Spectroscopic Investigation of Pr^{3+} Doped Zinc Lithium Bismuth Borate Glasses

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Optical absorption and fluorescence spectra of Pr^{3+} doped bismuth borate glasses having glass system (60-x)B_2O_3-10Bi_2O_3-20Li_2O-10ZnO-xPr_6O_{11} where x=1, 1.5 and 2 mol% have been recorded. Judd-Ofelt theory have been applied to compute oscillator strength and intensity parameters Ω_λ (λ=2, 4 and 6). These parameters have been used to calculate the radiative properties of glasses viz., spontaneous emission probability (A), radiative life time (τ_R), fluorescence branching ratio (β_R) and stimulated emission cross section (σ_p) of various emission lines have been evaluated. The results obtained suggest that these new materials can be considered as an interesting candidate for laser applications.

Keywords: Pr^{3+}:ZLiBiB Glasses, Judd-Ofelt theory, Laser Applications.

1. INTRODUCTION

Rare earth ion doped glasses as one kind of attractive laser materials have been received much attention and taken as important part in various areas presently such as fiber amplifiers, up-converters, lasers, electro optic device and optical fiber laser [1-7]. For laser applications the host glass must have low optical loss at the laser wavelength as well as high transparency at the pump wavelength/(s). Borate glasses are transparent, depending upon the composition, from the near ultraviolet to the near infrared (~300 nm to ~2.5 μm) which is sufficient for a wide variety of optical applications. This range can be further extended in the infrared region by the addition of heavy metal oxides such as PbO, Bi_2O_3 and Al_2O_3 to the borate glasses [8,9,10].

Addition of Bi_2O_3 to rare earth doped borate glasses at the moderate level increases the refractive index considerably [11,12]. Large line strengths and small fluorescence line widths are observed in the visible region for such bismuth – borate glasses, making them suitable laser materials for the visible region.

Further, in borate glasses the central rare earth ion is surrounded by BO_3 polymeric structure (boroxol ring) and BO_4 units. When Bi_2O_3 is added to the glass, a progressive conversion of BO_3 units to BO_4 units takes place. With the increase of BO_4 units surrounding the central rare earth ion, the glass becomes more covalent, enhances the line strengths, effective fluorescence line widths decreases and the refractive index of the material increases. A combined effect of all these factors is to yield stimulated emission cross-section larger than those for most of the oxide glasses [12,13,].

Covalency of the rare earth doped bismuth borate glass can be further increased by co-doping the glass with either Li_2O or ZnO [14,15]. With the help of suitable glass former and modifier, stimulated emission cross section and radiative life time for a particular laser transition can be varied in a laser glass according to the specific needs required for a particular laser application [16-19].

2. EXPERIMENTAL

Glasses with the batch compositions (60-x) B_2O_3-10Bi_2O_3-20Li_2O-10ZnO-xPr_6O_{11} with x=1, 1.5 and 2 mol% were prepared using melt quenching technique. All these chemicals are reagent grad and obtained from different standard companies with 99.99% purity. The row materials thoroughly mixed and ground in an agate pestle mortar in 15 g batches. The mixture was then melted in alumina crucibles in silicon carbide based an electrical furnace for 2h at 1050^0 C. The molten glass was then poured in a muffle furnace on to a steel mould and annealed at temperature of 350^0 C for 1 h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. Optically transparent and bubble-free glasses were selected for optical studies.

Glass densities were measured with xylene as an immersion liquid from the Archimedes's principle. The absorption spectra of these glasses were recorded between wavelength ranges 420-650 and 900-2350 nm with a Perkin-Elmer Lambda 750 UV/VIS/NIR Spectrophotometer at room temperature. The emission spectra of the glass samples were recorded using Varian Make Cary Eclipse fluorescence spectrophotometer in the spectral range 480-675 nm using the exciting wavelength 447 nm.

3. RESULT AND DISCUSSION

3.1. Absorption Spectra and Oscillator Strength

The optical absorption spectra of Pr^{3+} doped (60-x)B_2O_3-10Bi_2O_3-20Li_2O-10ZnO-xPr_6O_{11} (where x =1,1.5 and 2 mol%) glass sample are measured at room temperature in the wavelength ranges 420-650 and 900-2350 nm are shown in Figure 1. The optical absorption bands around the $^3P_2$ (445 nm), $^3P_1$ (470 nm), $^3P_0$ (483 nm), $^1D_2$ (591 nm), $^1G_4$ **(**1010 nm**),** $^3F_4$ (1441 nm), $^3F_3$ **(**1519 nm**)** and $^3F_2$ (1923 nm), are assigned from the ground state, $^3H_4$. Assignments to the various observed bands have been made by comparing their band positions with published article [20]. From the absorption spectra, experimental oscillator strengths have been calculated for all the absorption bands are given in Table 1, it is observed that, for the transition $^3H_4 \rightarrow {}^3P_2$ at 445 nm, the oscillator strength is very high compared with the other absorption transitions in all glasses. Thus, the transition $^3H_4 \rightarrow {}^3P_2$ is known as the hypersensitive transition and follows the selection rules $\Delta S = 0$, $\Delta L = 2$, and $\Delta J \leq 2$ [21].

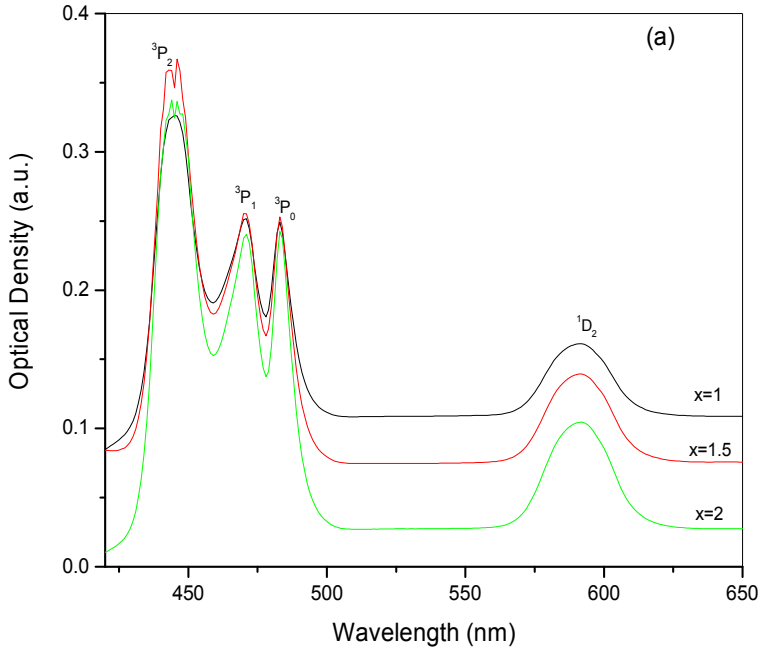

Fig. 1(a): Optical absorption spectra of Pr^{3+}:ZLiBiB glasses in UV-Vis region.

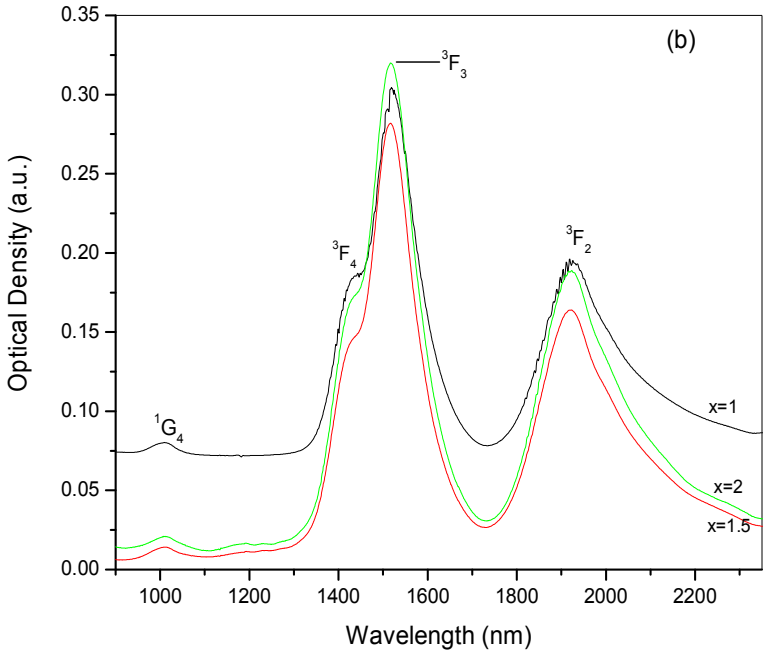

Fig. 1(b): Optical absorption spectra of Pr^{3+}:ZLiBiB glasses in NIR region.

Table 1: Measured ($f_{\exp} \times 10^{+6}$) and calculated ($f_{cal} \times 10^{+6}$) oscillator strength of Pr^{3+} ions in Zinc lithium bismuth borate glasses.

Energy level from $^3H_4 \rightarrow$	Glass-A		Glass-B		Glass-C	
	$f_{\exp}$	f_{cal}	$f_{\exp}$	f_{cal}	$f_{\exp}$	f_{cal}
$^3P_2$	10.107	3.608	9.446	2.819	8.663	2.507
$^3P_1$	3.875	3.788	3.466	2.846	3.038	2.344
$^3P_0$	3.335	2.448	2.796	1.824	2.256	1.474
$^1D_2$	2.142	1.086	1.826	0.848	1.733	0.751
$^1G_4$	0.284	0.315	0.228	0.246	0.208	0.218
$^3F_4$	3.243	3.628	2.646	2.856	2.365	2.559
$^3F_3$	6.964	6.253	5.558	4.871	4.935	4.290
$^3F_2$	3.315	2.982	2.676	2.301	2.412	2.060
r.m.s. deviation	± 2.368		± 2.420		±2.250	

3.2. Judd–Ofelt Intensity Parameters

The Judd–Ofelt intensity parameters Ω_λ (λ = 2, 4, and 6) were calculated by using the fitting approximation of the experimental oscillator strengths to the calculated oscillator strengths with respect to their electric dipole contributions [22,23]. The Judd-Ofelt parameters have been calculated by including $^3H_4 \rightarrow {}^3P_2$ transition but the agreements with experimental results are not good for $^3H_4 \rightarrow {}^3P_2$ transition. For other transitions, including the second hypersensitive transition ($^3H_4 \rightarrow {}^3F_2$ transition), the agreement is reasonable good. The values of Judd-Ofelt intensity parameters are given in Table 2. The lower value of Ω_2 for glass-C indicates that for smaller concentration of Bi_2O_3 (10 mol%), the asymmetry of the ligand field is minimum. The addition of Bi_2O_3 in the glass converts BO_3 units into BO_4 units. An increased formation of BO_4 units leads to close packing of oxygen atoms around the rare earth ion resulting in higher symmetry around the rare earth site. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 0.6 and 0.7 in the present glasses. This shows that these glasses are fairly rigid as compared to borosilicate glasses [24].

Table 2: Judd-Ofelt intensity parameters (Ω_2, Ω_4 and Ω_6) of Pr^{3+}: ZLiBiB glasses.

Glass	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)	Ω_4 / Ω_6
A	1.219	3.758	5.495	0.683
B	0.976	2.797	4.332	0.646
C	0.991	2.261	3.900	0.579

3.3. Fluorescence Spectra

Figure 2 represents the excitation spectrum of (1 mol%) Pr^{3+} ions doped glass, which was measured by monitoring an intense emission at 610 nm. There are three obvious excitation peaks from the excitation spectrum, and these are assigned to the electronic transition with ground level $^3H_4$ to higher energy level of Pr^{3+} , i.e., $^3H_4 \rightarrow {}^3P_2$ (447 nm), $^3H_4 \rightarrow {}^3P_1$ (471 nm) and $^3H_4 \rightarrow {}^3P_0$ (484 nm), based on energy levels. From these excitation transitions, 447 nm wave length has been selected for the measurement of emission spectrum (though the observed three excitation bands are with nearly equal intensity).

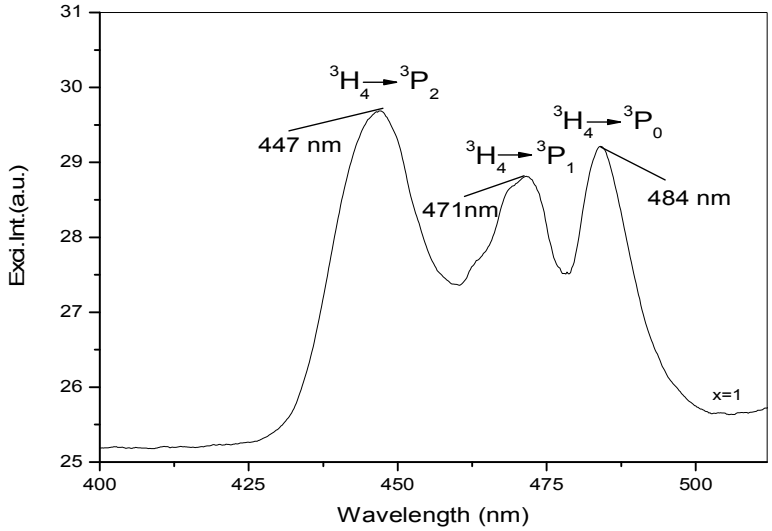

Fig. 2: Excitation spectrum of (1 mol%) Pr^{3+} ions doped glass.

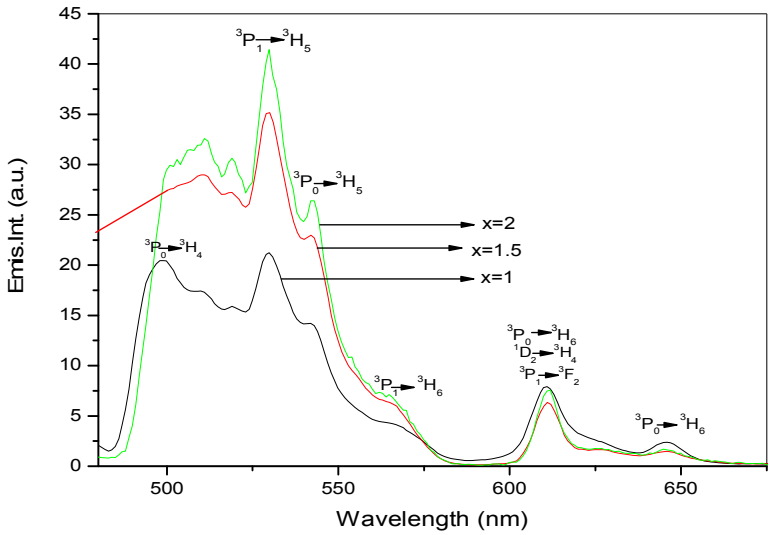

Fig. 3: Emission spectrum of Pr^{3+} : ZLiBiB glasses.

Figure 3 shows the emission spectra of Pr^{3+}: ZLiBiB glasses. As a consequence of which, six fluorescence bands around 499, 530, 542, 567, 611 and 645 nm, have been assigned ($^3P_0 \rightarrow {}^3H_4$), ($^3P_1 \rightarrow {}^3H_5$), ($^3P_0 \rightarrow {}^3H_5$), ($^3P_1 \rightarrow {}^3H_6$), ($^3P_0 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3F_2$) and ($^3P_0 \rightarrow {}^3F_2$), for glass-A respectively.

While praseodymium doped glass-B and glass-C reports fluorescence spectrum with five peaks namely ($^3P_1 \rightarrow {}^3H_5$), ($^3P_0 \rightarrow {}^3H_5$), ($^3P_1 \rightarrow {}^3H_6$), ($^3P_0 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3F_2$) and ($^3P_0 \rightarrow {}^3F_2$), respectively for two glass specimens. They are also assigned to various transitions on basis of energy consideration as shown in Table 3.

Table 3: Emission peak wavelengths ($\lambda_{p,}$), radiative transition probability (A_{rad}), branching ratio (β), stimulated emission cross-section ($\sigma_p(\Delta\lambda_{eff})$), total radiative transition probability (A_T) and radiative life time (τ_r) for various transition in Pr^+ ions doped ZLiBiB glasses.

Tran-sition	λ_{max} (nm)	ZLiBiB 1			ZLiBiB 2			ZLiBiB 3		
		A_{rad} (s^{-1})	β	σ_p (10^{-20} cm^2)	A_{rad} (s^{-1})	β	σ_p (10^{-20} cm^2)	A_{rad} (s^{-1})	β	σ_p (10^{-20} cm^2)
$^3P_0 \rightarrow {}^3H_4$	499	15616	0.5538	2.47	-	-	-	-	-	-
$^3P_1 \rightarrow {}^3H_5$	530	10520	0.3852	2.78	7992	0.3372	2.62	6705	0.3028	2.55
$^3P_0 \rightarrow {}^3H_5$	542	-	-	-	-	-	-	-	-	-
$^3P_1 \rightarrow {}^3H_6$	567	3761	0.1377	-	2970	0.1253	-	2680	0.1210	-
$^3P_0 \rightarrow {}^3H_6$	611	5279	0.1872	3.60	4160	0.1695	3.53	3753	0.1552	3.18
$^1D_2 \rightarrow {}^3H_4$	611	972	0.4479	0.66	758	0.3875	0.64	672	0.3594	0.57
$^3P_1 \rightarrow {}^3F_2$	611	1443	0.0528	0.98	1155	0.0487	0.98	1175	0.0531	1.00
$^3P_0 \rightarrow {}^3F_2$	645	4027	0.1428	3.27	3230	0.1316	-	3238	0.1357	-
	A_T ($^3P_0$) = 28200 s^{-1}, τ_{rad} ($^3P_0$) = 35 µs A_T ($^3P_1$) = 27308 s^{-1}, τ_{rad} ($^3P_1$) = 37 µs A_T ($^1D_2$) = 2170 s^{-1}, τ_{rad} ($^3P_0$) = 462 µs				A_T ($^3P_0$) = 24539 s^{-1}, τ_{rad} ($^3P_0$) = 41 µs A_T ($^3P_1$) = 23703 s^{-1}, τ_{rad} ($^3P_1$) = 42 µs A_T ($^1D_2$) = 1956 s^{-1}, τ_{rad} ($^3P_0$) = 511 µs			A_T ($^3P_0$) = 24184 s^{-1}, τ_{rad} ($^3P_0$) = 41 µs A_T ($^3P_1$) = 22144 s^{-1}, τ_{rad} ($^3P_1$) = 45 µs A_T ($^1D_2$) = 1870 s^{-1}, τ_{rad} ($^3P_0$) = 535 µs		

A comparison of fluorescence spectra of all glasses shows that the addition of Bi_2O_3 has enhanced the fluorescence intensity of the bands at 499, 611 and 645 nm considerable in glass-A. The fluorescence spectra has been used to drive radiative properties, which are more popularly known as laser parameters [25,26] viz., spontaneous emission probability (A), radiative life time (τ_R), fluorescence branching ratio (β_R) and stimulated emission cross section (σ_p) of the various emission transitions are calculated and are

presented in Table 3. It has already been noted that the conversion of BO_3 units to BO_4 units takes place when Bi_2O_3 is added to the glass, increase of BO_4 units surrounding the central rare earth ion, the glass becomes more covalent, enhances the line strengths, effective fluorescence line widths decreases and the refractive index of the material increases. A combined effect of all these factors is to yield stimulated emission cross-section larger than those for most of the oxide glasses.

The values of spontaneous emission probability (A) and stimulated emission cross-section (σ_p) are found to be maximum for the transition $^3P_0 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3H_5$ and $^3P_0 \rightarrow {}^3H_6$ for glass-A and transition $^3P_1 \rightarrow {}^3H_5$ and $^3P_0 \rightarrow {}^3H_6$ for glass (B and C), suggesting them to be the most probable laser transition. Next suitable transition for laser action is $^3P_0 \rightarrow {}^3F_2$ for glass A which also has relatively high value of A and σ_p parameters. $^3P_0 \rightarrow {}^3H_5$, $^3P_1 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3H_4$ and $^3P_1 \rightarrow {}^3F_2$ are relatively poor laser transitions for all glasses.

The high values of the fluorescence branching ratio for the transitions $^3P_0 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3H_5$ and $^1D_2 \rightarrow {}^3H_4$ for glass-A and the transitions $^3P_1 \rightarrow {}^3H_5$ and $^1D_2 \rightarrow {}^3H_4$ for glass (B and C) indicate them to contribute almost total fluorescence and hence, these appear to be equally promising laser transitions.

4. CONCLUSION

In summary, it is concluded, that we have successfully developed transparent, moisture resistant and more stable Pr^{3+} doped zinc lithium bismuth borate glasses for their optical characterization. The JO intensity parameters Ω_λ (λ = 2, 4, and 6) have been calculated from the measured oscillator strength of the absorption spectra of Pr^{3+}:ZLiBiB glasses. The spectroscopic quality factor (Ω_4/Ω_6), branching ratio (β_R) and the stimulated emission cross section (σ_p) values are calculated for present glasses. It could be observed that glass-A possess better values compared to the other two glass system (B and C). Stimulated emission cross section (σ_p) is the most important laser parameter. It signifies the rate of energy extraction from the laser materials. The high values of σ_p ~ 2.47 to 3.60 pm^2 for the transitions $^3P_0 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3H_5$ and $^1D_2 \rightarrow {}^3H_4$ confirm them to be laser transitions.

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