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Optical properties of praseodymium(III) in fluoroborate glasses

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Abstract : Optical absorption spectra of Pr^{3+} in certain fluoroborate glasses containing 1 mol % of Pr^{3+} as dopant are studied. Optical absorption spectra from both UV-VIS and NIR have been recorded and different energy levels have been identified. Using Judd Ofelt theory, the spectral intensities have been calculated and compared with theoretical values Radiative transition probabilities, lifetimes and branching ratios are reported for certain excited levels of Pr^{3+} in fluoroborate glasses The measured fluorescence levels have been characterized by determining their stimulated absorption cross sections

Keywords : Fluoroborate glasses, optical absorption spectra, radiative lifetimes

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1. Introduction

Heavy metal borate glasses have received great attention because of their potential applications and their importance in basic research view point. Rare earth ions can be easily incorporated into their borate glasses and a considerable research work has been done in the last few years. The studies of sensitizing Pr^{3+} ions by Tm^{3+} ions in phosphate glasses were reported by Joshi and Joshi [1]. Optical transitions of Pr^{3+} ions in fluorozirconate glass were studied by Adam and Sibley [2]. Previously, we have reported the optical absorption spectra and radiative intensities of Pr^{3+} ion in sulphate glasses [3]. Now, we are presenting certain physical and optical properties of Pr^{3+} doped fluoroborate glasses.

2. Experimental

The glasses of the following compositions were prepared by using standard quenching technique.

Glass A : $80B_2O_3 + 10Na_2O + 9LiF_2 + 1PrF_3$

Glass B : $80B_2O_3 + 10Na_2O + 9KF + 1PrF_3$

Glass C : $80B_2O_3 + 10Na_2O + 9ZnF_2 + 1PrF_3$

Glass D : $80B_2O_3 + 10Na_2O + 9BaF_2 + 1PrF_3$

Different proportions of various fluorides and borates are mixed and melted at 1000°C in an electrical furnace. The method of preparation of these fluoroborate glasses is similar to that given in earlier paper [4]. The densities of these glasses have been measured at room temperature with xylene as the immersion liquid. The refractive indices have been measured on a standard refractometer at $\lambda = 589.3$ nm. With these two measured physical quantities, a few other physical parameters have been determined using relevant expressions reported earlier [5]. Table 1 gives some of the physical properties of Pr^{3+} doped fluoroborate glasses.

Table 1. Various physical properties of Pr^{3+} in fluoroborate glasses.

Property	Glass A	Glass B	Glass C	Glass D
Average molecular weight M (gm)	64.37	67.27	71.34	77.82
Density d (gm cm^{-3})	2.683	2.356	2.126	2.892
Refractive index n_d	1.501	1.498	1.508	1.493
Molar refractivity R_M (cm^{-3})	7 069	8.326	10.008	7 820
Mean atomic volume V (g cm^{-3} atom^{-1})	3.55	4.28	4.96	3.95
Dielectric constant	2.253	2 244	2.274	2.229
Electronic polarizability (× 10^{+24} cm^3)	2.800	3.316	3.964	3.095
Pr^{3+} ion concentration N (× 10^{-22} ions cm^3)	2 511	2.110	1.795	2.239
Polaron radius r_p (Å)	1.376	1.458	1.539	1 430
Field strength (× 10^{-16} cm^2)	1.584	1.411	1.266	1.467
Reflection losses R (%)	4.012	3.974	4.102	3.910

The spectra were recorded in the UV-VIS and NIR regions on Hitachi U-3400 UV-VIS-NIR spectrophotometer. Figures 1 and 2 show the spectra of Pr^{3+} ion in Glass B. The spectra of the other glasses are not shown to save space. The band maxima could be measured accurately to 1 Å at 5000 Å and at 2 Å at 16660 Å. The wavelengths of the bands were converted into vacuum wavenumbers using NBS wavenumber tables [6].

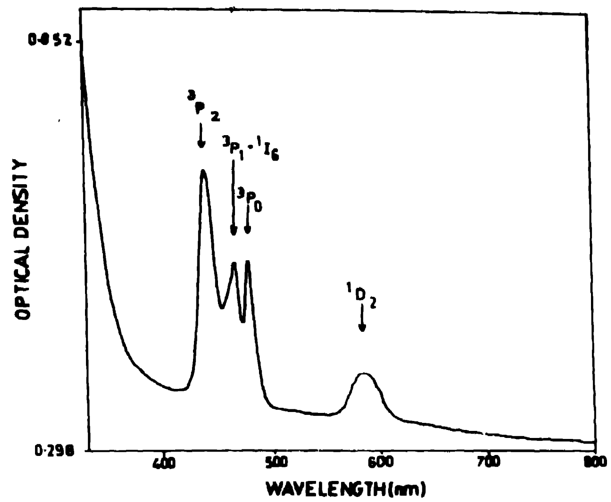

Figure 1. Absorption spectrum of Pr^{3+} in glass B (UV-VIS).

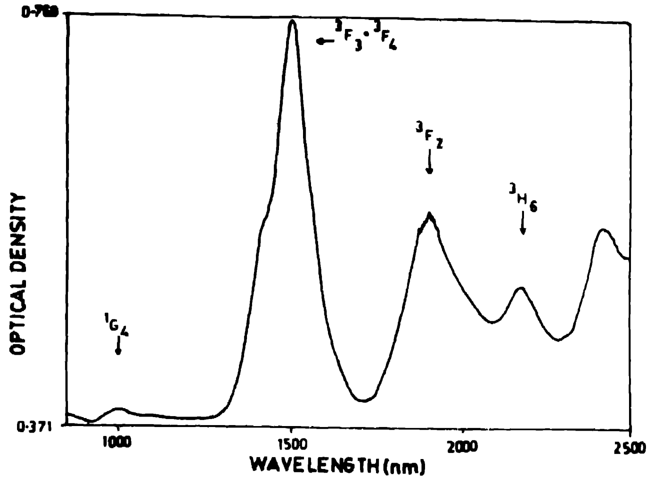

Figure 2. Absorption spectrum of Pr^{3+} in glass B (NIR).

3. Results and discussion

From the recorded optical absorption spectrum the evaluated Racah (E^1, E^2, E^3), spin-orbit (ξ_{4f}) and bonding (δ) parameters are presented in Table 2 for all the four glasses. It is observed that the bonding parameter is negative for all the four glasses.

The oscillator strengths of the absorption bands are measured using the following relation [7],

$$f_{\text{meas}} = 4.32 \times 10^{-9} \int \epsilon(\nu)\, d\nu,$$

where $\epsilon(\nu)$ is the molar extinction coefficient at the wave number ν (cm^{-1}). According to Judd-Ofelt theory [8,9]

$$f_{\mathrm{cal}} = \frac{\upsilon}{2J+1} \cdot \frac{8\pi^2 mc}{3h} \cdot \frac{(n^2+2)^2}{9n} \times \sum_{\lambda=2,4,6} \Omega_\lambda \left\langle \psi J \left\| U^\lambda \right\| \psi^1 J^1 \right\rangle^2 ,$$

where υ is the mean energy of the transition $\psi J \rightarrow \psi^1 J^1$. The matrix elements $\left\| U^\lambda \right\|$ have been evaluated for intermediate coupling [7]. The squared reduced matrix elements $\left\| U^\lambda \right\|^2$ are affected very small by changing the host material, so we have used the squared reduced matrix elements given in ref [10] for sulphate glasses. The measured and calculated oscillator strengths are listed in Table 3 for all the four glasses. Because of the band overlap, $^3F_3$ with $^3F_4$ and $^3P_1$ with $^1I_6$, the absorption bands were treated as two single bands and the matrix elements corresponding to the two transitions were combined and treated as single experimental point as has been done by Adam and Sibley [2].

Table 2. Racah (E^1, E^2, E^3) spin orbit (ξ_{4f}) and bonding (δ) parameters of Pr^{3+} in fluoroborate glasses

Parameter	Glass A	Glass B	Glass C	Glass D
E^1 (cm^{-1})	4748	4762	4751	4827
E^2 (cm^{-1})	20.45	20.79	20.69	20.62
E^3 (cm^{-1})	454.7	457.8	454.2	454.9
ξ_{4f} (cm^{-1})	814.22	818.6	809.7	801.1
δ	−0.63	−1.28	−0.69	−0.47

Table 3. Observed and calculated oscillator strengths ($f \times 10^6$) and Judd-Ofelt intensity parameters ($\Omega_\lambda \times 10^{20}$ (cm^2)) of Pr^{3+} ion in fluoroborate glasses

$S^1L^1J^1$	Glass A		Glass B		Glass C		Glass D	
	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^3H_6$	–	–	0.84	0.63	0.05	0.12	–	–
$^3F_2$	0.54	0.54	3.40	3.36	1.01	0.99	0.93	0.93
$^3F_3 + {}^3F_4$	1.99	2.01	8.61	8.97	3.28	3.39	3.64	3.70
$^1D_2$	0.26	0.22	3.08	0.98	0.83	0.37	0.63	0.41
$^3P_0$	0.54	0.52	4.08	4.84	1.85	2.00	1.23	1.63
$^3P_1 + {}^1I_6$	0.81	0.81	7.59	6.82	2.94	2.78	2.70	2.32
$^3P_2$	1.39	0.62	12.53	3.21	4.25	1.22	3.03	1.35
RMS deviation		+0.44		+5.55		+1.54		+1.11
Ω_2		0.24		0.17		−0.80		−0.55
Ω_4		0.91		8.41		3.45		2.80
Ω_6		1.26		4.23		1.55		1.99

Substituting f_{meas} for f_{cal} and using $\|U^{\lambda}\|^2$ values, Ω_λ parameters have been evaluated by the least squares method. These intensity parameters are also presented in Table 3. The quality of the fit can be expressed by root mean square (rms) deviation. The intensities of the bands of glass B are larger than those for other glasses, the asymmetric component of electric field acting on Pr^{3+} ion is greater in this glass. The Ω_2 parameter is very small for all the glasses, even negative for the glasses C and D. From the above data, it is concluded that the Judd-Ofelt treatment for Pr^{3+} transitions has resulted in poor agreement with experimental values as stated by Reisfeld and Jorgensen [11].

Electric (S_{ed}) and magnetic (S_{md}) dipole line strengths are calculated using the above intensity parameters and squared reduced matrix elements from the formula given in ref [12]. The radiative transition probability (A), for a transition is given by

$$A\left(\psi J, \psi^1 J^1\right) = \frac{64\,\pi^4 \nu^3}{3h\,(2J+1)} \times \left[\frac{n(n^2+2)^2}{9}\, S_{\mathrm{ed}} + n^3 S_{\mathrm{md}}\right],$$

here n is refractive index.

The total radiative relaxation rate (A_T) is

$$A_T(\psi J) = \sum_{\psi^1 J^1} A\,(\Psi J, \psi^1 J^1),$$

where the sum runs over all $\psi^1 J^1$ lower in the energy than ψJ.

The radiative lifetime T_R of a state is obtained from

$$T_R(\psi J) = \left[A_T(\psi J)\right]^{-1}.$$

Predicted total radiative relaxation rates (A_T) and radiative lifetimes (T_R) for the excited states $^3P_0$, $^3P_1$, $^1D_2$ and $^3F_3$ of Pr^{3+} ion in all the four fluoroborate glasses are presented in Table 4. It is observed that glass A is having highest lifetime values for all the fluorescent levels where as the glass B has lowest. The radiative lifetimes of $^3P_0$ and $^3P_1$ levels are nearly equal in each of the glasses and they are very small in comparison either with the $^1D_2$ or $^3F_3$ levels.

Table 4 Total radiative transition probabilities (A_T) and radiative lifetimes (T_R) (μs) for the excited states $^3P_0$, $^3P_1$, $^1D_2$ and $^3F_3$ of Pr^{3+} ion in fluoroborate glasses

State	Glass A		Glass B		Glass C		Glass D	
	A_T	T_R	A_T	T_R	A_T	T_R	A_T	T_R
$^3P_0$	5119	195	36583	27	12778	78	10927	91
$^3P_1$	5146	194	37967	26	15550	64	11094	90
$^1D_2$	404	2474	2138	467	575	1739	597	1678
$^3F_3$	107	9306	557	1794	201	4975	196	5083

Branching ratios (β) and integrated absorption cross sections (Σ) are compared for all the glasses in Table 5.

Table 5. Predicted branching ratios (β) and integrated absorption cross sections (Σ (cm^{-1})) for the excited states $^3P_0$, $^1D_2$ and $^3F_3$ of Pr^{3+} ion in fluoroborate glasses.

Transition	Glass A		Glass B		Glass C		Glass D	
	β_{ij}	$\Sigma\,(10^{-18})$	β_{ij}	$\Sigma\,(10^{-18})$	β_{ij}	$\Sigma\,(10^{-18})$	β_{ij}	$\Sigma\,(10^{-18})$
$^3P_0 \rightarrow {}^1D_2$	0	0	0	0.01	0	0.06	0	0.04
$^1G_4$	0.02	0.06	0.03	5.90	0.03	2.42	0.03	1.94
$^3F_4$	0.11	1.77	0.14	16.47	0.14	6.75	0.15	5.42
$^3F_3$	0	0	0	0	0	0	0	0
$^3F_2$	0.12	1.42	0.01	1.04	0.13	4.83	0.12	3.30
$^3H_6$	0.16	1.88	0.07	6.35	0.91	32.19	0.11	2.96
$^3H_5$	0	0	0	0	0	0	0	0
$^3H_4$	0.59	4.17	0.74	38.56	0.05	1.49	0.82	12.73
$^1D_2 \rightarrow {}^1G_4$	0.06	0.37	0.05	1.38	0.01	0.07	0.02	0.20
$^3F_4$	0.17	0.41	0.04	0.47	0.33	1.12	0.20	0.72
$^3F_3$	0.04	0.08	0.04	0.46	0.04	0.12	0.03	0.11
$^3F_2$	0.16	0.26	0.26	2.23	0.39	0.89	0.30	0.72
$^3H_6$	0.14	0.22	0.23	1.93	0.36	0.79	0.29	0.66
$^3H_5$	0	0	0.01	0.08	0.02	0.03	0.02	0.03
$^3H_4$	0.42	0.35	0.36	1.56	0.51	0.59	0.52	0.64
$^3F_3 \rightarrow {}^3F_2$	0.01	0.09	0.01	0.19	0.01	0.12	0.01	0.11
$^3H_6$	0.02	0.42	0.02	1.96	0.02	0.76	0.02	0.82
$^3H_5$	0.09	0.35	0.18	2.26	0.07	0.52	0.06	0.46
$^3H_4$	0.88	1.37	0.86	6.89	0.90	2.62	0.91	2.65

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References

[1] B C Joshi and M C Joshi *J. Non-Cryst. Solids.* **142** 171 (1992)

[2] J L Adam and W A Sibley *J. Non-Cryst. Solids.* **76** 267 (1985)

[3] S V J Lakshman and Y C Ratnakaram *J Non-cryst. Solids.* **101** 75 (1987)

[4] S V J Lakshman and Y C Ratnakaram *Phys. Chem. Glasses* **29** No. 1 (1988)

[5] S Buddhudu and F J Bryant *Spectrochem. Acta* **44A** 1381 (1988)

[6] C D Coleman, W R Bozman and W F Maggers *Table of Wavenumbers* (NBS Monograph, USA) Vol. 3 (1960)

[7] W T Carnall *Hand book on the Physics and Chemistry of Rare Earths* eds. K A Gschneidner (Jr) and L Eyring (Amsterdam : North Holland) (1979)

[8] B R Judd *Phys. Rev.* **127** 750 (1962)

[9] G S Ofelt *J. Chem. Phys.* **37** 511 (1962)

[10] Y C Ratnakaram *PhD Thesis* (S V University, Tirupati, India) (1987)

[11] R Reisfeld and C K Jorgensen *Lasers and Excited States of Rare Earths* (Berlin : Springer-Verlag) p 142 (1977)

[12] R Cases and M A Chamrro *J. Solid State Chem.* **90** 313 (1991)