Glass-Forming Region and Structure in SiS_2–Li_2S–LiX (X = Br, I)

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The glass-forming region in the SiS_2–Li_2S–LiX (X = Br, I) system, as determined by X-ray diffraction, has been extended to higher lithium content by the use of a direct liquid nitrogen quench. The base glass, $0.4SiS_2$–$0.6Li_2S$, was synthesized and doping up to $0.28SiS_2$–$0.42Li_2S$–$0.30LiBr$ and $0.24SiS_2$–$0.36Li_2S$–$0.40LiI$ was achieved. The properties of these glasses are compared to the glasses formed by previously reported quenching methods.

Vibrational assignments have been made from infrared investigation of the glasses using FT-IR. The basic glass network consists of SiS_4 tetrahedra while the addition of Li_2S as a network modifier produced nonbridging sulfur. Doping with lithium halide did not significantly change the glass network, i.e., no changes in IR peak positions were observed. However, the higher lithium ion concentration resulted in higher mobility and ionic conduction. © 1987 Academic Press, Inc.

Introduction

In recent years sulfide-based lithium ion-conducting glasses as solid electrolytes have been developed (*1–8*) because of the higher polarizability of the sulfide offering lower potential barriers for ion transport than their oxide counterparts. In particular, the SiS_2-based glasses allow more flexibility in synthesis techniques and have higher glass transition temperatures (~300°C) compared with the systems containing P_2S_5 (*1*) or B_2S_3 (*2*) as glass formers. Until now, the highest conductivities have been reported with the latter glass formers.

The glass-forming region in the SiS_2–Li_2S–LiX (X = Br, I) system has now been extended by the use of a direct liquid nitrogen quench, thereby producing glasses possessing high lithium ion concentration and mobility and exhibiting conductivities up to 1.8×10^{-3} S/cm at 25°C for $0.24SiS_2$–

$0.36Li_2S$–$0.40LiI$ glass (*6*). We report here the glass-forming regions in the ternary systems determined by X-ray diffraction (XRD) analysis and structural information by infrared spectroscopy (IR).

Experimental

Glass synthesis. The starting materials for the glasses were anhydrous reagent-grade SiS_2 (Cerac, 99.9%), Li_2S (Alfa, 99%), LiBr (Alfa, 99%), and LiI (Cerac, 99%). All preparations of the samples for glass synthesis, XRD, and IR were carried out in a helium-filled glove box (<2 ppm H_2O) because of the extremely hygroscopic nature of the starting materials as well as the glass products.

For the synthesis of the base (undoped) glass, appropriate amounts of SiS_2 and Li_2S were fully ground and mixed, placed in a vitreous carbon crucible, covered, and then

placed in a Vycor tube. The tube was heated in a vertical tube furnace for 1 hr under argon. The temperatures for melting the mixtures were 950–1100°C, which were chosen according to the compositions. Then the covered crucible containing the melt was removed from the tube and plunged directly into a liquid nitrogen bath.

LiX-doped glasses were synthesized by thoroughly mixing the base glass with LiBr or LiI in the molar ratios desired, and heating at 950°C followed by quenching as described above.

XRD analysis. X-ray diffraction analysis was performed to determine any crystallinity in the glass products. The powdered glass samples were sealed in plastic bags and removed from the glove box just prior to the XRD experiment. A Norelco–Philips diffractometer with CuK_α radiation was used.

Conductivity measurement. Powdered glass samples were pressed into pellets of 0.74-cm diameter with pressed powder TiS$_2$ electrodes on both sides using uniaxial pressing followed by isostatic pressing at ~3 kbar. Conductivity was measured using complex impedance over the frequency range 1–10^6 Hz. Details of the method were reported previously (*8*) and a comprehensive report of electrochemical properties will be published later.

IR investigation. Samples were prepared using a KBr pellet technique and infrared spectra were recorded using a Bio-Rad Digilab FTS-60 Fourier transform IR spectrometer. Because of the relatively high alkali ion mobility there was concern that an ion-exchange reaction might take place between Li$^+$ in the glass and K$^+$ in the pellet matrix. However, similar experiments using CsI and AgBr pellets showed no change in peak positions from those observed in KBr. Therefore, we conclude that any ion-exchange process must be slow compared to the time scale of the IR experiment. Particular care in the preparation of IR pellet

samples had to be taken because of the sensitivity to moisture noted earlier and the high sensitivity of the FT-IR spectrometer to hydrolysis products. The glass powder was mixed with anhydrous IR-grade KBr powder in a 1 : 100 weight ratio in the glove box. Then 130 mg of KBr powder, 100 mg of the glass/KBr mixture, and 130 mg of KBr powder were placed sequentially into the barrel of the die and were hand-pressed with the plunger after each layer. The die containing the sample was covered with two plastic bags, removed from the glove box, and pressed at 15,000 lb immediately before the IR measurement. Then the sandwich pellet sample was mounted in the dry nitrogen-filled compartment, and the absorption spectrum was obtained in the region 400–1300 cm^{-1} with a 2.0-cm^{-1} resolution.

Results and Discussion

Glass-forming region. The glass-forming region of the SiS$_2$–Li$_2$S–LiX (X = Br, I) systems are shown in Figs. 1 and 2. They are very similar in shape; only the glass region for the LiI system was somewhat wider than that for the LiBr system. The
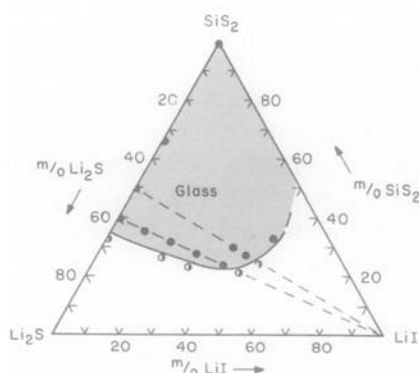

FIG. 1. Glass-forming region in Si$_2$S–Li$_2$S–LiI. Solid points indicate mixtures exhibiting no crystallinity by XRD. Partially solid points indicate mixtures exhibiting small amounts of crystalline LiI by XRD.

FIG. 2. Glass-forming region in $Si_2S-Li_2S-LiBr$. Solid points indicate mixtures exhibiting no crystallinity by XRD. Partially solid points indicate mixtures exhibiting small amounts of crystalline LiBr by XRD.
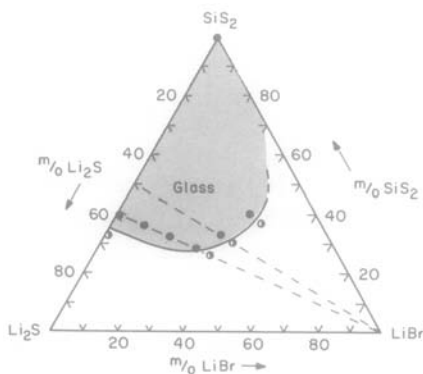
larger ionic radius and polarizability of the iodide ion compared to bromide probably contribute to the broader glass-forming region exhibited by LiI-doped glasses. Above 45 mole% LiI and 40 mole% LiBr, XRD analysis showed lines attributable to crystalline lithium halide.

With the direct liquid nitrogen rapid quenching method, the boundaries of the glass-forming region were extended to higher Li^+ content compared to conventional quenching reported previously (8), and the mole ratio for the dopant composition in the glasses reached 0.3 (LiBr) and 0.4 (LiI) even with the Li_2S-rich base glass composition of $0.4SiS_2-0.6Li_2S$. The resulting $0.24SiS_2-0.36Li_2S-0.40LiI$ glass exhibited a conductivity value of 1.8×10^{-3} S/cm at 25°C (6), which is one of the highest values ever reported for a Li^+-conducting sulfide glass or for any Li^+-conducting solid electrolyte at room temperature.

Our previous quenching method (8) for the preparation of SiS_2-Li_2S-LiX glasses ($X = I$, Br, Cl) was to immerse the entire Vycor tube into ice water or liquid nitrogen. With this quenching method, $0.4SiS_2-0.6Li_2S$ base glass could also be produced, but the maximum mole ratios for the dopant

were 0.2 (LiBr) and 0.3 (LiI). The conductivity was only 7.1×10^{-4} S/cm at 25°C for $0.28SiS_2-0.42Li_2S-0.30LiI$ glass, slightly lower than the value reported by Pradel and Ribes (7). These investigators reported that by using a twin-roller quenching technique, a base glass $0.4SiS_2-0.6Li_2S$ could be prepared. From this base glass they obtained a 0.3LiI doping level, and the conductivity of the resultant $0.28SiS_2-0.42Li_2S-0.30LiI$ glass was 8.2×10^{-4} S/cm at 25°C.

All of these results are summarized in Table I. It should be noted that the compositions of the base glasses containing a maximum amount of Li_2S as a glass network modifier were all identical. However, the quenching method reported here allowed higher values of LiI doping and consequently higher conductivities to be observed.

It should also be noted from Table I that the values of the conductivity of our present glasses are higher, even though activation energies are somewhat higher than those of Pradel and Ribes (7). This would imply that the present glasses have greater values for the preexponential term in the general conductivity equation

$$\sigma = A \exp(E_a/kT), \qquad (1)$$

TABLE I

COMPARISON OF THE RESULTS BY THREE DIFFERENT QUENCHING METHODS

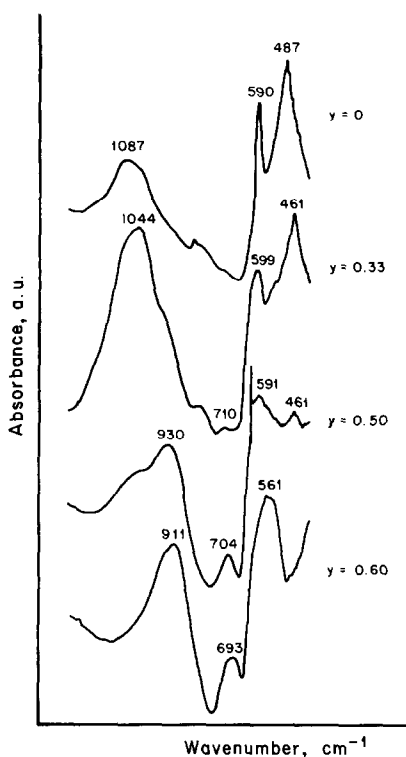| | Quenching method | | |
Composition	Twin-roller method (7)	Previously reported method (8)	Present method (6)
$(1 - y)SiS_2-yLi_2S$			
Max y	0.6	0.6	0.6
$\sigma_{25°C}$ (S/cm)	5.0×10^{-4}	1.5×10^{-4}	5.3×10^{-4}
E_a (eV)	0.25	0.36	0.33
log A	0.9	2.2	2.3
$(1 - x)(0.4SiS_2-0.6Li_2S)-xLiI$			
Max x	0.3	0.3	0.4
$\sigma_{25°C}$ (S/cm)	8.2×10^{-4}	7.1×10^{-4}	1.8×10^{-3}
E_a (eV)	0.27	0.31	0.28
log A	1.5	2.0	2.0

FIG. 3. FT-IR spectra for $(1 - y)\text{SiS}_2\text{-}y\text{Li}_2\text{S}$. Peak positions are given in wave numbers (cm^{-1}). (Note: the sharp peak at ~600 cm^{-1} for $y = 0.50$ is an instrumental artifact.)

IR spectra and glass structure. The IR spectra for the glass samples are shown in Figs. 3 and 4. The absorption bands of the spectra can be assigned to the vibrational modes in the glasses, and the changes observed in the spectra can be explained by comparing with previous studies involving silicate glasses (*10, 11*) and SiS₂ glass (*12, 13*).

There are three absorption bands in the spectrum of glassy SiS₂ (Fig. 3, $y = 0$). The highest-frequency peak at 1087 cm^{-1} can be identified as the stretching frequency for the Si–S–Si bridging bond in the tetrahedral framework of the glassy SiS₂. The lower-frequency peaks, 590 and 487 cm^{-1}, which are in good agreement with the results reported previously (*12*), involve bond-bending and bond-bending rock vibrations.

It should be noted that SiO₂ exhibits stretching frequencies near 1100 cm^{-1} (*10*)

where the preexponential term can be expressed as (*9*)

$$A = (ne^2d^2v_0/6kT) \exp\left[\left(\Delta S^* + \frac{\Delta S_d}{2}\right)\Big/ k\right].$$

(2)

In Eq. (2), ΔS_d and ΔS^* are entropy for the formation of the mobile ion and the activation entropy for its jump, d is the mean jump distance, and n is the bulk concentration of the mobile ion. Because the lithium ion bulk concentration in the present glasses is only slightly higher than that in the glasses reported by Pradel and Ribes (see Table I), any preexponential increase must be interpreted in terms of entropy and/or jump distance effects.
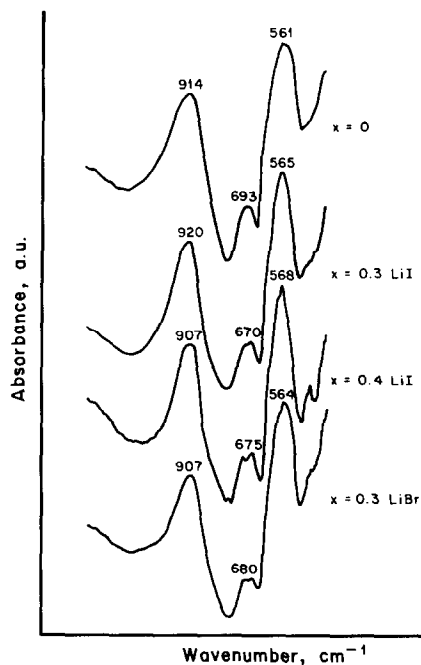

FIG. 4. FT-IR spectra for $(1 - x)(0.4\text{SiS}_2\text{-}0.6\text{Li}_2\text{S})\text{-}x\text{Li}X$. Peak positions are given in wavenumbers (cm^{-1}).

and that the observed band at 1087 cm^{-1} decreasing to 911 cm^{-1} as Li$_2$S increases might be due to SiO$_2$ impurity. As described under Experimental, the starting material was quoted as 99.9% pure, and the handling was quite rigorous (conductivity is extremely sensitive to moisture content). Finally, as a test of this possibility, 5% SiO$_2$ was added to the SiS$_2$ and the FT-IR spectrum recorded. Small new peaks at 1039, 1103, and 1198 cm^{-1} were observed. Thus, we conclude that the major peak at 1087 cm^{-1} can be attributed to SiS$_2$.

Two changes are clearly seen in the spectra of SiS$_2$–Li$_2$S glasses. First, the highest frequency of vibration decreased as the amount of Li$_2$S in the glasses increased. The variation may have resulted from the reduction of the force constant between Si and bridging S due to the presence of Li$_2$S as the glass network modifier. Second, a new absorption band appeared near 700 cm^{-1}, and its intensity increased gradually at the expense of the lowest band as the amount of Li$_2$S increased. One can assign the new band to the terminal stretching vibration of the Si–S$^-$ bond, i.e., a nonbridging S–Si stretching vibration, similar to the situation observed in the oxide analog.

On the other hand, the spectra of LiX-doped glasses (Fig. 4) showed that there was no discernible change in the absorption bands either when the amount of LiX increased up to 0.4 mole ratio or when LiI was replaced by LiBr. This result indicates that the LiX doping did not affect the basic structure of the glasses.

Thus, it can be concluded that in the SiS$_2$–Li$_2$S–LiX glasses, SiS$_4$ tetrahedra are the basic structural units of the glass network, and the addition of Li$_2$S as the glass modifier produces nonbridging sulfur. Addition of LiX as a dopant does not significantly change the glass network. However, this apparent lack of interaction with the glass network allows LiX additions to achieve higher lithium ion concentration and mobility (lower activation energy) and thereby increase ionic conduction in the glasses.

Conclusion

The rapid quenching method allowed a higher degree of disordered structure to remain in the glasses from the melts than in the conventional quenching method. Rapid quenching produced lower potential barriers for Li$^+$ transport in the glass, yielding higher ion mobility and conductivity. These glasses exhibited high preexponential terms in the conductivity equation, implying larger entropy terms or longer jumping distances than comparable glasses produced by other quenching techniques.

Second, a higher LiI saturation value, $x = 0.4$, in the doped glasses could be attained by the new rapid quenching method, even higher than the value reported for roller quenching. The more disordered structure combined with higher Li$^+$ content resulted in the exceptionally high conductivity value of 1.8×10^{-3} S/cm at 25°C for the 0.24SiS$_2$–0.36Li$_2$S–0.40LiI glass.

Acknowledgments

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