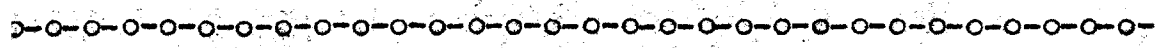


C H A P T E R - V

GENERAL DISCUSSION AND CONCLUSION

\*\*\*



## GENERAL DISCUSSION AND CONCLUSION

This chapter is devoted to the general discussion of the results obtained in the present investigation. Although some interpretations and inferences drawn from specific studies are described at the end of the preceding chapters, they are summarised and further discussed.

### 5-1 ABSORPTION CHARACTERISTICS:

#### A) Unfluxed & Fluxed Samples:

The absorption spectrum of undoped and unfluxed CaO found to exhibit a strong absorption band at about  $4000 \text{ \AA}^{\circ}$  alongwith weak bands at about  $4200 \text{ \AA}^{\circ}$ ,  $4400 \text{ \AA}^{\circ}$ ,  $4600 \text{ \AA}^{\circ}$ ,  $4800 \text{ \AA}^{\circ}$ ,  $5000 \text{ \AA}^{\circ}$ ,  $5400 \text{ \AA}^{\circ}$  and at  $5800 \text{ \AA}^{\circ}$  with decrease in absorption towards shorter wavelength side (below  $4000 \text{ \AA}^{\circ}$ ). Willi Lehmann (1) has reported a strong optical absorption at about  $6.5 \text{ eV}$  ( $= 191.2 \text{ nm}$ ) for purest CaO powder. Moreover, according to Willi Lehmann CaO phosphor cannot be excited optically across the band-gap using  $254 \text{ nm}$  ( $= 4.9 \text{ eV}$ ) radiations. The optical spectra in the present investigation has been studied in the wavelength range  $350 \text{ nm}$  ( $= 3.5 \text{ eV}$ ) to  $600 \text{ nm}$  ( $= 2.07 \text{ eV}$ ), the energy too small to excite the CaO across the band gap. Thus, absorption bands observed for unfluxed and undoped CaO could be attributed to the self activation of CaO, the lattice defects created during synthesis of phosphor at high temperature and/or to the presence of unknown impurities (2).

Addition of flux found to suppress the band at about 4000  $\text{\AA}^{\circ}$  with other bands remaining almost at the same wavelength and this suggests that incorporation of flux does not introduce new absorption centers but probably it causes for neutralization of the absorption centers responsible for 4000  $\text{\AA}^{\circ}$  band. Incorporation of flux in presence of either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  does cause for appearance and disappearance of some of the bands and to change amounts of absorption either towards shorter wavelength side or longer wavelength side, but observed effect is not systematic and significant. The observed effect might be due to the slight perturbations in peak positions and amounts of absorption within the limits of statistical variations.

B) CaO:Bi;Sm Phosphors (Fluxed):

Undoped CaO found to exhibit absorption bands at about 4200  $\text{\AA}^{\circ}$ , 4400  $\text{\AA}^{\circ}$ , 4600  $\text{\AA}^{\circ}$ , 4800  $\text{\AA}^{\circ}$ , 5000  $\text{\AA}^{\circ}$ , 5400  $\text{\AA}^{\circ}$  and at 5800  $\text{\AA}^{\circ}$ . Addition of activator  $\text{Bi}^{3+}$  does give rise to new absorption bands but the observed bands appear and disappear with an increase in  $\text{Bi}^{3+}$  concentration in an unsystematic manner. Moreover, higher concentration of  $\text{Bi}^{3+}$  found to increase the intensity of absorption bands in 3500  $\text{\AA}^{\circ}$  to 4500  $\text{\AA}^{\circ}$  wavelength range with the enhancement of absorption towards the longer wavelength side.

Incorporation and changing concentration of  $\text{Sm}^{3+}$  found to cause for appearance and disappearance of some of

the bands and also to change the band intensities, but the effect is unsystematic and small. Similar are the results obtained with addition of either  $\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  in the presence of each other.

Thus, it may be concluded that whatever effect has been observed with addition of activators  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  in peak positions, peak intensities, amounts of absorption either towards shorter wavelength side or longer wavelength side and also about the appearance and disappearance of some of the bands may be attributed to the slight perturbations in the peak positions and amounts of absorption within the limits of statistical variations, caused by activators.

#### 5-2 ORIGIN OF ABSORPTION BANDS & NATURE OF ABSORPTION CENTRES:

A comparison of absorption spectral results obtained for unfluxed and undoped CaO, fluxed CaO and for fluxed CaO:Bi:Sm samples reveal that whatever absorption bands observed for undoped and unfluxed CaO are seen to be almost for all other samples studied except the slight perturbation in peak positions, amounts of absorption and appearance and disappearance of some of the bands within the limits of statistical variations. Thus the observed absorptions bands is probably the property of defects present in host lattice and not that of flux or activator. The defects which are likely to be present in CaO lattice are  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  vacancies

or interstitials. To elucidate the nature of these defects EPR measurements have been carried out but as  $M_n^{2+}$  is found to be present invariably in all samples as a trace impurity, our efforts could not meet with success. The defects present in CaO lattice might be created during the synthesis of phosphor at high temperature and/or due to the presence of unknown trace impurity in ingredients.

5-3 EMISSION CHARACTERISTICS - Origin of Spectral Bands and Nature of Luminescence Centres:

A) Undoped & Unfluxed CaO:

It has been found that unfluxed and undoped CaO exhibits bands at about 4250  $\text{\AA}^{\circ}$  and at 5890  $\text{\AA}^{\circ}$ . The band at about 4450  $\text{\AA}^{\circ}$  is weaker while 5890  $\text{\AA}^{\circ}$  band is strong. The 5890  $\text{\AA}^{\circ}$  band is invariably observed for all samples and it has been attributed to  $M_n^{2+}$  impurity. The detailed discussion is left for the next section. The band at about 4250  $\text{\AA}^{\circ}$  might be due to self activation of CaO.

B) CaO (With Flux):

Addition of flux causes to give rise to additional band at about 5250  $\text{\AA}^{\circ}$  with other bands 4500  $\text{\AA}^{\circ}$  and 5890  $\text{\AA}^{\circ}$  remaining almost at same positions. The fluxes added are  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{Na}_2\text{SO}_4$  and NaF. We believe that out of  $\text{Na}^{1+}$ ,  $\text{SO}_2^{2-}$  and  $\text{F}^{1-}$  ions probably either  $\text{Na}^{1+}$  or  $\text{F}^{1-}$  ions are responsible for the 5250  $\text{\AA}^{\circ}$  band. However, as reported by

Shalgaonkar (2)  $\text{Na}^{1+}$  has closed shell structure and does not have any energy levels even with 10 eV of the ground state and as such the observed band will not be a characteristic property of  $\text{Na}^{1+}$  ion. Hence here we attribute the 4450  $\text{Å}^\circ$  band to the  $\text{F}^{1-}$  ion.

C) CaO:Bi (With Flux):

The emission spectra of CaO:Bi (fluxed) phosphors found to exhibit bands peaking at about 4250  $\text{Å}^\circ$ , 4500  $\text{Å}^\circ$ , 5250  $\text{Å}^\circ$  and 5890  $\text{Å}^\circ$ . The peak intensities of 5250  $\text{Å}^\circ$  and 5890  $\text{Å}^\circ$  are higher than the other ones.

The electron configuration of Bi atom is  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^{10}, 6s^2, 6p^3$  and the ground state of free ion is  $1s^0$ .  $\text{Bi}^{3+}$  enters in trivalent states losing  $6p^3$  electrons. The first excited state is due to  $6s, 6p$  electron configuration and that is P state.

According to L-S coupling scheme and Hunds rule the P state is further split into  $^3P_0, ^3P_1, ^3P_2$  and  $^1P_1$  (2). Transitions between these levels take place in accordance with the selection rule  $\Delta J = \pm 1$ . Consequently, the possible allowed transitions are  $^1P_1 \rightarrow ^1S_0$  and  $^3P_1 \rightarrow ^1S_0$  and the forbidden transitions are  $^3P_2 \rightarrow ^1S_0$  and  $^3P_0 \rightarrow ^1S_0$ .

The energy level diagram alongwith allowed and forbidden transition is shown in fig.5.1. The allowed transitions i.e.  $^1P_1 \rightarrow ^1S_0$  &  $^3P_1 \rightarrow ^1S_0$  should give emission at about 4470  $\text{Å}^\circ$  and 5120  $\text{Å}^\circ$  respectively (2,3). In fact such emissions have been

observed at about  $4500 \text{ \AA}^{\circ}$  and  $5250 \text{ \AA}^{\circ}$  for samples containing  $\text{Bi}^{3+}$  but these are found to overlap on the emission peaks corresponding to the fluxed CaO. The emission band found at about  $4250 \text{ \AA}^{\circ}$  may be due to a luminescence centre formed by  $\text{Bi}^{3+}$  impurity in co-operation with the other local defects.

D) CaO:Sm Phosphors (With Flux):

Incorporation and changing concentration of  $\text{Sm}^{3+}$  found to affect sensitively emission spectra. A new emission peak at about  $4250 \text{ \AA}^{\circ}$  has been observed and emission intensity continuously go on increasing towards the orange-red region with disappearance of peak at about  $5250 \text{ \AA}^{\circ}$ . Moreover, addition of  $\text{Sm}^{3+}$  found to cause decrease in intensity of a  $4500 \text{ \AA}^{\circ}$  peak.

Sm is one of the Lanthanide series of rare-earth elements having electron configuration  $(\text{Xe}) 4f^6, 5d^0, 6s^2$  and is characterised by unfilled 4f shell electrons shielded by  $5d^0, 6s^2$  electrons. The energy level diagram of  $\text{Sm}^{3+}$  ions in  $\text{LaCl}_3$  as given by G.F.Imbusch (4) is shown in fig.5.2. The transitions shown become allowed due to mixing a state when  $\text{Sm}^{3+}$  is incorporated in lattice. In fig.5.3 is shown the possible transitions of  $\text{Sm}^{3+}$  alongwith the emissions while energy term intervals between the six levels of the ground state are summarised in table 5.1. These results are reported by S.Makishima et.al (5) for  $\text{Sm}^{3+}$  in  $\text{BaTiO}_3$  matrix. From these results it is clear that

when  $\text{Sm}^{3+}$  is incorporated in any lattice it emit in orange-red region. Our results also show the similar emissions. However we could not attribute a particular emission to a specific transition because of limitations put by experimental procedure followed in recording the emission spectra.

E) Origin of 5890  $\text{A}^{\circ}$  Band:

The intense emission band around 5890  $\text{A}^{\circ}$  is found invariably for all samples. The same band was also observed by many workers in an undoped CaS and ZnS ( 2,6,7,8,9). At present there is great controversy regarding the origin of this band. Abhyankar (10) has reported this band in CaS:Ce phosphors to be due to  $\text{Na}^{1+}$  ions introduced through flux  $\text{Na}_2\text{SO}_4$ . Our samples also contain  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  and NaF as flux and hence it is tempting to attribute this band to  $\text{Na}^{1+}$  ions. But, as stated earlier Shalgaonkar has reported that  $\text{Na}^{1+}$  ion has closed shell structure and does not have any energy levels even within 1eV of the ground state and as such the observed band will not be the characteristic property of  $\text{Na}^{1+}$  ions. On the other hand Lalita et.al (11) reported that the deliberate addition of  $\text{M}_n^{2+}$  to CaS substitutes for  $\text{Ca}^{2+}$  to  $\text{M}_n^{2+}$  and gives rise to an emission band at about 5890  $\text{A}^{\circ}$ . Moreover, Lehmann (12) and Hadgal (9) have reported that an undoped CaS and ZnS contains  $\text{M}_n^{2+}$  as trace impurity and is responsible for emission at 5890  $\text{A}^{\circ}$ . Our EPR spectra of doped and undoped



CaO phosphors clearly show the presence of  $M_n^{2+}$  suggesting thereby the band at about  $5890 \text{ \AA}^0$  is a characteristic of  $M_n^{2+}$  impurity which might be present as a trace impurity in starting materials. This view is supported by the results of Shankar et.al (6) on CaS phosphors.

F) CaO:Bi:Sm Phosphors (With Flux):

When either  $Bi^{3+}$  or  $Sm^{3+}$  is added and varied in presence of each other both of them found to affect the emission spectra sensitively with giving their own characteristic emission.

5-4 MECHANISM OF ENERGY TRANSFER:

In luminescence transfer of energy from absorption centre to radiative center may take place either of one or more processes of the followings:-

- i) Cascade mechanism,
- ii) Resonance transfer,
- iii) Exciton migration, and;
- iv) Movement of charge carriers.

An insight into this can be had from absorption and emission spectra.

The measurements of emission spectra reveal that when activator  $Sm^{3+}$  is added to the host lattice, it absorbs the emission at about  $5250 \text{ \AA}^0$  and emit it as its own characteristic emission. These results thus implies that

the cascade mechanism of energy transfer is likely to be operative in CaO:Bi:Sm phosphors. Moreover, the transfer of energy with movement of charge carriers is also an expected process since, motion of electrons is involved during the excitation and emission processes. Here it should be mentioned that we could not draw any conclusion about the operativeness of resonance transfer and exciton migration mechanisms for the studies made in the present investigation.

#### 5-5 X-RAY DIFFRACTION STUDIES:

Lehmann (1) has reported that CaO crystallizes in the same cubic NaCl lattice as CaS. The x-ray diffraction pattern of CaO prepared by thermal reduction method in the present investigation shows a face centered cubic structure with lattice constant 'a' equal to  $8.71 \text{ \AA}$ . The analysis of XRD pattern obtained for fluxed CaO:Bi and CaO:Sm samples found to show the face centered cubic structure with shifting of peak positions towards the higher angle side and decrease in peak heights. The shifting of diffraction lines towards the higher angle side indicates the decrease of lattice constant 'a' with the addition of activators, while decrease in peak heights suggest the reduction in number of atoms in a plane. From the last result, the inference to be drawn is that  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  in CaO lattice probably take the  $\text{Ca}^{2+}$  sites. This is because  $\text{Sm}^{3+}$  and  $\text{Bi}^{3+}$  are trivalent and  $\text{Ca}^{2+}$  is divalent and as such the introduction of either

$\text{Bi}^{3+}$  or  $\text{Sm}^{3+}$  at lattice sites should result in reduction of number of atoms in a plane to maintain the neutrality of the crystal. Our results agree with the investigation of Willi Lehmann as CaO phosphors activated with  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  (1). The above conclusion is also supported by the ionic radii of  $\text{Ca}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$ . The ionic radii of  $\text{Ca}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  are  $0.99 \text{ \AA}$ ,  $0.99 \text{ \AA}$  and  $0.98 \text{ \AA}$  respectively. The difference in ionic radii is within 15 % and as such  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  can take easily the  $\text{Ca}^{2+}$  position at the lattice site.

#### 5-6 ELECTRON PARAMAGNETIC RESONANCE STUDIES:

The EPR measurement of prepared samples are carried out with a view to gain the information about the defect structure responsible for luminescence properties. However, in all samples studied the characteristic  $\text{Mn}^{55}$  spectrum is observed. We have not added  $\text{Mn}^{2+}$  as an activator but it might be present as a trace impurity and might have introduced through the starting material  $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ . Such EPR spectrum of  $\text{Mn}^{2+}$  as a trace impurity was observed by Shankar et.al (6) in CaS phosphors and by Hadgal (9) in  $(\text{Zn,Ca})\text{S}:\text{Bi}:\text{Dy}$  phosphors.

The EPR measurements of samples containing  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  were carried out but no signal corresponding to  $\text{Bi}^{3+}$  and/or  $\text{Sm}^{3+}$  is observed. This is since  $\text{Mn}^{2+}$  is very sensitive to EPR measurements and other impurities in its presence cannot

be detected. Same reasoning applies to the self activated and other defect centers present in CaO lattice.

Addition and change in percentage of  $\text{Sm}^{3+}$  found to change the crystal field surrounding the  $\text{Mn}^{2+}$  ion and to suppress the allowed and forbidden transitions except the transition corresponding to  $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$ . Thus indicating thereby probability of formation of the bonding of Sm atoms with the host lattice (9). No such results have been observed for  $\text{Bi}^{3+}$ . The spin Hamiltonian parameter of Mn has been calculated and it is found to be in good agreement with the results of other workers (9,13,14). The calculated value of 'g' varies between 1.99921 to 2.00277 but the observed variation is unsystematic and insignificant.

#### 5-7 CONCLUSIONS:

The principal findings of the present investigation may be summarised as follows -

- 1) The observed absorption bands is likely to be the property of host lattice defects. These defects are probably the  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  vacancies or interstitials created during the synthesis of phosphor at high temperature.
- 2) Whatever effect has been observed with addition of flux and activators ( $\text{Bi}^{3+}$ ,  $\text{Sm}^{3+}$ ) in peak positions, amounts of absorption and about the appearance and

disappearance of some of the bands may be due to the slight perturbation in the peak positions and amounts of absorption within the limits of statistical variation, caused by the flux and activators.

3) Addition of flux introduces a luminescence centre into the host lattice corresponding to a emission at about  $5250 \text{ \AA}^{\circ}$ . The defect could be attributed to the presence of  $F^{1-}$  ions in host lattice.

4) Spectral distribution of emitted radiation is significantly affected by the addition and change in percentage of  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$ .

5) Addition of  $\text{Bi}^{3+}$  introduces luminescence centres which give their own characteristic emission.

6) Addition of  $\text{Sm}^{3+}$  introduces luminescence centres which give their own characteristic emission.

7)  $\text{Bi}^{3+}$  and  $\text{Sm}^{3+}$  probably take the lattice site positions by replacing  $\text{Ca}^{2+}$  ions.

8) The band at about  $5890 \text{ \AA}^{\circ}$  is due to the  $\text{Mn}^{2+}$  trace impurity.

9) The prepared  $\text{CaO}:\text{Bi}:\text{Sm}$  phosphors crystallize in face centered cubic lattice with lattice constant  $a = 8.71 \text{ \AA}^{\circ}$ .

10) EPR measurements reveal the presence of  $\text{Mn}^{2+}$  as trace impurity.

- 11) There is no significant change in 'g' values.
- 12) A change in crystal field symmetry around the  $Mn^{2+}$  ions with change in percentage of  $Sm^{3+}$  points the formation of bendings of  $Sm^{3+}$  with the lattice.
- 13) The processes which are likely to be involved in transfer of energy from absorption centers to the emission centers are cascade mechanism and movement of charge carriers. Moreover, presence of resonance transfer and exciton migration are also possible mechanisms but it is not possible to draw any such conclusion from the present experimental investigation.
- 14) CaO is versatile as a phosphor host.

Table 5-1

Kind of $\text{Sm}^{3+}$ Interval	$\text{Sm}^{3+}$ at $\text{Ti}^{4+}$ sites		$\text{Sm}^{3+}$ in $\text{BaTiO}_3$ $\text{Sm}^{3+}$ at $\text{Ba}^{2+}$ sites		Expected ratio from a theory on the break- down of Russel-Saunders coupling for free $\text{Sm}^{3+}$
	$\text{cm}^{-1}$	ratio	$\text{cm}^{-1}$	ratio	
Energy Term					
${}^6H_{5/2}$ — ${}^6H_{7/2}$	1101	7	991	7	7
${}^6H_{7/2}$ — ${}^6H_{9/2}$	1431	9.1	1160	8.2	8.5
${}^6H_{9/2}$ — ${}^6H_{11/2}$	1531	9.8	1293	9.1	9.5
${}^6H_{11/2}$ — ${}^6H_{13/2}$	—	—	1332	9.5	10.1
${}^6H_{13/2}$ — ${}^6H_{15/2}$	—	—	—	—	10.1

Energy term intervals between the six levels of the ground state of  $\text{Sm}^{3+}$ .

REFERENCES

1. Lehmann, W.J. *Luminescence*, 6, (1973), 455-470.
2. Shalgaonkar, C.S., Ph.D. Thesis, Shivaji University, Kolhapur (1975).
3. Uehara, Y., *J. Chem. Phys.*, 50, 961 (1969).
4. Imbusch, G.F. " *Luminescence Spectroscopy* " Edited by Michael D. Lumb, pp. 21 (1978).
5. Makishima, S., et. al " *Luminescence of Organic and Inorganic Materials*", Edited by Hartmut P. Kallmann Graefe Marmor Spruch (1962).
6. Shankar, V., et al. *Indian J. Pure Appl. Phys.*, 14, 193 (1976).
7. Patil, M.G., Ph.D. Thesis, Shivaji University, Kolhapur (1981).
8. Ghosh, F.K. and Shankar, V., *Indian J. Phys.* 53A, 203 (1978).
9. Hadgal, R.R., Ph.D. Thesis, Shivaji University, Kolhapur (1982).
10. Abhyankar, M.D., Ph.D. Thesis, Saugar University, Sagar (1968).
11. Lalita, P.R. et. al, *Curr. Sci.*, 48, 719 (1979).
- 12) Lehmann, W., *J. Luminescence*, 20 95 (1979).



- 13) Awate, A.V., Ph.D. Thesis, Shivaji University, Kolhapur, (1975).
- 14) Ekbote, S.N. and Ranade, J.D., Indian J. Phys., 46, 529 (1972).

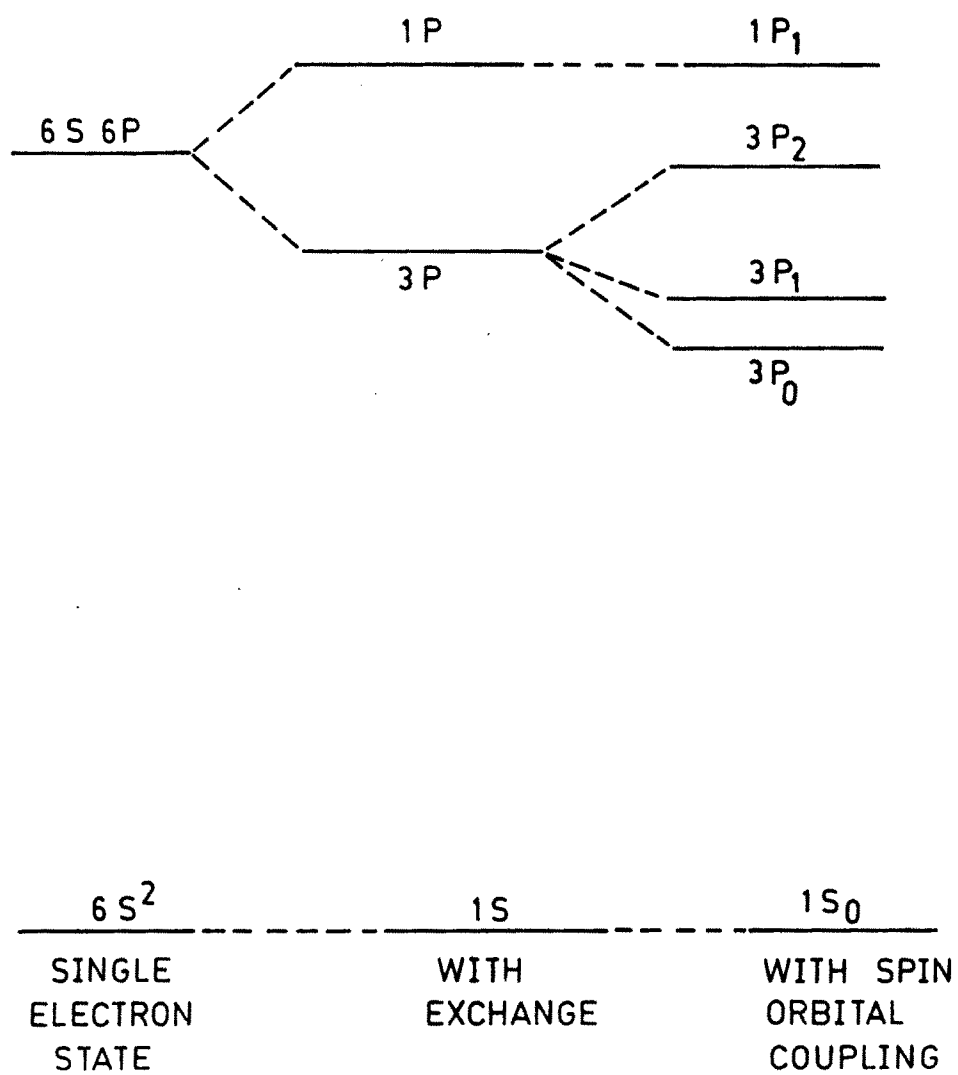


FIG. 5.1: ENERGY LEVELS OF THE FREE  $\text{Bi}^{3+}$  ION

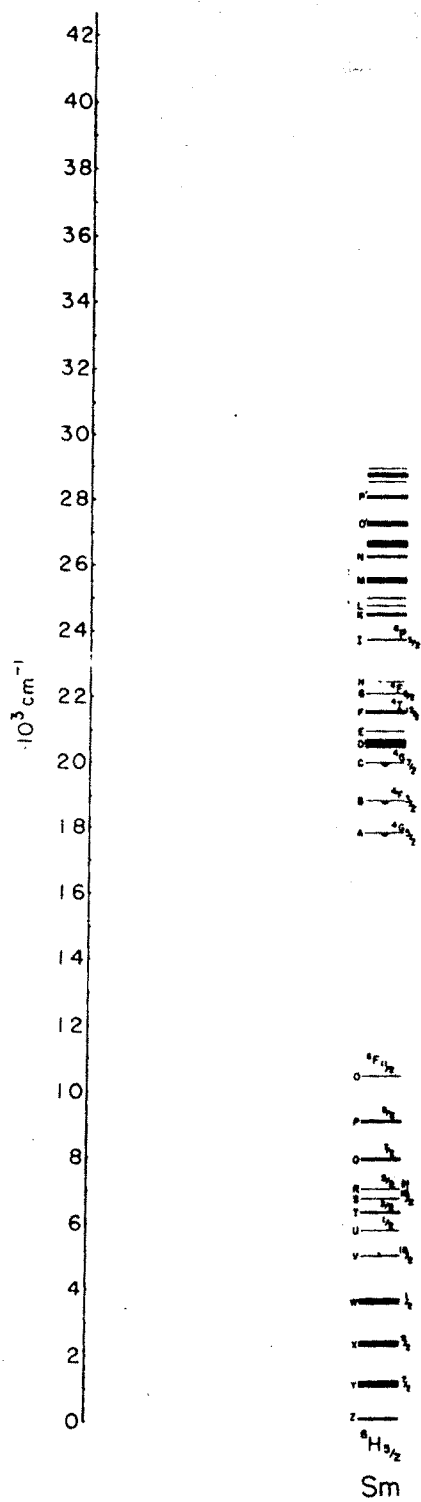


Fig. 5.2: Energy level diagram of  $\text{Sm}^{3+}$  ions in  $\text{LaCl}_3$ .

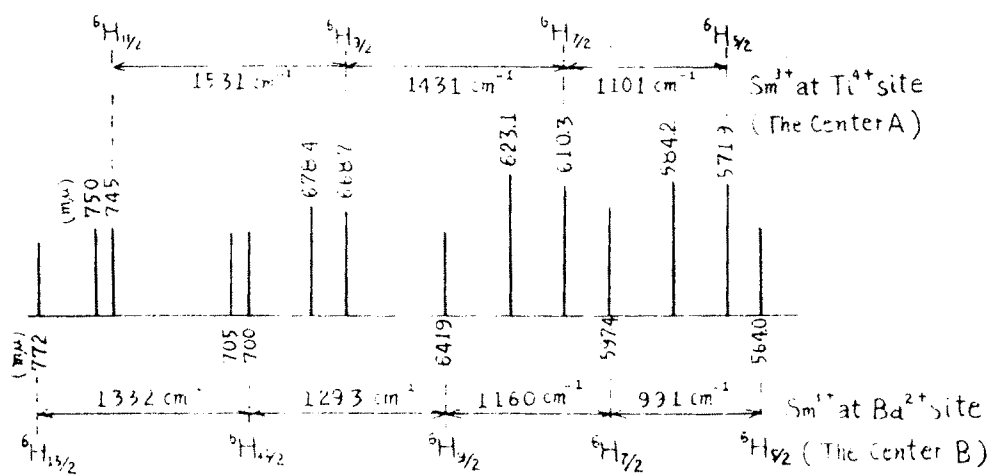


Fig. 5.3 Diagram of the emission spectrum of  $\text{Sm}^{3+}$  in a  $\text{BaTiO}_3$  matrix at  $-196^\circ\text{C}$ .