International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064, Impact Factor (2013): 4.438
www.ijsr.net

Physical and Optical Absorption Studies on Li_2O-Al_2O_3-P_2O_5 Glasses Doped with Sm_2O_3

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Abstract: ***Li_2O-Al_2O_3-P_2O_5 glasses doped with Sm_2O_3 have yielded useful applications in laser industry. Li_2O-Al_2O_3-P_2O_5 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 Li_2O-Al_2O_3-P_2O_5 pure glass and Li_2O-Al_2O_3-P_2O_5 glass doped with 1.0 mol% of Sm_2O_3 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 Li_2O-Al_2O_3-P_2O_5 glass doped with 1.0 mol% of Sm_2O_3 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: Li_2O-Al_2O_3-P_2O_5 glasses, Physical parameters, Optical absorption.

1. 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]. 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. Therefore, most glass scientists regard the term "glass" as covering all non crystalline solids that show a glass transition regardless of their preparation method. 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].

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 [4]. 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 [5]. Certain compositions of these glasses have large rare-earth stimulated emission cross-sections and low thermo optical coefficients (compared with silicate glasses) and are the materials of choice particularly for high power laser applications [6]. 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.

In the Periodic Table, elements from lanthanum (Z = 57) to lutetium (Z = 71) are known as lanthanides. These are f-block elements with $4f^n\ 5s^2\ 5p^6$ as the outer most electronic configuration of the trivalent states of these elements. As the 4f sub shell of these ions is filled there is shrinkage in the volume of these ions and this is known as lanthanide contraction. This contraction is due to imperfect shielding from the nuclear charge of one f electron followed by another electron. All the rare-earths exist in trivalent state and some occasionally in divalent and tetravalent states. These rare-earth ions are associated with the f-f and f-d transitions. Among these rare earth ions samarium (Sm^{3+}) is a good doping compound for improving the properties of prepared glass systems. In the present investigation we have prepared samarium (Sm_2O_3) doped Li_2O–Al_2O_3–P_2O_5 glass system and characterized by using different spectroscopic techniques.

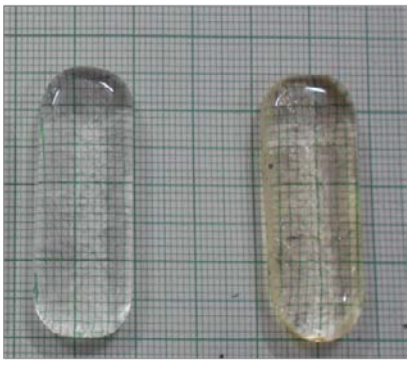
2. Experimental

In this study, the chosen composition is $(30–x)Li_2O–10Al_2O_3–60P_2O_5$: xSm_2O_3 with x=1.0 mol%.

The details of the compositions are:
ASm_0: 30 Li_2O –10Al_2O_3- 60P_2O_5
ASm_1: 29 Li_2O –10Al_2O_3- 60P_2O_5:1.0Sm_2O_3

Analytical grade reagents of P_2O_5, Li_2CO_3 Al_2O_3 and Sm_2O_3 powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar, calcinated at about 400°C for 2 h in a platinum crucible and subsequently melted in the temperature range of 1000 to 1100°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 250°C in another furnace. The samples prepared were mechanically ground and optically polished to the dimensions of 1 cm × 1 cm × 0.2 cm (Fig. 1).

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.



ASm_0 **ASm_1**

Figure 1: Images of pure and doped glasses of the Li_2O-Al_2O_3-P_2O_5 glass system

3. Results and Discussion

The composition of Li_2O–Al_2O_3–P_2O_5: Sm_2O_3 glass system is an admixture of glass formers, modifiers and intermediates. 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 oxygen's. Neighbouring phosphate chains are linked together by cross-bonding between the metal cation and two non-bridging oxygen atoms of each PO_4 tetrahedron [7, 8]. Physical parameters of Li_2O–Al_2O_3–P_2O_5 glasses doped with Sm_2O_3 are given in Table 1.

Table 1: Physical parameters of Li_2O–Al_2O_3–P_2O_5 glasses doped with Sm_2O_3

Glass	Denity (g/cm^3)	Avg. Mol. Wt. (g)	Mol. Vol (cm^3/mol)	r_i (A°)	r_{p_o} (A°)	N_i (10^{21}, ions/cm^3)	Field Strength (10^{15})	band gap (eV)
ASm_0	2.496	104.32	41.48	--	--	--	--	4.35
ASm_1	2.512	107.51	42.29	4.2	6.90	0.14	0.11	4.45

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 Li_2O–Al_2O_3–P_2O_5 pure glasses recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands (Fig. 2).

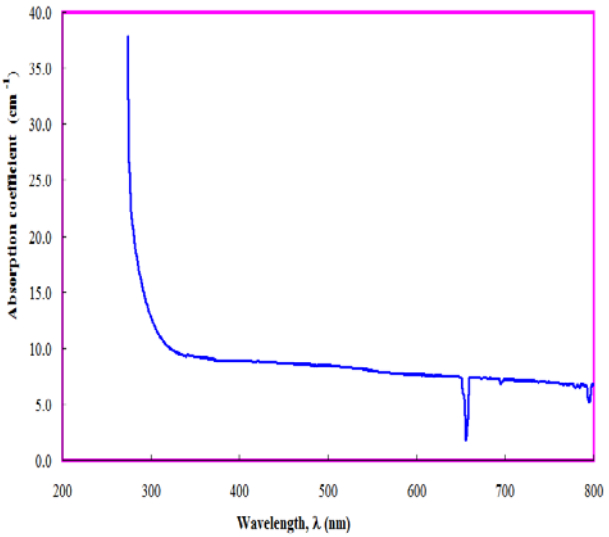


Fig. 2 Optical absorption spectra of Li_2O–Al_2O_3– P_2O_5 glass recorded at room temperature

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:

$$\alpha(\omega) \hbar \omega = C (\hbar \omega - E_o)^2 \text{ ------ (1)}$$

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 (E_0) obtained for Li_2O–Al_2O_3–P_2O_5 glasses.

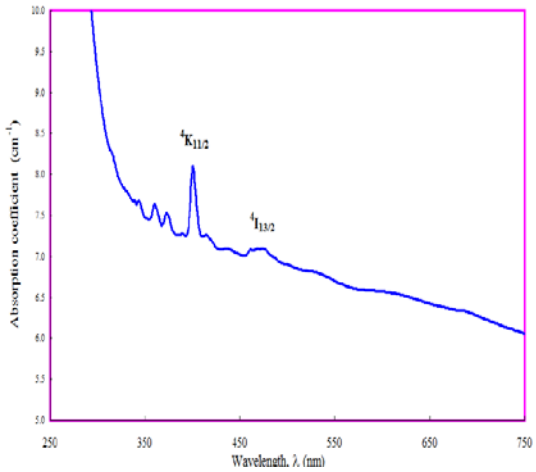


Fig. 3 Optical absorption spectra of $Li_2O–Al_2O_3–P_2O_5$ glasses doped with 1.0 mol % of Sm^{3+} recorded at room temperature in the visible region

The optical absorption spectra of $Li_2O–Al_2O_3–P_2O_5$: Sm^{3+} doped glasses recorded at room temperature in the wavelength region 300-2000 nm (Fig. 4) exhibited several absorption bands these levels are assigned to the following appropriate electronic transition [9, 10]:

Sm^{3+}: $^6H_{5/2} \rightarrow {}^4K_{11/2}$, $^4I_{13/2}$ (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)

Tauc plots of $Li_2O–Al_2O_3–P_2O_5$ glasses doped with of Sm^{3+} ions were drawn from Fig. 5 and optical band gap was estimated.

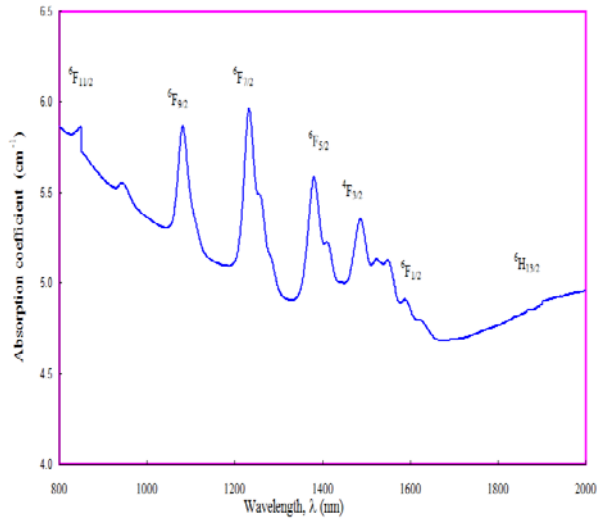


Fig. 4 Optical absorption spectra of $Li_2O–Al_2O_3–P_2O_5$ glasses doped with 1.0 mol % of Sm^{3+} recorded at room temperature in the NIR region

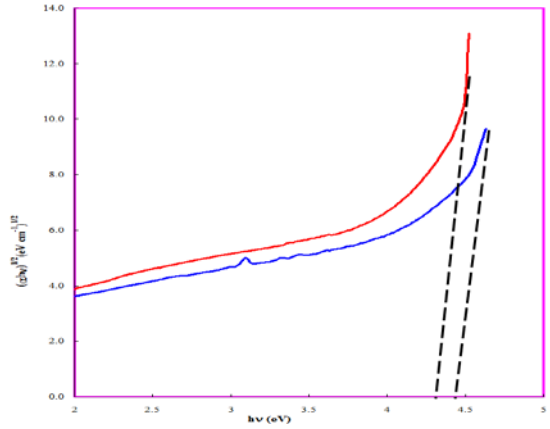


Fig. 5 Tauc plots for evaluating the optical band gap of $Li_2O–Al_2O_3–P_2O_5$ glasses doped with Sm^{3+} ions

4. Conclusion

$Li_2O–Al_2O_3–P_2O_5$ pure glass and $Li_2O–Al_2O_3–P_2O_5$ glass doped with 1.0 mol% of Sm_2O_3 systems are prepared by melt quenching method. The systematic studies like physical parameters evaluation and optical absorption behavior of $Li_2O–Al_2O_3–P_2O_5$ pure glass and $Li_2O–Al_2O_3–P_2O_5$ glass doped with 1.0 mol% of Sm_2O_3 systems have been carried out. The optical absorption spectra of $Li_2O–Al_2O_3–P_2O_5$ 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 and from the ground state $^6H_{5/2}$; these levels are assigned to the appropriate electronic transition.

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