

Physical and Optical Absorption Studies on LiF/NaF/KF-P₂O₅-B₂O₃ Glasses Doped with Sm₂O₃

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Abstract: LiF/NaF/KF-P₂O₅-B₂O₃ glasses doped with Sm₂O₃ have yielded useful applications in laser industry. LiF/NaF/KF-P₂O₅-B₂O₃ glasses doped with Sm₂O₃ have been synthesized by melt quenching method and the systematic studies like physical parameters evaluation and optical absorption behavior of LiF/NaF/KF-P₂O₅-B₂O₃ pure glass and LiF/NaF/KF-P₂O₅-B₂O₃ glass doped with 1.0 mol% of Sm₂O₃ systems have been carried out. The existence of Samarium 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-P₂O₅-B₂O₃ glass doped with 1.0 mol% of Sm₂O₃ is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state ⁶H_{5/2}; these levels are assigned to the appropriate electronic transition.

Keywords: LiF/NaF/KF-P₂O₅-B₂O₃, Melt quenching, Sm₂O₃, Spectroscopic Properties and Physical parameters.

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 [1]. 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. 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.

The literature survey on the formation of glass theories indicates that it was the Goldschmidt who proposed the theory of glass formation based on the examination of various glass systems that glasses of the general formula R_nO_m form most easily when the ratio of the ionic radius of the cat ion (R) to the oxygen (O) ion lies in the range 0.2 to 0.4. Since radius ratios in this range tend to produce cat ions surrounded by four oxygen ions in the form of tetrahedra, Goldschmidt believed that only melts containing tetrahedrally-coordinated cat ions form glasses during cooling. This contention was purely empirical, with no attempt to explain why tetrahedral coordination should be so favorable to glass formation.

Interest in amorphous phosphates was stimulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing [2]. The melting point and boiling point of P₂O₅ glasses are 560°C and 605°C respectively. Hypothetically P₂O₅ glass has a UV edge less than 150 nm (~ 8.27 eV). However, P₂O₅ glass generally contains water and shifts the edge towards longer wavelength. A comparative diagram of the UV edges of various glass formers is shown in Fig. 1.

P_2O_5 glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficients, low melting and softening temperatures and high ultra-violet transmission [3]. Certain compositions of these glasses have large rare-earth stimulated emission cross-sections and low thermo optical coefficients and are the materials of choice particularly for high power laser applications [4]. During the last two decades phosphate glasses have been investigated intensively, but there is still a great interest in developing new glasses related to the demands of both industry and technology. Many phosphate glasses are prone to crystallization or devitrification either during processing or in applications where they may be held at high temperatures for long periods. Therefore it would seem that a detailed study of the thermal behaviour of such glasses is of some importance. In the particular field of laser glasses, much recent work has concentrated on optimizing the glass compositions to give the best laser characteristics either for amplifier or oscillator configurations. However the poor chemical durability, high hygroscopic and volatile nature of phosphate glasses prevented them from replacing the conventional glasses in a wide range of technological applications [5, 6].

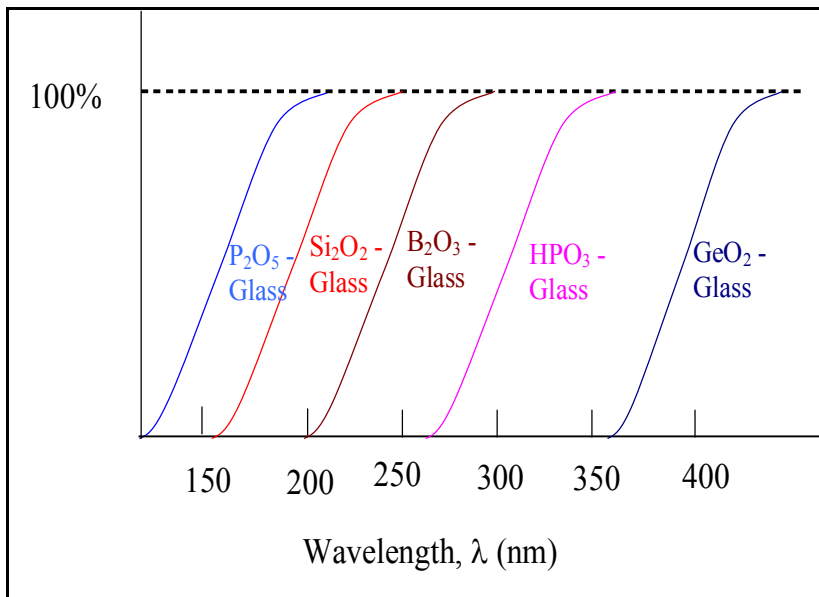


Fig. 1 Comparative diagram of the UV edges of various glass formers

In the present study $LiF/NaF/KF-P_2O_5-B_2O_3$ glasses doped with Sm_2O_3 have been synthesized by melt quenching method and the systematic studies like physical parameters evaluation and optical absorption behavior of $LiF/NaF/KF-P_2O_5-B_2O_3$ pure glass and $LiF/NaF/KF-P_2O_5-B_2O_3$ glass doped with 1.0 mol% of Sm_2O_3 systems have been carried out.

Experimental:

For the present study, the chosen composition is

$(20-x) LiF/NaF/KF-30P_2O_5-50B_2O_3: x Sm_2O_3$ with $x = 1.0$ mol%.

The details of the compositions are:

LPB₀: 20 LiF-30 P_2O_5 -50 B_2O_3

NaPB₀: 20 NaF-30 P_2O_5 -50 B_2O_3

KPB₀: 20 KF-30 P_2O_5 -50 B_2O_3

LPBSm: 19 LiF-30 P_2O_5 -50 B_2O_3 :1.0 Sm_2O_3

NaPBSm: 19 NaF-30 P_2O_5 -50 B_2O_3 :1.0 Sm_2O_3

KPBSm: 19 KF-30 P_2O_5 -50 B_2O_3 :1.0 Sm_2O_3

Analytical grade reagents of H_3BO_3 , P_2O_5 , LiF, NaF, KF and Sm_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 $\lambda = 589.3$ nm) using Abbe's refractometer with monobromo naphthalene as the contact layer between the glass and the refractometer prism.

Results and Discussion:

Some physical parameters useful for characterization LiF-P₂O₅-B₂O₃:Nd₂O₃ glasses are estimated from the measured value of density (*d*) and the average molecular weight \bar{M} , using the following Eqs.

The transition metal ion concentration (*N_i*) could be obtained from:

$$(i) N_i (10^{22} \text{ ions/cm}^3) = N_A M (\text{mol}\%) d / \bar{M} \text{ ----- (1)}$$

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

$$(ii) \text{ Inter - ionic distance } r_i (\text{\AA}) = \left[\frac{1}{N_i} \right]^{1/3} \text{ ----- (2)}$$

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

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:

$$(iv) \text{ Field strength } F_i (\text{cm}^{-2}) = \frac{z}{r_i^2} \text{ ----- (4)}$$

Table 1 Physical parameters of LiF/NaF/KF - P₂O₅ - B₂O₃ glasses doped with Sm₂O₃

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
LPBSm	2.732	102.60	37.56	8.42	3.39	1.68	1.483
NaPBm	2.714	107.25	39.52	8.56	3.44	1.59	1.479
KPBSm	2.706	111.92	41.36	8.69	3.50	1.52	1.474

P₂O₅ is a strong glass forming oxide, participates in the glass network with PO₄ structural clusters. The PO₄ 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 PO₄ tetrahedron [7]. The presence of such PO₄ units in the titled glass samples is evident from the IR spectral studies. B₂O₃ 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 [8-11]. Table 1 gives the information about the Physical parameters of LiF/NaF/KF-P₂O₅-B₂O₃ glasses doped with Sm₂O₃. 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.

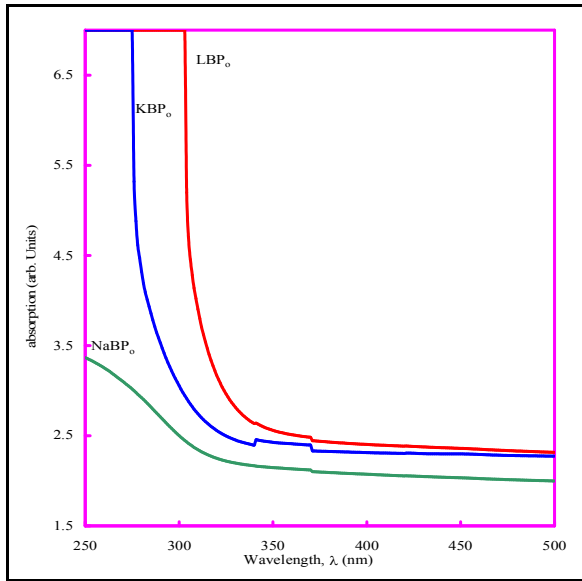


Fig. 2 Optical absorption spectra of LiF/NaF/KF–P₂O₃–B₂O₅ glasses in the visible and UV region

The optical absorption spectra of LiF/NaF/KF-P₂O₃-B₂O₃ pure glasses recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands (Fig. 2). From the observed absorption edges, we have evaluated the optical band gaps (E₀) of these glasses by drawing Tauc plot between $(\alpha \hbar \omega)^{1/2}$ and $\hbar \omega$ as per the equation:

$$\alpha(\omega) \hbar \omega = C (\hbar \omega - E_0)^2 \text{ ----- (5)}$$

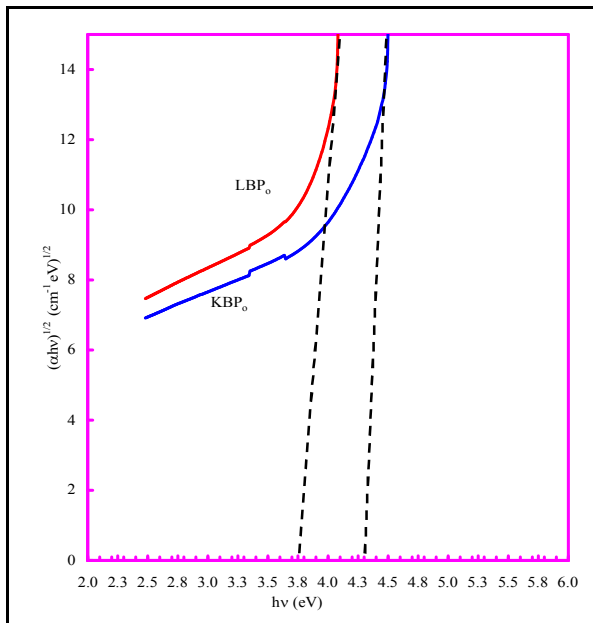


Fig. 3 Tauc plots of LiF/NaF/KF–P₂O₃–B₂O₅ glasses

Fig. 3 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 (E₀) obtained for LiF/NaF/KF-P₂O₃-B₂O₃ glasses. The optical absorption spectra of LiF/NaF/KF–P₂O₃–B₂O₃: Sm³⁺ doped glasses recorded at room temperature in the wavelength region 300-2000 nm (Fig. 4 & Fig. 5) exhibited several absorption bands these levels are assigned to the following appropriate electronic transition [12-16]:

Sm³⁺: $^6H_{5/2} \rightarrow ^6P_{5/2} + ^4K_{11/2}, ^4I_{13/2}$ (UV-visible region)
 $^6F_{11/2}, ^6F_{9/2}, ^6F_{7/2}, ^6F_{5/2}, ^6F_{3/2}, ^6F_{1/2}, ^6H_{15/2}$ (NIR region)

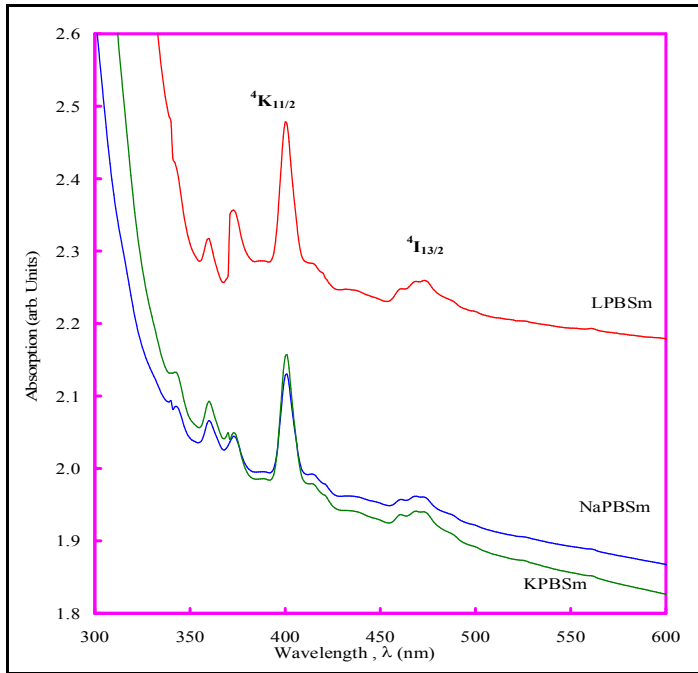


Fig. 4 Optical absorption spectra of LiF/NaF/Kf-P₂O₅-B₂O₃ glasses doped with 1.0 mol% of Sm₂O₃ (Visible region)

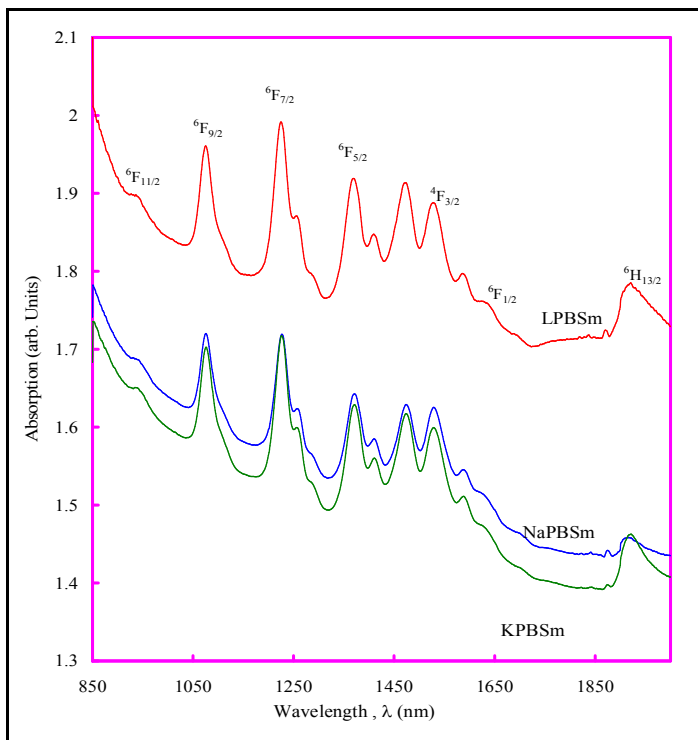


Fig. 5 Optical absorption spectra of LiF/NaF/Kf-P₂O₅-B₂O₃ glasses doped with 1.0 mol% of Sm₂O₃ (NIR region)

Conclusion:

LiF-Al₂O₃-B₂O₃ pure glass and LiF/NaF/KF-P₂O₅-B₂O₃ glass doped with 1.0 mol% of Sm₂O₃ systems are prepared by melt quenching method. The optical absorption spectra of LiF/NaF/KF-P₂O₅-B₂O₃ 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–P₂O₅–B₂O₃ glass doped with 1.0 mol% of Sm₂O₃ is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state ⁶H_{5/2}; these levels are assigned to the appropriate electronic transition.

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