

## ION TRANSPORT IN CHALCOGENIDE GLASSES: DYNAMICS AND STRUCTURAL STUDIES

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In this paper we attempt to summarise the state of our knowledge on ionic conductive chalcogenide glasses. The silver chalcogenide glass family has been chosen as an example. Measurements of <sup>110</sup>Ag tracer diffusion experiments ( $D_{Ag}$ ) and electrical measurements ( $\sigma_i$ ) carried out over an extremely large composition range elucidate the dc conductivity which depends on diffusion over long distances. The results show three distinctly different transport regimes: i) below the percolation threshold at  $x_c \approx$  few silver ppm the glasses are ionic insulators, ii) just above the percolation threshold ( $x_c < x < 1-3$  at % Ag)  $\sigma_i$  and  $D_{Ag}$  are very well described by a modified geometrical percolation model using a single parameter, the critical temperature  $T_o$ :  $\sigma_i(x) \propto x^{T_o/T}$ ,  $D_{Ag}(x) \propto x^{(T_o/T)-1}$ ,  $E(x) \propto k T_o \log(x/x_c)$ . This critical temperature, reflecting interconnectivity of "infinite" percolation clusters embedded in the glassy matrix depends on the structural organisation of the host matrix, iii) far above the percolation threshold the  $Ag^+$  ion transport depends on the Ag content but not on the host matrix. Accordingly only at low mobile ion content structure or, more precisely, dimensionality of the vitreous matrix seems to play a role in ionic transport properties of glasses. Concerning the ac conductivity the complete conductivity spectra ( $\log \sigma(\omega)$  vs  $\log f$  (Hz)), obtained in a very broad temperature and frequency ranges can be perfectly fitted by  $\sigma(\omega) = \sigma_{dc} + A\omega^{0.5} + B\omega^1 + C\omega^2$ . Thus at high frequencies (GHz range) and high temperatures the superlinear frequency dependence of the conductivity recently evoked to describe the data can be discarded. Moreover the existence of a high frequency plateau postulated by many models can be questioned.

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**Keywords:** Ion transport, Dc and ac conductivity

### 1. Introduction

The ionic mobility in glasses is at the origin of many applications in various domains (ion-exchange strengthening, chemical (micro) sensors, solid state (micro) batteries for electrochemical storage of energy, waveguides for integrated optical devices...). Thus, the survey of ionic transport in glasses is a topic of interest to the academic community as well to the glass industry.

Knowledge of mobile ion dynamics at both macroscopic and atomic levels is needed in order to answer the essential question: how can one link together structure, dynamics of ions and macroscopic properties of glasses? Only partial answers have been proposed to date.

The objective of this paper will be to summarise the state of our knowledge using the results that our group has obtained during the last years in the course of studying a family of fast ion conductive glasses, namely the silver chalcogenide glasses.

The following points will be emphasised:

- i) Variation of the conductivity with the mobile cation content ( $\sigma_{dc} \propto x_{(Ag)}$ , mechanisms of conduction).
- ii) Dynamic of ions ( $\sigma_{ac} \propto f$  (Hz) from few Hz to the IR frequencies).
- iii) The relationship between the glass structure (medium range order) and the conduction properties.

## 2. Experimental

Sample preparation and characterization, electrical conductivity and diffusion measurements, ion dynamic studies and structural investigations have been already described elsewhere (see for example publications 1-4).

## 3. Results and discussion

### 3.1. DC electrical conductivity

#### 3.1.1. Temperature dependence of conductivity dc ( $\sigma_{dc}$ )

Classically the electrical conductivity obeys the Arrhenius law  $\sigma_i = \sigma_o/T \exp(-E_{dc}/RT)$  where  $\sigma_o$  is the pre-exponential term,  $E_{dc}$  is the activation energy,  $R$  and  $T$  have their usual meaning. As an example, variations of the dc conductivity for 0.5 Ag<sub>2</sub>S-0.5 GeS<sub>2</sub> glass are shown in Fig. 1. Over the whole temperature range studied (350°C in this case, from 200°C to -150°C), a perfect linear variation is observed for  $\sigma_{dc}$  (at room temperature  $\sigma_{dc} = 10^{-4} \Omega^{-1}\text{cm}^{-1}$  et  $E_{dc} = 0.31 \text{ eV}$ ). For temperatures approaching  $T_g$  (near 300°C for this glass) a weak negative departure from the linearity has been observed for a number of fast ionic conductive glasses (5, 6). But this result remains controversial and requires further experimental confirmations (for the example chosen, the temperature dependence of the <sup>110</sup>Ag tracer coefficient shows a nearly perfect Arrhenius-type behaviour in the same temperature range (14)). It will not be discussed further in this paper.

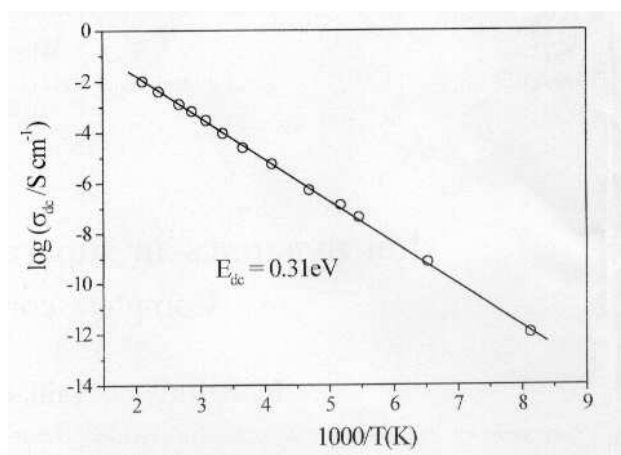


Fig. 1. Arrhenius variation of  $\sigma_{dc}$  for glass 0.5Ag<sub>2</sub>S-0.5GeS<sub>2</sub>. The lines are guides for the eyes.

As for many ionic solids conductors, ionic transport in glasses is a thermally activated process. For temperatures below the glass transition temperature  $T_g$ , structural relaxation times are much longer than the relaxation times for the mobile ions movements. Mobile cations move in a frozen network.

#### 3.1.2. Composition (mobile ion content) dependence of conductivity dc ( $\sigma_{dc}$ )

The ionic conductivity in glasses increases by many order of magnitude with increasing ion content (Fig. 2). For example for glasses belonging to the system  $x \text{ Ag}_2\text{S} - (1-x) \text{ GeS}_2$ , at room temperature  $\sigma_{dc}$  increases from  $6 \cdot 10^{-5} \Omega^{-1}\text{cm}^{-1}$  to  $10^{-3} \Omega^{-1}\text{cm}^{-1}$  when  $x$  varies from 0.3 to 0.55, ie conductivity is increased by a factor about 20 when the mobile ion content is increased by only a factor of 2. At the same time a decrease of activation energy is observed. In silver thiogermanate glasses  $E_{dc}$  varies from 0.36 to 0.32 eV. Different theories have been proposed to explain these drastic changes in the conductivity.

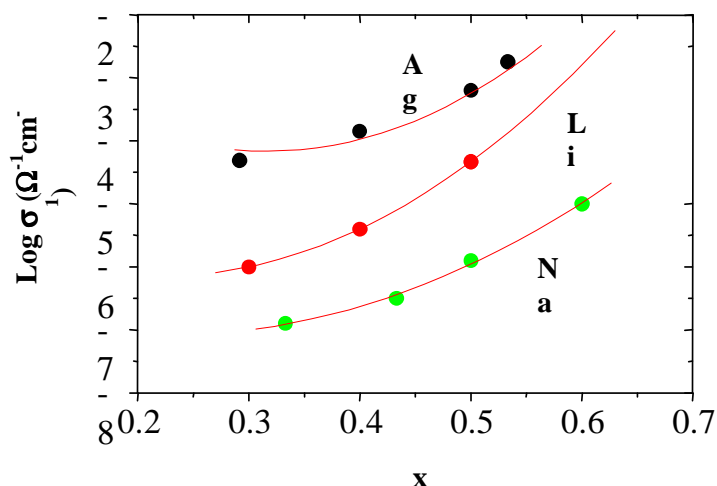


Fig. 2. Composition dependence of the conductivity for  $xM_2S-(1-x) GeS_2$  glasses ( $M= Ag, Li, Na$ ).

They can be divided into two categories:

- The strong electrolyte model, e.g. the Anderson and Stuart model (7) or others inspired by this model (8), in which the mobility of the ions varies according to their concentration and the temperature. All ions participate to the conduction.

- The weak electrolyte model, developed by Ravaine and Souquet (9) in which, on the contrary, the mobility is constant and independent of the concentration and the temperature. Only a fraction of the mobile ions in glass participate in the conduction.

Despite opposite assumptions similar predictions can be deduced from both models: an increase of the dielectric constant of the vitreous network induces an increase of the conductivity and a decrease of the activation energy. It was on the basis of this idea that the first sulfide glasses were synthesized in our group (10)

More recently dynamic structure (11) and jump relaxation (12) models have attempted to explain “quasi log-linear” composition dependence of the conductivity.

A simple ion transport regime operating over the entire composition range is usually proposed in these theories.

These approaches are supported by conductivity measurements covering only a narrow domain in composition, usually corresponding to the highest mobile cation content. This has been the natural focus of attention on obtaining the highest possible conductivity which was for many years the driving force for the research on conductive glasses.

Consequently experimental results covering a large range (several orders of magnitude) mobile ion concentration, which could be used to verify the theoretical predictions, are rather rare. This is especially true of data on tracer diffusion measurements which are essential to distinguish between the ionic or electronic transport at low or extremely low mobile ion contents. Moreover in a limited composition range, it is also difficult to distinguish between exponential or power-law isotherm composition dependence which play a key role in different theories.

Recently conductivity and  $^{110}Ag$  tracer diffusion measurements have been carried out for a number of silver chalcogenide glasses over a very wide composition range including  $Ag^+$  contents as small as few ppm [3, 13, 14]. As an example, glasses belonging to Ag-Ge-S systems have been studied from 0.008 to 25 % at. Ag. In such studies the conductivity increases by 9 orders of magnitude (from  $10^{-14}$  to  $10^{-5} \Omega^{-1}cm^{-1}$ ) with increasing mobile ion content. This enormous increase in the conductivity is accompanied by a dramatic decrease in the activation energy (from 1 to 0.4 eV). Figs. 3a and 3b show the conductivity isotherm variations at 298 K (Fig. 3a) and the same data plotted on a log-log scale at two temperatures 298 and 473 K (Fig. 3b). Figs. 4a and 4b show the  $^{110}Ag$  tracer diffusion measurements plotted on the same way for the same temperatures.

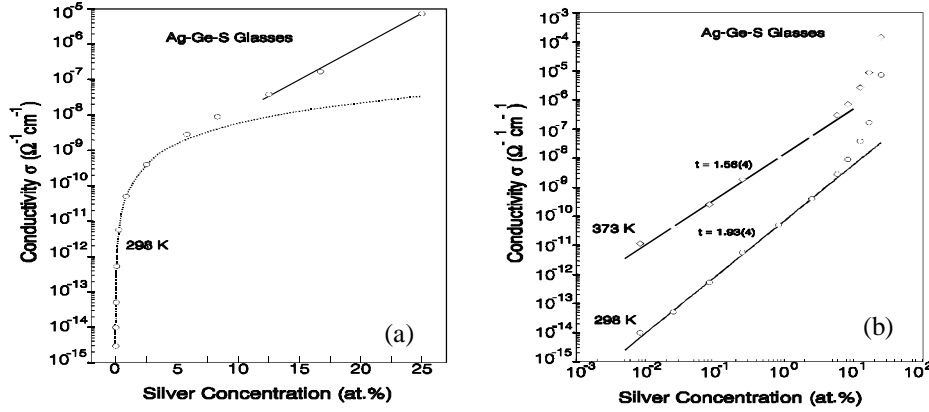


Fig. 3. Ionic conductivity  $\sigma_i(x)$  isotherms for Ag-Ge-S glasses plotted (a) on conventional way at 298 K and (b) on log-log scale at 298 and 373 K. Doted and solid lines represent the best fittings (Eq. 1 and 3). The percolation threshold is not sensibly different from 0% Ag hence a simple composition axis has been used in place of  $(x-x_c)$ .

In contrast to previous observations in which the phenomenon of percolation was unrecognized, in these glasses where the Ag ion content varies more than 3 order of magnitude (from 0.008 to 25 at %), at least three different ion transport regimes can be observed. i) Below the percolation threshold at  $x \approx 30$  ppm Ag, the glasses are ionic insulators. The silver ion transport number  $t_{Ag^+}$  is about 0,1 - 0,2. ii) Just above the percolation threshold for mobile ions the glass become predominantly ionic conducting ( $t_{Ag^+} > 0.6-0.8$  at  $x \geq 0.008$  at % and increases rapidly to 1 with  $x$ ). A characteristic feature of  $\sigma_i(x)$  and  $D_{Ag}(x)$  isotherms in the domain at  $x_c < x < 1-3$  at % Ag is a power-law composition dependence over  $\approx 2.5$  order of magnitude in silver concentration (Fig.3b and 4b).

$$\sigma_i(x, T) = \sigma_i(1, T) x^{t(T)} \quad (1)$$

$$D_{Ag}(x, T) = D_{Ag}(1, T) x^{t_D(T)} \quad (2)$$

where  $\sigma_i(1, T)$  and  $D_{Ag}(1, T)$  are the ionic conductivity and diffusion coefficient of a hypothetical phase at  $x = 1$ . The temperature dependent critical exponent  $t(T)$  and  $t_D(T)$  are related ( $t_D(T) = t(T) - 1$ ) according to the Nernst-Einstein equation ( $D_{Ag} \propto \sigma_i x^{-1}$ ). The Haven ratio,  $H_R = D_{Ag}/D_{\sigma}$ , decreases in this composition range from  $\approx 1$  to  $\approx 0.7$  (Fig. 5). This transport regime is attributed to percolation in the critical region just above the percolation threshold. Theoretical considerations (the dynamic structure model (15) and statistical (occupation) effects (16) on percolative ionic conduction) are also in good agreement with experimental findings. iii) Far above the percolation threshold at  $x > 10$  at % Ag,  $\sigma_i(x)$  and  $D_{Ag}(x)$  both exhibit positive deviations from the expected percolation behaviour (Fig. 3b and 4b) with an exponential law dependence ( $\sigma_i(x) = \sigma_i(o) e^{ax}$  [3]). At the same time the Haven ratio  $H_R$  becomes nearly constant  $H_R \approx 0.3$  (Fig. 5) indicating strongly correlated motion of the  $Ag^+$  ion. In this silver concentration domain, the ionic transport is not dependent any more on percolation pathway. Rather becomes network dependent with a strongly correlated motion of the  $Ag^+$  ions. This domain is called the modifier-controlled domain.

### 3.2. Ion dynamics - Complete conductivity spectra

Non-Debye relaxation is a characteristic of the ionic conductive glasses. It is often expressed by the Kohlraush-Williams-Watts (KWW) function in the time domain (17):

$$\phi(t) = \phi(o) \exp(-(t/\tau)^\beta) \text{ with } 0 < \beta < 1$$

Several earlier phenomenological expressions (Cole-Cole (18), Cole-Davidson (19) or Havriliak-Nagami (20)) also have been used to describe non-Debye relaxation in the frequency domain.

The frequency dependence of electrical conductivity in glassy is usually described by the so called "universal dynamic response" (UDR) first proposed by Jonscher (21).

$$\sigma(\omega) = \sigma_{dc} + A\omega^s \quad [4]$$

where  $0 < s \leq 1$  and  $\sigma_{dc}$  is the frequency independent conductivity.

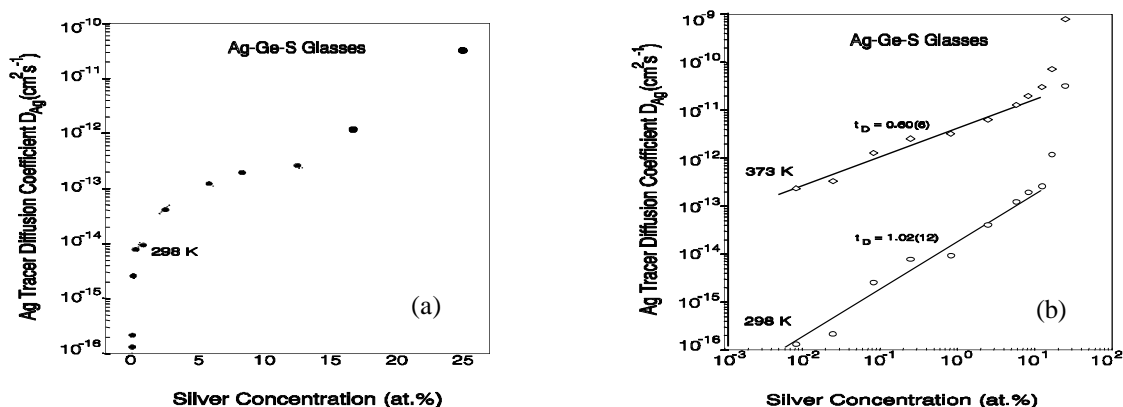


Fig. 4. Diffusion coefficient  $D_{Ag}(x)$  isotherms for Ag-Ge-S glasses plotted (a) on conventional way at 298 K and (b) on log-log scale at 298 and 373 K. Doted and solid lines represent the best fittings (Eq. 2). The percolation threshold is not sensibly different from 0% Ag hence a simple composition axis has been used in place of  $(x-x_c)$ .

Several models were developed to account for this behaviour. These models will be briefly discussed.

The coupling model proposed by Ngai (22) invokes the concept of correlated states between mobile species. In the case of ionic conductive glasses a correlation between mobile ions would take place after a critical time  $t_c$ . Consequently the relaxation rate would be a constant at very short time. For  $t > t_c$ , the relaxation would slow down and the time dependent relaxation rate would be expressed by  $w(t) = (1/\tau_0) (t/t_c)^{-P}$ ,  $\tau_0$  and  $t_c$  are thermally activated. The model predicts a power law behaviour for  $t > t_c$  and a plateau for  $t < t_c$ .

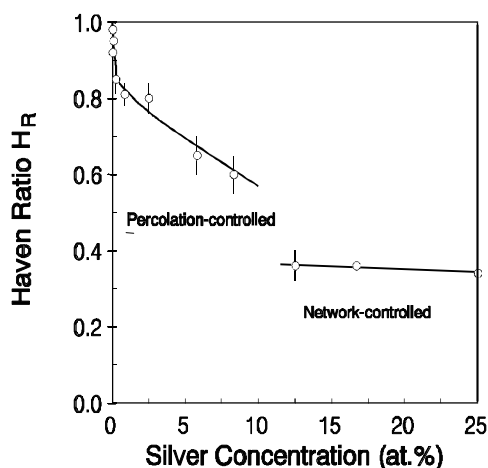


Fig. 5. Composition dependence of the Haven ratio  $H_R$  for Ag-Ge-S glasses. The lines are guides for the eyes.

The Jump Relaxation Model (JRM) developed by Funke (23) is based upon the existence of correlated forward-backward ion hops due to the retarded response of neighbouring species. The non-Debye character of the relaxation is due to the fact that the time constant of the back-hop process

increases as time progresses. This leads to a power-law dependence of the conductivity in the low frequency domain while a plateau should be observed in the high frequency region.

The Diffusion Controlled Relaxation Model (DCR) was proposed by Elliott (24). This model, based on interstitialcy mechanism, predicts a dispersive behaviour of conductivity with  $s = 0.5$  as a consequence of the  $t^{1/2}$  time dependence of the diffuse behaviour.

The "Counter Ion Model" (CIM) developed by Dieterich et al (25) and the "Diffusion Limited Percolation Model" (DLPM) proposed by Bunde et al (26) are based on lattice-gas model with inter-ion coulombic interactions. With such an assumption, Monte Carlo simulations of the diffusion of charged particles in disordered structures leads to a dispersive behaviour of conductivity with a sub-linear frequency exponent.

Recently conductivity measurements in the GHz region have shown a superlinear frequency dependence of the conductivity (1,27,28). The unified site relaxation model (USMR) (29) developed by combining the original JRM and some features of the dynamic structure model (DLPM) accounts for this apparent superlinear frequency dependence of the conductivity.

In addition all these models predict that  $A$  (eq. [4]) is thermally activated with an activation energy  $E_{ac}$  related to the dc activation energy  $E_{dc}$  by  $E_{ac} = E_{dc} (1 - s)$ . All of these models also predict the existence of high-frequency plateau

In summary the data indicate the presence of three conductivity regimes: the dc regime, a dispersive region where  $\sigma(\omega) = A\omega^s$  ( $s < 1$  and  $A$  is thermally activated with an activation energy  $E_{ac} = (1-s) E_{dc}$ ) and a third regime where  $\sigma(\omega) = B\omega^p$ . At high frequency and high temperature this regime shows a superlinear frequency dependence ( $p > 1$ ).

The characteristics of the third regime are still based upon very few experimental evidence. It is clear that systematic investigations of  $\sigma(\omega)$  as a function of frequency and temperature in very large temperature and/or frequency ranges are necessary to clarify this point. In a word to have a complete conductivity spectra become a necessity in order to support the models currently proposed.

What are the last data in this domain? Here again glasses belonging to  $Ag-Ge-S$  system and, more precisely, the glass with composition  $0.5 Ag_2S - 0.5 GeS_2$ , give us a good example (30).

Fig. (6) shows a log-log representation of the conductivity versus frequency in a very broad frequency range, from some Hz up to FIR frequencies (6 THz), and a large temperature domain (from 123 K to 473 K). When frequency was low enough, ie when the UDR (Jonscher law) applies,  $\sigma(\omega) \approx \sigma_{dc} + A\omega^s$ , to fit the experimental data led to an  $s$  value of 0.5. The parameter  $A$  was found thermally activated with an activation energy  $E_{ac} = 0.14$  eV. Within experimental error, it is in accordance with the value determined via  $E_{ac} = (1-s) E_{dc}$  ie 0.16 eV.

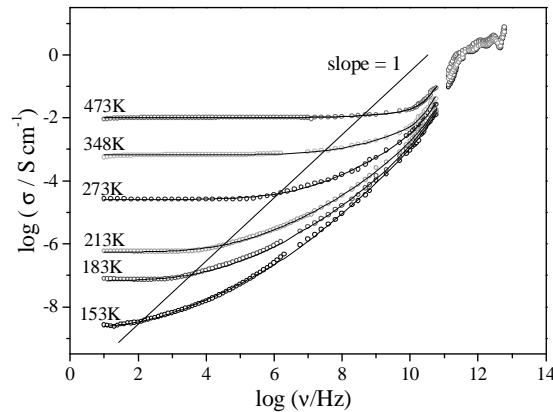


Fig. 6. Frequency dependent conductivity spectra for  $0.5Ag_2S-0.5GeS_2$  glass at various temperatures plotted on log-log scale. Straight line (slope 1) joins the crossover frequencies.

Solid lines represent the best fittings according to Eq. 5.

At higher frequencies, the power law from UDR was not adequate anymore to depict the spectra. It was necessary to add a second power law  $\sigma(\omega) \approx B\omega^p$ . The fit led to a value of the exponent  $p = 1$  (in agreement with Nowick results for the  $Na_2O-3SiO_2$  glass for example) (31). The  $B$  term was very slightly temperature dependent. There was no need of an exponent greater than one to account for the data. This observation contrasts previous results for silver conduction oxide glasses

(27) or for alkali borate glasses (32) as even for the same glass but measured in narrow frequency range (1).

At far infrared frequencies, the conductivity showed a frequency dependence in  $\omega^2$ . It corresponds to the low frequency flank of the lowest vibrational mode. So it was easy to extrapolate such a contribution to lower frequencies and to subtract it. The obtained spectra could then be solely interpreted in terms of a hopping motion of the ions. But even in this case no high frequency plateau could be observed.

Consequently (30), the complete spectra could be perfectly fitted by:

$$\sigma(\omega) = \sigma_{dc} + A\omega^{0.5} + B\omega^1 + C\omega^2 \quad (5)$$

The temperature frequency diagram displayed in Fig. (7) allows the visualisation of the four conductivity regimes. One can observe a narrowing of regime III (exponent 1) to the benefit of regime II and IV (exponents 0.5 and 2 respectively) when the temperature is increased.

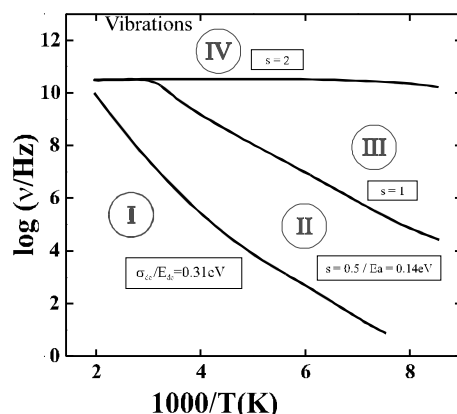


Fig. 7. Temperature-frequency diagram for 0.5Ag<sub>2</sub>S-0.5GeS<sub>2</sub> glass.

In conclusion these results show clearly the capital importance of reliable data measured in the widest temperature and frequency domains possible. Thus at high frequencies (GHz range) and high temperatures (in this case  $T > 150$  K) the superlinear frequency dependence of the conductivity recently evoked to describe the data can be discarded. Moreover from these data the existence of a high frequency plateau postulated by many models can be questioned.

### 3.3. Does the glass structure (intermediate-range order) play a role on conduction properties?

It is clear that in crystallized materials a relation exists between the structure of the material and its properties of ionic conduction. Beyond the type of conduction (vacancy (Schottky) interstitial (Frenkel) or interstitialcy mechanisms), one has a good idea of the structural characteristics that are leading to high ionic conductivity: i) a large number of empty equivalent sites should be available for the mobile ions to jump into, ii) the empty and occupied sites should have a similar potential energies with a low energy barrier between them iii) the structure should have in his framework open channels or preferential plane through which mobile ions may migrate.  $\alpha$ -AgI,  $\beta$ -alumina or material named NASICON are good illustrative examples of that.

In glass, because of the absence of long distance order, channel type arrangements or preferential planes favouring the diffusion of ions cannot exist. On the contrary, one can intuitively think that disorder should allow the existence of many vacant sites that are able to accept mobile ions and consequently to improve the conductivity. Finally, even if the structural units of the framework of glasses are well known (tetragonal Si, Ge, P... , trigonal As coordinations) the glass structure, ie the way of these units are linked, and even the coordination polyhedra for the mobile ions are still not very well known.

At this time what are our structural knowledge concerning silver chalcogenide glasses. Two systems will be chosen as example:

0.5 Ag<sub>2</sub>S - 0.5 GeS<sub>2</sub> glass: from silver isotopic-substitution neutron diffraction studies a structural model for the short and intermediate-range order has been proposed (4). Elongated tetrahedra are connected to two others through their apices, forming chain-like intermediate range ordering. The Ag<sup>+</sup> ions are presumed to sit between neighbouring chains, where they are coordinated by three S atoms (trigonal pyramids).

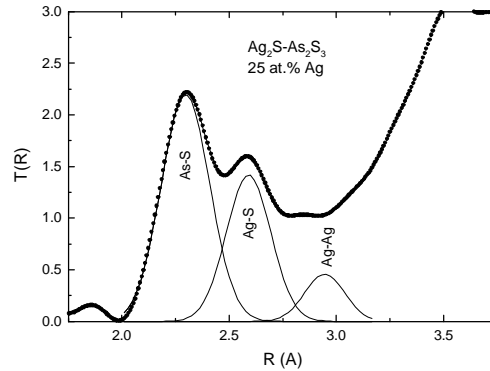


Fig. 8. Total pair correlation function  $T(R)$  for 0.5Ag<sub>2</sub>S-0.5As<sub>2</sub>S<sub>3</sub> glass. Fitting of peaks corresponding to coordination shells of As-S, Ag-S and Ag-Ag.

Ag<sub>2</sub>S - As<sub>2</sub>S<sub>3</sub> glasses: recent studies have been carried out using high-resolution neutron diffraction experiments at scattering vectors up to 40 Å<sup>-1</sup> (33) in order to find differences in the network structural organisation within the percolation and modifier controlled domains. In the percolation controlled domain ( $x \leq 1,2$  at % Ag) neither the short nor the intermediate-range order exhibits any significant transformations: the intensity of the first sharp diffraction peak (FSDP) at 1.25 - 1.35 Å exhibits relatively small changes as a function of the silver content, and the trigonal arsenic coordination and two-fold coordination of the sulphur species remain intact. In contrast, in the modifier-controlled domain, a nearly complete disappearance of As-As correlations at  $\approx 5$  Å, manifested by the strong decreases of the FSDP, has been observed indicating fragmentation of the host matrix. At the same time, the increase of the peak intensity near 3 Å (Ag-Ag correlation) reflects direct contacts of AgS<sub>3</sub> trigonal pyramids and formation of oligomeric silver-containing structural units. These structural units and their interconnections seem to be similar for many silver-rich chalcogenide glasses. As an example, total pair correlation functions  $T(R)$  for two chalcogenide glasses are shown. Fig. 8: 0.5 Ag<sub>2</sub>S-0.5 As<sub>2</sub>S<sub>3</sub> (25 at % Ag) glass (33); Fig. 9: 0.5 Ag<sub>2</sub>S-0.5 GeS<sub>2</sub> (33 at % Ag) glass (4).

We can use these structural data to examine the question of the relation between glass-structure and conductivity properties.

Let us consider first the percolation controlled domain. In this domain ( $x_c < x < 1-3$  at. % Ag) a power-law composition dependence characterises the variation of  $\sigma_i$  or  $D_{Ag}$  (eq. [1] and [2]) with Ag<sup>+</sup> content. Fig. 3b and 4b show that the slope of the log-log plot depends on the temperature. We have found that the slope of the plot, which define the power law exponent  $t(T)$  can be written as (14, 35).

$$t(T) = t_0 + T_0/T \equiv T_0/T$$

consequently equations [1] and [2] can be re-written giving the following expressions.

$$\sigma_i(x, T) \equiv \sigma_i(1, T) x^{T_0/T} = \sigma_0 \exp[-E_{dc}(x)/kT] \quad (6)$$

$$D_{Ag}(x, T) \equiv D_{Ag}(1, T) x^{(T_0/T)-1} = D_0 x^{-1} \exp[E_D(x)/kT] \quad (7)$$

$$E_{dc}(x) = E_D(x) = E(x) = E_0 - k T_0 \ln(x/x_c) \quad (8)$$

where  $T_0$  is a critical temperature. This critical temperature which could be extracted either from the  $t(T)$  or from the  $E(x)$  values, is a primordial parameter to describe the percolation phenomena in glasses (14, 35). The percolative ion-transport depends on the numbers of "infinite" percolation clusters, on the one hand, and on their interconnectivity, on the other.



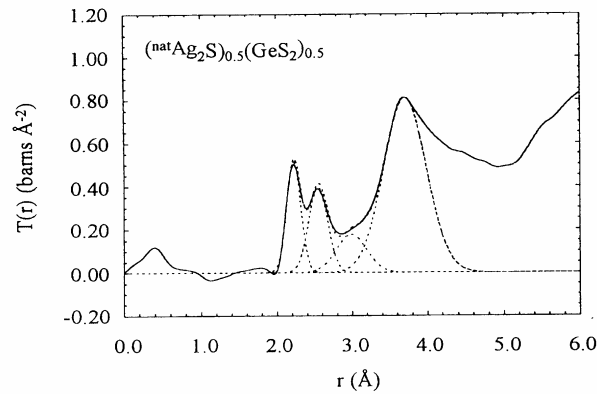


Fig. 9. Total pair correlation function  $T(R)$  for  $0.5\text{Ag}_2\text{S}-0.5\text{ GeS}_2$  glass. Fitting of peaks corresponding to coordination shells of Ge-S, Ag-S and Ag-Ag and Ag-Ge and Ge-Ge combined.

The second term in equation [8] represents a configuration entropy term, where  $\ln(x/x_c)$  reflects the number and  $T_0$  to the interconnectivity of conduction pathways. Plotting the critical temperature  $T_0$  versus the average local coordination number of the host matrix  $\langle n \rangle$ , a nearly linear decrease of  $T_0$  with decreasing  $\langle n \rangle$  is observed (Fig.10 ).

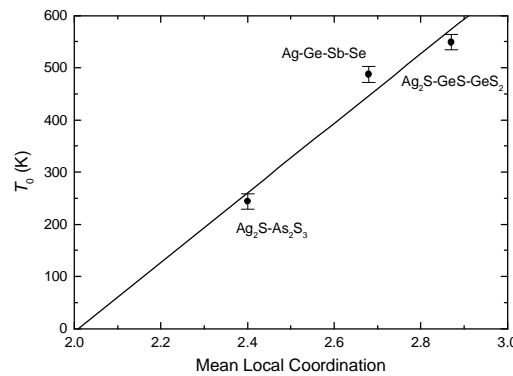


Fig. 10. Critical temperature  $T_0$ , characterising interconnectivity of percolation clusters, versus the average coordination number of the host matrix.

In conclusion, the ionic conductivity and tracer diffusion of silver chalcogenide glasses in the critical percolation domain ( $x_c \approx 30 \text{ ppm} < x < 1-3 \text{ at. \% Ag}$ ) are well described within the framework of modified geometrical percolation using a simple parameter  $T_0$  which reflects interconnectivity of "infinite" percolation clusters (macroscopic conduction pathways) embedded in the host matrix.

In the modifier-controlled domain far above the percolation threshold where i) Ag-Ag correlation can be observed in total pair correlation function  $T(R)$ , ii)  $\sigma_i(x)$  and  $D_{\text{Ag}}(x)$  exhibit positive deviations from percolation behaviour, the conductivity vs composition law is insensitive to the major changes in intermediate range order that occur when  $x_{\text{Ag}}$  is varied.

#### 4. Conclusions

The aim of this paper has been to summarise the state of our knowledge on ionic conductive chalcogenide glasses using silver chalcogenide glasses as an example.

Concerning the dc conductivity which expresses the long distance ionic diffusion,  $^{110}\text{Ag}$  tracer diffusion experiments ( $D_{\text{Ag}}$ ) and electrical measurements ( $\sigma_i$ ) carried out over an extremely large composition range show three distinctly different transport regimes i) below the percolation threshold at  $x_c \approx \text{few silver ppm} (\approx 30 \text{ ppm})$  the glasses are ionic insulators ii) just above the percolation

threshold ( $x_c < x < 1-3$  at % Ag)  $\sigma_i$  and  $D_{Ag}$  are very well described by a modified geometrical percolation model using a single parameter, the critical temperature  $T_o$  :  $\sigma_i(x) \propto x^{T_o/T}$ ,  $D_{Ag}(x) \propto x^{(T_o/T)-1}$ ,  $E(x) \propto k T_o \log(x/x_c)$ . This critical temperature, reflecting interconnectivity of "infinite" percolation clusters embedded in the glassy matrix depends on the structural organisation of the host matrix. iii) Far above the percolation threshold the  $Ag^+$  ion transport depends on the Ag content but not on the host matrix.

Accordingly only at low mobile ion content structure, or more precisely dimensionality of vitreous matrix seems to play an important role in ionic transport properties of glasses. For higher mobile cation content the conduction properties seem only governed by the amount of mobile species. In this concentration domain the structure of vitreous network does not seem to play any role.

Concerning the ac conductivity the complete conductivity spectra ( $\log \sigma(\omega)$  vs  $\log f$  (Hz)), obtained in a very broad temperature and frequency range, can be perfectly fitted by  $\sigma(\omega) = \sigma_{dc} + A\omega^{0.5} + B\omega^1 + C\omega^2$ . Thus at high frequencies (GHz range) and high temperatures the superlinear frequency dependence of the conductivity recently evoked to describe the data can be discarded. Moreover the existence of a high frequency plateau postulated by many models can be questioned.

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