

Spectral, Thermal and Raman Analysis of Tm³⁺ Doped in Bismuth Borate Glasses

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ABSTRACT: Glass sample of Zinc Lithium Calcium Niobate Alumino Bismuthborate: (30-x) Bi₂O₃:10ZnO:10Li₂O:10CaO:10Nb₂O₅:10Al₂O₃:20B₂O₃:xTm₂O₃. (where x=1,1.5 and 2 mol%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. DTA curve was analysed to evaluate the glass transition temperature, crystallization temperature and melting temperature. Raman, Optical absorption and fluorescence spectra were recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_λ ($\lambda=2, 4$ and 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: ZLCNABB Glasses, Thermal Properties, Raman Analysis Judd-Ofelt Theory,

I. INTRODUCTION

Rare earth doped ceramic glasses have attracted great interest recently due to their potential application in optical devices such as white light emitting diodes, light converting devices, frequency-conversion materials, waveguide laser and optical fiber amplifiers [1-7]. Glasses based on heavy metal oxide have received increased attention due to their manifold possible applications in the field of glass ceramics, thermal and mechanical sensors and layers for optoelectronics devices. Borate glass materials should have high refractive index, high density with good thermal and chemical stability. The up-conversion of phosphate glasses is also compressed because of their relatively large phonon energy [8-11]. Borate glasses can be a good matrix for fiber lasers because they exhibit good physical, optical and thermal properties. The addition of network modifier (NWF) Li₂O is to improve mechanical, thermal and electrical properties of such glasses. Zinc oxide is added in the glass matrix to increase glass forming ability and to ensure low rates of crystallization in the glass system [12-15].

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. I have studied on the absorption and emission properties of Tm³⁺ doped zinc lithium calcium niobate alumino bismuthborate glasses. The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelt theory, The laser parameters such as radiative probabilities(A), branching ratio (β), radiative life time(τ_R) and stimulated emission cross section(σ_p) are evaluated using J.O.intensity parameters(Ω_λ , $\lambda=2,4$ and 6).

II. EXPERIMENTAL TECHNIQUES

Preparation of glasses

The following Tm³⁺ doped bismuthborate glass samples (30-x) Bi₂O₃:10ZnO:10Li₂O:10CaO:10Nb₂O₅:10Al₂O₃:20B₂O₃:xTm₂O₃. (where x=1,1.5 and 2 mol%) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of Bi₂O₃, ZnO, Li₂O, CaO, Nb₂O₅, Al₂O₃, B₂O₃ and Tm₂O₃. They were thoroughly mixed by using an agate pestle mortar. then melted at 970°C by an electrical muffle furnace for 2h., After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of 250°C 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 %)
ZLCNABB (UD)	30 Bi ₂ O ₃ :10ZnO:10Li ₂ O:10CaO:10Nb ₂ O ₃ :10Al ₂ O ₃ :20B ₂ O ₃
ZLCNABB TM(1.0)	29 Bi ₂ O ₃ :10ZnO:10Li ₂ O:10CaO:10Nb ₂ O ₃ :10Al ₂ O ₃ :20B ₂ O ₃ :1Tm ₂ O ₃
ZLCNABB TM(1.5)	28.5 Bi ₂ O ₃ :10ZnO:10Li ₂ O:10CaO:10Nb ₂ O ₃ :10Al ₂ O ₃ :20B ₂ O ₃ :1.5 Tm ₂ O ₃
ZLCNABB TM(2.0)	28 Bi ₂ O ₃ :10ZnO:10Li ₂ O:10CaO:10Nb ₂ O ₃ :10Al ₂ O ₃ :20B ₂ O ₃ :2 Tm ₂ O ₃

ZLCNABB (UD) -Represents undoped zinc lithium calcium niobate alumino bismuthborate glass specimen.

ZLCNABB (TM) -Represents Tm³⁺ doped zinc lithium calcium niobate alumino bismuthborate glass specimens.

III. THEORY

3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [16].

$$f_{\text{expt.}} = 4.318 \times 10^{-9} \int \epsilon(\nu) d\nu \quad (1)$$

where, $\epsilon(\nu)$ 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 [17], using the modified relation:

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

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

3.2. Judd-Ofelt Intensity Parameters

According to Judd [18] and Ofelt [19] 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:

$$\frac{8\pi^2 m c \nu}{3h(2J+1)n} \frac{1}{n} \left[\frac{(n^2+2)^2}{9} \right] \times S(J, J') \quad (3)$$

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

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

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} ($\lambda=2, 4$ and 6) are known as Judd-Ofelt intensity parameters.

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:

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

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 $|4f^N(S', L') J' \rangle$ to a final manifold $|4f^N(S, L) J \rangle$ is given by

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

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

where, the sum is over all possible terminal manifolds. The stimulated emission cross-section for a transition from an initial manifold $|4f^N(S', L') J' \rangle$ to a final manifold $|4f^N(S, L) J \rangle$ 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 sample contain - B₂O₃ which is show 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.

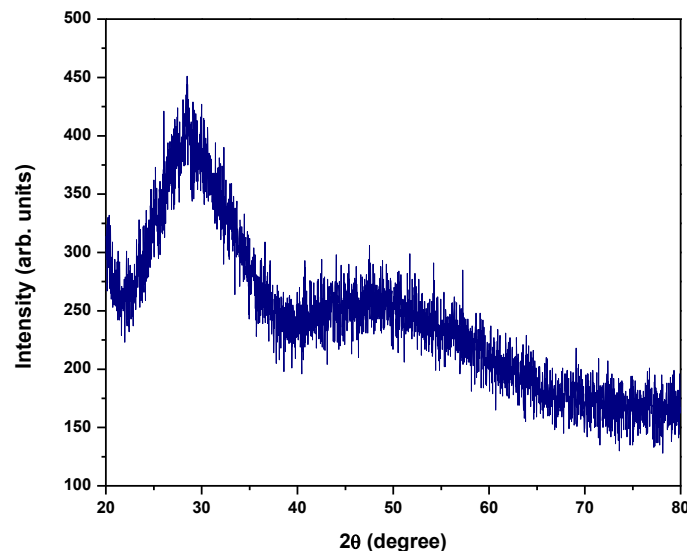


Fig. 1: X-ray diffraction pattern of ZLCNABB TM (1.0) glass.

4.2 Thermal Property

Differential thermal analysis checks the heat absorbed by glass samples during heating or cooling. Fig. 2 depicts the DTA thermogram of powdered ZLCNABB sample. The glass transition temperature (T_g), onset crystallization temperature (T_c), crystallization temperature (T_p), melting temperature (T_m), thermal stability (T_s), Balaji Parameter (B_p),

Hurbe's criterion (H_R) and reduced glass transition temperature (T_{rg}) were calculated. Shankar's parameter also calculated by using eq. (13). All the determined thermal parameters are given in table 2.

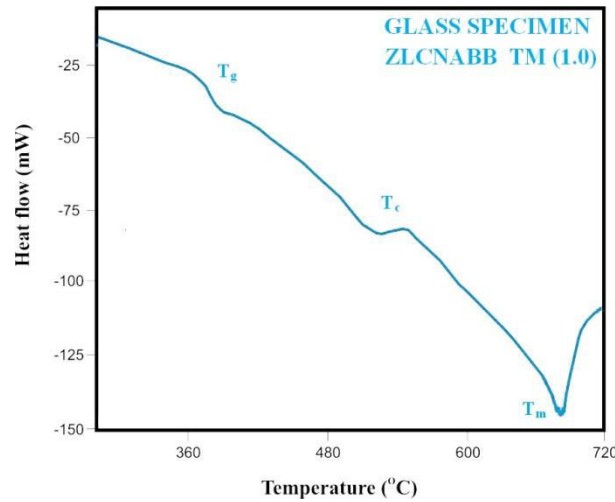


Fig.2: DTA curve of ZLCNABB TM (1.0) glass.

Table 2. Thermal parameters determined from the DTA traces of ZLCNABB TM glasses.

Sample Name	$T_g(^{\circ}C)$	$T_c(^{\circ}C)$	$T_p(^{\circ}C)$	$T_m(^{\circ}C)$	$T_s(^{\circ}C)$	$B_p(^{\circ}C)$	$H_R(^{\circ}C)$	$K_S(^{\circ}C)$	$T_{rg}(^{\circ}C)$
ZLCNABB TM (1.0)	375	510	549	686	135	3.462	0.222	34.636	0.547
ZLCNABB TM(1.5)	380	511	551	688	131	3.275	0.226	33.702	0.552
ZLCNABB TM(2.0)	386	513	555	693	127	3.024	0.233	32.987	0.557

The thermal stability of the glass samples can be calculated by difference between onset crystallization temperature and transition temperature [20].

$$\text{Thermal Stability } (T_s) = T_c - T_g \quad (9)$$

Balaji Parameter can be calculated using [20].

$$\text{Balaji Parameter } (B_p) = [(T_c - T_g) / (T_p - T_c)] \quad (10)$$

Hruby's criterion is calculated using the Hurby's relation [20].

$$\text{Hruby's criterion } (H_R) = [(T_p - T_c) / (T_m - T_c)] \quad (11)$$

Reduced glass transition temperature is given as [20].

$$\text{Reduced glass transition temperature } (T_{rg}) = T_g / T_m \quad (12)$$

Thermal Parameter is given as [20].

$$K_S = [(T_m - T_c) (T_c - T_g) / T_m] \quad (13)$$

4.3 Raman Spectrum

The Raman spectrum of zinc lithium calcium niobate alumino bismuthborate YZLCNABB TM(1.0) glass specimen has been presented in Figure 3. The spectrum peaks located at 445, 746, 985 and 1276 cm^{-1} . The band at 445 cm^{-1} is assigned to vibrations of Bi-O-Bi band of BiO_6 octahedral units. The band at 746 cm^{-1} is due to vibrations of metaborate group.

The band at 985 cm^{-1} is due to vibrations of orthoborate groups. The bands at 1276 cm^{-1} is due to the B-O stretching vibrations.

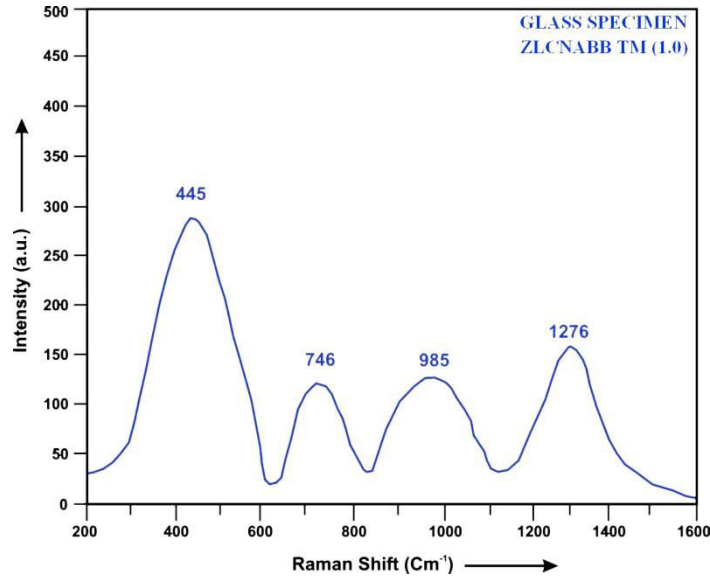


Fig. 3: Raman spectrum of ZLCNABB TM (1.0) glass.

4.4 Absorption Spectrum

The absorption spectra of ZLCNABB TM(1.0)glass specimen has been presented in Figure 4 in terms of optical density versus wavelength. Five absorption bands have been observed from the ground state 3H_6 to excited states 3F_4 , 3H_5 , 3H_4 , 3F_3 and 1G_4 for Tm^{3+} doped ZLCNABB glasses.

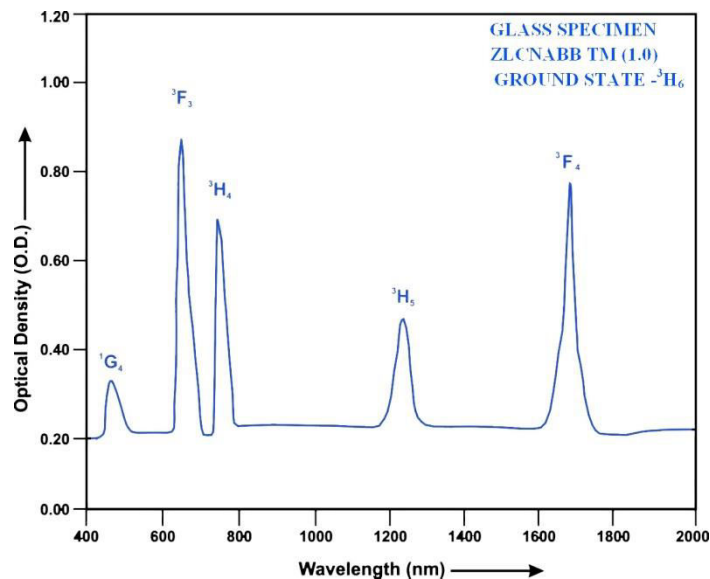


Fig. 4: Absorption spectrum of ZLCNABB TM (1.0) glass.

The experimental and calculated oscillator strength for Tm^{3+} ions in ZLCNABB glasses are given in Table 3.

Table 3: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Tm^{3+} ions in ZLCNABB glasses.

Energy level from 3H_6	Glass ZLCNABB TM(1.0)		Glass ZLCNABB TM(1.5)		Glass ZLCNABB TM(2.0)	
	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$	$P_{exp.}$	$P_{cal.}$
3F_4	1.89	1.91	1.87	1.89	1.85	1.88
3H_5	1.50	1.49	1.47	1.47	1.45	1.47
3H_4	2.06	2.11	2.04	2.09	2.01	2.08
3F_3	3.05	3.11	3.02	3.08	3.00	3.08
1G_4	0.85	0.91	0.83	0.91	0.80	0.90
r.m.s. deviation	± 0.0464		± 0.0509		± 0.0682	

*Low r.m.s.deviation values clearly indicate the accuracy of fitting.

The values of Judd-Ofelt intensity parameters are given in Table 4.

Table 4: Judd-Ofelt intensity parameters for Tm^{3+} doped ZLCNABB glass specimens.

Glass Specimen	$\Omega_2(\text{pm}^2)$	$\Omega_4(\text{pm}^2)$	$\Omega_6(\text{pm}^2)$	Ω_4 / Ω_6	
ZLCNABB TM (1.0)	7.079	8.786	5.987	1.468	P.W.
ZLCNABB TM (1.5)	7.040	8.685	5.932	1.464	P.W.,
ZLCNABB TM (2.0)	6.887	8.692	5.914	1.470	P.W.
TKWN (HO)	1.993	2.055	1.066	1.928	[21]

4.5. Fluorescence Spectrum

The fluorescence spectrum of Tm^{3+} doped in zinc lithium calcium niobate alumino bismuthborate glass is shown in Figure 5. There are nine broad bands observed in the Fluorescence spectrum of Tm^{3+} doped zinc lithium calcium niobate alumino bismuthborate glass. The wavelengths of these bands along with their assignments are given in Table 5. The peak with maximum emission intensity appears at 1810 nm and corresponds to the ($^3F_4 \rightarrow ^3H_6$) transition.

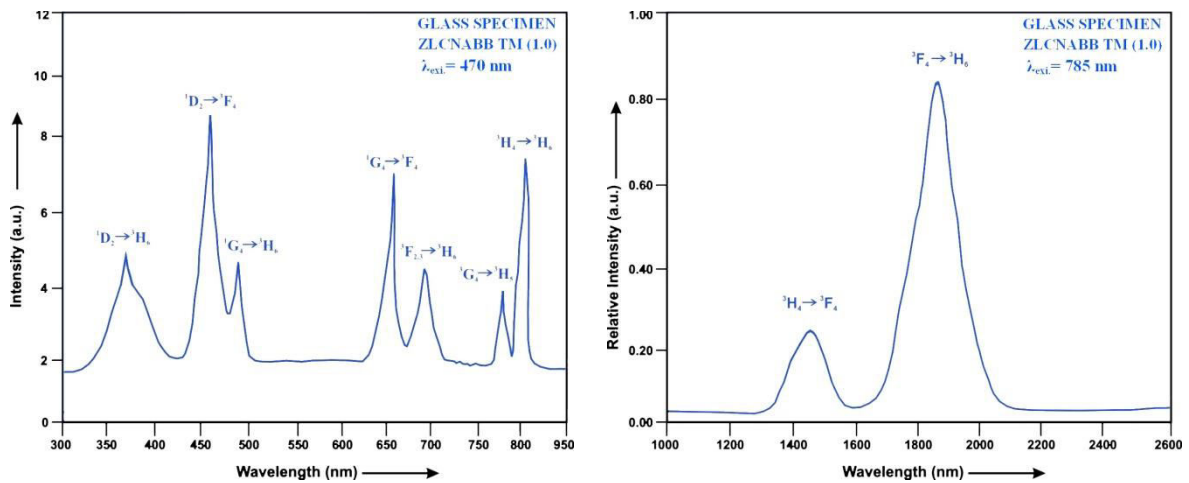


Fig. 5: Fluorescence spectrum of ZLCNABB TM (1.0) glass.

Table5: Emission peak wave lengths (λ_p),radiative transition probability (A_{rad}),branching ratio (β),stimulated emission cross-section(σ_p) and radiative life time(τ_R) for various transitions in Tm³⁺ doped ZLCNABB glasses

Transition	ZLCNABB TM (1.0)					ZLCNABB TM (1.5)					ZLCNABB TM (2.0)				
	λ_{max} (nm)	$A_{rad}(s^{-1})$	β	σ_p (10 ⁻²⁰ cm ²)	τ_R (us)	$A_{rad}(s^{-1})$	β	σ_p (10 ⁻²⁰ cm ²)	τ_R (us)	$A_{rad}(s^{-1})$	β	σ_p (10 ⁻²⁰ cm ²)	τ_R (10 ⁻²⁰ cm ²)		
¹ D ₂ → ³ H ₆	365	54302.40	0.6299	1.161	11.6006	53824.70	0.6292	1.161	11.6907	53911.50	0.6319	1.176	11.7210		
¹ D ₂ → ³ F ₄	455	17652.60	0.2048	2.262		17571.00	0.2054	2.306		17298.70	0.2028	2.326			
¹ G ₄ → ³ H ₆	480	2241.13	0.0260	0.519		2224.42	0.0260	0.534		2214.13	0.0259	0.557			
¹ G ₄ → ³ F ₄	651	731.37	0.0085	1.224		725.62	0.0085	1.314		725.67	0.0085	1.465			
³ F _{2,3} → ³ H ₆	689	5536.13	0.0642	2.307		5491.74	0.0642	2.321		5493.48	0.0644	2.374			
¹ G ₄ → ³ H ₅	785	2120.31	0.0246	2.393		2106.05	0.0246	2.433		2098.53	0.0246	2.517			
³ H ₄ → ³ H ₅	798	2807.80	0.0326	4.178		2789.38	0.0326	4.275		2773.94	0.0325	4.348			
³ H ₄ → ³ F ₄	1450	358.73	0.0042	3.675		356.22	0.0042	3.753		354.47	0.0042	3.805			
³ F ₄ → ³ H ₆	1810	452.24	0.0052	7.081		448.95	0.0052	7.107		446.67	0.0052	7.172			

V. CONCLUSION

In the present study, the glass samples of composition (30-x) Bi₂O₃: 10ZnO: 10Li₂O: 10CaO: 10Nb₂O₃: 10Al₂O₃: 20B₂O₃:xTm₂O₃. (where x =1, 1.5 and 2mol %) have been prepared by melt-quenching method. The large values of Balaji parameter indicate that the prepared glass samples have good thermal stability. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition (³F₄→³H₆) for glass ZLCNABB TM(2.0), suggesting that glass ZLCNABB TM(2.0) is better compared to the other two glass systems ZLCNABB TM(1.0) and ZLCNABB TM(1.5).

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