INTERNATIONAL JOURNAL OF ADVANCES IN PHARMACY, BIOLOGY AND CHEMISTRY

Research Article

# Optical absorption behavior of $KF–Al_2O_3–B_2O_3$ glass doped with $Ho_2O_3$

**MC. Rao*, T. Srikumar and Ch. Srinivasa Rao**

Department of Physics, Andhra Loyola College, Vijayawada-520008, Andhra Pradesh, India.

**ABSTRACT**

$KF–Al_2O_3–B_2O_3$ glasses mixed with 1.0 mol % of $Ho_2O_3$ 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 semi-conducting devices.

**Keywords:** $KF–Al_2O_3–B_2O_3$ glasses, $Ho_2O_3$, Optical, IR and Physical Properties.

## 1. INTRODUCTION

The recycling and valuation of wastes coming from industrial processes has become a worldwide concern, very important in the last few years and claims for a solution in the near future. In the past few years very intensive investigations have been employed for the development of different ferroelectric materials for application in electronic and optoelectronic. Because of excellent optical, piezoelectric, photo-elastic and photorefractive properties, lithium niobate crystals are of great interest. The vitrification process simulates the natural phenomenon of the glassing from volcanic rocks. These natural glasses contain toxic materials in their structure that have shown environmental inert as the time. These elements are absorbed in the chemically stable virtuous matrix[1]. The vitrification of hazardous residues has been industrially applied as the treatment of radioactive wastes[2] as the inertization of ashes from urban garbage incinerators[3-5].

Glass has been used due to its chemical and physical-chemical characteristics such as good behavior during fusion, homogeneity, durability and stability to several environmental conditions. In addition, glass shows an open amorphous structure and can easily be incorporated with a great number of elements of the periodic table. These characteristics are also interesting to the inertization of galvanic waste in the glass matrix that contains several different metals in its composition[6]. Glass can be made with excellent homogeneity in a variety of forms and sizes, from small fibers to meter-sized pieces. Furthermore, glass can be doped with rare earth ions and micro crystallites and a wide range of properties can be chosen to meet the needs of various applications. These advantages over crystalline materials are based on the unique structural and thermodynamic features of glass materials. A glass is defined as an inorganic product of fusion which has been cooled to a rigid condition without crystallization. According to this definition, a glass is a non crystalline material obtained by a melt-quenching process[7]. Nowadays, non crystalline materials that cannot be distinguished from melt-quenched glasses of the same composition are obtainable by using various techniques such as chemical vapor deposition, sol-gel process, etc.

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, 9]. According to Zachariasen[10] there are only five oxide materials which form the glass by themselves viz., $P_2O_5$, $B_2O_3$, $SiO_2$, $GeO_2$ and $As_2O_3$; two more non-oxide compounds viz., $As_2S_3$ and $BeF_2$ are also added to this list recently. Though, the glass materials do not possess the long-range periodicity but they retain short range order with $AO_3$ and $AO_4$ basic building blocks and follow certain rules proposed by Zachariasen. Basing on these rules, a continuous random network for a glass can be constructed. Reddy et al.[11] studied several physical properties and optical absorption and photoluminescence spectra of $Ho^{3+}$ doped PbO-$Al_2O_3$-$B_2O_3$ glasses have been studied. From the measured intensities of various absorption bands of these glasses the Judd-Ofelt parameters $\Omega_2$, $\Omega_4$ and $\Omega_6$ have been evaluated. The Judel-Oflet theory could successfully be applied to characterize the absorption and luminescence spectra of these glasses. From this theory various radiative properties like transition probability A, branching ratio $\beta_r$, the radiative life time $\tau_R$ and the emission cross-section $\sigma^E$ for various emission levels of these glasses have been determined and reported. An attempt has also been made to throw some light on the environment of $Ho^{3+}$ ions in PbO-$Al_2O_3$-$B_2O_3$ glass lattice.

## 2. MATERIALS AND METHOD

For the present study, the chosen composition is (30–x) KF–10$Al_2O_3$- 60$B_2O_3$: x$Ho_2O_3$ with x = 1.0 mol %.

The details of the compositions are:

**$Ho_0$: 30 KF–10$Al_2O_3$- 60$B_2O_3$**
**$Ho_1$: 29 KF–10$Al_2O_3$- 60$B_2O_3$:1.0$Ho_2O_3$**

Analytical grade reagents of $H_3BO_3$, KF and $Ho_2O_3$ powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar, calcinated at about 900°C for 2 h in a platinum crucible and subsequently melted in the temperature range of 1200 to 1250°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°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

$B_2O_3$ is a well known network former, participates in the network forming with $BO_3$ and $BO_4$ structural units. KF 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-$Al_2O_3$-$B_2O_3$: $Ho_2O_3$ 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)** $= \left[\frac{1}{N_i}\right]^{1/3}$

**(iii) Polaron radius $r_p$ (Å)** $= \frac{1}{2}\left[\frac{\pi}{6N_i}\right]^{1/3}$

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$^{-2}$)** $= \frac{z}{r_i^2}$

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[12]

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

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[12].

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. The optical absorption spectra of KF-$Al_2O_3$-$B_2O_3$ 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 $(\alpha\ \hbar\ \omega)^{1/2}$ and $\hbar\ \omega$ as per the equation:

$$\alpha(\omega)\hbar\omega = C(\hbar\omega - E_g)^2$$

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 KF−$Al_2O_3$−$B_2O_2$ glass is presented in Table.

The optical absorption spectra of KF-$Al_2O_3$-$B_2O_3$ glass doped with 1.0 mol % of $Ho_2O_3$ is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^5I_8$ (Fig. 3 & Fig. 4); these levels are assigned to the following appropriate electronic transition[13]:

**$^5I_8 \rightarrow {}^5G_2, {}^3K_6, {}^3H_6, {}^5G_4, {}^3K_7$, (near UV region)**
**$^5I_8 \rightarrow {}^5G_5, {}^3G_5, {}^5G_6, {}^3K_8, {}^5F_2, {}^5F_3, {}^5F_4, {}^5F_5$ ( in the Visible region)**
**$^5I_8 \rightarrow {}^5I_5, {}^5I_6, {}^5I_7$ ( in the NIR region)**

**Table: Physical parameters of KF - $Al_2O_3$ -$B_2O_3$ glasses doped with $Ho_2O_3$**

| Glass | Density ($g/cm^3$) | Refractive Index ($n_d$) | Dopant ion concentration $N_i$ ($10^{21}$, ions/$cm^3$) | Ionic radius $r_i$ (A°) | Polaron radius $r_p$ (A°) | Mol.vol ($cm^3$/mol) |
|---|---|---|---|---|---|---|
| $KAl_{10}$ | 2.178 | 1.467 | --- | --- | --- | 31.86 |
| $KHAl_{10}$ | 2.293 | 1.464 | 1.99 | 7.96 | 3.21 | 31.86 |

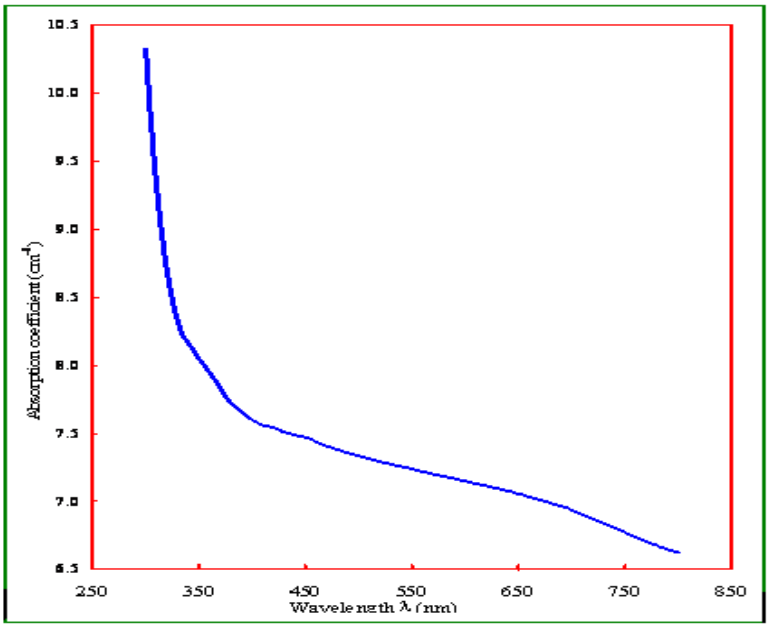


**Fig. 1: Optical absorption spectrum of KF-$Al_2O_3$-$B_2O_3$ glass system recorded at room temperature**

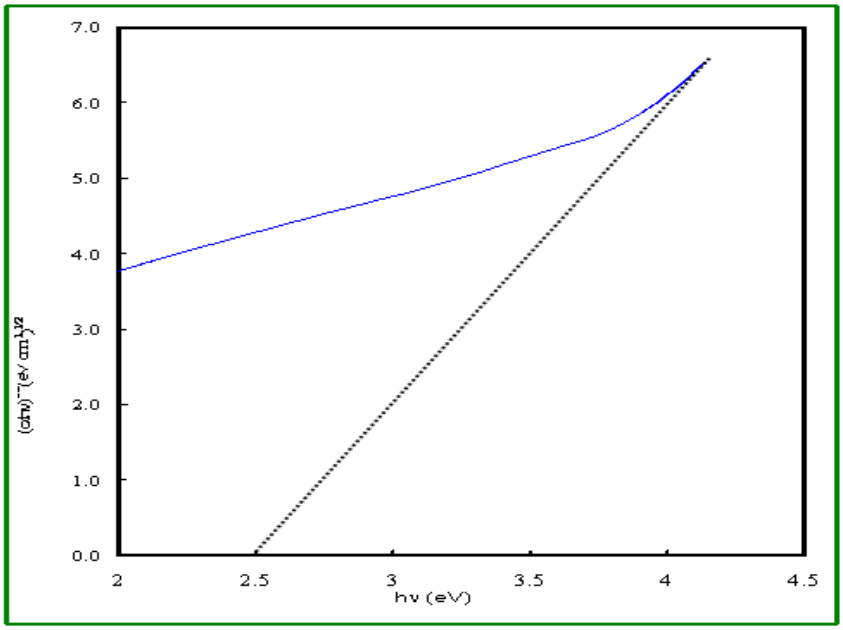


**Fig. 2: Urbach plot for evaluating the optical band gap of KF-Al2O3-B2O3 glass system**

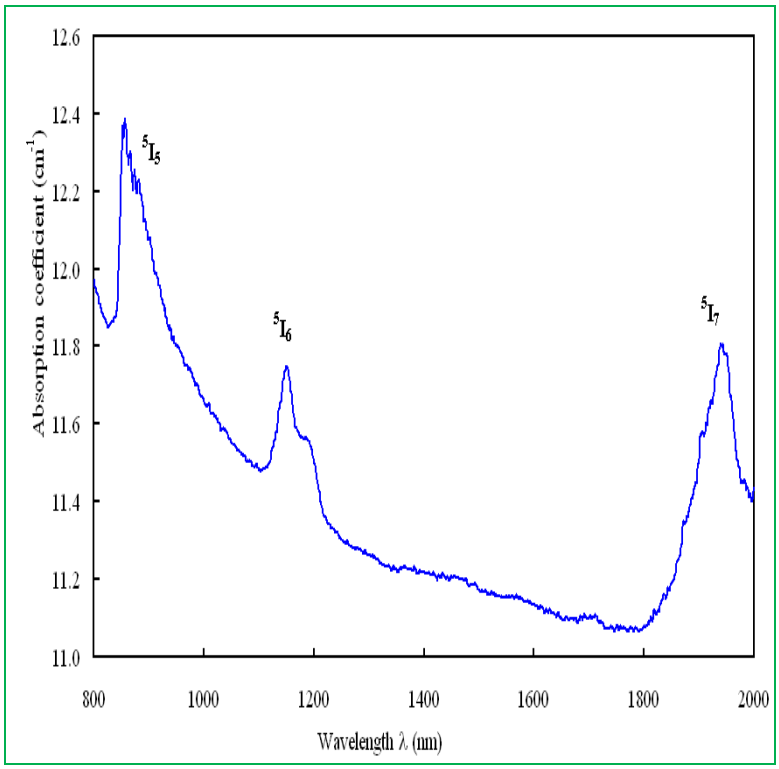


**Fig. 3: Optical absorption spectrum of KF-Al2O3-B2O3 glass system doped with 1.0 mol % of Ho2O3 recorded at room temperature**

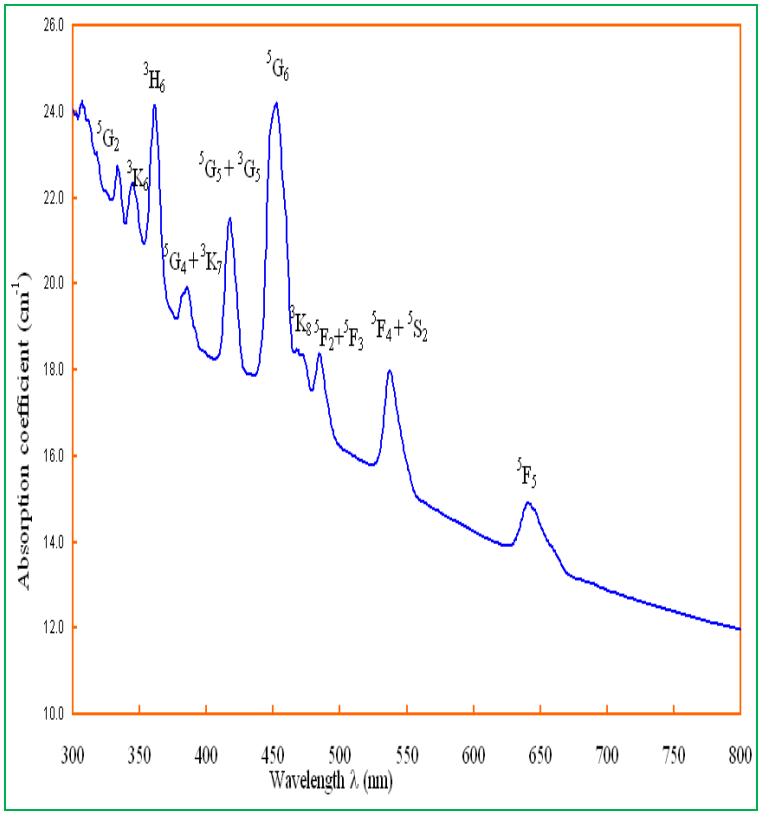


**Fig. 4: Optical absorption spectrum of KF-Al2O3-B2O3 glass system doped with 1.0 mol % of Ho2O3 recorded at room temperature (NIR region)**

## 4. CONCLUSIONS

KF-$Al_2O_3$-$B_2O_3$ pure glass and KF-$Al_2O_3$-$B_2O_3$ glass doped with 1.0 mol% of $Ho_2O_3$ systems are prepared by melt quenching method. The systematic studies like physical parameters evaluation and optical absorption behavior of KF-$Al_2O_3$-$B_2O_3$ pure glass and KF-$Al_2O_3$-$B_2O_3$ glass doped with 1.0 mol% of $Ho_2O_3$ systems have been carried out. The optical absorption spectra of KF-$Al_2O_3$-$B_2O_3$ 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 KF-$Al_2O_3$-$B_2O_3$ glass doped with 1.0 mol % of $Ho_2O_3$ is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^5I_8$; these levels are assigned to the appropriate electronic transition.

## 5. REFERENCES


1. Shackelford J F, Introduction to Materials Science for Engineers, Prentice Hall, New Jersey, USA, 1999.
2. Roth G, Weisennburger S, Nucl. Eng. Des., 2000; 202; 197.
3. Barbieri L, Bonamartini A C, Lancellotti I, J. Eur. Ceram. Soc., 2000; 20; 2477.
4. Scarinci G, Brusatin G, Barbieri L, Corradi A, Lancelotti I, Colombo P, Hreglich S, Dall Igna R, J. Eur. Ceram. Soc., 2000; 20; 2485.
5. Ferraris M, Salvo M, Smeacetto F, Augier L, Barbieri L, Corradi A, Lancellotti I, J. Eur. Ceram. Soc., 2001; 21; 453.
6. Verlag E G L, Praktische Galvanotechnik, Germany, 1970.
7. American Society for Testing Materials [ASTM], Standards on Glass and Glass Products, prepared by ASTM Committee C14, 1955.
8. Warren B E, J. Appl. Phys., 1942; 13; 602.
9. Weber M J, Handbook on the Physics and Chemistry of Rare Earth, Eds., North-Holland, Amsterdam, 1979.
10. Zachariasen W H, J. Am. Chem. Soc., 1932; 54; 3841.
11. Reddy M R, Raju S B, Veeraiah N, J. Phy. Chem. Solids, 2000; 61; 1567.
12. Devis E A Mott N F Philosophical Magazine, 1970; 22; 0903.
13. Nageswara Rao P, Raghavaiah B V, Krishna Rao D, Veeraiah N, Mat. Chem. Phy., 2005; 91; 381.