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Source / Izvornik: **Croatica Chemica Acta, 2017, 90, 657 - 665**

https://doi.org/10.5562/cca3330

ORIGINAL SCIENTIFIC PAPER

Croat. Chem. Acta **2017**, *90*(*4*), 657–665

DOI: 10.5562/cca3330

Mixed Ion-Polaron Glasses as New Cathode Materials

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RECEIVED: March 19, 2018 ⋆ REVISED: March 29, 2018 ⋆ ACCEPTED: April 3, 2018

THIS PAPER IS DEDICATED TO PROF. MLADEN ŽINIĆ ON THE OCCASION OF HIS 70TH BIRTHDAY

Abstract: Electrical transport in mixed ion-polaron glasses has been investigated in four series of glasses containing transition metal oxides (TMO) namely WO_3/MoO_3, and Na^+/Ag^+ ions with the composition $x WO_3$-$(30-0.5x)Na_2O$-$(30-0.5x)ZnO$-$40P_2O_5$, $x WO_3$-$(30-0.5x)Ag_2O$-$(30-0.5x)ZnO$-$40P_2O_5$, $x MoO_3$-$(30-0.5x)Na_2O$-$(30-0.5x)ZnO$-$40P_2O_5$, and $x MoO_3$-$(30-0.5x)Ag_2O$-$(30-0.5x)ZnO$-$40P_2O_5$, $0 \leq x \leq 60$ (mol%). The DC conductivity of Na-glasses up to 30 mol% of WO_3 and MoO_3 is almost identical due to the dominance of ionic conductivity. In this compositional region, the introduction of tungstate and molybdate units increases the mobility of sodium ions and compensates the decrease in sodium number density. On the other hand, with increasing WO_3 and MoO_3 content and decreasing Ag^+ ion concentration in Ag-glasses the DC conductivity decreases for few orders of magnitude. A significant difference in conductivity is observed for glasses with higher WO_3 and MoO_3 content. While for glasses containing WO_3 the conductivity rapidly increases due to a huge polaronic contribution indicating a turnover from predominantly ionic to polaronic transport, the conductivity for MoO_3-glasses decreases in the entire mixed compositional range suggesting dominant ionic transport. The changes in the conduction mechanism with the systematic alternation of the glass composition have been analyzed in correlation with the structural modifications and variations of molybdenum and tungsten in different oxidation states.

Keywords: mixed ion-polaron glasses, ionic and polaronic conductivity, electrical transport mechanisms, impedance spectroscopy.

INTRODUCTION

THE electrical transport in mixed ion-electron glasses has attracted much attention due to their potential technological application as battery electrodes,[1,2] high-temperature superconductors,[3] permeation membranes,[4] chemical sensors[5] and catalysts.[6] Among amorphous solids that show mixed ion-polaron conductivity, the oxide glasses possess several serious advantages mainly related to the ease of preparation, extreme compositional variability and consequently highly tunable properties. The common feature of all these glasses is the presence of highly mobile alkali (Na^+) or silver (Ag^+) ions in the combination with transition metal oxides (TMO) such as WO_3, MoO_3, V_2O_5 or Fe_2O_3. The electronic transport includes the transfer of electrons from the transition metal ions in lower to higher oxidation states. In this process electrons interact intensively with the surrounding structural network forming polarons and the transport mechanism is interpreted in terms of small polaron hopping.[7] Thus, the overall conductivity depends on concentration and mobility of mobile ions, amount of transition metal oxides as well as a fraction of transition metal ions in different oxidation states. While the content of alkali and transition metal oxides in glasses is controlled by the stoichiometry, the fraction of transition metal ions in different valence states depends strongly on the experimental conditions during glass preparation.

The electrical transport which encompasses two types of charge carriers, *i.e.* ions and polarons in the disordered glass structure is by no means simple. Besides the specific interactions between each type of charge carrier and its structural surroundings, there is an additional effect of their mutual interactions. The latter effect, known as ion-polaron effect,[8] can have a negative impact on overall conductivity since these interactions can result in neutral entities which do not participate in the electrical transport. Many studies have tried to explain various parameters that have an effect on the conductivity of such mixed conductors[9–11] but a conclusive and holistic physical picture of the mixed ion-electron transport has not yet been found. Furthermore, while the transition between predominantly ionic and predominantly polaronic conduction has been evidenced in many glass systems containing silver ions and transition metal oxides, the existence of mutual interactions between ions and polarons in oxide glasses is still a matter of debate.[12,13] It is important to mention that the behavior of silver ions in the mixed ionic-polaronic transport is different than that of the other monovalent cations. For example, in tellurite-based glasses containing Ag^+ ions, the DC conductivity is several orders of magnitude higher in comparison to the analogue glasses with alkali ions.[14] These findings suggest that Ag^+ transport is facilitated due to weak interactions with glass network. Therefore, it is clear that for understanding the highly complex dynamics of mixed charge carriers structural properties of the glass have to be considered. The aim of this study is to gain a deep insight into the nature of the electrical transport mechanisms in glasses containing either sodium or silver ions along with molybdenum or tungsten oxide by correlating changes in the conductivity with structural modifications that occurs with the systematic alternation of the glass compositions. It is of interest to study how two similar transition metal oxides modify phosphate network by incorporation of various tungstate and molybdate units and to identify their impact on the formation of different electrical pathways. The attractiveness of this study lies in the fact that these glass systems could be good candidates as solid state tunable materials exhibiting two electrical transport mechanisms.

EXPERIMENTAL

Four series of glasses with nominal compositions $x\mathrm{WO_3}$-(30-0.5x)$\mathrm{Na_2O}$-(30-0.5x)ZnO-40$\mathrm{P_2O_5}$, $x\mathrm{WO_3}$-(30-0.5x)$\mathrm{Ag_2O}$-(30-0.5x)ZnO-40$\mathrm{P_2O_5}$, $x\mathrm{MoO_3}$-(30-0.5x)$\mathrm{Na_2O}$-(30-0.5x)ZnO-40$\mathrm{P_2O_5}$, and $x\mathrm{MoO_3}$-(30-0.5x)$\mathrm{Ag_2O}$-(30-0.5x)ZnO-40$\mathrm{P_2O_5}$, $0 \leq x \leq 60$ (mol%) were prepared by conventional melt-quenching technique. The amorphous character of the glasses was confirmed by X-ray diffraction and detailed process of preparation was described elsewhere.[15,16] Two series of glasses containing WO_3 are labeled as Na-W and Ag-W whereas abbreviation for the glass series with MoO_3 is Na-Mo and Ag-Mo.

The structure of glasses was investigated by Raman spectroscopy. The fraction of molybdenum ions in 5+ valence states, Mo^{5+}/Mo_{tot}, was determined using Electron Spin Resonance (EPR) while the fraction of tungsten ions, W^{5+}/W_{tot}, was determined from the temperature dependence of magnetization, measured from 2 K to 300 K in constant magnetic field of 0.1 T. T by MPMS5 SQUID magnetometer. These methods enable determination of the small amount of the paramagnetic ions, important for glasses studied. Details on structural changes and fraction of tungsten and molybdenum in various valence states used to analyze the DC conductivity have been discussed in Refs. [15,16]. However, it should be mentioned that the focus in this paper is on examining the electrical conductivity of WO_3 and MoO_3 glass systems containing sodium and silver ions in correlation with structural changes but the analysis of structure described in Refs. [15,16] will not be presented herein.

Samples for electrical measurements were polished with SiC polishing papers. Gold electrodes, 7 mm in diameter, were sputtered onto both sides of 1 mm thick disks using Sputter Coater SC7620. Electrical properties were obtained by measuring complex impedance using an impedance analyzer (Novocontrol Alpha-AN Dielectric Spectrometer) over the frequency range from 0.01 Hz to 1 MHz and in the temperature range from 303 to 513 K. The temperature was controlled to an accuracy of ± 0.2 K.

RESULTS AND DISCUSSION

Electrical Properties

The composition of glasses studied in this paper and their electrical parameters are listed in Tables 1 and 2.

The conductivity isotherms measured at 303 K for series of glasses containing Na_2O (Na-W and Na-Mo), as well as Ag_2O (Ag-W and Ag-Mo) are shown in Figure 1 (a–b). Typically, each spectrum exhibits two domains; plateau at lower frequencies that correspond to the DC conductivity, *i.e.* long-range transport and an increase in conductivity at higher frequencies, called dispersion, related to the short-range transport of charge carriers. The conductivity spectra of glasses exhibit different features. First, DC conductivity for glasses free of transition metal oxides, Na-0TMO and Ag-0TMO, varies for almost four orders of magnitude. Lower value for DC conductivity of 7.87×10^{-13} $(\Omega\ \mathrm{cm})^{-1}$ is obtained for Na-0TMO whereas value of 2.97×10^{-9} $(\Omega\ \mathrm{cm})^{-1}$ is found for Ag-0TMO glass. The second difference is observed in the part of the spectra pertaining frequency-dependent conductivity, *i.e.* conductivity dispersion. While the dispersive behavior is visible in almost entire frequency range for glasses containing MoO_3, for glasses with higher WO_3 content the frequency-independent conductivity plateau becomes longer as shown in Figure 1 (a) for Na-50W and Ag-50W glasses. Finally, for binary 40P-60W glass, which is free of alkali or silver ions, the conductivity dispersion is shifted outside the frequency window leaving the DC conductivity plateau spanning over entire experimental frequency range. This result is related to a very fast polaron dynamics and consequently high conductivity in glasses containing higher amounts of WO_3.

Figure 2 (a–d) shows a compositional dependence of DC conductivity at various temperatures for glasses from all four series. For glasses Na-W and Ag-W, Figures 2 (a) and (c), the DC conductivity shows a minimum at about 30–40 mol% of WO_3 followed by a sharp increase in conductivity for higher WO_3 content reaching the highest conductivity value for binary 40P-60W glass. Therefore, observed minimum for Na-W and Ag-W glasses clearly reveals a changeover between predominantly ionic and predominantly polaronic conductivity. The change of the predominance in transport mechanisms is also visible in the shift of conductivity minimum to the higher WO_3 content, from 30 to 40 mol%, with increasing temperature indicating

Table 1. Glass composition, DC conductivity at 303 K, activation energy, pre-exponential factor and W^{5+}/W_{tot}, Mo^{5+}/Mo_{tot} fraction of the studied Na-series of glasses.

Glass	WO_3	Na_2O	ZnO	P_2O_5	σ_{DC} / (Ω cm)$^{-1}$ at 303 K	E_{DC} / eV	σ_0^* /(Ω cm)$^{-1}$ K	W^{5+} / W_{tot} / %
Na-0TMO	0	30	30	40	7.87×10^{-13}	0.92	5.63	0
Na-10W	10	25	25	40	1.44×10^{-12}	0.88	5.30	0.47
Na-20W	20	20	20	40	1.52×10^{-12}	0.87	5.08	0.55
Na-30W	30	15	15	40	5.84×10^{-13}	0.87	4.76	0.54
Na-40W	40	10	10	40	1.79×10^{-11}	0.63	2.07	0.86
Na-50W	50	5	5	40	1.29×10^{-8}	0.49	2.61	1.20
40P-60W	60	0	0	40	4.26×10^{-6}	0.37	3.18	1.45
	MoO_3	Na_2O	ZnO	P_2O_5				Mo^{5+} / Mo_{tot} / %
Na-10Mo	10	25	25	40	1.42×10^{-12}	0.88	5.27	2.31
Na-20Mo	20	20	20	40	1.61×10^{-12}	0.86	4.97	4.51
Na-30Mo	30	15	15	40	1.19×10^{-12}	0.85	4.76	5.88
Na-40Mo	40	10	10	40	5.61×10^{-13}	0.86	4.56	7.93
Na-50Mo	50	5	5	40	2.37×10^{-13}	0.82	3.44	9.12
40P-60Mo	60	0	0	40	2.75×10^{-11}	0.56	1.21	37.04

Table 2. Glass composition, DC conductivity at 303 K, activation energy, pre-exponential factor and W^{5+}/W_{tot}, Mo^{5+}/Mo_{tot} fraction of the studied Ag-series of glasses.

Glass	WO_3	Ag_2O	ZnO	P_2O_5	σ_{DC} / (Ω cm)$^{-1}$ at 303 K	E_{DC} / eV	σ_0^* /(Ω cm)$^{-1}$ K	W^{5+} / W_{tot} / %
Ag-0TMO	0	30	30	40	2.97×10^{-9}	0.69	5.32	0
Ag-10W	10	25	25	40	6.95×10^{-10}	0.69	4.85	–
Ag-20W	20	20	20	40	1.16×10^{-10}	0.74	4.89	0.42
Ag-30W	30	15	15	40	1.35×10^{-11}	0.78	4.62	0.51
Ag-40W	40	10	10	40	2.61×10^{-11}	0.63	2.29	0.80
Ag-50W	50	5	5	40	5.62×10^{-9}	0.49	2.33	1.00
	MoO_3	Ag_2O	ZnO	P_2O_5				Mo^{5+} / Mo_{tot} / %
Ag-10Mo	10	25	25	40	3.74×10^{-10}	0.72	4.91	2.88
Ag-20Mo	20	20	20	40	6.19×10^{-11}	0.76	4.83	4.12
Ag-30Mo	30	15	15	40	8.85×10^{-12}	0.77	4.28	5.71
Ag-40Mo	40	10	10	40	6.12×10^{-13}	0.84	4.26	961
Ag-50Mo	50	5	5	40	5.62×10^{-14}	0.89	3.96	15.07

stronger influence of temperature on the mobility of Na^+ and Ag^+ ions than on polarons which, in this narrow compositional range, leads to the changes of the relative contributions of the two conduction mechanisms to the total conductivity.

Further, as can be seen the DC conductivity in the range below minimum behaves differently for Na-W if compared to Ag-W glasses. Although the dominant conduction mechanism in both glasses is ionic, the decrease in Na_2O content in Na-W glasses keeps the overall conductivity constant whereas ionic conductivity decreases for approximately two orders of magnitude as Ag_2O content decreases in Ag-W glasses. The explanation for this lies in different mobility of Na^+ and Ag^+ ions. Considering that at low WO_3 content ionic conductivity is dominant, it is interesting to observe that Ag-glasses exhibit significantly higher conductivity than Na-glasses of analogous composition. This result suggests that the critical factor which determines ionic mobility in these glasses, and consequently their conductivity, is the interaction of mobile ions with the glass network. Similar Raman spectra of analogous glasses revealing the presence of tungstate octahedral units in the phosphate network[15,16] indicate that almost identical structural features in Na-W and Ag-W glasses are identified, which

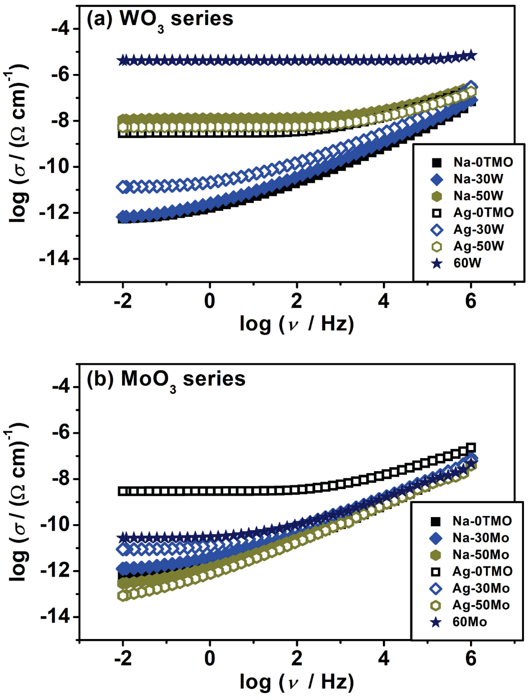

Figure 1. Conductivity spectra measured at 303 K for selected glasses containing (a) WO_3 and (b) MoO_3.

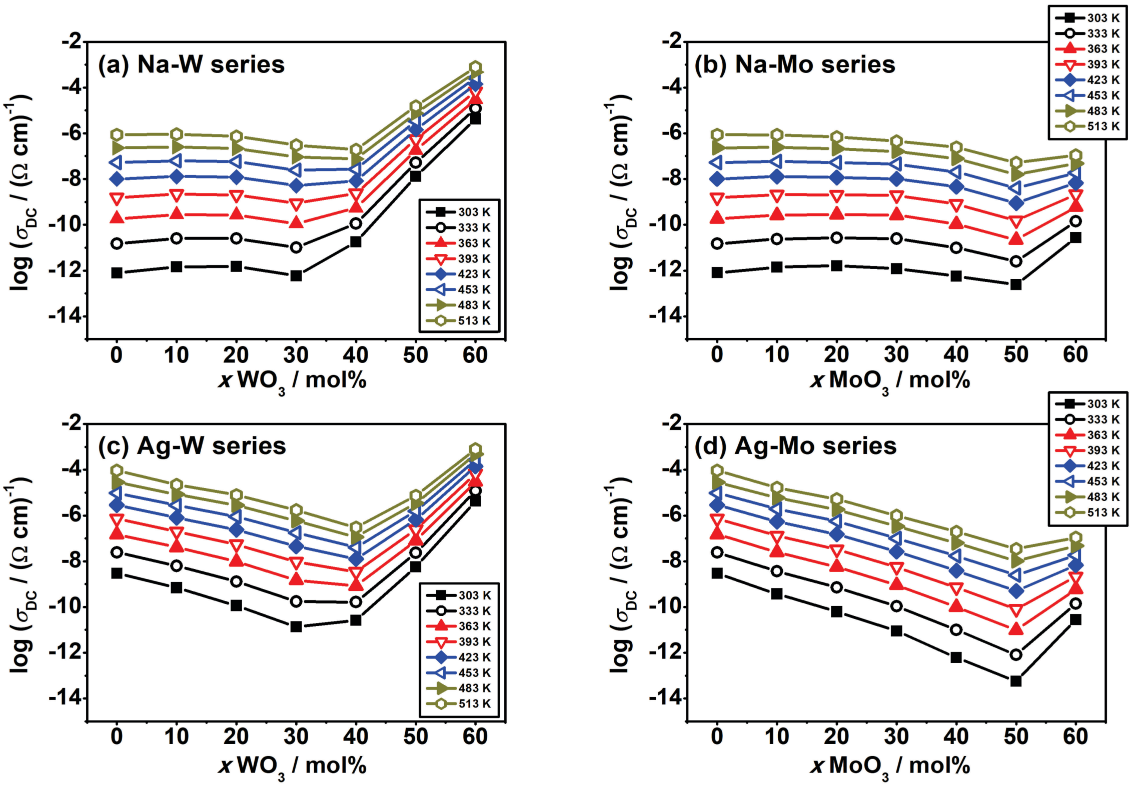

Figure 2. Compositional dependence of DC conductivity at various temperatures for glasses from all four series: (a) Na–W; (b) Na–Mo; (c) Ag–W, and (d) Ag–Mo.

further implies that similar local neighborhood is provided either for Na^+ or Ag^+ ions. In this context, it seems that Na^+ ions, lower in size than Ag^+, are tightly bonded to the non-bridging oxygens in depolymerized phosphate network. On the other hand, Ag^+ ions are loosely bonded to their immediate neighboring network making them highly mobile as their local excursions and diffusive motions are much larger which gives rise to the higher ionic conductivity. In other words, a high conductivity in these glasses is a result of the weak Coulomb interaction between Ag^+ and anion units in glass network leading to facilitated ionic transport. Thus, as expected, with a systematic replacement of Ag_2O with WO_3/MoO_3 the DC conductivity decreases confirming dominance of the ionic transport. However, it should be kept in mind that the mobility of Na^+ ions has an effect on the observed trend in Na-W glass conductivity rather than a polaronic contribution. It seems likely that any extent of polaronic conductivity for these glasses does not produce any negative impact on ionic one suggesting that it acts completely independently.

Different trend can be observed for Na-Mo and Ag-Mo glasses. The DC conductivity for Na-Mo glasses is almost constant in entire compositional range up to 50 mol% and similar in value to the conductivity of TMO-free glass. Such a behavior is due to an increase in polaronic conduction contribution which compensates ionic one, keeping the overall conductivity constant as can be seen in Figure 2 (b). Only slight increase in the conductivity was found for binary 40P-60Mo glass, which is by virtue of its composition a purely polaronic conductor. In contrast, as Ag_2O content in Ag-Mo glasses decreases the DC conductivity linearly decreases for approximately four orders of magnitude confirming that the electrical conductivity is entirely dominated by the highly mobile Ag^+ ions without any polaronic contribution except for the 40P-60Mo glass which does not contain Ag_2O.

Now, the fraction of tungsten and molybdenum ions in different oxidation states should be taken into consideration since the polaron transfer process is related to the hopping of electron through TM^{5+}-O-TM^{6+} bonds. From Figures 3 (a) and (b) it can be seen that with increasing WO_3 and MoO_3 content the W^{5+}/W_{tot} and Mo^{5+}/Mo_{tot} ratios also increase demonstrating an increase in polaronic number density as a general trend in all glasses investigated. The increase in the fractions of reduced Mo^{5+} and W^{5+} ions is related to the conditions in melting of the glasses such as a decrease of basicity with a decrease of alkali content as well as an increase in melting temperatures with increasing WO_3 and MoO_3 content.[15]

Although compositional dependence of these fractions show a similar trend for all series, the values of W^{5+}/W_{tot} are significantly lower than of Mo^{5+}/Mo_{tot}, as listed in Tables 1 and 2. Relative errors of the obtained values are less than 1%. Since the higher fraction of reduced transition metal ions results in the higher polaron number density and thus in the increase of polaronic conductivity[17] it is intriguing to observe a strongly opposite trend for 40P-60W and 40P-60Mo glasses. It is worth noted that the 40P-60W glass has drastically lower fraction of transitional metals in reduced form (W^{5+}/W_{tot} = 1.45 %) than 40P-60Mo glass (Mo^{5+}/Mo_{tot} = 37.04 %) and despite this it exhibits approximately six orders of magnitude higher polaronic conductivity. This surprising result is most probably related to the different structural modifications of glasses containing WO_3 and MoO_3. According to Raman spectra analyzed in our previously reported papers,[15,16] the incorporation of WO_3 into phosphate chains causes the formation of WO_6 clusters involved in W–O–W linkages which drastically facilitates the polaronic transport. It seems likely that the formation of continuous –W^{5+}–O–W^{6+}–O–W^{5+}- bridges strongly increases the probability of polaron transfer resulting in a very high conductivity. In addition, the clustering of the tungstate units has been identified in all glasses with $WO_3 \geq 30$ mol% which can explain a strong increase in conductivity in this compositional region. On the other hand, comparing structural modifications observed by the insertion of MoO_3 into phosphate network, it is noteworthy that the gradual change of MoO_6 octahedra to MoO_4 tetrahedra produces Mo–O–P connectivity throughout the entire compositional range except for binary 40P-60Mo glass.[15,16] Thus, in MoO_3 glasses the polaronic transport is hindered by the interlinkage of phosphate and molybdate units and this structural hindrance cannot be compensated with significantly high polaron number of density. In conclusion, it is clear that the key role for the polaronic transport in these glasses is the structure and not the parameter such as the fraction of W^{5+} or Mo^{5+} ions.

Going further in the interpretation of mechanisms of conduction within these glass series, the obtained complex impedance plots are analyzed and presented in Figure 4 (a–d). The changes in electrical transport in glass systems investigated are visible in the shape of complex impedance plots. As mentioned earlier behavior of the electrical transport of Na-Mo and Ag-Mo glasses varies from that of Na-W and Ag-W glasses showing a changeover from dominant ionic to dominate polaronic conductivity for the latest ones. Therefore, the concomitance of ionic and polaronic conduction found in WO_3 glasses produces two semicircles in the impedance plot as can be seen in Figures 4 (a) and (b) for Na-50W and Ag-50W. Such a behavior is typical for mixed ionic-polaronic conduction found in various materials where selectively blocking electrodes (blocking for one and non-blocking for another type of charge) are used.[9,18–22]

In these plots, a semicircle at higher frequency is attributed to the dielectric relaxation of the bulk, while additional semicircle at lower frequency is associated with chemical relaxation due to the unblocked polaronic diffusion.[15,21,22] As a matter of fact, the two observed complex impedance plots prove the coexistence of two different, ionic and polaronic, transport mechanisms in these glasses. However, it is important to point out that two separated impedance plots are only observed for Na-50W and Ag-50W glasses suggesting that the ratio of ionic and polaronic contributions for these particular glass compositions allows the separation of the two above-mentioned processes in the complex impedance plot. On the contrary, only one semicircle was found for Na-50Mo and Ag-50Mo glasses indicating that the polaronic contribution is hindered and yet not large enough to observe an additional low-frequency semicircle in a complex impedance plot, see Figures 4 (b) and (d).

It seems that the formation of strong cross-linking between phosphate and molybdenum units in Na-Mo and Ag-Mo glasses,[15,16] acts more like barriers than as pathways for an easy movement of polarons through the glass network. Indeed, a weaker connection of molybdenum units and absence of Mo–O–Mo bonds diminish the probability of the electron hopping through Mo^{5+}–O–Mo^{6+} bonds resulting in a reduction of polaronic contribution to the total electrical conductivity.

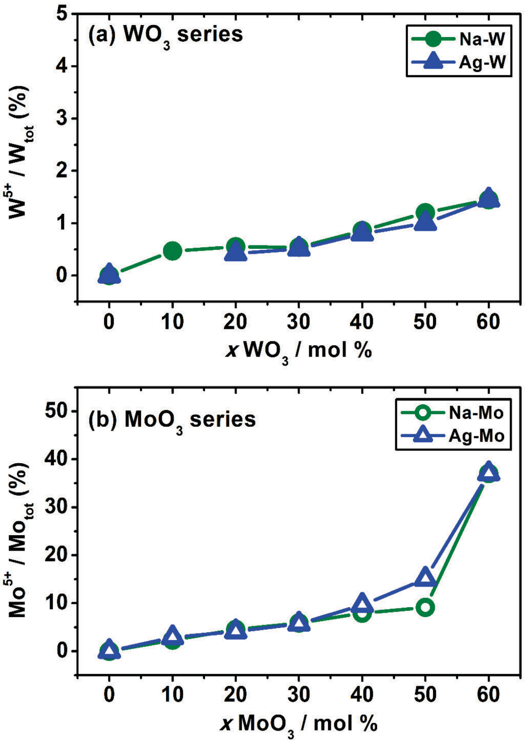

Figure 3. Compositional dependence of (a) W^{5+}/W_{tot} for both tungsten series of glasses (Na–W and Ag–W) and (b) of Mo^{5+}/Mo_{tot} for both molybdenum series of glasses (Na–Mo and Ag–Mo).

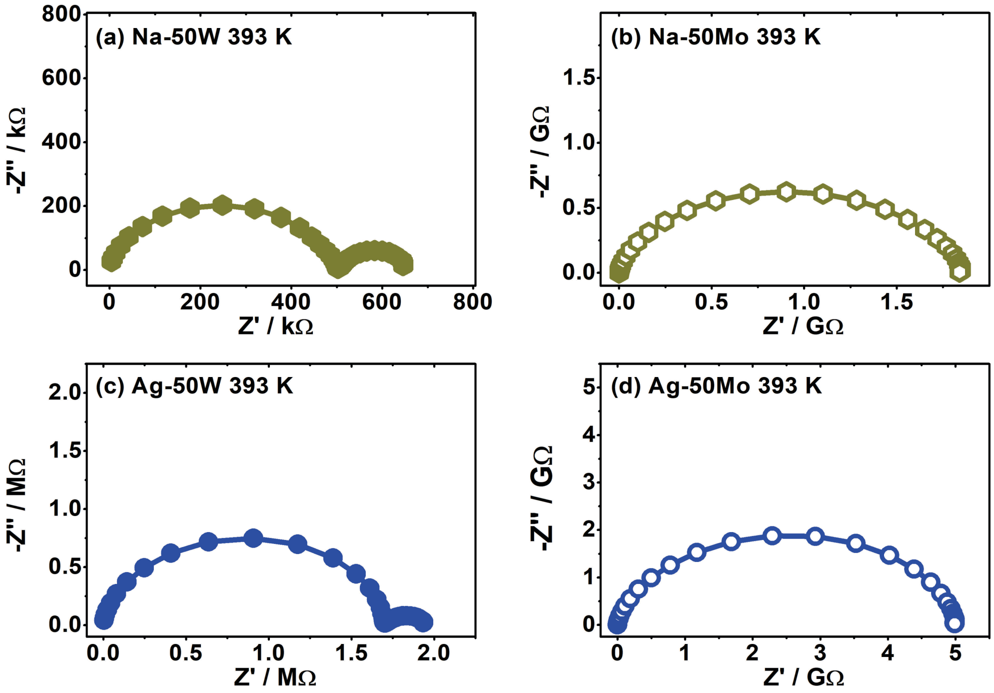

Figure 4. Complex impedance plots measured at 393 K for selected glasses containing (a–b) Na_2O (Na–W and Na–Mo) and (c–d) Ag_2O (Ag–W and Ag–Mo).

In Figure 5 (a–d) the Arrhenius plots for DC conductivity, and compositional dependence of pre-exponent, σ_0*, for all series of glasses are shown. The activation energy of DC conductivity, E_{DC}, for each sample was determined from the slope of log($\sigma_{DC}T$) *vs.* 1 / *T* using the equation:

$$\sigma_{DC}T = \sigma_0 \exp(-E_{DC} / k_B T) \tag{1}$$

where σ_{DC} is the DC conductivity, σ_0^* is the pre-exponent, k_B is the Boltzmann constant and *T* is temperature. The obtained values for σ_{DC}, σ_0^* and E_{DC} for all glasses investigated are listed in Tables 1 and 2. The compositional dependence of pre-exponential factor, σ_0^*, in Figures 5 (a) and (b) shows a steep decrease in the region between 30 and 40 mol% of WO_3 for Na-W and Ag-W glasses which corresponds to the region where the changeover between predominantly ionic and predominantly polaronic is observed. Such a behavior is directly related to the structural modifications that occur in the narrow compositional range where the WO_6 clusters are formed.[15,16] Similarly, for Na–Mo and Ag–Mo glasses the trend in pre-exponential factor, σ_0^*, correlates with DC conductivity which once again confirms that the structural changes in Na–W and Ag–W glasses are different in comparison to Na-Mo and Ag–Mo glasses.

In order to explain the complexity of mixed ion-polaron conduction in these four glass series, the Meyer-Neldel formalism was used.[23] The Meyer-Neldel rule is found to be valid for thermally activated processes in a wide range of materials such as ionic and mixed ionic-electronic glasses,[24–30] electronic amorphous or disordered semiconductors[31]. The correlation between the activation energy for DC conductivity (E_{DC}) and pre-exponential factor (σ_0*) is given by the following relation:

$$\log \sigma_0^* = aE_{DC} + b \tag{2}$$

where *a* and *b* are constants. Although the Meyer-Neldel relation represents an empirical model with the parameters that have no clear physical meaning,[32] the correlation observed in the investigated glasses point to the changes in the conduction mechanism. Indeed, the compositional dependence of pre-exponential factor, σ_0*, as a function of E_{DC} for all glasses containing WO_3 and MoO_3 in Figure 6 exhibits two distinct domains.

The Domain I contains the WO_3 glasses with high concentration of mobile ions ≥ 15 mol% of Ag_2O and Na_2O

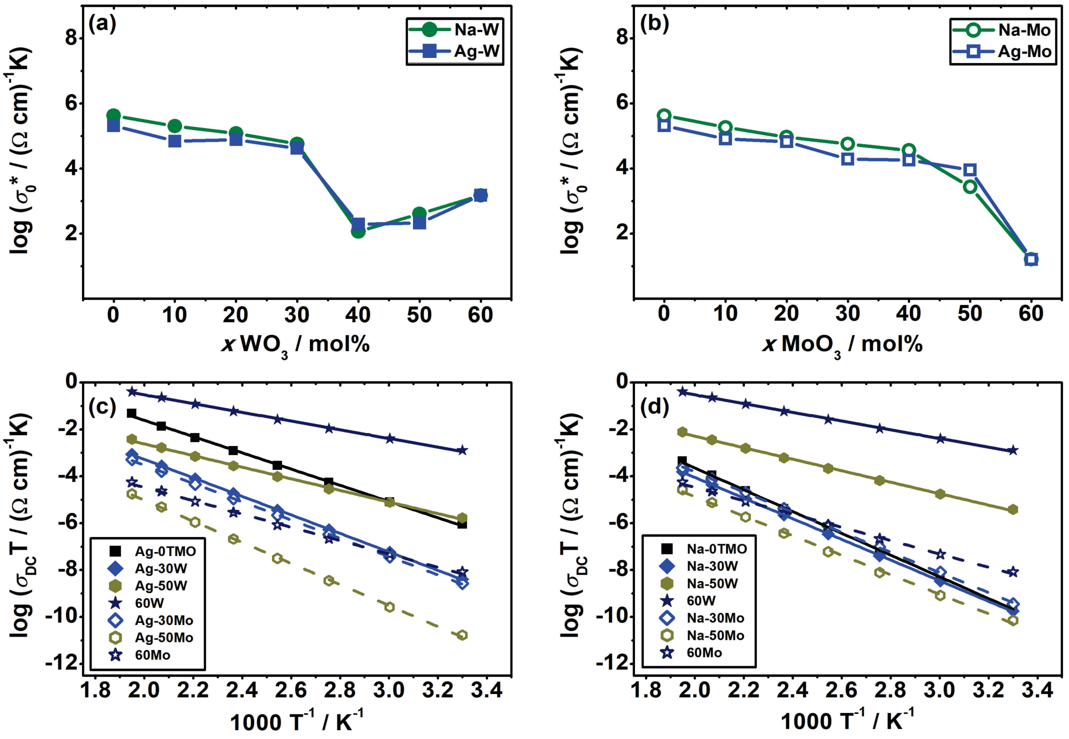

Figure 5. Compositional dependence of (a-b) pre-exponential factor, σ_0*, and (c-d) Arrhenius plots for selected glasses from tungsten (Na–W, Ag–W) and molybdenum (Na–Mo, Ag–Mo) series.

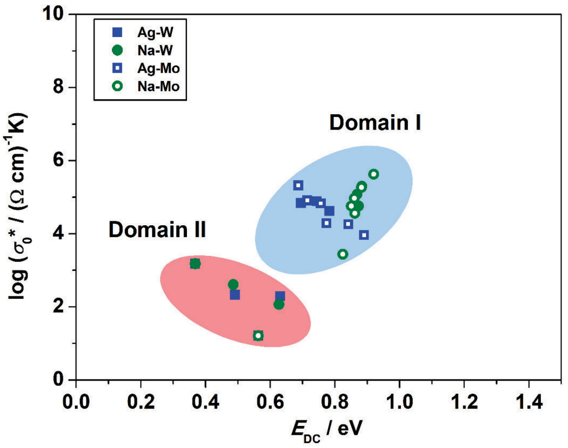

Figure 6. Dependence of pre-exponential factor, σ_0*, as a function of E_{DC} for all glasses.

whereas the rest of Na–W and Ag–W glasses fall into the Domain II. The observed trends in Domain I and Domain II coincidence with the ionic region below minimum in DC conductivity and polaronic region above the minimum, respectively, shown in Figures 2 (a) and (c). Different situation was found for MoO_3 containing glasses where all Na-Mo and Ag-Mo glasses lies in the Domain I except the binary polaronic 40P-60Mo glass which clearly departs to the Domain II. This result again leads to the conclusion that the contribution of polaronic transport produced in MoO_3 glasses either in Na-Mo or Ag–Mo is considerably low. The obtained results clearly show that the analysis of the activation energy dependence on the pre-exponential factor as proposed by Meyer-Neldel formalism allows an obvious identification of the dominance of ionic or polaronic conduction mechanism in the studied glasses.

CONCLUSION

The changes in the DC conductivity with systematic exchange of Na_2O and Ag_2O with WO_3/MoO_3 within four glass series: $x$$WO_3$-(30-0.5$x$)$Na_2O$-(30-0.5$x$)ZnO-40$P_2O_5$, $x$$WO_3$-(30-0.5$x$)$Ag_2O$-(30-0.5$x$)ZnO-40$P_2O_5$, $x$$MoO_3$-(30-0.5$x$)$Na_2O$-(30-0.5$x$)ZnO-40$P_2O_5$, and $x$$MoO_3$-(30-0.5$x$)$Ag_2O$-(30-0.5$x$)ZnO-40$P_2O_5$, $0 \le x \le 60$ (mol%) have been studied in correlation with the structural modifications that occur in these glasses. The results exhibit a different behavior of conductivity for sodium and silver glasses which contain WO_3 if compared to the MoO_3 glasses. The transition between predominantly ionic and predominantly polaronic conductivity is found for Na–W and Ag–W glasses, evidenced as a minimum at about 30–40 mol% of WO_3 content. The conductivity mechanism remains dominantly ionic below minimum due to the high mobility of sodium and especially silver ions whose transport is assisted by structural changes induced in the initial addition of tungstate and molybdate units to the phosphate network. A strong increase of DC conductivity for glasses with higher WO_3 content is a result of clustering of WO_6 octahedra *via* W–O–W bonds which facilitates the mobility of polarons. Therefore, enhanced transport through W^{5+}–O–W^{6+}–O–W^{5+} bonds in clusters suggests easier pathways for polarons resulting in a significant increase of the conductivity.

On the other hand, the conductivity for MoO_3 containing glasses behaves differently without any evidence of minimum in conductivity. For Na-Mo glasses the conductivity is kept almost constant whereas decreases in the entire mixed Ag–Mo compositional range. This indicates that the mobility of sodium and silver ions is different although the nature of electrical transport is dominantly ionic with no significant contribution of polaronic conductivity.

The addition of MoO_3 in entire mixed compositional range produces the P–O–Mo bonds forming a three-dimensional glass network which does not facilitate polaron transport but permits movement of ions and polarons through independent pathways.

Using the Meyer-Neldel formalism it was confirmed that the contribution of polaronic transport produced in MoO_3 glasses either in Na–Mo or Ag–Mo is considerably low. Furthermore, this study clearly shows that the cation-type, sodium and silver, differently interacts with structural glass network. Silver ions are loosely bonded to its neighboring network which makes them highly mobile as their excursions are much larger and diffusion higher resulting in very high ionic conductivity. This leads to the conclusion that the weak Coulomb interactions between silver ions and neighboring units facilitate the formation of easier conduction pathways for highly mobile silver ions that gives rise to the highest ionic conductivity of Ag rich glasses.

Acknowledgment. This work was supported by the Croatian Science Foundation; project IP-09-2014-5863. D.P. would like to acknowledge the partial support of Croatian Science Foundation; project UIP-2014-09-8276.

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