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Correlation between ion transport and network structure of Li_2O-P_2O_5 glasses

A. Chatterjee, A. Ghosh*

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

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ABSTRACT

In the present work we have studied ion transport and their correlation with network structure of Li_2O-P_2O_5 glasses. We have measured the ac conductivity of the glasses for wide ranges of temperature and frequency. The conductivity shows a crossover from dc to dispersive behavior with the increase in frequency. We have observed that the dc conductivity and the crossover frequency obey Arrhenius relation with same activation energy. We have calculated characteristic lengths of ion transport, such as the characteristic mean square displacement of mobile ions and the spatial extent of localized motion, within the framework of linear response theory. We have observed that both the length scales decrease with the increase in Li_2O content in the glasses. We have also investigated FTIR and Raman spectra to study the structure of glassy network and established a simple correlation between transport properties and network structure of the glasses.

1. Introduction

Ion conducting oxide glasses have attracted much attention due to their scientific importance and technological application in batteries, fuel cells, capacitors, chemical sensors etc. [1–10]. The introduction of alkali oxides (e.g., Na_2O, Li_2O, etc.) in oxide glasses de-polymerizes the glass network structure, forming non-bridging oxygen. The transport of alkali ions in these glasses occurs by the thermally activated hopping between non-bridging oxygen (NBO) [11–15]. Such transport mechanism is mainly due to the diffusion of mobile ions through the potential minima in the energy landscape of the glassy network. The height of these potential barriers depends on the Coulomb interaction between the alkali ions and the network structure of the glass [14,16]. It is observed that at low ion concentration ion conduction is primarily governed by the long range Coulomb interaction between mobile ions, while at higher ion concentration, the structural modification plays a dominant role in the conduction process. To understand the mechanism of ion transport in glasses is still a great challenge from scientific perspective due to inherent complexity of the glass structure [17,18]. The impedance spectroscopy has been extensively used to study ion dynamics in glasses [11,13,19]. It has been reported that the frequency dependent ac conductivity of several disordered materials shows a universal behavior [20]. The ac conductivity at low temperatures and higher frequencies exhibits a power-law behavior [21–24]. Many macroscopic as well as microscopic models have been developed to describe such typical behavior [11–13,16]. However, a concrete relationship between structure and conductivity is still lagging [25,26].

Among various glasses such as borates, phosphates, silicate, etc. [4,5], the phosphate glasses have been studied extensively due to their high ionic conductivity, low melting points, glass transition temperatures, strong glass forming ability, etc. [1,8–10,27–29]. The network structure of pure P_2O_5 glass is formed with PO_4 tetrahedra, which are connected through P–O–P linkages resulting in a polymeric structure [30,31]. The PO_4 tetrahedra are connected to their adjacent counterparts by three vertices corresponding to $P-O^-$ bonds, while the remaining vertex is occupied by a double bonded oxygen atom (DBO) $P{=}O$, which is also considered as non-bridging oxygen due to π bond delocalization [32–37]. The addition of alkali oxide de-polymerizes the phosphate network by converting bridging oxygen (BO) to non-bridging oxygen (NBO) [32]. The de-polymerization of phosphate network has been verified by ^{31}P Magic Angle Spinning Nuclear Magnetic Resonance [38–39] and X-ray photo electron spectroscopy [33,40,41]. The phosphate glasses are also very hygroscopic in nature due to the presence of $P-O^-$ linkage. The trapping of water molecules within the glassy network helps to form bonds with P or O atoms, which in turn de-polymerizes the phosphate network, a situation similar to the addition of alkali oxides to the glassy matrix [32,33].

In the present work, we have prepared binary lithium phosphate glasses of compositions xLi_2O-$(1-x)P_2O_5$, where $0.30 \le x \le 0.55$ and measured ac conductivity and dielectric spectra. We have calculated the characteristic mean square displacement of mobile lithium ions and the spatial extent of localized motion from the conductivity and dielectric

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* Corresponding author.
E-mail address: sspag@iacs.res.in (A. Ghosh).

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spectra respectively using linear response theory. We have also used FTIR and Raman spectroscopy to shed light into the network structure of the prepared glasses. At present there are a lot of works on material characteristics of phosphate glasses, especially binary alkali-phosphates [36,42,43,50,51]. However, the report on correlation between structure and transport properties through the use of microscopic length-scales is rare [11–13]. Here we have tried to correlate transport properties with the glassy network structure through the application of microscopic length-scales. Our present work will help to understand the complicated mechanism of ion dynamics in a comprehensive way for scientific as well as for technological purposes.

2. Experimental

Glasses of compositions $x Li_2O$-$(1-x)P_2O_5$, where $0.30 \leq x \leq 0.55$ were prepared by melt quenching technique. The required amounts of reagent grade chemicals Li_2CO_3 and $NH_4H_2PO_4$ (all from Sigma-Aldrich) were thoroughly mixed in a glove box in argon gas ambient. The mixtures were then preheated in alumina crucibles at 450 °C for 2 h in an electric furnace and melted at temperatures in the range 1000–1050 °C depending on the compositions and kept for 1 h for equilibrium. The melts were stirred several times to obtain homogeneity. The equilibrated and homogenous melts were rapidly quenched between two aluminum plates kept at room temperature and transparent sheets of glass samples were obtained. The glass samples were annealed at temperatures in the range 200–250 °C for one hour, depending on compositions, in an electric tube furnace in argon gas ambient, to remove residual stresses. Formation of glass was confirmed from X-ray diffraction patterns of the powdered samples taken in an X-ray diffractometer (Bruker, model D8 Advanced AXS) using Cu-K_α radiation with a scan speed 0.02°/s. The density of the prepared glasses was measured at room temperature with the help of Archimedes' principle using acetone as the immersion liquid. Fourier Transform Infrared (FTIR) spectra of these glasses were recorded at room temperature in the wave-number range 400–4000 cm^{-1}, using a FTIR spectrometer (Perkin Elmer, model Spectrum 100), with a resolution of 4 cm^{-1}. In order to get FTIR spectra the glass samples were finely grinded in powder form and mixed with KBr powder in the ratio 1:100 to form pellets. The unpolarized Raman spectra of the samples were recorded at room temperature in a confocal triple Raman spectrometer (Jovin-Yvon Horiba, model T64000) fitted with gratings of 1800 groove/mm and a TE cooled Synapse CCD detector. The samples were excited using Nd:YAG laser having 532 nm excitation wavelength. The electrical measurements such as capacitance and conductance of the samples were carried out in the frequency range from 10 Hz to 2 MHz in a LCR meter (QuadTech, model 7600 Plus) using a parallel electrode configuration in a wide temperature range of 243–483 K. Silver paste was applied on the parallel surfaces of the samples to serve as electrodes. The sample cell with parallel electrode configuration was placed inside a cryostat for measurements below room temperature. The temperature stability of the cryostat was of ± 0.1 K.

3. Results and discussion

The X-Ray diffraction (XRD) patterns of all the glass samples, presented in Fig. 1, show the characteristic wide haloes, revealing the amorphous nature of the glass samples.Fig. 2 shows the complex impedance or Nyquist plot (Z′-Z″, where Z′ and Z″ are the real and imaginary parts of the complex impedance Z*(ω)) of particular glass composition. The impedance plots are characterized by a semi-circle with a spike in the low frequency side due to electrode polarization. The intersection point of the semi-circle on real axis has been used to estimate the dc resistance. Such intersection points are found to shift towards lower Z′ values on increasing temperature, indicating that the dc resistance is thermally activated. The ionic conductivity (σ_{dc}) at different temperatures for all samples was obtained from the complex impedance plots. Fig. 3 shows reciprocal temperature dependence of the ionic conductivity for different compositions. It is observed that the dc conductivity follows Arrhenius relation:

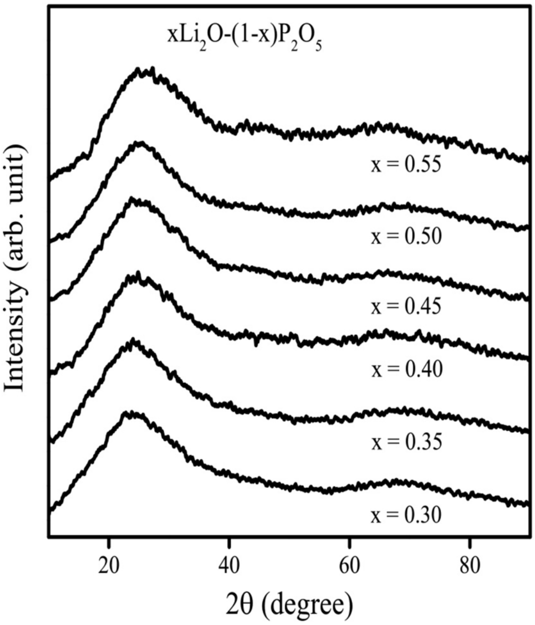

Fig. 1. XRD patterns of different compositions of $x Li_2O$-$(1-x)P_2O_5$ glasses taken at room temperature.

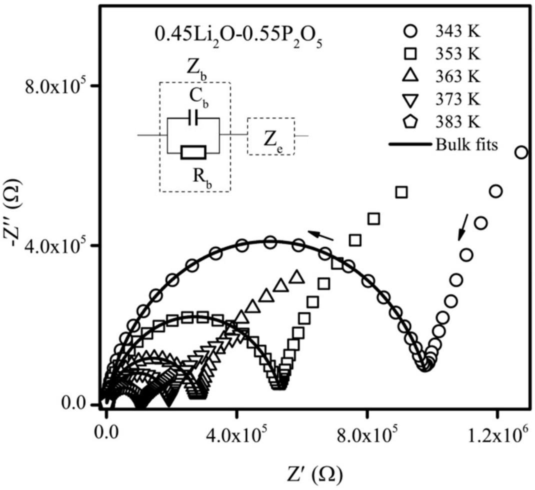

Fig. 2. Complex impedance plot (Z′-Z″) at different temperatures for the glass sample $0.45Li_2O$-$0.55P_2O_5$.The arrow directions indicate increase of frequency. The solid curve lines are the best fits to the semicircles with the equivalent circuit diagram, where C_b is the bulk capacitance and R_b is the bulk resistance, relates the bulk impedance (Z_b) only.

$$\sigma_{dc} = \sigma_0 \exp[-E_\sigma/k_B T], \tag{1}$$

where σ_o is the pre-exponential factor, E_σ is the activation energy, k_B is the Boltzmann constant and T is the absolute temperature. The values of the activation energy, obtained from the least squares straight line fits of the data to Eq. (1), are shown in Table 1. The variation of the dc conductivity at 363 K and the activation energy with Li_2O content is shown in Fig. 4. It is observed that the dc conductivity increases with increase in Li_2O content, while the activation energy follows opposite trend.

The real part of the ac conductivity spectra, σ′(ω) at several temperatures for a glass composition is shown in Fig. 5. It is observed that at low frequencies the conductivity is almost independent of frequency, while at high frequencies it shows dispersive behavior. The observed