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Spectroscopic Studies on LiF/NaF/KF-Al_2O_3-B_2O_3 glasses doped with Ho_2O_3

Ch.Srinivasa Rao, T.Srikumar, M.C.Rao*

Department of Physics, Andhra Loyola College, Vijayawada-520008, A.P., (INDIA)

ABSTRACT

LiF/NaF/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

LiF/NaF/KF-Al_2O_3-B_2O_3 glasses;
Ho_2O_3;
Optical;
IR and physical properties.

INTODUCTION

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 vitriûcation 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. The vitriûcation of hazardous residues has been industrially applied as the treatment of radioactive wastes as the inertization of ashes from urban garbage incinerators[1-3].

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[4]. The good formability is originated from the random network structure with

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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[5-7].

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[6]. The requirements of improving solid-state lasers, optoelectronic communication devices and color displays have inspired the research interest in rare earth ion doped glasses. The oxyûuoride glass ceramics doped with rare earth ions have been researched in the past decades. Their higher chemical and mechanical stabilities than ûuoride glass and lower phonon energy than oxide glass have been indicated[8-10].

EXPERIMENTAL

For the present study, the chosen composition is (30–x) LiF/NaF/KF–$10Al_2O_3$- $60B_2O_3$: xHo_2O_3 with x = 1.0 mol %.

The details of the compositions are:

Ho_0: 30 LiF/NaF/KF–$10Al_2O_3$- $60B_2O_3$

Ho_1: 29 LiF/NaF/KF–$10Al_2O_3$- $60B_2O_3$: 1.0Ho_2O_3

Analytical grade reagents of H_3BO_3, LiF/NaF/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 $\lambda = 589.3$ nm) using Abbe's refractometer with monobromo naphthalene as the contact layer between the glass and the refractometer prism.

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 LiF/NaF/KF-Al_2O_3-B_2O_3:

TABLE 1 : Physical parameters of LiF/NaF/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)
KABHo	2.293	1.464	1.99	7.96	3.21	31.86
LABHo	2.721	1.464	2.70	7.18	2.89	23.31
NaABHo	2.437	1.463	2.26	7.62	3.07	27.938

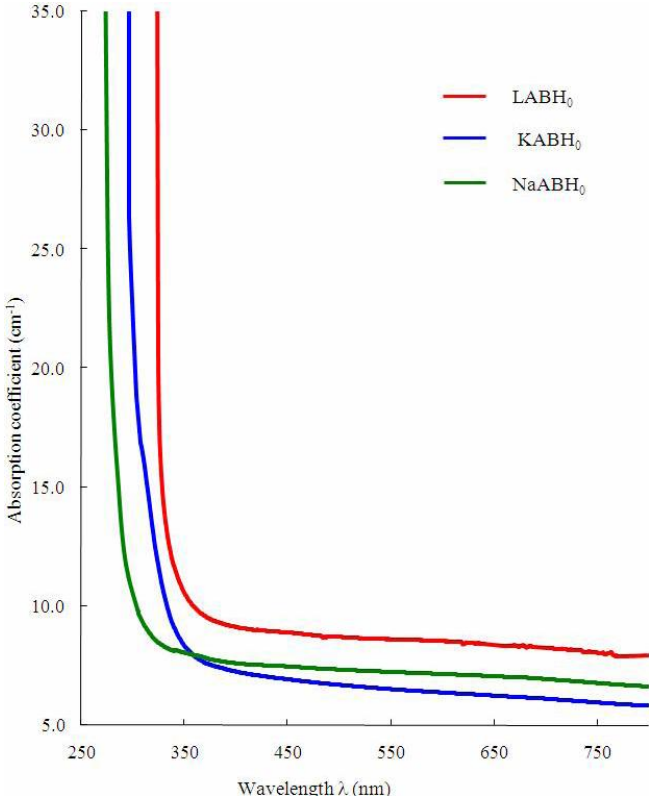

Figure 1: Optical absorption spectra of LiF/NaF/KF-Al_2O_3-B_2O_3 glass recorded at room temperature

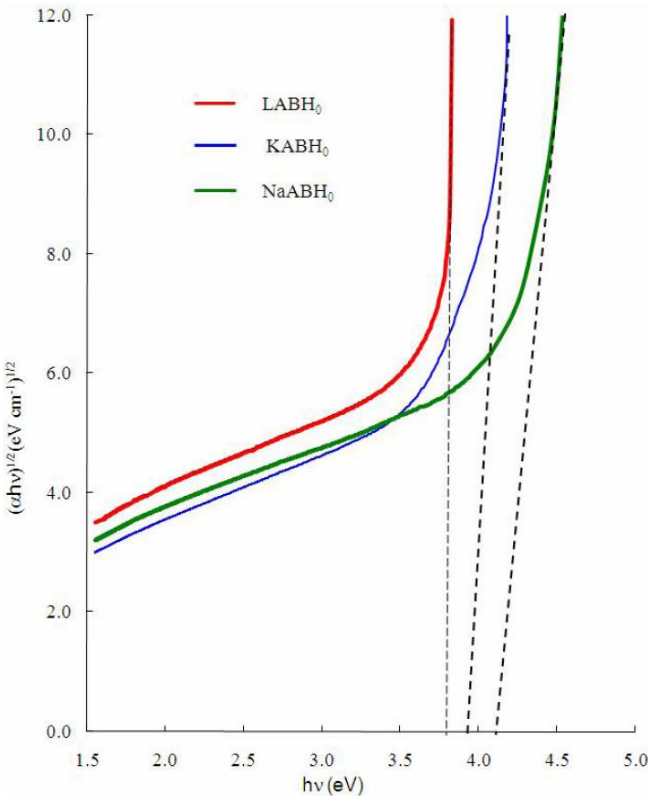

Figure 2 : Tau'c plots for evaluating the optical band gap of LiF/NaF/KF-Al_2O_3-B_2O_3 glass

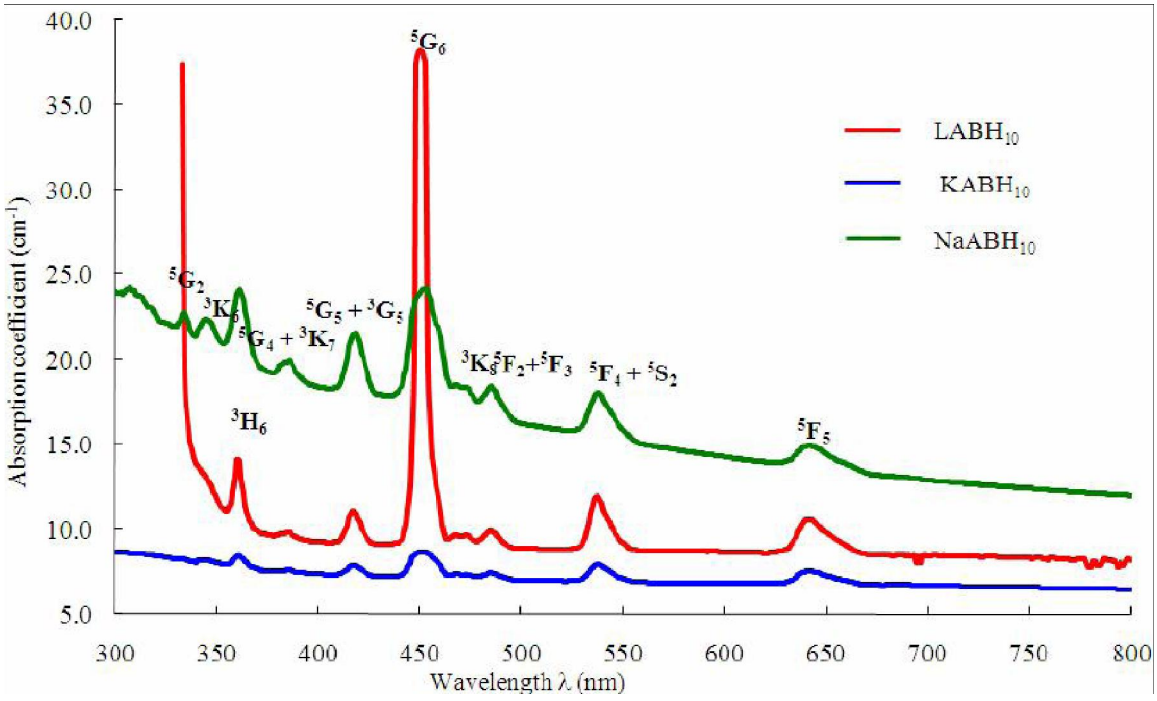

Figure 3 : Optical absorption spectra of LiF/NaF/KF-Al_2O_3-B_2O_3 glass doped with 1.0 mol% of Ho_2O_3 recorded at room temperature

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:

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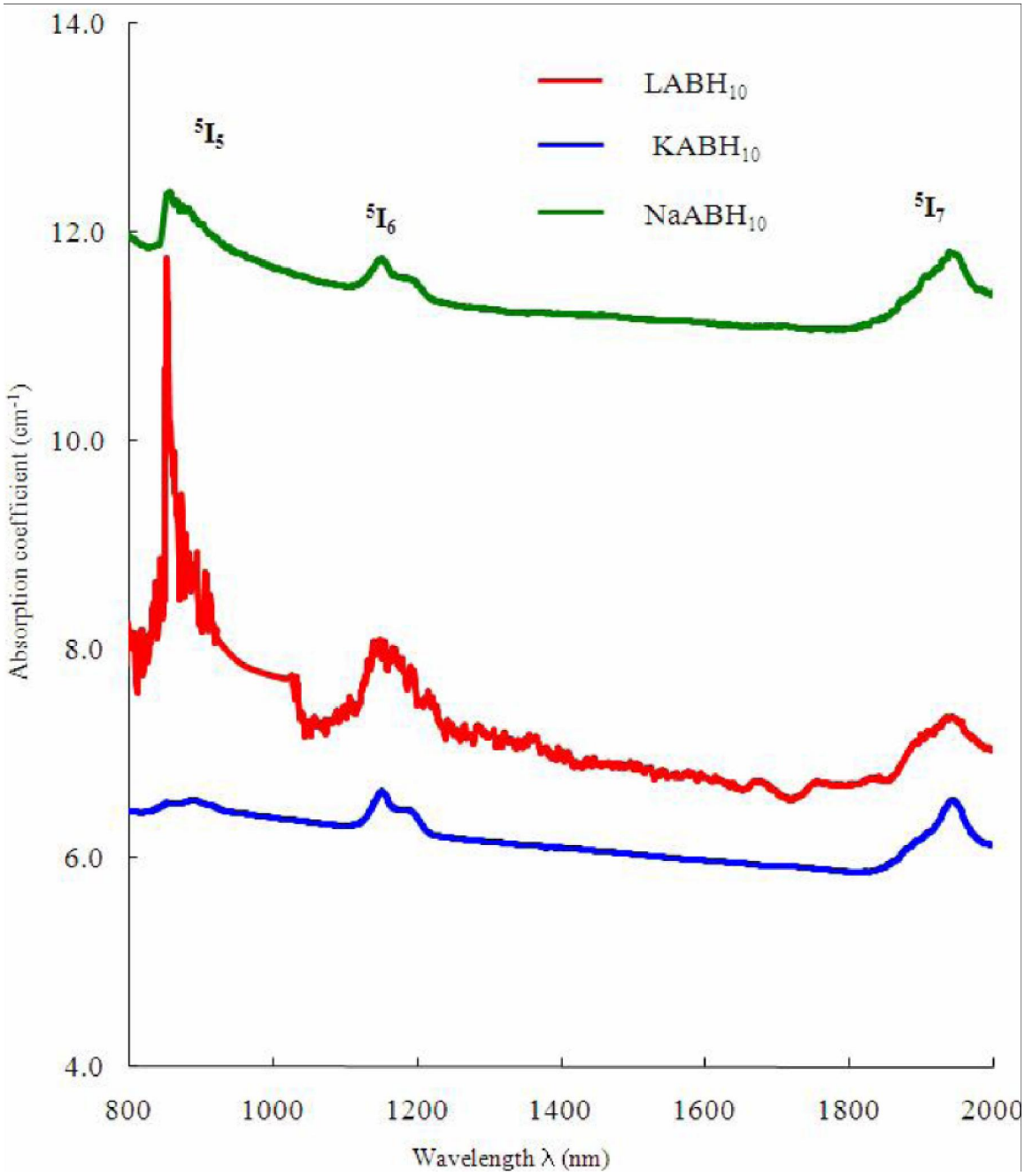

Figure 4 : Optical absorption spectra of LiF/NaF/KF-Al_2O_3-B_2O_3 glass doped with 1.0 mol% of Ho_2O_3 recorded at room temperature (NIR region)

(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 con-

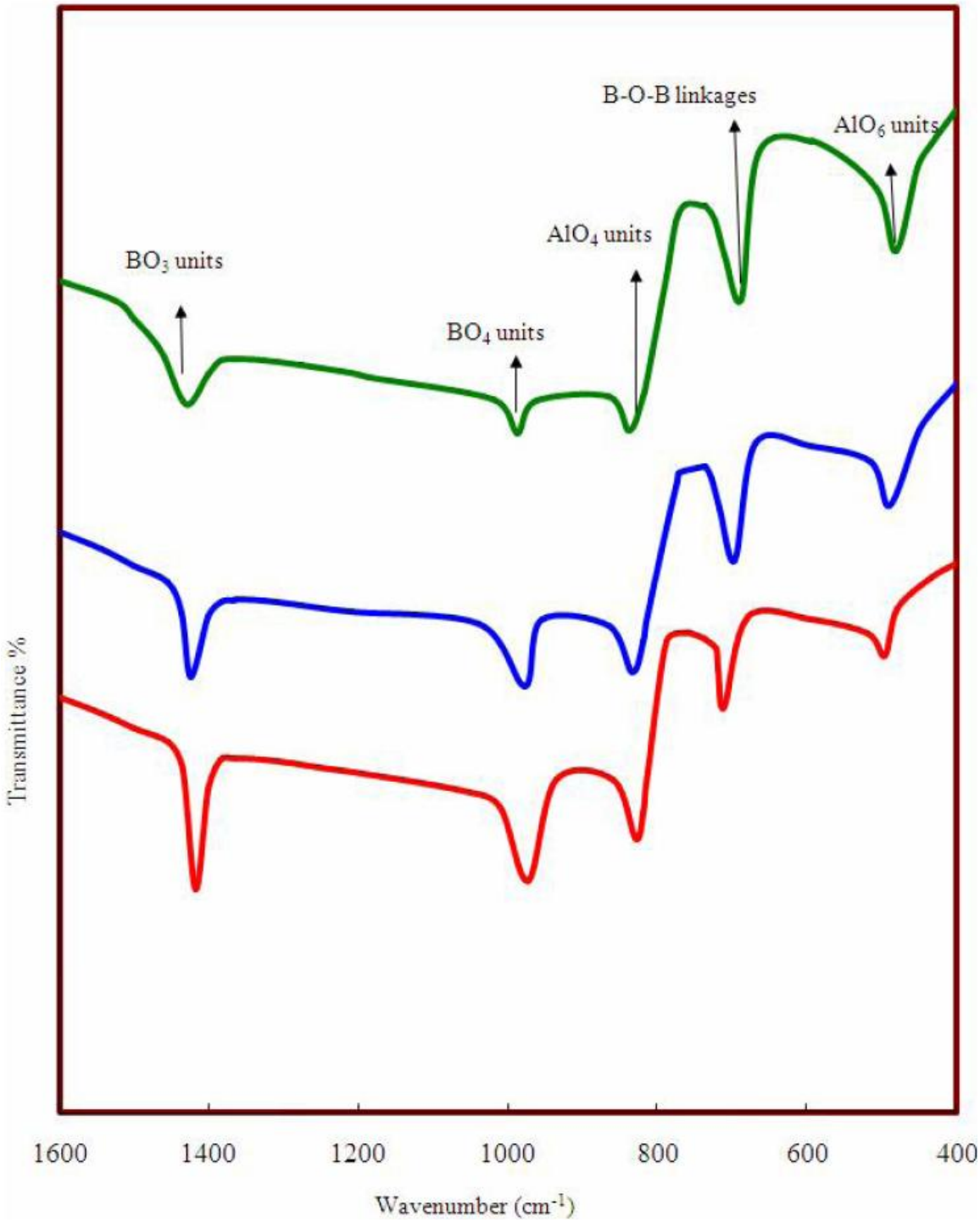

Figure 5 : FT-IR spectra of LiF/NaF/KF-Al_2O_3-B_2O_3 glasses

centration Ni, mean rare earth ion separation R_i and molar volume for all the glass samples were evaluated and presented in TABLE 1. 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[11,12]

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

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 re-

lated 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 are equals 2 and 3, respectively and for direct allowed and forbidden transitions are equals 1/2 and 2/3, respectively. 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. Figure 1 shows the optical absorption spectra of LiF/NaF/KF-Al_2O_3-B_2O_3 pure glasses 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 gaps (E_g) of these glasses by drawing Tauc plot between $(\alpha\ \hbar\omega)^{1/2}$ and ω as per the equation:

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

Figure 2 represents the Tau'c plot of this glass in which a considerable part of each curve is observed to be linear. The optical absorption spectra of LiF/NaF/KF-Al_2O_3-B_2O_3 glasses 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 $^5I_8$ (Figure 3 & Figure 4); these levels are assigned to the following appropriate electronic transition:

$^5I_8 \rightarrow {}^5G_2, {}^3K_6, {}^3H_6, {}^5G_4, {}^3K_7$, (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)

Figure 5 shows the FT-IR spectra of LiF/NaF/KF-Al_2O_3-B_2O_3: Ho_2O_3 glasses recorded at room temperature in the region 400-1600 cm^{-1}. The spectrum exhibit bands characteristic of symmetric and asymmetric stretching and bending vibrations borate groups, triply degenerate modes of phosphate ion PO_4^{3-}, P-O-P, Sulphate modes of vibrations. The bands observed at around 620, 612, 601, 592, 581 cm^{-1} are due to TiO_6 units. The bands observed at around 678, 671, 669, 664, 658 cm^{-1} are due to SO_4^{2-} (υ_2) units. The bands observed at around 724, 719, 717, 713, 709 cm^{-1} are due to B-O-B linkages. The bands observed at around 797, 783, 779, 772, 762 cm^{-1} are due to symmetric stretching of P-O-P and TiO_4 units. The bands observed at around 944, 938, 936, 933, 927 cm^{-1} are due to PO_4^{3-}, BO_4 units. The bands observed at around 1106, 1101, 1094, 1092, 1085 cm^{-1} are due to asymmetric stretching of P-O-P. The bands observed at around 1156, 1149, 1145, 1143, 1136 cm^{-1} are due to SO_4^{2-} (υ_1) units. The bands observed at around 1295, 1291, 1286, 1282, 1277 cm^{-1} are due to asymmetric stretching of PO^{2-}. The bands observed at around 1414, 1405, 1398, 1390, 1381 cm^{-1} are due to BO_3 units.

CONCLUSIONS

LiF/NaF/KF-Al_2O_3-B_2O_3 pure glass and LiF/NaF/KF-Al_2O_3-B_2O_3 glasses 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 LiF/NaF/KF-Al_2O_3-B_2O_3 pure glass and LiF/NaF/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 LiF/NaF/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 LiF/NaF/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. FT-IR spectra showed the characteristic vibrational modes of the prepared samples.

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