Optical properties of Pr³⁺ doped glasses, effect of host lattice

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Abstract : Glass base effect on optical absorption and luminescence properties of Pr^{3+} doped glasses have been studied in different hosts using modified J-O model proposed by Komienko *et al* Using modified J-O intensity parameters (Ω'_{λ}) radiative properties $(A, A_T \text{ and } \beta\%)$ and life times (τ_r) of the emitting levels ${}^{3}P_0$, ${}^{3}P_1$ and ${}^{1}D_2$ have been calculated and compared for different lattices. Theoretical results for oscillator strength obtained using this model show better agreement with experimental values.

Keywords : Pr³⁺ doped glasses, optical properties, effect of host lattice PACS Nos. : 78.66 Jg. 78.60 Ya

1. Introduction

The observed electric dipole transitions of the electronic configuration $4f^2$ of Pr^{3+} occur mainly from the excited states ${}^{3}P_{0,1,2}$ and ${}^{1}D_2$ to the ground and low lying excited states [1]. Compared to the optical 4f transitions of other rare earths ions, the electric dipole transitions ${}^{3}P_{0,1,2} \rightarrow {}^{3}H_4$ of Pr^{3+} exhibit short decay times of about few μ s. In several technical applications, such as Scintillators, fast luminescence is required. So Pr^{3+} is best suited as a dopant in X-ray conversion detectors for modern X-ray computed tomography [2]. Transitions from the ${}^{3}P_{0,1,2}$ levels are also used in phosphers. The other predominant transition ${}^{1}D_2 \rightarrow {}^{3}H_4$ of Pr^{3+} has a much larger decay time and laser action has been observed for this transition in $PrCl_3$ [3] and PrP_3O_{14} [4] etc. Smart et al [5] have reported that Pr^{3+} doped fluoride fibers exhibit lasing action in orange and red regions of spectrum when pumped with a Ti-Sapphire laser at 1010 and 835 nm's. Upconversion has also been demonstrated for Pr^{3+} ion in different glass hosts have also been studied [7].

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The Judd-Ofelt approximation has been successfully applied to most of the doped rare earth ions to explain their optical properties. However in the case of Pr^{3+} it is marked that there is a poor agreement between calculated and experimental oscillator strengths [8,9] and in some cases negative values are also obtained for Ω_2 parameter [10]. This is due to reason that some of the assumptions made in this approximation, in particular that the energy difference between excited configurations and each of the two levels involved in the electronic transition is the same, is probably not valid in the case of Pr^{3+} because 5d levels of it are at lower energies than in the other 4f ions. To improve upon this, some changes are needed in Judd-Ofelt formulae.

In the present work we report the absorption and fluorescence properties of Pr^{3+} in phosphate, tellurite, oxyfluoride and Zr based heavy metal fluoride (HMF) glasses where the results have been analysed using modified J-O theory [11a,11b]. A good agreement in the calculated and observed oscillator strength have been observed. The optical parameters for different transitions in different hosts are also compared.

2. Experimental

The composition of glasses are expressed by

PBK;	68P ₂ O ₅ .22BaO.8K ₂ O.2Pr ₂ O ₃
Ге.NaO;	72TeO.26Na ₂ O.2Pr ₂ O ₃
ABCP;	33AIF3.11AIPO4.30CaF2.24BaF2.2PrF3
ZrBAN;	55ZrF4.19BaF2.5AlF3.21NaF.2PrF3

Glasses are prepared using standard quenching technique. We weighed the glass and compared its weight with the weight of the mixture used. A very little change in the mass was found. This indicates that the composition of the glass is probably the same. The experimental details related to density and refractive index measurements are given in our earlier papers [12,13]. The stokes luminescence were obtained pumping Pr^{3+} glasses with a coherent innova 400 Ar⁺ ion laser (λ_{exe} is 476.5 nm). The dispersed spectra were obtained using 0.5 m Spex monochromator. The absorption spectra were recorded using Perkin Elmer-551 and Carl Zeiss Specard spectrophotometers.

3. Results and discussion

3.1. Absorption studies :

The absorption spectra of Pr^{3+} doped PBK, Te.NaO, ABCP, ZrBAN glasses at room temperature are shown in Figure 1. The spectra show nine absorption bands for the three glasses while in the case of tellurite glass only eight peaks are observed irrespective of the fact that 13 levels arise due to $4f^2$ configuration of Pr^{3+} . These bands arise due to electronic transition from the ground state manifold to various excited levels ${}^{3}P_{0,1,2}$, ${}^{1}D_{2}$, ${}^{1}G_{4}$, ${}^{3}F_{4,3,2}$ and ${}^{3}H_{6}$ and their positions and relative intensities changes with glass base are also reported by other workers ([14] and references therein). The wavelength of different absorption

peaks in different lattices are tabulated in Table 1. The transition ${}^{3}P_{2} \leftarrow {}^{3}H_{4}$ at 440 nm is hypersensitive and as can be seen from Figure 1, it has maximum intensity in the case of



Figure 1. Absorption spectrum of Pr^{3+} doped Zr based heavy metal fluonde (Z), tellurite (T), oxyfluonde (O), phosphate (P) glasses.

tellurite glass. The intensity of this peak in other glasses follows the order Te.NaO > Zr BAN > ABCP > PBK. The absorption peaks corresponding to the levels ${}^{3}P_{1}$, ${}^{3}P_{0}$ in the tellurite glass have nearly same optical intensity but in other glasses do not show any regularity. The energy of the ${}^{3}P_{0}$ is nearly the same for the PBK, TeNaO and ABCP glasses

Energy level	Free ion levels of Pr ³⁺	Pr ³⁺ ion in LaCl3 crystal [25]	ZrF2-CdF2 glass [21]	РВК	Te.NaO	ABCP	Zr BAN
³ P ₂	432	447	443	435	455	450	445
³ P1	454	475	468	471	470	473	470
³ P ₀	468	488	480	485	485	485	490
^I D ₂	577	598	588	588	585	585	589
$^{1}G_{4}$	1008	1020	1016	1012	-	1012	1011
${}^{3}F_{4}$	1459	1475	-	1465	1460	1471	1466
${}^{3}F_{3}$	1559	1579	1570	1560	1567	1560	1558
³ F ₂	1930	1932	1944	1935	1932	1929	1931
³ Н6	2401	2426	-	2488	2500	2500	2466

Table 1. Assignment of the peaks observed in visible, NIR absorption spectra of Pr^{3+} in different glasses (wavelengths in nm)

but shifts in lower energy side by almost 150 cm⁻¹ in the HMF glass due to nephlauxetic effect (see ref. [15]). A comparison of the NIR spectra shows that the band involving ${}^{1}G_{4}$ level of the Pr³⁺ appears broader in PBK glass in comparison to its width in ABCP glass but sharper in the case of HMF glass. The line corresponding to this level is totally absent in tellurite glass. A similar feature has been marked for ${}^{3}F_{2}$ and ${}^{3}H_{6}$ levels also. These

observations suggest that the intensity, position and band width of the optical transitions are host dependent. The optical density is increased when it is doped in HMF glass.

The oscillator strength (f) corresponding to different transitions were obtained by integrating the intensities of absorption bands. The absorption peaks are supposed to be pure Gaussian shape. The oscillator strength is given as [16],

$$f_{m} = \left(mc^{2} / \pi e^{2} N\right) \times \int \alpha(\lambda) d\lambda / \lambda^{2}$$
(1)

which in terms of energy reduces to

$$f_m = 9.20 \times 10^{-9} \varepsilon_{\max} \Delta v_{1/2},$$
 (2)

where ε_{\max} is the maximum value of molar extinction coefficient ε . $\Delta v_{1/2}$ is the half width of the line at $I_{\max}(v)/2$.

In order to get the theoretical value of oscillator strength, one calculates the Judd-Ofelt intensity parameters. The Judd-Ofelt theory is applicable to only those cases where the *f* levels splitting are smaller compared to *f*-*d* energy gap [16]. In Pr^{3+} however, this situation is different. As a result of this matrix elements $||U^4||$ and $||U^6||$ for the ${}^{3}F_{3}$ and ${}^{3}F_{4}$ transitions lying in the NIR region are found to be quite large. This gives very large value for Ω_4 and Ω_6 and a small value for Ω_2 . This predicts very large intensity for the bands near 1560 nm due to the ${}^{3}F$ levels. On the other hand when data for these bands are included in the fit a negative value for Ω_2 is obtained in all the cases except the HMF glass. Carnall *et al* [17,18] and Krupke [19] have also marked a negative value for Ω_2 for Pr^{3+} in LaF₃ lattice. Kornienko *et al* [11a] and Goldner and Auzel [11b] proposed a modification in Judd-Ofelt theory and called it as modified Judd-Ofelt model.

3.2. Modified Judd-Ofelt model :

In the Judd-Ofelt theory, the electric dipole line strength (S_{ed}) is given by

$$S_{ed}(\Psi_J, \Psi'_{J'}) = e^2 \sum \Omega_{\lambda} \left(\left\langle \Psi_J \| U^{\lambda} \| \Psi'_{J'} \right\rangle \right)^2, \qquad (3)$$

where Ω_2 , Ω_4 and Ω_6 are three Judd-Ofelt parameters. The values of these intensity parameters depend on impurity ions and the host lattice. $||U^{\lambda}||$ is called the reduced matrix element and its value is almost insensitive to lattice environment [20]. The reduced matrix elements $||U^{\lambda}||$ calculated by Weber [16] for Pr^{3+} in LaF₃ have therefore been used to derive the optical properties of Pr^{3+} in other lattices. This assumption is however not valid in all situations. Kornienko *et al* [11a] introduced a new formula to describe the experimental data which takes into account the dependence of Judd-Ofelt parameters on the energy level manifolds. The modified form of electric dipole line strength equation is

$$S_{ed}(\Psi_{J},\Psi_{J'}) = e^{2} \sum \Omega_{\lambda}' \left[1 + 2\alpha \left(E_{\Psi J} + E_{\Psi' J'} - 2E_{r}^{0} \right) \right] \\ \left(\left\langle \Psi_{J} \| U^{\lambda} \| \Psi_{J'}' \right\rangle \right)^{2}, \qquad (4)$$

 Ω'_{λ} are the modified Judd-Ofelt parameters ($\lambda = 2,4,6$). α is another parameter whose value in the case of Pr^{3+} is $[1/2 (E_{4f5d} - E_{4f})]$. Its value is found to be 10^{-5} cm⁻¹ [21]. $E_{\Psi J}$ and $E_{\Psi T}$ are the energies of the levels corresponding to the wave functions Ψ_J and $\Psi'_{J'}$, and E_r^0 is the energy of the center of gravity of $4f^2$ configuration of Pr^{3+} [for Pr^{3+} this value is given to be 10002 cm⁻¹ by Carnall *et al* (18)]. The Judd-Ofelt parameters Ω'_{λ} thus obtained are given in Table 2. The Ω'_{λ} values obtained here is positive in all the three cases.

Glasses		Ωź	Ω'_4	Ω' ₆	Ω'_4 / Ω'_6
РВК		0.24	5.91	3.62	1.69
TeNaO		2.90	6.72	1.85	3.63
ABCP		1.15	6.36	2.82	2.25
ZrBAN		0.28	5.72	1.73	3.30
35ZnO.65TeO ₂	[23] [*]	2.59	7.26	5.45	-
Li2O.2B2O3	[23]*	0.77	3.84	3.58	-
ZrBAN	[24]*	0.84	4.79	9.13	-
ZrBA	{26] [*]	0.06	5.05	6.92	-
Chlorophosphate	[27]*	4.38	1.86	4.15	-

Table 2. Judd-Ofelt intensity parameter ($\Omega_{\lambda} \times 10^{20} \text{ cm}^2$) of Pr³⁺ in PBK, Tc.NaO, ABCP and Zr.BAN glasses.

*These values are Ω_2 , Ω_4 and Ω_6 .

Table 3. Measured (f_a) and calculated (f_b) oscillator strength (× 10⁶) of Pr³⁺ in phosphate, tellurite, oxyfluoride and fluoride glasses.

Transition from	PBK		Te.f	Te.NaO		ABCP		Zr. BAN	
${}^{3}H_{4} \rightarrow$	fa	ſb	fa	ſb	fa	ſb	fa	ſb	
³ P ₂	5 00	4.88	7.21	6.22	5.12	6.99	4.21	3.30	
³ P ₁	1.58	1.29	2.10	2.85	1.92	0.58	2.00	1.15	
³ P ₀	2.00	1.86	3.52	2.80	2.81	2.92	4.86	3.59	
¹ D ₂	2.31	1.59	1.22	0.86	2.18	1.95	2.11	1.84	
¹ G ₄	0.12	0.32	-	-	0.32	1.39	0.33	0.41	
³ F ₄	1.02	1.33	1.21	2.93	1.63	2.61	2.31	2.40	
³ F ₃	5.32	5.18	6.92	6.32	4.32	5.21	3.52	3.81	
³ F ₂	1.93	1.84	2.54	3.81	0. 92	1.00	1.36	1.38	
³ H ₆	0.25	0.50	0.31	0.33	0.31	0.36	0.52	0.54	
R.m.s. × 10 ⁶	1.	06	2	2.12	3	.12	1	.52	

The oscillator strengths for different absorption bands in the four glasses were calculated using the modified value of Ω'_{λ} . They are compared with the experimental values also in Table 3. One can see from Table 3 that oscillator strength are in general,

lower in HMF glass than the other three. This is possibly due to fact that the crystal field affecting the Pr³⁺ ions is smaller in fluoride glasses than in the phosphate glasses [18].

3.3. Stokes luminescence :

As mentioned earlier fluorescence measurements have also been carried out at room temperature using 476.5 nm radiation of Ar⁺ laser (power 700 mW). This wavelength of Ar⁺ excites the ³P₁ level of Pr³⁺ since its energy (20981 cm⁻¹) is close to the energy of ³P₁ level (21118 cm⁻¹) [see Figure 2]. Therefore the fluorescence from ³P₁ to the ground state



Figure 2. Energy levels and fluorescence transitions in Pr³⁺ doped in PBK glass.

could not be observed as this line is overlapped with the exciting line. The fluorescence spectra of Pr^{3+} in the four glasses are shown in Figure 3. In total nine peaks could be observed. These lines arise due to the excited ${}^{3}P_{1}$, ${}^{3}P_{0}$ and ${}^{1}D_{2}$ levels to the ground state or low lying excited states [see Figures 2 and 3]. The wavelengths of the bands and their assignments, relative intensities in the four glasses are listed in Table 4. The band with maximum intensity in the emission spectrum is at 610 nm which corresponds to the transitions ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ and ${}^{3}P_{1} \rightarrow {}^{3}H_{6}$. The other bands are found to lie at 526, 545, 642, 681, 704 and 725 nm's. The intensities of the peaks are however found to vary from one glass to the other so much so that in some cases some of the peaks are completely absent.

For example, ${}^{3}P_{0} \rightarrow {}^{3}H_{5}$ transition in the tellurite glass is completely absent but it appears in the other glasses. Similarly in oxyfluoride glass the transition ${}^{3}P_{1} \rightarrow {}^{3}F_{4}$ does not appear.



Figure 3. Fluorescence spectrum of Pr^{3+} doped Zr based heavy metal fluoride (Z), tellurite (T), oxyfluoride (O), phosphate (P)

The bandwidths of the observed fluorescence lines also differ from glass to glass. The transition ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ appears sharper in heavy metal fluoride glass and its fluorescence

Table 4. Fluorescence line assignments, peak frequency (cm^{-1}) , effective bandwidths (cm^{-1}) and relative intensities of Pr^{3+} doped in tellurite, phosphate, oxyfluoride and fluoride glasses.

Transition		1	PBK		Т	TeNaO			ABCP			ZrBAN		
		v	Δν	I	v	Δv	1	v	Δv	1	ν	Δv	I	
${}^{3}P_{1} \rightarrow {}^{3}$	³ H5	19047	360	36	19011	310	42	18975	330	45	18975	250	47	
$^{3}P_{0} \rightarrow ^{3}$	³ H ₅ ⁽¹⁾	18858	130	17	-	-	-	18484	90	22	18484	92	19	
${}^{3}P_{0} \rightarrow {}^{3}$	³ H5 ⁽²⁾	17986	97	10	-	-	-	17986	90	12	17986	90	13	
${}^{3}P_{0} \rightarrow {}^{2}$	³ Н6	16666	350	69	16583	300	83	16722	310	80	16639	285	83	
${}^{1}D_{2} \rightarrow {}^{2}$	² H ₄	16420	341	80	16367	290	86	16393	355	82	16367	270	101	
${}^{3}P_{0} \rightarrow {}^{2}$	³ F ₂	15576	146	54	15601	140	59	15576	140	61	15576	142	70	
${}^{3}P_{1} \rightarrow {}^{3}$	³ F3	14706	178	8	14749	170	8	14684	168	13	14662	180	14	
${}^{3}P_{1} \rightarrow {}^{2}$	³ F4	14184	98	7	14168	88	10	-	-	-	14227	100	12	
${}^{3}P_{0} \rightarrow {}^{3}$	³ F4	13818	142	7	13778	130	9	13758	120	9	13831	105	13	

yield is also found to be maximum. This is probably because the fluoride host have lower phonon energy and hence non-radiative losses due to multiphonon relaxation giving better fluorescence efficiency.

3.4. Emission cross section and life time :

Laser materials are generally characterised on the basis of stimulated emission cross section, life time, branching ratio, transition probability *etc.*, for different transitions. In order to calculate these parameters we used the relation given by Saisudha and Rama Krishna [15]. The radiative transition probability and branching ratio for different transitions are given in Table 5 and stimulated emission cross section in Table 6.

	Transition	РВК		Te.N	aO	ABC	CP	Zr. BAN	
chergy		A	β	A	β	A	β	A	β
1_{D_2}	→								
³ H ₄	16420	1212	0.307	1011	0.266	1320	0.386	1518	0.460
3H5	14378	40.0	0.010	32.0	0.008	30.0	0.008	10.0	0.003
3 _{H6}	12282	750	0.190	850	0.224	750	0.219	690	0.209
$^{3}F_{2}$	16672	92 0	0 233	890	0.234	630	0.184	530	0.160
³ F1	10300	130	0.032	230	0.06	115	0.033	95 .0	0.028
³ F ₄	9825	770	0.195	650	0.171	420	0.122	320	0 097
$^{1}G_{4}$	7001	120	0 03	130	0.034	150	0 043	130	0.039
$^{3}P_{0}$	→								
³ H ₆	16666	3042	0.156	3146	0 154	2930	0 1 5 9	3295	0.166
$^{1}F_{2}$	15454	16022	0.826	17021	0.833	15048	0.821	16022	0.809
3 _{F4}	13583	220	0.001	120	0 006	240	0.013	330	0.016
$^{1}G_{4}$	10773	65.0	0.003	95 0	0.005	67.0	0.003	102	b 005
1D2	3768	32.0	0.02	46.0	0.002	40.0	0.002	50.0	0.003
³ P1	→								
$^{3}H_{4}$	21118	120	0.004	132	0 005	125	0.004	136	0 005
Ήs	18690	10452	0 359	9856	0 359	10280	0 37	11350	0 404
³ H ₆	16593	80.0	0.002	102	0 004	100	0 003	95.0	0 003
$^{3}F_{2}$	15991	5830	0.20	5680	0 207	5490	0 197	5620	0.200
³ F1	14616	12361	0.425	11362	0414	11463	0 413	10560	0 376
$^{3}F_{4}$	14125	70.0	0.003	80.0	0 002	82.0	0 002	80 0	0 003
$^{1}G_{4}$	11318	20 0	0.006	20.0	0.007	27.0	0.009	•20.0	0 007
D ₂	4312	150	0.005	153	0 006	162	0 006	156	0.005

Table 5. Radiative transition probabilities and branching ratio of the ${}^{3}P_{0}$, ${}^{3}P_{1}$ and ${}^{1}D_{2}$ excited states of ${}^{2}P_{1}^{3+}$ in phosphate, tellurite, oxyfluoride and Zr based fluoride glasses.

Table 6. Stimulated emission cross section of three intense bands and total transition probabilities of final state ${}^{1}D_{2}$, ${}^{3}P_{0}$, ${}^{3}P_{1}$ in different glasses

Glasses	Transition	Cross section $\sigma \times 10^{-20} \text{ cm}^2$	Total transition probabilities (<i>SA</i>)
Phosphate	${}^{1}D_{2} \rightarrow {}^{3}H_{4}$	42 3	3942
	${}^{3}P_{0} \rightarrow {}^{3}F_{2}$	22.1	19381
	${}^{3}P_{1} \rightarrow {}^{3}H_{5}$	31.0	29083
Tellurite	$^{1}D_{2} \rightarrow {}^{3}H_{4}$	43 15	3792
	${}^{3}P_{0} \rightarrow {}^{3}F_{2}$	20.16	20428
	${}^{3}P_{1} \rightarrow {}^{3}H_{5}$	32.10	27385
Oxyfluoride	$^{1}D_{2} \rightarrow {}^{3}H_{4}$	40.36	3415
	${}^{3}P_{0} \rightarrow {}^{3}F_{2}$	26 02	18325
	${}^{3}P_{1} \rightarrow {}^{3}H_{5}$	28.20	27729
Fluoride	$^{1}D_{2} \rightarrow {}^{3}H_{4}$	50.36	3293
	${}^{3}P_{0} \rightarrow {}^{3}F_{2}$	24.19	19799
	${}^{3}P_{1} \rightarrow {}^{3}H_{5}$	36.5	28026

The cross section values for ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$ (641 nm), ${}^{3}P_{1} \rightarrow {}^{3}H_{5}$ (525 nm) and ${}^{1}D_{2} \rightarrow {}^{3}H_{4}$ (609 nm) transitions in the HMF glass are 24 × 10⁻²⁰, 36.5 × 10⁻²⁰ and 50.36 × 10⁻²⁰ cm² respectively. The large cross section indicates that Pr doped HMF glass looks more promising for laser transitions. The radiative life time of the excited states ${}^{3}P_{0}$, ${}^{3}P_{1}$ and ${}^{1}D_{2}$ were also calculated and compared with the results given by Lakshman and Suresh Kumar [14] and Bunuel *et al* [22] in Table 7. These values are in reasonable agreement with the experimentally estimated values.

lon	Fluorescent level	ΡΒΚ τ _t (μs)	Te NaO τ ₁ (μs)	ABCP τ ₁ (μs)	Zr.BAN τ _r (μs)	Zn Na.P τ _f (μs) [14]	Zn.F ₂ CaF ₂ τ _f (μs) [22]
Pr ¹⁺	¹ D ₂	253	263	292	.303	369	$\tau_{exp} = 245$ $\tau_{cal} = 350$
	³ P ₀	51	48	54	50	47	$\tau_{exp} = 40$ $\tau_{cal} = 27$
	³ P1	34,	.36	36	35	47	

Table 7. Radiative life time (τ_t) of fluorecent levels 1D_2 , 3P_0 and 3P_1 in different hosts

4. Conclusion

Using modified J-O theory by Kornienko *et al* [11a], the intensity parameters, oscillator strength, transition probabilities and life time of the different levels of Pr^{3+} ion doped in PBK, Te-NaO, ABCP and HMF glasses have been calculated. These calculations show that among the four glasses selected, Zr based HMF glass is superior laser material.

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