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Lasing characteristics of Antimony Lead Borate Glasses Doped with Dysprosium and Erbium

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ABSTRACT

Lead antimony borate glasses of the composition 25 Sb_2O_3– (45−x) B_2O_3–30 PbO- x Re_2O_3 where Re =Dy & Er and x = 0 to 1.0 mol% in steps of 0.2 were prepared. Different physical parameters such as molar volume, density and oxygen packing density were calculated. The characterization of samples was done by X-ray diffraction and differential scanning calorimetric techniques. Fourier transform infra-red spectra and optical absorption spectra been investigated at room temperature have. Electronic polarizabilities were calculated using Lorentz -Lorentz equation. Various optical parameters for different emission levels of dysprosium and erbium ions have been evaluated.

Keywords*: *Lead antimony borte glasses, luminescence, Optical absorption, radiative parameter, rare earth doped glasses,

I. INTRODUCTION

Rare earth ion doped glasses have many applications in optical devices. The ability to emit intense radiation in the visible, NIR and IR spectral regions make the antimony lead borate glasses suitable for fabrications in photonics and electrochemical devices[1].

II. EXPERIMENTAL METHODS

Antimony lead borate glasses doped with dysprosium and erbium were prepared by the melt-quenching technique with the composition 25 Sb_2O_3– (45−*x*) B_2O_3–30 PbO – *x* Re_2O_3 where Re = Dy & Er and *x* = 0, 0.2, 0.4, 0.6, 0.8 and 1.0 and labeled as D0 to D10 and E0 to E10 respectively [2].

The samples were prepared by quenching method [2]. The samples were then ground and optical polished to the dimensions of 1 cm × 1 cm × 0.2 cm. Refractive index (n_d) of the samples was measured using an Abbe refractometer (at λ=589.3 nm) with mono bromo naphthalene as the contact layer between refractometer prism and the sample. The X-ray diffractograms of all the samples were recorded on Rigaku diffractometer mini flex with Cu-Kα radiation. The glass transition temperatures of these glasses were determined by DSC traces that were recorded using DSC Q20 (TA-Instruments). The FTIR transmission spectra of these glasses were recorded in the spectral range 400 – 4000 cm^{-1}. The absorption spectra is recorded in the spectral wavelength range of 300–1600 nm.

III. RESULTS

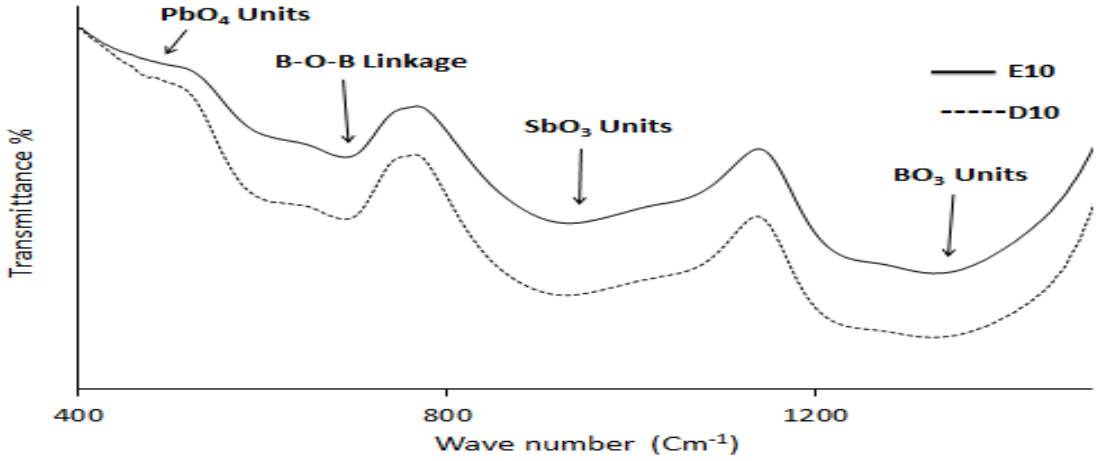

Fig.1 FTIR spectra of Antimony lead borate glasses doped with doped with Er^{3+} and Dy^{3+} ions for 1 mol %.

The FTIR spectra of both the systems exhibit bands at 463 cm^{-1} due to PbO_4 units, 689 cm^{-1} due to vibrations (bending) of B-O-B units, 931 cm^{-1} due to asymmetric stretching vibrations of B-O bonds in BO_4 units, 1330 cm^{-1} due to Boron- Oxygen bonds vibrations (stretching) in the tetrahedral BO_3 units of the borate network. Fig.1 shows the FTIR spectra of LAB glasses doped with Dy^{3+} and Er^{3+} ions. Various physical parameters and optical parameters were evaluated using standard equations [2,4]. The average molar refraction of the samples is known as specific refraction and calculated using Lorentz-Lorentz equation [3].

$$R_m = \left(\frac{n^2-1}{n^2+2}\right)V_m. \quad (1)$$

where V_m is molar volume and *n* is the refractive index.

The Lorentz-Lorentz equation presents the polarizability, i.e., the magnitude of response of the electrons to an electromagnetic field. When the material is exposed to intense light beams, the electronic polarization causes the optical non linearity. When Avogadro number N_A is introduced, the Lorentz –Lorentz equation can be written as

$$R_m = \left(\frac{n^2-1}{n^2+2}\right)V_m = \frac{4}{3}\pi N_A \alpha_e. \quad (2)$$

where α_m is the molar electronic polarizability in $Å^3$ and R_m is molar refraction in cm^3. Rearranging the terms, we can write electronic polarizability

$$\alpha_e = \frac{3}{4\pi}\left(\frac{R_M}{N_A}\right). \quad (3)$$

The various measured physical properties are presented in Table.1.

TABLE 1. Various physical properties of Dy^{3+} and Er^{3+} doped LAB glasses.

S. No	Parameter	Glass									
	Name of the Sample	D02	D04	D06	D08	D10	E02	E04	E06	E08	E10
1	Density ρ (g/cm^3)	5.35	5.360	5.371	5.381	5.392	5.061	5.155	5.296	5.406	5.4136
2	Refractive index(n) (experimental)	1.586	1.589	1.591	1.592	1.594	1.644	1.66	1.648	1.649	1.651
3	Molar Refraction (R_M)	11.39	11.26	11.037	10.86	10.64	12.89	12.14	11.88	11.705	11.755
4	Oxygen packing density(gm atom/L)	70.71	71.77	73.48	74.74	76.48	70.83	71.99	73.83	75.19	75.18
5	Re ion concentration N(x10^{21}/cm^3)	0.11	0.22	0.33	0.45	0.58	0.11	0.22	0.33	0.45	0.56
7	Polarizability (α_e)(x10^{-24}) (cm^3)	4.513	4.465	4.373	4.305	4.219	4.873	4.815	4.714	4.642	4.662
7	Cutoff Wavelength	358	360	362	364	366	355	356	357	358	359
8	Optical Bandgap Energy	3.449	3.436	3.418	3.398	3.374	3.423	3.421	3.417	3.414	3.412
9	Urbach Energy ΔE(eV)	0.564	0.6	0.64	0.68	0.722	0.488	0.521	0.591	0.628	0.673

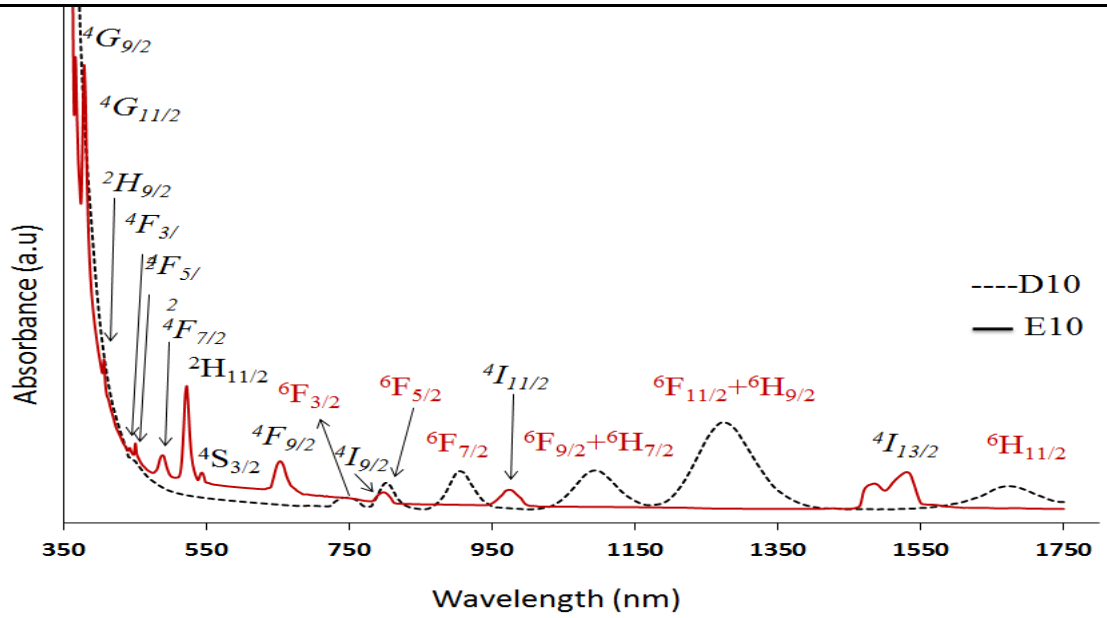

Fig.2. Optical absorption spectra antimony lead borate glasses doped with Er^{3+} (ground state $^4I_{15/2}$) and Dy^{3+} (ground state $^6H_{15/2}$) ions for 1 mol %.

Optical absorption spectra for dysprosium doped LAB glasses consist of six well resolved bands due to the transition from $^6H_{15/2}$ state to various exited states namely $^6H_{11/2}$ (1676 nm), $^6F_{11/2}$ + $^6H_{9/2}$ (1270 nm), $^6F_{9/2}$ + $^6H_{7/2}$ (1088 nm), $^6F_{7/2}$ (902 nm), $^6F_{5/2}$ (800 nm), $^6F_{3/2}$ (751 nm) whereas erbium doped glasses consist of twelve well resolved bands due to the transition from $^4I_{15/2}$ state to various exited states namely $^4I_{13/2}$ (1527 nm), $^4I_{11/2}$ (973 nm), $^4I_{9/2}$ (797 nm), $^4F_{9/2}$ (652 nm), $^4S_{3/2}$ (543 nm), $^2H_{11/2}$ (522 nm), $^4F_{7/2}$ (488 nm), $^4F_{5/2}$ (452 nm), $^4F_{3/2}$ (443nm), $^2G_{9/2}$ (408 nm), $^4G_{11/2}$ (378 nm), $^4G_{9/2}$(364 nm). The absorption bands are assigned by comparison with energy levels of Re^{3+} aqua-ion [5]. Fig.2 shows the optical absorption spectra antimony lead borate glasses doped with erbium with ground state $^4I_{15/2}$ and Dy^{3+} ions with ground state $^6H_{15/2}$ for one mol %.

The spectra obtained for all the glasses show identical characterization with the exception of their relative band intensities. The relation between the optical absorption coefficient α (ω) and optical band gap energy E_{opt} is given by the equation [6]

$$\alpha(\omega) = \frac{Const(\hbar\omega - E_{opt})^2}{(\hbar\omega)}. \quad (4)$$

This equation can be rearranged as

$$(\alpha\hbar\omega)^{1/2} = Const\ (\hbar\omega - E_{opt}). \quad (5)$$

Figure 3(a) shows variation of cutoff wavelength with mol % of dysprosium and erbium ions and Figure 3(b) variation of polarizability with mol % with mol % of dysprosium and erbium ions

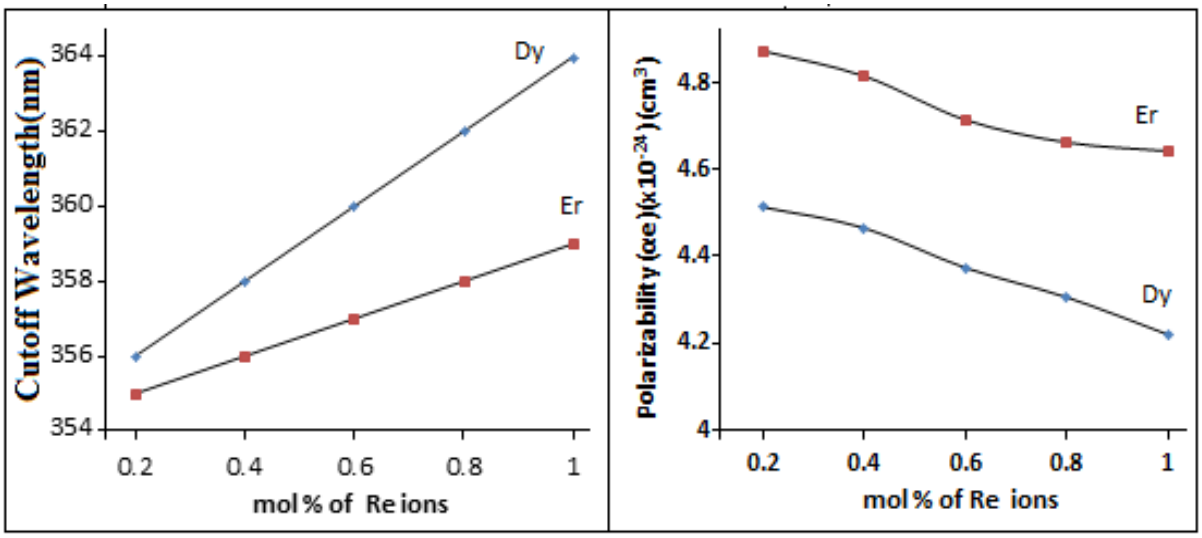

Figure 3: Variation of cutoff wavelength and polarizability with mol % of Dy^{3+} and Er^{3+} ions.

TABLE 2. Judd-Ofelt parameters ($\Omega \times 10^{-20}$ cm^2) in LAB glasses doped with erbium ions

Sample	J-O intensity parameters($\times 10^{-20}$ cm^2)		
	Ω_2	Ω_4	Ω_6
D02	2.270	0.940	1.310
D04	3.120	1.210	1.540
D06	3.290	1.010	1.020
D08	4.060	1.330	1.930
D10	5.810	1.130	2.680
E02	5.344	2.981	2.485
E04	5.639	3.126	2.591
E06	5.731	3.293	2.668
E08	5.877	3.338	2.724
E10	6.111	3.548	2.848

Optical band gap for all the glasses were evaluated by drawing Tauc plots between $(\alpha\hbar\omega)^{1/2}$ and $\hbar\omega$ using Equation 5. Cut of wavelength, optical band gap, Urbach energy, values were presented in Table 1. It is observed that the cut off wavelength, Urbach energy optical band gap of the glasses increases with increasing concentration of rare earth ions whereas optical band gap is decreasing.

TABLE 3. The branching ratios (β_R) and radiative decay times (τ_R) of Dy^{3+} (for $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition) Er^{3+} (for $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition) doped LAB glasses

	β_R		τ_R (μs)	
x	Dy^{3+}	Er^{3+}	Dy^{3+}	Er^{3+}
0.2	0.217	0.6711	2190	262
0.4	0.207	0.6711	2030	250
0.6	0.232	0.6709	1790	242
0.8	0.192	0.671	1460	237
1	0.168	0.6709	1220	225

The rms deviations between the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths were within the limits of experimental errors. The Judd-Ofelt parameters Ω_2, Ω_4 and Ω_6 were computed by the least square fitting analysis of the experimental oscillator strengths [7,8] and presented in Table 2. The values of Ω_λ follows the order $\Omega_2 > \Omega_6 > \Omega_4$ for disprosium doped glasses and $\Omega_2 > \Omega_4 > \Omega_6$ order for erbium doped glasses

IV. LUMINESCENCE PROPERTIES

Normalized luminescence spectra of Dy^{3+} doped antimony lead borate glasses with the excitation wavelength of 388 nm shows bands at 454nm, 484 nm, 576 nm and 666 nm corresponding to the transitions $^4I_{15/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and $^4F_{9/2} \rightarrow {}^6H_{11/2}$. Similarly Er^{3+} doped LAB glasses shows bands at 526nm, 547 nm and 665 nm corresponding to the transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (bright green) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (weak red) with the excitation wavelength of 380 nm. It should be noted that the emission at 547 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) considerably broadens towards the high energy side. Fig.4 shows the normalized luminescence spectra of Er^{3+} doped LAB glasses and Fig. 5 shows luminescence spectra of Dy^{3+} doped glasses.

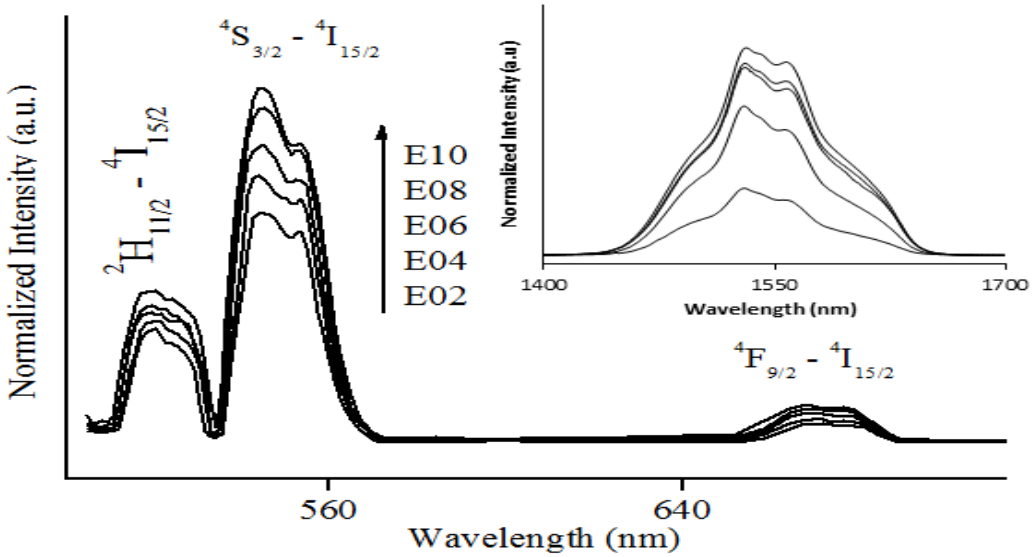

Fig. 4 Emission spectra of LAB glasses doped with Er^{3+} ions recorded at room temperature (λ_{ex} =388 nm). The inset shows IR Emission spectrum.

V. RADIATIVE PROPERTIES

The radiative properties such as, luminescence branching ratio (β_R), radiative lifetimes (τ_r) are calculated by using the standard relations [7,8] and presented in Table 3.

VI. CONCLUSIONS

There is no shift in the positions of bands in absorption spectra as well in FTIR spectra whereas intensity increase with the increase in rare earth ion concentration. It has been observed that the luminescence intensity of various emission bands increase with the concentration of rare earth ions which indicates that there is no luminescence quenching in these glasses within the concentration range studied.

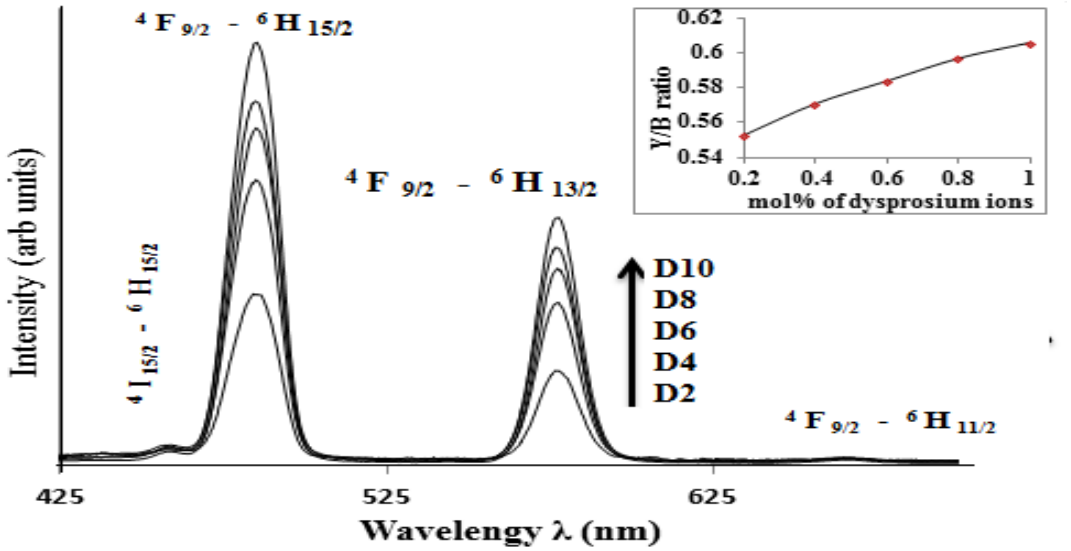

Fig.5 Emission spectra of LAB glasses doped with Dy^{3+} ions recorded at room temperature (λ_{ex} =388 nm). The inset shows Y/B ratio.

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