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Influence of MgO on structure and optical properties of alumino-lithium-phosphate glasses

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HIGHLIGHTS

- Alumino Lithium Phosphate glasses doped MgO were prepared by melting quenching method.
- The introduction of MgO results in depolymerization of the phosphate glasses confirmed via Raman spectroscopy.
- The dispersion of the glass was studied using the Wemple–DiDomenico method.
- The values of E_{opt} and ΔE were found to vary in a non-linear manner.

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ABSTRACT

MgO doped lithium alumino phosphate glasses (PLA: $P_2O_5+Li_2O+Al_2O_3+MgO$) were prepared by melt quenching technique. Raman spectra display three significant peaks at 698, 1164 and 1383 cm^{-1} attributed to: symmetric stretching vibrations of the bridging oxygen (BO) in the P–O–P chains, symmetric stretching vibrations of the PO_2 groups, and the asymmetric vibrations vas(PO_2) of the non-bridging oxygen (NBO) atoms, respectively. Also, the density, molar volumes and ion concentration have been discussed and correlated with the structural changes within the glassy matrix. Some optical constants such as refractive index and dispersion parameters (E_o: single-oscillator energy and E_d: dispersive energy) of the glasses were determined. Finally, the values of the optical band gap for direct and indirect allowed transitions have been determined from the absorption edge studies. It is deduced that the values of E_{opt} increase with increasing MgO content. It was assigned to structural changes induced from the formation of non-bridging oxygen. The Urbach energy (ΔE) was found to decrease from 0.578 to 0.339 eV with increasing MgO content from 0.5 to 2 mol.

1. Introduction

Lithium alumino phosphate glasses have recently become of more interest owing to their technological significance in the recycling of nuclear waste, high energy capacitors, and other electro chromic devices [1]. High thermal stability and transparency of these glasses constitute also underlying properties for the exploitation of these host materials in photonics and optoelectronics applications. Addition of Li_2O into the phosphate glass system introduces coordinated defects along with non-bridging oxygen ions, and acts also as network modifier and breaks P–O–P linkages. It has been reported that adding Al_2O_3 to phosphate glass improves their physical properties and its chemical stability [2]. On the other hand, Al_2O_3 well increases the cross-linking between PO_4 tetrahedra in the glass which results in moisture free and thermally stable glass with low thermal coefficient of expansion that are used for ion exchange planar waveguide devices [3]. The physical properties of phosphate glasses can be improved by introducing alkaline earth such as magnesium, which provides higher chemical durability. For practical applications, we have shown [4] that MgO additions play a dominant role for the creation of multicomponent invert phosphate glasses used as resorbable bone implant material.

The present study illustrates the correlation between structural and optical properties of lithium alumino phosphate glass system with varying MgO content. A systematic study has been performed to understand the variation of optical band gap and Urbach energy as a function of composition in mixed magnesium lithium alumino phosphate glasses. Other optical and physical parameters, i.e.,

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enhancement of density, molar volume and dispersion parameters were also evaluated as supplements to throw more light to elucidate the role of magnesium ions and their structural modifying ability of the glass network.

2. Material and methods

Lithium alumino phosphate glasses doped MgO were prepared by the melt quenching technique. High purity $NH_4H_2PO_4$ (99.9%), Li_2CO_3 (99.99%), Al_2O_3 (99.99%) and MgO (99.9%) were used as starting materials. The compositions (in mol.%) of glasses used in the present study were $(66-2x/3)P_2O_5$–$(33-x/3)Li_2O$–$(1)Al_2O_3$–(x)MgO (referred as PLA0, PLA1, PLA2, PLA3 and PLA4, for $x=0$, 0.5, 1, 1.5 and 2 mol%, respectively). The ratio 1:2 of Li_2O to P_2O_5 was kept constant for all glasses. Small constant addition of Al_2O_3 was added to the batches to prevent accidental devitrification during the cooling and annealing of the samples because lithium glasses are very sensitive to variations in temperature and Al_2O_3 stabilizes the preparation process. About 6 g of the batch composition was thoroughly ground in an agate mortar and this homogeneous mixture was taken into a platinum crucible and heated in an electric furnace at 950 °C for 2 h. The melt was air quenched by pouring it onto a preheated brass mold and kept for annealing at 250 °C for 3 h in order to remove thermal strains and then slowly allowed to cool to room temperature (RT). After that, these glass samples were polished to get good transparency and flat surfaces for optical measurements.

The X-ray diffraction patterns of all these Lithium alumino phosphate glasses show broad and diffused humps which indicate the vitreous nature of all the synthesized glassy materials. These results were clarified and published in the previous work [5].

Micro Raman measurements were carried out using a HORIBA Jobin Yvon spectrometer Raman LABRAM HR. The excitation wavelength's were 325 nm and 632.8 nm from He–Cd laser and He–Ne laser, respectively. Spectroscopic Ellipsometry (SE) measurements were performed using an automatic ellipsometer SOPRA GES5. The system uses a 75 W xenon lamp, a rotating polarizer, an autotracking analyzer, a double monochromator, and as detectors: a photomultiplier detector and a AlGaAs:P photodiode. Data were collected in the 1.0–5.0 eV photon energy region with the resolution of 10 meV at an incidence angle $\Phi_0=73°$. The optical properties were studied according to UV–Vis–NIR spectrum with Perkin-Elmer Lambda 950 spectrophotometer in the wavelength range of 250–1200 nm at room temperature, taking air as reference. All the optical measurements were carried out at room temperature.

Density (ρ) of the prepared glass samples was measured at room temperature by standard Archimedes method (apparent weight loss) using acetone as the immersion fluid.

3. Results and discussion

3.1. Raman spectra

For the UV excitation (325 nm), the Raman spectra reveal four main bands at about 324, 698, 1164 and 1383 cm^{-1}, reported in Fig. 1 A. The band centered at about 1383 cm^{-1} are assigned to the asymmetric vibrations vas (PO_2) of the non-bridging oxygen atoms bonded to phosphorus atoms (O–P–O) in metaphosphate chains (Q^2) [6]. With regard to higher wave numbers, a strong band is present at approximately 1164 cm^{-1}. This band may be ascribed to the vibrations of phosphate units vs (PO_2) [7]. Characteristic feature of phosphate structural units (at about 698 cm^{-1}) is assigned

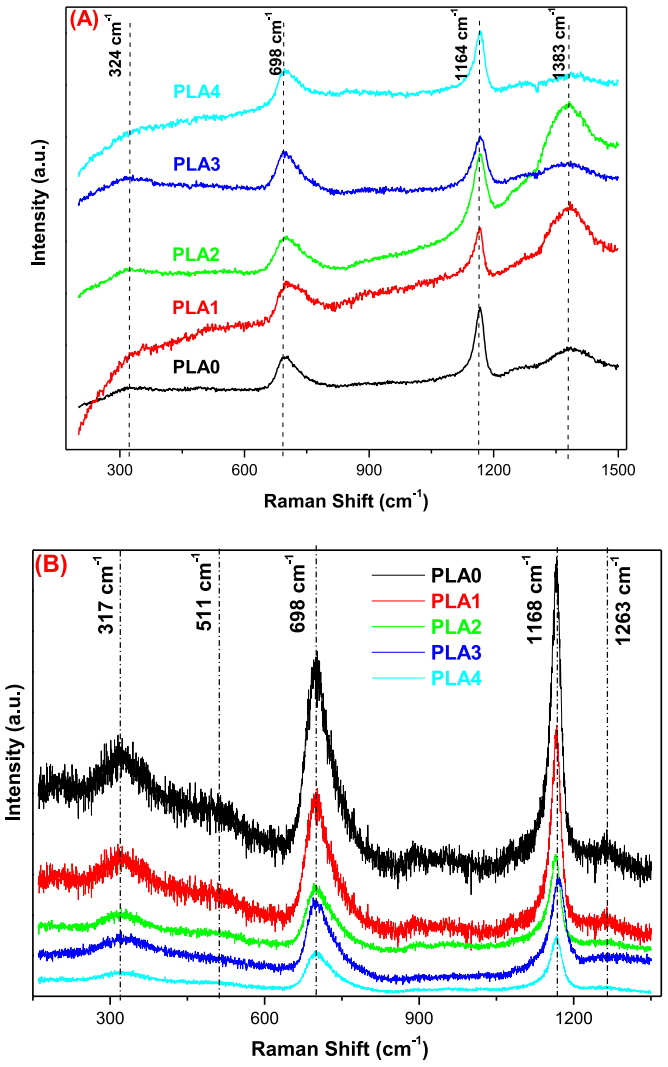

Fig. 1. Raman spectra of PLA0, PLA1, PLA2, PLA3 and PLA4 glasses under: (A) 325 nm and (B) 632.8 nm excitation.

to the symmetrical stretching vibration of bridging oxygen atoms between Q^2 units [8].

For excitation with 632.8 nm wavelength, all the Raman spectra show the presence of the same peaks with a small shift for some peaks [5]. Comparing both spectra of Fig.1 A and B, we can observe the absence of the band situated at 511 cm^{-1} and attributed to the O–P–O bending vibration [9]. Fig. 1B shows a strong band located at 698 cm^{-1} and 1168 cm^{-1}. The bands located at 698, 1168 and 1263 cm^{-1} decrease in intensity with increasing MgO content. This evolution of Raman spectra implies progressive depolymerization of the phosphate network with increasing magnesium concentration. Karakassides et al. [10] have noted that the relative decrease in intensity was more pronounced for vibrations related to P–NBO bonds (e.g. $(PO_3)_{sym}$) than P–BO bonds (e.g. POP_{sym}). In fact, the result implies an increase in the chemical durability of the glass network [11].

3.2. Density and molar volume

The density of the present glasses was estimated according to Archimedes principle with acetone as buoyant liquid using the following relationship: