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Research Article

Optical Absorption Behaviour of $NaF–Al_2O_3–B_2O_3$ Glass Doped with Ho_2O_3

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ABSTRACT

$NaF–Al_2O_3–B_2O_3$ 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 semiconducting devices.

Keywords: $NaF-Al_2O_3-B_2O_3$ Glass, Ho_2O_3, Experimental, IR and Physical Parameters.

1. INTRODUCTION

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. 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. Some components called network modifiers can also participate in glass formation by acting to modify the glass properties. These components do not form networks but occupy thermodynamically stable sites or act as a replacement for a part of `network former'. Glass formation is possible, in principle, for a system of any composition provided that it contains sufficient of the component called `network former'. Thus, a wide variety of multi-component glasses can be prepared to attain the desired properties by adjusting the chemical composition at a level below 1%. Since an active ion doped in a glass occupies a similar position to the modifier ions, the absorption and emission spectra from the ion, if any, are broader than those from active ions doped in a crystalline material is a feature which is often advantageous in the preparation of a special glass[1].

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[2, 3]. 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 oxyfluoride glass ceramics doped with rare earth ions have been researched in the past decades. Their higher chemical and mechanical stabilities than fluoride glass and lower phonon energy than oxide glass have been indicated[4-7].

Ramesh Babu et al.[8] studied transparent glasses, obtained through melt quenching technique, with composition 30LiF-10SrO-(60-x)B2O3and conductivity σ -xMnO, with $0 \leq x \leq 3$ mol% (x = 0, 1, 1.5, 2, 2.5 and 3), were characterized by X-ray diffraction (XRD) and then they were analyzed for physical, spectroscopic studies (optical absorption,

electron spin resonance (ESR) and FTIR) and dielectric properties (dielectric constant ε′, loss tanδ etc.). The results were analyzed and correlated with each other in the light of local environment and oxidation states of manganese ion in the glass network. The increase in the area of optical absorption peak and ESR signal intensity indicate that both Mn^{2+} and Mn^{3+} ions exist in octahedral symmetry are increased with increasing MnO dopant in the glass matrix. The semi conducting nature of the glass network is found to increase due to the considerable increase in BO_3, MnO_6 structural units whenever B_2O_3 in the host glass is gradually replaced by MnO.

2. MATERIALS AND METHOD

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

The details of the compositions are:

Ho_0: 30 NaF-10Al_2O_3- 60B_2O_3
Ho_1: 29 NaF-10Al_2O_3- 60B_2O_3:1.0 Ho_2O_3

Analytical grade reagents of H_3BO_3, NaF 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. NaF 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:

$$\text{(i) } N_i \ (10^{22} \text{ ions /cm}^3) = N_A \, M \text{ (mol\%) } d / \overline{M}$$

From the N_i values obtained, the polaron radius (r_p) and inter-ionic distance (r_i) of transition metal ions could be evaluated:

$$\text{(ii) Inter - ionic distance } r_i \text{ (Å)} = \left[\frac{1}{N_i}\right]^{1/3}$$

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

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:

$$\text{(iv) Field strength } F_i \text{ (cm}^{-2}) = \frac{z}{r_i^2}$$

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[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. The optical absorption spectra of NaF-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 $(\square\ \hbar\ \square)^{1/2}$ and $\hbar\ \square$ as per the equation:

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

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 NaF-Al_2O_3-B_2O_2 glass is presented in Table.

The optical absorption spectra of NaF-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[10]:

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

4. CONCLUSIONS

NaF-Al_2O_3-B_2O_3 pure glass and NaF-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 NaF-Al_2O_3-B_2O_3 pure glass and NaF-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 NaF-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 NaF-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.

Table: Physical parameters of NaF - 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)
$NaAl_{10}$	2.392	1.464	---	---	---	26.99
$NaHAl_{10}$	2.437	1.463	2.26	7.62	3.07	27.938

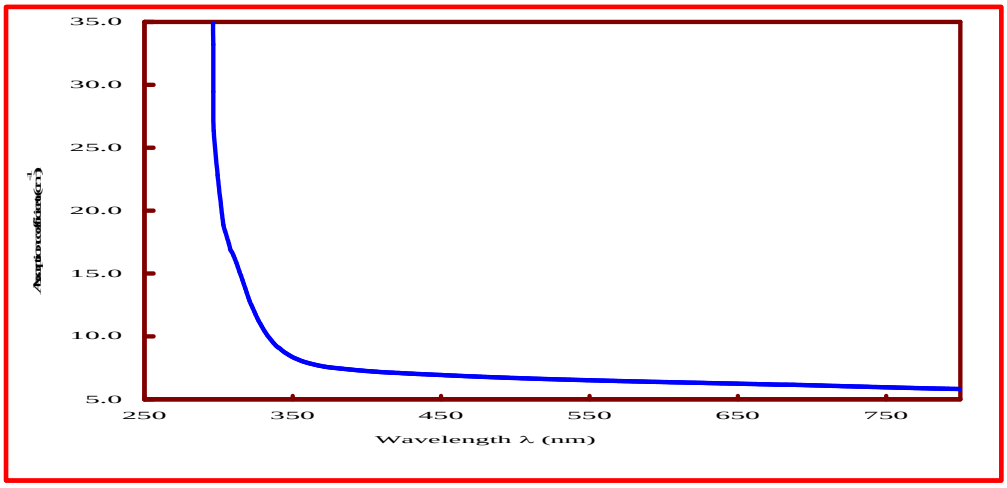

Fig. 1: Optical absorption spectrum of NaF-Al_2O_3-B_2O_3 glass system recorded at room temperature

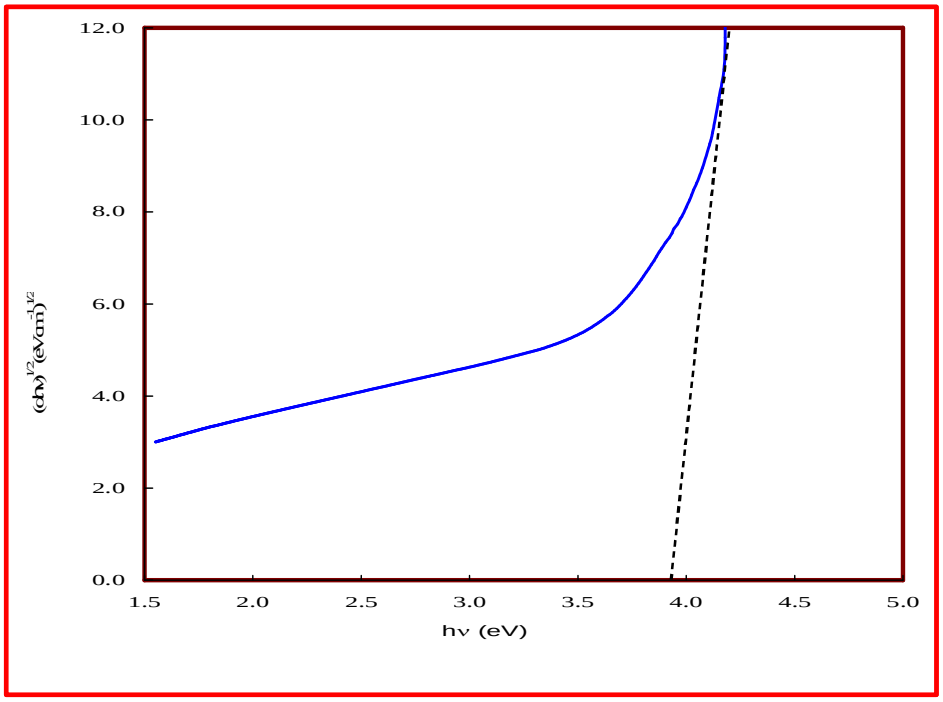

Fig. 2: Urbach plot for evaluating the optical band gap of $NaF-Al_2O_3-B_2O_3$ glass system

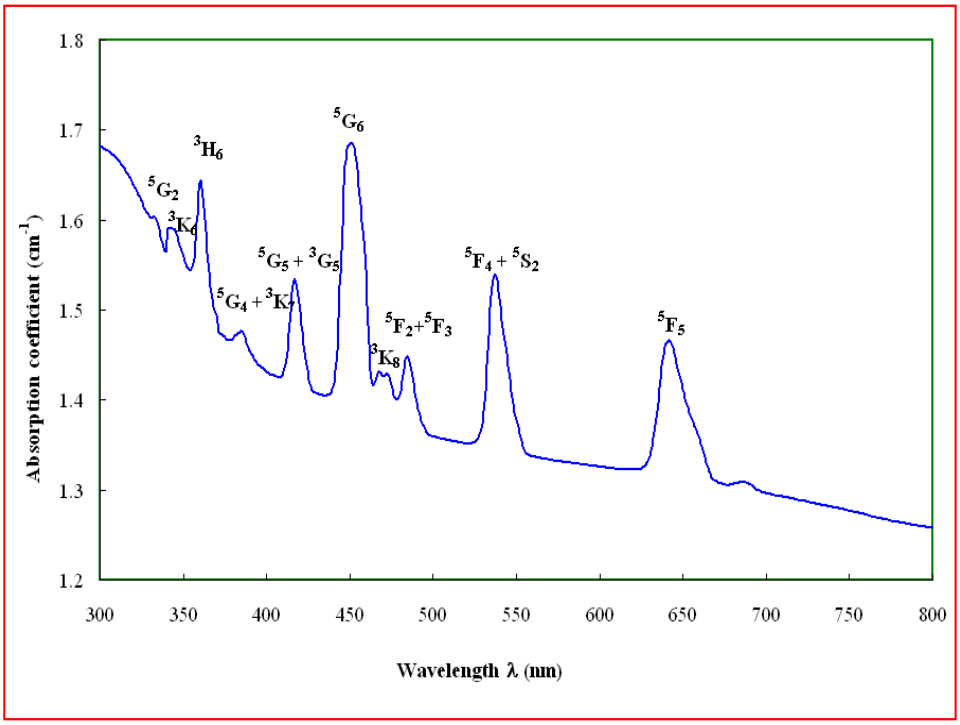

Fig. 3: Optical absorption spectrum of $NaF-Al_2O_3-B_2O_3$ glass system doped with 1.0 mol % of Ho_2O_3 recorded at room temperature

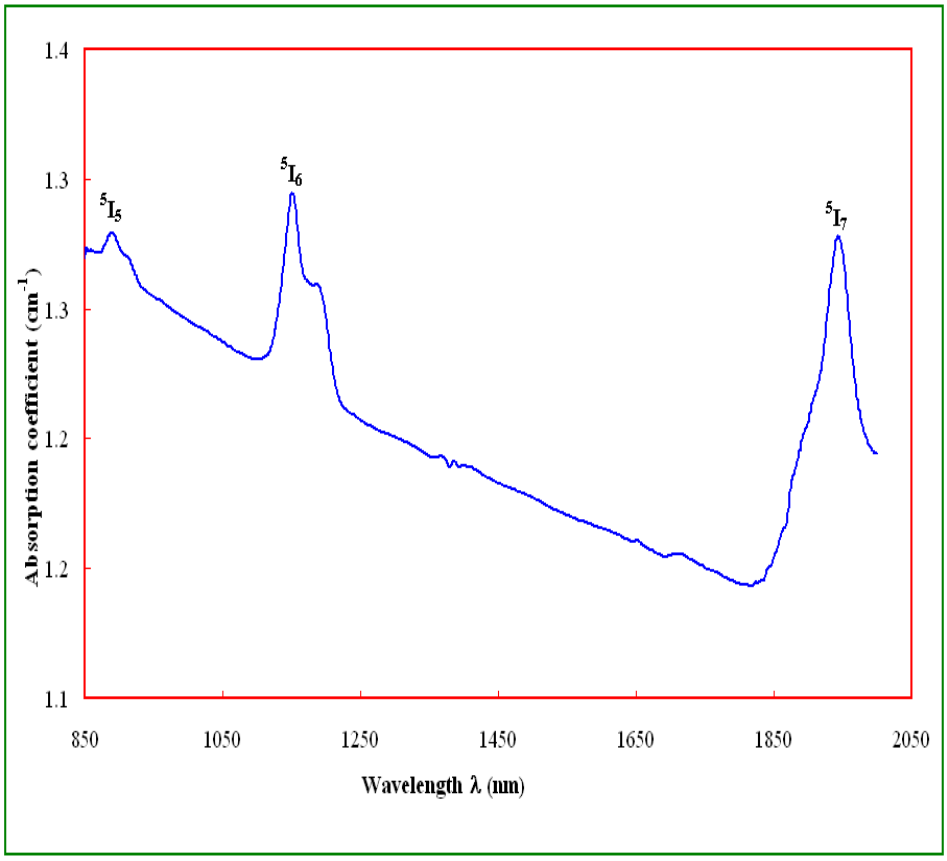

Fig. 4: Optical absorption spectrum of NaF-Al_2O_3-B_2O_3 glass system doped with 1.0 mol % of Ho_2O_3 recorded at room temperature (NIR region)

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