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Spectroscopic Properties of Nd^{3+} Doped Zinc Lithium Bismuth Borate Glasses

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ABSTRACT

Zinc lithium bismuth borate glasses containing Nd^{3+} in (25- x): Bi_2O_3:20Li_2O:20ZnO: 35B_2O_3:xNd_2O_3 (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by x-ray diffraction studies. Optical absorption spectra were recorded at room temperature for all glass samples. Slater-Condon parameters F_k (k=2, 4, 6), Lande's parameter ξ_{4f} and Racah parameters E^k (k=1, 2, 3) have been computed. Using these parameters energies and intensities of these bands has been calculated. Judd-Ofelt intensity parameters Ω_λ (λ=2, 4, 6) are evaluated from the intensities of various absorption bands of optical absorption spectra. Using these intensity parameters various radiative properties like spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross–section of various emission lines have been evaluated. The stimulated emission cross section (σ_p) for the transition ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) is found to be in the range 2.75– 2.86 × 10^{-20} cm^2. The σ_p values are comparatively large suggesting the possible utilization of these materials in laser applications.

Keywords: ZnLiBiB Glasses, Optical Properties, Judd-Ofelt Theory, Rare earth ions.

1. INTRODUCTION

Glasses based on heavy metal oxide (HMO) are becoming an important class of materials for optoelectronic application[1,2]. Among various glasses, borate glasses are excellent host matrices because boric oxide (B_2O_3) acts as a good glass former and flux material[3]. Bismuth oxide contained host glass matrix improves chemical durability of the glass[4]. Despite, the Bi_2O_3 is not a classical network former, it exhibits some superior properties like high refractive index, high density, high optical basicity and large polarizability[5]. Bismuth based oxide glasses have attracted the attention of the scientific community, due to their important applications in the field of glass ceramics, thermal and mechanical sensors, reflecting windows[6-9]. Some of recent studies indicate that bismuth borate glass could be a good choice as a host material to achieve a flat gain for dense wave length division multiplexing application[10]. Nd^{3+} doped materials have proven to be among the most efficient candidates for photonic devices, such as lasers, microchop lasers and planer wave guides[11-13]. Glass scientists have started exploring the potential of Nd^{3+} doped heavy metal oxide glasses, because it has emerged as an excellent lasing medium at 1μm to 1.34 μm.

A survey of the literature shows that there are many reports available on ternary bismuth borate glasses[14-16]. Bismuth in glasses plays a dual role as a glass network former (NWF) at high concentration and a modifier (NWM) at low concentration[17].

In the present work, the absorption spectra of Nd^{3+} doped ZnLiBiB glasses have been investigated. From the spectral data various energy interaction parameters like Slater-Condon parameters F_k (k=2, 4, 6), Lande's parameter ξ_{4f} and Racah parameters E^k (k=1, 2, 3) have been computed. The Judd-Ofelt theory has been applied to compute the intensity parameters Ω_λ (λ=2, 4, 6).To understand the laser efficiency of these materials, the value of spectroscopy quality factor (Ω_4/ Ω_6) has been evaluated. These intensity parameter have been used to evaluate optical properties such as spontaneous emission probability, branching ratio, radiative life time and stimulated emission cross section. Large stimulated emission cross section is one of the most important parameters required for the design of high peak power solid state lasers. The effect of bismuth borate matrix on the fluorescence properties of Nd^{3+} is investigated. The compositional dependence of the stimulated emission cross section of the ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) transition of Nd^{3+} is discussed.

2. EXPERIMENTAL

The following Nd^{3+} doped bismuth borate glass samples (25−x) Bi_2O_3: $20Li_2O$: $20ZnO$:$35B_2O_3$:xNd_2O_3 (where x =1, 1.5, 2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of Bi_2O_3, Li_2O, ZnO, and B_2O_3 and Nd_2O_3. They were thoroughly mixed by using an agate pestlemortar.Then melted at 1060˚C by an electrical muffle furnace for 2 hours. After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of 350˚C for 2 h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in Table 1.

Table 1. Chemical composition of the glasses.

Sample	Glass composition (mol %)
ZnLiBiB (UD)	$25Bi_2O_3$:$20Li_2O$:20ZnO:$35B_2O_3$
ZnLiBiB (ND1)	$24Bi_2O_3$:$20Li_2O$:20ZnO: $35B_2O_3$:$1Nd_2O_3$
ZnLiBiB (ND1.5)	$23.5Bi_2O_3$:$20Li_2O$:20ZnO: $35B_2O_3$:$1.5Nd_2O_3$
ZnLiBiB (ND2)	$23Bi_2O_3$:$20Li_2O$:20ZnO: $35B_2O_3$:$2Nd_2O_3$
ZnLiBiB (UD)—	Represents undoped Zinc Lithium Bismuth Borate glass specimens
ZnLiBiB (PR)—	Represents Nd^{3+} doped Zinc Lithium Bismuth Borate glass specimens

3. RESULTS AND DISCUSSION

3.1. XRD Measurement

Figure 1 presents the XRD pattern of the samples shows no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

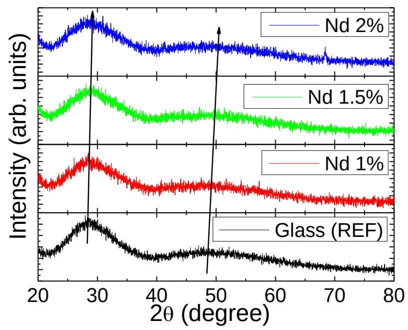

Fig.1: X-ray diffraction pattern of Bi_2O_3:Li_2O: ZnO: B_2O_3:Nd_2O_3 glasses.

3.2. Physical Properties

Table 2 Various Physical Properties of Nd^{3+} doped ZnLiBiB glass specimens

Physical properties	ZnLiBiB (ND01)	ZnLiBiB (ND1.5)	ZnLiBiB (ND02)
Refractive Index n, at 589.3 nm	1.888	1.889	1.891
Density, d (g/cm)	3.4	3.9	4.02
Thickness, t (cm)	0.233	0.255	0.256
Average molecular weight M(g)	161.826	161.172	160.530
Rare earth ions concentration N($\times 10^{21}$ions/cms)	1.265	2.186	3.016
Dielectric Constant (ε)	3.56	3.57	3.58
Optical Dielectric Constant (pdt/dp)	2.56	2.57	2.58
Molar Volume V_m (gm/cm^3)	47.596	41.328	39.933
Reflection losses (R)	9.454	9.469	9.498
Molar refractvity (R_m)	21.936	19.062	18.448
Energy gap(E_g)	3.726	3.105	2.789
Polaron radius (r_p)(A^0)	5.813	5.805	5.789
Interionic distance (r_i)(A^0)	9.246	7.7054	5.570
Electronic polarizability α_e(10^{-23}ions cm^{-3})	0.1829	0.1830	0.1833
Field strength F($10^{16}\times$cm^{-2})	0.168	0.264	0.329
Optical basicity (Λ)	0.7853	0.7862	0.7872
Molarpolarizability(α_m)	8.705	7.564	7.321
Oxide ions polarizability($\alpha_O^{2-(n)}$) Å^3	3.574	3.051	2.935
Oxygen packing density(OPD)	46.22	53.23	55.09
Metallization criterion(M)	0.5391	0.5388	0.5380

The measured density, molar volume and refrective index of Nd^{3+} doped zinc lithium bismuth borate glass samples for different concentrations are shown in Table 2. Based on the measurement of density, molar volume and refrective index various physical parameters e.g. electronic polarizability, ionic concentrations, polaron radius, molar refraction, Inter-ionic distance and field strength, etc. are calculated and are also listed in Table 2.

The density and refractive index increases with an increase in concentration of Nd_2O_3. The other two properties of polarizability and optical basicity also rise over the doping concentration. Increase in optical basicity results in increasing ability of oxide ions to donate electrons to surrounding cation. The electrons polarizability shows a general trend of increase with increase in refractive index.

3.3. Absorption spectra

The absorption spectra of ZnLiBiB (ND 01) glass, consists of absorption bands corresponding to the absorptions from the ground state $^4I_{9/2}$ of Nd^{3+} ions. Nine absorption bands have been observed from the ground state $^4I_{9/2}$ to excited states $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{5/2}$, $^4G_{7/2}$, $^4G_{9/2}$, and $^2G_{9/2}$ for Nd^{3+} doped ZnLiBiB(ND 01)glass.

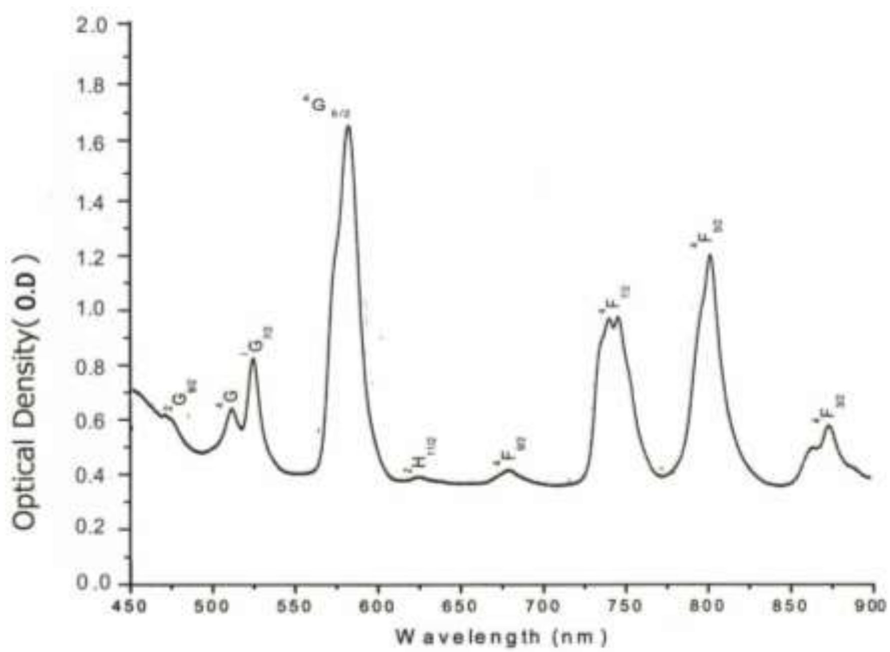

Fig.2: Vis-NIR absorption spectra of ZnLiBiB (ND 01) glass.

The experimental and calculated oscillator strengths for Nd^{3+} ions in zinc lithium bismuth borate glasses are given in Table 3.

Table 3. Measured and calculated oscillator strength ($P^m \times 10^{+6}$) of Nd^{3+} ions in ZnLiBiB glasses.

Energy level from $^3H_4$	Glass ZnLiBiB (ND01)		Glass ZnLiBiB (ND1.5)		Glass ZnLiBiB (ND02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^4F_{3/2}$	3.328	3.326	3.225	3.046	3.135	2.957
$^4F_{5/2}$	8.123	8.203	7.391	7.614	7.282	7.527
$^4F_{7/2}$	9.420	9.742	8.860	9.145	8.734	9.176
$^4F_{9/2}$	0.598	0.514	0.564	0.480	0.554	0.477
$^2H_{11/2}$	0.188	0.145	0.178	0.136	0.15	0.136
$^4G_{5/2}$	24.140	24.443	22.100	22.424	20.100	20.545
$^4G_{7/2}$	4.120	4.866	3.150	4.467	2.100	4.277
$^4G_{9/2}$	2.016	2.116	1.800	1.952	1.600	1.904
$^2G_{9/2}$	0.920	2.739	0.720	2.520	0.54	2.457
R.m.s.deviation	0.674		0.765		0.999	

The various energy interaction parameters like Slater-Condon parameters F_k (k=2, 4, 6), Lande's parameter ξ_{4f} and Racah parameters E^k (k=1, 2, 3) have been computed using partial regression method and formula described elsewhere[18]. The ratio of Racah parameters E^1/E^3 and E^2/E^3 are about 9.4 and 0.034 respectively. Which are almost equal to the hydrogenic ratio[19]. This implies that Nd^{3+} ions at different doping concentrations are subjected. Computed values of Slater-Condon, Lande, Racah, nephelauexetic ratio and bonding parameter for Nd^{3+} doped ZnLiBiB glass specimens are given in Table 4.

Table4. Computed values of Slater-Condon, Lande, Racah, nephelauexetic ratio and bonding parameter for Nd^{3+} doped ZnLiBiB glass specimens.

Parameter	Free ion	ZnLiBiB ND01	ZnLiBiB ND1.5	ZnLiBiB ND02
$F_2(cm^{-1})$	331.16	286.24	290.70	297.53
$F_4(cm^{-1})$	50.71	57.25	56.77	56.11
$F_6(cm^{-1})$	5.154	3.46	3.68	4.01
$\xi_{4f}(cm^{-1})$	884.0	918.53	916.78	912.95
$E^1(cm^{-1})$	5024.0	4464.52	4537.21	4645.70
$E^2(cm^{-1})$	23.90	15.41	16.24	17.47
$E^3(cm^{-1})$	497.0	486.73	486.32	486.55
F_4/F_2	0.1531	0.2000	0.1954	0.1886
F_6/F_2	0.0155	0.0121	0.0127	0.0135
E^1/E^3	10.1086	9.1725	9.3297	9.5483
E^2/E^3	0.0481	0.0317	0.0334	0.0359
β'		0.8644	0.8778	0.8984
$b^{1/2}$		0.2604	0.2472	0.2254

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. In the present case the three Ω_λ parameters follow the trend $\Omega_2 < \Omega_6 < \Omega_4$. 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 ion site and to the changes in their rare earth oxygen covalence[20]. Where as Ω_4 is related to the rigidity of the host.
The values of Judd-Ofelt intensity parameters are given in Table 5.

Table 5. Judd-Ofelt intensity parameters for Nd^{3+} doped ZnLiBiB glass specimens.

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6
ZnLiBiB ND01	2.246	5.715	2.928	1.952
ZnLiBiB ND1.5	2.059	5.216	2.758	1.891
ZnLiBiB ND02	1.660	5.030	2.776	1.812

3.4. Fluorescence Spectrum

The fluorescence spectrum of Nd^{3+}doped in zinc lithium bismuth borate glass is shown in Figure 3. There are two broad bands ($^4F_{3/2}\rightarrow{}^4I_{9/2}$) and ($^4F_{3/2}\rightarrow{}^4I_{11/2}$) respectively for glass specimens.

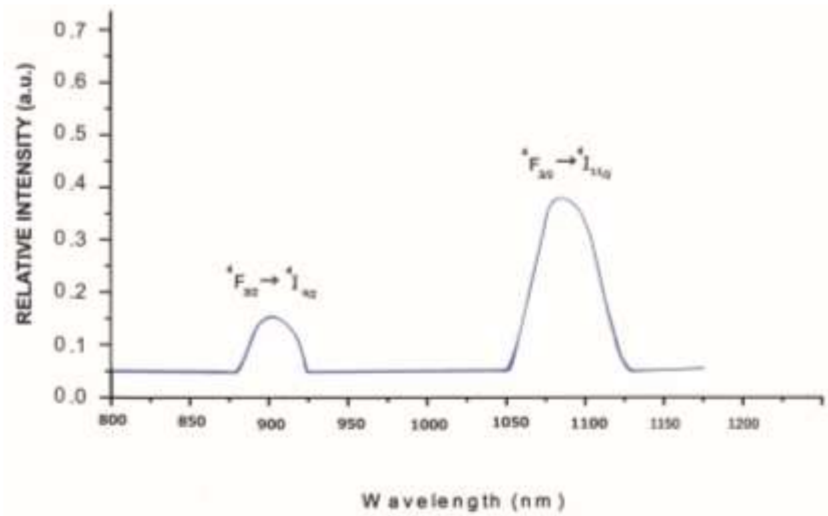

Fig.3: Fluorescence spectrum of ZnLiBiB glasses doped with Nd^{3+}.

A comparison of calculated σ values for bismuth borate glasses with those reported[21,22] for silicate, and phosphate, shows that bismuth borate glasses are best glasses. The wavelengths of these bands along with their assignments are given in Table 6.

Table 6. Emission peak wave lengths (λ_p), radiative transition probability (A_{rad}), branching ratio (β_R), stimulated emission crosssection (σ_p), and radiative life time (τ) for various transitions in Nd^{3+} doped ZnLiBiB glasses.

		ZnLiBiB(ND01)				ZnLiBiB(ND01)				ZnLiBiB(ND01)			
Transition	λ_p(nm)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(μs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(μs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-20}cm^2$)	τ_R(μs)
$^4F_{3/2}\rightarrow{}^4I_{9/2}$	905	2333.57	0.5747	2.648	246.28	2140.62	0.5711	2.543	266.79	2081.61	0.5660	2.529	271.92
$^4F_{3/2}\rightarrow{}^4I_{11/2}$	1075	1726.90	0.4253	2.861		1607.71	0.4289	2.755		1596.00	0.4340	2.749	

4. CONCLUSION

In the present study, the glass samples of composition (25−x) Bi_2O_3:20Li_2O: 20ZnO:35B_2O_3:xNd_2O_3 (where x =1, 1.5, 2 mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition ($^4F_{3/2}\rightarrow^4I_{11/2}$) for glass ZnLiBiB (ND 01), suggesting that glass ZnLiBiB (ND 01) is better compared to the other two glass systems ZnLiBiB (ND1.5) and ZnLiBiB (ND02). The large stimulated emission cross section in bismuth borate glasses suggests the possibility of utilizing these systems as laser materials.

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