Spectroscopic Properties of Dy^{3+} Doped Lead Lithium Cadmium Tantalum Magnesium Bismuth Borate Glasses

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Abstract

Glass sample of Lead Lithium Cadmium Tantalum Magnesium Bismuth Borate (35-x) Bi_2O_3:10PbO:10Li_2O:10CdO:10Ta_2O_5:10MgO:15B_2O_3: x Dy_2O_3. (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. Optical absorption and fluorescence spectra were recorded at room temperature for all glass samples. Judd-Ofelt intensity parameters Ω_λ (λ=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: LLCTMBB Glasses, Optical Properties, Judd-Ofelt Theory, Rare earth ions.

Introduction:

Bismuth borate glasses doped with trivalent rare-earth ions are very important because they show strong luminescence due to their small cutoff phonon frequencies and scientific application [1-4].Rare earth doped bismuth borate glasses and glass ceramics are of increasing interests in various optical applications, because of their optical, liner and non liner properties. The performance and relatively low cost of borate glasses make them attractive for most of the ordinary laser applications [5-7].

Among various glasses, borate glasses are excellent host matrices because boric oxide (B_2O_3) acts as a good glass former and flux material. The structure of vitreous B_2O_3 consists of a random network of boroxyl rings and BO_3 triangles connected by B-O-B linkages. Borate glass forming ability over wide range of composition, higher bond strength, high transparency, low melting point and good rare earth ion solubility [8, 9]. The addition of network modifier (NWF) Li_2O is to improve both electrical and mechanical properties of such glasses. With the presence of property modifying (MgO) with B_2O_3 glass network could significantly improve different properties like mechanical strength, thermal stability and chemical durability [10-14].

The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. We have studied on the absorption and emission properties of Dy^{3+} doped lead lithium cadmium tantalum magnesium bismuth borate 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, λ=2,4 and 6).

Experimental:

Preparation of glasses:

The following Dy^{3+}doped bismuth borate glass samples (35-x) Bi_2O_3:10 PbO: 10Li_2O:10 CdO: 10Ta_2O_5: 10MgO: 15B_2O_3: xDy_2O_3. (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 Bi_2O_3, PbO, Li_2O, CdO,

Ta_2O_5, MgO, B_2O_3 and Dy_2O_3. They were thoroughly mixed by using an agate pestle mortar. then melted at 1050^0C 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 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 %)
LLCTMBB (UD)	$35Bi_2O_3$:10PbO:$10Li_2O$:10CdO:$10Ta_2O_5$:10MgO:$15B_2O_3$.
LLCTMBB (DY1)	$34Bi_2O_3$:10PbO:$10Li_2O$:10CdO:$10Ta_2O_5$:10MgO:$15B_2O_3$.1 Dy_2O_3.
LLCTMBB (DY1.5)	$33.5Bi_2O_3$:10PbO:$10Li_2O$:10CdO:$10Ta_2O_5$:10MgO:$15B_2O_3$.1.5 Dy_2O_3.
LLCTMBB (DY2)	$33Bi_2O_3$:10PbO:$10Li_2O$:10CdO:$10Ta_2O_5$:10MgO:$15B_2O_3$. 2 Dy_2O_3.

LLCTMBB (UD) -Represents undoped Lead Lithium Cadmium Tantalum Magnesium Bismuth Borate glass specimens.

LLCTMBB (DY)-Represents Dy^{3+} doped Lead Lithium Cadmium Tantalum Magnesium Bismuth Borate glass specimens.

Theory:

Oscillator Strength:

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation [15].

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

where, ε (*v*) is molar absorption coefficient at a given energy *v* (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 [16], using the modified relation:

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

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

Judd-Ofelt Intensity Parameters:

According to Judd [17] and Ofelt [18] 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, *v* 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=2,4and 6) are known as Judd-Ofelt intensity parameters.

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'> to a final manifold │4f^N (S, L) J >| is given by:

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

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

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

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

where, the sum is over all terminal manifolds.

The radiative life time is given by

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

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 │4f^N (S, L) J >| is expressed as

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

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

Results and Discussion:

XRD Measurement:

Figure 1 presents the XRD pattern of the sample contain - Bi_2O_3 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

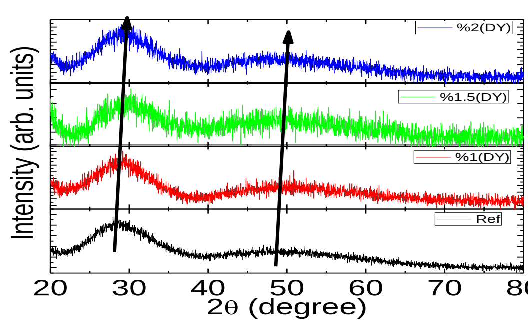

Fig.1: X-ray diffraction pattern of Bi_2O_3: PbO: Li_2O: CdO: Ta_2O_5: MgO: B_2O_3: Dy_2O_3.

Absorption Spectrum:

The absorption spectra of Dy^{3+}doped LLCTMBB glass specimens have been presented in Figure 2 in terms of Intensity versus wavelength. Thirteen absorption bands have been observed from the ground state $^6H_{15/2}$ to excited states $^6H_{13/2}$, $^6H_{11/2}$, $^6H_{9/2}+^6F_{11/2}$, $^6H_{7/2}+^6F_{9/2}$, $^6F_{7/2}+^6H_{5/2}$, $^6F_{5/2}$,$^6F_{3/2}$, $^6F_{9/2}$,$^4I_{15/2}$, $^4G_{11/2}$, $^6F_{7/2}+^4I_{13/2}$, $^6M_{19/2}+4(P,D)_{3/2}$ and $^4G_{9/2}+^6P_{3/2}$ for Dy^{3+}doped LLCTMBB glasses.

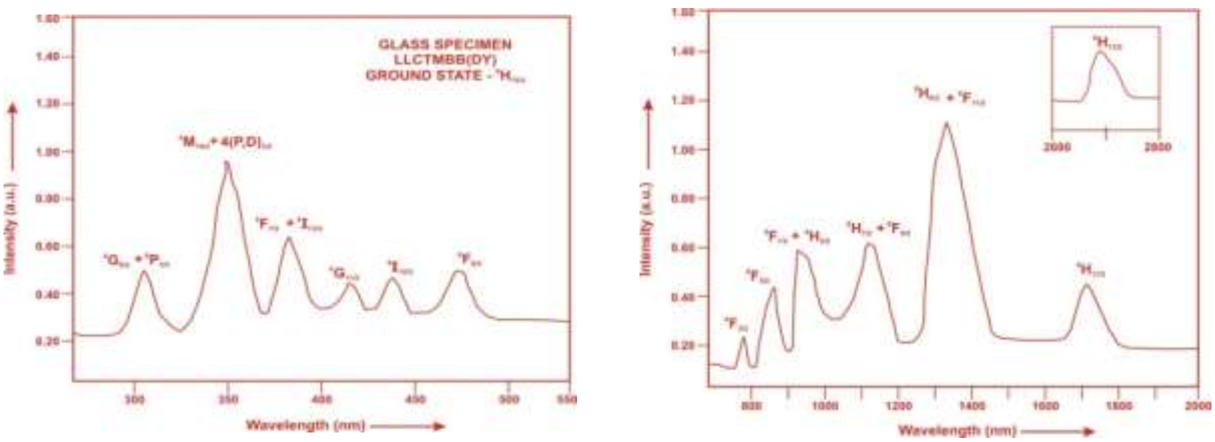

Fig.2: Absorption spectrum of Dy^{3+}doped LLCTMBB glasses

The experimental and calculated oscillator strength for Dy^{3+} ions in LLCTMBB glasses are given in **Table 2.**

Table 2: Measured and calculated oscillator strength ($P_m \times 10^{+6}$) of Dy^{3+}ions in LLCTMBB glasses.

Energy level from $^6H_{15/2}$	**Glass LLCTMBB (DY01)**		**Glass LLCTMBB (DY1.5)**		**Glass LLCTMBB (DY02)**	
	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.	P_{exp}.	P_{cal}.
$^6H_{13/2}$	1.95	2.34	1.93	2.33	1.90	2.32
$^6H_{11/2}$	1.32	1.91	1.30	1.90	1.26	1.87
$^6H_{9/2}+^6F_{11/2}$	10.15	10.04	10.12	10.01	10.07	9.96
$^6H_{7/2}+^6F_{9/2}$	5.45	5.14	5.42	5.12	5.40	5.10
$^6F_{7/2}+^6H_{5/2}$	4.62	4.58	4.60	3.56	4.56	3.52
$^6F_{5/2}$	1.20	1.59	1.18	1.57	1.16	1.55
$^6F_{3/2}$	0.19	0.30	0.17	0.29	0.13	0.28
$^6F_{9/2}$	0.26	0.27	0.24	0.26	0.22	0.25
$^4I_{15/2}$	0.24	0.66	0.21	0.65	0.18	0.64
$^4G_{11/2}$	0.18	0.17	0.16	0.16	0.13	0.15
$^6F_{7/2}+^4I_{13/2}$	3.35	3.56	3.32	3.54	3.28	3.51
$^6M_{19/2}$+4(P,D)3/2	7.85	9.99	7.82	9.98	7.78	9.97
$^4G_{9/2}+^6P_{3/2}$	1.50	1.99	1.46	1.98	1.42	1.95
r.m.s. deviation	0.7287		0.7361		0.7531	

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

In the Lead Lithium Cadmium Tantalum Magnesium Bismuth Borate glasses Ω_2, Ω_4 and Ω_6 parameters decrease with the increase of x from 1 to 2 mol%. The order of magnitude of Judd-Ofelt intensity parameters is $\Omega_2 > \Omega_4 > \Omega_6$ for all the glass specimens. The high values obtained for Ω_2 in all glasses indicate that the Dy^{3+} ion is subjected to higher covalency with low symmetry. The spectroscopic quality factor (Ω_4 /Ω_6) related with the rigidity of the glass system has been found to lie between 1.298 and 1.346 in the present glasses.

The values of Judd-Ofelt intensity parameters are given in **Table 3.**

Table 3: Judd-Ofelt intensity parameters for Dy^{3+} doped LLCTMBB glass specimens

Glass Specimen	$\Omega_2(pm^2)$	$\Omega_4(pm^2)$	$\Omega_6(pm^2)$	Ω_4/Ω_6	Ref.
LLCTMBB (DY01)	2.362	1.467	1.130	1.298	P.W.
LLCTMBB (DY1.5)	2.352	1.468	1.118	1.313	P.W.
LLCTMBB (DY02)	2.326	1.479	1.099	1.346	P.W.
NLTB(DY)	9.86	3.39	2.41	1.407	[19]
LLTB(DY)	8.75	2.62	2.07	1.266	[20]
PKMAF(DY)	7.04	1.73	1.57	1.102	[21]

Excitation Spectrum:

The Excitation spectra of Dy^{3+}doped LLCTMBB glass specimens have been presented in Figure 3 in terms of Excitation Intensity versus wavelength. The excitation spectrum was recorded in the spectral region 315–465 nm fluorescence at 575nm having different excitation band centered at 322,353, 365, 385, 425, 454 and 473 nm are attributed to the $^6P_{3/2}$, $^6P_{7/2}$, $^4P_{3/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$ and $^4F_{9/2}$ transitions, respectively. The highest absorption level is $^4I_{13/2}$ and is at 385nm.So this is to be chosen for excitation wavelength.

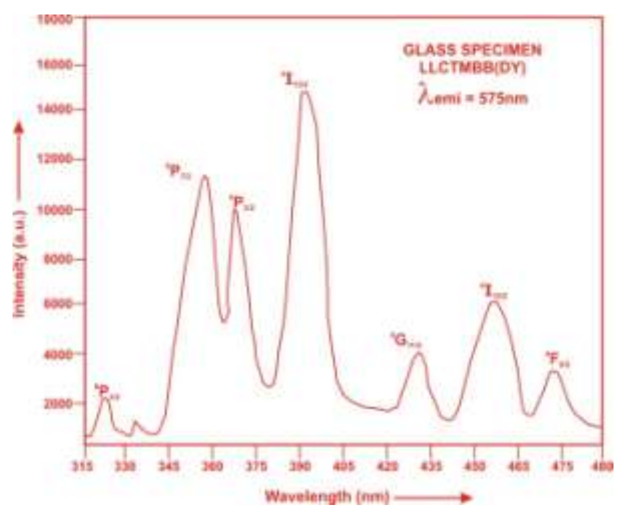

Fig.3: Excitation spectrum of doped with Dy^{3+} LLCTMBB glasses.

Fluorescence Spectrum:

The fluorescence spectrum of Dy^{3+}doped in Lead Lithium Cadmium Tantalum Magnesium Bismuth Borate glass is shown in Figure 4. There are three broad bands observed in the Fluorescence spectrum of Dy^{3+}doped Lead Lithium Cadmium Tantalum Magnesium Bismuth Borate glass. The wavelengths of these bands along with their assignments are given in Table 6. The peak with maximum emission intensity appears at 485nm, 575 nm and 665 nm and corresponds to the ($^4F_{9/2}\rightarrow{}^6H_{15/2}$), ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) and ($^4F_{9/2}\rightarrow{}^6H_{11/2}$) transition.

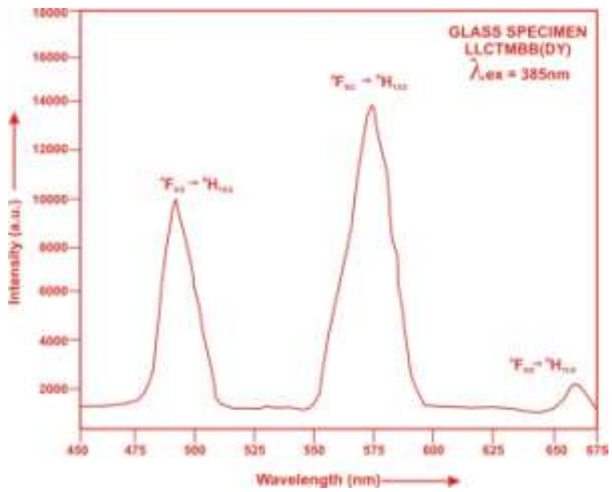

Fig. 4: Fluorescence spectrum of doped with Dy^{3+} LLCTMBB glasses.

Conclusion:

In the present study, the glass samples of composition (35-x) Bi_2O_3:10PbO:10 Li_2O:10 CdO: $10Ta_2O_5$:10MgO:15 B_2O_3:xDy_2O_3 (where x =1, 1.5and 2mol %) have been prepared by melt-quenching method. The value of stimulated emission cross-section (σ_p) is found to be maximum for the transition ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) for all glass specimens. This shows that ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) transition is most probable transition.

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Table4: 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 Dy^{3+} doped LLCTMBB glasses.

Transition		**LLCTMBB DY 01**				**LLCTMBB DY 1.5**				**LLCTMBB DY 02**			
	λ_{max} (nm)	**$A_{rad}(s^{-1})$**	**β**	**σ_p (10^{-20} cm^2)**	**$\tau_R(\mu s)$**	**$A_{rad}(s^{-1})$**	**β**	**σ_p (10^{-20} cm^2)**	**τ_R (μs)**	**$A_{rad}(s^{-1})$**	**β**	**σ_p (10^{-20} cm^2)**	**τ_R (10^{-20} cm^2)**
$^4F_{9/2}\rightarrow{}^6H_{15/2}$	485	97.3987	0.2065	0.165		96.664	0.2058	0.160		95.6674	0.2056	0.154	
$^4F_{9/2}\rightarrow{}^6H_{13/2}$	575	338.453	0.7174	1.211	2119.68	337.170	0.7179	1.175	2129.32	334.045	0.7180	1.136	2149.53
$^4F_{9/2}\rightarrow{}^6H_{11/2}$	665	35.9168	0.07613	0.145		35.8005	0.07623	0.143		35.5065	0.07632	0.138	