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Structure and Ion dynamics of P_2O_5-CaO-Na_2O-ZnO glass

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Abstract : Phosphate glass system of $47P_2O_5$–30.5CaO–(22.5-x)Na2O–xZnO (x=1, 2, 3, 4 and 5) have been prepared by melt quenching technique. From the Raman analysis, the glass structure has been analyzed. Purity of glasses has been confirmed from EDX analysis. The conductivity and ion dynamics of the glasses have been studied over a wide range of frequency (42Hz to 1 MHz) and temperature of 200°C to 250°C. The frequency and temperature dependent dielectric properties of the glasses have been analyzed in terms of imaginary part of dielectric modulus.
Keywords: Glass, Raman spectroscopy, dielectric modulus and activation energy.

Introduction

Phosphate glasses have attracted great attention due to their potential applications in different fields like electrolyte, biomedical, etc.,[1]. Glass is a thermodynamically non-equilibrated, 'frozen' liquid. Glass electrolytes have been widely studied in the recent past due to several important technological advantages such as absence of grain boundaries, isotropic nature, ease of composition modification, tailoring in desired shapes and good ionic conductivity due to long range disorder[2]. Simple phosphate glasses could not be able to study due to their poor chemical durability from the application point of view[3]. So, studies on phosphate glasses with suitable glass modifiers have been concentrated by the researchers. The role of the most commonly used sodium oxide (Na_2O) and calcium oxide (CaO) can have a significant effect on the glass structure and properties[4, 5]. Further sodium act as dynamic ion for the conduction[6]. Ionic ortho and pyrophosphate glass melts with ZnO and Na_2O exhibit high glass forming ability[7]. The aim of the present work is to investigate the structure, ac conductivity and dielectric behavior of $47P_2O_5$–30.5CaO–(22.5-x)Na_2O–xZnO (x=1, 2, 3, 4 and 5) glass system.

Experiments

Glasses of $47P_2O_5$ - 30.5CaO - (22.5-x) Na_2O – x ZnO (x = 1, 2, 3, 4, 5) were prepared by conventional melt quenching technique. The nomenclature of the samples are PZ01, PZ02, PZ03, PZ04 and PZ05 corresponding to ZnO concentration of 1, 2, 3, 4 and 5 mol% respectively. $NH_4H_2PO_4$, $CaCO_3$, Na_2CO_3 and

ZnO were taken as raw materials. Required amount of chemicals were thoroughly mixed and preheated at 350ºC for three hours. The preheated mixture was then melted in a platinum crucible at 950ºC for two hours in order to achieve bubble free liquid in an air atmosphere using a muffle furnace. The molten liquid was poured on the stainless steel plate and rapidly pressed by another plate to get glasses in disc form for electrical analysis. Raman spectra are observed by NANO FINDER 30 SOLAR TII, Laser Raman spectrometer. The surface of the phosphate glasses was analysed by SEM of model JSM-5610LV (JEOL, Japan) equipped with energy dispersive analysis by X-rays (EDX). AC impedance measurement on the glasses of thickness 1.9 mm and diameter 9-10 mm has been carried out in the temperature range of 200ºC–250ºC, over the frequency range of 42Hz – 1MHz using the computer controlled HIOKI 3532-50 LCR HiTESTER. The silver paste was applied uniformly on the two opposite surfaces of the prepared glass for the impedance analysis.

Result and Discussion

The structure of pure phosphate glass is considered to be a random network of Q^3 tetrahedra of phosphorus with the three single and one double bonded oxygen. Addition of oxide modifiers results in the depolymerization of the glass network by the creation of bond to the single bonded oxygen and the transitions from Q^3 -» Q^2 and/or Q^1 and/or Q^0. The Raman spectra of all phosphate glasses are shown in Figure 1. All spectra show bands at about 350 cm^{-1}, 700 cm^{-1}, 1170 cm^{-1}, 1025 cm^{-1} and 1260 cm^{-1}. There is no significant effect on the structure of the phosphate glasses with the addition of ZnO. The broad bands in the range 300 – 400 cm^{-1} in the spectra of all glasses are assigned to bending vibrations. The band in the frequency region near 700 cm^{-1} is due to stretching vibrations of the bridging oxygen (BO) (Q^2) chain connected with two PO_2 tetrahedra (Q^2) and the band at about 1170 cm^{-1} is related to the symmetric stretching of two NBO in the Q^2 phosphate structures bonded to PO_2 [8, 9]. The weak asymmetric stretching of PO_2 appears at 1260 cm^{-1}. The band at 1025 cm^{-1} has been assigned to the symmetric stretching vibration of PO_3 [10]. In the glass containing 5% of ZnO, the bond at 1025 cm^{-1} is almost disappeared and is due to the decreasing of PO_3 in the phosphate tetrahedra.

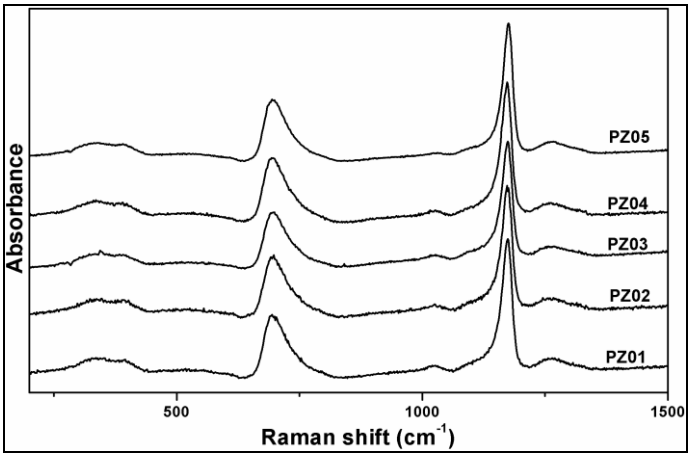

Figure 1: Raman spectra of the glass at different concentrations of ZnO.

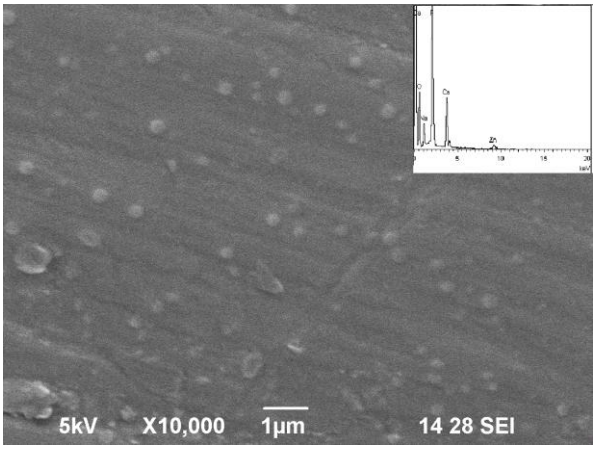

Figure 2: SEM image of PZ01 and inset (2): EDX of the glass PZ05.

Figure 2 shows that the SEM micrograph of the glass PZ01. The surface of the glass does not show explicitly any microcrystalline structures. As a result, it predicts the amorphous nature of the glass. The EDX is performed on phosphate glass. The inset figure 2 represents the EDX of the glass PZ01. It can be noticed that no peaks correspond to any impurity element, other than those supposed to be present in the glass. From the EDX analysis the purity of the material is confirmed. All other glasses are also exhibit the similar SEM and EDX.

The electrical conductivity of the glass system for different concentration of ZnO is shown in Figure 3. The electrical conductivity of the phosphate glasses depends on the concentration of sodium ions which are mobile charge carrier [11]. Hence, the electrical conductivity of the glass system might be decreased by reducing the number of mobile sodium ions that are replaced by ZnO. The conductivity has been observed in the glasses, and at lower concentrations of ZnO content (σ_{dc} (PZ01) = 2.26 X 10^{-8} Scm^{-1}, σ_{dc}(PZ02) = 1.23 X 10^{-8} $Scm^{-1}$and σ_{dc}(PZ03) = 1.02 X 10^{-8} Scm^{-1} at 200°C). Moreover, the conductivity of the materials strongly relies on ion mobility more than the concentration of mobile ions [12]. So, addition of ZnO in the network may weakening the network by making single bond with two oxygen in the glass network at higher concentration. Further, author suggested that the addition of oxygen along with the Zn has been increasing the number of non-bridging oxygen in the glass network. This non-bridging oxygen enhances the ion dynamics in the glass networks and it causes more ionic conduction. So, the conductivity increases with increase of ZnO at higher concentrations of ZnO (σ_{dc}(PZ04) = 1.34 X 10^{-8} $Scm^{-1}$and σ_{dc}(PZ05) = 2.90 X 10^{-8} Scm^{-1} at 200°C).

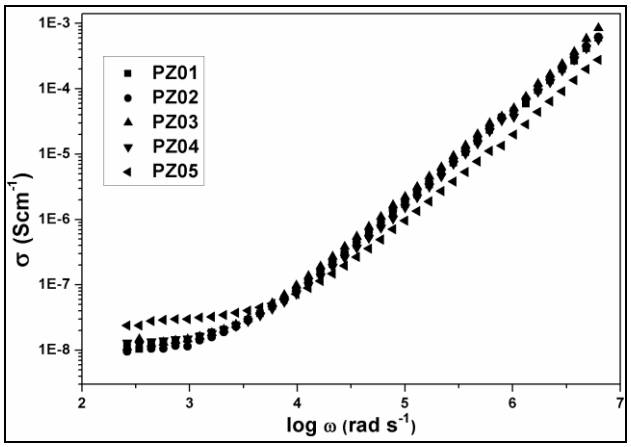

Figure 3: Conductivity spectra of the glass at different concentrations of ZnO.

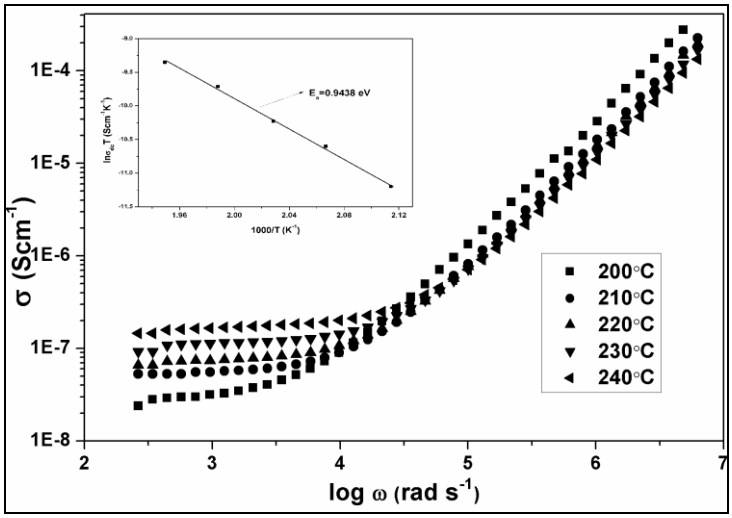

Figure 4: Conductivity of PZ05 as a function of temperature, inset (4): Arrhenius conductivity plot of PZ05.

Variation of conductivity with respect to frequency at different temperature for the sample PZ05 is shown in figure 4. It is observed that the conductivity have been increased with increase of temperature. This implies that the conduction phenomena are thermally activated. Same kind of thermal activation process has

also been observed in all the glass samples (not shown). It has also been observed that the DC region shifts towards higher frequencies as temperature increases which also confirms the thermally activated process. The temperature dependent conductivity follows the Arrhenius behavior and plot is shown in the inset figure 4. The temperature dependent conductivity is fitted and activation energy of the materials is calculated from the equation $\sigma = \sigma_0 \exp(-E_a/kT)$, where ″$E_a$″ is the activation energy, ″k″ is the Boltzmann constant and ″T″ is the absolute temperature. The activation energies of the glasses are found to be 0.88 eV, 0.80 eV, 0.67 eV, 0.82 eV and 0.94 eV for the PZ01, PZ02, PZ03, PZ04 and PZ05 respectively.

Another approach of analyzing ion dynamics is the study of electric stress (ie., electric modulus) effected by the change of dipole moment in an ac field. The electric modulus can be stated as M*(ω) = M' + iM", where M' is the real part of the electric modulus, M" is the imaginary part of electric modulus. The electric modulus is related to the complex dielectric permittivity [13] as:

$$M'' = \frac{\varepsilon''}{\varepsilon'^2+\varepsilon''^2}$$

$$M' = \frac{\varepsilon'}{\varepsilon'^2+\varepsilon''^2}$$

wherein ε' and ε" are the real and imaginary parts of the dielectric complex spectrum. The variation of imaginary part of electric modulus with respect to frequency is shown in figure 5.

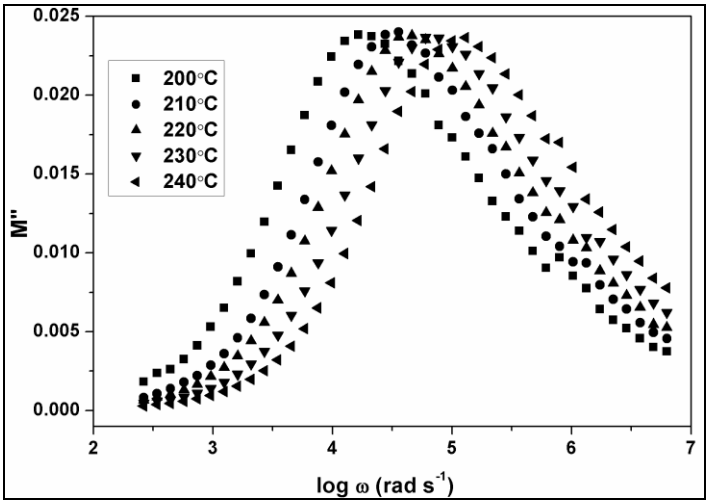

Figure 5: Imaginary modulus vs log ω of glass PZ01.

From the figure 5, the peak in the imaginary part of modulus is found to be shifted towards higher frequency with increase of temperature and is attributed to the thermally activated ion dynamics of the glass (PZ05). The presence of relaxation-peaks in the M" plot indicates that the samples are ionic conductors [14]. The spectra describes two regions, the frequency region below ω_{max} determines the range in which charge carriers are mobile over long distances and is due to the hopping of ions. For region above ω_{max}, the carriers are confined to potential wells and are mobile over short distances associated with polarization process [15].

Conclusion

Phosphate based glass system were prepared by rapid quenching technique. Higher concentrations of ZnO modifier in the glass network produced non-bridging oxygen and it could enhance the conductivity. Activation energy and the conductivity of the system were calculated. Imaginary modulus spectra confirmed the samples are ionic conductors.

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