Mixed Glass Former Effect in the System 0.3Li$_2$S−0.7[(1−*x*)SiS$_2$−*x*GeS$_2$]: A Structural Explanation

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A mixed glass former effect has been observed in the glassy system 0.3Li$_2$S−0.7[(1−*x*)-SiS$_2$−*x*GeS$_2$], where $0 \leq x \leq 1$. It corresponds to a large enhancement of ionic conductivity for compositions $0.50 \leq x \leq 0.64$. The variations of the electrical characteristics are closely related to those of the glass transition temperature and the density. Structural investigations by Raman and SAXS techniques have been carried out on this system. The results indicate that the high conducting glasses belonging to the central composition region, i.e., $0.50 \leq x \leq 0.64$, are phase separated, forming entities with a composition close to GeS$_2$ which are embedded in a matrix close to Li$_2$SiS$_3$, while glasses from the limiting composition ranges, i.e., $0 \leq x < 0.50$ and $0.64 < x \leq 1$, are homogeneous.

Introduction

During the past decades, ionic conductive glasses gave rise to extensive studies because of their interest as solid electrolytes for batteries or electrochromic devices, for example. Many investigations aimed at the preparation of glasses with a very high conductivity. Different ways were explored such as the dissolution of a halide salt in a glass containing a network former and modifier or the replacement of oxygen by more polarizable atoms, i.e., S or Se. The so-called "mixed former" effect can be another way to obtain a large enhancement of the conductivity in a glass. Nonlinear variations of conductivity versus composition with the presence of one or two maxima were indeed observed in some families of glasses when a network former was replaced by another, the total modifier content being constant. This effect was mainly observed and studied in borophosphate glasses.[1−3] According to Raman and NMR studies[4,5] the enhancement of the conductivity was related to the appearance of BPO$_4$ entities. Another explanation based upon the weak electrolyte theory and the assumption of a hindered phase separation was proposed to account for the mixed glass former effect, when the variation of the conductivity with the composition presented two maxima,[6] i.e., in sodium and silver borophosphate and in lithium borotellurate glasses.[7]

Some years ago a mixed glass former effect was shown for the first time in a family of chalcogenide glasses with composition 0.3Li$_2$S−0.7[(1−*x*)SiS$_2$−*x*GeS$_2$].[8,9] At the same time, the investigation by DSC, density measurements, and Raman spectroscopy indicated that the enhancement of the conductivity was related to a structural change in the glasses and a phase separation was suggested. However, no direct experimental data were given to prove such a phase separation.

In this work the above-mentioned system was reinvestigated. In particular, a structural study of several glasses was made by small-angle X-ray scattering (SAXS), which is a suitable technique for examining the homogeneity of the glass on a scale from 10 to 1000 Å.

Small-Angle X-ray Scattering. The SAXS scattered intensity I is a function of the value of the scattering vector $q = 4\pi \sin(\theta)/\lambda$, where 2θ is the scattering angle and λ is the incident X-ray wavelength.

According to standard scattering theories[10] and neglecting incoherent scattering, which is small for SAXS, the intensity of the scattered waves for a statistically isotropic dilute system with no long range order is given by

$$I(q) = V(\Delta\rho)^2 \int_V 4\pi r^2 \, dr \, \gamma_0(r) \sin(qr)/qr \qquad (1)$$

where V is the scattering volume, $\Delta\rho$ is the electron density fluctuation, and $\gamma_0(r)$ is the characteristic function introduced by Debye and Bueche.[11]

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Calculating the second moment of the intensity we can obtain the so-called invariant Q[10]

$$\int_0^\infty I(q)q^2\,\mathrm{d}q = 2\pi^2 V(\Delta\rho)^2 = Q \qquad (2)$$

which does not depend on special features of the structure but only on the mean square fluctuation of the electron density.

Porod[10] has shown that the scattering tail intensity (i.e., at high q values) for particles with a well-defined surface S tends to a constant value:

$$I(q) \to 2\pi S(\Delta\rho)^2/q^4 \qquad (3)$$

The practical application of eq 3, for example, to deduce the amount of interfaces, requires the measurements of absolute intensities. If these are not available, the intensity can be normalized by the invariant Q to obtain the specific surface:

$$S/V = \pi\lim_{q\to\infty} I(q)q^4/Q \qquad (4)$$

From the specific surface we can also calculate the radius for spherical particles, sometimes called Porod radius R_P.

More generally, in the case of a system with a random distribution of scattering entities in a homogeneous matrix,[11] the characteristic function is given by

$$\gamma_0(r) = \exp(-r/a) \qquad (5)$$

where a is a correlation length, related to correlated fluctuations of the electronic density $\Delta\rho$.[12] In relative units the intensity can be expressed by

$$I(q) = I(0)/(1 + q^2a^2)^2 \qquad (6)$$

Experimental Section

Hygroscopic glasses from the family $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ with compositions $x = 0$, 0.14, 0.28, 0.43, 0.5, 0.57, 0.64, 0.71, 0.86, and 1 were prepared using the twin roller quenching technique according to the procedure described elsewhere.[8] The amorphous nature of the materials thus obtained was checked by X-ray diffraction. The vitreous transition temperature, T_g, was measured by differential scanning calorimetry (Mettler Instrument) using a heating rate of 10 °C/min and taking the onset of the change in the baseline as T_g. The densities of the glasses were determined by pycnometry using benzene.

The electrical characteristics were obtained by impedance spectroscopy using a HP 4192A impedance meter. The measurements were performed on films obtained by twin roller quenching. The electrodes were graphite-reinforced polyethylene disks. The temperature range investigated extended from −50 to 150 °C.

Raman spectra were recorded at room temperature in the range 50–500 cm^{-1} using an Omar 89 Dilor spectrophotometer (the wavenumber accuracy of all sharp bands is ±4 cm^{-1}). The sample, contained in a sealed Pyrex ampule, was excited with an argon ionized laser (Spectra Physics 164-300 mW) at 514.5 nm.

Preparation of glasses with the twin roller quenching technique allowed samples to be obtained with the optimal thickness of about 50–100 μm for SAXS measurements. Because of their highly hygroscopic character, all samples were covered with a capton foil. The experiments were carried out on the D22 beamline at LURE, Orsay (France), in a setup
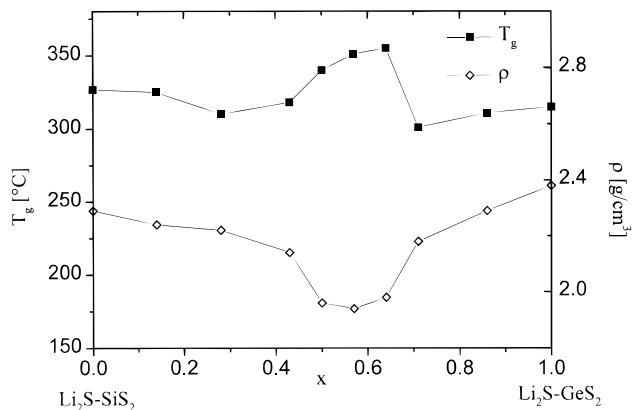

Figure 1. Variations of the glass transition temperature T_g and of the density ρ with composition x in the glassy system $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$.

described elsewhere.[13] A pinhole collimation and an energy selection at 9000 eV were obtained by slits and a double Ge(111) monochromator. The distance between the sample and the linear gas detector was 1625 mm. All spectra were corrected for the primary intensity of the beam, sample to detector distance, solid angle, counting time, detector dead time, sample absorption, and thickness. The spectra are in relative but consistent units.

Results

Glasses were obtained in the whole composition range in the system $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$. Figure 1 shows the variations of the glass transition temperature T_g and of the density ρ, respectively, when SiS_2 is substituted by GeS_2 in the glassy matrix. Nonlinear variations were observed in both cases. While the first additions of a second glass former (GeS_2 in Li_2S-SiS_2, i.e., $x < 0.5$, or SiS_2 in Li_2S-GeS_2, i.e., $x > 0.64$) induced a smooth decrease in both T_g and ρ, any further additions, i.e., $0.5 \le x \le 0.64$, led to a sudden change in the curves with a large increase in T_g corresponding to a large decrease in ρ.

The conductivity at room temperature $\sigma_{25°C}$ and the activation energy for conduction E_a derived from Arrhenius plots of conductivity ($\sigma = \sigma_0 \exp(-E_a/kT)$ for each glass are plotted as a function of x in Figure 2. Note that the preexponential factor σ_0 is almost constant and $\log(\sigma_0 [Scm^{-1}] = 1.8)$. Therefore any change in σ is related to a change in the activation energy E_a. The variations of the electrical characteristics, as shown in Figure 2, are closely related to those of T_g and ρ. A sudden break in the curves corresponding to a large increase in conductivity of about 2 orders of magnitude and a decrease in activation energy are indeed observed for the same compositions, i.e., $0.5 \le x \le 0.64$. Even though they contain only 30 mol % in modifier Li_2S, these glasses exhibit electrical characteristics very similar to those of glasses containing much larger amounts of modifier in the limiting binary systems $yLi_2S-(1-y)SiS_2$ (e.g., $y = 0.5$, $\sigma_{25°C} = 1 \times 10^{-4}$ Scm^{-1}, $E_a = 0.32$ eV) and $yLi_2S-(1-y)GeS_2$ (e.g., $y = 0.63$, $\sigma_{25°C} = 1.5 \times 10^{-4}$ Scm^{-1}, $E_a = 0.34$ eV).

Raman spectra were collected for all glasses, see Figure 3. The Raman spectra of glasses GeS_2 and

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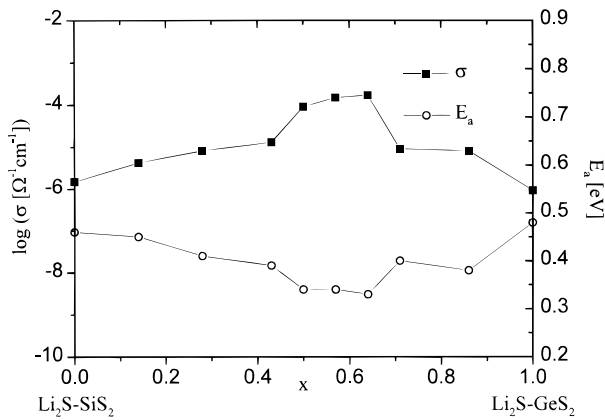
Figure 2. Variations of the conductivity at room temperature $\sigma_{25°C}$ and of the activation energy for conduction E_a with composition x in the glassy system $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$.

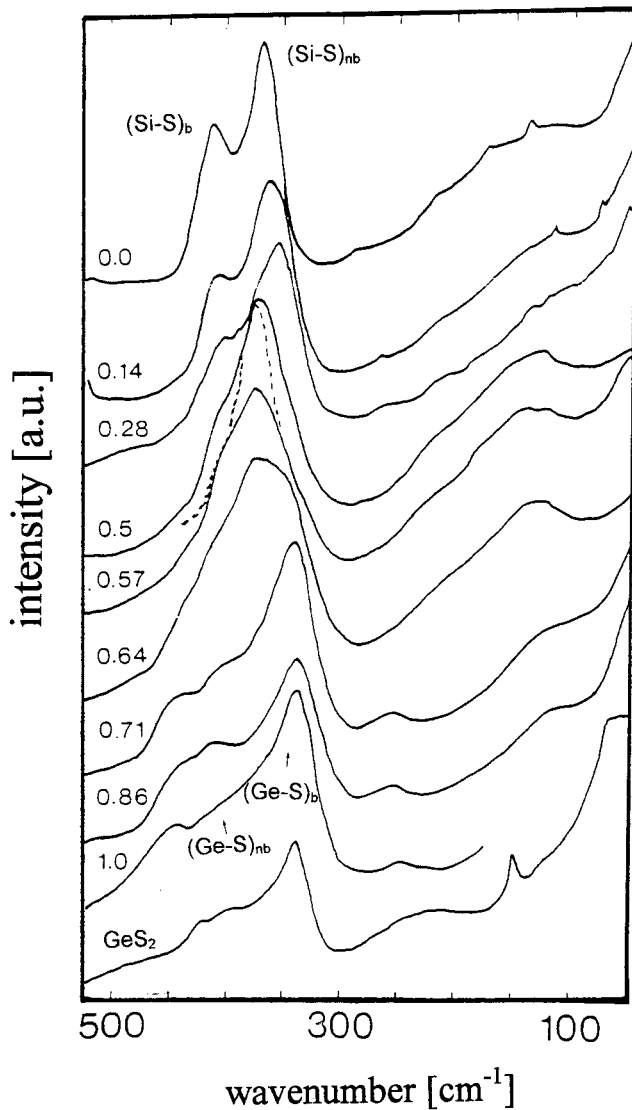**Figure 3.** Raman spectra for $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ glasses (the dotted line corresponds to the Raman spectrum of glass Li_2SiS_3).

Li_2SiS_3 (dotted line) are also reported for comparison. Structural studies of the glasses $yLi_2S-(1-y)SiS_2$ and $yLi_2S-(1-y)GeS_2$ by Raman spectroscopy have already been reported in the literature[9,14] and have shown that

the glasses are built up with tetrahedral units SiS_4 and GeS_4, respectively. For thiogermanate glasses, the larger peak at ~340 cm^{-1} was attributed to the stretching mode of the vibrations of bridging Ge−S bonds while the terminal stretching vibrations of nonbridging Ge−S$^-$ bonds were located in the frequency range ~425 cm^{-1}. For thiosilicate glasses, the stretching vibrations of bridging Si−S bonds appear as a peak located at high frequency (~410 cm^{-1}) while the large peak at lower frequency which shifted to higher frequency and increased in relative intensity when increasing the amount of modifier (368 cm^{-1} for $y = 0.3$ and 377 cm^{-1} for $y = 0.5$) was attributed to stretching vibrations of nonbridging Si−S$^-$ bonds. All the peaks characteristic of thiogermanate and thiosilicate glasses appear in a very narrow frequency range and they largely overlap. However, the general evolution of the spectra of the $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ glasses can be commented on.

First, three domains corresponding to different spectra evolutions can be observed. For the first substitution of a glass former by the other one i.e., for $0 \leq x < 0.50$ and $0.64 < x \leq 1$, a smooth change in the spectra is observed which is in agreement with the smooth changes observed for thermal and electrical characteristics in the same composition ranges. The first addition of germanium in the Li_2S-SiS_2 glass mainly led to a broadening of the Raman spectra. It probably results from the appearance of the peak characteristic of Ge−S bridging bonds at ~340 cm^{-1}. In the same way, the peak at ~408 cm^{-1} appearing in the Raman spectra when some silicon is introduced into Li_2S-GeS_2 is probably indicative of the appearance of Si−S bridging bonds in the glassy matrix. A sudden change in the Raman spectra is observed when the ratio Si/Ge is close to 1, i.e., for $0.5 \leq x \leq 0.64$. For $x = 0.5$, the Raman spectrum becomes narrower and the main peak suddenly shifts to higher frequency close to the frequency of the vibrations of Si−S$^-$ nonbridging bonds in glassy Li_2SiS_3. Raman spectra of Li_2SiS_3 and of glass with composition $x = 0.5$ are indeed very similar, even though the second one is broader. This feature can be related to the presence of additional Ge−S bonds in the second glass. It is consistent with the further broadening of the Raman spectra when more Ge is substituted for Si in the glassy matrix, i.e., for $x = 0.57$ and 0.64.

SAXS experiments were carried out on five selected glasses covering the three composition domains mentioned earlier, i.e., $x = 0.14$ and 0.43 for range I where $0 \leq x < 0.5$, $x = 0.57$ and 0.64 for range II where $0.50 \leq x \leq 0.64$, and $x = 0.86$ for range III where $0.64 < x \leq 1$. All $I = f(q)$ spectra recorded for these glasses present a monotonic decay of the scattered intensity as shown in Figure 4. However, the scattering is higher for samples belonging to range II than for samples belonging to limiting ranges I and III. The composition domains where important modifications are observed in Raman spectra and thermal and electrical characteristics correspond to composition domains where a change in the scattered intensities appears.

Satisfactory fits to the Debye−Bueche model (eq 6 plus a small constant background) were obtained only for glassy compositions lying in ranges I and III. In this
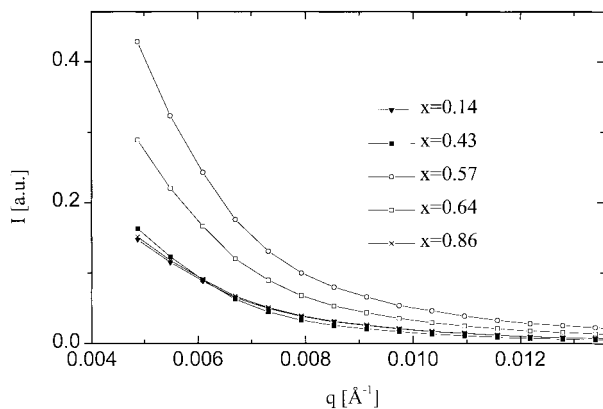
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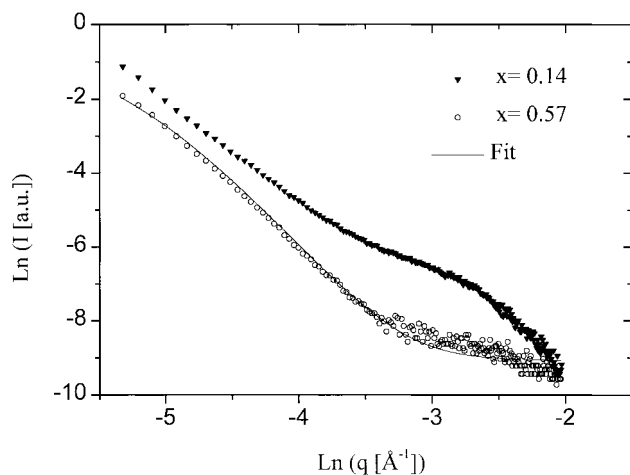**Figure 4.** SAXS spectra for $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ glasses.

Figure 5. Examples of scattering intensities for samples in the region I ($x = 0.14$) and samples in the region II ($x = 0.57$). For samples in the region III, the intensity curves are similar to those for samples in the region I and correspond to a Debye−Bueche model.

case correlation lengths of approximately 200 Å were found. These results indicate that there is no sharp phase boundary in these glassy matrixes.

On the other hand the curves obtained for samples of the central domain II obey Porod's law (eq 3). The corresponding Porod radius, R_P, of about 50 Å is indicative of the size of the aggregates present in the glass. Figure 5 shows examples of scattering curves that satisfy either the Debye−Bueche model (regions I and III) or Porod's law (region II).

Discussion

The glassy system $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ clearly shows an important mixed glass former effect with an increase of conductivity of about 2 orders of magnitude for the most conductive glass compared to that of the limiting compositions. The curve "conductivity vs composition" shows only a maximum which is similar to the results obtained on lithium borophosphate and unlike those reported for sodium and silver borophosphate or lithium borotellurate where two maxima were observed. The assumption of an hindered phase separation as proposed by Kone[6] therefore can be discarded. The increase in conductivity concerns the range II in which the substitution Si/Ge is close to 1/1, i.e., $0.50 \leq x \leq 0.64$. In fact, a sudden change of all the

investigated properties occurs for glasses belonging to this central region.

The analysis of SAXS data indicates that Porod's law applies to samples belonging to range II whereas the Debye−Bueche model is valid for glasses belonging to ranges I and III. These results indicate that a phase separation with the presence of aggregates with Porod radius of ~50 Å with sharp interfaces exists in region II, while homogeneous glasses with only weak inhomogeneities with a correlation length of ~200 Å are obtained in the two limiting ranges, i.e., $x < 0.5$ and $x > 0.64$.

These results are in agreement with the density measurements which indicate a lower density for the phase-separated glasses of the range II compared to the homogeneous glasses of limiting regions. It, therefore, appears that the first additions of Si (or Ge) in the limiting glasses $0.3Li_2S-0.7GeS_2$ (or SiS_2) result in a progressive substitution of Ge by Si (or vice versa) in the glassy matrix without any important structural change as indicated by smooth changes in the properties of the materials (Tg, ρ, nature of bondings, σ, and E_a). A phase separation appears suddenly when the substitution ratio Ge/Si is close to 1. An analysis of the experimental data (Tg, Raman spectra, and conductivity) shows that the phase separation cannot be understood by the appearance of a glass containing the two limiting compositions. This rather leads us to propose that the glasses of composition $0.5 \leq x \leq 0.64$ are phase separated with a phase close in composition to GeS_2 embedded in a phase close in composition to Li_2SiS_3. The Raman spectrum of glass $x = 0.5$ indeed shows the disappearance of the peak at 368 cm^{-1} related to stretching vibrations of Si−S$^-$ bonds in $0.3Li_2S-0.7SiS_2$ glass in favor of a peak at 377 cm^{-1} related to the same bonds but in the more modified glass $0.5Li_2S-0.5SiS_2$ (Li_2SiS_3). This peak remains unchanged in the Raman spectra of the two other compositions in range II. On the whole, the Raman spectra of glasses of the central region can be described as the sum of the Raman spectrum of Li_2SiS_3 and that of pure GeS_2 (Figure 3). Note that the Raman effective sections of the different entities have a strong influence on the relative intensities of the different peaks in glasses. In particular, Tenhover et al.[15] calculated the ratio of Raman effective sections for SiS_4 and GeS_4 entities, i.e., $S(SiS_4)/S(GeS_4)$ = 0.26 in $Si_xGe_{1-x}S_2$ glasses. The dominance of peaks attributed to GeS_2, especially for glass $x = 0.64$, can be understood by a larger Raman effective section for Ge-containing entities.

The electrical characteristics of the glasses of the central range also lead us to discard the presence of two phases with the composition of the limiting glasses (I and III). In this case, the conductivity would not be larger by 2 orders of magnitude than that of the most conducting limiting glass, i.e., $0.3Li_2S-0.7SiS_2$. On the other side, a glass containing insulating GeS_2 aggregates embedded in a phase close to Li_2SiS_3 might have a conductivity close to the most conducting phase, i.e., 10^{-4} Scm^{-1} as it is observed in glasses with $0.5 \leq x \leq 0.64$, if a percolation threshold is reached. In fact, the percolation must have occurred since the volume

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fraction of each phase is about 0.5 in the central region II ($\rho(Li_2SiS_3) \approx 2.2$ g cm^{-3} and $\rho(GeS_2) \approx 2.8$ g cm^{-3}). The strong increase in Tg is also in favor of a strong structural change with appearance of a more rigid phase and does not support the coexistence of the two limiting compositions in the glasses of the range II.

The above results can be closely related to experimental data reported for lithium germanosilicate glasses which are the oxide counterparts of the thiogermanosilicates under investigation in this work.[16]

The germanosilicate glasses arouse some interest because of their potential interest for fabrication of optical fibers, and therefore, their refractive indexes and densities were usually the properties investigated. In the course of these studies some singularities were observed. In the case of lithium glasses, they were attributed to a phase separation due to the Li tendency to place itself preferentially on Si-based tetrahedra rather than on Ge-based tetrahedra. One of the resulting glassy "phases" had then the composition of a defined crystalline phase, i.e., the lithium disilicate. On the other hand, for the system $0.33Li_2O-0.67[xSiO_2-(1-x)GeO_2]$, a composition which corresponds to lithium disilicate, homogeneous glasses were obtained with a statistical distribution of Li on Si- or Ge-based tetrahedra. In the case of the lithium thiosilicate systems, a crystalline thiodisilicate phase does not exist but the metathiosilicate Li_2SiS_3 phase does exist.[17] It is striking to note that a phase separation is observed for the system $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ with the tendency to produce a glassy "phase" with composition Li_2SiS_3. On the other hand, homogeneous glasses are obtained in the whole composition range in the case of the system $0.5Li_2S-0.5[(1-x)SiS_2-xGeS_2]$, a composition which corresponds to the metathiosilicate Li_2SiS_3.[8,9] It appears, therefore, that the mixed glass former effect observed in glasses $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ results from a phase separation and the presence of an insulating glassy "phase" ($\sim GeS_2$) embedded in a second glassy "phase" which contains almost all the modifier ions ($\sim Li_2SiS_3$). This result is in agreement with the fact that the mixed glass former effect appears only in some families of glasses. In some case, the substitution of a glass former by another occurs without apparition of phase separation as in the system $0.5Li_2S-0.5[(1-x)SiS_2-xGeS_2]$ and a monotonic variation of the conductivity is observed. In the same way a mixed glass former effect is not expected when a phase separation with a homogeneous distribution of the modifier ions in the two glassy "phases" occurs. This could be the case

for lithium borosilicate glasses reported by Levasseur.[18] In this case a phase separation occurs and a monotonic evolution of conductivity is observed. A last point can be underlined: the mixed glass former effect observed in borophosphates shows different aspects for sodium[6] and silver glasses[2] on one hand (with the presence of two maxima) and for lithium glasses[1] on the other hand (with the appearance of a maximum only as it is in lithium thiogermanosilicates). Since it is known that the tendency for glasses to phase separate increases when the cation size decreases, one might suggest that these results support the idea that the presence of one maximum is indicative of a phase separation while the presence of two maxima could be related to a hindered phase separation as proposed by Kone.[6]

Conclusion

Glasses of the $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ system were obtained over the whole composition range, $0 \leq x \leq 1$, by the twin roller quenching technique. A large enhancement of ionic conductivity of about 2 orders of magnitude for glasses belonging to the central region ($0.50 \leq x \leq 0.64$) showed the existence of a mixed glass former effect. The variations of the electrical characteristics were closely related to those of the glass transition temperature and the density.

Structural investigations by Raman and SAXS techniques were carried out in order to explain this phenomenon. Both Raman and SAXS data indicated important structural changes for glasses belonging to the central region compared to those belonging to the limiting compositions rich in one of the two formers SiS_2 or GeS_2. While Raman and SAXS data were consistent with homogeneous matrixes for glasses belonging to the limiting regions ($0 \leq x < 0.50$ and $0.64 < x \leq 1$), they pointed toward phase separation for glasses in the central region ($0.5 \leq x \leq 0.64$). SAXS analysis indeed indicated the presence of aggregates or clusters of 50 Å in size in this case, while Raman spectra could be described as the sum of the Raman spectra of GeS_2 and Li_2SiS_3 phases. The existence of these two entities for glasses of the central region is in agreement with the fact that these glass compositions show a high ionic conductivity close to that of Li_2SiS_3.

Therefore, the whole result gives strong support for the explanation that the mixed glass former effect in the system $0.3Li_2S-0.7[(1-x)SiS_2-xGeS_2]$ is caused by a phase separation with one phase containing almost all the modifier cations.

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