

FRACTAL DIMENSIONALITY OF ION CONDUCTION IN GLASS-NANOCOMPOSITES

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Abstract. We have reported the variation of dc conductivity with annealing time and the imaginary part of modulus spectra of Ag^+ ions in the frequency range 40 Hz-110 MHz of the heat-treated sample $0.70\text{AgI}-0.15\text{Ag}_2\text{O}-0.015\text{Cu}_2\text{O}-0.135\text{MoO}_3$ at room temperature. We have observed that the variation of dc conductivity with annealing time shows a linear relationship, which indicates that ion conduction process is independent of the annealing time. We have also observed that the variation of relaxation time with annealing time follows a proposed power law from which the fractal dimensionality of the ion motion is predicted. The stretched exponent, obtained from the imaginary part of modulus spectra is found to vary with the annealing time which indicates the change in structure during annealing.

1. Introduction

Superionic solids embedded with nanocomposites exhibit the remarkable behavior of selective ion mobility [1]. Apart from a few crystalline materials such as Rb_4AgI_5 , the highest ionic conductivity at room temperature have been achieved in AgI doped glasses and composites [1,2]. The glassy conductors are of particular interest for technological applications such as batteries, sensors etc. due to their ease of preparation, their stability, and the large available composition ranges. In order to understand the ionic transport phenomena, it is essential to find a connection between the microscopic structure and the ionic conductivity. Oxide superionic glasses have a random network structure with physical void spaces and, therefore, can be exploited as nanotemplates in which distributed nanostructured can be grown.

Different transport models, such as the weak electrolyte model [3], the random site model [4], the dynamic structure model [5] and the diffusion pathway model [6,7] have been proposed to explain the high ionic conductivity of superionic glasses. Basically they involve some indirect assumptions regarding the microscopic structure and the local environment of the mobile cations. So in order to make out the origin of the diffusion mechanism using different models, it is essential to obtain more insight about their structures and the nature of

the conduction pathways. So far, regarding the ion conduction in glasses and glass-nanocomposites, our knowledge is limited to some empirical relations. The conductivity is achieved by highly polarizable anion, e.g., I_2 , in combination with a polarizable metal ion, e.g., AgI. Mustarelli *et al* [8,9] successfully showed that the addition of AgI to the molybdate glassy matrix causes a successive increase of the silver ions in mixed coordination state, I.Ag.O, and the mobile Ag^+ cations are responsible for ionic conductivity. Sanson and co-workers [10] showed that the temperature dependence of EXAFS exhibited original insights into the behavior of the local environment of iodine resulting the increase of the Ag^+ ions diffusion when temperature increases.

In this letter, we have shown, for the first time, how the ionic conductivity as well as the dimensionality of the ionic transport of selective iodomolybdate glassnanocomposite depends upon the temperature and the time duration of heat-treatment of the sample or annealing time. Here we have proposed an empirical model based on which we can predict it.

2. Experimental

Glass-type sample of compositions $0.70AgI-0.15Ag_2O-0.015Cu_2O-0.135MoO_3$ has been prepared from the reagent grade chemicals AgI, $AgNO_3$, Cu_2O , and MoO_3 . The mixtures of these chemicals in appropriate proportions were held at $400\text{ }^\circ\text{C}$ for 2 h for denitrogenation of $AgNO_3$ and melted in the temperature $750\text{ }^\circ\text{C}$ in a high temperature electric furnace. The melts were equilibrated for 2 h and were finally quenched between two aluminum plates. Transparent glass samples of thickness $\sim 1\text{ mm}$ were obtained. Glass formation was confirmed from X-ray diffraction study. The differential scanning calorimetry (DSC) was carried out to determine the glass transition temperature (T_g). T_g is found to be $90\text{ }^\circ\text{C}$. Next the as-prepared sample has been passed through a heat treatment of constant temperature $130\text{ }^\circ\text{C}$ ($T_g + 40\text{ }^\circ\text{C}$) but different time duration or annealing time 1h, 2h, 5h, 12h, and 24h respectively. The impedance spectroscopy measurements of these samples (as-prepared and heat-treated) were carried out at room temperature, in the frequency range of 40 Hz-110 MHz using an Agilent 4294A Precision Impedance Analyzer with the Cp-Rp configuration, indicated for samples of high resistance, where Cp represents the capacity and Rp the resistance of a parallel RC equivalent circuit. The analytical background used to determine the electric permittivity characteristics of these samples is discussed in the literature [11].

3. Results and discussion

Fig. 1 shows the variation of dc conductivity with annealing time. It is observed in Fig. 1 that with increase of annealing time, the dc conductivity falls down. This can be explained from their structural point of view. Minami *et al* [12,13] exhibited that in the iodomolybdate glass matrices, α -AgI phases are stabilized at room temperature and above $147\text{ }^\circ\text{C}$, α -AgI phases are transformed into β -AgI phases. So it may be concluded from the above fact that at $130\text{ }^\circ\text{C}$, the mixed phases of α -AgI and β -AgI might be present in the sample under investigation and their sizes control the dc conductivity. The solid straight line in Fig. 1 represents the best fitted curve of the experimental data. As the Fig. 1 shows a linear relationship between dc conductivity and annealing time, it may be stated that conduction process is independent of the annealing time within this range of the experiment.

In order to analysis the electrical impedance data, the modulus formalisms [14-16] are also adopted. An electric modulus M^* at a particular frequency (ω) and temperature is defined in terms of reciprocal of complex dielectric permittivity ϵ^* as

$$M^*(\omega) = 1/\epsilon^*(\omega). \quad (1)$$

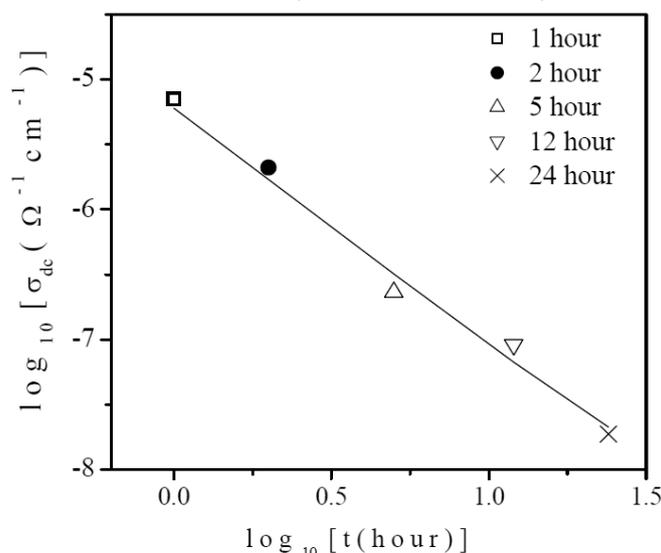


Fig. 1. dc conductivity of 0.70AgI-0.15Ag₂O-0.015Cu₂O-0.135MoO₃ heat-treated samples shown as a function of different annealing time.

The modulus $M^*(\omega)$ can also be expressed as a Fourier transformation of a relaxation function $\phi(t)$:

$$M^*(\omega) = M_\infty \left[1 - \int_0^\infty dt \exp(-i\omega t) \left(-d\phi/dt \right) \right], \quad (2)$$

where M_∞ is the reciprocal of high frequency dielectric constant ϵ_∞ . The function $\phi(t)$ is usually taken as Kohlrausch - Williams - Watts function [15], given by

$$\phi(t) = \exp[-(t/\tau_m)^\beta], \quad 0 < \beta \leq 1, \quad (3)$$

where β is the stretched exponent, whose value tends to unity for Debye type of relaxation and τ_m is the conductivity relaxation time. We have presented the imaginary modulus spectra at different annealing time for a particular glass-nanocomposite as shown in Fig. 2. The imaginary modulus M'' exhibits a maximum M''_{\max} which corresponds to the conductivity relaxation frequency ω_m . It is further noted that the position of M''_{\max} shifts towards lower frequencies as the annealing time is increased. The stretched exponents (β) are obtained from the full width at half maxima [17] of each curves in Fig. 2. The conductivity relaxation time τ_m are obtained from the reciprocals of the conductivity relaxation frequency ω_m because of the fact $\omega_m \tau_m = 1$ for Debye type of relaxation.

Fig. 3 shows the variation of the non-exponential parameter β with annealing time. It is noted in Fig. 3 that the values of β are found to increase with the increase of annealing time for the same composition. These variations of β indicate that the conductivity relaxation is highly non-exponential and the structure of the as-prepared sample is changed. Comparing the values of β of the present glass-system with those (~ 0.50) of phosphate glasses [18], we note that the values of β of the silver molybdate glasses are slightly smaller than those for the phosphate glasses at room temperature, it shows high β value (0.53) at higher annealing time. This might arise from the structural differences of these glasses as mentioned in the introduction.

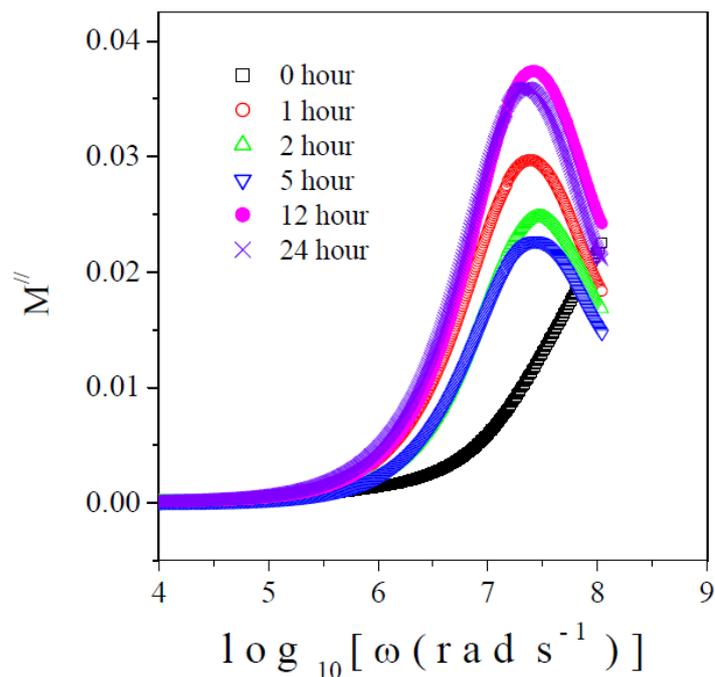


Fig. 2. Imaginary modulus spectra of $0.70\text{AgI}-0.15\text{Ag}_2\text{O}-0.015\text{Cu}_2\text{O}-0.135\text{MoO}_3$ as prepared and heat-treated samples at room temperature.

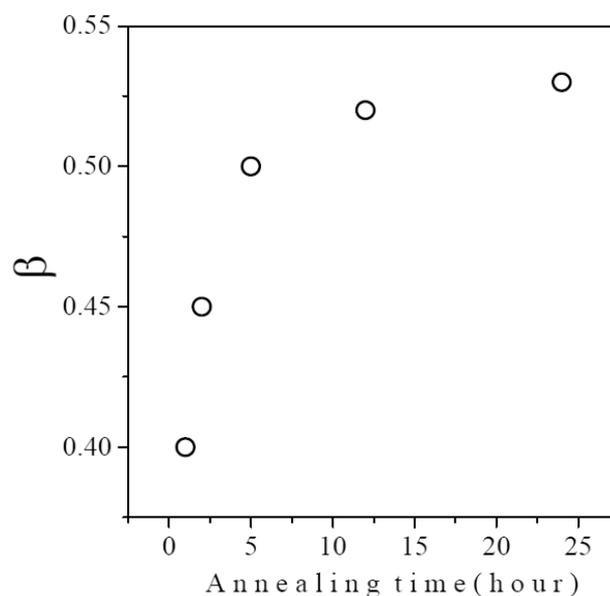


Fig. 3. Variation of β shown as a function of different annealing time of $0.70\text{AgI}-0.15\text{Ag}_2\text{O}-0.015\text{Cu}_2\text{O}-0.135\text{MoO}_3$ heat-treated samples.

The variation of conductivity relaxation time (τ_m) with annealing time is shown in Fig. 4. It has been observed in Fig. 4 that τ_m increases with the increase of annealing time. This directly indicates that conductivity relaxation time and dc conductivity (Fig. 1) show opposite behavior with annealing time.

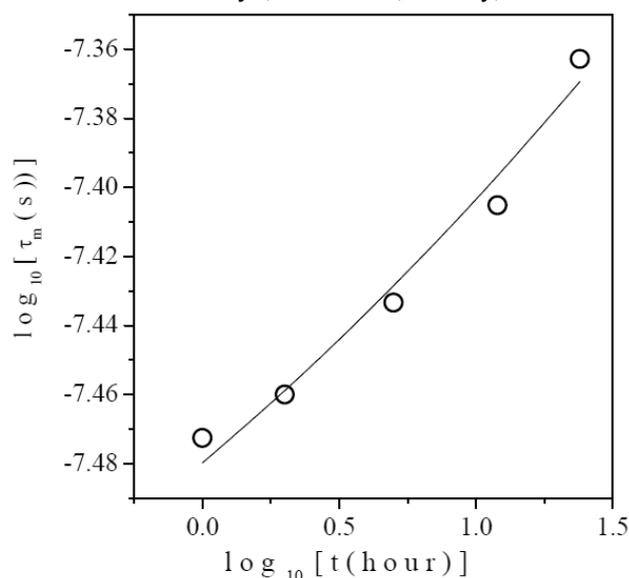


Fig. 4. Variation of the relaxation time as a function of different annealing time of 0.70AgI-0.15Ag₂O-0.015Cu₂O-0.135MoO₃ heat-treated samples.

The experimental data in Fig. 4 are fitted with a proposed power law:

$$\tau_m = \tau_0 [(t/t_{av})^n + 1], \quad (4)$$

where τ_m is the conductivity relaxation time, τ_0 is the pre-factor, t is the annealing time, t_{av} is the average annealing time and n is the power. The solid line in Fig. 4 represents the best fitted curve by Eq. (4). From the fitting, the values of τ_0 and n are obtained as 2.1×10^{-8} s and 0.185 respectively. Like other power law [19] models, n may also be related to the dimensionality [15] of conduction pathways. Sidebottom [20] successfully shows that the value of the power of frequency is $\sim 2/3$ and does not depend significantly on composition as well as temperature indicating a three dimensional motion of Ag^+ ions in the iodomolybdate glass-nanocomposite when an electric field is applied. It agrees with the numerical value of n that the dimensionality might be fractal. It is noted that the fractal dimension of metallic glasses is close to the fractal dimension of quasicrystals [21] (2.72), which exhibits a quasiperiodic long-range order and are characterized by a hierarchy of atomic clusters [22], showing the structural similarity between metallic glasses and quasicrystals [23]. In the present system, α -AgI and β -AgI nanocrystals might be present in the heat-treated samples as discussed in the introduction. The pre-heated sample must show three dimensional conduction pathways [20]. When the as-prepared sample is heated at 130 °C at different annealing time, the α -AgI and β -AgI nanocrystals might be broken into fractal growth thereby reducing the conduction pathways. This fractal growth might resist the Ag^+ conduction. As a consequence of this, the dc conductivity decreases (Fig. 1). It directly indicates that when the sample under investigation undergoes heat treatment at different annealing time, the dimensionality of ion conduction is reduced.

4. Conclusion

The variation of dc conductivity with annealing time and the imaginary part of modulus spectra of Ag^+ ions in wide frequency ranges of the heat-treated sample have been studied at

room temperature. It is observed that the variation of dc conductivity with annealing time follows a linear relationship, which indicates that ion conduction process is independent of the annealing time. We have also observed that the variation of relaxation time with annealing time follows a proposed power law from which the fractal dimensionality of the ion motion is predicted. But the reason of this surprising result is still under investigation. The stretched exponent is found to vary with the annealing time which indicates the change in structure during annealing.

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