Optical Absorption Behavior of Li_2O-Al_2O_3-P_2O_5Glasses Mixed with Nd_2O_3

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Abstract: ***Li_2O-Al_2O_3-P_2O_5glasses mixed with Nd_2O_3 have yielded useful applications in laser industry. Li_2O-Al_2O_3-P_2O_5glasses mixed with Nd_2O_3have been prepared by melt quenching method and the systematic studies like 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 Nd_2O_3 systems have been carried out. The existence of Nd^{3+}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 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: Li_2O-Al_2O_3-P_2O_5, Melt quenching, Nd2O3, Spectroscopic properties

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 [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. 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. 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 Neodymium (Nd^{3+}) is a good doping compound for improving the properties of prepared glass systems. Ajith Kumar et al. [2] studied the optical absorption spectrum of Nd^{3+} ions in phosphate glasses of varying matrix environments has been recorded in the ultra violet, visible and near infrared region. From the absorption spectra, various spectroscopic parameters such as Slater-Condon (F_2, F_4 and F_6), spin-orbit ($\xi 4f$), Racah (E^1, E^2 and E^3), nephelauxetic (β), bonding (δ) and Judd-Ofelt (J–O) ($\Omega 2$, $\Omega 4$ and $\Omega 6$) intensity parameters were evaluated. De la Rosa-Cruz et al. [3] studied the spectroscopic properties of Nd^{3+} in barium fluoroborophosphate glassy matrix have been analyzed by fitting the experimental data with the standard Judd–Ofelt theory. Various spectroscopic parameters, viz. radiative transition probabilities, radiative decay time, fluorescence branching ratios, electric dipole line strengths, stimulated emission cross-sections and optical gain of the principal fluorescence transition from the $^4F_{3/2}$ metastable level were obtained to evaluate the potential of the samples as laser material. Results show that addition of borate content to the fluorophosphate matrix will reduce the fluorescence spectral properties of Nd^{3+}.In the present investigation we prepared Neodymium (Nd_2O_3) doped Li_2O–Al_2O_3–P_2O_5 glass systems using melt quenching technique and characterized by different spectroscopic studies.

2. Experimental

For the present study, the chosen composition is (30–x)Li_2O–$10Al_2O_3$-$60P_2O_5$: xNd_2O_3 with x = 1.0 mol%.
The details of the compositions are:
Nd_0: 30 Li_2O –$10Al_2O_3$- $60P_2O_5$
Nd_1: 29 Li_2O –$10Al_2O_3$- $60P_2O_5$:$1.0Nd_2O_3$
Analytical grade reagents of P_2O_5, Li_2CO_3 Al_2O_3 and Nd_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 1200°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 1cm× 1cm× 0.2 cm (Fig. 1).

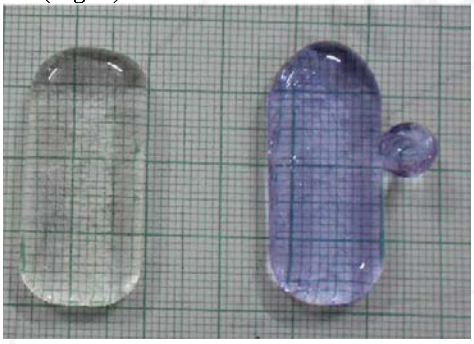

Fig. 1 Images of pure and doped glasses of the Li_2O-Al_2O_3-P_2O_5 glass system

3. Characterization

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.

4. Results and Discussion

The composition of Li_2O – Al_2O_3 – P_2O_5: Nd_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 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. The presence of such PO_4 units in the titled glass samples is evident from the IR spectral studies [4, 5]. Among various rare earth ions, Nd^{3+} doped glasses that give rich emission in the ultraviolet, visible and near infrared region (at ~2.0 μm). The introduction of Neodymium ions in the glass network will create bond defects liberating non bridging oxygen atoms (NBOs) and also suitable cations for giving rich emission. So these glasses are best candidates for lazing materials.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 1.

Table 1 Physical parameters of Li_2O–Al_2O_3–P_2O_5 glasses doped with Nd_2O_3

Glass	Density (g/cm^3)	Avg. Mol. Wt. (g)	Mol. Vol (cm^3/mol)	r_i (A°)	r_p (A°)	N_i (10^{21}, ions/cm^3)	Field Strength (10^{15})	band gap (eV)
Nd_0	2.514	104.32	41.48	- -	--	- -	--	4.35
Nd_1	3.041	107.69	35.41	39.55	15.67	0.17	0.12	4.80

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_5pure glass recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands (Fig. 2).

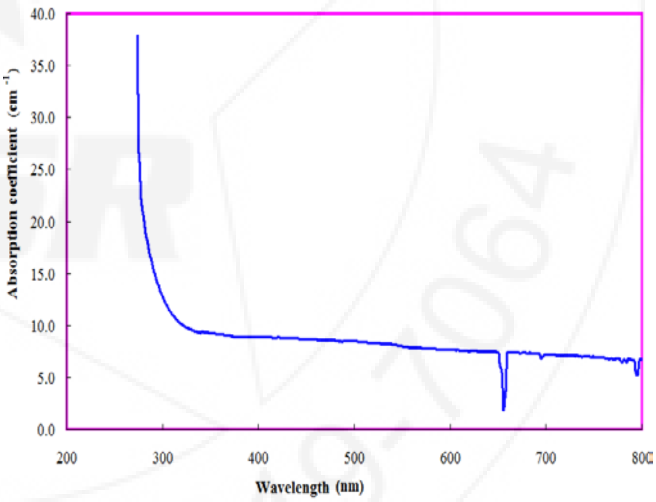

Fig. 2 Optical absorption spectra of Li_2O–Al_2O_3–P_2O_5 glassrecorded at room temperature

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_5glass is presented in Table 1.

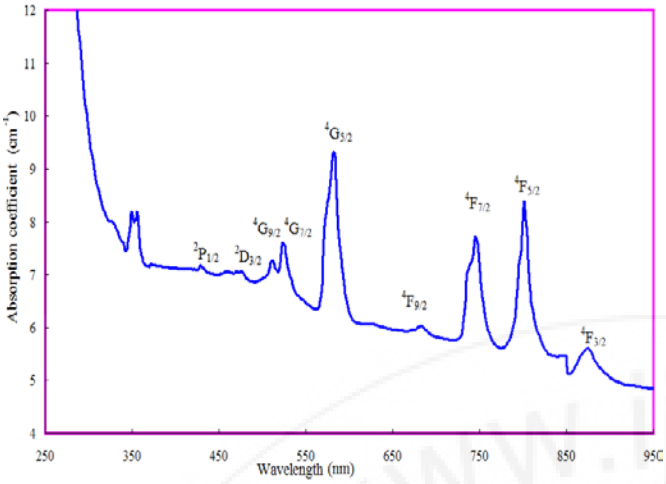

Figure 3: Optical absorption spectra of Li_2O–Al_2O_3–P_2O_5 glasses doped with1.0 mol % of Nd^{3+} Recorded at room temperature in the visible Region

The optical absorption spectra of Li_2O– Al_2O_3–P_2O_5glass 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 following appropriate electronic transition

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

Tauc plots of Li_2O–Al_2O_3–P_2O_5 glasses doped with of Sm^{3+} ions were drawn from Fig. 4 and optical band gap was estimated.

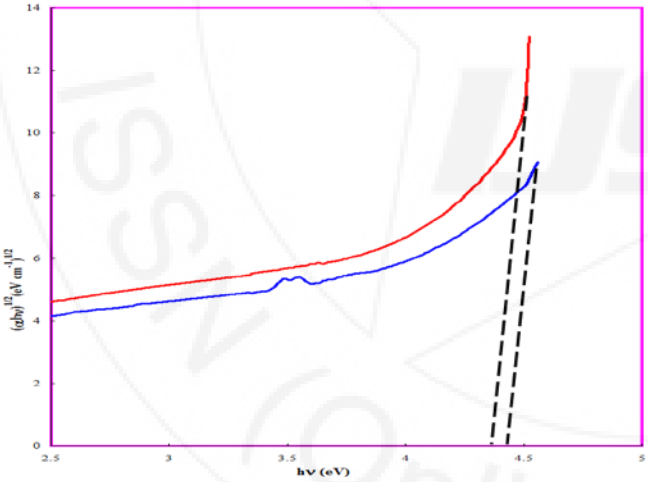

Figure 4: Tauc plots for evaluating the optical band gap of Li_2O–Al_2O_3–P_2O_5 glasses doped with Nd^{3+} ions

5. Conclusion

Li_2O–Al_2O_3–P_2O_5pure glass and Li_2O–Al_2O_3–P_2O_5glass doped with 1.0 mol% of Nd_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_5pure glass and Li_2O–Al_2O_3–P_2O_5glass doped with 1.0 mol% of Nd_2O_3 systems have been carried out. Optical absorption spectra of Li_2O–Al_2O_3–P_2O_5pure glass recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands. The optical absorption spectra of Li_2O–Al_2O_3–P_2O_5glass 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.Summing up the entire work presented in this project it is felt that the study of various physical and spectroscopic properties of Li_2O–Al_2O_3–P_2O_5glasses doped with Nd_2O_3 have yielded some valuable information which will be useful for the practical applications of these materials in the laser industry.

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