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Ion transport and structure in chalcogenide glasses

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Abstract

Ion-conducting chalcogenide glasses have been chosen to illustrate three specific electrical effects in glasses and their relationship with the glassy structure. Firstly, the variation of conductivity with the mobile cation content was investigated for glasses from the systems $\text{Ag}_2\text{S}-\text{GeS}_2$, $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ and $x\text{Ag}_2\text{S}-60\text{GeS}-(40-x)\text{GeS}_2$. Electrical conductivity and field emission scanning electron microscopy measurements, carried out over an extremely large composition range, show clearly the role of the macroscopic structure in the electrical properties. Two conductivity regimes are observed and the change from the low conductivity regime to the high conductivity regime in the phase separated glasses $\text{Ag}_2\text{S}-\text{GeS}_2$ and $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ occurs when the regions containing the Ag-rich phase start to connect. Secondly, a mixed glass former effect was observed in the glassy system $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$ ($0 \leq x \leq 1$), corresponding to an enhancement of the ionic conductivity for the central region $0.5 \leq x \leq 0.64$. Structural investigations by Raman and small angle x-ray scattering (SAXS) techniques indicate that the glasses from the limiting composition ranges are homogeneous while glasses belonging to the central region are phase separated into two compounds with compositions close to GeS_2 and Li_2SiS_3 . Finally, glasses with composition $0.5[(1-x)\text{Rb}_2\text{S}-x\text{Ag}_2\text{S}]-0.5\text{GeS}_2$ show clear manifestations of a mixed cation effect. SAXS measurements show that the glasses are homogeneous and extended x-ray absorption fine structure investigations indicate that each mobile cation, Ag^+ or Rb^+ , maintains its own specific environment. On the other hand, Raman spectra indicate a non-linear structural change of the glass matrix upon cation mixing with a rearrangement of the local GeS_4 tetrahedra to form chains.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

Ionic mobility in glasses is at the origin of many applications in different domains such as ion-exchange strengthening, chemical (micro) sensors, solid state (micro) batteries, the electrochemical storage of energy and waveguides for integrated optical devices. Thus, a survey of ionic transport in glasses is a topic of interest to the academic community as well as to the glass industry. Knowledge of the mobile ion dynamics at both macroscopic and atomic levels is needed in order to answer the essential question: how can one link together structure and electrical properties in glasses? Only partial answers have been proposed to date.

The objective of the paper is to summarize the state of our knowledge by using the results obtained by our group over the last few years in the course of studying a family of fast ion conducting glasses based on chalcogenide systems. The following points will be emphasized.

- (i) The variation of the dc electrical conductivity with the mobile cation content, σ_{dc} versus x , over an extremely large composition range in glasses from the systems $\text{Ag}_2\text{S}-\text{GeS}_2$, $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ and $\text{Ag}_2\text{S}-\text{GeS}-\text{GeS}_2$.
- (ii) The mixed glass former effect for $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_{2x}\text{GeS}_2]$ glasses ($0 \leq x \leq 1$).
- (iii) The mixed cation effect for $0.5[(1-x)\text{RbS}_2 - x\text{Ag}_2\text{S}]-0.5\text{GeS}_2$ glasses ($0 \leq x \leq 1$).

2. Experimental procedures

The sample preparation procedures have been described elsewhere [1–6]. The electrical conductivity measurements for glasses prepared by the twin roller quenching technique are described in [4]. In the case of conventionally prepared bulk-quenched glasses, the samples used for the electrical conductivity measurements were pieces of 5–30 mm² in area and 0.4–0.7 mm in thickness. The sides of the samples were ground parallel and platinum or gold electrodes were sputtered onto the opposite sides. Measurements of the impedance modulus, Z , and the phase angle, θ , in the frequency range from 100 Hz to 200 kHz were carried out for samples having resistance $R \leq 10 \text{ M}\Omega$ using a General Radio 1693 *RLC* digibridge. Measurements of the dc conductivity were performed for samples with higher resistance using a Keithley 617 electrometer. Both methods (dc conductivity measurements at lower temperature and ac impedance measurements at higher temperature) gave the same results for insulating glasses. The temperature range of the electrical measurements was usually from 20 to 180 °C. A calibrated thermocouple was used to determine the cell temperature.

Field emission–scanning electron microscopy (FE–SEM) measurements were performed on a LEO-982 instrument with an acceleration voltage varying from 1 to 5 kV and a magnification of 5000 \times –2000 \times using finish fracture of glass samples. Raman spectra were recorded at room temperature using an 89 Dilor spectrophotometer and a Fourier-transform (FT) Raman instrument (Bruker RFS 100). Silver (25 514 eV) and rubidium (15 200 eV) K edge extended x-ray absorption fine structure (EXAFS) spectra were measured in transmission mode at LURE (Orsay, France) on the D44 beam line of the DCI storage ring operating at 1.85 GeV with an average current of 25 mA. All of the experiments were performed at a temperature of 35 K. Small angle x-ray scattering (SAXS) measurements were carried out on the D22 beam line at LURE. Both the SAXS theory and data treatment are described elsewhere [5].

3. Results and discussion

3.1. Variation of the conductivity with the mobile cation content

For many years the driving force for research on ion-conducting glasses was to obtain the highest possible conductivity. Consequently, a large number of researchers focused their

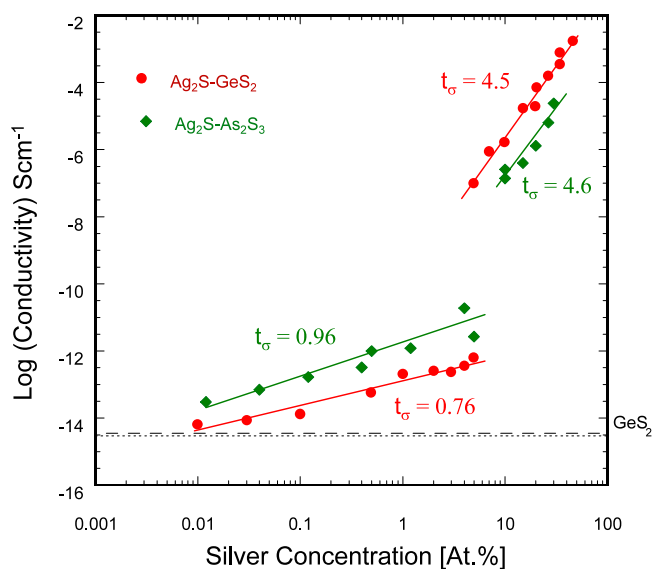


Figure 1. Evolution of the room temperature conductivity with Ag content in glasses from the $\text{Ag}_2\text{S-GeS}_2$ [1, this paper] and $\text{Ag}_2\text{S-As}_2\text{S}_3$ [3, 12] systems.

studies on conductivity measurements covering only a narrow domain in composition, usually corresponding to the highest mobile cation content. Different theories, such as the strong electrolyte model [7], weak electrolyte model [8] and dynamic structure model [9], have been proposed to explain the observed composition dependence of the conductivity. A single regime for ion transport operating over the entire composition range is usually invoked in these theories. However, experimental data covering a large range of mobile cation concentration (several orders of magnitude), which could be used to verify the theoretical predictions, are rather rare to date [2, 3, 10, 11]. Our contribution to this problem includes studies on three families of silver-conducting sulfide glasses, i.e. $\text{Ag}_2\text{S-GeS}_2$, $\text{Ag}_2\text{S-As}_2\text{S}_3$ and $x\text{Ag}_2\text{S-60GeS-(40-x)GeS}_2$.

The variation of room temperature conductivity with composition, plotted on a log-log scale for $\text{Ag}_2\text{S-GeS}_2$ [1, this paper] and $\text{Ag}_2\text{S-As}_2\text{S}_3$ [3, 12] glasses, is shown in figure 1. The data clearly show two different conductivity domains, with a strong increase of four to five orders of magnitude in the conductivity occurring at about 5 at.% cation content. On the other hand, figure 2 shows the variation of room temperature conductivity with composition for another glass family, i.e. $x\text{Ag}_2\text{S-60GeS-(40-x)GeS}_2$, with the silver content varying between 0.008 and 25 at.% [2]. In this case a change in the behaviour of the conductivity is indeed observed at about 5 at.% silver but it corresponds only to a shoulder in the plot and not to a sudden break with a large increase in value.

An FE-SEM investigation of the glasses has also been carried out. While all the $x\text{Ag}_2\text{S-60GeS-(40-x)GeS}_2$ glasses are homogeneous down to 5 nm, the highest resolution of the instrument used, the $\text{Ag}_2\text{S-GeS}_2$ and $\text{Ag}_2\text{S-As}_2\text{S}_3$ glasses showed phase separation. As an example, figure 3 shows the FE-SEM images of two $\text{Ag}_2\text{S-GeS}_2$ glasses, one with 5 at.% silver and the other with 7 at.% silver corresponding to compositions having small and high conductivities respectively. While regions of the Ag-poor phase (dark in the micrographs) are connected in the glass with 5 at.% silver, regions of the Ag-rich phase (white in the micrographs) are connected in the silver-rich glass. As a matter of fact, the FE-SEM micrographs clearly indicate that the change in the conductivity regime occurs when the regions of the Ag-rich

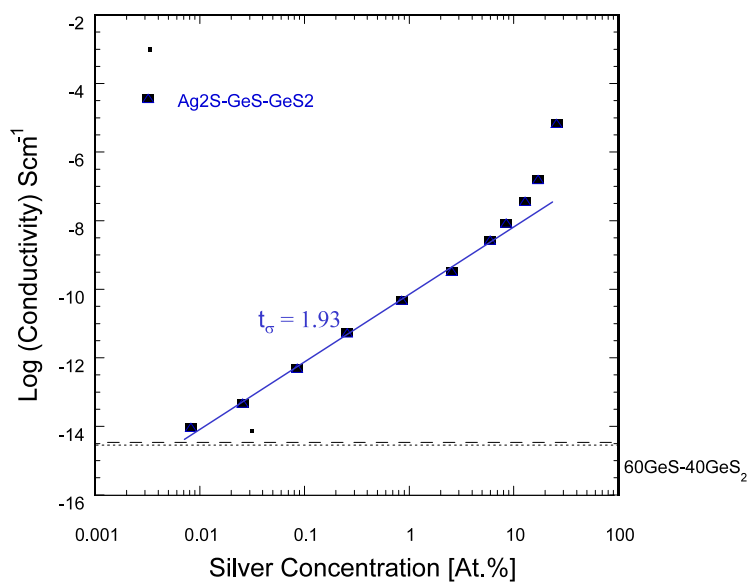


Figure 2. Evolution of the room temperature conductivity with Ag content in $x\text{Ag}_2\text{S}-60\text{GeS}-(40-x)\text{GeS}_2$ glasses [2].

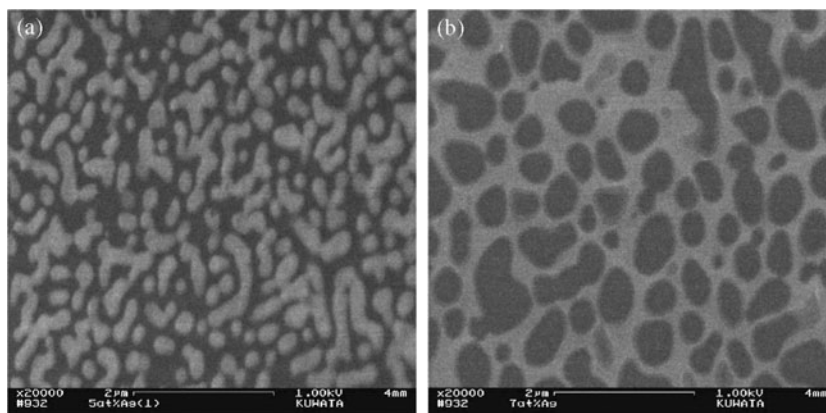


Figure 3. FE-SEM micrographs of two glasses from the system $\text{Ag}_2\text{S}-\text{GeS}_2$ containing (a) 5 at.% Ag or (b) 7 at.% Ag.

phase start to connect in either the $\text{Ag}_2\text{S}-\text{GeS}_2$ or $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ glasses. This behaviour is characteristic of a percolation threshold with the Ag-poor phase (Ag-rich phase) being responsible for the conductivity at low silver (high silver) content.

In an early study of $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ and $x\text{Ag}_2\text{S}-60\text{GeS}-(40-x)\text{GeS}_2$ glasses made using electromotive force measurements [10], the change in conductivity behaviour at about 5 at.% silver was attributed to a change in the nature of the charge carriers from electrons or holes to ions. However, this interpretation does not fully agree with the recent findings from tracer diffusion coefficient measurements carried out on these two glass families [2, 13]. The latter investigation indicates a close relationship between the variation of both the conductivity and ion diffusion coefficients. Firstly, plots of the diffusion coefficients against composition show

very similar behaviour to those for conductivity with a change occurring at about 5 at.% Ag, corresponding to a sudden break in the case of the phase separated $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ glasses [13] and to a smooth evolution for the homogeneous $x\text{Ag}_2\text{S}-60\text{GeS}-(40-x)\text{GeS}_2$ glasses [2]. Moreover, the variation of the conductivity and diffusion coefficients with silver concentration ([Ag] in at.%) for all of the glasses can be fitted in the same way, i.e. by a power law in either the low or high conductivity domains (see figures 1 and 2). The available composition range in the high conductivity domain is not large enough to allow a unique fitting of the curves such that an exponential variation cannot be discarded [2]. However, in the low conductivity domain, the values for the exponents t_σ and t_D obtained by fitting the conductivity and diffusion coefficient plots with the equations $\sigma([\text{Ag}]) \propto [\text{Ag}]^{t_\sigma}$ and $D([\text{Ag}]) \propto [\text{Ag}]^{t_D}$, respectively, are reliable (figures 1 and 2). The values of t_D are 1.02 at room temperature and -0.29 at 118.8°C for the $x\text{Ag}_2\text{S}-60\text{GeS}-(40-x)\text{GeS}_2$ [2] and $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ [13] glasses respectively.

Therefore, even though a reinvestigation of the nature of the conductivity at low silver content is probably needed, the previously described investigation clearly indicates a change in the silver diffusion mechanism between glasses with low and high silver contents. This change, which can be understood in terms of a percolation threshold between a Ag-poor phase and a Ag-rich one in phase-separated glasses, also exists in homogeneous glasses. Further investigation of the structure of these glasses might bring new insight into this behaviour.

3.2. Mixed glass former effect

The mixed former effect [5] refers to a non-linear enhancement of the conductivity versus composition relation in glasses containing two network formers when one former is replaced by another and the total modifier content is held constant. This effect aroused some interest a decade ago since it appeared to be a way of obtaining glasses with large conductivity. The mixed former effect has been mainly observed and studied in borophosphate glasses where it was attributed to the appearance of BPO_4 entities [14, 15]. Our contribution to this problem concerns a study of the Li-conducting glassy chalcogenide family $\text{Li}_2\text{S}-\text{SiS}_2-\text{GeS}_2$ [4, 5, 16].

$0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$ glasses were prepared over the whole composition range, $0 \leq x \leq 1$, by using the twin roller quenching technique. A large enhancement of the ionic conductivity by about two orders of magnitude for glasses belonging to the central region ($0.50 \leq x \leq 0.64$) shows the existence of a mixed glass former effect (figure 4). The change in the ionic conductivity, σ , is related to a change in activation energy, E_a , since the pre-exponential factor remains constant ($\log(\sigma_0[\text{S cm}^{-1}]) = 1.8$). The variation of the electrical characteristics is closely related to that of the glass transition temperature, T_g , and the density. While the glass transition temperature increases suddenly for glasses of the central region ($T_g \sim 350^\circ\text{C}$ compared with 327°C for $x = 0$ and 315°C for $x = 1$), the density decreases down to $\sim 1.94 \text{ g cm}^{-3}$ for the same glasses (compared to 2.29 and 2.38 g cm^{-3} for $x = 0$ and 1 respectively).

Structural investigations by SAXS and Raman techniques have been carried out in order to understand this phenomenon. SAXS experiments show that samples belonging to the central region scatter more than samples belonging to the limiting regions. Moreover, the scattering data for glasses in the limiting regions (figure 5) could be accounted for by the Debye-Bueche model which considers the diffuse electronic fluctuations in the medium under study. On the other hand, the scattering data for glasses in the central region (figure 5) could be fitted by using Porod's law which describes the scattering by particles with well defined surfaces. In this case the SAXS analysis indicates the presence in the glass of aggregates or clusters of 50 \AA in size. The SAXS data are, therefore, consistent with homogeneous matrices for glasses belonging to the limiting regions ($0 \leq x < 0.50$ and $0.64 < x \leq 1$) and point towards

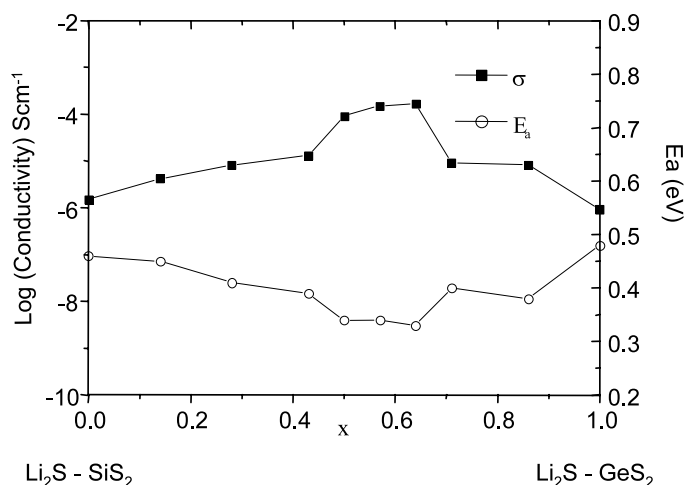


Figure 4. Variation with composition x of the conductivity at room temperature, σ , and of the activation energy for conduction, E_a , in the glassy system $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$. Lines are drawn to guide the eye.

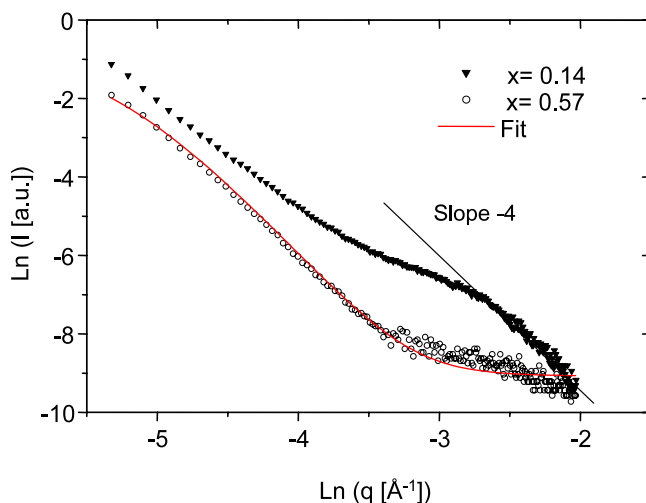


Figure 5. Examples of SAXS intensities for a sample from the limiting region ($x = 0.14$) and a sample from the central region ($x = 0.57$) in the glassy $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$ system. The line corresponds to a fit of the SAXS data for sample $x = 0.14$ using the Debye-Bueche model.

phase separation for glasses in the central region ($0.5 \leq x \leq 0.64$). Raman spectra of the $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$ glasses with $0 \leq x \leq 1$ are shown in figure 6. For the substitution of one glass former by another in the ranges $0 \leq x < 0.50$ and $0.64 < x \leq 1$, a smooth change in the spectra is observed. A sudden change in the shape of the spectra is, however, observed when the Si/Ge ratio is close to 1, i.e. when $0.5 \leq x \leq 0.64$. Indeed, the Raman spectrum of the $x = 0.5$ glass shows the disappearance of the peak at 368 cm^{-1} , related to the stretching vibrations of non-bridging $\text{Si}-\text{S}^-$ bonds in $0.3\text{Li}_2\text{S}-0.7\text{SiS}_2$ glass, in favour of a peak at 377 cm^{-1} related to the same bonds but in the more heavily modified

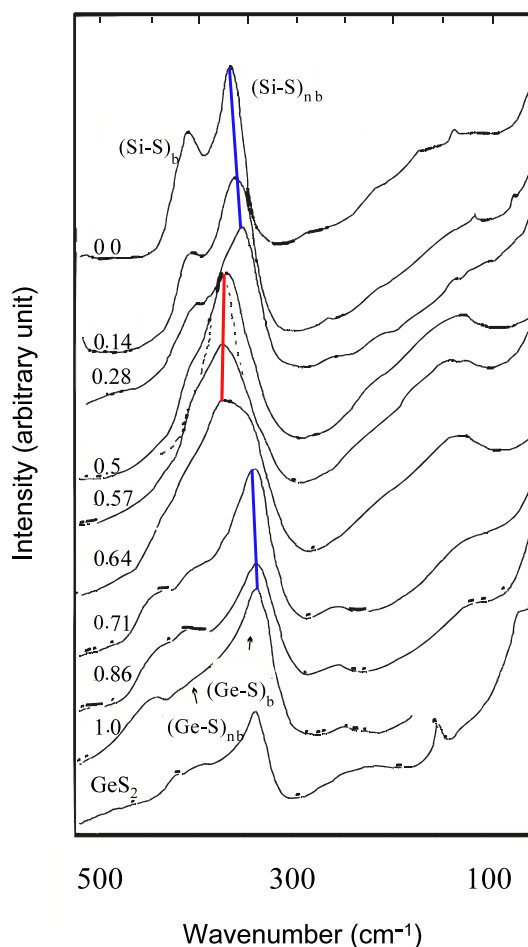


Figure 6. Raman spectra for glasses in the system $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$ ($0 \leq x \leq 1$).

glass $0.5\text{Li}_2\text{S}-0.5\text{SiS}_2$ (the Raman spectrum of glassy Li_2SiS_3 is shown by the dotted curve in figure 6). The peak at 377 cm^{-1} remains unchanged in the Raman spectra of the other glasses in the central region. The broadening of the Raman spectra when more Ge is substituted for Si is consistent with an increasing number of Ge-S bonds in the glass. As a whole, the Raman spectra of the glasses in the central region can be described by the sum of the Raman spectra of the pure GeS_2 and Li_2SiS_3 phases. The observation of these two entities for glasses in the central region is in agreement with the SAXS conclusion that the glasses are phase separated. Moreover, one can understand their high ionic conductivities, close to that of Li_2SiS_3 , if the glasses comprise insulating GeS_2 aggregates embedded in a continuous phase of composition close to Li_2SiS_3 .

On the whole, the results give strong support to the explanation that the mixed glass former effect in the system $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$ is caused by phase separation with one phase containing almost all of the modifier cations. As in borophosphate glasses, our investigation of the $\text{Li}_2\text{S}-\text{SiS}_2\text{GeS}_2$ system clearly indicates that an explanation of the mixed former effect lies in the structure of the glasses.

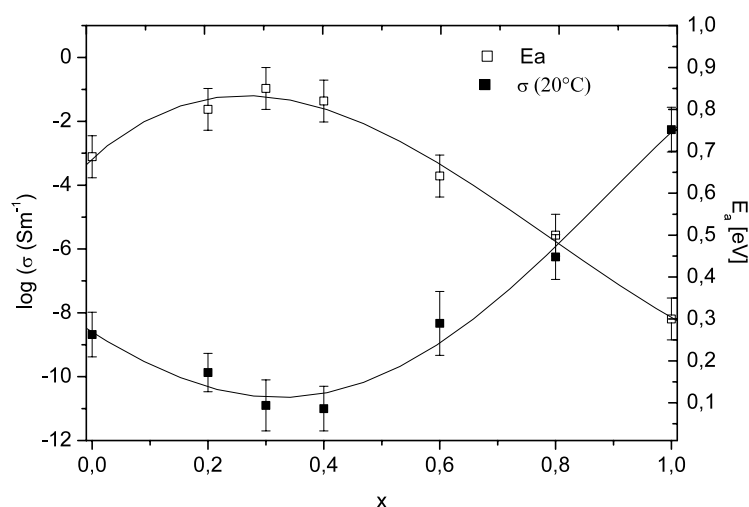


Figure 7. Electrical conductivity at 20 °C, σ , and activation energy, E_a , as a function of composition for $0.5[(1-x)\text{Rb}_2\text{S}-x\text{Ag}_2\text{S}]-0.5\text{GeS}_2$ glasses. Lines are drawn to guide the eye.

3.3. Mixed cation effect

The mixed cation effect [6] is probably the best known and most controversial effect that can be found in ion-conducting glasses. It corresponds to a non-linear variation of the electrical characteristics when one modifier is replaced by another and the total modifier content is kept constant. While this effect has been reported many times for oxide glasses, our contribution has been to show its existence in chalcogenide glasses, and more specially in the $\text{Li}_2\text{S}-\text{Na}_2\text{S}-\text{SiS}_2$ and $\text{Rb}_2\text{S}-\text{Ag}_2\text{S}-\text{GeS}_2$ systems [6, 17, 18]. In the present paper we will focus on our investigation of the second system.

The non-linear evolution of the electrical parameters, σ_{dc} and E_a , with composition for the $0.5[(1-x)\text{Rb}_2\text{S}-x\text{Ag}_2\text{S}]-0.5\text{GeS}_2$ glasses is shown in figure 7. The glass transition temperature also exhibits a negative deviation from additivity with composition, closely related to that of the electrical characteristics. Structural investigations by several techniques have been carried out. Firstly, SAXS experiments showed that the Rb–Ag thio germanate glasses are homogeneous over the entire composition range since no significant scattering at small angles was observed. Secondly, an EXAFS investigation was undertaken at both the Ag and Rb K edges. The Ag K-edge Fourier-filtered experimental signals for all of the $0.5[(1-x)\text{Rb}_2\text{S}-x\text{Ag}_2\text{S}]-0.5\text{GeS}_2$ glasses had a very similar shape, suggesting that the silver environment in the mixed cation glasses is rather similar. Quantitative results indicate that each silver atom is surrounded by 2.8 sulphur atoms at an average distance of 2.5 ± 0.01 Å. In the same way, the high degree of similarity shown by the Rb K-edge Fourier oscillations for the different compositions indicates that Rb also has a similar environment in all of the glasses. Quantitative results give an average number of 4.2 sulphur atoms surrounding Rb with an average distance of 3.38 ± 0.01 Å. The EXAFS investigations therefore indicate that Rb^+ and Ag^+ cations form their own specific local environments, which are not affected by the presence of the dissimilar cation. The present results are in agreement with the original EXAFS findings of Greaves for mixed alkali silicate glasses [19] and more recent EXAFS data of Huang and co-workers [20] for $\text{Rb}_2\text{O}-\text{Ag}_2\text{O}-\text{GeO}_2$ glasses, the oxide analogues of $\text{Rb}_2\text{S}-\text{Ag}_2\text{S}-\text{GeS}_2$ glasses.

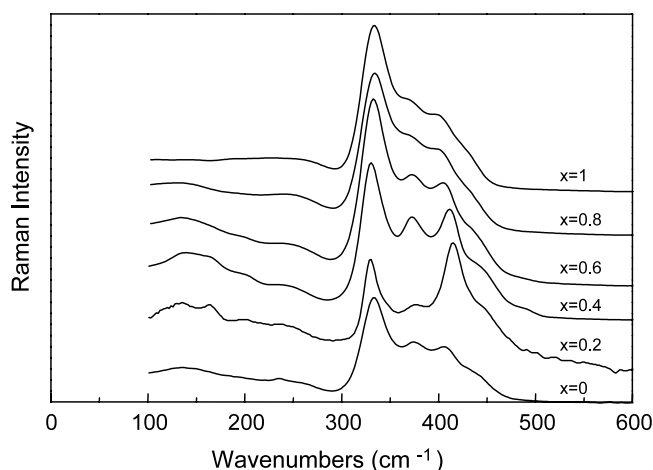


Figure 8. FT Raman spectra of $0.5[(1-x)\text{Rb}_2\text{S}-x\text{Ag}_2\text{S}]-0.5\text{GeS}_2$ glasses.

On the other hand, a non-linear structural evolution of the glass matrix with composition is pointed out by the Raman spectra shown in figure 8. The Raman spectra of the modified thiogermanate glasses can be understood in terms of the vibrational characteristics of thiogermanate tetrahedral units Q^n containing $4-n$ terminal bonds, Ge-S^- , and n bridging bonds, Ge-S , per germanium atom. With the help of previous Raman studies of thiogermanate glasses [21, 22], the high frequency features at $370-375$, $400-405$ and $425-440\text{ cm}^{-1}$ of the Rb-Ag thiogermanate Raman spectra can be attributed to the frequencies $\nu(\text{Ge-S}^-)$ of Q^1 , Q^2 and Q^3 thiogermanate tetrahedral units, respectively. The most intense feature at 333 cm^{-1} is attributed to the stretching vibration of bridging bonds $\nu(\text{Ge-S})$. The features of the Raman spectra show clearly the coexistence of the different Q^n species at these meta-thiogermanate compositions, where normally one would expect only the Q^2 arrangements. To explain this result it was proposed [22] that the following equilibria occur in the melt and are partially quenched into the glassy state:



If we now consider the relative intensity of the different features, it appears that the band at 415 cm^{-1} in the range of $\nu(\text{Ge-S}^-)$ for Q^2 units gains in intensity in the composition range $0.2 \leq x \leq 0.4$, i.e. in the same composition range where T_g and the electrical parameters exhibit their extreme values. The clear increase of the relative intensity of the Q^2 band upon cation mixing can be interpreted in terms of a progressive shift of the equilibria described in equations (1) and (2) to the left for mixed cation glasses. Therefore, cation mixing appears to result in a more homogeneous glass structure, since Q^2 units are formed at the expense of Q^4 , Q^3 and Q^1 species. Such a process should lead to dissimilar cations occupying neighbouring sites, which can be dynamically exchanged upon providing the required site mismatch energy.

The investigation of the mixed cation effect in the Rb-Ag thiogermanate glasses indicates a close relationship between the evolutions of both the electrical characteristics and the structure. In this case, the Raman results point towards a rearrangement of the local GeS_4 tetrahedra to form chains, i.e. to a change in the medium range order of the glasses.

4. Conclusion

Three different families of ion-conducting chalcogenide glasses, that show three specific electrical effects, have been studied.

In the first family, which comprises the systems $\text{Ag}_2\text{S}-\text{GeS}_2$, $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ and $x\text{Ag}_2\text{S}-60\text{GeS}-(40-x)\text{GeS}_2$, the modifier content was varied from very low concentration to high concentration, allowing a study of the conductivity evolution over several decades in concentration. Two different conductivity regions as a function of the cation content were observed and the conductivity in these regions shows a power law dependence. FE-SEM measurements of the $\text{Ag}_2\text{S}-\text{GeS}_2$ and $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$ glasses show clearly that the change from the low concentration region to the high concentration region is related to phase separation. Indeed, the change in the conductivity regime occurs when regions of the Ag-rich phase start to connect.

The second family, i.e. the $0.3\text{Li}_2\text{S}-0.7[(1-x)\text{SiS}_2-x\text{GeS}_2]$ glasses ($0 \leq x \leq 1$), show a mixed glass former effect. This corresponds to an enhancement of the ionic conductivity for glasses with $0.5 \leq x \leq 0.64$. The phenomenon was again shown to be related to phase separation. Indeed, a structural investigation by Raman and SAXS indicates that glasses from the limiting composition ranges are homogeneous while glasses belonging to the central region are phase separated into two compounds with compositions close to GeS_2 and Li_2SiS_3 .

The third family, i.e. glasses with the composition $0.5[(1-x)\text{Rb}_2\text{S}-x\text{Ag}_2\text{S}]-0.5\text{GeS}_2$ ($0 \leq x \leq 1$), show clear manifestations of a mixed cation effect (minima in the conductivity and T_g variations with x , maximum in the activation energy variation with x). In this case, SAXS measurements show that the glasses are homogeneous. However, the phenomenon could still be related to a change in the medium range order in the glasses since a Raman investigation indicates a non-linear structural evolution of the glass matrix upon cation mixing with a rearrangement of the local GeS_4 tetrahedra to form chains.

Overall, the present investigation points towards a close correlation between structural organization in glasses and specific electrical effects such as the variation of conductivity with cation content, the mixed glass former effect and the mixed cation effect.

Acknowledgments

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References

- [1] Robinel E, Carette C and Ribes M 1983 *J. Non-Cryst. Solids* **57** 49
- [2] Bychkov E, Tsegelnik V, Vlasov Yu, Pradel A and Ribes M 1996 *J. Non-Cryst. Solids* **208** 1–20
- [3] Bychkov E, Bychkov A, Pradel A and Ribes M 1998 *Solid State Ion.* **113–115** 691
- [4] Deshpande V, Pradel A and Ribes M 1988 *Mater. Res. Bull.* **23** 379–84
- [5] Pradel A, Rau C, Bittencourt D, Armand P, Philippot E and Ribes M 1998 *Chem. Mater.* **10** 2162
- [6] Rau C, Armand P, Pradel A, Varsanis C P, Kamitsos E I, Granier D, Ibanez A and Philippot E 2001 *Phys. Rev. B* **63** 184–204
- [7] Anderson O and Stuart D 1954 *J. Am. Ceram. Soc.* **37** 573
- [8] Ravaine D and Souquet J L 1977 *Phys. Chem. Glasses* **18** 27
- [9] Maass P, Bunde A and Ingram M D 1994 *J. Non-Cryst. Solids.* **172–174** 1222
- [10] Kawamoto Y, Nagura N and Tsuchihashi S 1974 *J. Am. Ceram. Soc.* **57** 489
- [11] Patel H K and Martin S W 1992 *Phys. Rev. B* **45** 10292
- [12] Kazakova E A and Borisova Z U 1980 *Fiz. Khim. Stekla* **6** 424

- [13] Drugov Yu, Tsegelnik V, Bolotov A, Vlasov Yu and Bychkov E 2000 *Solid State Ion.* **136/137** 1091
- [14] Tsuchiya T and Moriya T 1980 *J. Non-Cryst. Solids* **38/39** 323
- [15] Scagliotti M, Villa M and Chiodelli G 1987 *J. Non-Cryst. Solids* **93** 350
- [16] Pradel A and Ribes M 1989 *Mater. Chem. Phys.* **23** 121
- [17] Pradel A and Ribes M 1994 *J. Non-Cryst. Solids* **172–174** 1315
- [18] Gee B, Eckert H, Pradel A, Taillades G and Ribes M 1997 *J. Non-Cryst. Solids* **215** 32
- [19] Greaves G N 1985 *J. Non-Cryst. Solids* **71** 203
- [20] Huang W C, Jain H and Marcus M A 1994 *J. Non-Cryst. Solids* **180** 40
- [21] Barrau B, Ribes M, Maurin M, Kone A and Souquet J-L 1980 *J. Non-Cryst. Solids* **37** 1
- [22] Kamitsos E I, Kapoutsis J A, Chryssikos G D, Taillades G, Pradel A and Ribes M 1994 *J. Solid State Chem.* **112** 255