulfur vacancies and also donate free electrons. Sulfur vacancies trap these electrons forming F$^+$ centers. The EPR signal intensity corresponding to the F$^+$ center also increased with doping concentration of Dy^{3+} ions (Fig. 3).

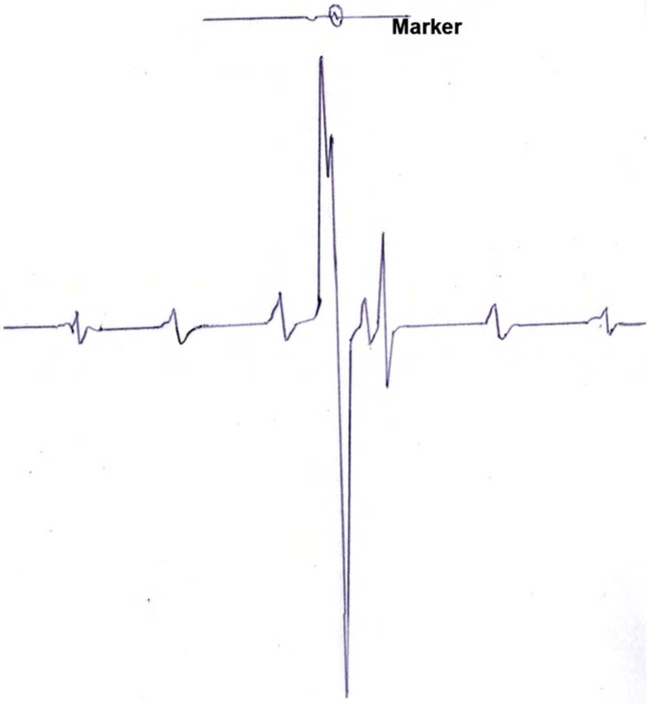

Fig. 2. EPR spectrum of SrS:Dy,Cl phosphor for 0.25 at.% of Dy doping concentration.

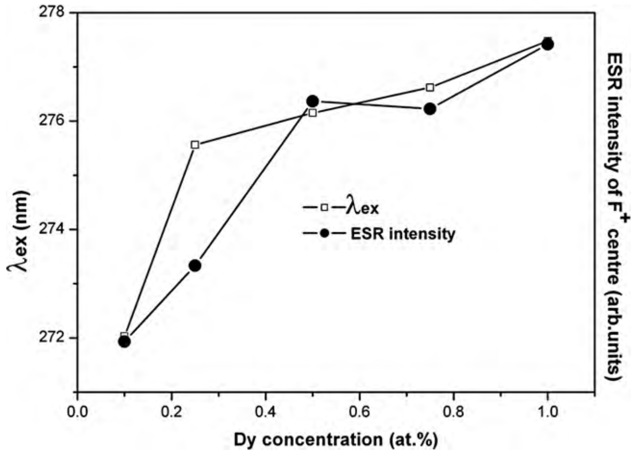

Fig. 3. EPR intensity of F$^+$ center and excitation peak as a function of doping concentration.

3.3. Photoluminescence spectra of SrS:Dy,Cl

Photoluminescence emission spectrum of Dy^{3+} in the SrS powder under excitation of 274 nm is shown in Fig. 4. Due to transitions of the internal 4f electrons in Dy^{3+} we get sharp emission lines. These are characteristic lines of Dy^{3+} [11,12]. The lines at 481, 574, 664 and 756 nm correspond to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$, and $^6H_{9/2}$ transitions, whereas the transitions $^4F_{7/2} \rightarrow {}^6H_{13/2}$, $^6H_{11/2}$, $^6H_{7/2}$, $^6H_{5/2}$ and $^6F_{7/2}$ lead to the emission lines at 457, 486, 580, 657 and 669 nm respectively. This confirms our earlier statement that the dysprosium luminescent impurities are incorporated as Dy^{3+} state in the host lattice.

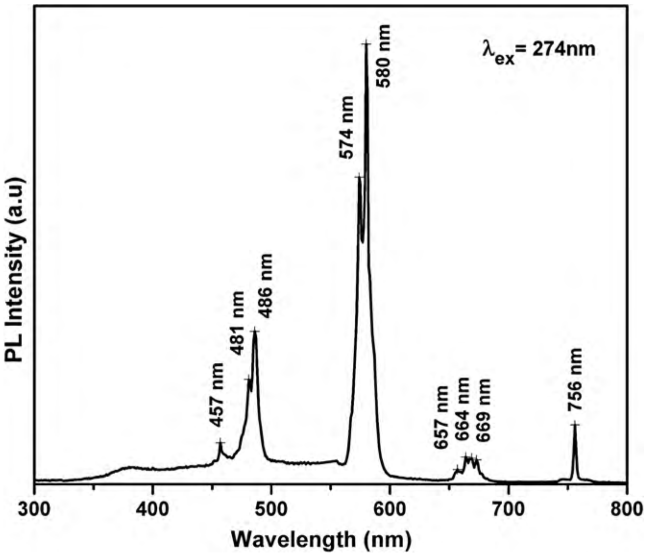

Fig. 4. PL spectrum of SrS:Dy,Cl phosphor with 0.25 at.% of Dy at $\lambda_{ex} = 274$ nm.

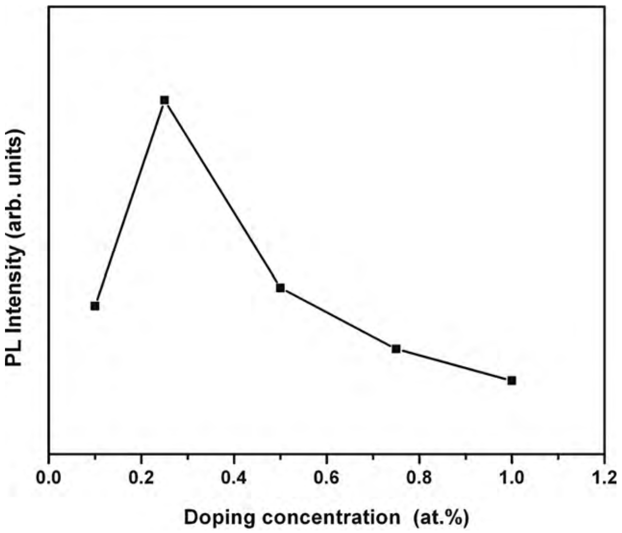

Fig. 5. Variation of PL intensity with doping concentration of Dy in SrS:Dy,Cl.

The resultant of PL emission from the sample is yellow with chromaticity coordinates $x = 0.40$, $y = 0.42$. Elizebath etal. [11] reported two fluorescence bands at 480 and 571 nm (${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^6H_{13/2}$) with Dy^{3+} in an oxalate matrix. Kirsh and Townsend [12] reported a broad line for two allowed transitions ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ and ${}^4F_{7/2} \rightarrow {}^6H_{11/2}$ centered at 485 nm. Also they obtained a single broad line for ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ and ${}^4F_{7/2} \rightarrow {}^6H_{7/2}$ transitions centered at 580 nm. In the present work all emission lines were recorded with good resolution.

The effect of concentration on PL intensity was also studied. Dysprosium doping concentration was varied from 0.1 to 1 at.%. The emission intensities increased with the doping concentration and maximum was observed for a concentration of 0.25 at.% and thereafter decreased (Fig. 5).This decrease can be attributed due to concentration quenching.

3.4. Photoluminescence excitation spectra

PLE and PL spectra of undoped SrS is shown in Fig. 6. Excitation intensity was found to be maximum at 278 nm for an emission wavelength of 381 nm.The PLE spectra of the doped samples (Fig. 7) with different concentrations of Dy were also recorded at room temperature with λ_{em} at 486 nm. The excitation spectra of all samples are broad centered around 275 nm which corresponds to the band to band excitation of SrS host matrix which has a band gap ~4.4 eV. This result suggests that the Dy^{3+} luminescent center is excited via the energy transfer from the host matrix. The excitation peak gets shifted to larger wavelengths as doping concentration is increased (Fig. 3).

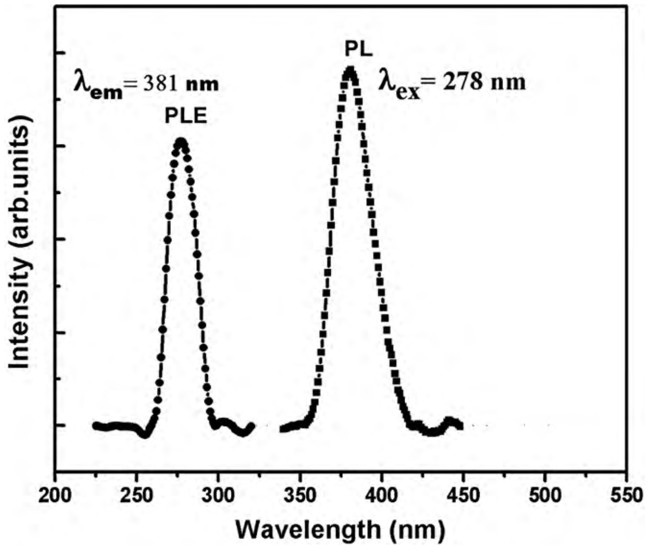

Fig. 6. PLE and PL spectrum of pure SrS at room temperature.

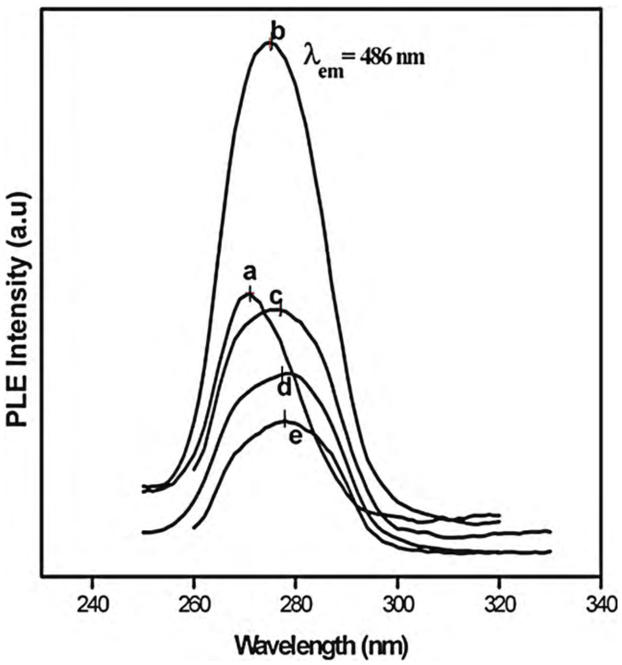

Fig. 7. PLE spectra of SrS:Dy,Cl phosphors for various doping concentrations, $\lambda_{em} = 486$ nm: (a) 0.1 at.%, (b) 0.25 at.%, (c) 0.5 at.%, (d) 0.75 at.% and (e) 1 at.%.

On doping an additional broad excitation band is observed indicating the existence of centers where absorption starts at longer wavelengths which could be related to defect states (Fig. 8). Inset of this figure shows the defect related broad excitation band for different doping concentrations. Doping by $DyCl_3$ introduced many

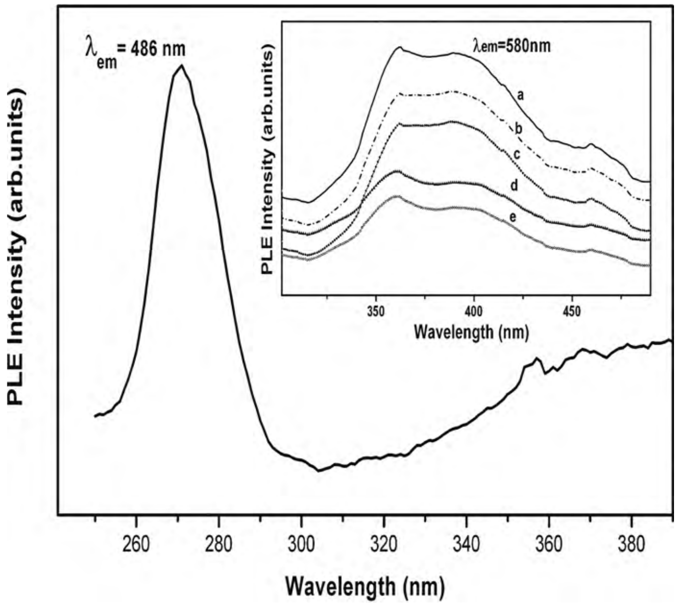

Fig. 8. PLE spectrum of SrS, Dy:Cl for 0.1 at.% Dy concentration ($\lambda_{em} = 486$ nm). Inset shows the PLE spectrum of different samples for $\lambda_{em} = 580$ nm.

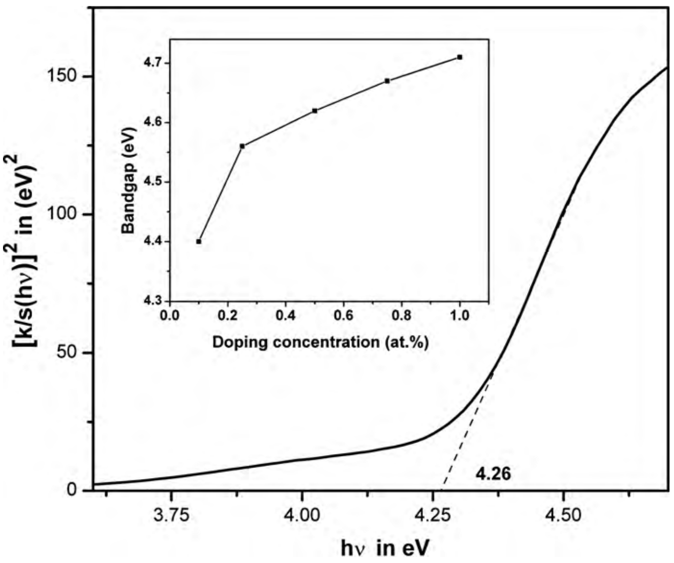

Fig. 9. Plot of $((k/s)\ h\nu)^2$ vs. $h\nu$ of undoped SrS. Inset shows variation of band gap with doping concentration of SrS:Dy,Cl.

defect levels in SrS host matrix. The Cl^- can form a donor level just below the conduction band, the density of which increases with the doping concentration of Dy^{3+} ions since dysprosium is introduced in the form of $DyCl_3$. In ZnS this level was found at 0.46 eV below the conduction band [13,14]. EPR spectrum confirms the existence of F^+ center. The absorption at 385 nm may be due to sulfur vacancies since it is also seen in the photoluminescence emission of pure SrS. Another defect of chlorine at sulfur vacancies (Cl_S) can also be introduced below the conduction band for charge compensation. These tail band states cause the gradual red shift in (λ_{ex}) peak with increase in doping concentration.

3.5. Diffuse reflectance and conductivity measurements

Fig. 9 is the plot of $h\nu$ vs. $\{(k/s)/h\nu\}^2$ obtained from diffuse reflectance spectra of pure and doped SrS powder, k and s being the absorption and scattering coefficients respectively. The ratio k/s was calculated from reflectance spectra via Kubelka–Munk equation [15,16]. The band gap is found to increase with increase of Dy^{3+} doping concentration (inset of Fig. 9). This could be related to the Burstein–Moss shift. The optical gap is defined as the minimum energy needed to excite an electron from valance band to conduction band. In pure undoped crystals the optical gap equals the energy separation between the band edges. On heavy doping (Dy^{3+} and Cl^-) the donor electrons occupy states at the bottom of the conduction band. Since Pauli's principle prevents states that being doubly occupied, the optical band gap is given by energy difference between states with Fermi momentum in the conduction band and valance band. This type of blocking of low energy transitions is known as Burstein–Moss effect [17,18]. The conductivity of the dysprosium doped SrS samples shows an increase in conductivity (Table 1). This confirms that there is increase in carrier concentration on increasing the Dy^{3+} concentration and hence the BM shift.

Table 1
Variation of conductivity with doping concentration.

Doping concentration (at.%)	Conductivity ($\times 10^{-6}$ S m^{-1})
Pure SrS	7.95×10^{-3}
0.1	1.78
0.25	7.2
0.5	8.2
0.75	9.5
1.0	11.2

3.6. Conclusion

The optical properties of Dy doped SrS powder phosphor for various concentrations have been investigated. PL intensity is maximum for a doping concentration of 0.25 at.%. ESR spectrum consists of two signals one due to Dy^{3+} ion and other due to F^+ center. Room temperature PLE spectra show a monotonic red shift with increasing doping concentration. This is due to the near band edge fluctuations caused by randomly distributed doping impurities. But absorption edges show a blue shift with increasing doping concentration which is BM shift due to doping induced increase in carrier concentration.

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