OPTICAL ABSORPTION AND STRUCTURAL STUDIES OF Pr^{3+} DOPED CADMIUM BISMUTH BORATE GLASSES IN VISIBLE AND NEAR INFRARED REGIONS

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Glasses having composition $20\text{CdO} \cdot x\text{Bi}_2\text{O}_3 \cdot (79.5-x)\text{B}_2\text{O}_3 \cdot 0.5\text{Pr}_6\text{O}_{11}$ with x varying from 15 to 35 mol% have been synthesized. Optical absorption and fluorescence spectra were measured at ambient temperature. A close correlation is observed between the Bi_2O_3 content and the spectroscopic properties such as Judd-Ofelt intensity parameters Ω_λ ($\lambda = 2, 4, 6$), radiative and structural properties of prepared glasses doped with Pr^{3+} ion. The variation of Ω_2 with Bi_2O_3 content has been attributed to changes in the asymmetry of the ligand field at the rare earth (RE) ion site (due to structural change) and to changes in RE-O covalency, whereas the variation of Ω_6 has been related to the variation in RE-O covalency. Following the luminescence spectra, various radiative properties like transition probability (A_{rad}), radiative lifetime (τ_r), branching ratio (β_r) and stimulated emission cross section (σ) have been calculated. The branching ratio for $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transition of Pr^{3+} glass system arrive at 41 to 40%, respectively, and the predicted spontaneous radiative transition probability rates are high and varies from 14032 to 14864 s^{-1} . In addition, the glass stability is improved in which the substitution of B_2O_3 for Bi_2O_3 strengthens the glass network structure. The bismuth based glass as a host for Pr^{3+} ion doped suggesting their suitability for laser applications.

Keywords: Glasses; Optical Materials; Spectroscopic Properties.

1. Introduction

Glasses based on heavy metal oxides (HMO) are becoming an important class of materials for optoelectronic applications. The large mass, low field strength and high polarizability of bismuth gives some special significance to glasses that are developed. Also bismuth oxide has the ability to form stable glasses over a wide range of concentration due to its dual role, as glass former and modifier. Among the rare earth ions, trivalent praseodymium ions (Pr^{3+}) have different applications due to a large number of available absorption bands in the UV, visible and near infrared regions. It is used for optical amplifiers, up-converters and other electro optic devices [1-3]. Spectral properties of Pr^{3+} ions doped glasses have been widely investigated because the energy levels of Pr^{3+} ions are such that the emission spectrum also ranges from UV to infrared. Pr^{3+} ions

doped glass fiber are currently used as promising device for optical communication system based on 1.3 μm radiation [4]. Laser action has been observed for $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition [5-7] of the Pr^{3+} ions. The intensity of the transitions for the rare earth ions has been calculated by using the Judd-Ofelt theory [8-9]. This theory defines a set of three intensity parameters Ω_λ ($\lambda = 2, 4, 6$) which are sensitive to the environment of the rare earth ions. These intensity parameters have been used to calculate important optical properties such as radiative transition probability for spontaneous emission, radiative life time of the excited state, branching ratio and stimulated emission cross-section. The intensity parameter Ω_2 is an indicator of the covalency of the rare earth-oxygen bond and it is sensitive to the structural changes in the glass. In bismuth borate glasses, Ω_2 varies due to the conversion of three coordinated boron atoms (B_3) to four coordinated boron atoms (B_4) and the change in the number of non-bridging oxygens ions ($\text{NBO}'\text{s}$). In this paper, we have studied the effect of bismuth oxide on the absorption, emission and structural properties of Pr^{3+} doped cadmium bismuth borate glasses. We have chosen this heavy metal based glasses to incorporate the Pr^{3+} ions because these glasses have large glass forming region, high refractive index, good physical and chemical stability and large transmission window [10-12].

2. Experimental Details

Pr^{3+} doped glasses having composition $20\text{CdO} \cdot x\text{Bi}_2\text{O}_3 \cdot (79.5-x)\text{B}_2\text{O}_3 \cdot 0.5\text{Pr}_6\text{O}_{11}$, ($15 \leq x \leq 35$, x in mol%) were prepared by using melt-quench technique. The 15g batches of analar grade chemicals were taken in appropriate proportion and were melted at 1150°C for 40 minutes. The glass samples were obtained by pouring and quenching the melt in between two stainless steel plates held at room temperature (RT). The amorphous nature of the prepared samples was confirmed by recording X-ray diffraction patterns using Miniflex-II (Rigaku) X-ray diffractometer. The refractive index (n) of the polished samples was measured by the Brewster angle method using He-Ne laser (632nm). The optical absorption spectra of all the polished samples were recorded at RT in the wavelength range 300-3200 nm using a spectrophotometer (Varian-Carry 5000). The emission spectra were recorded using a spectrofluorometer (JobinYvon Fluorolog-3) at an excitation wavelength of 450 nm. The IR spectra of all the samples were recorded in the range 400-4000 cm^{-1} at RT with a spectral resolution of 4 cm^{-1} using FTIR spectrometer (Shimadzu FTIR 8001PC).

3. Results and Discussion

The optical absorption spectra of CBBP1 glass sample are shown in Fig. 1. From this spectra, absorption bands at 442, 470, 482, 586, 886, 1422, 1518, and 1866 nm are observed and these bands are assigned to following transitions for Pr^{3+} ion: $^3\text{H}_4 \rightarrow ^3\text{P}_{2,1,0}$, $^3\text{H}_4 \rightarrow ^1\text{D}_2$, $^3\text{H}_4 \rightarrow ^1\text{G}_4$, and $^3\text{H}_4 \rightarrow ^3\text{F}_{4,3,2}$ respectively.

Fig. 1 Optical absorption spectra of Pr^{3+} doped $20\text{CdO} \cdot 15\text{Bi}_2\text{O}_3 \cdot 64.5\text{B}_2\text{O}_3 \cdot 0.5\text{Pr}_6\text{O}_{11}$ (CBBP1) glass

The observed absorption bands can be divided into three groups; transition from $^3\text{H}_4 \rightarrow ^1\text{G}_4$ and $^3\text{H}_4 \rightarrow ^3\text{F}_{4,3,2}$ in the infrared region, the $^3\text{H}_4 \rightarrow ^1\text{D}_2$ transition at 586 nm and $^3\text{H}_4 \rightarrow ^3\text{P}_{2,1,0}$, complex group of transitions in violet to blue region. For calculating oscillator strength of the overlapped peaks, the area of the peaks was estimated by extrapolating up to the base line. In order to estimate the intensities for the transitions $^3\text{H}_4 \rightarrow ^3\text{P}_{2,1,0}$, it is first noted that the base line for the absorption is rising towards the higher frequency side. Since the peaks are distinct we extended the two sides of individual lines linearly to this base line and measured each such triangular area. In the region of overlap, the proportion of intensity contributed by different transitions is so adjusted that the relative intensities as estimated by the peak height are not unduly modified. The experimental oscillator strengths, which measure the intensity of absorption transitions from the ground $^3\text{H}_4$ level to various excited levels, have been measured by relation $f_{\text{expt}} = 4.318 \times \int \epsilon(\nu) d\nu$ and the values are given in Table 1. The transitions $^3\text{H}_4 \rightarrow ^3\text{P}_2$ and $^3\text{H}_4 \rightarrow ^3\text{F}_2$ of Pr^{3+} ions have been labeled as hypersensitive transitions as these transitions are strongly dependent on the neighbouring ligands [13] and these obey the selection rules: $\Delta S = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$ [14].

Table 1. Oscillator strength for some transitions from the indicated levels to the ground level $^3\text{H}_4$, with their root mean square deviation (δ_{RMS}), which indicates the fit quality of theoretical and experimental results and Judd-Ofelt intensity parameters for Pr^{3+} ions, doped CBBP glasses.

Transition from ground state $\rightarrow ^3\text{H}_4$	λ nm	Oscillator strength (10^{-8})									
		CBBP1		CBBP2		CBBP3		CBBP4		CBBP5	
		f_{expt}	f_{cal}	f_{expt}	f_{cal}	f_{expt}	f_{cal}	f_{expt}	f_{cal}	f_{expt}	f_{cal}
$^3\text{P}_2$	442	388	383	377	337	306	296	269	297	234	251
$^3\text{P}_1$	470	442	395	389	381	325	364	307	304	284	295
$^3\text{P}_0$	482	169	261	142	208	138	162	133	129	109	115
$^1\text{D}_2$	586	289	267	256	227	248	227	207	220	183	198
$^1\text{G}_4$	886	385	383	382	338	323	363	261	298	249	284
$^3\text{F}_3$	1518	395	412	269	223	254	238	241	260	201	251
$^3\text{F}_2$	1886	233	219	217	197	150	130	113	123	99	101
$\delta_{\text{RMS}} (10^{-6})$		2.06		2.34		3.09		2.048		4.01	
$\Omega_2 (10^{-20}\text{cm}^2)$		5.15		5.57		7.17		7.63		7.82	
$\Omega_4 (10^{-20}\text{cm}^2)$		4.14		2.91		2.69		2.41		1.98	
$\Omega_6 (10^{-20}\text{cm}^2)$		3.63		2.73		2.21		2.38		1.67	

The oscillator strength of these peaks shows a peculiar behavior, the strength decreases as Bi_2O_3 concentration increases from 15 to 35 mol%. Using the experimental oscillator strengths, the host dependent Judd-Ofelt intensity parameters Ω_λ ($\lambda=2,4,6$) and calculated oscillator strength for observed electric dipole transitions within the $4f^2$ configuration

have been determined using the Eq. $f_{\text{cal}}(\Psi J; \Psi' J') = \frac{8\pi^2 m c \nu}{3h(2J+1)} \left[\frac{(n^2+2)^2}{9n} \right] \times$

$\sum_{\lambda=2,4,6} \Omega_\lambda (\Psi J \| U^\lambda \| \Psi' J')^2$ with the help of least square fit procedure and also presented

in Table 1. It has been noted that the Judd-Ofelt theory is not very successful in case of Pr^{3+} ion as the energy levels corresponding to the ground configuration $4f^2$ and the first excited $4f^1 5d^1$ state differ very little in energy. Because of this small energy separation, a negative value for the Ω_2 parameter has been reported [15] and there is usually a poor agreement between the theoretically estimated and experimentally measured results for various optical parameters [15]. The Judd-Ofelt parameters have been recalculated after including/excluding $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transition but it was noted that neither the calculated oscillator strength nor the δ_{rms} deviation showed any significant improvement. Therefore, in the present work the Judd-Ofelt parameters have been calculated by including $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transition. Further, no unphysical (like negative) values for Ω_2 have been found but the agreement with experimental results is not good for $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transition. For other transition, including the second hypersensitive transition ($^3\text{H}_4 \rightarrow ^3\text{F}_2$), the agreement is reasonably good. Table 1 shows that Ω_2 increases whereas Ω_4 and Ω_6 decrease with increase in the Bi_2O_3 content in the host glasses. These intensity parameters reflect the local structure and bonding in the vicinity of rare earth ions to some extent. As

a general conclusion, Ω_2 parameter increases with asymmetry of the local structure and with the degree of covalency of the lanthanide-ligand bonds, whereas Ω_6 parameter decreases with the tendency of covalency. In addition, Ω_4 parameter is believed to be related to the bulk properties of the samples [16]. It has been experimentally observed in the similar glasses doped with Sm^{3+} ions [17], with the addition of Bi_2O_3 , the BO_3 units in the glass convert to 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 ion site and hence increase in the value of Ω_2 . Fig. 2 shows the fluorescence spectra for CBBP1 to CBBP5 glass samples recorded at RT ($\lambda_{\text{ext}} = 450$ nm). This figure shows four peaks around 483, 498, 612, and 651 nm. These fluorescence peaks are assigned to $^3\text{P}_1 \rightarrow ^3\text{H}_4$, $^3\text{P}_0 \rightarrow ^3\text{H}_{4,6}$ and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transitions, respectively.

Fig. 2 Emission spectra of Pr^{3+} doped $20\text{CdO} \cdot x\text{Bi}_2\text{O}_3 \cdot (79.5-x)\text{B}_2\text{O}_3 \cdot 0.5\text{Pr}_6\text{O}_{11}$ (CBBP) glasses

The first and most interesting observation is that the intensity of the fluorescence peak at 482 nm corresponding to $^3\text{P}_1 \rightarrow ^3\text{H}_4$ transition increases with increasing Bi_2O_3 concentration (maximum when $x = 30$ mol%). The another important observation is that the last two peaks $^3\text{P}_0 \rightarrow ^3\text{H}_6$ and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ have very low intensity for CBBP1 glass and the intensity for these transitions increases with increase in Bi_2O_3 content in the host glasses. The enhancement of the fluorescence intensity is probably attributed due to structural change in the glass network on substitution of B_2O_3 by Bi_2O_3 . The fluorescence spectra have been used to derive radiative parameters like radiative transition probability

(A_{rad}), branching ratio (β_r), radiative life time of excited state (τ_r) and stimulated cross-section (σ) etc. and these parameters are presented in Table 2. It has already been noted that the conversion of BO_3 units to BO_4 units takes place with the increase of Bi_2O_3 content, so it is seems that the existence of BO_4 units are more suitable for fluorescence.

Table 2. The peak wavelength (λ_p), radiative transition probability (A_{rad} (s^{-1})), branching ratio (β_r , (%)), ,stimulated emission cross-section (σ , (10^{-20} cm^2)), total radiative transition probability (A_T (s^{-1})), radiative life time (τ_r , (μs)) and the total emission cross-section (σ_t (10^{-20} cm^2)) for various transitions in CBBP, Pr^{3+} doped glasses.

Transitio	λ_p	CBBP1			CBBP2			CBBP3			CBBP4			CBBP5		
		A_{rad}	β_r	σ	A_{rad}	β_r	σ	A_{rad}	β_r	σ	A_{rad}	β_r	σ	A_{rad}	β_r	σ
ns																
$^3\text{P}_1 \rightarrow ^3\text{H}_4$	483	2613	0.07	2.48	2702	0.07	3.64	2789	0.07	3.95	2845	0.07	4.79	2912	0.07	5.47
$^3\text{P}_0 \rightarrow ^3\text{H}_4$	498	10997	0.32	3.58	11058	0.31	3.79	11358	0.31	4.26	11528	0.31	4.85	11624	0.31	5.16
$^3\text{P}_0 \rightarrow ^3\text{H}_6$	612	6513	0.19	1.26	6705	0.19	1.58	6894	0.19	2.14	6924	0.19	3.09	7109	0.19	3.98
$^3\text{P}_0 \rightarrow ^3\text{F}_2$	652	14032	0.41	8.58	14241	0.41	9.29	14578	0.40	10.25	14784	0.40	13.57	14864	0.40	15.08
$A_T(\text{s}^{-1})$		34155			34706			35619			36081			36509		
$\tau_r(\mu\text{s})$		29.27			28.81			28.07			27.72			27.39		
σ_t		15.90			18.30			20.60			22.30			29.69		

Therefore high spontaneous emission probability and large branching ratio, low maximum phonon energy is a necessary condition for obtaining fluorescence emission because the emission efficiencies for a rare-earth ion are strongly related to the non-radiative losses from relative excited states. Table 2 shows that the predicted spontaneous emission probability for the transition $^3\text{P}_0 \rightarrow ^3\text{F}_2$ increases from 14032 to 14864 s^{-1} with increase in Bi_2O_3 concentration. The branching ratio (β_r) is evaluated for each transition and values are presented in Table 2. This table shows that the branching ratio (~41%) for this emission is much larger than other transitions, so this transition ($^3\text{P}_0 \rightarrow ^3\text{F}_2$) of Pr^{3+} ions is reasonably efficient in the present host. It is observed that σ increases with increase in Bi_2O_3 content. Therefore, the large stimulated emission cross-section in the present glass is an attractive feature for low-threshold, high gain applications and can be utilized to obtain continuous wave (CW) laser action. It has been reported that in Sm^{3+} and Er^{3+} doped zinc/cadmium bismuth borate [10-12, 17], the radiative transition probabilities and the stimulated emission cross-section are large. Therefore the present Pr^{3+} doped cadmium bismuth borate glasses may be utilized as potential laser materials. The IR spectra of the prepared glasses are shown in Fig. 3. From this figure it is observed that the intensity of the band around 510 cm^{-1} , corresponding to *Bi-O-Bi* vibration of distorted [*BiO*₆] octahedral units [18] increases and the band shifts to lower wave numbers with increase in Bi_2O_3 content. The non appearance of the vibration band around 840 cm^{-1} corresponding to [*BiO*₃] polyhedra [19] implies that only [*BiO*₆] octahedral units build up the bismuthate structure of the investigated glasses.

Fig. 3 IR spectra of Pr^{3+} doped $20\text{CdO} \cdot x\text{Bi}_2\text{O}_3 \cdot (79.5-x)\text{B}_2\text{O}_3 \cdot 0.5\text{Pr}_6\text{O}_{11}$ (CBBP) glasses

The band corresponding to the bending vibration of $B-O-B$ in $[\text{BO}_3]$ units shifts from 670 cm^{-1} (CBBP1) to 685 cm^{-1} (CBBP5) [20-21]. This shift may be due to the influence of the electrostatic field associated with the strongly polarizing Bi^{3+} ions. The increase in Bi_2O_3 content results in the increase of the electron cloud density around oxygen of $[\text{BO}_3]$ units, thereby, leading to an increase in the roll torque of $B-O-B$ bond and consequently contributes to the shifting of the bending vibration $B-O-B$ bond towards higher wave number. The infrared spectral range $900\text{--}950 \text{ cm}^{-1}$ is typical for the stretching vibration of $[\text{BO}_4]$ units [22]. The existence of $[\text{BO}_4]$ units indicates that the addition of Bi_2O_3 into the glass replacing B_2O_3 causes a progressive conversion of $[\text{BO}_3]$ units to $[\text{BO}_4]$ units. The band between $1200\text{--}1400 \text{ cm}^{-1}$ is assigned to the stretching vibration of $[\text{BO}_3]$ units [20].

4. Conclusions

The radiative properties of Pr^{3+} ions doped cadmium bismuth borate glasses have been studied. Effect of bismuth oxide on the absorption and emission spectra were investigated with the help of Judd-Ofelt theory. The variation of Judd-Ofelt intensity parameters are discussed and correlated to the structural changes in the glass network. Fluorescence intensity is enhanced with the addition of bismuth oxide. The radiative properties like spontaneous emission probability, radiative life time, branching ratio and stimulated emission cross-section in the present glasses has been determined. The branching ratio for $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transition in the present glass is 41% and the predicted spontaneous radiative transition rate is as high as 14864 s^{-1} for CBBP5 sample. This is beneficial for achieving laser action in Pr^{3+} doped cadmium bismuth borate glasses. Further, the radiative emission probability for Pr^{3+} ions this glass is as high as in zinc/cadmium bismuth borate glasses, which have been successfully used as laser material. This indicates that the present Pr^{3+} doped cadmium bismuth borate glasses can act as potential laser material.

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