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Conductivity spectra of silver-phosphate glass nanocomposites: Frequency and temperature dependency

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ABSTRACT

A series of glass nanocomposite systems of the composition xAgI–$(1-x)$ $(0.5Ag_2O–0.5P_2O_5)$ for $x = 0.1$, 0.2, 0.3 and 0.4 have been prepared by conventional melt quenching route. The X-ray diffraction patterns indicate the amorphous nature of all the glassy samples with the presence of a certain amount of crystallinity, superposing over broad peaks. Different types of bonds, existing within present system have been identified by FT-IR measurement. The dc and ac conductivity decreases with AgI content. The values of activation energy for dc conductivity and activation energy for crossover frequency are very close to each other, which specify that the same mechanism is responsible for the electrical conduction. The ionic conduction depends on the Ag_{ion}–Ag_{ion} separation (R), which increases with a rise in AgI content. The absence of grain boundary effect is observed from complex impedance plots. The formation of the cation-electron pair with increasing AgI content is expected to block the diffusive or hopping path, which indicates fall in conductivity. Correlated barrier hopping (CBH) model is the appropriate mechanism for ac conduction process. The temperature and composition scaling of conductivity spectra reveals that the conductivity relaxation is independent of temperature but depend on composition i.e., the structure of the glass nanocomposites.

1. Introduction

Recently, phosphate glassy systems and their nanocomposites, have attracted considerable attention to the researchers and technologists owing to their implementations in various fields such as infrared lasers, optical fibre amplifiers, energy converters, optoelectronic-devices and bio-medical applications [1–6]. In many glassy systems [1], it has been observed that ionic conductivity increases when other oxides replace network former. Similarly, ionic conductivity is found to increase when alkali or other ion conducting salt is doped gradually in the host matrix [7,8]. Study of electrical transport of P_2O_5 doped system [7] may reveal the effect of addition of alkali salt in the temperature and frequency dependent conductivity. Raman and impedance spectroscopic studies of phosphate glassy system containing Li_2O [9] correlated successfully between the structural and electrical properties. Structural and dynamic properties of phosphate glasses have extensively studied by Martin et al. [10]. Formation of bridging oxygen may increase in the volume of interstitial spaces, which attributes the diffusion process of Ag^+ ions [11]. Study of ionic conductivity of P_2O_5 doped glassy systems [11] reveals that it depends upon local structural disorder caused by structural transition.

Ac conductivity of glassy system may be analyzed by Jonscher's universal power law [12].

$$\sigma(\omega) = \sigma_o + A\omega^S \quad (1)$$

where, A is the pre factor, S is the frequency exponent and σ_o is the low frequency or dc conductivity.

The nature of variation of frequency exponent with temperature may suggest the ac conduction mechanism [7–9]. Scaling behaviour [13] of ac conductivity points to the direction where the conduction mechanism is dependent upon temperature and composition. Different formalisms have been employed by researchers [7–9] to explain ion transport phenomena in alkali oxide glassy systems and their nanocomposites. However, proper explanation has been hardly emerged and

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it is still under deep study.

The purpose of the present work is to investigate ac conductivity of AgI doped P_2O_5 glassy nanocomposites using various phenomenological and microscopic approaches. The electrical conduction of the present glassy system has been discussed and correlated with their microstructures.

2. Experimental procedure

The glassy nanocomposites, xAgI-$(1-x)$ $(0.5Ag_2O\text{-}0.5P_2O_5)$ with $x = 0.1$, 0.2, 0.3 and 0.4 have been prepared by melt quenching route [1]. The appropriate amount of silver iodide (AgI), silver oxide (Ag_2O) and phosphorous pentoxide (P_2O_5) powders have been thoroughly mixed and preheated in an alumina crucible and the mixtures were then melted in an electric furnace in the temperature range from 950 °C to 1000 °C depending upon the composition. The melts have been equilibrated for 30 min and quenched between two aluminium plates. Partially transparent glass-nanocomposites of thickness ~1 mm have been obtained. X-ray diffraction (XRD) patterns of the samples were recorded using a Seifert (model 3000P) X-ray diffractometer. The distribution of different nanocrystallites has been confirmed from the XRD-peaks. The FT-IR spectra of the samples were recorded on a Shimadzu FTIR 8400S spectrometer. The electrical conductivity measurements of the as-prepared samples have been carried out at various temperatures by complex impedance method. For this, the samples of about 1 mm thickness have been used and the measurements were made by the two-probe method. The sample inside the sample-holder has been kept in contact with two polished, cleaned and spring-loaded copper electrodes (Joy-Crucible made). The complex impedance measurements were carried out using Hioki LCR tester (Model No.3532–50) in the frequency range 42 Hz to 5 MHz at various temperatures.

3. Results and discussions

3.1. X-ray diffraction studies

XRD patterns in Fig. 1(a) of all as-prepared glass-nanocomposites illustrate broad and diffused scattering, which confirm their amorphous nature. It can be perceived from the Fig. 1(a) that the XRD patterns for $x = 0.3$ and 0.4 show no sharp peaks. The lack of sharp peaks in the XRD patterns of these glassy compositions reveal the short-range order. Sharp peaks in Fig. 1(a) for $x = 0.1$ and 0.2 clearly exhibit existence of crystallinity or long-range order. The individual diffraction peaks have been recognized and indexed through assessment and crosschecking with the available literature data. The sizes of nanocrystallites (d_c) have been estimated by the Debye-Scherrer equation [14].

$$d_c = \frac{0.89\ \lambda}{\beta\ \cos\ \theta} \tag{2}$$

where, λ is the wavelength (1.54 Å) of the Cu-K_α X-ray radiation used, θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM). The different nanocrystallites, such as $Ag_4P_2O_7$ [15], $Ag_5P_3O_{11}$ [16], Ag_2O [17] and Ag_3PO_4 [18] have been identified. The average size of individual crystallites has been calculated and presented in Fig. 1(b). It is note-worth that average size of each crystallite decreases with a rise in the concentration of AgI. It is also noted from Fig. 1(a) that with the incorporation of AgI, the structure of as-prepared glassy systems becomes more amorphous. To explore structural transformation with more incorporation of AgI in the compositions, dislocation density of the present system has been estimated. Here, dislocation is the span of the dislocation lines per unit volume of crystallite, which is crystallographic anomaly or a defect formed within the crystallite. The dislocation density (δ) in the sample is estimated using the relation [19,20].

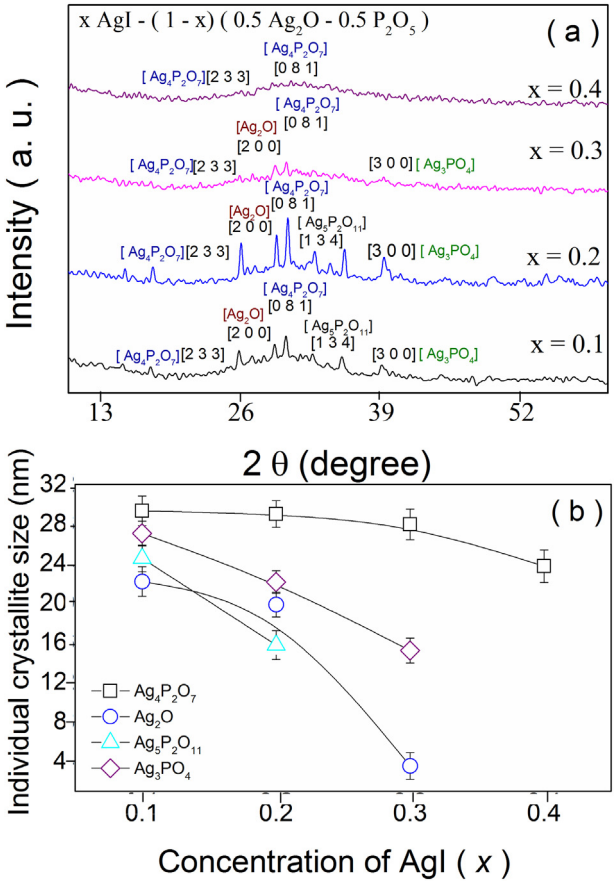

Fig. 1. (a) X-ray diffraction patterns of all the glass nanocomposites with different values of x (different phases and indexing are labelled at the peak positions); (b) individual crystallites with composition. Possible errors have been indicated using error bars.

$$\delta = \frac{1}{d_c^{\,2}} \tag{3}$$

where, d_c is the size of the crystallite. Moreover, diffraction line broadening as shown in Fig. 1(a) is not only due to formation of crystallites, but also due to strain contributions [21]. The strain-induced broadening in the glassy samples due to crystal imperfections and distortions [14] may be expressed as

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{4}$$

Here, ε is the mean strain and β is the peak width owing to the micro-strain. Mean crystallite size (d_c), dislocation density (δ) and the lattice strain (ε) have been illustrated in Fig. 2 with compositions. It is ascertained from Fig. 2 that as the mean size of the crystallites decreases, the dislocation density and lattice strain of the as-prepared glass nanocomposites are found to increase. The enhancement of these values indicates the modification of structure and formation of new nanocrystallites [1]. In view of Fig. 1, it is suggested that these new nanocrystallites may be oriented in such a manner that they are not detected by XRD study. Here, glassy samples with higher AgI content may be termed as “X-ray amorphous materials”. It needs further study in near future.

3.2. Study of Fourier transform infrared spectroscopy (FT-IR)

Fig. 3 shows the FT-IR spectra of all as-prepared samples in the frequency range 1400–400 cm^{-1}, which provides some important information about the structural changes with the inclusion of AgI