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Optical Absorption Studies of Nd^{3+} Doped Yttrium Zinc Lithium Bismuth Borate Glasses

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Abstract

Yttrium Zinc lithium bismuth borate glasses containing Nd^{3+} in (20- x): Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40B_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. The spectroscopic quality factor related with the rigidity of the glass system is also discussed.

Keywords: Bismuth borate glasses, Energy interaction parameters, Optical absorption, Judd-Ofelt Theory,

1. INTRODUCTION

Bismuth borate glasses have received considerable attention in the past few years due to the synthesis of new glass compositions with high chemical stability. The improvement of chemical stability stimulated the application of bismuth borate glasses in several fields of materials science, such as optoelectronics, photonics and optical fiber communications [1-5]. Among different glass matrices, scientific interest on bismuth borate glasses is attributed to their favorable properties such as ,high refractive index, high density, low melting temperature, large third order nonlinear optical susceptibility[6-9].

It has been reported that yttrium zinc lithium bismuth borate glasses containing Bi_2O_3 as the network intermediate (NWI) to the glass network former B_2O_3 (NWF) posses high refractive index, high density and high infrared transparency. The addition of network modifier (NWF) Li_2O is to improve both electrical and mechanical properties of such glasses [10, 11]. Despite, the Bi_2O_3 is not a classical network former, it exhibits some superior properties like high refractive index, high optical basicity and large polarizability [12].

In the present work, the absorption spectra of Nd^{3+} doped YZnLiBiB 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 ($\Omega_4/\ \Omega_6$) has been evaluated.

2. EXPERIMENTAL

The following Nd^{3+} doped bismuth borate glass samples (20- x): Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40B_2O_3:xNd_2O_3 (where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of Bi_2O_3, Li_2O, ZnO, Y_2O_3, B_2O_3 and Nd_2O_3. They were thoroughly mixed by using an agate pestlemortar. Then melted at 1150˚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 400˚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 %)
YZnLiBiB (UD)	20Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40B_2O_3
YZnLiBiB (ND1)	19Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3: 40B_2O_3:1Nd_2O_3
YZnLiBiB (ND1.5)	18.5Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3: 40B_2O_3:1.5Nd_2O_3
YZnLiBiB (ND2)	18Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3: 40B_2O_3:2Nd_2O_3

YZnLiBiB (UD)—Represents undoped Yttrium Zinc Lithium Bismuth Borate glass specimens

YZnLiBiB (ND)—Represents Nd^{3+} doped Yttrium 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.

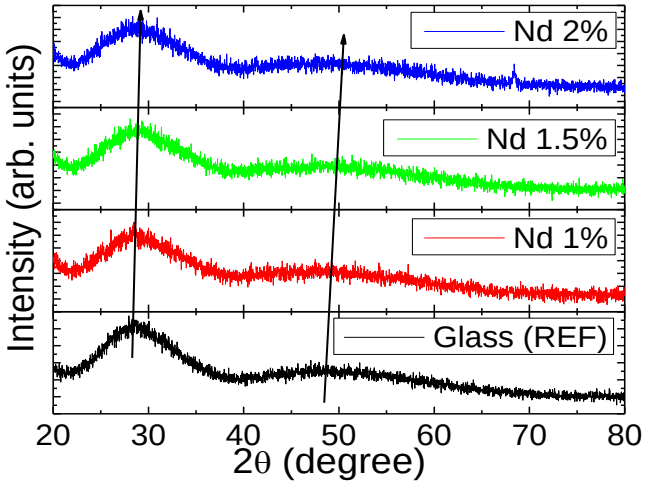

Figure 1. X-ray diffraction pattern of Bi_2O_3:Li_2O: ZnO: Y_2O_3: B_2O_3 :Nd_2O_3 glasses.

3.2. Physical Properties

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

Table 2: The physical and optical properties of Nd^{3+}: YZnLiBiB glasses

Physical properties	YZnLiBiB(ND 01)	ZYnLiBiB(ND 1.5)	YZnLiBiB(ND 02)
Refractive Index (n)	1.892	1.893	1.895
Density (ρ) $\left(gm/cm^3\right)$	3.528	3.546	3.554
Thickness(Z)	0.262	0.263	0 .264
Averagemolecularweight M $\left(g\right)$	159.025	158.378	157.730
Rare earth ions concentratio(N)	1.630	2.451	3.279
Dielectric Constant (ϵ)	3.580	3.583	3.591
OpticalDielectricConstant $p\frac{dt}{dp}$	2.580	2.583	2.591
MolarVolume (V_m) $\left(gm/cm^3\right)$	44.846	44.660	44.380
Reflection losses(R_L)	9.513	9.528	9.558

Molar refractivity ($R_{m)}$	20.734	20.664	20.567
Polaron radius R_p $\left(A^0\right)$	3.659	3.191	2.888
Interionic distance(R_i) $\left(A^0\right)$	9.080	7.920	7.169
Electronic polarizability (α_e)	0.1833	0.1835	0.1838
Field strength (F)	1.957	2.583	3.165
Optical basicity (Λ)	0.7549	0.7558	0.7566
Molar polarizability(α_m) $\times 10^{-24} cm^3$	8.228	8.200	8.162
Oxide ions polarizability ($\alpha_O^{2-(n)}$) A^0	3.102	3.086	3.065
Oxygen packing density(OPD)	53.516	53.739	54.078
Metallization criterion (M)	0.5377	0.5373	0.5366
Energy gap(E_g)	5.782	5.774	5.758

The density increase with an increase in concentration of Nd_2O_3. The electrons polarizability shows a general trend of increase with increase in refractive index.

3.3. Absorption spectra

The absorption spectra of Nd^{3+} doped YZnLiBiB glasses, 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 YZnLiBiB glasses.

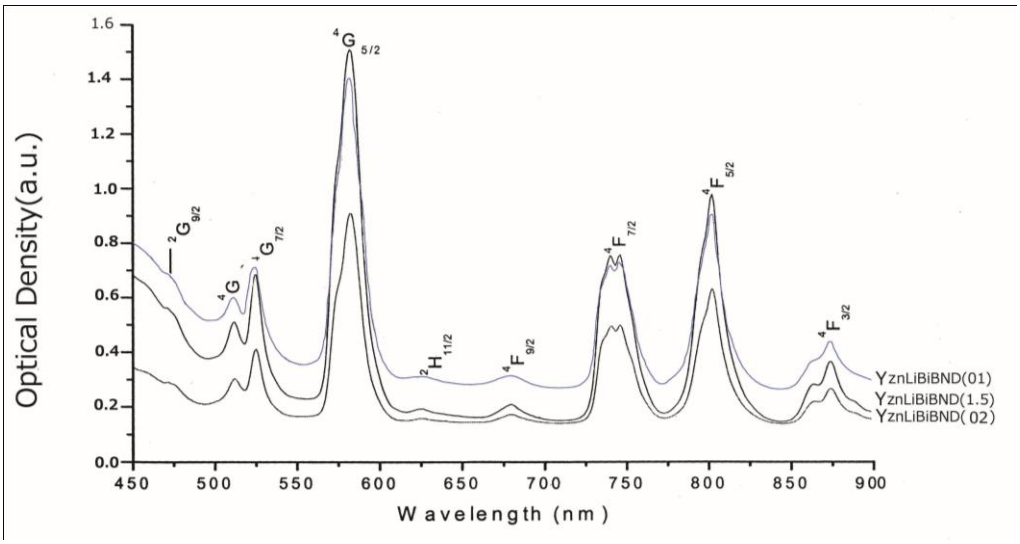

Figure 2. Vis-NIR absorption spectra of YZnLiBiB (ND) glasses.

The experimental and calculated oscillator strengths for Nd^{3+} ions in yttrium zinc lithium bismuth borate glasses are given in **Table 3**. The observed relatively small values of these deviations confirm the validity and applicability of Judd-Ofelt theory for the present glasses.

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

Energy level from $^4I_{9/2}$	**Glass YZnLiBiB (ND01)**		**Glass YZnLiBiB (ND1.5)**		**Glass YZnLiBiB (ND02)**	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^4F_{3/2}$	4.126	3.605	3.816	3.348	3.612	3.321
$^4F_{5/2}$	9.213	9.749	8.561	9.044	8.125	8.479
$^4F_{7/2}$	9.42	9.224	8.602	8.561	7.582	7.732
$^4F_{9/2}$	0.612	0.756	0.602	0.702	0.6	0.646
$^2H_{11/2}$	0.216	0.210	0.204	0.196	0.198	0.181
$^4G_{5/2}$	25.12	25.247	24.14	24.341	24.02	24.291
$^4G_{7/2}$	4.6	5.189	3.80	4.867	3.6	4.803
$^4G_{9/2}$	2.86	2.568	2.4	2.391	2.1	2.306
$^2G_{9/2}$	0.98	2.344	0.91	2.180	0.89	2.152
R.m.s.deviation	0.570		0.602		0.614	

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[13].The ratio of Racah parameters E^1/E^3 and E^2/E^3 are about 10.239 and 0.050 respectively. Which are almost equal to the hydrogenic ratio [14]. 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 YZnLiBiB glass specimens are given in **Table 4**.

Table 4. Computed values of Slater-Condon, Lande, Racah, nephelauexetic ratio and bonding parameter for Nd^{3+} doped YZnLiBiB glass specimens.

Parameter	**Free ion**	**YZnLiBiB ND01**	**YZnLiBiB ND1.5**	**YZnLiBiB ND02**
$F_2(cm^{-1})$	331.16	327.68	330.52	330.97
$F_4(cm^{-1})$	50.71	49.83	49.43	49.41
$F_6(cm^{-1})$	5.154	5.15	5.31	5.32
$\xi_{4f}(cm^{-1})$	884.0	889.45	890.55	890.57
$E^1(cm^{-1})$	5024.0	4973.14	5023.53	5026.35
$E^2(cm^{-1})$	23.90	23.81	24.40	24.45
$E^3(cm^{-1})$	497.0	489.55	488.89	488.97
F_4/F_2	0.1531	0.1521	0.1496	0.1493
F_6/F_2	0.0155	0.0157	0.0161	0.0161
E^1/E^3	10.1086	10.1586	10.2754	10.2795
E^2/E^3	0.0481	0.0486	0.0499	0.0500
β'		0.9895	0.9987	0.9994
$b^{1/2}$		0.0725	0.0251	0.0169

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 Ω_2 parameter is affected by the covalency, the Ω_6 parameter is related to the with the rigidity of the glass hosts. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 1.19 and 1.35 in the present glasses. This shows that these glasses are fairly rigid as compared to NGBNd [15] and TLF glasses [16]. The values of Judd-Ofelt intensity parameters are given in **Table 5**.

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

Glass Specimen	**Ω_2(pm^2)**	**Ω_4(pm^2)**	**Ω_6(pm^2)**	**Ω_4/Ω_6**	**Ref.**
YZnLiBiB ND01	3.575	5.766	4.864	1.185	p
YZnLiBiB ND1.5	3.579	5.357	4.507	1.189	p
YZnLiBiB ND02	3.568	5.410	4.02	1.346	p
NGBNd	5.75	3.44	3.73	0.92	[15]
TLF	5.61	4.17	5.44	0.77	[16]

4. CONCLUSION

In the present study, the glass samples of composition (20−x) Bi_2O_3:15Li_2O: 15ZnO:10Y_2O_3:40B_2O_3:xNd_2O_3 (where x =1, 1.5, 2 mol %) have been prepared by melt-quenching method. The spectroscopic quality factor related with the rigidity of the glass system has been found to lie between1.19 and 1.35 in the present glasses, which is fairly large as compared to other glasses. The large values of spectroscopic quality factor (**Ω_4/Ω_6**) make them suitable for optical devices.

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