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Compositional dependence of optical properties of Pr^{3+} ions in lithium borate glasses

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Abstract

Optical properties of Pr^{3+} ions in six different lithium borate glasses have been systematically investigated. The observed energy levels have been analysed by using a free ion model Hamiltonian. From the experimental values of oscillator strengths and calculated matrix elements, the Judd–Ofelt parameters were obtained and their compositional dependence was investigated systematically. The predicted lifetime for fluorescent levels decreases with decreasing content of Li_2CO_3. However, lifetime increases with increasing content of LiF. Out of six glasses examined, $49.5LiF+49.5H_3BO_3+1Pr_2O_3$ glass exhibits comparatively better predicted radiative properties. © 1998 Elsevier Science S.A.

Keywords: Optical properties; Pr^{3+}; Lithium borate glass; Lifetime

1. Introduction

The physical and optical properties of lanthanide ions in Li-based crystalline [1–3] and non-crystalline materials [4] have received great attention in the recent literature.

Praseodymium ions in crystals and glasses are by far the most widely investigated systems, because the Pr-doped systems exhibit very rich emission spectra extending from the UV to the infrared [1,5], Pr:glass fibres are currently viewed as the most promising candidates for a 1.3-μm communication window [6], the $4f^2$ electronic structure of Pr^{3+} ion is relatively very simple so that its electronic structure is widely used to define and test theoretical models to understand and estimate lanthanide–ligand radiation interaction mechanisms [7,8], etc.

To account for the emission properties and the important $^1G_4 \rightarrow {}^3H_4$ transition at 1.3 μm of Pr^{3+}, the Judd–Ofelt (JO) model [9,10] has been applied to most of the Pr^{3+}:systems, although the JO model raises some problems [11,12]. This paper reports the effect of glass composition (lithium/borate/fluoride) on energy level intensities, JO parameters and, in turn, radiative properties for fluorescent levels of Pr^{3+} ions.

2. Experimental methods

Good optical quality praseodymium-doped lithium borate (L*n*BP, $n=4$, 5, 6 and 7) and lithium fluoroborate (L*x*FBP, $x=2$, 5) glasses were prepared with the following compositions:

L4BP	$59.5Li_2CO_3+39.5H_3BO_3+1Pr_2O_3$
L5BP	$49.5Li_2CO_3+49.5H_3BO_3+1Pr_2O_3$
L6BP	$39.5Li_2CO_3+59.5H_3BO_3+1Pr_2O_3$
L7BP	$29.5Li_2CO_3+69.5H_3BO_3+1Pr_2O_3$
L2FBP	$24.75Li_2CO_3+24.75LiF+49.5H_3BO_3+1Pr_2O_3$
L5FBP	$49.5LiF+49.5H_3BO_3+1Pr_2O_3$

The above compositions were melted in the range of 900–950°C and then air quenched. These glasses were annealed at 350°C. Optical measurements were made using an Hitachi U-3400 spectrophotometer at room temperature. The refractive indices were measured using an Abbe refractometer at sodium wavelength.

3. Theoretical methods

The model Hamiltonian that was used to study the electronic energy level structure of Pr^{3+} and the fitting procedure for the observed and calculated energy level

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schemes have been carried out as detailed elsewhere [13,14]. Following the same procedure as in Ref. [11,12,14], the JO analysis and, in turn, radiative properties for the fluorescent levels of Pr^{3+}:LBP (L*n*BP and L*x*FBP) glasses have been estimated.

4. Results and discussions

4.1. Energy levels

The room temperature optical absorption spectra between 400–600 and 900–2500 nm are shown in Fig. 1a and Fig. 1b, respectively, for Pr^{3+}:LBP glasses. The assigned bands shown in Fig. 1 are associated with the electronic transitions from the ground state ($^3H_4$). These band positions and relative intensities are similar to those reported for Pr^{3+}:glasses [11–14].

In all the six Pr^{3+}:LBP glasses $^3H_4 \rightarrow {}^3H_6$, $^3F_{2,3,4}$, $^1G_4$, $^1D_2$ and $^3P_{0,1,2}$ levels have been observed, except for Pr^{3+}:L4BP glass where the $^1G_4$ level is missing. These observed levels have been analysed by fitting with the free ion model Hamiltonian [13,14] in three different ways. In the first fit, all the observed levels for respective systems have been used and varied only electrostatic (F^k, k=2, 4, 6) and spin-orbit (ξ) interaction parameters and fixed remain interaction parameters of two-body configuration (α, β, γ), spin-other-orbit (M^j, j=0, 1, 2) and electrostatically correlated spin-orbit (P^k). In the second fit α and β parameters are also allowed to vary freely. However, in this fit the other parameters are fixed as the number of freely vary parameters should not exceed the number of levels used in the fit. In the third fit, common levels of eight energy levels observed in all six glasses have been used and varied only F^k and ξ. The observed and calculated band positions and best fit parameters obtained in the second fit are shown in Table 1 for Pr^{3+}:L5BP and L5FBP glasses.

In all these fits, it is found that the trends of the free ion parameters are similar but took slightly different magnitudes. The σ values for the data sets obtained in the second fit are found to be relatively smaller than those values obtained in the first and third fits. For example, the $\sigma(N)$ value for Pr^{3+}:L5BP for first, second and third are found to be $\pm$116(9), $\pm$29(9) and $\pm$122(8), respectively. It is also noticed that the magnitudes of the free ion parameters are comparatively smaller for fluoride contents (L*x*FBP) than that of the oxide contents (L*n*BP) of LBP glasses.

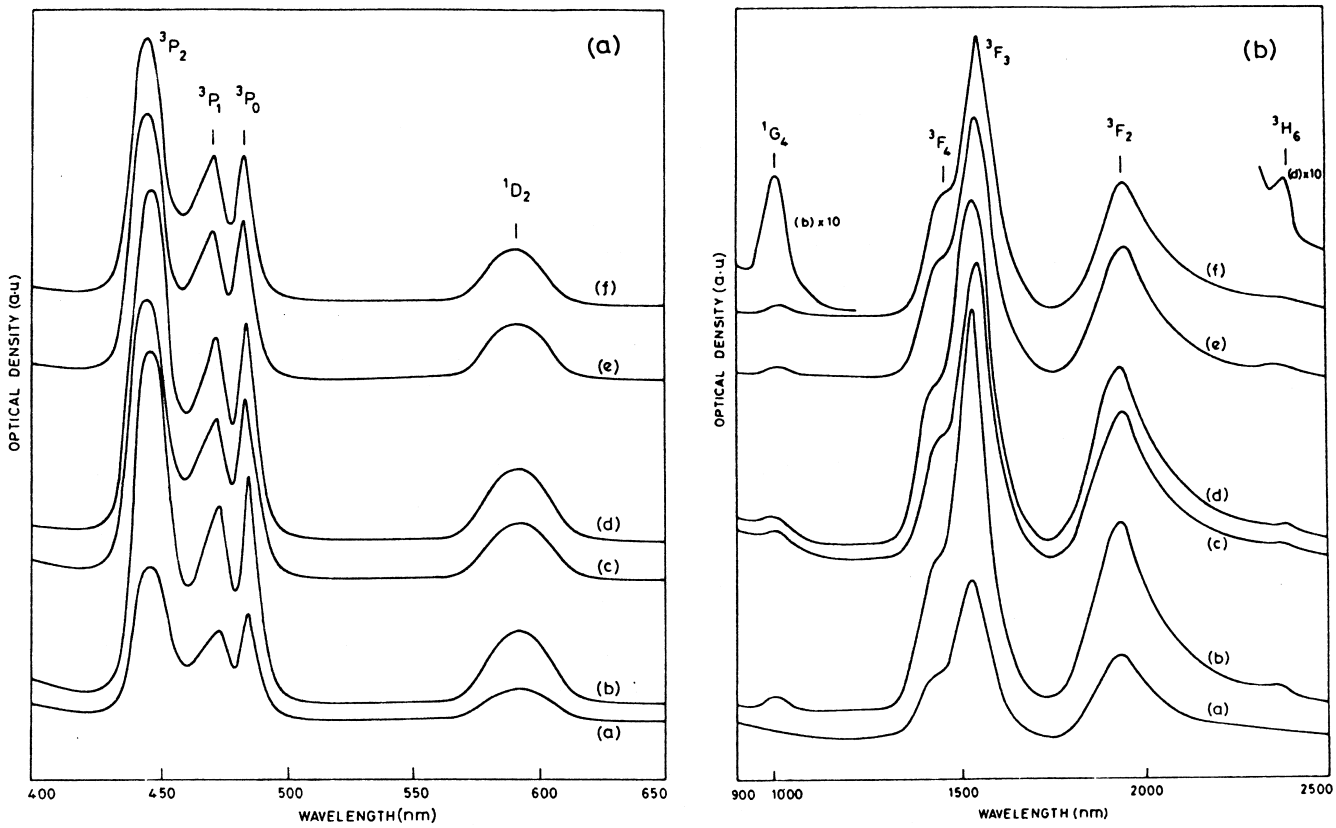

Fig. 1. Absorption spectra of Pr^{3+} ions in (a) L4BP, (b) L5BP, (c) L6BP, (d) L7BP, (e) L2FBP and (f) L5FBP glasses.

Table 1
Experimental (E_{exp}) and calculated (E_{cal}) energies and free ion parameters for Pr^{3+}:L5BP and L5FBP glasses[a]

Level	L5BP		L5FBP		Free ion	L5BP	L5FBP
	E_{exp}	E_{cal}	E_{exp}	E_{cal}			
$^3H_4$	0	−24	0	−22	E_{AVG}	9988	9995
$^3H_5$	—	2074	—	2067	F^2	68979	69229
$^3H_6$	4245	4268	4231	4252	F^4	52397	52030
$^3F_2$	5184	5177	5185	5188	F^6	34614	34291
$^3F_3$	6567	6567	6580	6570	α	15	14
$^3F_4$	6977	6990	6958	6973	β	−1141	−1102
$^1G_4$	9989	9983	9946	9939	γ	[1454]	[1454]
$^1D_2$	16 883	16 889	16 932	16 936	ξ	748	745
$^3P_0$	20 648	20 646	20 747	20 756	M^0	[2.00]	[2.00]
$^3P_1$	21 155	21 213	21 295	21 321	P^2	[236]	[236]
$^1I_6$	—	21 348	—	21 376	N	9	9
$^3P_2$	22 434	22 372	22 507	22 468	σ	±29	±19

[a]All values are in cm^{-1}. N denotes the number of E_{exp} used in parametric fits. The E_{cal} values are obtained using the parameter values listed for respective systems. In all the fits $M^2=0.56M^0$, $M^4=0.38M^0$, $P^4=0.75P^2$ and $P^6=0.50P^2$ are fixed. The values shown in square brackets were held fixed during the fit. σ represent the r.m.s. deviation between observed and calculated energies [13,14].

4.2. Judd–Ofelt analyses and radiative properties

The experimental oscillator strengths have been analysed by using JO theory [9,10] as carried out earlier [11,12,14]. The observed and calculated oscillator strengths for Pr^{3+}:LBP glasses are shown in Table 2. The JO parameters are collected in Table 3. As noticed for other Pr systems, $^3P_2$ transition possesses maximum intensity and fits poorly between experimental and calculated values and also the fit gives Ω_2 with negative sign. The JO parameters have been evaluated for various constraints while fitting the calculated to experimental oscillator strengths to know the dependence between the sign of the Ω_2 and the nature of the transitions that are used in the least-squares fit. It is found that the exclusion of $^3P_2$ and $^3F_2$ transitions yield positive sign for the Ω_2 value, whereas inclusion of either/both of these transitions yield a negative sign for the Ω_2 value. It is also found that significant differences are found in the magnitude of Ω_λ, in particular, Ω_2 value changes to higher values, whereas moderate changes are noticed for Ω_4 and Ω_6.

The predicted lifetimes (τ_R) for $^3P_1$, $^3P_0$ and $^1D_2$ levels of Pr^{3+}:LBP glasses are compared with the values of extensively studied Pr^{3+}:ZnF_2–CdF_2 glass [11] in Table 3. The radiative properties have been predicted using the negative value of Ω_2 (as obtained in the fit) and also by assuming $\Omega_2=0$ [15]. As seen from Table 3 for L4BP and set A of Pr^{3+}:ZnF_2–CdF_2, the τ_R values are almost similar for $^3P_1$ and $^3P_0$ levels but significant changes are noticed for $^1D_2$ transition. The same trend (with respect to set A) is noticed even for Pr^{3+}:ZnF_2–CdF_2 glass either with the modified JO theory [16], set B and set D of Table 3, or by using transition intensities obtained both from absorption and emission measurements, set C. It is also found that the τ_R values predicted by assuming $\Omega_2=0$ are also close to experimental τ_R for Pr^{3+}:ZnF_2–CdF_2 glass, though the

Table 2
Experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths ($\times10^{-6}$) for Pr^{3+}:LBP glasses

Level	L4BP		L5BP		L6BP		L7BP		L2FBP		L5FBP	
	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^3H_6$	0.01	0.38	0.01	0.52	0.01	0.59	0.02	0.74	0.01	0.47	0.01	0.41
$^3F_2$	1.47	1.48	2.19	2.19	2.39	2.39	3.11	3.11	1.83	1.82	1.63	1.63
$^3F_3$	4.09	3.84	5.21	5.17	5.78	5.72	7.26	7.26	4.37	4.44	3.96	3.94
$^3F_4$	1.32	1.82	2.30	2.53	2.58	2.84	3.52	3.73	2.22	2.27	1.91	2.07
$^1G_4$	—	—	0.18	0.25	0.12	0.29	0.19	0.36	0.19	0.22	0.15	0.20
$^1D_2$	0.92	0.64	1.34	0.87	1.41	0.97	1.83	1.23	1.18	0.76	1.03	0.68
$^3P_0$	1.87	2.86	2.76	3.50	2.88	3.72	3.40	4.32	2.14	2.70	1.56	2.23
$^3P_1$	2.52	2.88	3.78	3.53	4.00	3.76	4.87	4.35	3.31	2.73	2.58	2.25
$^3P_2$	5.28	2.03	7.33	2.75	8.20	3.10	10.06	3.91	6.48	2.44	5.53	2.16
N[a]	8		9		9		9		9		9	
σ[a]	±1.23		±1.57		±1.74		±2.10		±1.39		±1.17	

[a]See footnote of Table 1 for explanation.

Table 3
Judd—Ofelt parameters (Ω_λ) and lifetimes (τ_R) for Pr^{3+}:glasses

Glass	Ω_λ ($\times 10^{-20}$ cm^2)			N^a	σ^a	τ_R (μs)		
	Ω_2	Ω_4	Ω_6			$^3P_1$	$^3P_0$	$^1D_2$
Present								
L4BP	−1.02	4.63	2.66	8	1.24	39.0	45.8	1013.0
	0.00	4.63	2.66			35.3	40.5	722.3
L5BP	−0.56	5.64	3.76	9	1.57	28.1	32.3	556.5
L6BP	−0.53	5.97	4.29	9	1.75	26.1	30.0	508.1
L7BP	−0.01	6.89	5.57	9	2.11	22.0	25.3	416.3
L2FBP	−0.26	4.42	3.55	9	1.39	36.9	42.4	697.4
L5FBP	−0.002	3.68	3.27	9	1.17	45.1	51.9	830.2
Reported for ZnF_2–CdF_2 [11][b]								
Set A	−2.19	5.33	7.96	7	3.69	34.9	42.8	736.1
	0.00	5.33	7.96			29.7	34.6	472.4
Set B	0.55	4.75	13.80	7	1.67	26.5	31.1	329.0
Set C	0.72	4.80	7.93	11	2.68	30.5	35.2	441.4
Set D	0.80	4.58	13.88	11	1.19	26.6	31.1	321.9
Exp.						—	40	340

[a]See footnote of Table 1 for explanation.
[b]Set A refers to JO theory and set B to modified JO theory [16] for absorption data only. Set C refers to JO theory and set D refers to modified JO theory both for absorption and emission data.

differences between experimental and calculated τ_R still exist in either case. However, the radiative properties obtained either by using modified JO theory [16] or combined absorption and emission JO analyses are found to be similar to those results obtained from the assumption of $\Omega_2=0$ when it is negative. Due to lack of experimental facilities, we could not measure lifetime for Pr:LBP glasses.

As seen from the trends of Ω_λ for LBP, the Ω_2 decreases while Ω_4 and Ω_6 increase when Li_2CO_3 content decreases in L*n*BP glasses, and also when LiF content increases Ω_λ values decrease for L*x*FBP glasses. The τ_R for all the fluorescent levels of $^3P_1$, $^3P_0$ and $^1D_2$ found to decrease in the order of L4BP→L5BP→L6BP→L7BP for L*n*BP glasses. In the case of L*x*FBP glasses, Ω_λ decreases with increase in content of LiF and, accordingly, τ_R value increases.

5. Conclusions

Absorption spectra of Pr^{3+}:LBP glasses have been measured and used to evaluate Judd–Ofelt parameters. The free ion parameters are found to be dependent on the number of levels considered and number of parameters varied in the energy level fits. Systematic variations between Ω_λ and glass compositions for Pr^{3+}:LBP glasses are noticed, though the resulting negative sign for Ω_2 has no meaning. In the case of negative sign for Ω_2, the radiative properties may also be predicted by assuming $\Omega_2=0$ when emission data are not available. Radiative lifetimes for $^3P_1$, $^3P_0$ and $^1D_2$ levels decreases with decreasing content of Li_2CO_3, whereas it increases with increase in content of LiF. The fluoride content glasses of lithium borates exhibit higher τ_R than those of neat oxide content glasses of lithium borates.

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