On Luminescent Properties of SrS: Sm Phosphor Using Nitrogen Laser Excitation

Thomas Baby and V.P.N.Nampoori
Laser Division, Department of Physics
Cochin University of Science and Technology
Cochin 682022

Abstract

The fluorescence emission spectrum of SrS: Sm phosphor in the visible region is recorded. It consists of three groups of emission bands which are well resolved into discrete lines. On the basis of the crystal field theory, the splitting pattern of Sm^{3+} energy levels in SrS lattice is evaluated.

Key words: fluorescence, spectroscopy

Introduction

Alkaline earth sulphide phosphors activated by specific metallic impurities gained considerable practical importance after the discovery of infrared stimulation and sensitized luminescence (Tomaschek 1944; Rothschild 1934). A good deal of work has been done on the luminescence properties of SrS phosphors doped with a number of activators. However, investigations on SrS: Sm phosphors carried out till date are inadequate and in certain cases, controversial as well. These facts motivated us to undertake a fresh investigation of fluorescence spectrum of SrS: Sm phosphor. The primary objective of this paper is to interpret the site of the luminescent centre and the levels involved in the emission, on the basis of the crystal field theory.

The samples were prepared by the techniques previously described in our earlier paper on the flourescence of SrS: Ce and BaS: Ce phosphors (Thomas Baby, Thomas & Nampoori 1985). High purity SrS was used as the base material. A number of samples with varying samarium concentrations were prepared by doping the base material with the required

amounts of samarium oxide and carbon (reducing agent) in the presence of sodium thiosulphate as flux. The mixture was fired at 950^0C 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 10mm radius and 3 mm thickness.

The phosphors were excited using a pulsed Nitrogen Laser (337.1 nm) of peak power 250 KW. Fluorescence spectra were recorded using a 0.5m Jarrel-Ash monochromator coupled with PMT, pre-amplifier and a chart recorder. All the measurements were carried out at room temperature. Several samples were prepared by varying the parameters like activator concentrations, firing temperature, firing time and concentration of flux. In this paper, we report the effect of crystal field on the energy level structure of Sm^{3+} in SrS lattice.

The Sm^{3+} emission in SrS consists of three groups of intense lines (Table 1) in the region 550-675 nm (Fig.1). These bands are attributed to the well known transitions $4_{G_{5/2}} \rightarrow 6_{H_{5/2}}, 4_{G_{5/2}} \rightarrow 6_{H_{7/2}}$ and $4_{G_{5/2}} \rightarrow 6_{H_{9/2}}$(Marfunin 1979). The occurrence of the sub levels is due to the splitting of the free ion term of the Sm^{3+} under the influence of the ligands of the surrounding ions. In the present case, since SrS crystallises in $NaCl$ structure (Keller & Pettit 1959), an impurity ion occupying as Sr^{2+} site will experience a cubic crystal field with octahedral co-ordination. In such an environment (Lea,Leask & Wolf 1962), the free ion terms with $J = 5/2$ and $J = 7/2$ will split into two and three sub levels respectively. So evidently, the first group of emission bands will consists of four lines and the second will comprise of six lines.

Table 1. Wavelengths and assignment of fluorescence emission bands
in SrS: Sm phosphor

Group	Level Transitions	Wavelength (nm)	Wavenumber (ν)cm^{-1} Observed	Calculated
$^4G_{5/2} \rightarrow ^6 H_{5/2}$	$8 \rightarrow 7$	5561	17982	17982
	$7 \rightarrow 7$	5597	17867	17867
	$8 \rightarrow 8$	5669	17640	17643
	$7 \rightarrow 8$	5705	17528	17528
$^4G_{5/2} \rightarrow ^6 H_{7/2}$	$8 \rightarrow 7$	5963	16770	16740
	$7 \rightarrow 7$	6015	16625	16625
	$8 \rightarrow 6$	6035	16570	16600
	$7 \rightarrow 6$	6066	16485	16485
	$8 \rightarrow 8$	6051	16525	16525
	$7 \rightarrow 8$	6097	16401	16410
$^4G_{5/2} \rightarrow ^6 H_{9/2}$	$8 \rightarrow 8^{(1)}$	6436	15538	15538
	$7 \rightarrow 8^{(1)}$	6483	15425	15423
	$8 \rightarrow 8^{(2)}$	6498	15389	15389
	$7 \rightarrow 8^{(2)}$	6539	15293	15274
	$8 \rightarrow 6$	6570	15221	15267
	$7 \rightarrow 6$	6622	15101	15152

An analysis of the crystal field splitting can be made by following the method suggested by Zhong and Bryant (1980). Lea et al. (1962) have shown that within a manifold of
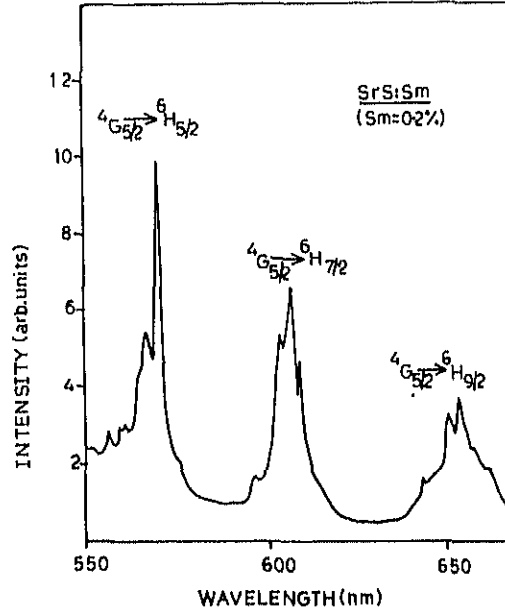

Figure 1: Fluorescence spectrum of SrS:Sm phosphor.

angular momentum J of $4f^n$ configuration the general operator equivalent potential with cubic symmetry has the form

$$H = B_4(O_4^0 + 5O_4^0) + B_6(O_6^0 - 21O_6^4) \tag{1}$$

where x,y,z axes have been chosen along the $< 100 >, < 010 >, < 001 >$ directions, respectively. Using the notation of Lea et al. (1962) the Hamiltonian is then

$$H = W\left(x\frac{O_4}{F(4)} + (1 - |x|)\frac{O_6}{F(6)}\right) \tag{2}$$

where

$$O_4 = O_4^0 + 5O_4^4, \quad O_6 = O_6^0 - 21O_6^4$$
$$B_4 F(4) = W_x, \quad B_6 F(6) = 1 - |x| \tag{3}$$

and $-1 \leq x \leq 1$, when x runs from -1 to +1. The Hamiltonian covers all possible combinations of the fourth and sixth degree terms. The scale and pattern of the crystal field splittings are determined by the coefficients B_4 and B_6 which are

$$B_4 = A_4 < r^4 > \beta_., \quad B_6 = A_6 < r^6 > \gamma \tag{4}$$

where $< r^4 >$ and $< r^6 >$ are the mean fourth and sixth powers of the radii of the $4f$ electrons of the impurity ion and β and γ are the Steevan's multiplicative constants (Steevans 1952).

The geometrical coordination factors A_4 and A_6 are given by the point charge crystal field model. Freeman and Watson (1962) gave the respective values of $< r^4 >$ and $< r^6 >$ for the Sm^{3+} ion as 1.897 a_H^4 and 8.7775 a_H^6 (a_H is the Bohr radius) respectively. Here the values of W and x are both positive since the Sm^{3+} ion in SrS experiences an octahedral crystal field.
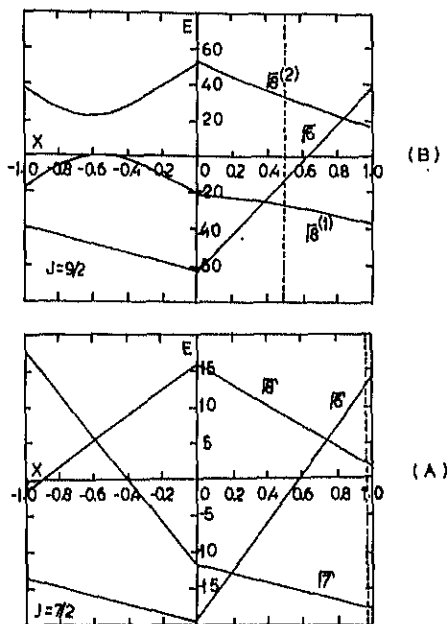
Figure 2: (A and B). The splitting pattern of the $^6H_{7/2}$ and $^6H_{9/2}$ manifold of the Sm^{3+} ion in the SrS lattice. E is in cm^{-1} and x is a dimensionless parameter defined in the text. The broken lines indicate the values of x used to evaluate the scale factor $W(in cm^{-1})$ required for the experimental determination of crystal field parameters.

In order to identify the various sub levels giving rise to the six lines occurring in the $^4G_{5/2} \rightarrow ^6H_{7/2}$ level and also to find out the level separation between these sub levels, an analysis of the spectrum has been carried out. It is found that these six lines can be grouped into two sets consisting of three lines, each group being separated by an average amount of 115 cm^{-1}. The lines in each group are found to be separated by 75 cm^{-1} and 140 cm^{-1} (Fig.3). The splitting pattern of the $^6H_{7/2}$ level of the Sm^{3+} ion in a cubic field is given in (Fig.2A). An exact fit with the above pattern occurs for the scale factor $W = 6.08 cm^{-1}$ and $x = 0.97$. Using the Equations (3) and (4) the crystal field parameters calculated are $B_4 = 0.98$, $B_6 = 2.38 x 10^{-5}$, $A_4 < r^4 >= 393$ cm^{-1}.

For the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition, the separation is found to be 115 cm^{-1}. The lines in each group are separated by 122 cm^{-1} and 149 cm^{-1} respectively. The splitting pattern of $^6H_{9/2}$ level of Sm^{3+} ion is shown in Fig.2B. For this group, the best fit is obtained when $W = 2.249 cm^{-1}$ and $x = 0.52$ giving $B_4 = 0.019$., $B_6 = 1.79 \times 10^{-5}$ and $A_4 < r^4 >= 7.79 cm^{-1}$.

Thus the values of $A_4 < r^4 >$ obtained using the experimentally measured W and x from Equations (2) and (4) which coincides with the values of $A_4 < r^4 >$ obtained theoretically

Figure 3: The energy level scheme showing the various sub levels and transitions which give to the fluorescence spectrum of SrS:Sm.

from the point charge crystal field calculations. The model suggests that Sm^{3+} dissolves in SrS substitutionally.

References

Freeman,A.J. and Watson,R.E. 1962,Phys.Rev.**187**,2058.

Keller,S.P.and Pettit,G.D. 1959,J.Chem.Phys.**30**,434.

Lea,K.R., Leask,M.J.M. and Wolf W.P. 1962, J.Phys.Chem.Solids **23**, 1381.

Marfunin,A.S. 1979, Spectroscopy, Luminescence and Radiation Centres in the Minerals, Springer Verlag Publishers, New York, 207.

Rothschild,S. 1934, Z.Phys., **35**, 557.

Steevans 1952,Proc.Phys.Sov.A**65**,209.

Tomaschek,R. 1944, Reichsber Phys., **1**, 139.

Thomas Baby, Thomas R. and Nampoori, V.P.N. 1985, Proc.DAE Symposium on quantum electronics, BARC, Bombay, 180.

Zhong,C.Z. and Bryant,F.J. 1980, J.Phys.C**13**,4797.