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Silver ion transporting mechanism in superionic conducting AgI–Ag₂O–TeO₂ glasses

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Abstract. Superionic conducting glasses in the ternary AgI–Ag₂O–TeO₂ system have been prepared and investigated by different techniques. Comparison between conductivities of the present glasses and those of glasses in other different systems has been carried out. The obtained results revealed that the optimum value of conductivity at room temperature is of the order of 10^{-2} S cm⁻¹ at about 60 mol% AgI for all the considered superionic systems, regardless of their composition or types. The highest conduction at about 60 mol% AgI was correlated to the creation of maximum pathways which favour the Ag⁺ ion transporting mechanism. Formation of some crystalline phases from AgI at higher concentrations (>60 mol% AgI) was considered the main reason for decreasing the conduction of AgI-rich glasses. Some specific structural models have been proposed to explain the Ag⁺ ion transport mechanism in the AgI–Ag₂O–TeO₂ glasses.

1. Introduction

Several electrical studies on glassy materials [1–3] have revealed that glasses need not necessarily be insulators, but can be superionic conductors under certain circumstances. This development has certainly opened up a whole new field of both fundamental investigations and applications [4–6]. However, incorporation of alkali halides or metal halides in the modified glasses [1, 4, 7–10] was considered the predominant factor playing the role of enhancing the conductivity of the conventional glasses to reach values characterized the superionic materials. From a fundamental point of view there is much to be learnt about the structure and properties of these glasses.

Glasses containing alkali or metal halide are considered to be able to confer the superionic phenomenon at certain high temperature [1, 7, 11]. On the other hand, glasses containing silver halide, particularly silver iodide, can provide superionic behaviour at room temperature. In this respect, the existence of silver ion conducting glasses with high electrical performance in doped borate [7, 12, 13], phosphate [14, 15], molybdate [16], molybdophosphate [17, 18] and even in non-oxide glasses [9, 10] has encouraged one to undertake the research of new Ag⁺ ion conductors in tellurate glasses.

From the viewpoint of application [19–22], glasses containing TeO₂ as a network former are considered to be important. This is because they offer a high refractive index [19] and good optical transmission in the infrared region [20–22], in addition to their tendency for inducing superionic behaviour when they doped with metal halides [23, 24]. Although there have been many investigations [1–10] to study the superionic behaviour in glassy systems, not much is known about this phenomenon in tellurate glasses. Therefore, in this article, some of

the structures and properties of superionic AgI–Ag₂O–TeO₂ materials will be described with emphasis on current and potential applications.

2. Experiment

2.1. Glass preparation and measurements

The composition of the glasses prepared were in the ternary system AgI–Ag₂O–TeO₂ with a molar ratio of Ag₂O/TeO₂ = 1 and an AgI content between 20 and 80 mol%. The glass samples were prepared by melting the calculated quantities (mol%) of reagent grades AgNO₃, AgI and TeO₂ (Aldrich, USA) in porcelain crucibles. The mixtures were melted in an electric furnace for 30 min in the temperature range 650–800 °C depending on composition. The crucible was covered to reduce volatilization losses, the batches being occasionally mixed by swirling the melt to obtain a bubble free and homogenous glass. The melt was poured onto a stainless steel plate and pressed with another plate to obtain a thin disc (0.1–0.15 mm in thickness). The obtained glassy samples were then annealed at a temperature 50 °C lower than the glass transition temperature in order to relieve internal stresses.

X-ray diffraction patterns were obtained at room temperature using an x-ray diffractometer, type Philips PW 1724. The x-ray investigations confirm the amorphous structure of the all samples containing ≤60 mol% AgI, since all samples in this region are investigated by x-ray diffraction, while there are tendencies to crystallization in glasses with higher AgI content.

The electrical conductivity was measured as a function of temperature using an impedance meter (type Tesla BM 507). The conductivity can be described by the well known Arrhenius law $\sigma = \sigma_0 \exp -E_a/KT$ for all samples in the range between 300 K and 30 K below T_g. The flat surfaces of the sample were coated with silver and used as electrodes. Thermal expansion measurements were carried out using a dial gauge with 0.01 mm sensitivity. The same heating rate (5 °C min⁻¹) to just above the softening point was used for all the measurements. The glass transition temperature was determined with a Shimadzu DTA 50 thermal analyser at heating rate of 10 K min⁻¹. Microhardness measurements were performed using an FM 7 microhardness tester. At least ten indentations were made for each sample. The molar volume was determined from density measurements which were carried out using the Archimedes method with xylene as an immersion fluid.

3. Results

The investigation of superionic glasses in the system Ag₂O–AgI–TeO₂ has revealed that the conductivity is improved due to the effect of increasing AgI content to up to 60 mol%. Figure 1(a) shows the variation of room temperature conductivity (σ_{rt}) with increasing AgI content. It can be observed from this figure that σ_{rt} increases as the amount of AgI increases to reach a maximum value at about 60 mol% silver iodide and then decreases with further AgI addition. The change of the associated activation energy for ionic conduction (E_a) with AgI content is shown also in figure 1(b). This figure shows a gradual decreasing of E_a to reach a minimum at about 60 mol% AgI and then increases with further increasing AgI content (>60 mol%).

The influence of the change of glass composition on both thermal expansion coefficient (α) and molar volume (V_m) of the glasses is represented in figure 2. It can be realized that both V_m and α increase with increasing AgI content to reach saturated values for AgI ≤ 60 mol%.

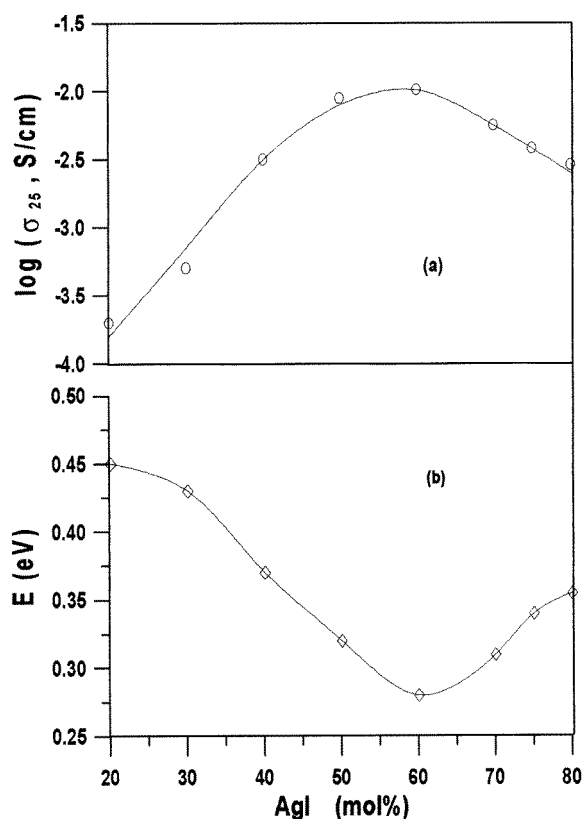


Figure 1. Composition dependencies of both room temperature conductivity (curve a) and the associated activation energy (plot b).

Figures 3(a) and (b) show the variation of the glass transition temperature (T_g) and the microhardness number (H_v) of the glasses with the change of AgI concentrations. Clear decreasing trends of both T_g and H_v can be observed with increasing the amount of AgI.

Figure 4 shows the x-ray diffraction patterns at room temperature for samples containing different AgI contents (60, 70, 75 and 80 mol%). The amorphous nature of all glasses of ≤ 60 mol% AgI is verified. All the spectra of glasses in this region (≤ 60 mol% AgI) showed similar shape, therefore, the spectrum of one of these glasses (AgI = 60 mol%) is presented in figure 4 as an example for glasses containing a single phase. While in the patterns of samples with more than 60 mol% AgI, the crystalline phases are clearly to be observed.

Figure 5 presents a comparison of conductivity of glasses in different systems containing AgI. The conductivity (σ_{rt}) belonging to the region ≤ 60 mol% AgI showed a similar compositional dependence. σ_{rt} for each system increases with increasing AgI content to reach its optimized value at about 60 mol% AgI. Moreover at this AgI content (60 mol%), the conductivity for all the considered systems shows no noticeable differences (i.e. the conductivity is changed more or less very little from one system to another).

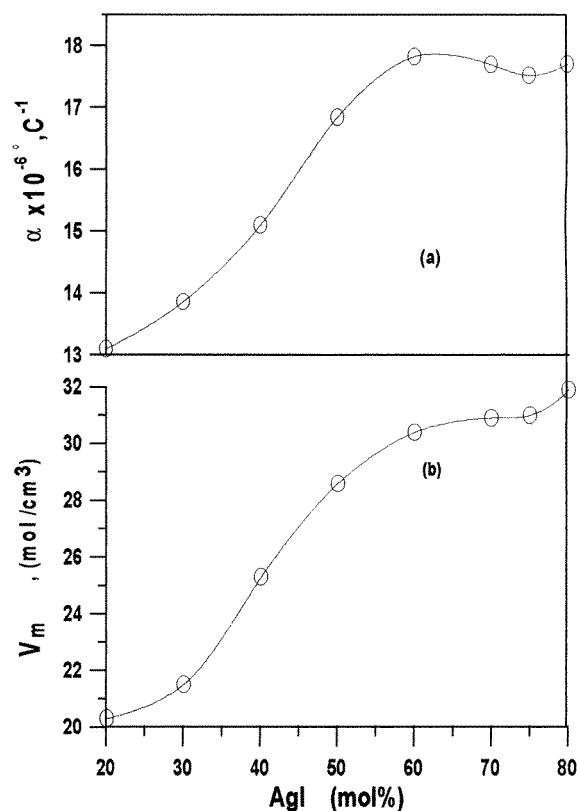


Figure 2. Influence of the change of glass composition on both thermal expansion coefficient (α), plot a, and molar volume (V_m), plot b, of the glasses.

4. Discussion

A knowledge of the structure of TeO_2 glasses is an important prerequisite for a full understanding of their physical properties. Therefore, both short and intermediate range orders in tellurate glasses are important to review before discussing the present results.

The structure of tellurite glasses has been examined by many authors [19, 25–29]. It is proposed that Te in TeO_2 glass is coordinated by four oxygen atoms to form TeO_4 tetrahedral units. The four coordination of Te is found to decrease with the addition of modifier oxide [19, 25]. This coordination change is considered to be due to the ability of the modifier oxide to break some of the Te–O–Te bonds and consequently TeO_3 units with non-bridging oxygen atoms (NBOs) should be formed. Creation of NBOs in telluride network is reported to depend mainly on both the value and the type of modifier oxide [19, 25]. Increasing the latter leads to increasing TeO_3 groups at the expense of the number of TeO_4 units and this enables the glassy matrix to dissolve the AgI salt [23, 24, 30–32]. Dissolution of AgI in the Te network is considered to be very important in obtaining glasses characterized with their high room temperature conductivity (superionic glasses).

Introduction of AgI to the Ag_2O – TeO_2 network does not affect the fourfold coordination of tellurium, but it surely induces changes in the intermediate range order. This is particularly

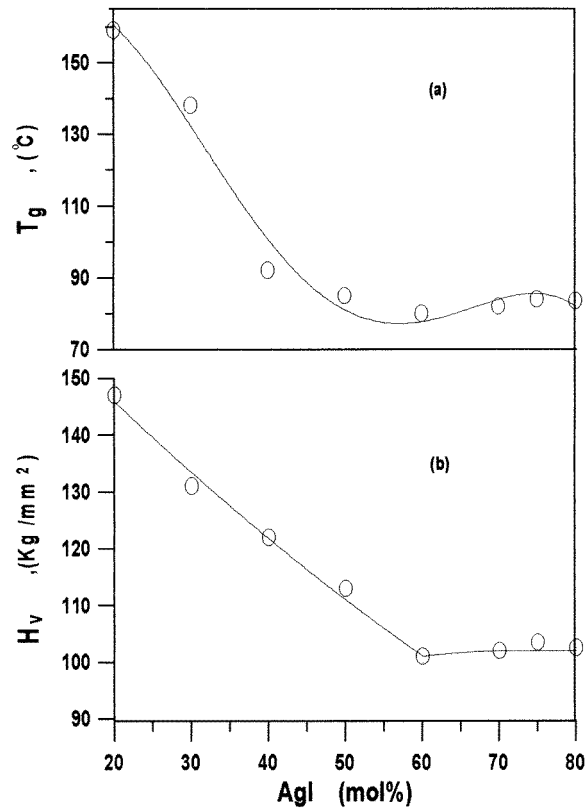


Figure 3. Variation of glass transition temperature (T_g) and microhardness (H_v) with the change of AgI content.

manifested by the partial elongation, weakening or destroying the Te cyclic arrangement. This structural rearrangement helps the tellurite network to be able to accommodate the bulky AgI [23,24,30]. Generally, accommodation of iodine ions in glasses is considered the most dominant factor which is responsible for improving the conductivity of different glassy materials [17, 32–35]. In the following discussion I try to extract the role of Ag ions in transporting the electric current and enhancing the conductivity of tellurite glasses by the effect of iodine accommodations. Moreover, the following discussion distinguishes glasses with low AgI content (≤ 60 mol%) from those with higher AgI, since the experimental results in the first region (≤ 60 mol%) showed different behaviours from that of glasses of higher AgI concentrations.

4.1. Glasses with AgI ≤ 60 mol%

Figure 1 shows the variation of room temperature conductivity, σ_{rt} , and the activation energy for ionic conduction, E_a , as a function of AgI concentration. The σ_{rt} is found to vary over about three orders of magnitude with the variation of AgI at the expense of both Ag₂O and TeO₂ contents. The conductivity increases with increasing AgI to reach a maximum value at about 60 mol% AgI and then decreases. On the other hand, the activation energy is observed

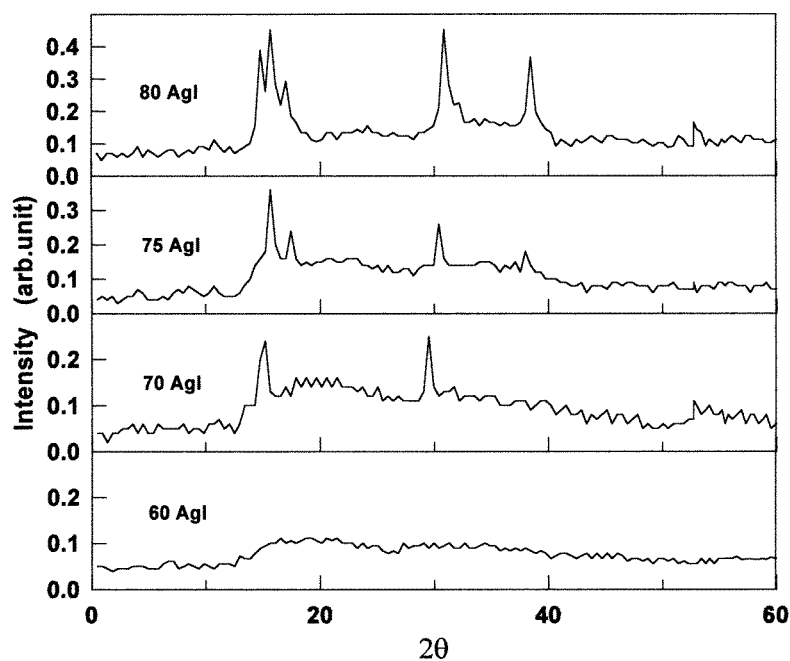


Figure 4. X-ray diffraction patterns at room temperature for samples containing 60, 70, 75 and 80 mol% AgI.

to decrease with AgI reaching a minimum value and then increases. The most remarkable observation in both E_a and σ_{rt} is that the position of the minimum in E_a is nearly the same as that of the maximum σ_{rt} of the glasses studied. This result suggests that the change of conductivity is predominantly governed by the decrease in E_a by the effect of iodine accommodation. To interpret these behaviours, it is useful to discuss the effect of replacing AgI with both TeO_2 and Ag_2O on the conduction mechanism and correlates the change of the latter with that of the other studied physical properties.

Although the total content of Ag^+ cation decreases when Ag_2O is replaced by AgI, the electrical conductivity is shown to be improved and strongly dependent on AgI concentration, figure 1(a). This behaviour may lead to the Ag^+ cation associated with the iodine ion being much more mobile than that associated with oxygen. However, the enhanced conductivity would then be caused by a change in the mobility of Ag cations by the effect of I ions [23].

Based on the above arguments one would expect that not all Ag^+ cations are effective in transporting the electric current. The Ag^+ cations originating from AgI are ionically bonded with I ions at the interstitial sites in the network structure [36], and are mobile under the effect of an electric field. On the other hand, the Ag^+ cations originating from Ag_2O are considered to be covalently bonded with oxygen atoms constituting the skeleton of the glass network and less mobile [36]. Therefore, it is considered that silver cations associated with I ions play the primary role in the cationic conduction of the glasses studied. This is because the Ag^+ cations in the iodide sites have less energy for migration than the Ag^+ cations in the oxide sites. Therefore increasing of AgI content at the expense of Ag_2O and/or TeO_2 should contribute more Ag^+ cations at iodide potential and simultaneously reduce the number of less mobile Ag^+ ions in the oxide potential, where the free energy for ion migration is more. Then, the above

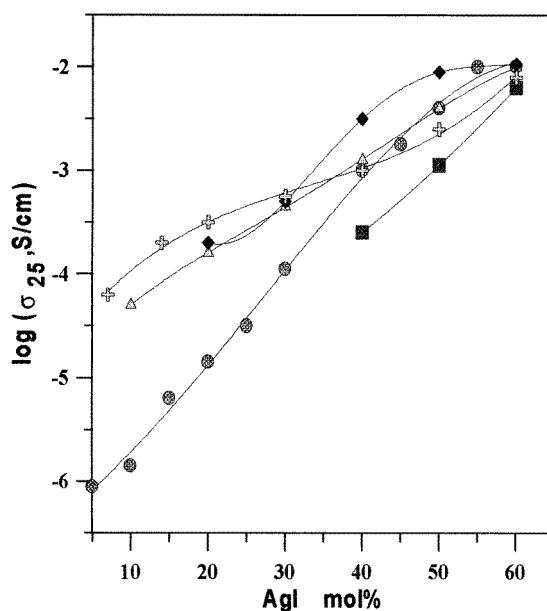


Figure 5. Comparison of different conductivity data. (◆) this work, (●) AgI–Ag₂O–P₂O₅, (■) AgI–Ag₂O–MoO₃, (▲) AgI–Ag₂S–P₂S₃ and (+) AgI–Ag₂O–B₂O₃ [40–42].

considerations may lead to the conclusion that increase of iodine content in the TeO₂ network can enlarge the Ag⁺ cation diffusion process with a possible minimum activation energy. This conclusion is further supported by the dependence of E_a on AgI content (figure 1(b)). It can be observed from this figure that the enhancement in conductivity (figure 1(a)) is generally dominated by decreasing the activation energy. However, it is known that [23, 24, 37, 38] if the oxide ion is replaced by the larger and more polarizable iodine ion, significant decreases in activation energy are achieved leading to considerably greater conductivities, figure 1(b). These behaviours may provide evidence that the presence of I ions in the TeO₂ network decreases the jump distance of the migrating Ag⁺ cations. This may be considered due to the ability of I ions to weaken or open the glass network structure through formation pathways which in turn increases the mobility of the charge carrying species [24].

Evidence for the weakening of the TeO₂ network structure by iodine ions can be obtained from the change of some other studied physical properties, e.g. increasing AgI content leads to an extra increase of both thermal expansion coefficient and molar volume, figures 2(a) and (b). Because the ionic radius of the I ion ($r = 2.2$ nm) is larger than that of both oxygen ($r = 0.132$ nm) and Te ($r = 0.7$ nm), an increase of I ion concentration is therefore expected to lead to an expansion of the glass network and corresponding increase of molar volume. These behaviours have been observed as seen in figures 2(a), (b). In addition, in order to accommodate the larger I ion, the glass structure may be forced to form an open structure [37] by clustering some of the TeO₃ and TeO₄ groups and this makes I ions easy to locate in the interstices. This concept has been reported previously in halide containing borate glasses [37, 38].

The expansion increment with AgI content may lead to a reduction of the total bond strength of the glass structure. This was confirmed by decreasing of both the glass transition temperature (T_g) and the hardness number of the glass (H_v) with increasing AgI content,

figures 3(a), (b). Based on the bond strength consideration, the decreasing trends of T_g and H_v can be explained satisfactorily by a reduction in the degree of polymerization of the cross linking density in the tellurate network structure with replacement of AgI with both TeO_2 and Ag_2O . This is really expected because increasing AgI concentration in the glass is accomplished by increasing the concentration of the ionic Ag–I bonds at the expense of covalently bonded Te–O and Ag–O types.

4.2. AgI-rich glasses

In contrast with the AgI-rich glasses of previous work [32, 39], the present results showed a similar behaviour to those known from observations on different glass systems [32, 39]. In the composition region >60 mol%, inflections in some physical parameters, e.g. conductivity and the associated activation energy, are observed, see figure 1. It is clear from this figure that when the concentration of AgI exceeds 60 mol%, the activation energy increases markedly, with a concomitant drop in conductivity. On the other hand, the glass transition temperature, T_g , and the hardness number, H_v , of the glasses in this region ($60 < \text{AgI} \leq 80$ mol%) are seen to be saturated, figures 3(a), (b).

The observations presented above may be considered as evidence or guides for the formation of some ordered phases from AgI. This fact is surely confirmed from the x-ray diffraction spectra of the glasses studied in this compositional range, see figure 4. This figure shows the x-ray diffraction patterns at room temperature for samples containing different AgI contents (60, 70, 75 and 80 mol%). In this system the halo patterns due to the glass state are only observed for glasses containing $\text{AgI} \leq 60$ mol% (the spectrum of the glass containing 60 mol% AgI is presented in figure 4 as an example), while in the patterns of the samples with more than 60 mol% AgI the crystalline phases of AgI can be clearly observed (figure 4). The intensity of the peaks characterizing these crystallite phases is found to increase with the extra addition of AgI. This may reflect the increasing degree of crystallinity with increasing AgI concentrations.

In correlation to the arguments based on the x-ray results, the decreasing trend in the conductivity for $\text{AgI} > 60$ mol% must be related to the formation of low conductivity crystalline phases from AgI [32]. Then, the increase of total AgI content in the glass samples ($X = 70, 75, 80$ mol%) is accomplished by a decrease of its content in the glass phase. Therefore, it seems that the observed decrease of overall conductivity of glasses for high AgI content is caused not only by the presence of the low conductivity crystalline phases but also by lowering of the electrical conductivity of the glassy phase.

The arguments based on the change of the above discussed physical properties lead one to focus on the glass forming region capable of yielding the optimized conductivity. To clarify this fact in more detail, a comparison of conductivity of glasses in different systems containing AgI [40–42] was useful to consider, see figure 5. From this figure the conductivity belonging to the region ≤ 60 mol% showed similar composition dependencies. σ_{rt} for each system increases with increasing AgI content to reach its limiting value ($\approx 10^{-2} \text{ S cm}^{-1}$) at a certain level of AgI (≈ 60 mol%). It seems that the conductivity at 60 mol% AgI does not differ so much among glasses in the different systems. However, the appearance of the maximum conductivity around 60 mol% AgI may lead us to conclude that a maximum limit of the well formed void spaces or pathways made up by iodine ions is altered at this value regardless of the type of glass network. As a matter of fact, one would expect that the glasses enriched with AgI should present the general necessary properties of good candidates for superionic substances. In this regard, the investigated glass of 60 mol% AgI is recommended for this purpose, since this material displayed highest conductivity at room temperature.

Distinct models [43, 44] have been applied to explain the electrical behaviour and the ion transport mechanism in superionic conducting glasses. These phenomenological models were considered to give a better description of the mechanism of the ion migration in the glassy materials. In this respect, the results of the present study (discussed above) lend support to the view that the more weakened, opened and expanded TeO₂ network is considered the main reason for enhancing the electrical conductivity of the glasses in the region of AgI \leq 60 mol% AgI. This may be considered to be due to formation of pathways when I ions are accommodated. Therefore, the open network model [43] is suggested to be the most promising one to explain the conductivity enhancement due to iodine accommodations in the glasses containing \leq 60 mol% AgI. On the other hand, more addition ($>$ 60 mol%), as reported above, leads to decreasing the conductivity of the glasses due to formation of crystalline phases from AgI. In this case the crystalline or cluster-tissue model [44] would explain the electrical behaviour of the glasses in this region.

5. Conclusion

The main role of iodine ions in improving the conductivity of AgI–Ag₂O–TeO₂ glasses has been discussed in terms of increasing mobility of the Ag⁺ cation through formation of some void spaces or pathways in the tellurite network structure. The optimized value of conductivity is achieved at a certain limit of AgI content (60 mol%). At this concentration the homogeneity configuration or the growth of amorphous nature of the glass is expected to be predominant. Therefore, the ionic conductivity improves to 60 mol% AgI.

Conductivities of the glasses in the present work are compared to previously reported data. The most remarkable result of this comparison is that the conductivities at 60 mol% AgI do not differ very much among these glasses. It is therefore suggested that 60 mol% AgI is the critical concentration, regardless of the type of glass, to obtain an amorphous structure rather than microcrystalline phases. This result combined with x-ray diffraction of glass reveals significant correlations. The amorphousness of these materials increases their interest as superionic glasses in a wide range of applications, while at higher AgI concentration some crystalline phases from AgI are detected. The decrease of conductivity and increase of the activation energy for ionic conduction, therefore, seems to be related to the presence of these ordered structures in the region $60 \leq$ AgI \leq 80 mol%. Structural models compatible with the discussion are proposed to explain the Ag⁺ ion transport mechanism in the investigated glasses.

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