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AC, DC and impedance measurements of some oxide glasses

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ABSTRACT

AC,DC and impedance measurements of (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3,[where x = 0, 15, 20, 25,30,35,40 and 45] superionic glasses have been studied in the frequency range (50 Hz-5 MHz) and in the temperature range 303-503K. The frequency dependence of the total conductivity(σ_t) for the investigated samples was carried out at different ambient temperatures. The temperature dependence of ac conductivity $\sigma_{ac}(\omega)$,and dc conductivity (σ_{dc}) were studied, where Arrhenius behavior has been observed for all the glass, and the corresponding activation energies ΔE_{ac}, E_{dc}, respectively have been obtained. The bulk conductivity (σ_b)of the samples has been carried out at different temperatures, from impedance plots, where the activation energy ΔE_b can be obtained. From the frequency dependence of the ac conductivity of the investigated samples, $\sigma_{ac}(\omega)=A\omega^s$, the frequency exponent s and the maximum barrier height W_m have been deduced at different compositions. The results are interpreted in terms of the correlated barrier hopping (CBH),Funke, and Minami models.

KEYWORDS

Oxide glass;
Ionic conduction;
Impedance measurements;
AC conductivity;
DC conductivity.

INTRODUCTION

Growing interest has developed in the recent years to study the fast ion conducting glasses due to their potential applications in various electrochemical devices such as batteries sensors. This type of material is not only have high ionic conductivity but also have many other advantages over their crystalline counterparts,such as, ease in preparation, wide selection of composition and glass forming region, absence of grain boundaries and inert to atmosphere[1-3]. The electrical conductivity, σ, of many solids was given[4-8] to consists of a frequency independentand a strongly frequency dependent components, the former being the dc conductivity σ_{dc} while the later one is called the ac conductivity$\sigma_{ac}(\omega)$.

The ac conductivity study at variable frequencies and temperatures give useful information about the mobile ion diffusion and short time phenomena due to local motion of mobile ions[9-10]. The interpretation of the ac conductivity measured in the ionic solids is still the subject of controversy since no model has been fully recognized as sufficiently powerful or informative[11]. Many of the research works concerning the ionic conductivity of glasses have been widely investigated in the view of their unique transport properties and its application to solid state ionic devices[12-14]. Oxide glasses containing transition metal ions, such as Fe_2O_3 have attracted great attention because of their use in electrochemical, electronic and electro-optic devices[15-17]. The dielectric properties of oxide glasses in the formAgI AgO Fe_2O_3 P_2O_3 have been earlier studied[18], while their electrical properties,upon our limit knowledge, have not yet been studied. The present work aim to investigate the electrical conductivity and the complex impedance of the glassy system $(50-x)P_2O_5$-xAgI-$40Ag_2O$-$10Fe_2O_3$,[where x= 0, 15, 20, 25,30,35,40 and 45 mol %].

EXPERIMENTAL DETAILS

Preparation of samples

The glassy system $(50-x)P_2O_5$-xAgI-$40Ag_2O$-$10Fe_2O_3$ [where x = 0,15, 20, 25,30,35,40 and 45 mol %] were prepared by melting mixtures of $NH_4H_2PO_4$, AgI, Ag_2O and Fe_2O_3 in the powder form. The mixture was heated in purceline crucbles at a temperature ranging from 250°C to 350°C for two hours in order to gas evolution ceased. After that, the temperature was raised gradually to 950°C and left for 6 hours in order to chemical reaction is completed. Then the melt was shaked several times to ensure the homogenity. The melt was poured on a steel plate kept at (0°C). Silver paste, which show ohmic contact with glass samples, was used for coating the desired electrode area. The sample before measurements was left at room temperature for about 10 hrs. The solid electrolyte glass $20P_2O_5$-30AgI-$40Ag_2O$-$10Fe_2O_3$ was pulverized into very small grain sizes. The solid electrolyte powder was pressed under the desired pressure to obtain pellet of 12 mm diameter and 1 mm thickness. The blocking electrode material is Ag_2S where was mixed with electrolyte glass powder in a weight ratio of 2 : 3. It was pressed together with the solid electrolyte layer into a two-layered pellet. Silver paste, which showed ohmic contact with solid electrolyte layer, used to coating the surface of the solid electrolyte layer as a negative electrode.

A.C. measurements

The ac measurements have been carried out in the range of frequency from (500 Hz to 5 MHz). The values of impedence (Z), capacitance (C), Resistance (R), and phase angle (ϕ) are directely read by using a programmable automatic RCL meter (HIOK 3532 LCR HITESTER). The total conductivity (σ_t) were calculated by using the data of Z, C, R andϕ at any frequency F. The total conductivity $\sigma_t$of the sample was calculated by using the following relation ;

$$\sigma_t = \frac{d}{A} \cdot \frac{1}{R} \qquad (1)$$

where d is the thickness of the sample, A is the cross-sectional area of the sample and R is the resistance of the sample.

RESULTS AND DISCUSSION

The effect of frequency on the total conductivity

Figure 1 shows the frequency dependence of the total conductivity$\sigma_t(\omega)$ in the frequency range (50 Hz - 5 MHz) for the glass system $(50-x)P_2O_5$-xAgI-$40Ag_2O$-$10Fe_2O_3$[where x=0, 15, 20, 25, 30, 35, 40 and 45] at different ambient temperatures. With decreasing frequency, the conductivity decreases and approaches the direct-current conductivity σ_{dc}. The general behaviour can be divided into three regions :

1- At low frequency range,the conductivity,which refers to the dc conductivity(σ_{dc}), is nearly frequency independent which may be attributed to the randum distribution of the ionic charge carriers via activated hopping. The observed variation of conductivity with frequency is due to electrode polarization effects at the electrode and glass interfaces. As the frequency decreases, more and more charges accumulation occurs at the electrode and glass interface,which leads to adrop in conductivity at low frequency[19]. The low frequency conductivity is found to be strongly dependent on temperature for all investigated samples.

2- In the intermediate frequency region, the conductivity is almost found to be frequency independent and is supposed to be true dc conductivity.

3- At high frequency range the conductivity obeys a power law.

The variation of σ_t with frequency could be expressed by the following relation[20]:

$$\sigma_t=\sigma_{dc}+\sigma_{ac}(\omega)=\sigma_{dc}+A\omega^s \qquad (2)$$

where σ_{dc}, is the dc conductivity, which is independent of frequency(extrapolation of σ_t at $\omega = 0$) and $\sigma_{ac}(\omega)$isthe ac conductivity.

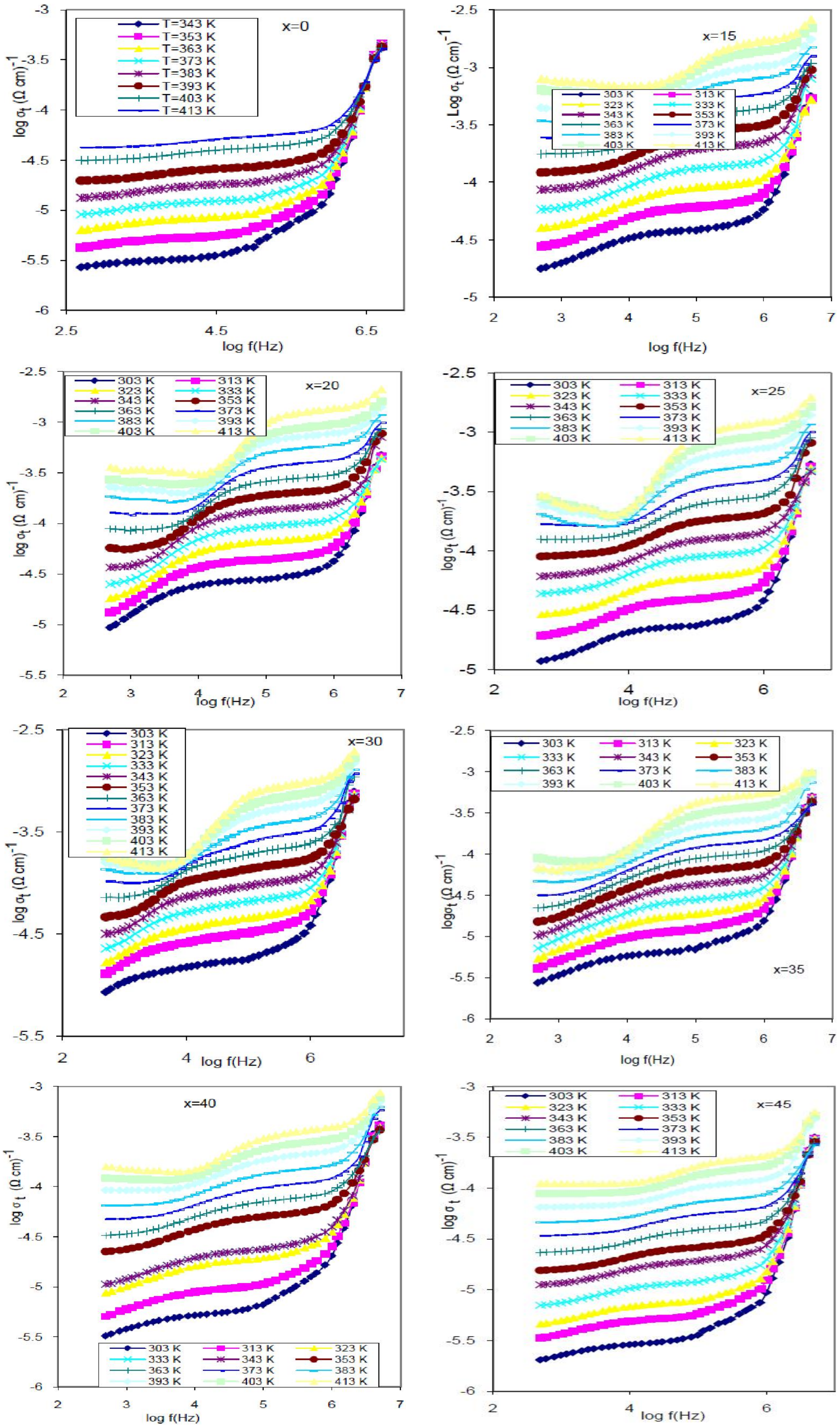

Figure 1 : The frequency dependence of the total conductivity of the sample(50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3, [Where x = 0 , 15 , 20, 25,30,35,40 and 45].

The plateau of the conductivity at minima are assumed to equivalent to the dc conductivity for the sample at each temperature. These values of the dc conductivities are plotted as a function of the ambient temperatures as given in Figure 2. It can be noticed that the curves show straight lines obeying the relation:

$$\sigma_{dc} = \sigma_o \exp(\Delta E_{dc}/kT) \qquad (3)$$

Where σ_o is the pre-exponentional factor, ΔE_{dc} isthe activation energy due to dc conductivity, k is the Boltzmann's constant and T is the ambient temperature. The activation of dc conductivity with increasing temperature may be attributed to the fast diffusion involving low-energy barriers for the motion of Ag^+ ions in the microdomains of AgI_4 clusterswhich are embedded in the glass matrix[21]. Also, the total interaction between the Ag^+ and I^- ions including both ionic and covalent bonding in the AgI^4 cluster, is very small. This characteristic electronic state[22] of the Ag^+ ion is one of the causes of the fast movement of Ag^+ ions in AgI-based superionic glasses. In addition, the Ag^+ ion has a $(4d)^{10}$ configuration of electrons which results in "soft outer shell" and may be distorted and fitted to the conduction path. This flexibility of the outer shell is believed to be one of the origions of the height ionic conductivity of AgI related compounds. As the concentration of the xAgI content increases, the concentration of the microdomains increases which leads to an increase of the conductivity. The influence of adding AgI at the expence of P_2O_5 on ΔE_{dc} of the investigated sample is given in TABLE 1. It can be noticed that ΔE_{dc} decreases as AgI content increases, which may be attributed to the increasing in the concentration of AgI ions in the glassy matrix, which may lead to the observed decrease in ΔE_{dc}.

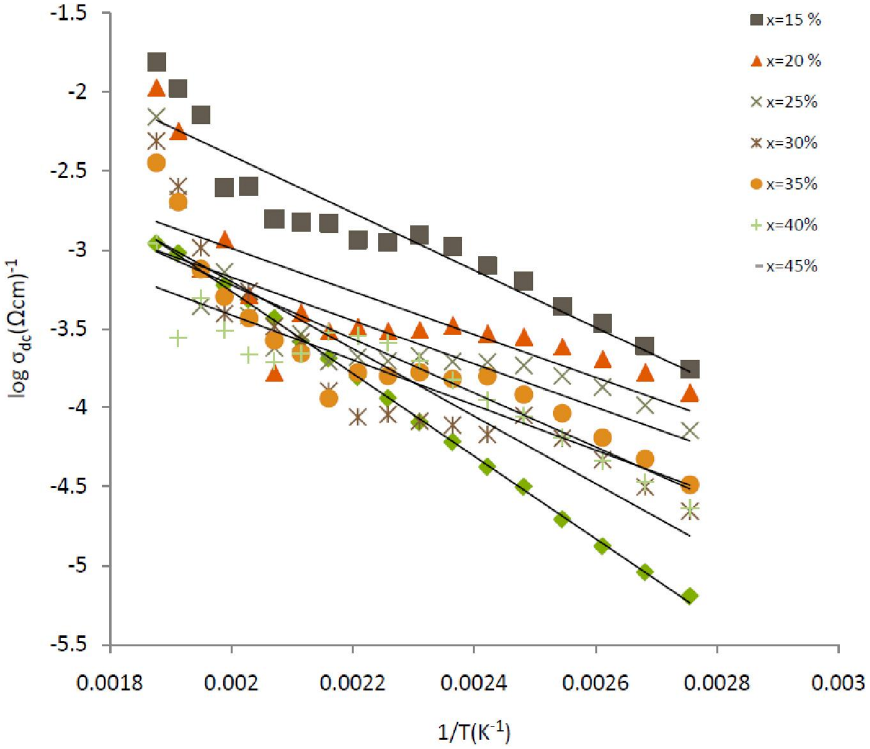

Figure 2 : The temperature dependence of the dc conductivity of the sample (50-x)P_2O_5-xAgI-40Ag_2O-10Fe_2O_3, [Where x = 0 , 15 , 20, 25,30,35,40 and 45].

At high frequency range the conductivity exibits despersion which increase roughly in a power law form and eventually becomes almost linear at even higher frequncies[23,24]. The changeover of the conductivity is shifted towards higher frequency with increase in temperature because mobile ions acquire more thermal energy and cross the barrier more easily. It is known that the frequency dependent of the ac conductivity $\sigma_{ac}(\omega)$in all amorphous sloids and glass follows the power law[25]:

$$\sigma_{ac}(\omega) = A\omega^s \qquad (4)$$

Where A is a pre-exponentional constant and s is the frequency exponent factor. The experimental value of the exponent s can be obtained as :

$$s=\frac{d(\ln\sigma)}{d(\ln\omega)} \tag{5}$$

The temperature dependence of the frequency exponent s is shown in Figure 3. The values of sare found to be in the range from 0.149 to 2.3. It can be noticed that s decreases with increasing the ambient temperature,which is in agreement with the proposed correlated barrier hopping (CBH) model[26]. In this model the bipolaron (i.e. two electrons hopping between charged defectsD$^+$ and D$^-$)has been proposed to explain the frequency dependent of the ac conductivity. Mott and Davis[25] interpreted the power law in terms of hopping between pairs of isolated sites close to the Fermi-level and with a random distribution of seperation distance R_a from each other. Funke[27] proposed that, in the case of strucrurally disdorded materials, if an ion performs a hop to neighbouring vacant sites, there is high probability for that ion to hop back to its previous position (unsuccessful hop) but if the neighbourhood then becomes relaxed with recpect to the ion position, the ion stays on the new site, and the initial forward hop has proved successful. The electrons in the charged defect states hop over the columbic barrier whose maximum height (W_m) can be obtained from the equation:

$$s=1-\frac{6kT}{[W_m-kT\ln(1-\omega\tau_o)]} \tag{6}$$

Where τ_o is the Debye relaxation time,is of the order 10^{-13}s[20] and k is the Boltzmann constant. The values of W_m are given in Figure 4 as a function of the ambient temperature, at different compositions of the investigated sample. It can be noticed that as the ambient temperature increases, W_m tends to increases which may be attributed to thethermal activation of the phonon-phonon scattering which arise from the thermal excitation.

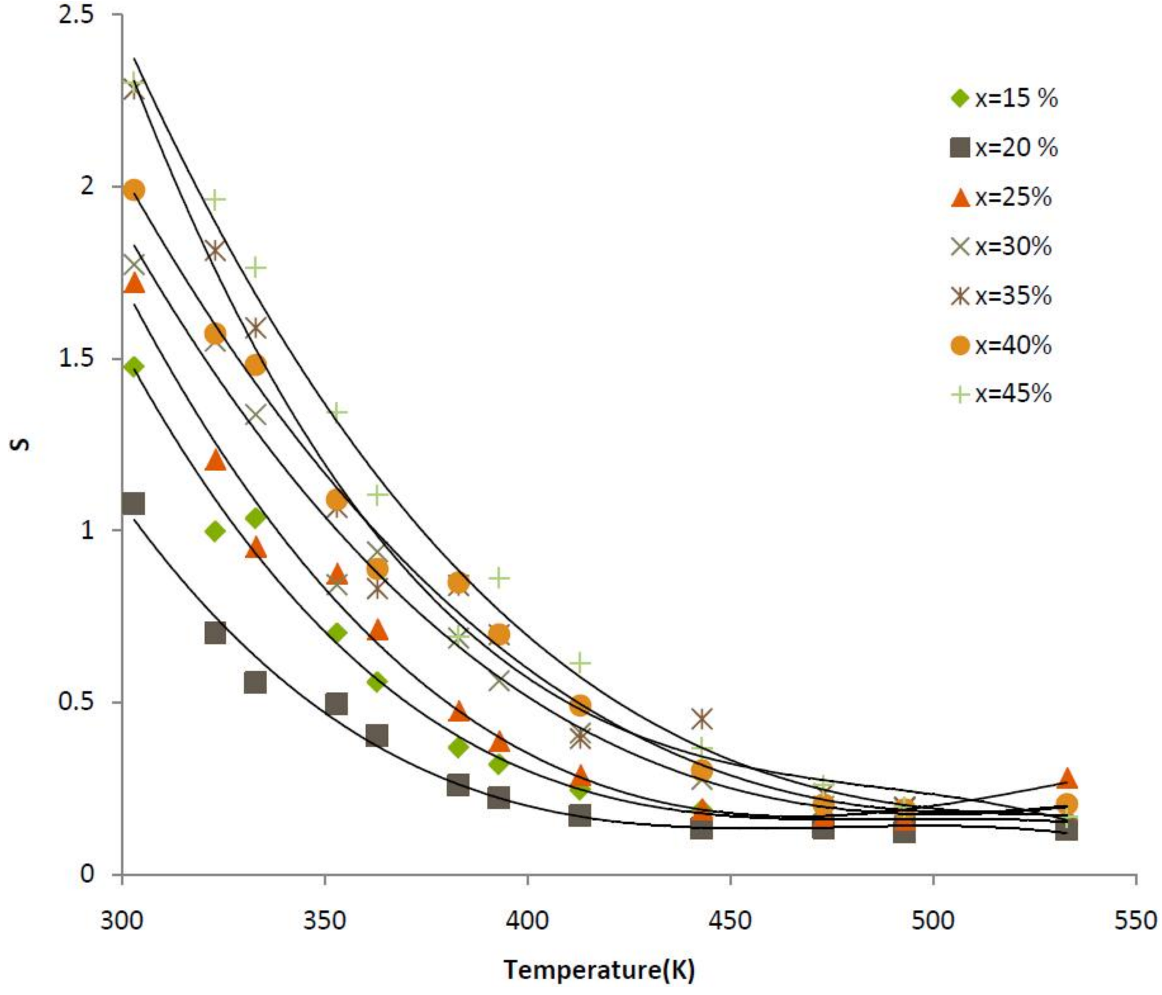

Figure 3 : The temperature dependence of the exponent s for the investigated samples.

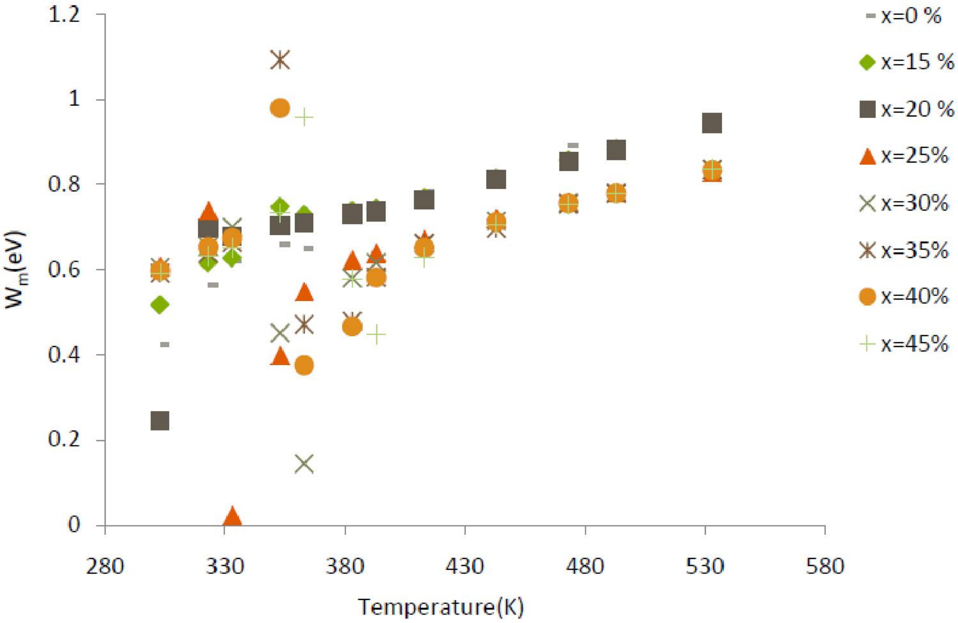

Figure 4 : The temperature dependence of the maximum barrier height, W_m at different compositions of the

The effect of temperature on the AC conductivity

Figure 5 shows The temperature dependence of the AC conductivity at different frequencies for the sample $35P_2O_5$-15AgI-$40Ag_2O$-$10Fe_2O_3$ as a representative one. It can be noticed that the behavior of the ac conductivity can be represented by a set of straight lines. These lines shows that the ac conductivity increases with increasing temperature. This may be due to the hopping of electrons affected by the electric field and the thermal excitation energy in the high temperature range. The activation energies for conduction at different constant frequencies for all glasses prepared were calculated using Arrhenius equation[28]:

$$\sigma_{ac}(\omega) = A \exp(-\Delta E_{ac} / kT) \qquad (7)$$

Where A is the pre-exponential factor, ΔE_{ac} is the activation energy due to ac conductivity, k is the Boltzmann constant and T is the ambient temperature. The values of ΔE_{ac} at different compositions and constant frequency (0.05 kHz) are given in TABLE 1, where it can be noticed that as the AgI content increase, ΔE_{ac} tends to decrease which may be attributed to the increasing behavior in the conductivity. When the temperature was increased, $\sigma_{ac}(\omega)$ increases because of structure relaxation and the Ag^+ ions attached to the non-bridging oxygens are released and become mobile leading to the increase of the mobile ion concentration. In addition, the increase of σ_{ac} with increasing xAgI content may be due to the contribution of silver salt (AgI) and glass modifier oxide (Ag_2O) through the following dissociation reaction[29]: $AgI = Ag^+ + I^-$ and $Ag_2O = Ag^+ + OAg^-$

Impedance and bulk conductivity results

The plots of Z“, (imaginary part of impedance), against Z‘, (real part of impedance), for the for the glass system, $(50-x)P_2O_5$-xAgI-$40Ag_2O$-$10Fe_2O_3$, [x=0,5,10,15,20,30 35 40 and 45], have been studied and Figures 6,7 and 8 are given as a representative ones. The plots show semicircles, with centerslying below Z‘ –axis. The real and the imaginary parts of the impedance are given by:

$$Z' = \frac{R}{(1+\omega^2R^2C^2)} \quad \& \quad Z'' = \frac{\omega R^2C}{(1+\omega^2R^2C^2)} \qquad (8)$$

Where ω =2πf is the angular frequency of the electrical signal. It can be noticed that the radius of the semicircles decreases with increase in temperature indicating relaxation time of relaxing species borne out by frequency explicit plots. The spectra of all samples show a single semicircle at high frequency, confirming their good homoginity[30-32]. Two parts of complex impedance diagram, arc and straight line, can be observed for some compositions and temperatures, as a result of two different effects-conduction and polarization. Two different effects determine the electrical behavior of studied glass – the bulk conductivity as a result of electron hopping and the effect of the near-electrode process. In the low frequency region of complex impedance, the arc (right-hand side of each plot) is sometimes incomplete and display a spike or part of straight line which is a characteristic of interfacial impedance caused by the accumulation of charge carriers at the blocking electrode on the sample. The semicircle at the higher frequency range (left-hand side of each plot) is characteristic of a parallel combination of bulk resistance R_b and the bulk capacitance C_b of the material[3,33,34]. The intersection of Z' – axis represents the sample bulk resistance R_b (at the infinite frequency) from which bulk conductivityσ_b can be obtained. It is clear from the complex impedance plots that with the increase in temperature, the intercept of the low frequency arc on the real axis shifts towards the origion, i.e.,the bulk resistance of the sample decrease with increase of temperature and thus conductivity increases[35]. The obtained values of $\sigma_b$are thermally activated with increasing temperature and obeys Arrhenius equation which can be expressed by the following relation ;

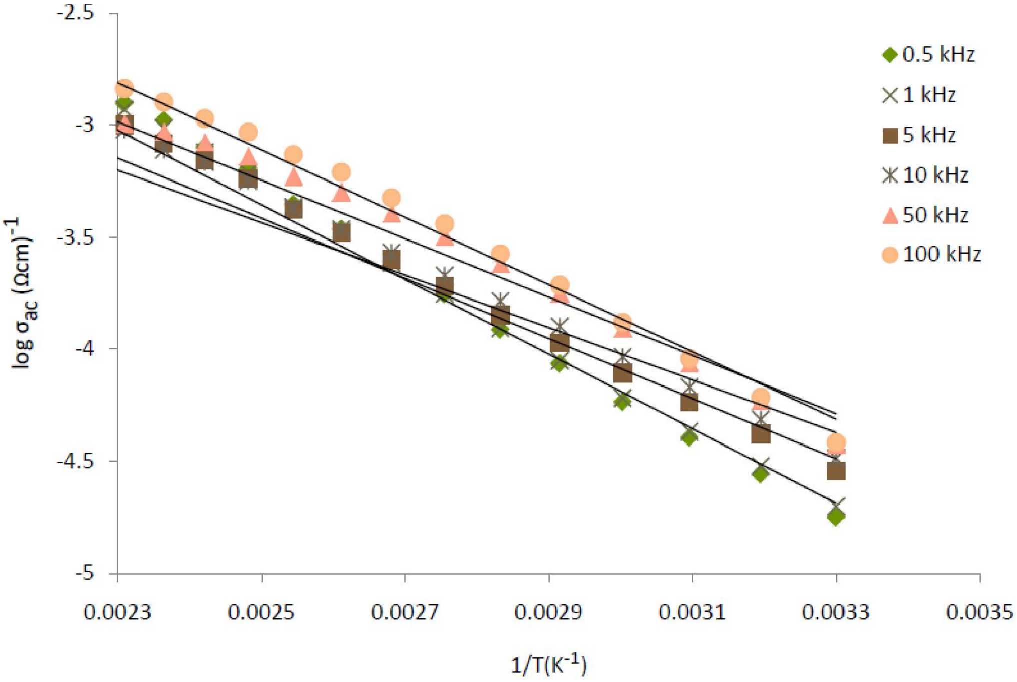

Figure 5 : The temperature dependence of the ac conductivity for the sample x=15 %.

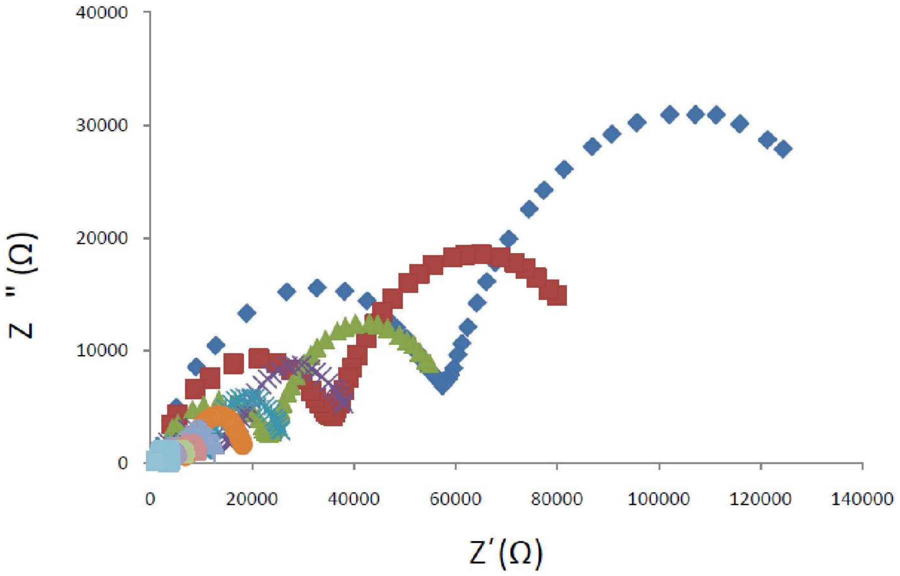

Figure 6 : Complexiimpedance plots for x= 15 % glass sample.

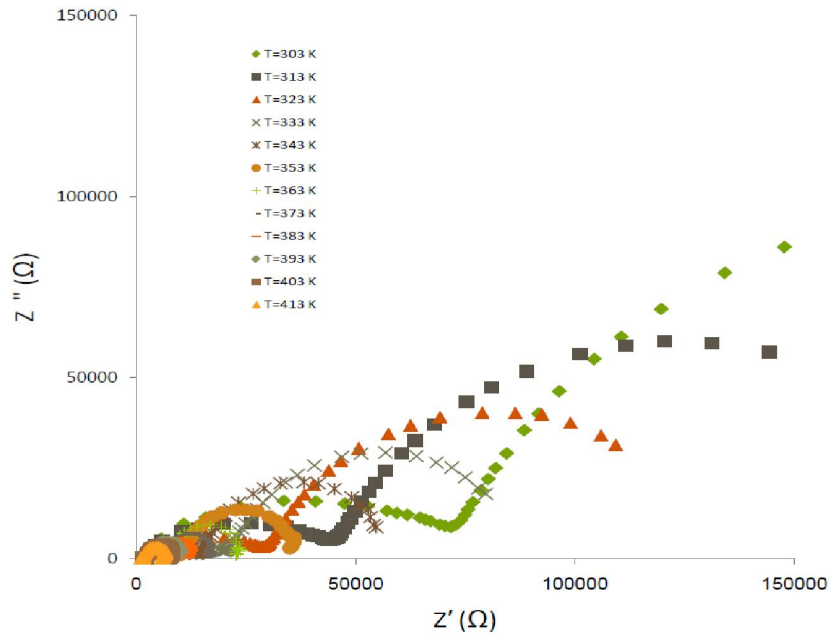

Figure 7 : Complex impedance plots for x=20 % glass sample.

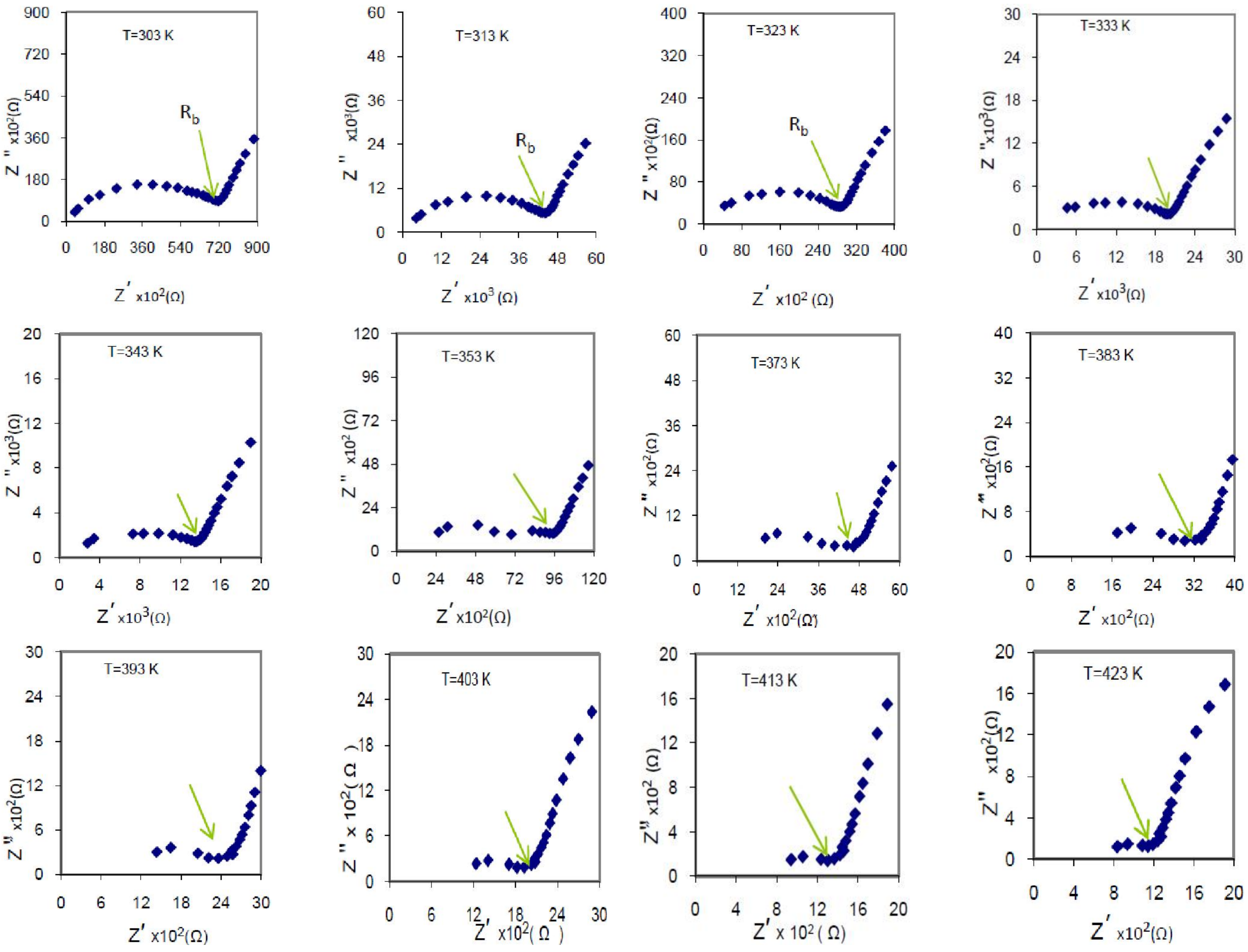

Figure 8 : The effect of temperature on the impedance plots for x=20 %.

$$\sigma_b = A\exp(-\Delta E_b / KT) \qquad (9)$$

Where A is constant and ΔE_b is the apparent activation energy. Figure 5 shows the relation between the bulk conductivity σ_b and the ambient temperature. The activation energies, at different compositions, are determined by the least square fitting of relation (9) and listed in TABLE 1. It is also noticed that, the bulk conductivity σ_b increases with increase the xAgI content.

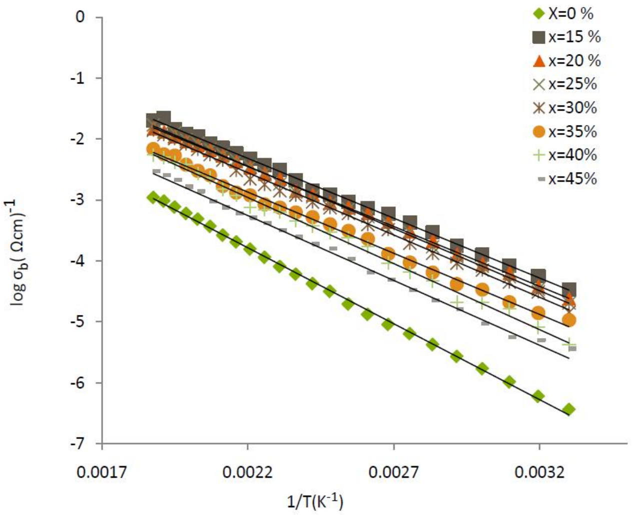

Figure 9 : The temperature dependence of the bulk conductivity of the investigated samples.

TABLE 1 : The activation energy corresponding to the ac, dc and bulk conductivity at different composition of the investigated sample.

Composition (at%)	ΔEdc (eV)	ΔEac (eV)	ΔEb (eV)
0	0.2253	0.214	0.380
15	0.1564	0.169	0.390
20	0.1051	0.169	0.391
25	0.1176	0.176	0.406
30	0.1186	0.176	0.406
35	0.1839	0.1731	0.398
40	0.1476	0.1869	0.431
45	0.1232	0.1836	0.422

The increasing of bulk conductivity(σ_b)with temperature can be interpreated by Minamimodel[36]. This model suggested the occurrence of Ag^+ ions with different mobilities in AgI-based superionic glasses in three types of Ag^+ ions: (i) Ag^+ ions are bonded to the oxygen atoms of the network, (ii) Ag^+ ions interact weakly with the network oxygen atoms and (iii) Ag^+ ions are surrounded by I^- ions only. Silver ions of the last type have maximum mobility and contribute mostly to ionic conduction. When the temperature was increased to higher values, the conductivity reaches to higher values because of Ag^+ ions (which interact weakly to the oxygen atoms of the network) may release and contribute in conduction with the Ag^+ ions (which surrounded by I^- ions) leads to increase the concentration of Ag^+ mobile ions.

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