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

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Abstract: *Zinc lithium bismuth borate glasses containing Er^{3+} in (25- x): Bi_2O_3:20Li_2O:20ZnO: 35B_2O_3:xEr_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 and fluorescence spectra were recorded at room temperature for all glass samples. 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.*

Keywords: *Amorphous nature, Optical Properties, Judd-Ofelt Theory, Rare earth ions.*

I. Introduction

Glasses doped with various rare –earth ions are important materials for fluorescent display devices, optical detectors, optical fibers and optical amplifiers [1-3].Among the other heavy metal oxide glasses, bismuth borate glasses have wide range of applications in the field of glass ceramics, layers for optical and electronic devices, thermal and mechanical sensors, reflecting windows [4,5], Glasses containing heavy metal oxides exhibits good non-linear optical properties and good chemical durability [6,7]. The past literature shows that the rare earth ions find more important application in the preparation of the laser materials [8, 9].

Among various glasses, borate glasses are excellent host matrices because boric oxide (B_2O_3) acts as a good glass former and flux material [10]. ZnO is a wide band gap semiconductor and has received increasing research interest. It is an important multifunction material due to its specific chemical, surface and micro structural properties. It is used in various applications such as gas sensor, varistors, catalysts etc [11]. Er^{3+} ion is the most studied among the rare earth ions and the up conversion process of this ion in various kinds of host materials has been investigated [12-16].

In this work, the spectroscopic properties of Er^{3+} -doped (25- x): Bi_2O_3:20Li_2O:20ZnO: 35B_2O_3:xEr_2O_3 (where x=1, 1.5,2 mol %) glasses were investigated for operation at the 1.55 μm wavelength. The optical properties, the absorption spectra, fluorescence spectra of Er^{3+} of the glasses were investigated. The J-O intensity parameters render significant information regarding local structure and bonding in the vicinity of rare-earth ions. The parameter Ω_2 is related with the symmetry of the glass hosts while Ω_6 is a measure of the covalency in the network [17].

II. Experimental Techniques

Preparation of glasses

The following Er^{3+} doped zinc lithium bismuth borate glass samples (25-x) Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: xEr_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 Er_2O_3. All weighed chemicals were powdered by using an Agate pestle mortar and mixed thoroughly before each batch (10g) was melted in alumina crucibles in silicon carbide based an electrical furnace.

Silicon Carbide Muffle furnace was heated to working temperature of 1050^0C, for preparation of Zinc Lithium Bismuth Borate glasses, for two hours to ensure the melt to be free from gases. The melt was stirred several times to ensure homogeneity. For quenching, the melt was quickly poured on the steel plate & was immediately inserted in the muffle furnace for annealing. The steel plate was preheated to100^0C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350^0C for 2h 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)	25 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3
ZnLiBiB (Er 1)	24 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 1 Er_2O_3
ZnLiBiB (Er 1.5)	23.5 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 1.5 Er_2O_3
ZnLiBiB (Er 2)	23 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 2 Er_2O_3

ZnLiBiB (UD)—Represents undoped Zinc Lithium Bismuth Borate glass specimens
ZnLiBiB (Er) -Represents Er^{3+} doped Zinc Lithium Bismuth Borate glass specimens

III. Theory

3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [18].

$$f_{expt.} = 4.318 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \qquad (1)$$

where, $\varepsilon(\nu)$ is molar absorption coefficient at a given energy ν (cm^{-1}), to be evaluated from Beer–Lambert law. Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated, using the modified relation [19].

$$P_m = 4.6 \times 10^{-9} \times \frac{1}{cl} \log \frac{I_0}{I} \times \Delta\upsilon_{1/2} \qquad (2)$$

where c is the molar concentration of the absorbing ion per unit volume, I is the optical path length, $\log I_0/I$ is absorbtivity or optical density and $\Delta\upsilon_{1/2}$ is half band width.

3.2. Judd-Ofelt Intensity Parameters

According to Judd [20] and Ofelt [21] theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial J manifold $|4f^N (S, L) J\rangle$ level and the terminal J' manifold $|4f^N (S'L') J'\rangle$ is given by:

$$\frac{8\Pi^2 mc\bar{\upsilon}}{3h(2J+1)} \frac{1}{n}\left[\frac{(n^2+2)^2}{9}\right] \times S(J, J') \qquad (3)$$

where, the line strength S (J, J') is given by the equation

$$S(J, J') = e^2 \sum_{\lambda=2,4,6} \Omega_\lambda \langle 4f^N (S, L) J \| U^{(\lambda)} \| 4f^N (S', L') J' \rangle^2 \qquad (4)$$

In the above equation m is the mass of an electron, c is the velocity of light, ν is the wave number of the transition, h is Planck's constant, n is the refractive index, J and J' are the total angular momentum of the initial and final level respectively, Ω_λ (λ = 2, 4 and 6) are known as Judd-Ofelt intensity parameters which contain the effect of the odd-symmetry crystal field terms, radial integrals and energy denominators. $\| U^{(\lambda)} \|^2$ are the matrix elements of the doubly reduced unit tensor operator calculated in intermediate coupling approximation. Ω_λ parameter can be obtained from least square fitting method [22]. The matrix element $\| U^{(\lambda)} \|^2$ that are insensitive to the environment of rare earth ions were taken from the literature [23].

3.3.Radiative Properties

The Ω_λ parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time (τ_R), and laser parameters like fluorescence branching ratio (β_R) and stimulated emission cross section (σ_p). The spontaneous emission probability from initial manifold $|4f^N (S', L') J'\rangle$ to a final manifold $|4f^N (S, L) J\rangle$ is given by:

$$A[(S', L') J'; (S, L) J] = \frac{64\pi^2 \nu^3}{3h(2J'+1)} \left[\frac{n(n^2+2)^2}{9}\right] \times S(J', J) \qquad (5)$$

Where, $S(J', J) = e^2 [\Omega_2 \| U^{(2)} \|^2 + \Omega_4 \| U^{(4)} \|^2 + \Omega_6 \| U^{(6)} \|^2]$

The fluorescence branching ratio for the transitions originating from a specific initial manifold $|4fN (S', L') J'>$ to a final many fold $|4f^N (S, L) J>$ is given by

$$\beta[(S', L') J'; (S, L) J] = \sum_{S L J} \frac{A[(S' L)]}{A[(S' L') J' (S L)]} \quad (6)$$

where, the sum is over all terminal manifolds.

The radiative life time is given by

$$\tau_{rad} = \sum_{S L J} A[(S', L') J'; (S,L)] = A_{Total}^{-1} \quad (7)$$

where, the sum is over all possible terminal manifolds. The stimulated emission cross -section for a transition from an initial manifold $|4f N (S', L') J'>$ to a final manifold $|4fN (S, L) J>|$ is expressed as

$$\sigma_p(\lambda_p) = \left[\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right] \times A[(S', L') J'; (\bar{S}, \bar{L}) \bar{J}] \quad (8)$$

where, λ_p the peak fluorescence wavelength of the emission band and $\Delta\lambda_{eff}$ is the effective fluorescence line width.

IV. Result and Discussion

4.1. XRD Measurement

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

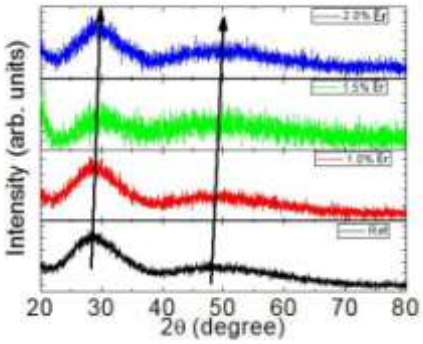

Fig.1: X-ray diffraction pattern of ZnLiBiB (ER) glasses.

4.2. Absorption spectra

The absorption spectra of ZnLiBiB (ER) glasses, consists of absorption bands corresponding to the absorptions from the ground state $^4I_{15/2}$ of Er^{3+} ions. Ten absorption bands have been observed from the ground state $^4I_{15/2}$ to excited states $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$, $^2H_{9/2}$ and $^4G_{11/2}$ for Er^{3+} doped ZnLiBiB(ER) glasses.

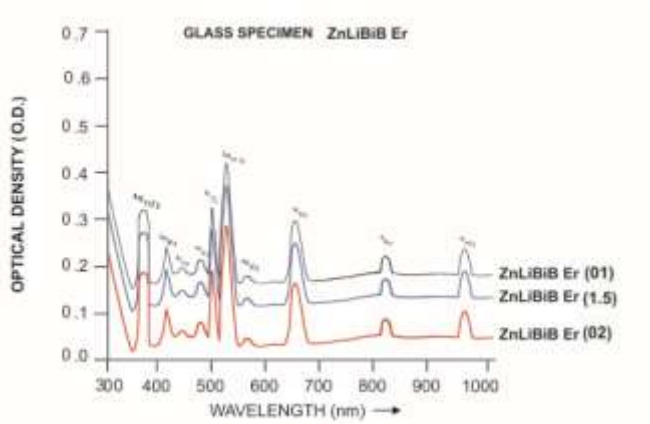

Fig.2: Vis-NIR absorption spectra of ZnLiBiB (ER) glasses.

The experimental and calculated oscillator strengths for Er^{3+} ions in zinc lithium bismuth borate glasses are given in **Table 2**

Table 2. Measured and calculated oscillator strength ($P^m \times 10^{+6}$) of Er^{3+} ions in ZnLiBiB glasses.

Energy level	Glass ZnLiBiB (ER01)		Glass ZnLiBiB (ER1.5)		Glass ZnLiBiB (ER02)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
$^4I_{11/2}$	0.81	0.67	0.78	0.63	0.76	0.51
$^4I_{9/2}$	0.42	0.81	0.38	0.80	0.32	0.46
$^4F_{9/2}$	2.14	1.23	2.1	1.17	1.7	0.89
$^4S_{3/2}$	0.36	0.60	0.32	0.56	0.21	0.46
$^2H_{11/2}$	6.40	2.43	6.2	2.26	5.2	1.78
$^4F_{7/2}$	5.20	2.01	5	1.89	4.1	1.51
$^4F_{5/2}$	0.64	0.76	0.62	0.71	0.51	0.58
$^4F_{3/2}$	0.32	0.47	.30	0.44	0.21	0.36
$^2H_{9/2}$	1.66	0.88	1.6	0.83	0.88	0.66
$^4G_{11/2}$	4.84	6.69	4.4	6.25	3.22	4.91
R.m.s.deviation	1.763		1.740		1.490	

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 [24]. The ratio of Racah parameters E^1/E^3 and E^2/E^3 are about 10.35 and 0.049 respectively. Which are almost equal to the hydrogenic ratio [25]. This implies that Er^{3+} ions at different doping concentrations are subjected. Computed values of Slater-Condon, Lande, Racah, nephelauexetic ratio and bonding parameter for Er^{3+} doped ZnLiBiB glass specimens are given in **Table 3**.

Table3. Computed values of Slater-Condon, Lande, Racah, nephelauexetic ratio and bonding parameter for Er^{3+} doped ZnLiBiB glass specimens.

Parameter	Free ion	ZnLiBiB ER01	ZnLiBiB ER1.5	ZnLiBiB ER02
$F_2(cm^{-1})$	441.680	433.887	433.483	434.069
$F_4(cm^{-1})$	68.327	67.018	67.091	67.515
$F_6(cm^{-1})$	7.490	7.044	7.016	7.098
$\xi_{4f}(cm^{-1})$	2369.400	2415.794	2417.019	2413.232
$E^1(cm^{-1})$	6855.300	6661.704	6654.207	6687.888
$E^2(cm^{-1})$	32.126	31.349	31.258	31.246
$E^3(cm^{-1})$	645.570	643.513	643.835	644.810
F_4/F_2	0.15470	0.15446	0.15477	0.15554
F_6/F_2	0.01696	0.01623	0.01619	0.01635
E^1/E^3	10.61899	10.35209	10.33527	10.37187
E^2/E^3	0.049764	0.048715	0.048550	0.048458
β'		0.9824	0.9814	0.9828
$b^{1/2}$		0.0938	0.0964	0.0927

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 $\Omega_4 < \Omega_6 < \Omega_2$. 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 [26].
The values of Judd-Ofelt intensity parameters are given in **Table 4**.

Table 4. Judd-Ofelt intensity parameters for Er^{3+} doped ZnLiBiB glass specimens.

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6
ZnLiBiB ER01	0.796	0.122	0.744	0.164
ZnLiBiB ER1.5	0.732	0.124	0.726	0.171
ZnLiBiB ER02	0.595	0.100	0.589	0.170

4.3. Fluorescence Spectrum

The fluorescence spectrum of Er^{3+}doped in zinc lithium bismuth borate glass is shown in Figure 3. There are four broad bands ($^4F_{7/2}\rightarrow{}^4I_{15/2}$), ($^2H_{11/2}\rightarrow{}^4I_{15/2}$) ($^4S_{3/2}\rightarrow{}^4I_{15/2}$) and ($^4F_{9/2}\rightarrow{}^4I_{15/2}$) respectively for glass specimens.

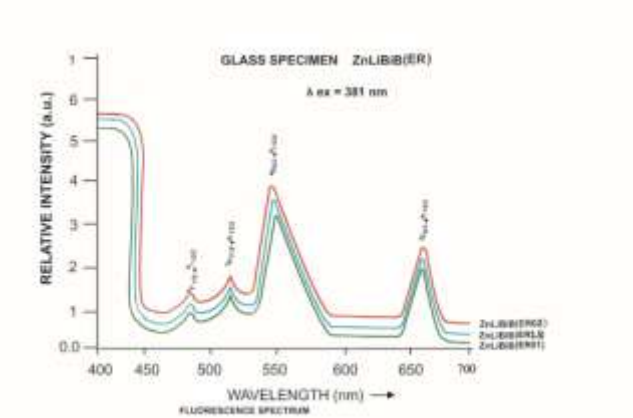

Fig.3: Fluorescence spectrum of ZnLiBiB glasses doped with Er^{3+}.

Table 5. 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 Er^{3+} doped ZnLiBiB glasses.

	ZnLiBiB(ER01)					ZnLiBiB(ER1.5)				ZnLiBiB(ER02)			
Transition	λ_p(nm)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-22}cm^2$)	τ_R(μs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-22}cm^2$)	τ_R(μs)	$A_{rad}(s^{-1})$	β_R	σ_p ($10^{-22}cm^2$)	τ_R(μs)
$^4F_{3/2}\rightarrow{}^4I_{13/2}$	485	2527.06	0.4232	0.582		2385.02	0.4214	0.537		1936.96	0.4214	0.427	
$^4H_{11/2}\rightarrow{}^4I_{13/2}$	530	1669.72	0.2796	0.449	167.46	1555.54	0.2749	0.403	176.70	1264.31	0.2751	0.0325	217.57
$^4S_{3/2}\rightarrow{}^4I_{13/2}$	550	1106.22	0.1853	0.271		1082.37	0.1913	0.263		878.82	0.1912	0.0212	
$^4F_{9/2}\rightarrow{}^4I_{13/2}$	657	668.45	0.1119	0.292	246.28	636.26	0.1124	0.275	266.79	516.20	0.1123	0.0219	271.92

V. Conclusion

In the present study, the glass samples of composition (25−x) Bi_2O_3:20Li_2O: 20ZnO:35B_2O_3:xEr_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 ($^4F_{7/2}\rightarrow{}^4I_{15/2}$) for glass ZnLiBiB (ER 01), suggesting that glass ZnLiBiB (ER 01) is better compared to the other two glass systems ZnLiBiB (ER1.5) and ZnLiBiB (ER02).

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