LASER INDUCED FLUORESCENCE OF BaS:Sm PHOSPHOR AND ENERGY LEVEL SPLITTING OF Sm^{3+} ION

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Fluorescence of BaS:Sm phosphor has been studied using a pulsed Nitrogen laser (337.1nm) as the excitation source. The spectrum consists of a broad band in the region 540-660nm superposed by the characteristic Sm^{3+} lines. Energy level splitting pattern of Sm^{3+} due to crystal field effects has been calculated and relevent field parameters are evaluated. Analysis shows that Sm^{3+} takes up Ba^{2+} substitutional sites.

Study of luminescence and related properties of alkaline earth sulphide phosphors is important in the context of the development of display devices and also will be helpful in understanding the effect of crystal field on free-ion energy levels. Amongst the class of sulphide phosphors CaS has been studied extensively [1-3]. While such investigations are very limited in the case of SrS and BaS. We have been studying the synthesis and characterisation of alkaline-earth sulphide phosphors for the last few years [4]. In this paper we report the results obtained from the study of BaS:Sm phosphor under N_2 laser excitation. Unlike the earlier reports on Sm doped BaS phosphors [5] we observed the characteristic Sm^{3+} ion emission superposed over a broad emission band due to the host material.

Phosphor samples were prepared by the reduction of $BaSO_4$ in Carbon atmosphere, giving an initial firing at 950 $^\circ$C for about one hour. To a weighed amount of BaS thus obtained, the flux $Na_2S_2O_3$ (2 mol % by wt.) and the dopant in the form of aqueous solution of $SmCl_3$ in proper concentrations (5 mol % by wt. to 0.001 mol % by wt. of BaS) were added, well mixed and the mixture was then slowly heated and dried. The resulting mass was crushed and refired at 1050 $^\circ$C for 90 min. under reduced pressure (10^{-2} Torr.). The powder thus obtained was pressed into disc pellets of 10mm dia. and 2mm thickness.

Samples were excited using 337.1nm radiation from a pulsed nitrogen laser system (peak power 300KW, 10 ns pulse width, 25pps). Fluorescence spectra were recorded in a perpendicular direction using 0.5m grating monochromator(Jarrel Ash) having an EMI 9683 KQB PMT with S20 cathode as detector along with a highly stabilised power supply(EMI model PM 28B) followed by a low-noise preamplifier and omniscribe chart recorder. All measurements were carried out at RT.

The fluorescence spectra (fig. 1) revealed three groups (A,B,and C) of well seperated bands superposed over the broad emission band (550-650m) of BaS phosphor. The overall emission show the usual concentration quenching of fluorescence above an optimum Sm^{3+} conc.(0.5 mol % by wt. of BaS). The observed three groups of emission lines at 560nm (group A), 600nm (group B), and 650nm (group C) regions can be attributed to Sm^{3+} transitions from $^4G_{5/2}$ to various lower levels viz. $^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ [6]. Fine structure revealed in these bands are due to the crystal field interaction on free-ion energy levels of Sm^{3+}.

BaS with 3.8eV band gap undergoes a direct band-to-band transition under N_2 laser excitation(337.1nm). Electrons and holes generated in the process will migrate through BaS lattice and will be trapped by Sm^{3+} ions followed by radioactive recombinations of electrons and holes. Also the observed increase in fluorescence emission of BaS:Sm phosphor suggests there is an effective energy
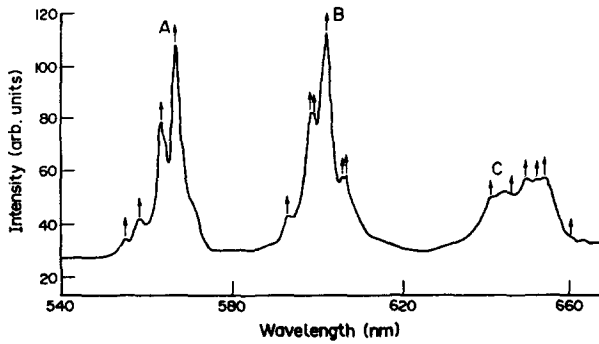
Fig.1. Fine structure spectrum of BaS:Sm Phosphor

Free-ion terms with J=5/2 will split into two sublevels viz. Γ_8 and Γ_7 in octahedral crystal field. The four lines observed in the group A is due to $^4G_{5/2} \to {}^6H_{5/2}$ transitions of Sm^{3+} ion can therefore be explained by taking into consideration the doublet structure of upper and lower levels with separation $114cm^{-1}$ and $274cm^{-1}$ respectively. The six lines observed in the group B are 4 transitions due to the radiative de-excitation $^4G_{5/2} \to {}^6H_{7/2}$ between the two sublevels of $^4G_{5/2}$ (Γ_8 and Γ) and the three sublevels of $^6H_{7/2}$ (Γ_6, Γ_8 and Γ_7) having multiplet separation $74cm^{-1}$ and $177cm^{-1}$. Similarly the six lines of the group

transfer between BaS host lattice centers to Sm^{3+} centers. Since BaS has NaCl structure, Ba^{2+} site will experience a cubic crystal field with octahedral co-ordination. Free-ion energy levels of Sm^{3+} ions in Ba^{2+} site will split into sub-levels due to crystal field effect.

Analysis of crystal field splitting can be made by the method used by Zhong and Bryant [7] and Pillai and Vallabhan [8] in the analysis of EL spectra. Within a manifold of angular momenta J of $4f^n$ electron configuration, the general operator equivalent potential with cubic symmetry can be written as [9]

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

where O_l^m are the usual spherical harmonic functions.

Using the modified notation,

$$\mathcal{H} = W\left[x\left(\frac{O_4}{F(4)}\right) + 1 - |x| \left(\frac{O_6}{F(6)}\right) \right] \quad\text{---- (2)}$$

where $O_4 = O_4^0 + 5 O_4^4$; $O_6 = O_6^0 - 21 O_6^4$ ----(3.a) and $F(4)$ and $F(6)$ are defined through the relations, $B_4F(4)=Wx$; $B_6F(6)=1-|x|$ ----(3.b) with $-1 \le x \le 1$, and W the scale factor.

The pattern of crystal field splitting is determined by B_4 and B_6 which are given by

$$B_4 = A_4 \langle r^4 \rangle \beta \quad\text{and}\quad B_6 = A_6 \langle r^6 \rangle \gamma \quad\text{---- (4)}$$

where $\langle r^4 \rangle$ and $\langle r^6 \rangle$ are the mean fourth and sixth powers of the radii of 4f electrons of Sm^{3+} ion and β and γ are the Steevan's multiplicative constants [10]. A_4 and A_6 are the geometrical co-ordination factors and are given by the point charge crystal field model. Freemann and Watson [11] gave $\langle r^4 \rangle$ and $\langle r^6 \rangle$ values of Sm^{3+} ion as $1.897 a_H^4$ and $8.775 a_H^6$ respectively (a_H - the Bohr radius).
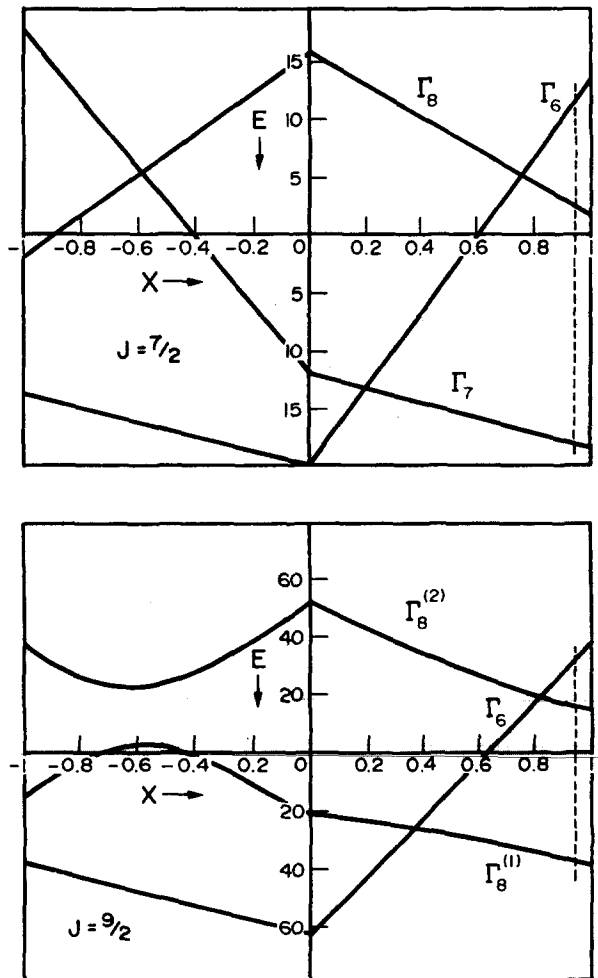

Fig.2. The splitting pattern $^6H_{7/2}$ and $^6H_{9/2}$ manifold of Sm^{3+} ion in BaS lattice. E is in cm^{-1}; x is a dimensionless parameter defined in the text. The broken lines indicate the values of x used to evaluate the scale factor W (in cm^{-1}) required for the experimental determination of crystal field parameters.

Table .1.

Transitions involved corresponding to the fine structure spectrum of Sm^{3+} in BaS lattice.

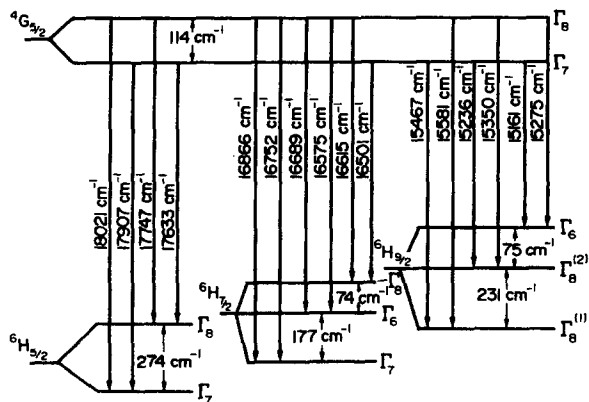| Group	Transitions Upper state --->lower state	Wavelength (nm)	Wavenumber (ν cm^{-1}) Observed	Calculated
A	Γ_8 ---> Γ_7	554.9	18021	18021
	Γ_8 ---> Γ_8	563.3	17752	17747
$^4G_{5/2}$--->$^6H_{5/2}$	Γ_7 ---> Γ_7	558.3	17911	17907
	Γ_7 ---> Γ_8	567.1	17633	17633
B	Γ_8 ---> Γ_7	592.7	16866	16866
	Γ_8 ---> Γ_8	599.2	16888	16869
$^4G_{5/2}$--->$^6H_{7/2}$	Γ_8 ---> Γ_6	601.9	16614	16615
	Γ_7 ---> Γ_7	597.0	16750	16752
	Γ_7 ---> Γ_8	603.0	16583	16575
	Γ_7 ---> Γ_6	606.0	16501	16501
C	Γ_8 ---> $\Gamma_8^{(1)}$	641.8	15581	15581
	Γ_8 ---> $\Gamma_8^{(2)}$	651.5	15349	15350
$^4G_{5/2}$--->$^6H_{9/2}$	Γ_8 ---> Γ_6	654.7	15274	15275
	Γ_7 ---> $\Gamma_8^{(1)}$	646.8	15469	15467
	Γ_7 ---> $\Gamma_8^{(2)}$	656.2	15239	15236
	Γ_7 ---> Γ_6	659.5	15163	15161

Fig.3. Energy level multiplet structure of Sm^{3+} in BaS lattice. Term values are given as obtained from the analysis. Various transitions are also shown.

C can be attributed to the transition $^4G_{5/2} \to {}^6H_{9/2}$ where $^6H_{9/2}$ split into three sublevels viz. $\Gamma_6, \Gamma_8^{(2)}$ and $\Gamma_8^{(1)}$ with multiplet separation as 75cm^{-1} and 231cm^{-1}. These lines are then compared with splitting pattern for J=7/2 and J=9/2 terms (fig. 2). The multiplet structures of the observed energy levels assigned for Sm^{3+} in BaS (as given in Table 1 and fig. 3) can be best fitted with theoretical prediction by taking x=0.955 and the scale factor W=8.442cm^{-1} for $^4G_{5/2} \to {}^6H_{7/2}$ transitions and W=11.84cm^{-1} for $^4G_{5/2} \to {}^6H_{9/2}$ transitions. Calculations gave the releventcrystal field parameters as :B$_4$=0.13436; B$_6$=3.015x10^{-4}; A$_4\langle r^4\rangle$=53.74 cm^{-1}for J=7/2 term and B$_4$=0.188453; B$_6$=2.114x10^{-4}; A$_4\langle r^4\rangle$=75.345cm^{-1} for J=9/2 term respectively.

In conclusion, we analysed the fine structure of Sm^{3+} in BaS lattice by laser induced fluorescence. The splitting patterns obtained for Sm^{3+} energy levels in BaS lattice show the activator ions(Sm^{3+}) occupies Ba^{2+} substitutional sites. Calculated values of the crystal field parameters using the experimental data support this fact.

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