Tl\textsuperscript{+} ion conducting glasses in the Tl-Ge-S system

M. Bokova\textsuperscript{a,b,*}, I. Alekseev\textsuperscript{c}, E. Bychkov\textsuperscript{a,b}

\textsuperscript{a}Univ Lille Nord de France, Lille F-59000, France
\textsuperscript{b}ULCO, LPCA, EAC CNRS 4493, Dunkerque F-59140, France
\textsuperscript{c}St. Petersburg University, St. Petersburg 199034, Russia

Abstract

Tl\textsuperscript{+} ion conducting glasses in the (Tl\textsubscript{2}S)\textsubscript{x}(GeS)\textsubscript{50-x/2}(GeS\textsubscript{2})\textsubscript{50-x/2} system, where Tl\textsubscript{2}S concentration changes between 0 \leq x \leq 50, were analysed. The glass transition temperature decreases significantly with increasing x from 358 °C (x = 0) to 160 °C (x = 50), indicating a strong depolymerisation of germanium-sulphur network. Raman spectroscopy studies confirm this conclusion, reflected by changes in corner- and edge-sharing GeS\textsubscript{4} tetrahedra, GeS\textsubscript{4-n}Ge\textsubscript{n} tetrahedral units having Ge-Ge bonds at \approx 2.45 Å, and the appearance of non-bridging sulphur species. \textsuperscript{204}Tl tracer diffusion, dc conductivity and ac impedance measurements have been used to study ionic and total conductivity in the glasses. The glasses belong to ionic conductors and their conductivity increases drastically with increasing thallium concentration, ranging between 10\textsuperscript{-17} S cm\textsuperscript{-1} for the 50GeS-50GeS\textsubscript{2} matrix and 10\textsuperscript{-8} S cm\textsuperscript{-1} for Tl\textsubscript{2}S-rich glasses at 298 K, the activation energy decreases from 1.11 to 0.63 eV, respectively.

Keywords: chalcogenide glasses; ionic conductivity; Raman spectroscopy

1. Introduction

Chalcogenide glasses containing Ag\textsuperscript{+}, Li\textsuperscript{+}, Na\textsuperscript{+} or Cu\textsuperscript{+} exhibit very high ionic conductivity which makes them suitable for many applications, i.e., all-solid-state batteries, chemical sensors, etc [1-7]. Little is known about ion transport of heavy alkali cations or Tl\textsuperscript{+} except for a few communications [8-10]. In this paper we will present Tl\textsuperscript{+} ion conducting glasses in the (Tl\textsubscript{2}S)\textsubscript{x}(GeS)\textsubscript{50-x/2}(GeS\textsubscript{2})\textsubscript{50-x/2} system, where Tl\textsubscript{2}S concentration changes between 0 \leq x \leq 50. The main reason to choose this system was the
availability of large and homogeneous bulk glasses over the whole concentration range [11]. Thallium doped glasses were characterized by DSC measurements, Raman spectroscopy, $^{203}$Tl tracer diffusion, dc conductivity and ac impedance measurements.

2. Experimental details

2.1. Glass preparation

The Tl-doped glasses were prepared by mixing appropriate quantities of germanium (Aldrich 99.999%), sulphur (Aldrich 99.998%) and thallium (Fluka 99.99%). The mixtures were sealed under vacuum ($10^{-6}$ mbar) in a cleaned silica tube (with a inner diameter of 7 mm and a wall thickness of 1.5 mm), heated slowly to 900 °C at 1 K min$^{-1}$ heating rate and maintained at this temperature for a few days with repeated stirring of the melt. Once homogeneous, the glasses were cooled down to 800°C and quenched in water at 20°C. To avoid the high vapour pressure of the sulphur during initial steps of the synthesis, prolonged heating at 300, 500 and 800°C was necessary. Sample masses of 3 g were obtained. The quenched samples were annealed at 20-30°C below the glass transition temperature, $T_g$, for 24 h. Compositions of $(\text{Tl}_x \text{S})_y (\text{GeS})_{50-x/2} (\text{GeS}_2)_{50-x/2}$ glasses were synthesised for values of $x = 0, 10, 20, 30, 40, 50$ mol.%. All the samples have a dark coloured and shiny appearance. The amorphous nature of the samples was verified at room temperature by the neutron diffraction technique using the GEM diffractometer at the ISIS pulsed neutrons source at the Rutherford-Appleton Laboratory, UK.

2.2. DSC measurements

Differential scanning calorimetry, DSC, experiments were carried out using a Seiko SSC 5200 instrument at a heating rate of 10 K min$^{-1}$ in the temperature range from 20 to 600 °C. Samples of 10 to 15 mg, encapsulated in a standard aluminium pan, were used for DSC measurements. An empty aluminium pan was served as a reference, and high purity nitrogen N$_2$ as the purge gas. DSC traces were used to obtain the glass transition temperature $T_g$, as the temperature corresponding to the intersection of two linear portions adjoining the transition elbow of the DSC trace.

2.3. Raman spectroscopy measurements

Raman spectra over the spectral range 80–1200 cm$^{-1}$ were taken at room temperature using an LABRAM Dilor spectrometer (Jobin Yvon Horiba Group) equipped with a triple monochromator, liquid nitrogen cooled charge-coupled device (CCD) detector and a microscope. Raman scattering was excited using a 632.8 nm He–Ne laser with a typical power of 1mW or 0.1mW. Usually, from 2 to 4 spectra were measured for each sample at different positions and with different laser power in order to verify the sample homogeneity and the absence of photo-induced phenomena. The measurements of several spectra were especially important for Tl-rich sample where the photo-crystallization was observed under the laser beam with a power of 1mW.

2.4. Conductivity measurements

The dc conductivity of the samples with high resistance was measured using a Hewlett Packard 4339B high resistance meter with the voltage of 100 volts. For the thallium rich samples having resistance $R \leq 10$ MΩ, the ac conductivity was measured using a Hewlett Packard 4194A impedance meter.
The impedance modulus $Z$ and the phase angle $\theta$ were obtained in the frequency range from 100 Hz to 15 MHz. Both methods (dc conductivity measurements at lower temperatures and ac impedance measurements at higher temperatures) gave the same results for thallium rich glasses. The temperature range of the electrical measurements was usually from 20 to 200 °C or less depending on $T_g$ and glass resistivity. Further details on conductivity measurements were published previously [12].

2.5. $^{204}$Tl tracer preparation

The $^{204}$Tl tracer (the half-life $t_{1/2} = 3.783$ y) was produced by the $^{203}$Tl(n,\gamma)$^{204}$Tl nuclear reaction. The TlNO$_3$ target (144 mg, 99.9% chemical purity) was irradiated in a water channel of a research reactor of St. Petersburg Nuclear Physics Institute using thermal neutrons with an average flux of $8.0(2) \times 10^{13}$ n cm$^{-2}$ s$^{-1}$. After irradiation, the final (end of bombardment) specific $^{204}$Tl gamma activity was 0.3 mCi mg$^{-1}$, the radiochemical purity was 99.9%. The irradiated target was dissolved in 5 mL of 2 M HNO$_3$. The $^{204}$TlNO$_3$ solution for tracer measurements was further prepared by dilution of the primary solution using 0.04 M HNO$_3$. The typical thallium content in the last solution was below 300 $\mu$g mL$^{-1}$.

2.6. Tracer diffusion measurements

The quenched samples of different compositions, prepared as rectangular plates, were polished using abrasive powder, the samples sides were ground parallel. Typical thickness of the samples was 800-1800 m, the thickness uncertainty was ± 5 $\mu$m. A drop of radioactive $^{204}$TlNO$_3$ solution was deposited onto one face of the sample, kept there for 80 min, wiped with a filter paper, washed with distilled water and ethyl alcohol, and then dried. The samples were annealed in a furnace at 140 °C (the temperature measurements uncertainty was ± 2°C) for a period of 23 d.

A high-purity Ge detector (GX1018, Canberra Ind., USA) was used to measure the initial and residual gamma activity of the sample before and after sectioning. Spectrometer calibration in the energy range from 0.020 MeV to 1.600 MeV was carried out using $^{109}$Cd, $^{152}$Eu, $^{241}$Am sources with different activities. The gamma activity of the samples was determined using characteristic $^{204}$Hg photopeaks in the energy range 60–80 keV, whose quantum efficiency was 0.095–0.789%. The samples were placed in a polyethylene cell (the radioactive face in the bottom) in a well-defined fixed geometry. The measurements of the initial and residual (after each sectioning) gamma activity were carried out for 1000 s. A Genie 2000 program (Canberra Ind., USA) was used for data analysis. Other details concerning tracer diffusion measurements were published elsewhere [2, 7].

3. Results and discussions

3.1. Glass-forming ability and thermal properties of Tl-Ge-S glasses

Diffraction pattern of the sample with $x = 40$ exhibit only broad features characteristic of glassy and amorphous materials. For the other samples with Tl$_2$S content below 40 mol.%, $0 \leq x \leq 40$, the Bragg peaks were not observed. The low intensity Bragg peaks appear for the sample with $x = 50$ and correspond to crystalline germanium. Nevertheless, the glass phase remains predominant for this sample. Therefore, we estimate the limit of glass formation in the (Tl$_2$S)$_x$(GeS)$_{50-x/2}$(GeS$_2$)$_{50-x/2}$ system to be at $x \approx 50$ mol.% in our conditions of glass synthesis and quenching. Our glass forming region is larger than that obtained by Linke (Fig. 1) [11].
A single glass transition is observed for all the samples, indicating a homogeneous glass nature on macroscopic and mesoscopic scale. The composition dependence of $T_g$ is plotted in Fig. 2. As expected, the glass transition temperature decreases significantly with increasing $x$ from 358 °C ($x = 0$) to 160 °C ($x = 50$), indicating a strong depolymerisation of germanium-sulphur network. This behaviour is very similar to that observed with increasing modifier cation concentration in binary vitreous system [4, 8]. The obtained results are consistent with an increase of modifier atoms reducing the number of bridging sulphur atoms, thus creating a more broken-up network structure.

Fig. 2. Composition dependence of glass transition temperature $T_g$ for $(\text{Tl}_2\text{S})_x(\text{GeS})_{50-x/2}(\text{GeS}_2)_{50-x/2}$ glasses. The solid line is drawn as a guide for the eye.

### 3.2. Raman spectroscopy results

The typical Raman spectra of $(\text{Tl}_2\text{S})_x(\text{GeS})_{50-x/2}(\text{GeS}_2)_{50-x/2}$ glasses are shown in Fig. 3. The Raman spectra represent basically two regions below and above 200 cm$^{-1}$. The low-frequency ‘bond-bending’ region is related to translational (T), rotational (R), E, and lower $F_2$ motions of the GeS$_2$ tetrahedra [13].
The spectral features of this region are broad and unresolved. We do not use therefore the region below 150 cm\(^{-1}\) in further data analysis and subtracted the related features as a background. The background was fitted by a Voigt function and subtracted from the experimental data. The intensity of Raman spectra was normalized to the most intense peak.

The spectrum of glassy \((\text{GeS})_{50}(\text{GeS}_2)_{50}\) is in accordance with previously published results for Ge-rich thiogermanate glasses [14-16]. The broad poorly resolved Raman features in the 350–430 cm\(^{-1}\) range are essentially attributed to Ge–S vibrations in the corner-chairing (CS-) and edge-chairing (ES-) \(\text{GeS}_{x/2}\) tetrahedra from \(\text{GeS}_2\) glassy structure. Among the peaks, the peak at 347 cm\(^{-1}\) was assigned to the symmetric breathing \(A_1\) mode of S atoms at CS-\(\text{Ge(S}_{1/2})_4\) tetrahedra and its companion line at 374 cm\(^{-1}\) and the mode at 410 cm\(^{-1}\) to symmetric stretching and vibrations in ES-\(\text{Ge(S}_{1/2})_4\) tetrahedra. In the low-frequency region, the features at 255 cm\(^{-1}\) and at 225 cm\(^{-1}\) with a shoulder at \(\approx 200\) cm\(^{-1}\) were consistent with existence of \(\text{GeS}_{x/z}\text{Ge}_n\) tetrahedral units with fewer than four S atoms having Ge-Ge bonds at \(\approx 2.45\) Å [14, 15]. Finally, a weak feature at \(\approx 290\) cm\(^{-1}\) can be attributed to a-Ge, since the asymmetric peak 290 cm\(^{-1}\) was already observed in the Raman spectra of Ge films [17]. The detection of crystalline germanium phase in the diffraction pattern of \((\text{Tl}_2\text{S})_{50}(\text{GeS})_{25}(\text{GeS}_2)_{25}\) glass is consistent with this Raman mode attribution.

![Raman spectra of the \((\text{Tl}_2\text{S})_{(50-x/2)}\text{GeS} (50-x/2)\text{GeS}_2\) glasses.](image)

Fig. 3. Raman spectra of the \((\text{Tl}_2\text{S})_{(50-x/2)}\text{GeS} (50-x/2)\text{GeS}_2\) glasses.

There are several changes in Raman spectra with thallium addition. The \(A_1\) mode at 347 cm\(^{-1}\) for glassy \((\text{GeS})_{50}(\text{GeS}_2)_{50}\) gradually shifts to higher frequency region with thallium concentration up to 363 cm\(^{-1}\) for \(x = 50\). This result is opposite to those observed previously, where the \(A_1\) mode shifted to
lower frequency region with the addition of the network modifier in the $x$Mg$_2$S$_{(1-x)}$GeS$_2$ systems [5, 18, 19]. The $A_1$ mode shift is accompanied by parabolic behaviour of Raman modes intensities at 255 cm$^{-1}$ and 200 cm$^{-1}$ with the minimum at $x = 20$ and non-monotonous variation of the feature intensity at 225 cm$^{-1}$. All these changes in Raman spectra indicate the transformation of glassy thiogermanate matrix with thallium addition. A new feature appears at $\approx 422$ cm$^{-1}$ for $x \geq 10$. This feature can be attributed to Ge–S terminal bond vibrations. Its intensity increases and the feature shifts to lower frequencies with increasing Tl$_2$S concentration (397 cm$^{-1}$ for $x=50$). Such behaviour is consistent with breaking of Ge–S–Ge bridges and the creation of non-bridging sulphur Ge–S terminal bonds. This phenomenon was observed for $x$Mg$_2$S$_{(1-x)}$GeS$_2$ stoichiometric compositions where M = Ag, Tl, Li, Na, K, Rb, Cs [1, 3-6, 8, 18, 19]. The creation of germanium–sulphur tetrahedra with one Ge–S$^-$ bond (GeS$_{3/2}$S$^-$), two Ge–S$^-$ bonds (GeS$_{2/2}$S$_2^{2-}$) or three Ge–S$^-$ bonds (GeS$_{1/2}$S$_3^{3-}$) was proposed and explained by the development of Raman modes ranging from 480 to 400 cm$^{-1}$ [4, 18, 19]. Generally, its position shifts to lower frequencies as the number of bridging sulphur per Ge atom decreases. Another new feature at $\approx 300$ cm$^{-1}$ appears and shifts up to 330 cm$^{-1}$ with thallium content. The appearance of this Raman mode with cation addition was not observed earlier. Nevertheless, this mode can also be discussed in terms of the vibrational characteristics of thiogermanate tetrahedral units containing terminal bonds. The existence of this feature can be explained by the complexity of the non-stoichiometric (GeS)$_{50}$GeS$_{250}$ host matrix and by the shift of $A_1$ mode to lower frequency region with the addition of the network modifier in the $x$Mg$_2$S$_{(1-x)}$GeS$_2$ systems.

3.3. Electric conductivity and preliminary $^{204}$Tl tracer diffusion results

The temperature dependence of total electrical conductivity, determined either by the complex impedance method ($\sigma \geq 10^{-9}$ S cm$^{-1}$) or from dc measurements ($\sigma < 10^{-9}$ S cm$^{-1}$) for the (Tl$_2$S)$_x$(GeS)$_{50-x/2}$GeS$_{250-x/2}$ glasses is presented in Fig. 4. The conductivity follows the Arrhenius law:

$$\sigma = \sigma_0 \exp \left( - \frac{E_\sigma}{kT} \right)$$

(1)

where $\sigma_0$ is the pre-exponential factor, $E_\sigma$ the activation energy, $k$ the Boltzman constant and $T$ the temperature. The room-temperature conductivity $\sigma_{298}$, $E_\sigma$, $\sigma_0$ were calculated from a least-square fit of the data to Eq.(1). The room-temperature conductivity increases drastically with increasing thallium concentration from the values which are typical of insulating glasses ($10^{-17}$ S cm$^{-1}$ for the 50GeS-50GeS$_2$ matrix) to the values which are characteristic of rather low ion-conducting vitreous alloys ($10^{-8}$ S cm$^{-1}$ for Tl$_2$S-rich glasses). A similar behaviour has been observed in the cases of the silver or alkali doped thiogermanate glasses [4, 8]. The increase in the conductivity is accompanied by a decrease in the activation energy from 1.11 to 0.63 eV. In contrast, the values of the pre-exponential factor do not change significantly within the experimental uncertainty.

Penetration profiles for $^{204}$Tl tracer diffusion in the (Tl$_2$S)$_x$(GeS)$_{50-x/2}$GeS$_{250-x/2}$ glasses obey the usual solution of Fick’s law for an infinitesimally thin deposit of radioactive isotope on a semi infinite specimen [20]

$$1 - \frac{A(a,t)}{A_0} = \text{erf}(q),$$

(2)
where

\[ q = \frac{a}{2\sqrt{D_T t}} \]

\( A(a,t) \) is the residual activity of the sample after a thickness \( a \) was removed, \( t \) is the diffusion anneal time, \( A_0 \) is the initial residual activity, \( D_T \) is the tracer diffusion coefficient, and \( \text{erf}(q) \) is the Gauss error function. Experimentally determined values of \( A(a,t) \) and \( A_0 \) yield \( q \) values which, when plotted vs. \( a \), produce a straight line passing through the origin. The thallium tracer diffusion coefficients \( D_T \) can be determined from the slope of the penetration profiles according to Eq. (3). Figure 5 shows that the conductivity and tracer diffusion isotherms at 140 °C for the Tl-rich glasses (\( x = 40 \) and 50 mol.% Tl\(_2\)S) are very similar. These results are consistent with the assumption that thallium doped thiogermanate glasses exhibit Tl\(^+\) cation conductivity.

Figure 6 presents a comparison between the room temperature conductivity values for our \( (\text{Tl}_2\text{S})_x(\text{GeS})_{50-x/2}(\text{GeS}_2)_{50-x/2} \) glassy system and \( x\text{Mg}_x\text{S}_y-(1-x)\text{GeS}_2 \) stoichiometric thiogermanate glasses, where \( \text{M}=\text{Ag, Li, K, Rb, Cs} \). The ionic conductivity increases with increasing concentration of alkali cations and decreases with the cation size. In each glass series, the glass with the highest cation atomic fraction has the highest conductivity. The light alkali cations exhibit high conductivity at room temperature (\( 10^{-5} \) and \( 10^{-6} \) S cm\(^{-1}\) for the lithium and sodium thiogermanate glasses, respectively [4, 6]) attributed to smaller ionic radius. The conductivities for the heavy alkali thiogermanate glasses are several
orders of magnitude lower and are comparable with thallium doped glasses which is explained by the larger cation size. The same trend is observed for the activation energy variation. Figure 7 shows the dependence of activation energy on cation (M⁺) radius for the same cation concentration. The activation energy increases with ionic radius. Silver ion behaves differently compared to alkalis due to its electronic structure. It should be noted that thallium behaviour is similar to heavy alkalis.

![Graph](image_url)

**Fig. 5.** Composition dependences of the diffusion coefficient \( D_{Tl} \) (●) and conductivity \( \sigma_{140} \) (○) for the \((Tl_2S)_x(\text{GeS})_{50-x/2}(\text{GeS}_2)_{50-x/2}\) glasses at 140°C

![Graph](image_url)

**Fig. 6.** Comparison of room temperature conductivity for the \((Tl_2S)_x(\text{GeS})_{50-x/2}(\text{GeS}_2)_{50-x/2}\) glass system (open circles) and for the \(x\text{Mg}_2S_{(1-x)}\text{GeS}_2\) (M = Ag, Li, Na, K, Rb, Cs) systems (solid symbols) taken from [4, 8]. The lines are drawn as guides for the eye.
0.6 0.8 1.0 1.2 1.4 1.6
0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Activation energy $E_a$ (eV)

$R_M$ (Å)

Ag
K
Li
Na
Rb
Tl

Fig. 7. Dependence of $E_a$ on cationic (M⁺) radius for the thallium doped glass in the (Tl₂S)$_x$(GeS)$_{50-x/2}$ (GeS₂)$_{50-x/2}$ system (open circle) and for the $x$Mg₂S-(1-$x$)GeS$_2$ (M=Ag, Li, Na, K, Rb) systems (solid symbols) taken from [4, 8] for the cation concentration of 13.33 at.%. Values were extrapolated for silver, lithium and sodium glasses and measured for thallium, potassium and rubidium alloys. The solid line is a guide for the eye.

4. Conclusions

Tl⁺ ion conducting glasses in the (Tl₂S)$_x$(GeS)$_{50-x/2}$ (GeS₂)$_{50-x/2}$ system, where Tl₂S concentration changes between 0 $\leq x \leq 50$, have been analyzed. The glass transition temperature decreases significantly with increasing $x$ from 358 °C ($x = 0$) to 160 °C ($x = 50$), indicating a strong depolymerisation of germanium-sulphur network. Raman spectroscopy studies confirm this conclusion, reflected by changes in corner- and edge-sharing GeS₄ tetrahedra, GeS₄-Ge₄ tetrahedral units having Ge-Ge bonds at $\approx 2.45$ Å, and the appearance of non-bridging sulphur species. $^{204}$Tl tracer diffusion, dc conductivity and ac impedance measurements have been used to study ionic and total conductivity in the (Tl₂S)$_x$(GeS)$_{50-x/2}$ (GeS₂)$_{50-x/2}$ glasses. The glasses belong to ionic conductors and their conductivity increases drastically with increasing thallium concentration, ranging between $10^{-17}$ S cm$^{-1}$ for the 50GeS-50GeS₂ matrix and $10^{-8}$ S cm$^{-1}$ for Tl₂S-rich glasses at 298 K; the activation energy decreases from 1.11 to 0.63 eV, respectively.

Acknowledgements

The authors are grateful to Dr. Alex C. Hannon (ISIS Facility, UK) and Myriam Moreau (University of Lille I, France) for help with neutron diffraction and Raman spectroscopy measurements, respectively. This work was supported by the European Commission within the Interreg IVA 2 Seas programme, CleanTech project.

References


