Solid State Communications, Vol. 81, No. 4, pp. 367–369, 1992.
Printed in Great Britain.

0038–1098/92 $5.00 + .00
Pergamon Press plc

FLUORESCENCE EMISSION OF SrS : Eu^{2+} PHOSPHOR-ENERGY LEVEL SPLITTING OF Eu^{2+}

Thomas Baby* and V.P.N. Nampoori

Laser Division, Department of Physics, Cochin University of Science and Technology,
Cochin-682 022, India

(*Received* 6 *July* 1991 *by A. Okiji*)

A method of preparation of strontium sulphide phosphors doped with europium is given. Nitrogen laser excited fluorescence emission spectra of these phosphors in the visible region are recorded. A band with line structure in the region 350–430 nm and a new broad band at 460 nm are observed. The splitting pattern for the ^6P levels of Eu^{2+} are given.

IN RECENT years, it has become apparent that in certain hosts, Eu^{2+} exhibits fluorescence emission spectrum characterized by sharp lines. The presence of such sharp line spectra has caused detailed experimental measurements and theoretical analysis by various workers. The luminescence properties of Eu^{2+} activated alkaline earth phosphors (e.g. Ca, Sr and Ba) have been studied and it was found that the emission spectrum constitutes of a $4f^7$–$4f^7$ line spectrum in the near ultraviolet region [1–6].

Prizibram [7] claimed that in the divalent europium halides, the fluorescent emission consists of a blue band and sharp lines in the red region. This was in contrast with the results of Gobrecht [8] who attributed the blue band to Eu^{2+} and the red lines to Eu^{3+}. Freed and Katcoff [9] had results essentially in agreement with Prizibram with their work on $EuCl_2$. On the other hand, Brauer [10] reported that the emission from Eu^{2+} and Eu^{3+} falls in the same wavelength region. According to Brauer, Eu as a trace, is divalent in the alkaline earth sulphides and trivalent in the alkaline earth oxides. Jaffe and Banks [11] have also reported similar results. Keller [12] had shown that Eu^{2+} can be converted into Eu^{3+} and vice versa by changing the conditions of firing. Furthermore, under certain conditions, samples can be obtained which have measurable amounts of both divalent and trivalent europium.

Thus the investigation on Eu activated phosphors is surprisingly rare, and a few publications are not always in agreement with each other. Our investigations were made to clarify the reported contradictions and to interpret the optical spectra of Eu^{2+} in the SrS : Eu phosphor system. A probable energy level scheme is given from the observed spectra.

The samples were prepared following the technique as described in our earlier reports [13, 14]. High purity SrS (Reidel, Germany) was used as the base material. A number of samples with varying europium concentrations (0.1, 0.2, 0.4, 0.8, 1 and 1.4 wt %) were prepared by doping the base material with the required amounts of europium oxide (99.99% purity, from IRE, India) and carbon (reducing agent) in the presence of sodium thiosulphate (flux). The mixture was fired at 950°C for about one hour. Efficient phosphors were obtained by quenching the fired samples to room temperature. The powder thus obtained was converted into pellets of 10 mm radius and 3 mm thickness.

The phosphors were excited using a home made pulsed nitrogen laser (337.1 nm) of peak power 700 kW [15, 16]. Fluorescence emission spectra were recorded on a strip chart recorder (Omnigraphic) using a 0.5 m Jarrel Ash monochromator coupled to an EMI 9683 KQB photomultiplier tube (PMT) having S-20 cathode. Output from the PMT was amplified using a low-noise high gain preamplifier. All the measurements were carried out at room temperature.

The fluorescence emission spectra of SrS : Eu^{2+} are shown in Fig. 1. Spectra reveal several narrow lines which are superimposed on the broad band emission peaking at 380 nm and a broad band at 460 nm. The 460 nm band is not observed using conventional u.v. excitation sources. The band intensity at 380 nm gets enhanced at the cost of 460 nm. The 460 nm band disappears completely at 0.8% of Eu concentration. There is no perceptible shift in the peak wavelength of both the bands with the change of activator concentrations. In the case of undoped SrS

---

[*] On leave from The Rubber Research Institute of India, Kottayam 686 009, India.

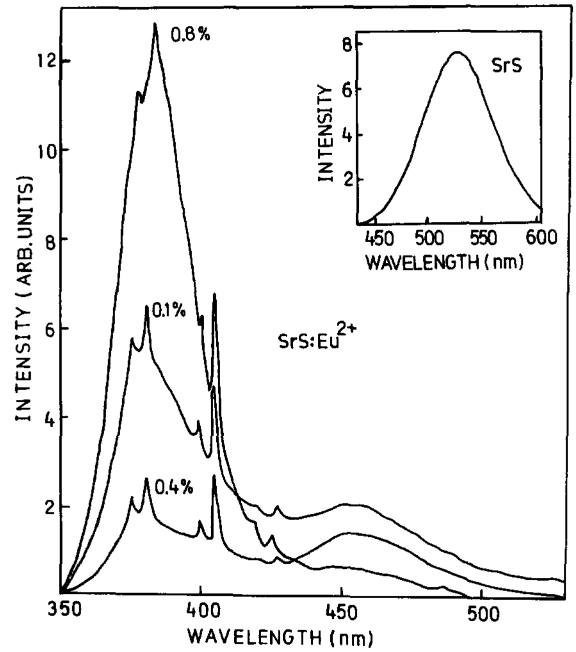

Fig. 1. Fluorescence emission spectra of SrS : Eu^{2+} phosphors for different Eu concentrations (in wt %): (1) 0.1% (2) 0.4% and (3) 0.8%. Inset shows the fluorescence emission spectrum of undoped SrS.

sample, only a broad band at 520 nm is observed (inset of Fig. 1). The sample does not show any characteristic fluorescence emission in the red region. This indicates that Eu goes into the SrS lattice as Eu^{2+}.

The phosphors exhibit a broad and strong fluorescence band resulting from the $5d \rightarrow 4f$ transition as well as sharp line emission which has been assigned to $4f(^6P_i) \rightarrow 4f(^8S_{7/2})$ transitions (here $i = 3/2$, $5/2$ and $7/2$). As in the case of fluorite type crystals doped with divalent europium [17], the broad band in the optical spectra of alkaline earth sulphides is due to the transition from the $4f^7\,(^8S_{7/2})$ ground state to the states in the $4f^6 5d$ configuration of the Eu^{2+} ion. The presence of both $5d \rightarrow 4f$ and $4f \rightarrow 4f$ transition indicates the proximity of the lowest excited $5d$ and $4f^7\,(^6P_{7/2})$ levels [4, 18].

A schematic configuration coordinate diagram Eu^{2+} in which the lowest excited $5d$ and $4f^7\,(^6P_i)$ levels are included is shown in Fig. 2. The diagram is similar to that proposed by Blasse [19] except that ^6P_i level was fixed lower than that of $4f^6 5d$. Our observations show that ^6P_i should lie above $4f^6 5d$. The change in relative position of the $5d$ and ^6P_i levels is due to the difference in host lattice. Strong $5d \rightarrow 4f$ band emission occurs when the $5d$ level is significantly lower than the $^6P_{7/2}$ level while the $4f \rightarrow 4f$ line emission appears when the reverse is true. Both $5d \rightarrow 4f$ and $4f \rightarrow 4f$ transition occurs when the energy levels are close together as in the present case. Thus the broad band at 460 nm is attributed to the $5d \rightarrow 4f$ transition, while the band with line structure in the region 350–430 nm corresponds to $^6P_i \rightarrow {}^8S_{7/2}$ transitions. This implies that $5d$ level lies at about 1706 cm^{-1} lower than the $^6P_{7/2}$ state (Fig. 3b).

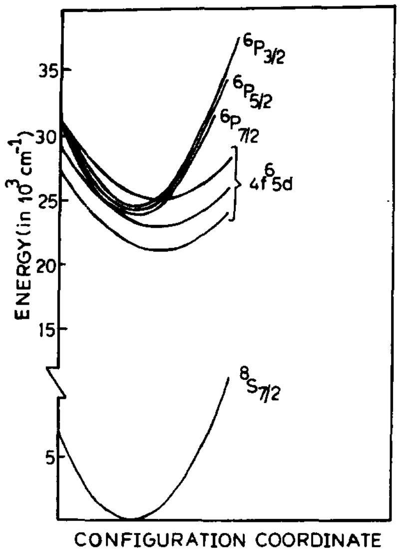

Fig. 2. Schematic configuration coordinate diagram of Eu^{2+}. Curves were placed as indicated in text. Stark splitting is not shown.

The wavelengths and assignments of the observed fluorescence emission in the 350–430 nm region are given in Table 1. In order to identify the various sublevels giving rise to the six lines occurring in the $^6P_i \rightarrow {}^8S_{7/2}$ levels, an analysis of the spectrum has been carried out following the method suggested by Lea *et al.* [20] and Zhong and Bryant [21]. The method has been applied successfully to analyse the photoluminescence and electroluminescence spectra [14, 22]. It is found that the six lines can be attributed to transitions from various Stark levels of $^6P_{7/2}$, $^6P_{5/2}$ and

Table 1. Wavelength and assignments of ^{6}P *levels of* Eu^{2+}

Group	Wavelength	Wavenumber (ν cm^{-1})	
		Observed	Calculated
$^6P_{7/2} \rightarrow {}^8S_{7/2}$	427.3	23 403	23 445
	420.0	23 810	23 810
	404.9	24 697	24 660
$^6P_{5/2} \rightarrow {}^8S_{7/2}$	399.6	25 025	25 025
	380.3	26 295	26 295
$^6P_{3/2} \rightarrow {}^8S_{7/2}$	375.1	26 660	26 660

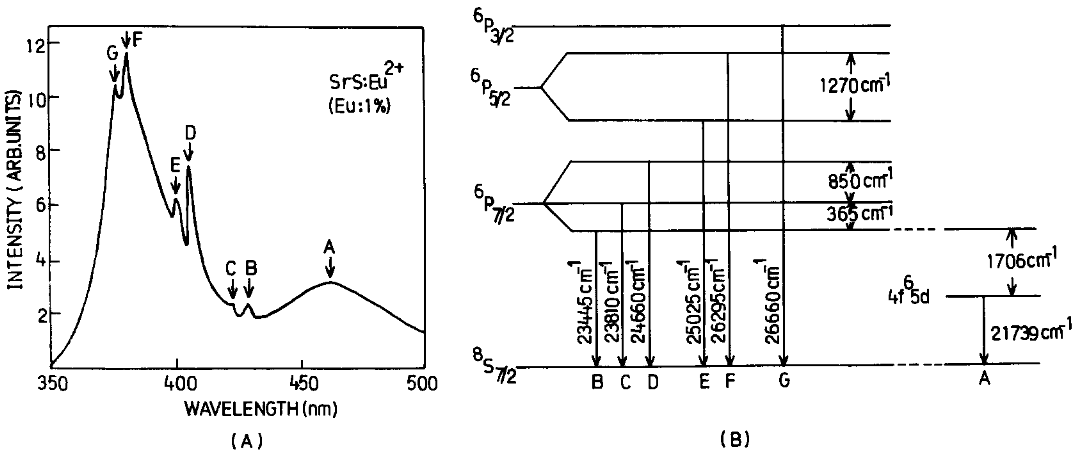

Fig. 3. (a) Fluorescence emission spectrum of SrS : Eu^{2+} (Eu : 1%). (b) Energy level scheme showing the various sublevels and transitions which give rise to the fluorescence emission spectrum in Eu^{2+}.

$^6P_{3/2}$ to $^8S_{7/2}$. The present analyses show that $^6P_{7/2}$ and $^6P_{5/2}$ split into triplet and doublet, respectively, due to the crystal field interactions while $^6P_{3/2}$ and $^8S_{7/2}$ do not show any splitting. Details of the analyses are given in earlier reports [14, 20–22]. The relevant energy level diagram is shown in Fig. 3(b).

In conclusion, we have observed a new broad band ($5d \rightarrow 4f$) as well as sharp line emissions ($4f \rightarrow 4f$) of divalent europium doped in SrS phosphors. The energy level scheme for these transitions in Eu^{2+} ion is also presented.

Acknowledgements – The authors are grateful to Dr T.M.A. Rasheed for many valuable discussions. They are also thankful to Professor K. Babu Joseph for providing them with necessary facilities to carry out this work. Financial assistance from the Ministry of Human Resources and Development (New Delhi) is gratefully acknowledged.

REFERENCES

1. J.L. Sommerdijk, J.M.P.J. Verstegen & A. Bril, *J. Lumin.* **8,** 502 (1974).
2. J.M.P.J. Verstegen & J.L. Sommerdijk, *J. Lumin.* **9,** 297 (1974).
3. J.M.P.J. Verstegen, J.L. Sommerdijk & A. Bril, *J. Lumin.* **9,** 420 (1974).
4. B. Tanguy, P. Merle, M. Pezat & C. Fouassier, *Mater. Res. Bull.* **9,** 831 (1974).
5. A.L.N. Stevels, *J. Lumin.* **17,** 121 (1978).
6. G. Blasse, A. Bril & J. de Vries, *J. Electrochem. Soc.* **115,** 977 (1968).
7. K. Prizibram, *Z. Physik.* **107,** 709 (1937).
8. H. Gobrecht, *Ann. Physik.* **28,** 673 (1937).
9. S. Freed & S. Katcoff, *Physica* **14,** 17 (1948).
10. P. Brauer, *Z. Naturforsch.* **6a,** 561 (1951).
11. P.M. Jaffe & E. Banks, *J. Electrochem. Soc.* **102,** 518 (1955).
12. S.P. Keller, *J. Chem. Phys.* **30,** 556 (1959).
13. Reethamma Thomas & V.P.N. Nampoori, *Solid State Commun.* **68,** 821 (1988).
14. Reethamma Thomas & V.P.N. Nampoori, *Solid State Commun.* **73,** 803 (1990).
15. Thomas Baby, T. Ramachandran, P. Radhakrishnan, V.P.N. Nampoori & C.P.G. Vallabhan, *Measur. Sci. Technol.* **2,** 873 (1991).
16. Thomas Baby, T. Ramachandran, K. Sathianandan, V.P.N. Nampoori & C.P.G. Vallabhan, *Rev. Sci. Instrum.* **62**(9), 2076 (1991).
17. J. Hernandez, A, W.K. Cory & J. Rubio, O, *J. Chem. Phys.* **72**(1), 198 (1980).
18. T. Kobayasi, S. Mroczkouski & J.F. Owen, *J. Lumin.* **21,** 247 (1980).
19. G. Blasse, *Phys. Status Solidi* **55,** 131 (1973).
20. K.R. Lea, M.J.M. Leask & W.P. Wolf, *J. Phys. Chem. Solids* **23,** 1381 (1962).
21. C.Z. Zhong & F.J. Bryant, *J. Phys. C: Solid State Phys.* **13,** 4797 (1980).
22. S.M. Pillai & C.P.G. Vallabhan, *Phys. Status Solidi* (*b*) **134,** 383 (1986).