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Electrical conductivity and dielectric properties of MgO doped lithium phosphate glasses

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ABSTRACT

The electrical and dielectrical properties of Li_2O-P_2O_5-Al_2O_3 doped with MgO glasses were measured using complex impedance spectroscopy. IR study reveals the influence of gradual increase in MgO content on the glass structure. The Nyquist diagrams were investigated in terms of equivalent circuits due to resistors and constant phase elements (CPE). Constant-phase elements (CPE) were used in equivalent electrical circuits for the fitting of experimental impedance data. Complex impedance analysis showed the behavior of a dielectric relaxation non-Debye type. The ac conductivity increases with temperature following the Arrhenius law, with single apparent activation energy for conduction process. The variation of conductivity and high temperature activation energy with composition revealed the possibility of ionic contribution to the conductivity and a transition from predominantly polaronic conductive regime to ionic conductive regime around 1.5 mol% of MgO in lithium phosphate glasses. The frequency dependence of the electric conductivity follows a simple power law behavior, according to relation $\sigma_{ac}(\omega) = \sigma(0) + A\omega^s$, where $s < 1$. It was evident that the electrical transport process in the system was due to the hopping mechanism. The frequency and temperature dependence of the electrical modulus as well as dielectric loss parameters have exhibited a relaxation character.

1. Introduction

Lithium phosphate glasses were gained great attention during the last decades due to their wide range of compositional and structural possibilities. The low melting and glass transition temperatures, the high electrical conductivity and the high thermal expansion coefficient of these glasses enable their use in laser host matrices, lithium microbatteries or in electro-optical systems [1–3]. Recently, a large number of phosphate glasses have been studied and their structure, properties, conductivities and dielectric behavior have been ascertained [4,5]. The study of electrical conductivity of phosphate glasses has been subject of extensive investigation due to their potential applications in solid state batteries [6,7].

Among all glasses, lithium phosphate glasses are widely studied because of their potential application in solid state batteries [8]. Since lithium is light and highly electropositive, lithium-based glasses find potential applications in high energy density solid state batteries [9]. With the addition of Li2O, the conductivity of these glasses has been found to increase. When more than one glass former is used, there is an increase in conductivity due to mixed former effect [10,11]. Further addition of lithium halides increases the conductivity of these glasses [12,13].

It has been reported that adding Al_2O_3 to phosphate glass improves their physical properties and its chemical stability [14]. On the other hand, Al_2O_3 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 [15].

However, for the study, the glass systems are considered as ionic glasses due to the existence of alkaline earth ions (Mg^{2+}) with no more than one valence state. Hence, electrons jumping from low valency state to other higher valency state are not taking place. Glass is a complex material and until today there has been no theory of ionic transport which is accepted widely. Thus, ionic diffusion in ionic conducting glass material has been an issue of interest because of its importance in technological uses. Therefore, a better understanding of its electrical conductivity is required [16].

The study on dielectric properties such as dielectric constant, loss and ac conductivity of phosphate glasses over a wide range of frequency and temperature is expected not only to reveal comprehensive information regarding the nature and origin of the loss occurring in these materials as well as conduction mechanism but also to provide information on the structural aspect of the glasses [17,18].

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In this contribution we present the results of electrical and dielectric investigation of a Lithium phosphate glasses as function of temperatures. Ac electrical measurements show that the values of conductivity are higher than those studied at room temperature in previous work [19].

The aim of the present study is to investigate the structural, electrical and dielectric properties in lithium phosphate glass with various concentrations of MgO in which the function of frequency is (40 Hz–6 MHz) and the temperature (533 to 568 K) using FTIR and impedance spectroscopy.

2. Experimental

Lithium 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 are $(66\text{-}2x/3)\ P_2O_5–(33\text{-}x/3)Li_2O–(1)Al_2O_3–(x)$ MgO (referred as PLA0, PLA1, PLA2 and PLA3, for $x = 0$, 0.5, 1 and 1.5 mol%, respectively). The ratio 1:2 of Li_2O to P_2O_5 was kept constant for all glasses. 1 mol% 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 is taken into a platinum crucible and heated in an electric furnace at 950 °C for 2 h. The melt was quickly quenched to room temperature by pouring on a preheated stainless steel plate and kept for annealing at 250 °C for 3 h. The glass samples were covered with another stainless steel plate after that slowly cooled down to room temperature. The annealing process sought to minimize the internal mechanical stress and obtain glasses with good mechanical stability. The sample has the form of a disk with $(d = 1 \pm 0.1)$ mm diameter and $(e = 0.75 \pm 0.1)$ mm thickness.

The amorphous nature of these glass samples was established and confirmed using X-ray diffraction (XRD) [19].

Infrared spectra of all glasses were collected in the range of 400–4000 cm^{-1} using a Perkin-Elmer (FTIR 2000) spectrometer at 4 cm^{-1} resolution. The IR spectra absorption measurements were done using the KBr pellet technique. The spectrum of pure KBr was subtracted from each glass spectrum to correct the background.

Electrical conductivity measurements were performed as a function of both temperature (533 to 568 K) and frequency (40 Hz–6 MHz) using an Agilent 4294A impedance analyzer.

3. Results and discussion

3.1. FTIR analyses

Fig. 1 shows the FTIR spectra in the frequency range between 400 and 2000 cm^{-1} of five samples. They are similar to those reported for other phosphate glasses [20]. The band at ~1634 cm^{-1} reflected the bending vibrations of P—OH bonds [21]. The band at ~1734 cm^{-1} in the glass may be assigned to water-bending mode [21,22]. Moreover, the absorption bands near 1369 cm^{-1} has been assigned to the asymmetric stretching vibration of the P═O bonds [23]. The bands near 1242 cm^{-1} is assigned to asymmetric stretching mode of the two non-bridging oxygen atoms bonded to phosphorus atoms, the O–P–O or $(PO_2)_{as}$ units, in the phosphate tetrahedral [24,25] and the stretching mode of P═O double bonds [25,26]. These two bands, $(PO_2)_{as}$ and P═O, are overlapped to form the broaden bands in the spectra. The band at around 1147 cm^{-1} is assigned to the PO_2 symmetric stretching mode, $(PO_2)_{str}$ [25]. The band around ~1078 cm^{-1} is asymmetric stretching vibration mode of P—O—P non-bridging oxygen group. The band at ~900 cm^{-1} is asymmetric stretching vibration of P—O—P [27]. The

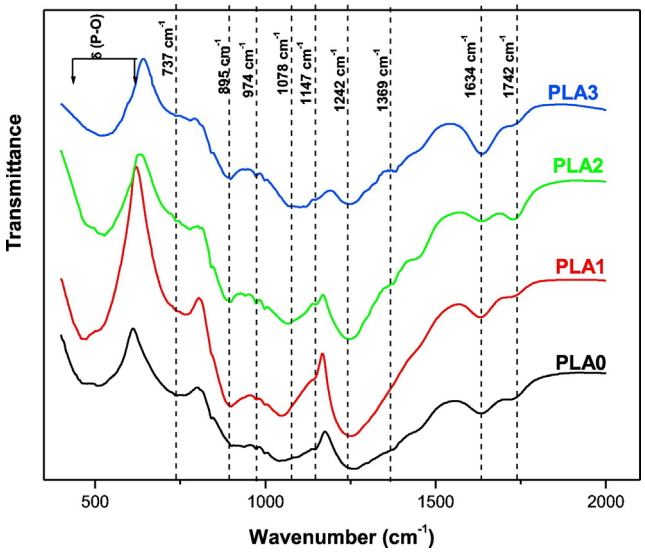

Fig. 1. IR spectra of P_2O_5-Li_2O-Al_2O_3 glasses doped MgO at room temperature.

band near 895 cm^{-1} has been assigned to P—O^- groups, the phosphate-non-bridging oxygen portion of PO_4 tetrahedra in a chain structure [28]. The absorption bands near 895 and 737 cm^{-1} are assigned to the asymmetric stretching and the symmetric stretching modes of the in-chain P—O—P linkages, (P—O—P) as and $(P—O—P)_{str}$, respectively [29,30].

At low frequency, the spectra show a strong broad absorption band near 522 cm^{-1} which can be composed of two component bands near 450–500 cm^{-1} and 530–550 cm^{-1} assigned to deformation modes of PO_4^{3-} groups [31] and the bending mode of O—P—O linkages [32] respectively.

On the other hand, the intensity bands around ~1078 cm^{-1} and near 895 cm^{-1} increase with MgO amount. The result reveals an increase of non-bridging oxygen (NBO) group, which implies an increase in the chemical durability of the glass network [33–35].

All these facts are consistent with the results of Raman spectra studied in previous work [19,36].

3.2. Impedance analysis

Fig. 2 shows complex impedance cole-cole plots for PLA0 (case 0 mol% MgO) glasses at different temperatures. A theoretical curve fitting and experimental data are measured. A good agreement between

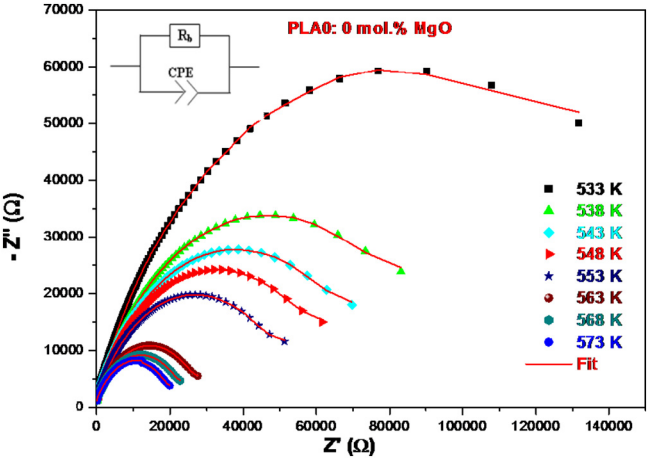

Fig. 2. Experimental impedance diagrams of PLA0 glasses at different temperatures with inset the corresponding equivalent circuit.

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