

Praseodymium Ion Doped Sodium Borosilicate Glasses: Energy Interaction and Radiative Properties

Y. K. Sharma*, R. K. Singh, Sudha Pal

Department of Physics, S.B.S. Govt. Post Graduate College, Rudrapur, India

Abstract Sodium borosilicate glasses of the final composition (in wt.%) 68.94 SiO₂ -22.55 Na₂O- 1.91 CaO -4.96 K₂O – 0.85 B₂O₃ -0.29 As₂O₃- x Pr₆O₁₁ (where x = 0.1,0.3 and 0.5) have been prepared by melt quenching technique. The absorption and fluorescence spectra have been recorded at room temperature. Energy interaction parameters i.e. Slater-Condon, Racah, Nephelauxetic ratio (β') and bonding parameters ($b^{1/2}$) have been computed from observed energy band to study the nature of bonding in doped glasses. The intensities of the $4f \leftrightarrow 4f$ transitions in the absorption spectra have been analyzed by the Judd-Ofelt theory. Using the fluorescence data and JO parameters, various radiative properties for different emission lines have been computed. The values of A, β and σ_p for $^3P_0 \rightarrow ^3H_4$ and $^3P_0 \rightarrow ^3F_2$ transition are maximum, suggesting that they can be used as a most probable laser transitions. The values of σ_p for the transition $^3P_0 \rightarrow ^3F_2$ is high due to the presence of As₂O₃ in glass.

Keywords Sodium borosilicate glass, Absorption spectrum, Fluorescence Spectrum, Energy Parameters, Judd-Ofelt Parameters and Radiative Properties

1. Introduction

Spectral studies of rare-earth ions in glass systems are of considerable interest [1] due to their potential applications in lasing materials, fiber optics materials and wavelength converting devices. The laser potential can be evaluated from small sample by obtaining related information, such as covalence of doped ions, radiative and non-radiative properties, branching ratios and stimulated emission cross section. It is possible to improve the laser transitions of the ionic level by the proper choice of the host materials. In recent years [2], much attention has been focused on the search for new rare earth doped materials to be used as hosts for optical devices. Rare earth doped heavy metal fluoride glasses are transparent from ultraviolet to the infrared region. They can be easily prepared and a range of concentration of transition metal and rare earth ions can be incorporated into the glass. Fluoride [3-5] glasses have smaller multiphonon emission rates and are chemically stable. They are also stable against atmospheric moisture [4, 6-8]. Praseodymium ion is considered to be serious contender for laser applications due to its large number of available transitions in the UV, visible and NIR regions. Laser action in praseodymium doped crystalline hosts has been demonstrated [9, 10].

In this paper, a new kind of praseodymium doped sodium

borosilicate glasses has been prepared. The spectral analysis of praseodymium doped sodium borosilicate glasses has been investigated. From the observed absorption band Slater-Condon, Racah, nephelauxetic ratio and bonding parameters have been computed to study the nature of bonding in doped glasses. Judd-Ofelt theory has been applied for the $f \leftrightarrow f$ transitions of praseodymium ions to evaluate Judd – Ofelt intensity parameters, Ω_λ ($\lambda = 2,4,6$), which in turn have been used to calculate various radiative properties like, spontaneous transition probability (A), fluorescence branching ratio (β), radiative life time (τ) of various excited states and stimulated emission cross - section (σ_p) of various emission lines.

2. Experimental Procedure

Sodium borosilicate glasses of the final composition (in wt.%) 68.94 SiO₂-22.55 Na₂O - 1.91 CaO - 4.96 K₂O – 0.85 B₂O₃ - 0.29 As₂O₃ - x Pr₆O₁₁ (where x = 0.1,0.3 and 0.5) have been prepared by the melt quenching technique [11] from reagents of analytical grade in 10 g batches. The rare-earth oxides (99.99% pure) were obtained from the Indian Rare Earth Ltd. Batches containing 0.0, 0.1, 0.3 and 0.5 mol.% of Pr³⁺ in the base glass materials were mixed in an agate pestle mortar for two hours and were thermally treated for 6 h in an alumina crucible up to 950±25°C. Homogeneity of the melt was ensured by stirring the melt with an alumina rod from time to time. The melt was quenched by pouring it into a rectangular shaped brass mould placed on a pre heated (200°C) heavy copper plate. The glass specimens so

* Corresponding author:

dryksharma@yahoo.com (Y. K. Sharma)

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prepared were taken away after 24 h and annealed for three hours at 300°C so as to remove stresses and to give them thermal stability and strength. Samples of the size 15 x 10 x 1.5 mm³ were cut and polished on all sides to make the faces flat and parallel. The initial and final polishing of the samples was done with the help of fine powder of cerium oxide. These samples were again annealed at 250°C for further removing mechanical stresses developed during polishing. The glass samples so prepared were of good optical quality and were transparent. X-ray diffractogram of the glass sample was studied with “RIGAKU X-ray diffractometer Geigerflex D/max-B” system. The X-ray diffractogram showed no prominent peaks indicating the absence of a crystalline phase (Fig.1).

The absorption spectra have been recorded in terms of

relative absorption (I_o/I) vs wavelength (nm), where I_o is the intensity of the radiation transmitted through the undoped glass specimen and I is the intensity of the radiation transmitted through the doped glass specimen of the same thickness.

The density ‘ ρ ’ of the glass samples were determined by Archimedeś displacement method, using xylene as the immersion liquid and sensitive ADAIR DUTT analytical microprocessor based electronic single pan digital top loading balance ‘Model AD – 180’. The refractive index of glass specimens were measured on an Abbé refractometer (ATAGO3T). An ordinary lamp was used as the light source. The path length was measured to the nearest of 0.01cm with the help of a micrometer.

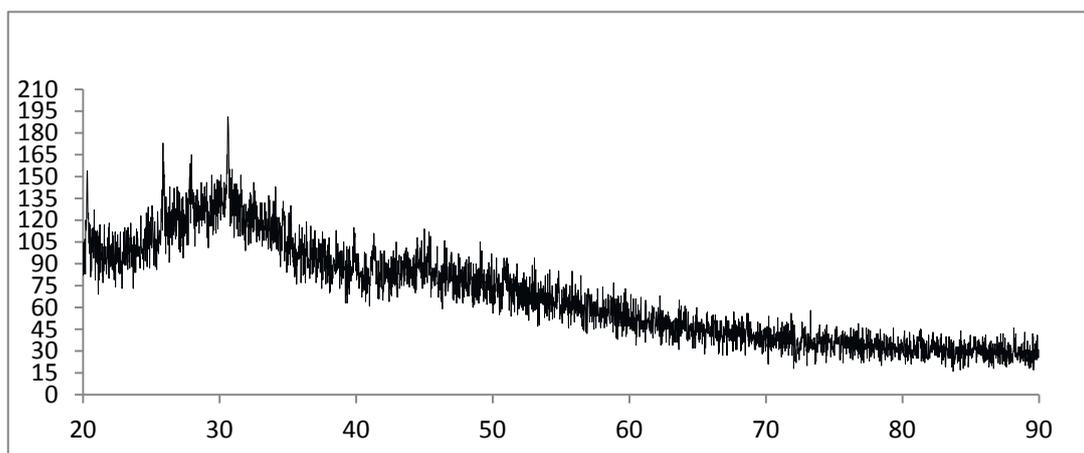


Figure 1. XRD of sodium borosilicate glass specimen

3. Results and Discussion

Physical Properties:

Various physical properties of praseodymium doped sodium borosilicate glasses for different concentration were measured and collected in table 1. Density and average molecular weight increases with increasing concentration of praseodymium ion. The relation of Refractive index, Dielectric constant, Optical dielectric constant and Reflection losses for different concentration of praseodymium ion is 0.1 wt.% = 0.5 wt.% < 0.3 wt.% in Table 1.

Table 1. Physical properties of Praseodymium doped sodium borosilicate glasses for different concentration

Physical Properties	0.1 wt%	0.3% wt%	0.5% wt%
Refractive (Pr) index	1.68	1.681	1.68
Density	4.437	4.854	5.107
Thickness	0.343	0.354	0.34
Average Molecular Weight.	63.323	65.365	67.407
Dielectric Constant	2.822	2.826	2.822
Optical Dielectric Constant	1.822	1.826	1.822
Molar Volume Vm(g/cm ³)	14.271	13.466	13.199
Molar refractivity	5.392	5.095	4.987
Reflection Losses	6.04	6.43	6.04

Absorption Spectra:

The spectral measurements were carried out by spectrophotometer method. The absorption spectra in spectral range 300-900 nm were recorded on UV-visible double beam spectrophotometer Model-220 and in spectral range 1000-2200nm were recorded on Hitachi absorption spectrophotometer model F-330. The absorption spectrum of Pr^{3+} doped sodium borosilicate glass in the spectral range 350-2200 nm has been shown in Fig 2. The absorption bands, on the basis of energy separation of energy levels of Pr^{3+} free ion and the observed intensity of the bands, have been assigned to transitions from ground state $^3\text{H}_4$ to different energy levels. Eight absorption bands have been observed from the ground state $^3\text{H}_4$ to excited states $^3\text{F}_2$, $^3\text{F}_3$, $^3\text{F}_4$, $^1\text{G}_4$, $^1\text{D}_2$, $^3\text{P}_0$, $^3\text{P}_1$ and $^3\text{P}_2$ in sodium borosilicate glass. The band positions agree with previous reported data on Pr^{3+} ion in

other glass systems [12]. From the observed absorption band various energy parameters have been computed.

Energy Interaction Parameters:

Wong [13, 14] suggested that the energy, E_j , having particular value of the interaction parameter F_k and ζ_{4f} can be expanded as a Taylor series expansion for a small variation of the energies. In the first order approximation the energy E_j of the j^{th} level is given [13, 14] by

$$E_j (F_k, \zeta_{4f}) = E_{0j} (F_k^0, \zeta_{4f}^0) + \sum_{k=2,4,6} \frac{\partial E_j}{\partial F_k} \Delta F_k + \frac{\partial E_j}{\partial \zeta_{4f}} \Delta \zeta_{4f} \quad (1)$$

where E_{0j} is the zero order energy of j^{th} level.

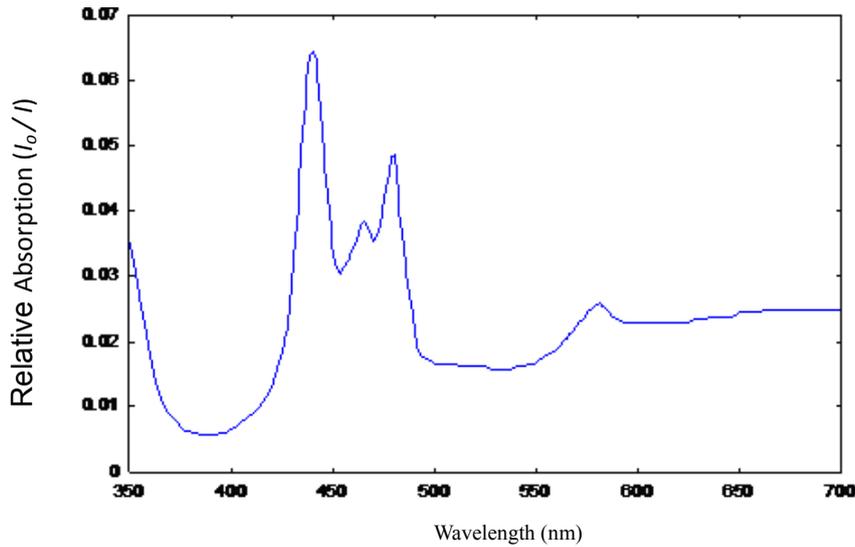


Figure 2(a). Absorption spectrum of Pr^{3+} (0.5wt%) doped sodium borosilicate glass in the range 350 to 700nm

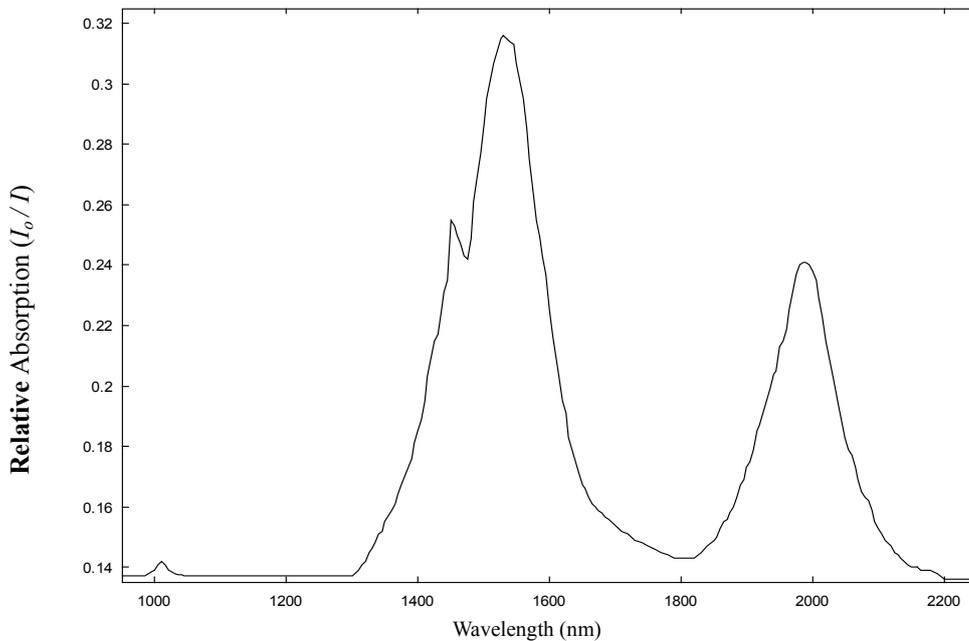


Figure 2(b). Absorption spectrum of Pr^{3+} (0.5 wt%) doped sodium borosilicate glass in the range 1000 to 2200nm at room temperature

Table 2. Experimental and calculated energy, zero order energies and partial derivatives of the energy levels with respect to F_k and ζ_{4f} parameters for Pr^{3+} ion [25]

Bands	E_{0j} (cm ⁻¹)	$\partial E_j / \partial F_2$	$\partial E_j / \partial F_4$	$\partial E_j / \partial F_6$	$\partial E_j / \partial \zeta_{4f}$	E_{exp} (cm ⁻¹)	E_{cal} (cm ⁻¹)
³ F ₂	4757	15.40	13.64	-249	0.909	4830	4841.29
³ F ₃	6102	15.00	14.65	-274	2.983	6353	6195.92
³ F ₄	6784	10.24	43.97	-188	3.146	6898	6854.37
¹ G ₄	10009	0.04	112.10	-4	5.792	9900	10041.85
¹ D ₂	16972	45.97	-37.63	510	2.906	17164	17224.70
³ P ₀	20412	70.17	81.81	-1253	1.905	20824	20783.47
³ P ₁	20990	70.07	80.66	-1278	3.974	21231	21372.62
³ P ₂	22220	67.56	68.42	-1077	5.029	22624	22595.66

The values of zero order energy (E_{0j}) and partial derivatives $\partial E_j / \partial F_k$ and $\partial E_j / \partial \zeta_{4f}$ for the observed levels of Pr^{3+} calculated by Wong [13, 14] and collected in Table 2. The values of ΔF_k and $\Delta \zeta_{4f}$ have been computed using Eq.1 by partial regression method. The values of F_k and ζ_{4f} are then evaluated using equations

$$F_k = F_k^0 + \Delta F_k$$

$$\zeta_{4f} = \zeta_{4f}^0 + \Delta \zeta_{4f} \quad (2)$$

where F_k^0 and ζ_{4f}^0 are zero order values of corresponding parameters.

Racah has introduced new operators which have simple transformation properties under the groups of transformation employed in classify the wave functions. The electrostatic energy E_c can be written as:

$$E_c = \sum_{k=1} e_k E^k \quad (3)$$

Where e_k is expectation value of new operator the Racah parameters E^k can be expressed as linear combination of F_k :

$$E^1 = 1/9(70F_2 + 231F_4 + 2002F_6) \quad (4)$$

$$E^2 = 1/9(F_2 - 3F_4 + 7F_6) \quad (5)$$

$$E^3 = 1/3(5F_2 + 6F_4 - 91F_6) \quad (6)$$

the integrals F_k and E_k are treated as parameters to be determined from the observed energy levels. This method has been used by various groups [15-20]. The Racah parameters, E^k , can be calculated using Eqs. 4 – 6.

In order to justify the present calculation the E_j values, E_{cal} have been calculated by substituting the calculated values of F_k and ζ_{4f} parameters. The root mean square (r m s) deviation (σ) between calculated (E_{cal}) and experimental (E_{exp}) energies of the levels has been calculated which is defined by

$$\sigma = \left[\sum_i \frac{\Delta E_i^2}{N} \right]^{1/2} \quad (7)$$

where ΔE_i is the difference between observed and calculated values of energies of the i^{th} level and N is the number of experimental levels fitted.

The bands due to electronic transitions of an ion have been found to shift to longer wave length (red shift) on complexation or putting it in the crystal field of the ligand. In the case of rare earth ions the metal 4f orbitals, being shielded ones, expand to a lesser degree.

The ratio of Slater Condon parameters of glass and free ion is known as nephelauxetic effect and is quantitatively measured in terms of nephelauxetic ratio (β') defined by [21-23]

$$\beta' = \frac{F_k^g}{F_k^f} \quad (8)$$

where g and f refer to the glass and free ions respectively in the present case. If β' is less than one, it indicates covalent bonding, while greater than one indicates ionic bonding. Henrie and Choppin [24] have defined another bonding parameter $b^{1/2}$ in terms of β' , given by

$$b^{1/2} = \left[\frac{1 - \beta'}{2} \right]^{1/2} \quad (9)$$

A real value of $b^{1/2}$ indicates covalent bonding. This parameter is very useful for comparative study for bonding.

The values of various energy interaction parameters viz Slater – Condon (F_k), Racah (E^k) and Lande' (ζ_{4f}) parameters have been computed by using eqs.1-7 the observed energies of the bands, the values of zero order energies (E_{0j}) and partial derivatives by the help of partial regression and least square method. The partial derivatives for praseodymium ion and observed energy of absorption band with their assignment have been collected in Table 2.

Zero order parameters

$F_2 = 305.0 \text{ cm}^{-1}$, $F_4 = 51.88 \text{ cm}^{-1}$, $F_6 = 5.321 \text{ cm}^{-1}$, $\zeta_{4f} = 730.5 \text{ cm}^{-1}$.

The values of F_k , E^k and ζ_{4f} parameters have been collected in Table 3. In the present glass specimens, the relation among different F_k parameters found as $F_2 > F_4 > F_6$. It is interesting to note that the observed values of $F_4/F_2 \sim 0.138$ and $F_6/F_2 \sim 0.015$ are nearly same as calculated considering radial eigen function to be hydrogenic ($F_4/F_2 \sim 0.14$ and $F_6/F_2 \sim 0.015$) [26]. The E^k parameters have been

given in Table 3, deduced from F_k parameters. The ratio of E^1/E^3 and E^2/E^3 are about 9.890 and 0.052 respectively, which are almost equal to the hydrogenic ratio. The values of nephelauxetic ratio (β') and bonding parameter ($b^{1/2}$) are 0.964 and 0.133 respectively (Table 3). The values of β' and $b^{1/2}$ is indicating covalent bonding. R.M.S deviation (σ) values is ± 95.53 . It's indicating that energies are justifying Taylor series expansion.

Table 3. Slater-Condon, Lande', Racah, Nephelauxetic ratio and bonding parameters for Pr^{3+} doped sodium borosilicate glass specimens with different concentrations and compare with free ion values

Parameters	Free ion	0.1 wt. %	0.3 wt. %	0.5 wt. %
F_2 (cm^{-1})	322.09	310.26	309.83	310.14
F_4 (cm^{-1})	44.46	42.83	42.77	42.81
F_6 (cm^{-1})	4.867	4.68	4.68	4.68
ζ_{4f} (cm^{-1})	741.00	733.87	736.76	736.13
E^1 (cm^{-1})	4728.92	4555.30	4548.87	4553.42
E^2 (cm^{-1})	24.75	23.82	23.79	23.81
E^3 (cm^{-1})	478.10	460.56	459.91	460.37
F_4/F_2	0.14	0.138	0.138	0.138
F_6/F_2	0.02	0.015	0.015	0.015
E^1/E^3	9.89	9.89	9.89	9.89
E^2/E^3	0.05	0.05	0.051	0.05
β'	0.963	0.961	0.962
$b^{1/2}$	0.135	0.137	0.136

R M S value = ± 95.53

Judd -Ofelt Intensity Parameters:

The intensities of absorption transitions are measured in terms of P_{exp} which represents the oscillator strength. In the case of absorption band, it is given [27] by

$$P_{\text{exp}} = 2303 \text{ mc}^2 / N \pi e^2 \int \epsilon d\nu$$

$$P_{\text{exp}} = 4.318 \times 10^{-9} \times \int \epsilon \nu d\nu$$

$$P_{\text{exp}} = 4.6 \times 10^{-9} \times \epsilon \times \Delta \nu_{1/2} \quad (10)$$

where ϵ is the molar absorptivity of a band at the energy. The molar absorptivity at a given energy is computed from the Beer-Lambert law $\{\epsilon = 1/cl (\log I_0/I)\}$

$$P_{\text{exp}} = 4.6 \times 10^{-9} \times (1/cl) \log (I_0/I) \times \Delta \nu_{1/2} \quad (11)$$

where c is the molar concentration of the absorbing ion per unit volume, l is the path length and $\log (I_0/I)$ is the absorptivity or optical density and $\Delta \nu_{1/2}$ is half band width. However, for a solid material it is generally expressed in terms of line strength S_{exp} which is related to oscillator strength P_{exp} by

$$P_{\text{exp}} = \{8\pi^2 m \bar{c} \bar{\nu} / 3h (2J+1)\} (1/n) [(n^2 + 2)^2 / 9] S_{\text{exp}} \quad (12)$$

where $\bar{\nu}$ is the average energy of the transition in cm^{-1} , J is the total angular momentum of the initial level, the factor $(n^2 + 2)^2 / 9$ represents the local field correction for an ion

embedded in a dielectric medium of refractive index, n , under the tight binding approximation and the other symbols have their usual meaning.

The oscillator strength, P_{exp} , of these transitions may be due to electric dipole, magnetic dipole or electric quadrupole or contribution from more than one of these modes. Thus the oscillator strength of the observed absorption band is given by

$$P_{\text{exp}} = P_{\text{ed}} + P_{\text{md}} + P_{\text{eq}} \quad (13)$$

where P_{ed} , P_{md} and P_{eq} refer to oscillator strengths due to electric dipole, magnetic dipole and electric quadrupole transitions respectively. The values of P_{eq} ($\sim 10^{-11}$) and P_{md} ($\sim 10^{-9}$) are very small in comparison with P_{ed} ($\sim 10^{-6}$).

It is interesting to note that f-f transitions if considered as magnetic dipole transitions, are parity allowed and in R-S coupling scheme they follow the selection rules [28]:

$$\Delta L = 0, \Delta S = 0, \Delta J \leq 1, (J' = 0 \rightarrow J'' = 0)$$

Similar selection rules are followed by electric quadrupole transitions. Since both these modes have very small values of oscillator strength, it is clear that the contribution is mainly from electric dipole mode. However, for true electric dipole transitions the initial and final levels should have different parity, whereas no parity change is involved in f-f transitions. Hence for f-f transitions, though electric dipole transitions are forbidden, both magnetic dipole and electric quadrupole transitions are allowed ones. Considering the observed intensities of these bands it is proposed that the induced electric dipole transitions may be operative.

The basic idea of Judd - Ofelt theory is that the intensity of the forbidden f-f electric dipole transition can arise from the admixture of opposite parity configuration into the $4f^N$ configuration, thus relaxing the parity restricted selection rule.

The odd part of the crystal field potential is considered as a perturbation for mixing states of different parity into the $4f^N$ configuration. In simple form the line strength (S_{cal}) of an electric dipole transition between initial J manifold $|f^N(\alpha, S, L) J\rangle$ and terminal J' manifold $|f^N(\alpha', S', L') J'\rangle$ is given by

$$S_{\text{cal}} = \sum_{\lambda=2,4,6} \Omega_{\lambda} | \langle f^N(\alpha, S, L) J | U^{(\lambda)} | f^N(\alpha', S', L') J' \rangle |^2 \quad (14)$$

where $|f^N(\alpha, S, L) J\rangle$ are the basis states in the LS coupling scheme and α represents an extra quantum number that might be necessary to describe the states completely, $U^{(\lambda)}$ are the unit tensor operators of rank ' λ ', which are doubly reduced to yield the matrix elements $\langle || U^{(\lambda)} || \rangle$ in the intermediate coupling [29], and Ω_{λ} are the phenomenological Judd - Ofelt intensity parameters which specify the electric dipole moment between any two electronic levels and contain implicitly the odd symmetric crystal field terms, radial integrals, and perturbation denominators. An attempt has been made by Quimby and Miniscalco [30] to further modify the theory, though the basic consideration remains the same.

In order to test the validity of Judd-Ofelt approach, employed to interpret the spectral intensities, a reduced chi-square test between S_{exp} and S_{cal} values has been performed. The reduced chi-square is given [31] by

$$\text{Reduced chi-square} = \sum (S_{cal} - S_{exp})^2 / \xi' - 3 \quad (15)$$

where ξ' is the number of absorption bands used in computation. The low value of this statistical parameter is a measure of the goodness of fit.

On the basis of Judd-Ofelt theory [32, 33] the electric-dipole line strength as a sum of products of phenomenological intensity parameters Ω_λ and matrix elements of tensor operator U^λ connecting states of $4f^n$ configuration. The Judd-Ofelt approach [32, 33] is applicable to transition between starks levels. The experimental line strengths (Table 4) S_{exp} for different bands and reported values of unit tensor matrix elements U^λ (Table 4) for Pr^{3+} ions, may be put in Eq 14 to get as many

Equations as the number of bands. Then partial regression and least square method are used to obtain the Judd-Ofelt intensity parameters. The resulting values of Ω_2, Ω_4 and Ω_6 have been collected in Table 5. The calculated line strength agrees very well with the experimental values. The trends of Ω_λ parameters is found to be $\Omega_2 > \Omega_4 < \Omega_6$. Sharma et al [11] and Ratnakran et al [17] have shown that Ω_4 and Ω_6 are structure dependent parameters. They are related to the rigidity and stability of the glass matrix in which the rare earth ions are situated. Spectroscopic quality factor Ω_4/Ω_6 in fluoride glass is ~ 2.0 , in the soda lime silicate glass is ~ 1.83 , and in the present glass is 0.429. Table 5 shows that similar values of Ω_4 / Ω_6 were observed in reported data. This indicates that the present glass is fairly rigid. They are more stable and rigid as compared to fluorophosphate and tellurites glasses. The low value of the goodness of fit (0.17) shows the applicability of Judd-Ofelt theory.

Table 4. Experimental (S_{exp}) and calculated line strength (S_{cal}) with their differences (ΔS) for various absorption bands of Pr^{3+} doped sodium borosilicate glass specimen

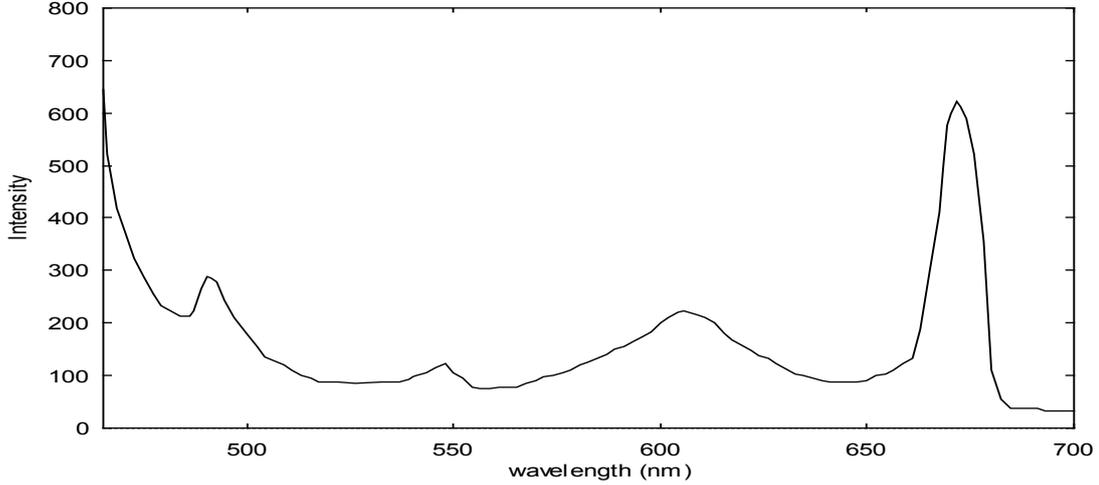
Absorption bands	U Matrix			Experimental O.S. ($P_{exp}10^{-6}$)			Line Strengths					
	$\ U^2\ ^2$	$\ U^4\ ^2$	$\ U^6\ ^2$	0.1%	0.3%	0.5%	0.1%		0.3%		0.5%	
							$S_{exp} 10^{-20}$	$S_{cal} 10^{-20}$	$S_{exp} 10^{-20}$	$S_{cal} 10^{-20}$	$S_{exp} 10^{-20}$	$S_{cal} 10^{-20}$
3F_2	0.8089	0.4032	0.1177	4.76	7.28	9.70	5.310	5.380	8.133	8.276	10.832	11.034
3F_3	0.0654	0.3469	0.6983	6.25	10.27	14.6	5.310	4.880	8.725	8.011	12.396	11.388
3F_4	0.0187	0.0500	0.4849	2.67	4.20	6.01	2.080	2.840	3.286	4.645	4.699	6.622
1G_4	0.0012	0.0072	0.0266	0.77	1.20	1.70	0.419	0.166	0.654	0.273	0.926	0.389
1D_2	0.0026	0.0170	0.0520	1.68	2.73	3.86	0.527	0.334	0.857	0.547	1.213	0.779
3P_0	0.0000	0.1728	0.0000	1.36	2.24	3.16	0.352	0.385	0.580	0.661	0.818	0.944
3P_1	0.0000	0.1707	0.0000	2.66	4.28	6.15	0.676	1.050	1.088	1.782	1.564	2.537
3P_2	0.0000	0.0362	0.1355	3.39	5.60	8.11	0.809	8.184	1.337	1.346	1.933	1.924

Table 5. Judd-Ofelt intensity parameters for Pr^{3+} ion in different host materials

Host Materials	$\Omega_2 (10^{-20})$	$\Omega_4 (10^{-20})$	$\Omega_6 (10^{-20})$	Ω_4 / Ω_6	Reference
Sodium borosilicate (0.1 wt.%)	4.747	2.228	5.445	0.491	Present
Sodium borosilicate (0.3 wt.%)	7.028	3.825	8.914	0.429	Present
Sodium borosilicate (0.5 wt.%)	9.061	5.466	12.744	0.428	Present
$Ca_5 (PO_4)_3 F$	0.32	1.59	3.82	0.42	34
$LiYF_4$	0.00	8.07	7.32	1.10	35
$BaYbF_8$	1.50	8.70	5.90	1.47	35
LaF_3	0.12	1.77	4.78	0.37	36
$LiPrP_4O_{12}$	1.82	2.83	6.54	0.43	35
$YAlO_3$	2.00	6.00	7.00	0.86	35
PrP_3O_{14}	1.34	1.19	6.09	0.20	35
$Sr_5 (PO_4)_3 F$	1.18	2.99	1.82	1.64	36

Table 6. Spontaneous emission probability (A), fluorescence branching ratio (β), radiative life time (τ), and stimulated emission cross section (σ_p) for Pr^{3+} doped Sodium borosilicate Glass

Transitions	λ (nm)	$[U^{(2)}]^2$	$[U^{(4)}]^2$	$[U^{(6)}]^2$	$\Delta\lambda_{\text{eff}}$ (nm)	A (Sec. ⁻¹)	β	τ ($\mu\text{sec.}$)	σ_p (pm^2)
$^3\text{P}_0 \rightarrow ^3\text{H}_4$	490.1	0.0000	0.1713	0.0000	7.14	10197.1	0.336	98.1	3.79
$^3\text{P}_0 \rightarrow ^3\text{H}_5$	547.8	0.0000	0.0000	0.0000	11.30	0.0	0.0	---	0.0
$^3\text{P}_0 \rightarrow ^3\text{H}_6$	605.5	0.0000	0.0000	0.0726	33.69	5600.4	0.188	178.6	1.03
$^3\text{P}_0 \rightarrow ^3\text{F}_2$	671.7	0.2942	0.0000	0.0000	11.95	14491.1	0.478	69.0	2.89

**Figure 3.** Fluorescence spectrum of Pr^{3+} (0.5 wt%) doped sodium borosilicate glass specimen and excitation wavelength 445 nm

Fluorescence Spectra:

The fluorescence spectra of Pr^{3+} doped sodium silicate glass specimens has been recorded in terms of wavelength (nm) vs relative fluorescence (au) (Fig.3). The most intense band in the absorption spectra around 445 nm ($^3\text{H}_4 \rightarrow ^3\text{P}_2$) have been used for the excitation of Pr^{3+} ions. As a consequence of which, four fluorescence bands around 492, 547, 605 and 672 nm in 0.1 wt.%, 489.0, 546.0, 604.8 and 670.0 nm in 0.3 wt.%, and 490.1, 547.8, 605.5 and 671.7 nm in 0.5 wt% respectively have been observed. They have been assigned to the transitions $^3\text{P}_0 \rightarrow ^3\text{H}_4$, $^3\text{P}_0 \rightarrow ^3\text{H}_5$, $^3\text{P}_0 \rightarrow ^3\text{H}_6$ and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ respectively. Addition of As_2O_3 has increased their intensities considerably. This may be due to intermixing of electronic levels of Pr^{3+} with molecular orbitals of As_2O_3 resulting, the increase in the population of the excited state of Pr^{3+} . Such effect has also been observed by Reisfeld et al. [37] in the case of Sm^{3+} ion. The fluorescence peak wavelength (λ_p) and the effective line width of the fluorescence peak ($\Delta\lambda_{\text{eff}}$) of the observed fluorescence bands for different glasses have been collected in Table 6.

4. Radiative Properties

The radiative properties of rare earth ions have been theoretically studied by Krupke [38] and Jacob and Weber [39] in relation to Judd - Ofelt intensity parameters in

absorption spectra and fluorescence spectra. These properties are often called laser parameters.

Spontaneous emission probability (A)

The spontaneous emission probability from an initial manifold $|f^N(\alpha', S', L') J' \rangle$ to a terminal manifold $|f^N(\alpha, S, L) J \rangle$ is given by

$$A = \frac{64\pi^4 e^2}{3h(2J'+1)\lambda_p^3} n \left[\frac{(n^2+2)^2}{9} \right] \times \sum_{\lambda=2,4,6} \Omega_{\lambda} | \langle f^N(\alpha', S', L') J' || U^{(\lambda)} || f^N(\alpha, S, L) J \rangle |^2 \quad (16)$$

Fluorescence branching ratio (β)

The Fluorescence branching ratio for the transitions originating from a specific initial J' manifold $|f^N(\alpha', S', L') J' \rangle$ is defined as

$$\beta = \frac{A}{\sum_{\alpha, S, L, J} A} \quad (17)$$

Radiative lifetime (τ)

The radiative life time τ for a transition is reciprocal of spontaneous emission probability 'A', for radiative decay from the initial J' manifold $|f^N(\alpha', S', L') J' \rangle$. It is given by

$$\tau = A^{-2} \quad (18)$$

Stimulated emission cross - section (σ_p)

The stimulated emission cross – section σ_p , for the transition from initial J' manifold $|f^N(\alpha', S', L') J' \rangle$ to a terminal J manifold $|f^N(\alpha, S, L) J \rangle$, having a probability A is expressed as

$$\sigma_p = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{\text{eff}}} A \quad (19)$$

where λ_p is the peak fluorescence wavelength and $\Delta\lambda_{\text{eff}}$ is the effective line width of the fluorescence, defined by

$$\Delta\lambda_{\text{eff}} = \frac{\int I(\lambda) d\lambda}{I_{\text{max}}} \quad (20)$$

where $I(\lambda)$ is fluorescence intensity at wavelength λ .

The effective line width is a measure [40] of a combination of the extent of the stark splitting of the initial and terminal J manifold and the inhomogeneous broadening resulting from the site – to – site variations of the local field.

In order to choose a suitable material for laser action, it is necessary to study the various transitions giving rise to fluorescence and computes its laser parameters utilizing the absorption and fluorescence data. Spontaneous emission probability (A), branching ratio (β), radiative life time (τ), and stimulated emission cross-section (σ_p) have been computed by using eqs. 16-19 by putting the values fluorescence wave length, reduced matrix elements for the relevant transition and the values of Ω_2 , Ω_4 and Ω_6 (Table 5).

These all laser parameters are collected in Table 6. The σ_p is an important laser parameter. Its value signifies the rate of energy extraction from the laser material and is generally used to predict laser action rare earth doped materials prepared on laboratory scale. The values of σ_p for the all transitions ${}^3P_0 \rightarrow {}^3H_4$, ${}^3P_0 \rightarrow {}^3H_6$ and ${}^3P_0 \rightarrow {}^3F_2$ are collected in Table 6. The values of A , β and σ_p for ${}^3P_0 \rightarrow {}^3H_4$ transition are maximum, suggesting that it can be used as a most probable laser transition. From table 6 shows the highest values of σ_p for the transition ${}^3P_0 \rightarrow {}^3F_2$, suggesting that under suitable circumstances, it can be used as a laser transition. The values of σ_p for the transition ${}^3P_0 \rightarrow {}^3F_2$ is high due to the presence of As_2O_3 in glass. It has its own luminescence spectrum [41] ranging from 590 nm to 650nm with its peak at 630 nm and ${}^3P_0 \rightarrow {}^3H_5$ is found to be zero due to the value of A . In the present glass system Pr^{3+} gets surrounded by $[AsO_4]^{3-}$ in the second coordination sphere. Since the negative charge of $[AsO_4]^{3-}$ tetrahedral is not properly compensated by the positive charge of alkali ion, $[AsO_4]^{3-}$ tetrahedral provide a fluorine type structure in the glass network thereby decreasing the covalent character between the Pr^{3+} and oxygen atoms provided by $[SiO_4]$ tetrahedra. With the decrease in covalency, Ω_6 parameter increases because of the inverse relationship [42] between the two and as a consequence of it, σ_p for the transition ${}^3P_0 \rightarrow {}^3F_2$ increases.

5. Conclusions

In this paper we have calculated various physical properties of sodium borosilicate glass with different concentrations. The absorption spectra of Pr^{3+} ions doped glasses have been analyzed on the basis of energy interaction and Judd-Ofelt theory. Eight absorption bands have been observed in the visible and IR region. The relation among different Slater –Condon (F_k) parameters found as $F_2 > F_4 > F_6$. It is interesting to note that the observed values of $F_4/F_2 \sim 0.138$ and $F_6/F_2 \sim 0.015$ are nearly same as calculated considering radial eigen function to be hydrogenic. Racah (E^k) parameters deduced from F_k parameters. The values of nephelauxetic ratio (β') and bonding parameter ($b^{1/2}$) are less than 1. This suggest that the values of β' and $b^{1/2}$ is covalent bonding. R.M.S deviation (σ) values is ± 95.53 . It is justifying Taylor series expansion. Judd-Ofelt parameter increases on increasing concentration of Pr^{3+} ion. The trends of Ω_k parameters is found to be $\Omega_2 > \Omega_4 < \Omega_6$. Ω_4 and Ω_6 are structure dependent parameters. Spectroscopic quality factor (Ω_4/Ω_6) in the present glass is 0.429. Compare the values of Ω_4/Ω_6 with reported laser crystals and found results in between. This indicates that the present glass is fairly rigid. They are more stable and rigid as compared to fluorophosphate and tellurites glasses. The low value of the goodness of fit (0.17) shows the applicability of Judd-Ofelt theory. The values of A , β , τ and σ_p computed for the transitions ${}^3P_0 \rightarrow {}^3H_4$, ${}^3P_0 \rightarrow {}^3H_6$ and ${}^3P_0 \rightarrow {}^3F_2$. The values of A , β and σ_p for ${}^3P_0 \rightarrow {}^3H_4$ and ${}^3P_0 \rightarrow {}^3F_2$ transition are maximum, suggesting that they can be used as a most probable laser transitions. The values of σ_p for the transition ${}^3P_0 \rightarrow {}^3F_2$ is high due to the presence of As_2O_3 in glass. In the present glass system Pr^{3+} gets surrounded by $[AsO_4]^{3-}$ in the second coordination sphere. Since the negative charge of $[AsO_4]^{3-}$ tetrahedral is not properly compensated by the positive charge of alkali ion, $[AsO_4]^{3-}$ tetrahedral provide a fluorine type structure in the glass network thereby decreasing the covalent character between the Pr^{3+} and oxygen atoms provided by $[SiO_4]$ tetrahedra. With the decrease in covalency, Ω_6 parameter increases because of the inverse relationship between the two and as a consequence of it, σ_p for the transition ${}^3P_0 \rightarrow {}^3F_2$ increases.

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