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Physical And Optical Absorption Studies Of LIF/NAF/KF-P_2O_5- B_2O_3 Glasses Doped With ND_2O_3

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Abstract: LiF/NaF/KF-P_2O_5-B_2O_3 glasses doped with Nd_2O_3 have yielded practical applications in the laser industry. LiF/NaF/KF-P_2O_5-B_2O_3 glasses doped with Nd_2O_3 have been synthesized by melt quenching method and the systematic studies like physical parameters evaluation and optical absorption behavior of LiF/NaF/KF–P_2O_3–B_2O_5 pure glass and LiF/NaF/KF–P_2O_5–B_2O_3 glass doped with 1.0 mol% of Nd_2O_3 systems have been carried out. The presence of niobium ions in these glasses is expected to influence their physical properties to a large extent since these ions exist in different valence states. The optical absorption spectra of LiF/NaF/KF–P_2O_5–B_2O_3 glass doped with 1.0 mol% of Nd_2O_3 is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^4I_{9/2}$; these levels are assigned to the appropriate electronic transition.
Keywords: LiF/NaF/KF–P_2O_3–B_2O_5, Melt quenching, Nd_2O_3, Spectroscopic properties, Physical parameters.

Introduction:

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 [1]. The macroscopic properties of a glass such as optical transmission and absorption, refraction of light, thermal expansion, etc. are observed always equally in all directions, provided that the glass is free from stress and strain. That is, a glass is an isotropic material, whereas crystalline materials are generally anisotropic. 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].

According to Zachariasen [4] 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 [5]. 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. During the last few decades a large variety of inorganic glasses have been developed with an attempt to achieve suitable optical, electrical and mechanical characteristics. These characteristics are associated with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, IR transmission performance and their ability to accept rare earth and transition metal ions for their use in solid-state devices. Work along these lines was carried out on a number of glasses giving valuable information [6-10]. In the present study (20–x) LiF/NaF/KF-

$30P_2O_5$-$50B_2O_3$ glasses doped with Nd_2O_3 have been synthesized by melt quenching method and the systematic studies like physical parameters evaluation and optical absorption behavior of LiF/NaF/KF–P_2O_3–B_2O_5 pure glass and LiF/NaF/KF–P_2O_5–B_2O_3 glass doped with 1.0 mol% of Nd_2O_3 systems have been carried out.

Experimental:

In the present study, the chosen composition is (20-x) LiF/NaF/KF-$30P_2O_5$-$50B_2O_3$: xNd_2O_3 with x = 1.0 mol%. The details of the compositions are:

LPB_0: 20 LiF–$30P_2O_5$–$50B_2O_3$
$NaPB_0$: 20 NaF–$30P_2O_5$–$50B_2O_3$
KPB_0: 20 KF–$30P_2O_5$–$50B_2O_3$
LPBNd: 19 LiF–$30P_2O_5$–$50B_2O_3$:$1.0Nd_2O_3$
NaPBNd: 19 NaF–$30P_2O_5$–$50B_2O_3$:$1.0Nd_2O_3$

Analytical grade reagents of H_3BO_3, P_2O_5, LiF, NaF, KF and Nd_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 x 1 cm x 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.

Results and Discussion:

Some physical parameters useful for characterization LiF–P_2O_5–B_2O_3:Nd_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 / $\overline{M}$ ---------- (1)

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) = $\left[\frac{1}{N_i}\right]^{1/3}$ ---------- (2)

(iii) Polaron radius r_p (Å) = $\frac{1}{2}\left[\frac{\pi}{6N_i}\right]^{1/3}$ ---------- (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}) = $\frac{z}{r_i^2}$ ---------- (4)

P_2O_5 is a strong glass forming oxide, participates in the glass network with PO_4 structural clusters. The PO_4 tetrahedra are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross-bonding between the metal cation and two non-bridging oxygen atoms of each PO_4 tetrahedron [11]. The presence of such PO_4 units in the titled glass samples is evident from the IR spectral studies. B_2O_3 is also a strong glass former, when it is mixed in the phosphate glasses, the tetrahedral boron entities dominate in the phosphate-rich domain where as trigonal boron entities prevail in the borate-rich side and form easily B–O–P bridges. The highest stability occurs for fully polymerized glasses and can be related to the energetics of the reaction B–O–B + P–O– P = 2(B–O–P); this relation also suggests that the B–O–P linkage is more stable relatively than the mixture of B–O–B and P–O–P linkages [12, 13]. Table 1 gives the information about the Physical parameters of LiF/NaF/KF–P_2O_5–B_2O_3 glasses doped with Nd_2O_3.

Table 1 Physical parameters of LiF/NaF/KF–P_2O_5–B_2O_3 glasses doped with Nd_2O_3

Glass	Density (g/cm^3)	Ave. Mol. Wt. (g)	Mol.vol (cm^3/mol)	r_i (A°)	r_p (A°)	N_i (10^{21}, ions/cm^3)	Refractive Index
LPB_0	2.663	93.37	34.67	…..	…..	…..	1.475
$NaPB_0$	2.683	104.18	38.83	…..	…..	…..	1.469
KPB_0	2.672	109.01	40.80	…..	…..	…..	1.464
LPBNd	2.730	102.47	37.54	8.41	3.39	1.68	1.481
NaPBNd	2.704	107.13	39.62	8.57	3.45	1.59	1.476

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 LiF/NaF/KF–P_2O_3–B_2O_5 pure glasses 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_o) of these glasses by drawing Tauc plot between $(\alpha \hbar\omega)^{1/2}$ and $\hbar\omega$ as per the equation:

$$\alpha(\omega)\hbar\omega = C(\hbar\omega - E_o)^2 \qquad \text{----------} \qquad (5)$$

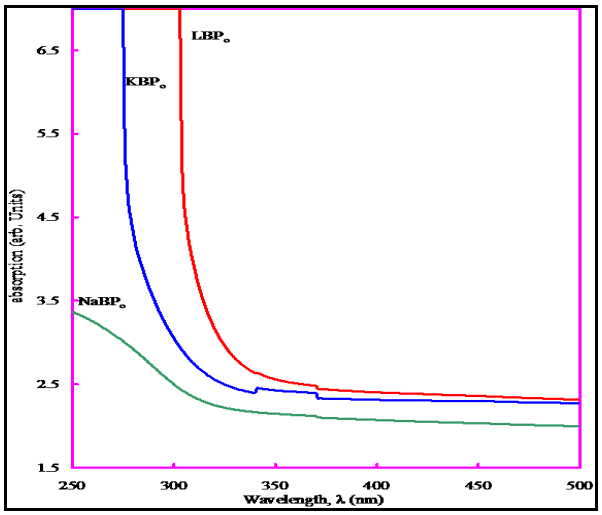

Fig. 1 Optical absorption spectra of LiF/NaF/KF–P_2O_3–B_2O_5 glasses in the visible and UV region

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_0) obtained for LiF/NaF/KF–P_2O_3–B_2O_5 glass is presented in Table 1. The optical absorption spectra of LiF/NaF/KF–P_2O_5–B_2O_3: Nd^{3+} doped glasses recorded at room temperature in the wavelength region 300-2000

nm (Fig. 3) exhibited several absorption bands these levels are assigned to the following appropriate electronic transition [14, 15]:

Nd^{3+}: $^4I_{9/2} \rightarrow {}^2P_{1/2}$, $^2D_{3/2}+{}^4G_{11/2}$, $^4G_{9/2}+{}^4G_{7/2}$, $^4G_{5/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$ and $^4F_{3/2}$

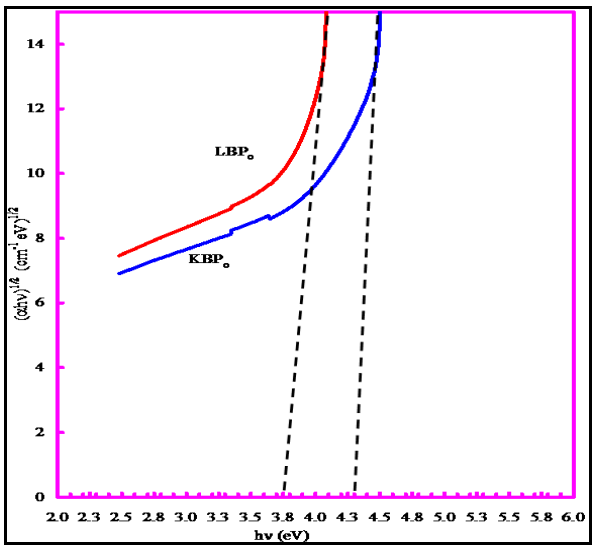

Fig. 2 Tauc plots of LiF/NaF/KF–P_2O_3–B_2O_5 glasses

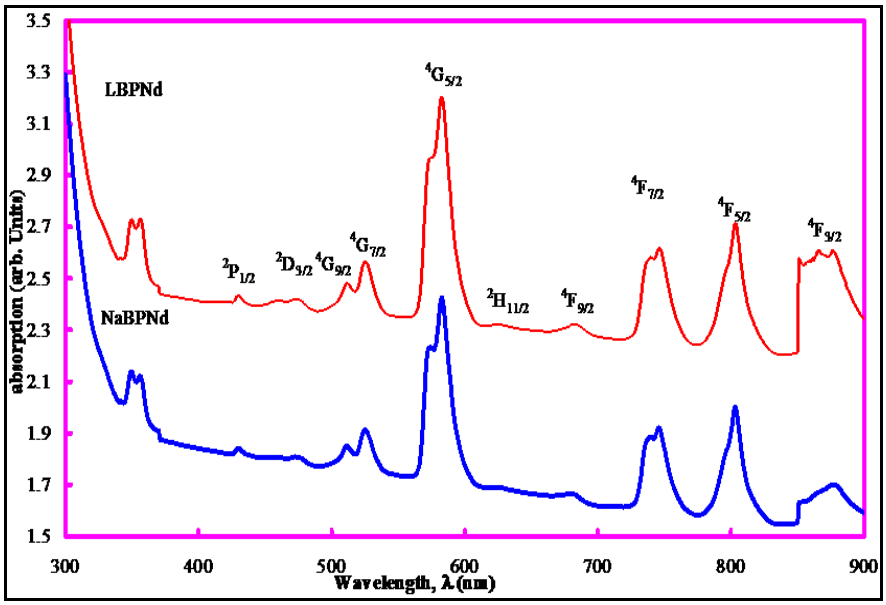

Fig. 3 Optical absorption spectra of LiF/NaF/KF–P_2O_3–B_2O_5 glasses doped with 1.0 mol% of Nd_2O_3 in the visible and UV region

Conclusion:

LiF-Al_2O_3-B_2O_3 pure glass and LiF/NaF/KF–P_2O_5–B_2O_3 glass doped with 1.0 mol% of ND_2O_3 systems are prepared by melt quenching method. The optical absorption spectra of LiF/NaF/KF–P_2O_5–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–P_2O_5–B_2O_3 glass doped with 1.0 mol% of Nd_2O_3 is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^4I_{9/2}$; these levels are assigned to the appropriate electronic transition.

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