Optical and Physical Investigations of Lanthanum Bismuth Borate glasses doped with Ho$_2$O$_3$

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Abstract. Holmium doped 10La$_2$O$_3$-15Bi$_2$O$_3$-(75-x) B$_2$O$_3$ (Ho$^{3+}$: LBB) glasses have been prepared by melt quench technique and the impact of holmium ions concentration on optical and physical properties of present glasses have been examined. Ho$^{3+}$ dependent density, molar volume, refractive index, rare earth ion concentration, polaron radius, inter ionic distance, field strength and energy band gap are calculated and tabulated. Amorphous nature of the all glasses has been confirmed by XRD patterns. The room temperature (RT) Uv-Vis absorption spectrum doped with 1 mol% of Ho$_2$O$_3$ exhibit eight prominent bands centred at 895, 641, 537, 486, 472, 467, 451 and 416 due to transition between ground state to various excited states. The results show that, the density is increases and molar volume of the glasses is decreases with an increase in Ho$_2$O$_3$ concentration and consequently generate more non-bridging oxygen (NBOs) in the glass matrix. The Urbach energy is increases with holmium concentration which exemplifies the degree of disorder present in the LBB glasses. The considerable increase in field strength observed in present glasses is attributed to occurrence of strong bridge between Ho$^{3+}$ and B$^-$ ions and this strong bridge is possibly due to the displacement between Ho$^{3+}$ and oxygen atoms which are generated from the conversion BO$_3$–BO$_4$ units.

1. Introduction

In recent decades, Vitreous materials doped with rare earths (REs) have attracted persistent interest due to unique luminescent behaviours and wide applications of REs in illumination, solid-state lasers and so on [1]. Further, these REs doped vitreous materials proving to be good luminescence materials since they have high emission efficiencies due electronic transitions between 4f–4f and 4f–5d of RE ions [2]. The 4f–4f transition gives an especially sharp fluorescence pattern from the ultraviolet (UV) to the infrared region. This is attributed to shielding effects of the outer 5s and 5p orbital on the 4f electrons [2]. However, enhancing the physical and optical properties of RE doped inorganic glasses received intense interest due their potential applications in optical devices and laser technology [3]. One of the notable example is modern solid state optical technology, which is based on glass materials doped with lanthanides. Such optical materials offer a wide range of applications in the area of telecommunication, x-ray imaging, sensors, colour displays, infrared detection, medical diagnostics, data storage and solid-state lasers [3, 4]. Among several glass formers, Borate is one of the good and most well-known glass formers. It possesses several attractive features such as high transparency, good host for alkali, alkaline earth and rare-earth ions, higher relative stability and most importantly it is inexpensive [4]. Glasses which consist of heavy metal oxides (HMO, such as PbO, Bi$_2$O$_3$, Sb$_2$O$_3$, Nb$_2$O$_5$, TeO$_2$, GeO$_2$, WO$_3$) and heavy metal fluorides (HMF, like PbF$_2$, BiF$_3$, SbF$_3$, TeF$_4$ etc) are more promising for photonics and optoelectronics due to its low melting temperature (600°C–800°C) [5], extensive glass formation range, high refractive index, high physical and chemical stability, high nonlinear optical property and also the intensity and quantum efficiency of luminescence from the excited states of rare-earth ions can be tuned to several orders when glasses host with HMO and
HMF. Among HMOs, Bi\textsuperscript{3+} has been widely investigated since the third order nonlinear optical susceptibility (\(\chi^3\)) of bismuth oxide is 1.5 times larger than lead oxide \[6\] and also the higher valent oxides Bi\textsubscript{2}O\textsubscript{3} can be used as a network modifier since the cation produces important structural changes due to its highest valence \[2\]. Furthermore, Saisudha \[7, 8\] had investigated the spectroscopic properties of Nd\textsuperscript{3+}, Sm\textsuperscript{3+}, and Dy\textsuperscript{3+} ions in various borate glasses and concluded that the borate glasses consist of bismuth oxide have large stimulated emission cross sections and may be used as laser host materials. Of several RE ions, much attention has been paid towards Ho\textsuperscript{3+} ions, since the Ho\textsuperscript{3+} doped glasses are expected to demonstrate the prominent emissions in infrared (IR) region along with visible emissions. And also, to our knowledge, the effect of Ho\textsuperscript{3+} concentration on optical and physical properties of lanthanum bismuth borate glasses has not been studied in detail.

The present work reports, the influence of Ho\textsubscript{2}O\textsubscript{3} concentration on the physical and optical properties of LBB glasses.

2. Experimental
The glasses of nominal composition xHo\textsubscript{2}O\textsubscript{3}-10La\textsubscript{2}O\textsubscript{3}-15Bi\textsubscript{2}O\textsubscript{3}-(75-x) B\textsubscript{2}O\textsubscript{3}, where x=0, 0.5, 1, 2 mol\% of Ho\textsubscript{2}O\textsubscript{3} (hereafter named as LBB-0, LBB-1, LBB-1, LBB-3 respectively) have been prepared using high purity La\textsubscript{2}O\textsubscript{3}, Bi\textsubscript{2}O\textsubscript{3}, H\textsubscript{3}BO\textsubscript{3} chemicals by melt quenching technique. Exact amounts of AR grade La\textsubscript{2}O\textsubscript{3} (SDFCL, 99.99%), Bi\textsubscript{2}O\textsubscript{3} (SDFCL, 99.99%), and H\textsubscript{3}BO\textsubscript{3} (SDFCL, 99.99%), were mixed in a porcelain crucible and melted at 1180\textdegree C for 30 min. The molten liquid was then poured between two brass moulds and pressed each other. The prepared glass samples were kept for annealing at 400\textdegree C for 3h to make samples free from thermal stresses. The samples were cut into proper shape and polished for further studies.

The glassy nature of samples was confirmed by XRD measurements (Rigaku Ultima IV) using Cu-K\textalpha radiations (\(\lambda = 0.154 \text nm\)) with copper filters operating at 40 kV and 100 mA. The 2\texttheta range was 0\textdegree– 80\textdegree with step size of 0.2\textdegree and a resolution of 0.01\textdegree. The optical absorption spectra were recorded using PekinEleder Lambda-35 Uv-Vis spectrometer in the range of 200 – 1100 nm equipped with a deuterium lamp and halogen lamp with a resolution of 1 nm. The refractive indices of the glasses were measured using Abbe’s refractometer (Model CL: 1.30-1.81) with a sodium vapour lamp as the source of light, emitting the light of wavelength, \(\lambda = 589.3 \text{ nm (D line)}\) and having monobromonaphthalene as the contact layer between the sample and prism of the refractometer. All measurements were done at room temperature (RT).

The optical absorption coefficient \(\alpha (\lambda)\) of the samples was calculated by using the following relation \[9\]:

\[
\alpha(\lambda) = 2.303 \left[ \frac{A}{d} \right]
\]

Where, A and d are the absorbance and the thickness of the samples respectively.

The optical bandgap \(E_g\), describe the direct and indirect energy difference between valence and conduction band of glasses and is obtained from the equation \[9\]:

\[
\alpha h\nu = B(h\nu - E_g)^n
\]

Where, \(\alpha\) is the absorption coefficient, \(h\nu\) is the incident photon energy, \(B\) is the electronic transition constant and \(n\) values are 1/2 and 2 for direct and indirect allowed transitions respectively.

Density of the glasses were measured by using Archimede’s principle with toluene as the immersion liquid,

\[
\rho = \frac{W_a}{W_a - W_b} \times \rho_t
\]

Where, \(W_a\) is weight of the glass sample in air and \(W_b\) is the weight of the glass sample when immersed in toluene (\(\rho_t = 0.8669 \text{ g cm}^{-3}\)). Here Toluene is preferred as immersion liquid due to its superior chemical stability against hygroscopic attack to the glass and toxicity is relatively low.
The molar volume ($V_m$) was calculated from the expression,

$$V_m = \frac{M}{\rho}$$  \hfill (4)

Where, $M$ is the average molecular weight and $\rho$ is the density of the glass samples.

The molar refractivity ($R_M$) was obtained from the expression,

$$R_M = \frac{\varepsilon - 1}{\varepsilon + 2} V_m$$  \hfill (5)

Where, $V_m$ is the molar volume and $\varepsilon$ is dielectric constant of the glasses respectively.

The electronic polarizabilities ($\alpha_e$) of the glasses were calculated with the help of Lorentz–Lorenz equation,

$$\alpha_e = \frac{3}{4\pi N_A} R_M$$  \hfill (6)

Where, $N_A$ is the Avogadro’s number, $R_M$ is the molar refractivity of the glass sample. The RE ion concentration was calculated using,

$$N = \frac{x \times \rho \times N_A}{M_i}$$  \hfill (7)

Where, $x$ is the mol % of dopant (here it is $Ho_2O_3$).

Polaron radius was calculated from the expression,

$$r_p = \frac{1}{2} \left[ \frac{\pi}{6N} \right]^{\frac{1}{3}}$$  \hfill (8)

Inter - ionic distance of Ho$^{3+}$ ions was calculated from the equation,

$$r_i = \left[ \frac{1}{N} \right]^{\frac{1}{3}}$$  \hfill (9)

Dielectric constant of the glasses was calculated from,

$$\varepsilon = n^2$$  \hfill (10)

Where, $n$ is the refractive index of the glass samples.

Reflection loss in the samples was obtained from the expression,

$$R(\%) = \left( \frac{n - 1}{n + 1} \right)^2 \times 100$$  \hfill (11)

The field strength of Ho$^{3+}$ ions was obtained via,

$$F = \frac{Z}{r_p^2}$$  \hfill (12)

Where, $Z$ is the charge on the rare earth ion.

All the physical parameters calculated using above expressions are enlisted in table 1.

3. Results and Discussion

The typical X-ray diffraction pattern of the glasses is shown in figure 1 and which presents a broad hump between $40^0$ to $50^0$ without any sharp peak, confirms the amorphous nature of the glass samples. The XRD profiles of all samples are nearly the same.
Figure 1: XRD patterns of LBB glasses

Figure 2: Variation of refractive index of LBB glasses with different Ho$_2$O$_3$ content.

Figure 3: Variation of density and molar volume of LBB glasses doped with different concentration of Ho$_2$O$_3$.

The addition of Ho$_2$O$_3$ in to the glass matrix increases the refractive index (RI) from 1.456 to 1.626 as shown in figure 2. It is demonstrated that, the incorporation of RE ions in to the glass matrix disturbs the vibration of boron and oxygens atoms which induces large scale disruption in the network by converting bridging oxygen to non-bridging oxygen [10]. The formation of non-bridging oxygens affords a larger polarizability over the covalent bonds of bridging oxygen by imparting a higher refractive index [11]. In general, the ionic refractivity of non-bridging oxygens in oxide glasses is larger than that of bridging oxygens [12]. Therefore, the considerable increase in refractive index possibly due to increase in number of non-bridging oxygen [13]. This increase in RI with respect to different concentration of Ho$^{3+}$ ions attributed to the illustrious modifications in the glass network structure [14]. From the figure 3, it is observed that, the substitution of Ho$_2$O$_3$ in to the glasses is gradually enhances the glass density and reduces the molar volume. The remarkable increase in density is attributed to; (i) increase in molar mass of Ho$_2$O$_3$, (ii) increase in the average molecular weight of oxide ions in the glass due to Ho$_2$O$_3$, has a higher relative molecular weight than that of B$_2$O$_3$, (iii) The replacement of La and Bi ions by Ho$^{3+}$ ions having higher atomic mass. The molar volume depends on the rates of change of both density and molecular weight. However, the rate of increase in density is greater than the rate of increase in molecular weight which results in decreasing in molar volume with the increase in Ho$_2$O$_3$ content. It may be assumed that the increase in Ho$_2$O$_3$ concentration at the expense of B$_2$O$_3$ results in decrement in bond length or inter-ionic spacing between the RE ions which may be due to the increase in the stretching force constants of the bonds inside glass network [15].
Table 1: Physical properties and inter-ionic properties of LBB glasses at different concentration of Ho\textsubscript{2}O\textsubscript{3}.

| Properties                        | Glasses     |
|-----------------------------------|-------------|
|                                   | LBB-0 | LBB-1 | LBB-2 | LBB-3 |
| Physical Properties               |        |       |       |       |
| Refractive index, n               | 1.456  | 1.504 | 1.605 | 1.626 |
| Average molecular weight, M\textsubscript{(gmol\textsuperscript{-1})} | 154.691 | 156.231 | 157.772 | 160.855 |
| Density, ρ (gcm\textsuperscript{-3}) | 4.41  | 4.503 | 4.871 | 4.899 |
| Molar volume, V\textsubscript{m} (cm\textsuperscript{3}) | 35.077 | 34.694 | 32.390 | 32.834 |
| Molar refractivity, R\textsubscript{M} (cm\textsuperscript{3}) | 9.534 | 10.273 | 11.155 | 11.622 |
| Electronic Polarizability, α\textsubscript{e} (Å\textsuperscript{3}) | 3.778 | 4.070 | 4.418 | 4.605 |
| Reflection loss, R (%)            | 3.447  | 4.051 | 5.393 | 5.682 |
| Dielectric constant, ε            | 2.119  | 2.262 | 2.576 | 2.643 |
| Inter-ionic properties            |        |       |       |       |
| RE ion concentration, N (x10\textsuperscript{22} ions cm\textsuperscript{-3}) | -     | 0.868 | 1.859 | 3.668 |
| Polaron radius, r\textsubscript{p} (Å) | 1.960 | 1.521 | 1.212 |       |
| Inter-ionic distance, r\textsubscript{i} (Å) | -     | 4.865 | 3.774 | 3.009 |
| Filed strength, F (x10\textsuperscript{15} cm\textsuperscript{-2}) | -     | 7.80  | 12.960 | 20.395 |

Significant reduction in the inter-ionic distance and Polaron radius (shown in table1) with the increase of holmium concentration is attributed to the clogging of Ho\textsuperscript{3+} ions in the glass host. As a result, the field strength is enhanced considerably due to the existence of strong link between the Ho\textsuperscript{3+} and B\textsuperscript{-} ions and the this link between Ho\textsuperscript{3+} and B\textsuperscript{-} ions is further attributed to the possible displacement between the Ho\textsuperscript{3+} and lately generated oxygen atoms from the conversion of BO\textsubscript{3}–BO\textsubscript{4} units [3] which leads to a more compact boron network in LBB glass systems.

Figure 4: Optical absorption spectrum of LBB-2 glass.
Figure 4, represents the absorption spectrum of LBB-2 (doped with 1 mol % of Ho\textsubscript{2}O\textsubscript{3}) glass sample recorded in the wavelength range of 200–1100 nm at RT. The observed absorption bands of Ho\textsuperscript{3+} ions are centred at 895, 641, 537, 486, 467, 451, and 416 nm are attributed to the 4f–4f transitions of Ho\textsuperscript{3+} ions from the ground \( ^5\text{I}_8 \) level to \( ^5\text{I}_5 \), \( ^5\text{F}_5 \), \( ^5\text{S}_2+^5\text{F}_4 \), \( ^5\text{F}_3 \), \( ^5\text{F}_2 \), \( ^3\text{K}_6 \), \( ^5\text{G}_6+^5\text{F}_1 \) and \( ^5\text{G}_5 \) excited levels respectively. These transitions were assigned by comparing the band positions in the absorption spectra with those reported in the literature [13, 14]. Among various absorption transitions of the Ho\textsuperscript{3+} ion, the absorption bands assigned to the \( ^5\text{I}_8 \rightarrow ^5\text{G}_6 \) transitions centred at 454 nm is referred as hypersensitive transition [17]. This transition obey the selection rules |ΔS| = 0, |ΔL| ≤ 2 and |ΔJ| ≤ 2 and which is very responsive to the surrounding environment of the Ho\textsuperscript{3+} ions.

**Figure 5:** Typical plot of \((ahv)^2\) v/s \(hν\) for direct bandgap measurements.

**Figure 6:** Typical plot of \((ahv)^{1/2}\) v/s \(hν\) for indirect bandgap measurements.

**Figure 7:** variation of direct and indirect bandgap energies in LBB glasses at different concentration of Ho\textsubscript{2}O\textsubscript{3}

Figures 5 and 6, depicts the typical plots of \(hν\) dependence of \((ahv)^2\) and \((ahv)^{1/2}\) respectively and same tendency have been observed for different concentration of Ho\textsubscript{2}O\textsubscript{3} in LBB glasses (not shown here). The variation of direct and indirect bandgap energy values for different mol % of Ho\textsubscript{2}O\textsubscript{3} is shown in figure 7, it is observed that, the direct and indirect bandgap energies are decreases with substitution of Ho\textsubscript{2}O\textsubscript{3} in to the glass matrix. The incorporation of Ho\textsubscript{2}O\textsubscript{3} causes the new structural changes in the glasses and creates greater number of non-bridging oxygens (NBOs) which results in reduction of the bandgap [18]. The decrease in bandgap energies is turn attributed to the increase in Ho\textsuperscript{3+} concentration may enhance the degree of localization via creation of defect in the charge...
distribution and drive the energy levels of the nearest oxygen ions closer to the top of the valence band and thereby raise donor centers in the glass matrix [3]. This increase in donor centers results in decrease in energy band gap [19].

![Figure 8](image1.png) **Figure 8:** Typical plot of ln(α) v/s hv used to calculate the Urbach energy.

![Figure 9](image2.png) **Figure 9:** Variation of Urbach energy with different concentration of Holmium.

Figure 8 presents a typical plot of ln(α) v/s hv, the values of Urbach energy calculated from the inverse slope. The increase in Urbach energy with the increase of Ho2O3 concentration shown in figure 9 is attributed to the formation of bonding defects and non-bridging oxygen. However, the increase in Urbach energy with the increase of Ho2O3 content manifests the degree of disorder in LBB glasses [14].

The Urbach energy values of LBB glasses are well within the range of 0.046–0.66 eV for amorphous semiconducting materials [20]. In general, it is assumed that the position of absorption edge depends on the oxygen bond strength in the glass formation network [21]. Consequently, with addition of Ho2O3 into the host glass changes the oxygen bonding in the network (by the formation of NBOs) which in turn changes the absorption characteristics.

4. **Conclusion**

The glasses of varied concentration of holmium doped lanthanum bismuth borate glass samples (Ho3+: LBB) have been fabricated by conventional melt quench technique. XRD profiles were confirmed the amorphous nature glasses. The role of holmium ions on optical and physical properties of the 10La2O3–15Bi2O3–(75-x) B2O3 glasses are investigated. With increase in holmium concentration the refractive index is increases and is found highest at 2 mol% of Ho2O3, whereas direct and indirect band gap energies decreases with increasing Ho2O3 concentration. The increment in density and decrement in volume is observed with respect to the concentration of Ho3+. All these attenuations observed in present glasses are ascribed to the growth of non-bridging oxygen. Due to the existence of strong link between Ho3+ ions and B ions, the significant increase in field strength has been observed. Further, with the variation of holmium concentration, the Urbach energy is increasing which exemplify the degree of disorder present in the glasses. The results, in particular, the high refractive index and density revealed that, the present glasses may contribute towards the development of glasses useful in solid state lasers and broadband devices.

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