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Investigation of Structure and Ion Dynamics of a Lithium Ion Conducting Borophosphate Glass

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ABSTRACT

Lithium ion conducting borophosphate glass has been synthesized by melt quenching technique. The thermal and structural characterizations of the glass have been performed. The glass is structurally and thermally stable which is suitable for its applicability as glassy electrolyte for solid state batteries. The detailed investigation of the ion transport mechanism has been performed by employing conductivity spectroscopy measurements. The conductivity of the glass is moderate in room temperature but can be increased up to 3×10^{-6} $\Omega^{-1}cm^{-1}$ at 413 K which predicts its application in high temperature battery application. The frequency and temperature dependent conductivity data have been analysed in the context of Jonscher model and random barrier model.

Keywords: glass; electrolyte; lithium ion battery; ion dynamics

1. Introduction

Ion conducting solids like glasses, polymers are playing an important role in modern technology. These materials are important to fabricate solid state batteries, fuel cells supercapacitors and different types of sensors, etc. [6,21]. Investigation of ion transport through such type materials is necessary for further advancement in this field. Materials are divided into two categories namely crystalline solids and amorphous solids on the basis of atomic arrangement. For investigation of electron conduction through the crystals several well established theories like free electron theory, band theory exit. Formulation of these theories is quite simple as electrons move through a matrix which can be considered as three dimensional periodic arrays of ion cores. However, if we consider the motion of ions through a non-periodic matrix such as glasses, then formulation of theory becomes complicated. That is why no broadly accepted model exists for ion conduction in disordered materials [6,21].

Atoms in the glass forming materials such as SiO_2, P_2O_5, B_2O_3, etc. are held together by strong covalent bonds [8]. To prepare ion conducting glasses some alkali oxides such as Li_2O, typically known as modifier are incorporated into the glass forming matrix. The alkali oxide breaks the oxygen bonds connected between the two Si or P atoms in host glass matrix. As a result two Li cations are connected with two oxygen atoms with a negative charge. This bond is ionic bond which is weaker than the covalent bond. Thus, ions can easily dissociate with application of thermal energy. The non-bridging oxygen atoms act as charge compensating sites of the lithium ions. These ions can “hop” from one of these sites to another if some electric field is applied. There are

several ways to probe ion transport phenomena in disordered solids such as ac electrical conductivity spectroscopy, spin lattice relaxation measurements, etc. [10]. The present paper aims to investigate the lithium ion dynamics from ac conductivity studies.

A model glass system has been synthesized for the study of lithium ion conduction mechanism. This system is mixed former kind of glass consisting of phosphate and borate species. There are some specific reasons to select such type of glass system. Recently, much attention is being focused on solid state lithium ion batteries [9, 13, 20, 22]. The term solid state is used in the sense that all components of this battery should be in solid state to prevent leakage or sudden burst of the battery. The electrolyte of this kind of batteries should be purely ion conducting dielectric type of materials. That is why, ion conducting polymers or glasses are used as electrolytes. Polymers are promising electrolytes for battery, but there arises some problems in using polymer type of materials as its thermal stability is very poor due to low glass transition temperature although it provides high ionic conductivity in room temperature to facilitate the charge transfer process [2, 17]. On the other hand, glass is a highly stable material although its ionic conductivity is very less in room temperature [12, 18]. The glass system that has been synthesized shows high thermal stability and moderate ionic conductivity at room temperature. The present paper is devoted regarding the structural information and electrical properties of this glass.

2. Experimental section

The Glass sample of the composition $0.45Li_2O$-$0.05ZnO$-$0.20B_2O_3$-$0.30P_2O_5$ was synthesized by melt quenching route. The chemicals such as Li_2CO_3, ZnO, H_3BO_3 and $NH_4H_2PO_4$ were used as raw materials. The precursors in appropriate molar ratio were mixed and ground in agate mortar with pestle. The mixture was calcined for 4 hours at 450 ^oC in a muffle furnace. The mixture was melt at 1200 ^oC. The melt was equilibrated for half an hour at the melting temperature. Finally, the melt was rapidly quenched between two aluminium plates held under atmospheric conditions. The x-ray diffraction (XRD) pattern of the sample was measured in an x-ray diffractometer (Rigaku miniflex 600) using Cu-Kα radiation (0.154 nm wavelength) at a scan rate of 0.02 degree per second. Density of the glass sample was measured using Archimedes principle and using acetone as immersion liquid. Differential scanning calorimetric measurements were carried out with in a NETZSCH DSC 214 differential scanning calorimeter (DSC) under nitrogen atmosphere. The FTIR spectrum of the sample was recorded by an FTIR spectrometer (Shimadzu, IRAffinity 1S). To carry out electrical measurements a small piece of glass was taken and silver paste was coated on both sides to form a parallel plate capacitor. The frequency dependent electrical conductivity measurements of the glass were performed by using an LCR meter (model E4980A) in the frequency range 20 Hz to 2 MHz and in the temperature range 293 - 413 K in 10 K interval.

3. Results and discussions

Fig. 1 shows the x-ray diffraction spectrum of the glass. The sample exhibits amorphous hump which indicates the amorphous nature of the sample. No diffraction peaks are observed which rules out the possibility of formation of crystallinity in the glass matrix [4, 5]. The experimental curves for heat flow and heat capacity obtained from differential scanning calorimetry measurement is shown in Fig. 2.The sample shows the baseline

shift in both heat flow and heat capacity curve. The value of the glass transition temperature (T_g) is 405 ^oC which was obtained from the baseline shift of heat flow curve.It may be noted that discontinuity in the heat capacity curve indicates that the glass transition is a second order transition. However, it is a matter of debate that it is truly second order or not [8]. The high value of the glass transition temperature indicates the high thermal stability for the glass sample [14].

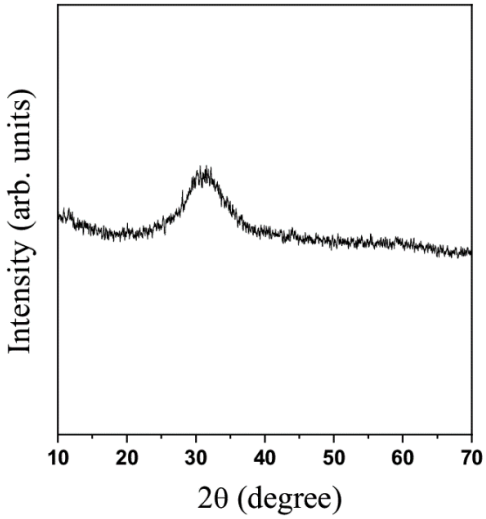

Figure 1: X-ray diffraction pattern of the glass sample.

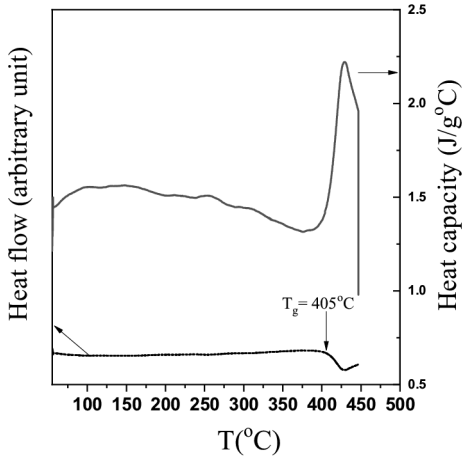

Figure 2: Heat flow and heat capacity curve obtained from DSC measurement.

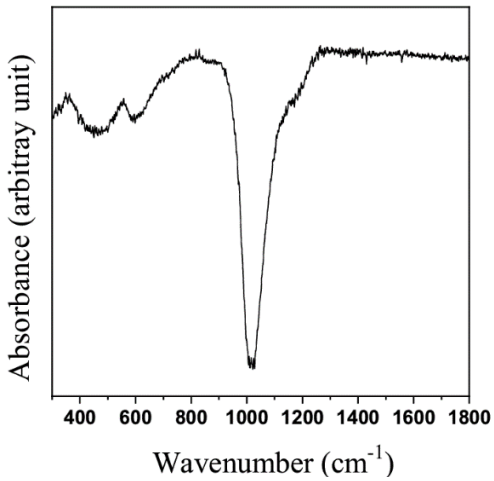

Figure 3: FTIR spectrum of the sample recorded at room temperature.

Fig. 3 shows the FTIR spectrum for the sample. The bending vibration of P-O-P or P-O-B appears close to 457 cm^{-1}[16, 17]. The bending vibration of B-O-B bridge and the symmetric stretching of P-O-P bridge appears in the same region (~600 cm^{-1}) for this sample. A strong band appears at 1000 cm^{-1} which corresponds to B-O stretching of BO_4 units [15, 16].Strong intensity of this band indicates the presence of this unit in a large amount with respect to other units. It is worthy to mention that the BO_4 units results in cross-linked network in the glass matrix through P-O-B bonds with bridging oxygen species. As a result enhancement of structural stability is observed in the glass matrix [15, 16]. Presence of BO_4 units also increases the ionic conductivity [15, 16]. A weak band appears at 1184 cm^{-1}. This band corresponds to the B-O stretching of BO_3 units [3, 15, 16]. Presence of non-bridging oxygen in BO_3 units acts as a trap for the charge carriers. Therefore, it reduces the mobility of the charges by trapping them. BO_3 units also open up the network like structure which results in decrease of thermal stability [15, 16]. The weak band corresponding to BO_3 units indicates that its presence is negligible with respect to other units.

Fig. 4 represents the real part of the conductivity spectra of the sample at different temperatures. The spectra resembles to those observed in case of other ion or electron conducting solids [6]. It has been observed that shape of the conductivity spectra of ion or electron conducting disordered materials is almost universal in nature [21]. It can be noted from Fig. 4 that there is a levelling off of the conductivity spectra in the extreme low frequency region which arises from the presence of silver electrode that blocks the mobile silver ions in the sample to flow in the external circuit [21].Therefore, a pile up of mobile ions occurs in one side of the sample electrode interface, whereas in the other side of the interface a depletion zone is formed that contains opposite charge to the mobile ion. This phenomenon is commonly known as electrode polarization effect and this property is solely due to electrode sample interface and therefore in no way it reflects any property of the sample [21]. It is observed that at low frequency region just after the polarization part the real part of the conductivity is almost independent of frequency and this part of conductivity corresponds to the frequency independent conductivity or dc conductivity. However, if we still move further in frequency scale a

rapid increase of conductivity is observed after the dc conductivity part. This part of the conductivity corresponds to the dispersive conductivity or ac conductivity.There is a crossover frequency, at which the dispersion in the conductivity starts.

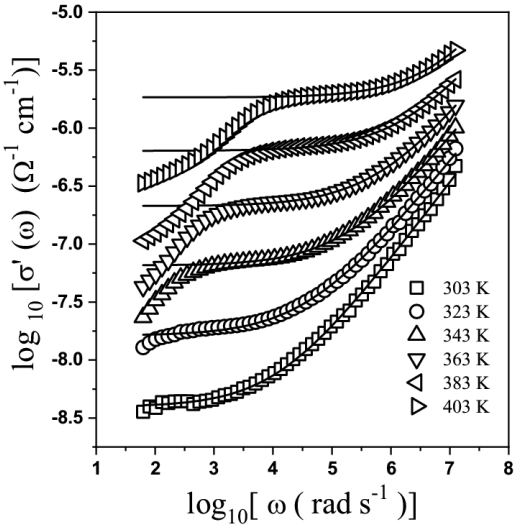

Figure 4: Frequency dependent conductivity spectra of the sample at different temperature. The solid lines are fit to the curves according to Eq. 1.

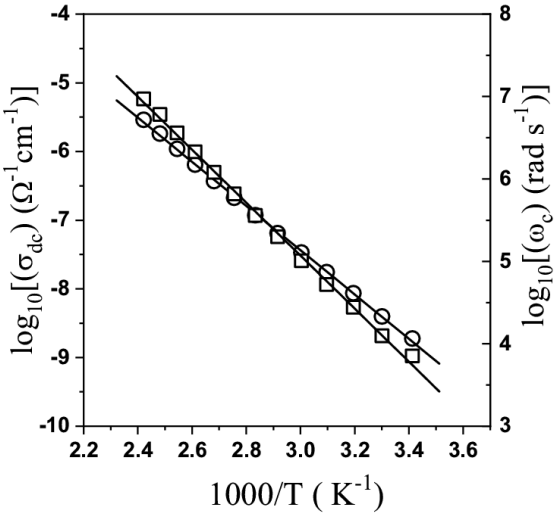

Figure 5: Temperature dependence of the dc conductivity (σ_{dc}) and crossover frequency (ω_c) is shown for the sample.

Fig. 4 clearly shows that the crossover frequency shifts towards higher values with increase of temperature. In several reports, it has been observed that in frequency window below a few MHz and moderate temperature range which is well below to the glass

transition temperature, Jonscher type of power law is used to describe the real part of the conductivity spectra [11]. The equation describing this power law is given below [1]

$$\sigma'(\omega) = \sigma_{dc}\left(1 + \left(\frac{\omega}{\omega_c}\right)^n\right) \quad (1)$$

Here, σ_{dc} denotes the dc conductivity, ω_c denotes the crossover frequency and n denotes the frequency exponent. The conductivity data of the sample at different temperatures were fitted to Eq. 1, excluding the polarization part. The parameters such as σ_{dc}, ω_c, and n were obtained at different temperatures for the sample. The resulting fit of the data is described by the solid lines in Fig. 4.

The temperature dependence of the dc conductivity and crossover frequency is shown in Fig. 5. It is observed that the both parameters are thermally activated in nature. It may be noted that the activation energy corresponding to the dc conductivity and crossover frequency is same and equal to 0.64 (±0.01) eV. It has been observed that the value of the frequency exponent n is 0.65 (±0.03). The value of n does not vary significantly with temperature. The room temperature conductivity of the glass is 4×10^{-9} $\Omega^{-1}cm^{-1}$ and it increases up to 3×10^{-6} $\Omega^{-1}cm^{-1}$ at 413 K. Thus, moderate conductivity has been achieved. Such type of glassy electrolyte may be suitable in high temperature battery application.

The Jonscher power law model is widely used model in literature [6, 21]. However, this model is empirical in nature. There is no sound theoretical basis of the model. However, the random barrier model (RBM) proposed by Dyre stands on comprehensive explanation of ion conduction theory [6, 7]. RBM considers that hopping of the charge carriers is performed in a randomly varying energy landscape inside the glassy matrix. The charge carriers must have to overcome a critical percolation energy barrier to perform long range motion. The time τ_e taken by a charge carrier to overcome the barrier may be expressed as

$$\tau_e \propto \exp(E_c/k_B T) \quad (2)$$

Here E_c denotes activation energy barrier. In this model the characteristic frequency that indicates the onset of dispersive conductivity from the dc conductivity can be expressed as

$$\omega_c \propto {\tau_e}^{-1} \quad (3)$$

RBM model leads to analytical formulae for the complex conductivity function based on two physical parameters: one is the dc conductivity σ_{dc} and the other is the characteristic time τ_e. Within this framework, the complex conductivity function ($\sigma^*(\omega)$) can be expressed by

$$\sigma^*(\omega) = \sigma_{dc}\left[\frac{i\omega\tau_e}{\ln(1+i\omega\tau_e)}\right] \quad (4)$$

The real part of the conductivity spectra have been fitted with Eq. 4 after separating the real part [19]. The fitted conductivity spectra are shown in Fig. 6. It is observed that precise fit has been obtained. The values of the parameters such as σ_{dc} and τ_e were estimated in the temperature range 293 K to 413 K. The temperature dependence of σ_{dc} and τ_e is shown in Fig. 7. It is observed that the σ_{dc} is thermally activated with an activation energy (E_c) of 0.64 (±0.01) eV which is same as that obtained from Jonscher model. The parameter τ_e is thermally activated with an activation energy(E_τ) of 0.60 (±0.01) eV which is slightly less than that of dc conductivity.

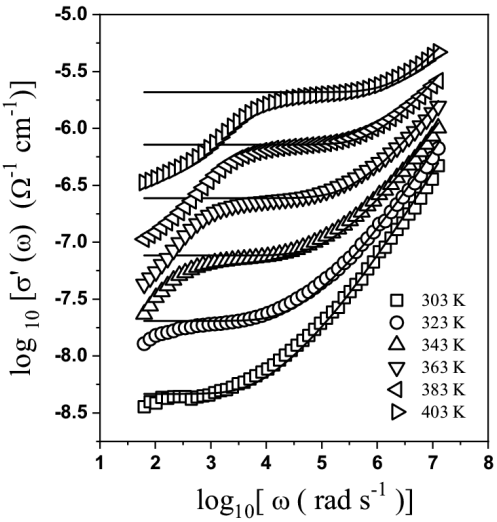

Figure 6: Fitting of the frequency dependent conductivity spectra at different temperature according to RBM model given in Eq. 4.

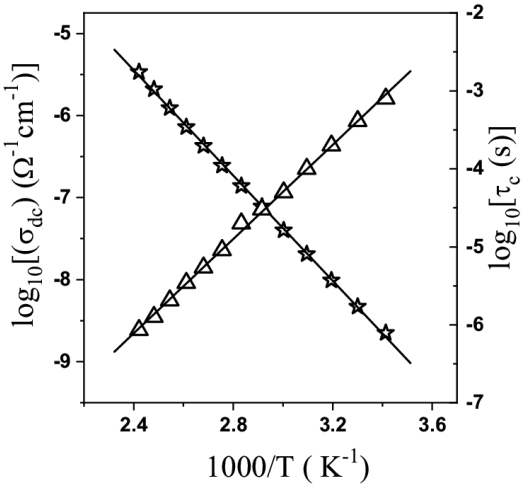

Figure 7: Temperature dependence of the dc conductivity (σ_{dc}) and characteristic time (τ_e) obtained from fitting of RBM model is shown for the sample.

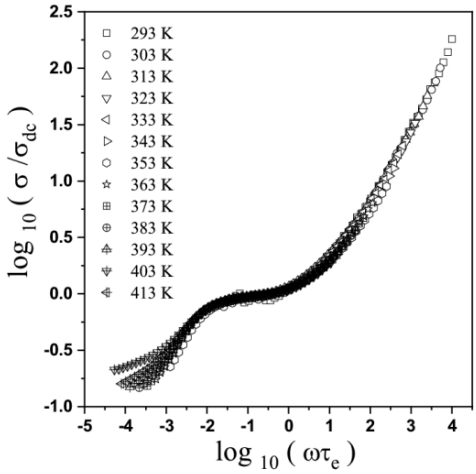

Figure 8: Scaling of conductivity spectra according to RBM formalism is shown.

The conductivity spectra at different temperatures have been scaled according to the RBM model [19]. It has been observed that the conductivity spectra superpose on a master curve. The superposition of the spectra indicates that ion transport mechanism is independent of the temperature. It may be noted that superposition has not been obtained in the polarization region as RBM model is not valid for sample electrode interface effect.

4. Conclusions

In conclusion, it may be inferred that the lithium ion conducting glassy material with high thermal and structural stability has been synthesized. High conductivity can be achieved at high temperatures. Such type of material can be used as electrolytes of lithium ion battery which can work at very high temperature condition. The ion dynamics for this glass has been investigated in details. Theoretical models such as Jonscher and RBM model have been used to explain ion transport mechanism. The superposition of the conductivity spectra in the context of RBM model suggests that the dynamics of the ion does not depend on temperature.

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