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**Research Article**

# Optical Absorption Behavior of LiF–Al$_2$O$_3$–B$_2$O$_3$ Glass Doped with Ho$_2$O$_3$

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**ABSTRACT**
LiF–Al$_2$O$_3$–B$_2$O$_3$ glasses mixed with 1.0 mol % of Ho$_2$O$_3$ were synthesized by melt quenching method. The physical parameters such as rare earth ion concentration, mean rare earth ion separation and molar volume for the prepared glass samples were evaluated. The spectroscopic properties like optical and IR studies have been undertaken. The study of optical absorption, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of the materials. The optical absorption studies revealed that all possible absorption transitions are observed in the spectrum from the ground state $^5I_8$. These transitions spread over near UV, Visible and NIR regions. The IR spectral studies showed the conventional bands due to borate groups, AlO$_4$ and AlO$_6$ structural units. These glasses find potential applications as laser materials, IR domes, optical fibres, modulators, memory devices, photonic devices for communication, advanced computer applications and as semiconducting devices.

**Keywords:** LiF-Al$_2$O$_3$-B$_2$O$_3$ Glass, Ho$_2$O$_3$, Experimental, IR and Physical Parameters.

## 1. INTRODUCTION

Inorganic glass materials generally possess high transparency, good formability and tunable chemical composition range. Since glass has no grain boundary, which is a characteristic of liquid, attained high transparency of glass makes it to be a fundamental material for our daily life, for examples, window, display panel glass and optical glass fibres. The good formability is originated from the random network structure with interstitial free volume, and therefore, large and long glassy material can be prepared much easier than inorganic crystal. Note that the term "random" in glass means a lack of the long range ordering. Actually in glass there is a short-range ordering of atoms that constitute various coordination polyhedra. Thus, the short-range ordering in amorphous is basically identical to that in crystal. On the other hand, the random network of glass closely correlates with the chemical composition diversity, which in turn allows us to tailor physical property and various functionalities. The diversity is also a unique characteristic of amorphous glass materials.

Crystalline and glassy borate compounds, undoped and doped with rare earth and transition elements, are very promising materials for quantum electronics and non-linear optics, scintillators and

thermoluminescent (TL) dosimeters as well as γ and neutron detectors[1-3]. This also concerns lithium tetraborate (Li$_2$B$_4$O$_7$) single crystals, which are characterized by extremely high radiation stability, good TL properties and high transparency in a wide spectral range from vacuum UV to far IR[4-6]. Rare-earth ions such as Eu$^{3+}$, Eu$^{2+}$, Er$^{3+}$, Nd$^{3+}$, Tm$^{3+}$, Sm$^{3+}$, Yb$^{3+}$, etc., show high luminescence efficiency in a variety of host materials with emission in a broad spectral range and widely used as activator centres in laser and luminescent materials, including borate and tetraborate crystals and glasses with different chemical compositions. In particular, compounds activated with Tb$^{3+}$ and Dy$^{3+}$ is considered as effective luminescent materials in green and yellow-blue spectral ranges, respectively[7].

A study of the physical properties including spectroscopic, dielectric properties etc., of the glasses is of considerable importance because of the insight it gives into the fundamental process-taking place in them. In fact, the physical properties of the glasses are to a large extent controlled by the structure, composition and the nature of the bonds of the glasses. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition, doping etc., is of

considerable interest in the application point of view[8].

## 2. MATERIALS AND METHODS

For the present study, the chosen composition is $(30–x)$ LiF–10Al$_2$O$_3$- 60B$_2$O$_3$: xHo$_2$O$_3$ with x = 1.0 mol%.

The details of the compositions are:

Ho$_0$: 30 LiF–10Al$_2$O$_3$- 60B$_2$O$_3$
Ho$_1$: 29 LiF–10Al$_2$O$_3$- 60B$_2$O$_3$: 1.0 Ho$_2$O$_3$
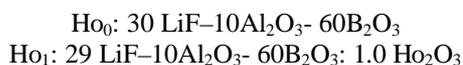
Analytical grade reagents of H$_3$BO$_3$, LiF and Ho$_2$O$_3$ powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar, calcinated at about 900$^o$C for 2 h in a platinum crucible and subsequently melted in the temperature range of 1200 to 1250$^o$C in an automatic temperature microprocessor controlled furnace for about 30 minutes. The resultant bubble free melt was then poured in a pre–heated brass mould and annealed at 300$^o$C in another furnace. The samples prepared were mechanically ground and optically polished to the dimensions of 1 cm × 1 cm × 0.2 cm. The density of the glasses was determined to an accuracy of (± 0.0001) by the standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.1 mg using Ohaus digital balance Model AR2140 for evaluating the density. The optical absorption spectra of the glasses were recorded to a resolution of 0.1 nm at room temperature in the spectral wavelength range covering 250-900 nm using JASCO Model       V-670 UV-VIS-NIR spectrophotometer. The refractive index (n) of the samples was measured (at λ = 589.3 nm) using Abbe's refractometer with monobromo naphthalene as the contact layer between the glass and the refractometer prism.

## 3. RESULTS AND DISCUSSION

B$_2$O$_3$ is a well-known network former, participates in the network forming with BO$_3$ and BO$_4$ structural units. LiF do act as modifier like any conventional modifiers and create bonding defects. In some of the recent investigations  it has also been reported that K$^+$ and Li$^+$ ions in floro salt glass matrices experience mixed oxygen-fluorine coordination and do not induce any defects in the glass network.

Some physical parameters useful for characterization KF-Al$_2$O$_3$-B$_2$O$_3$: Ho$_2$O$_3$ glasses are estimated from the measured value of density (d) and the average molecular weight $\overline{M}$ , using the following Eqs.

The transition metal ion concentration (N$_i$) could be obtained from:

(i) N$_i$  $(10^{22}$ ions /cm$^3$)   = N$_A$ M (mol%) d / $\overline{M}$

From the N$_i$ values obtained, the polaron radius ( r$_p$ ) and inter-ionic distance ( r$_i$ ) of transition metal ions could be evaluated:

(ii) Inter - ionic distance r$_i$ (Å)  $= \left[ \dfrac{1}{N_i} \right]^{1/3}$

(iii) Polaron radius r$_p$ (Å)     $= \dfrac{1}{2} \left[ \dfrac{\pi}{6N_i} \right]^{1/3}$

The field strength ( F$_i$ ) of transition metal ion  in the glass matrix is described through the oxidation number (z) and the ionic radii (r$_i$) of the transition metal ions  by:

(iv) Field strength F$_i$ (cm$^{-2}$)    $= \dfrac{z}{r_i^2}$

From the measured values of the density and average molecular weight M of the samples, various other physical parameters such as rare earth ion concentration Ni, mean rare earth ion separation R$_i$ and molar volume for all the glass samples were evaluated and presented in Table.

The study of optical absorption, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of the materials. The absorption coefficient α(ν) is related to transmitted intensity , incident intensity  and the thickness of the sample (t) as[9]

$$\alpha(\nu) = (1/t) \ln (I_i/I_t)$$

Optical band gap energy is an important parameter which reflects the optical behavior of a sample in terms of its transparency towards electromagnetic radiations. The optical band gap energy (E$_g$) is related to the absorption coefficient α(ν) as

$$\alpha h\nu = B(h\nu - E_g)^r$$

In this equation ν is the frequency of incident radiation and B is a constant named as band tailing parameter. The value of the index r suggests the nature of transitions taking place in the sample. For indirect allowed and forbidden transitions r equals 2 and 3, respectively, and for direct allowed and forbidden  transitions r equals  1/2  and  2/3, respectively[9].

The study of optical absorption, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of the materials. It is possible to determine whether the optically induced transition is direct or indirect and allowed or forbidden by analysis of the absorption edge. The optical absorbance of glass system has been studied in the vicinity of the fundamental absorption edge.

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The optical absorption spectra of LiF-Al$_2$O$_3$-B$_2$O$_3$ pure glass recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands (Fig. 1). From the observed absorption edges, we have evaluated the optical band gaps (E$_g$) of these glasses by drawing Tauc plot between $(\Box \hbar \Box)^{1/2}$ and $\hbar \Box$ as per the equation:

$$\Box(\Box)\hbar \Box = C (\hbar \Box - E_g)^2$$

Fig. 2 represents the Tau plot of this glass in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap (E$_g$) obtained for LiF-Al$_2$O$_3$-B$_2$O$_2$ glass is presented in Table.

The optical absorption spectra of LiF-Al$_2$O$_3$-B$_2$O$_3$ glass doped with 1.0 mol% of Ho$_2$O$_3$ is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^5$I$_8$ (Fig. 3 & Fig. 4); these levels are assigned to the following appropriate electronic transition[10]:

$^5$I$_8$ → $^5$G$_2$, $^3$K$_6$, $^3$H$_6$, $^5$G$_4$, $^3$K$_7$, (near UV region)

$^5$I$_8$ → $^5$G$_5$, $^3$G$_5$, $^5$G$_6$, $^3$K$_8$, $^5$F$_2$, $^5$F$_3$, $^5$F$_4$, $^5$F$_5$ ( in the Visible region)
$^5$I$_8$ → $^5$I$_5$, $^5$I$_6$, $^5$I$_7$ ( in the NIR region)

## 4. CONCLUSIONS
LiF-Al$_2$O$_3$-B$_2$O$_3$ pure glass and LiF-Al$_2$O$_3$-B$_2$O$_3$ glass doped with 1.0 mol % of Ho$_2$O$_3$ systems are prepared by melt quenching method. The systematic studies like physical parameters evaluation and optical absorption behavior of LiF-Al$_2$O$_3$-B$_2$O$_3$ pure glass and LiF-Al$_2$O$_3$-B$_2$O$_3$ glass doped with 1.0 mol % of Ho$_2$O$_3$ systems have been carried out. The optical absorption spectra of LiF-Al$_2$O$_3$-B$_2$O$_3$ pure glass recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands. From the observed absorption edges, we have evaluated the optical band gap. The optical absorption spectra of LiF-Al$_2$O$_3$-B$_2$O$_3$ glass doped with 1.0 mol % of Ho$_2$O$_3$ is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^5$I$_8$; these levels are assigned to the appropriate electronic transition.

### Table: Physical parameters of LiF - Al$_2$O$_3$ -B$_2$O$_3$ glasses doped with Ho$_2$O$_3$

| Glass | Density (g/cm$^3$) | Refractive Index (n$_d$) | Dopant ion concentration N$_i$ (10$^{21}$, ions/cm$^3$) | Ionic radius r$_i$ (A$^\circ$) | Polaron radius r$_p$ (A$^\circ$) | Mol.vol (cm$^3$/mol) |
|---|---|---|---|---|---|---|
| LiAl$_{10}$ | 2.663 | 1.462 | --- | --- | --- | 22.44 |
| LiHAl$_{10}$ | 2.721 | 1.464 | 2.70 | 7.18 | 2.89 | 23.31 |
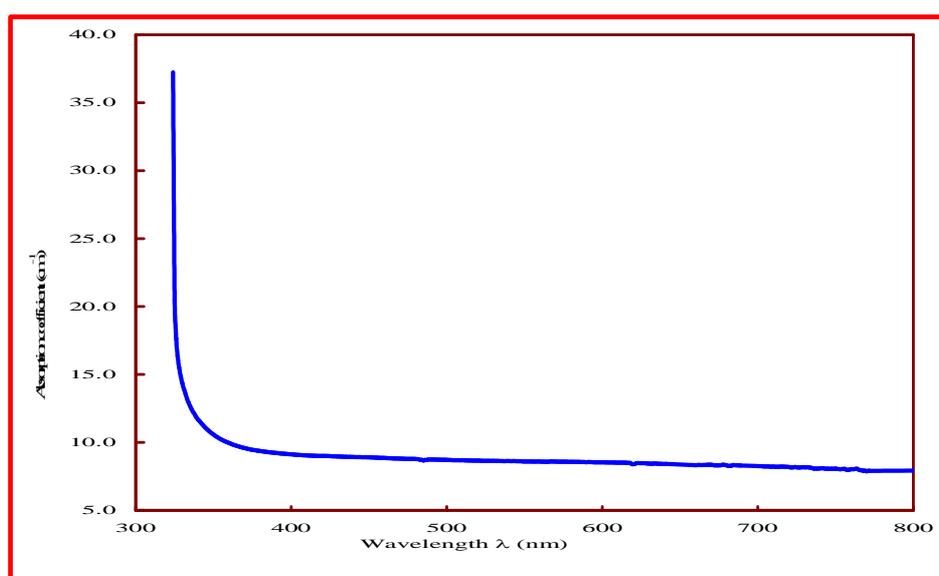


**Fig. 1: Optical absorption spectrum of LiF-Al$_2$O$_3$-B$_2$O$_3$ glass system recorded at room temperature**
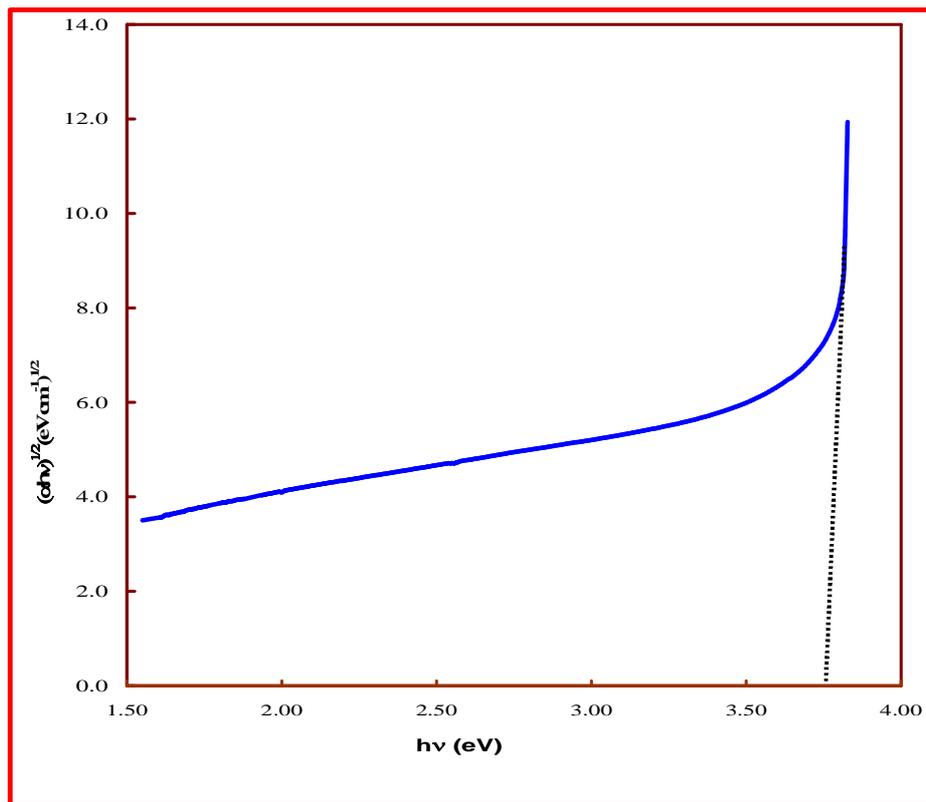
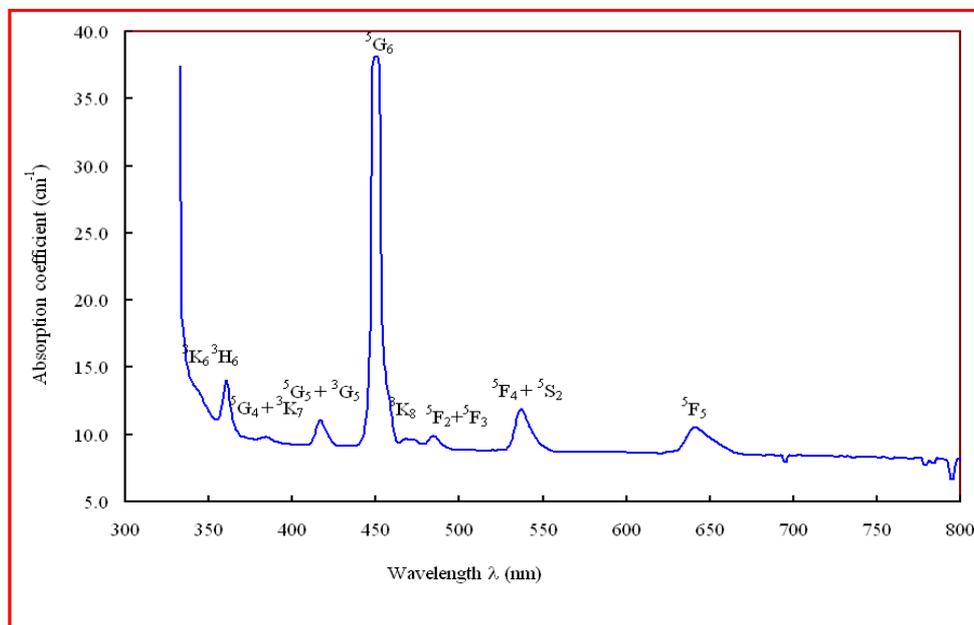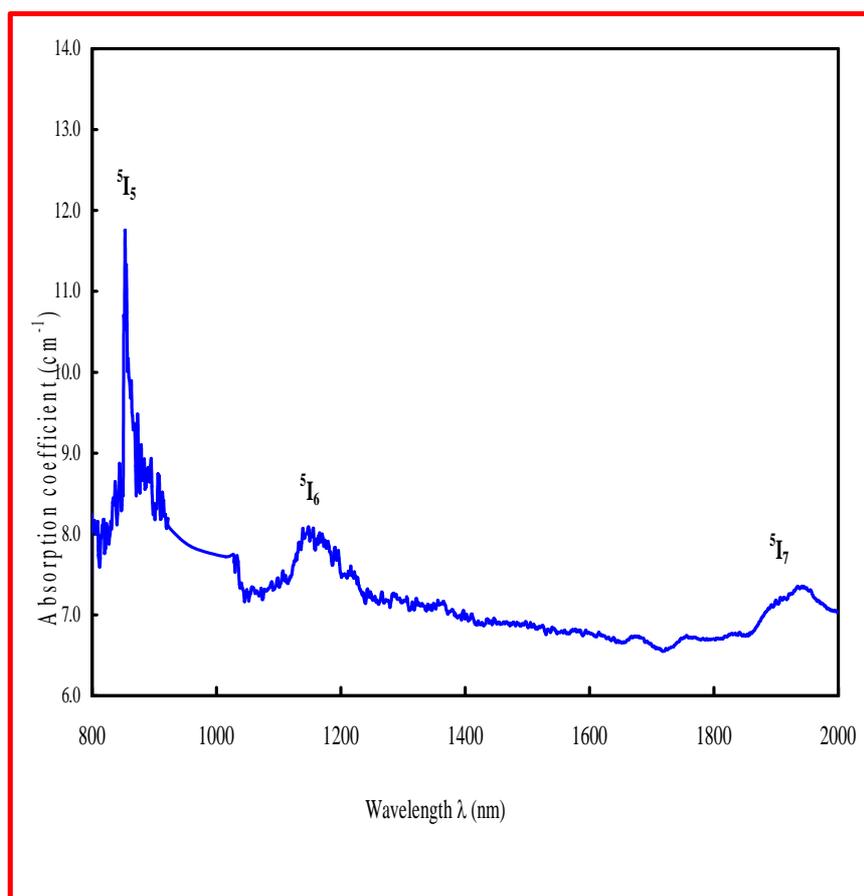**Fig. 2: Urbach plot for evaluating the optical band gap of LiF-Al$_2$O$_3$-B$_2$O$_3$ glass system**



**Fig. 3: Optical absorption spectrum of LiF-Al$_2$O$_3$-B$_2$O$_3$ glass system doped with 1.0 mol % of Ho$_2$O$_3$ recorded at room temperature**

**Fig. 4: Optical absorption spectrum of LiF-Al$_2$O$_3$-B$_2$O$_3$ glass system doped with 1.0 mol % of Ho$_2$O$_3$ recorded at room temperature (NIR region)**

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