Short Range Structural Models of the Glass Transition Temperatures and Densities of 0.5Na2S + 0.5[xGeS2 + (1 – x)PS5/2] Mixed Glass Former Glasses

Christian Michael Bischoff
Iowa State University, bischoff@iastate.edu

Katherine Schuller
Iowa State University

Steve W. Martin
Iowa State University, swmartin@iastate.edu

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Abstract
The 0.5Na2S + 0.5[xGeS2 + (1 – x)PS5/2] mixed glass former (MGF) glass system exhibits a nonlinear and nonadditive negative change in the Na+ ion conductivity as one glass former, PS5/2, is exchanged for the other, GeS2. This behavior, known as the mixed glass former effect (MGFE), is also manifest in a negative deviation from the linear interpolation of the glass transition temperatures (Tg) of the binary end-member glasses, x = 0 and x = 1. Interestingly, the composition dependence of the densities of these ternary MGF glasses reveals a slightly positive MGFE deviation from a linear interpolation of the densities of the binary end-member glasses, x = 0 and x = 1. From our previous studies of the structures of these glasses using IR, Raman, and NMR spectroscopies, we find that a disproportionation reaction occurs between PS7/24- and GeS32- units into PS43- and GeS5/21- units. This disproportionation combined with the formation of Ge4S104+ anions from GeS5/21- groups leads to the negative MGFE in Tg. A best-fit model of the Tgs of these glasses was developed to quantify the amount of GeS5/21- units that form Ge4S104+ molecular anions in the ternary glasses (~5–10%). This refined structural model was used to develop a short-range structural model of the molar volumes, which shows that the slight densification of the ternary glasses is due to the improved packing efficiency of the germanium sulfide species.

Disciplines
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Comments
Short Range Structural Models of the Glass Transition Temperatures and Densities of 0.5Na$_2$S + 0.5[xGeS$_2$ + (1 - x)PS$_{5/2}$] Mixed Glass Former Glasses

Christian Bischoff,$^\dagger$ Katherine Schuller,$^\ddagger$ and Steve W. Martin$^{\ast,\S}$

Department of Materials Science and Engineering Iowa State University Ames, Iowa 50011, United States

ABSTRACT: The 0.5Na$_2$S + 0.5[xGeS$_2$ + (1 - x)PS$_{5/2}$] mixed glass former (MGF) glass system exhibits a nonlinear and nonadditive negative change in the Na$^+$ ion conductivity as one glass former, PS$_{5/2}$, is exchanged for the other, GeS$_2$. This behavior, known as the mixed glass former effect (MGFE), is also manifest in a negative deviation from the linear interpolation of the glass transition temperatures ($T_g$) of the binary end-member glasses, $x = 0$ and $x = 1$. Interestingly, the composition dependence of the densities of these ternary MGF glasses reveals a slightly positive MGFE deviation from a linear interpolation of the densities of the binary end-member glasses, $x = 0$ and $x = 1$. From our previous studies of the structures of these glasses using IR, Raman, and NMR spectroscopies, we find that a disproportionation reaction occurs between PS$_{7/2}$ and GeS$_2$ units into PS$_4$ and GeS$_{1/2}$ units. This disproportionation combined with the formation of Ge$_4$S$_{10}^4$ cations from Ge$_{5/2}^2$ groups leads to the negative MGFE in $T_g$. A best-fit model of the $T_g$ of these glasses was developed to quantify the amount of Ge$_{5/2}^2$ units that form Ge$_4$S$_{10}^4$ molecular anions in the ternary glasses ($\sim 5\% - 10\%$). This refined structural model was used to develop a short-range structural model of the molar volumes, which shows that the slight densification of the ternary glasses is due to the improved packing efficiency of the germanium sulfide species.

INTRODUCTION

Reliable energy storage systems are required to meet the demand for renewable energy. Global conversion and use of energy is currently ~15 TW and is expected to double by 2050. The typical electrical power profile of renewable energy sources, chiefly solar and wind, are cyclic in nature. To enable these renewable energy sources to help meet the rapidly growing worldwide demand for low cost and abundant electricity requires the development of new energy storage technologies. Electrochemical energy storage systems, such as batteries, are attractive energy storage systems for use with renewable energy systems as they can be low cost, scalable, safe, energy dense, and compatible with a wide range of deployments from home to neighborhood to city level installations. Currently, rechargeable lithium-ion batteries depend on liquid electrolytes that foster lithium dendrite growth, leading to severe safety concerns in large grid scale energy storage applications. The development of solid electrolytes with sufficient alkali ion conductivities, at least 10$^{-4}$ S/cm at 25 °C, may offer a solution to this safety problem. Alkali ion conducting glasses, especially those based on ubiquitously available and hence very low cost sodium, may enable new types of solid state sodium batteries that may be able to meet these challenging design constraints. On a volumetric basis, typical sodium batteries have very comparable energy densities to typical lithium-ion batteries.

In the search for new, low cost, easily prepared, and high conductivity Na$^+$ ion conducting solid electrolytes, a rare coincidence of high ionic conductivity with improved physical and electrochemical properties of glassy solid electrolytes can be achieved by mixing two glass former cations, such as B and P, at constant fraction of the mobile cation and this effect has become known as the mixed glass former effect (MGFE). For this reason, we have begun an in-depth study of the MGFE in both oxide and sulfide glasses. Currently, the structures and properties of sodium modified MGF systems that are being studied include B$_2$O$_3$, SiO$_2$, P$_2$O$_5$, SiS$_2$, GeS$_2$, and P$_2$S$_5$ glass formers and these are being characterized in an effort to better understand and exploit the MGFE to enable the development of optimized solid electrolytes for next-generation solid state sodium batteries.

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MGF glasses are found to exhibit the first ever reported negative MGFE in the ionic conductivity, it is of great interest to determine whether this negative MGFE is present in other physical properties. To this end, in this study we report the composition dependence of the glass transition temperature, \( T_g \) and the density, \( \rho \), of these \( 0.5\text{Na}_2\text{S} + 0.5\text{[xGeS}_2 + (1-x)\text{PS}_5/2] \) MGF glasses and a detailed atomic level model that is not only able to fully interpret the composition dependence of the \( T_g \) and density, but in so doing we are able to refine our previously published model\(^{23} \) of the composition dependence of the various short-range order (SRO) thiophosphate and thiogermanate structures present in these glasses. This refinement has enabled the distinction between molecular-like, Ge\(^{3M} \), and network-like, Ge\(^{3B} \), thiogermanate SRO structures in these glasses which we find are critical to the accurate modeling of the composition dependence of the \( T_g \) of these glasses.

**EXPERIMENTAL METHODS**

**Sample Preparation.** All syntheses were carried out in a high purity \( \text{N}_2 \) glovebox, where \( \text{O}_2 \) and \( \text{H}_2\text{O} \) levels are below 10 ppm and typically below 1 ppm. Since high purity \( \text{Na}_2\text{S} \) is not commercially available, it was synthesized in our laboratory by the thermal decomposition of \( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \). The \( \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O} \) was placed in a vitreous carbon crucible that was placed in a stainless steel reaction chamber. This reaction chamber was then placed in a vertical crucible furnace so that the sample was within the heated section of the furnace and the top sealing section of the reaction chamber extends outside the furnace. The reaction chamber was sealed with a water cooled rubber O-ring gasketed stainless steel top and connected to a vacuum pump. The hydrated crystalline material was then slowly heated under vacuum up to 150 °C over a period of at least 2 h, after which the temperature was slowly increased to 650 °C and held for approximately 20 h. The reaction chamber containing the now dehydrated \( \text{Na}_2\text{S} \) was transferred to the glovebox and unloaded. IR spectroscopy and X-ray diffraction (XRD) were used to confirm the absence of contaminant oxides and the phase purity, respectively, of the material. Glassy Ge\(_2\text{S}_3\) was prepared by reacting stoichiometric amounts of germanium powder and sulfur in an evacuated silica ampule at 900 °C for approximately 16 h. The ampule was air quenched to room temperature and glassy Ge\(_2\text{S}_3\) was obtained. Phosphorus pentasulfide (\( \text{P}_2\text{S}_5 \)) is commercially available and was used as received (99.9% Sigma-Aldrich).

Glass batches of 3 to 4 g were made by combining appropriate amounts of the starting material powders to create the \( y\text{Na}_2\text{S} + (1-y)\text{GeS}_2 \) and \( y\text{Na}_2\text{S} + (1-y)\text{PS}_5/2 \) binary glasses. The binary sodium thiophosphate glasses were planetary milled prior to melting to minimize evaporation of \( \text{PS}_5/2 \), by inducing the precrystallization of the \( \text{Na}_2\text{S} \) and \( \text{PS}_5/2 \).\(^{24,25} \) The binary sodium thiogermanate compositions were melted and quenched to the glassy state without prior milling. The ternary \( y\text{Na}_2\text{S} + (1-y)\text{xGeS}_2 + (1-x)\text{PS}_5/2 \) glasses were prepared by mixing the appropriate ratio of the binary \( 0.5\text{Na}_2\text{S} + 0.5\text{GeS}_2 \) and \( 0.5\text{Na}_2\text{S} + 0.5\text{PS}_5/2 \) glasses. These mixtures were then melted in covered vitreous carbon crucibles for 3–5 min inside a mullite muffle tube furnace at 550–800 °C hermetically connected to the side of the glovebox, where lower temperatures were used for the thiophosphate-rich glasses and the higher temperatures were used for the thiogermanate-rich glasses. The samples were then removed from the furnace and allowed to cool to room temperature inside the crucible. Mass losses were recorded and in all cases found to be less than 2 wt % and the glasses were then remelted at the same temperature for an additional 3 min and quenched to room temperature between brass plates (>10^3 °C/s). All samples were transparent and showed no visual signs of crystallization and/or phase separation.

**Glass Transition Temperatures.** Differential scanning calorimetry, DSC, measurements were performed using a Perkin-Elmer Pyris 1 DSC that had previously been calibrated to the indium and tin melting points (±1 °C) on ~20 mg sample hermetically sealed in aluminum sample pans. Scans on the as-quenched glass were heated and cooled at a rate of 20 °C/min. For each composition, two samples were prepared and examined by DSC, the first of which was heated from room temperature past the \( T_g \) of the glass until the crystallization onset. The second sample pan was then heated from room temperature to 20–50 °C above the \( T_g \) of the glass, but below the crystallization onset temperature, \( T_c \), cooled to room temperature, heated above the \( T_g \) cooled to room temperature, and finally heated past the \( T_g \) of the glass until crystallization onset. This temperature cycling ensured a common thermal history for all glass compositions. \( T_s \) were then determined by averaging three calculated onset temperatures from the final heating step. Figure 1 shows an example DSC thermogram for the \( x = 0 \) glass and the onset tangent construction used to determine the \( T_g \) of the glasses.

**Density.** Densities were determined using the Archimedes method on annealed bulk glass samples inside a high purity \( \text{N}_2 \) glovebox. The immersion fluid used was mineral oil (Fisher Scientific) with a measured density of 0.866 ± 0.001 g/cm\(^3\). The density of the mineral oil was determined before each measurement using a stainless steel calibration sphere of known density. In this way, slight fluctuations in the density due to temperature or contamination could be monitored and avoided. Sodium metal flakes were submerged in the mineral oil to capture dissolved oxygen and moisture during storage in the glovebox. Replicate measurements on three glass samples were averaged for each glass composition and in this way the accuracy of the density measurements was found to ±0.01 g/cm\(^3\).
RESULTS

Glass Transition Temperatures. Figure 2 shows the composition dependence of the $T_g$ values of the $0.5\text{Na}_2\text{S} + 0.5[x\text{GeS}_2 + (1-x)\text{PS}_{5/2}]$ glasses. At $x = 0$, the $T_g$ is $187 ^{\circ}\text{C}$ and at $x = 1$, the $T_g$ is $237 ^{\circ}\text{C}$. All ternary compositions show a $T_g$ depression relative to the linear interpolation behavior between the end-member glasses. The maximum deviation from this linear behavior is observed at $x = 0.3$.

Density. The composition dependence of densities of the $0.5\text{Na}_2\text{S} + 0.5[x\text{GeS}_2 + (1-x)\text{PS}_{5/2}]$ glasses is shown in Figure 3. The density of the $x = 0$ glass is $2.03 \text{g/cm}^3$ and, with the exception of the $x = 0.2$ glass, the density shows a small positive deviation from linearity when GeS$_2$ is exchanged for PS$_{5/2}$ across the entire composition range. The density of the $x = 1$ glass is $2.47 \text{g/cm}^3$. As seen in Figure 3, the densities of the ternary compositions do not deviate significantly from linear interpolation behavior between the end-member glasses.

DISCUSSION

Composition Dependence of $T_g$. The $0.5\text{Na}_2\text{S} + 0.5[x\text{GeS}_2 + (1-x)\text{PS}_{5/2}]$ glasses exhibit a negative deviation in $T_g$ relative to the linear interpolation behavior between the end-member glasses. The $T_g$ of the $x = 1$ sodium thiogermanate glass is significantly higher than that of the $x = 0$ sodium thiphosphate glass because in the former, the SRO structure, the Ge$^2$ group, has two bridging sulfurs (bS) per network former (Ge) whereas in the latter, the SRO group, P$^1$, see Figure 4 and Figure 5 below, only possesses a single bS unit.

![Figure 2](https://example.com/figure2.png)

![Figure 3](https://example.com/figure3.png)

![Figure 4](https://example.com/figure4.png)

![Figure 5](https://example.com/figure5.png)
bridge bonds such as in bS in these glasses or in bridging oxygens (bO) in oxide glasses, for example as those studied by Christensen et al.\textsuperscript{13,18,19,26}

In order to compare these assumptions to the composition dependence of the $T_g$ data of these glasses, the atomic level SRO structures of the glasses must be considered; the average number of bS in these glasses must be determined to evaluate if the observed trend in $T_g$ is consistent with the proposed hypothesis, that is that the negative deviation in the $T_g$ suggests that the ternary glasses possess smaller numbers of bS and therefore larger numbers of nonbridging sulfurs (nbS) than a linear interpolation between 2 per Ge and 1 per P of the binary glasses. Hence, in the present case, where the $T_g$ exhibits a negative trend below the linear extrapolation between the $T_g$ of the two binary glasses, this suggests that the average connectivity of the ternary glasses is less than that of the two binary glasses.

To investigate this hypothesis, we begin with the representations of local phosphorus environments in the glasses studied that are shown in Figure 4 and local germanium environments that are shown in Figure 5. These SRO glass structures are identified as $J$, where $J$ is the glass-forming cation (P, Ge), and $n$ is the number of bS. From the composition of the glass and our structural studies of them,\textsuperscript{25} at $x = 0$, Na$_2$PS$_{5/2}$, the structure is predominantly comprised of P\textsuperscript{1} groups with 0.5 bS per phosphorus, while the $x = 1$ glass, Na$_2$GeS$_3$, is predominantly comprised of Ge\textsuperscript{2} groups with two bS per germanium. It is important to note that, by definition, every bS is shared between two glass-forming cations, so each glass-forming cation accounts for only half of each bS. Since Ge\textsuperscript{2} groups have one more bS than P\textsuperscript{1} groups, the connectivity of the Ge\textsuperscript{2} structure is greater than that of the P\textsuperscript{1} structure, and thus, this may explain why the $T_g$ of the $x = 1$ glass is greater than that of the $x = 0$ glass. Indeed, with two bS shared between every two Ge centers, it is expected that such Ge\textsuperscript{2} units form long chain structures, whereas the P\textsuperscript{1} group with only one bS shared between two P centers exhibits almost no network connectivity forming the molecular anion Na$_2$P$_2$S$_2$ and presumably the low $T_g$ of this glass is associated with this weak connectivity.

Formally, this can be investigated by determining the number of moles of bS, $N_{bS}$, in the 0.5Na$_2$S + 0.5[xGeS$_2$ + (1 − $x$)GeS$_2$] glass series and can be calculated from eq 1,

$$N_{bS}(x) = N_b(x) - N_{nbS3}(x) - N_{nbSNa+}(x)$$

where $N_b$ is the total number of moles of sulfur, $N_{nbS3}$ is the number of moles of nbS due to doubly bonded sulfur in phosphorus species, see Figure 4, and $N_{nbSNa+}$ is the number of moles of “normal” nbS associated with Na\textsuperscript{+} ions. For the 0.5Na$_2$S + 0.5[xGeS$_2$ + (1 − $x$)GeS$_2$] glasses to satisfy charge neutrality, $N_{nbSNa+}$ = 1 for all glasses $x$. $N_b$ and $N_{nbS3}$ are determined using eq 2 and eq 3, respectively.

$$N_b(x) = \frac{1}{4}(7 - x)$$

(2)

$$N_{nbS3}(x) = \frac{1}{2}(1 - x)$$

(3)

Substitution of eq 2 and eq 3 into eq 1 and simplification yields eq 4.

$$N_{bS}(x) = \frac{1}{4}(1 + x)$$

(4)

As may be expected, eq 4 yields a linear interpolation of $N_{bS}$ between $N_{bS} = 0.25$ at $x = 0$ and $N_{bS} = 0.5$ at $x = 1$ because the number of Na\textsuperscript{+} ions is held constant for the entire glass series. In order to understand why the $T_g$ of the ternary MGF glasses exhibit a negative depression relative to linear interpolation behavior between the end-member glasses, the amount and type of bS at each composition must be considered.

SRO-Adjusted Bridging Sulfur Model of $T_g$. In our previous paper on the atomic level structures of the glasses in this series, an atomic fraction model of the various SRO structures present in these ternary MGF glasses was developed to describe structures of the 0.5Na$_2$S + 0.5[xGeS$_2$ + (1 − $x$)GeS$_2$] glass system.\textsuperscript{25} The composition dependence of the atomic fractions of all of the phosphorus SRO structures, Figure 6, were determined by deconvolution and integration of $^{31}$P MAS NMR spectra for the various phosphorus groups. The fractions of the various germanium SRO structures were approximated through charge neutrality considerations where the sum of all of the negative charges of the thiophosphate and thiogerminate SRO groups in the glass must equal −1 because there are only +1 positive charges in the glass. The IR and Raman vibrational spectra were in good agreement with the type and fraction of the germanium SRO structures predicted from charge neutrality. As described above, the model that was consistent with the IR, Raman, and NMR spectra for the phosphorus SRO structures and charge neutrality constraints for the germanium SRO structures showed that the unequal sharing of Na\textsuperscript{+} in the 0.5Na$_2$S + 0.5[xGeS$_2$ + (1 − $x$)GeS$_2$] glasses could be accounted for by the disproportionation reaction given in eq 5.

$$P^1 + Ge^2 \rightarrow P^0 + Ge^3$$

(5)

Now, because the formed SRO structures, more networked depolymerized P\textsuperscript{0} groups and more network polymerized Ge\textsuperscript{3} groups, must maintain the overall same number of nbS, again charge neutrality must be held, the observed negative deviation in the $T_g$ may be an indication that secondary effects may be occurring in these glasses such that the overall network connectivity of the glasses is decreased.

One possible source of network degradation in the face of the overall number of nbS remaining constant in these glasses is...
that it may be caused at the intermediate range order (IRO) level, that comprising the second and higher coordination spheres of the network forming cations P and Ge. The suggestion here is that not all bS are equal in that if the bS do not “propagate” out into the longer range structure of the glass, then the rigidity of the network will not necessarily be increased and Tg may not increase. We have such a possibility in these glasses through the formation Ge3S10−x molecular anions.28–34 These structural groups are superstructures of Ge3 groups which we have shown must be present to properly account for all of the vibrational spectral features of these glasses and for this reason are included in our SRO model of the structures of these glasses. As seen in Figure 6, these units possess 1.5 bS per germanium, as expected for this composition, but none-the-less do not constitute fully network bridging bS structures in these glasses. The vibrational spectra showed strong evidence of these molecular anions being present in these glasses, but the relative amounts of Ge3 groups forming branchi networks, hereafter denoted Ge3B, and Ge3 groups forming discrete Ge3S10−x molecular anions, hereafter denoted Ge3M, could not be separately determined from the IR and Raman spectra alone.23 Hence, in our previous paper reporting the structure of these glasses, we could only report the total amount of Ge3 groups in the glasses.23 We now show that we can use the negative MGFE deviation of the Tg of these glasses to address the so far unanswered question of the relative fractions of Ge3B and Ge3M units in these glasses. It is to this question that we now turn.

Under these considerations, presumably, the formation of Ge3M groups would produce a glass network that is less cohesive, less connected, than a glass network with only Ge3B structures. We hypothesize, therefore, that the formation of totally depolymerized P0 and non-network forming Ge3M units leads to the Tg depression exhibited by these ternary glasses in the 0.5Na2O + 0.5[xB2O3 + (1 − x)GeS2] glass system. Christensen et al. showed that there was strong correlation between the number of bO and the Tg of the 0.35Na2O + 0.65[xB2O3 + (1 − x)PS5/2] glasses.19 It is reasonable to assume that a similar correlation exists here between bS and the Tg in the MGFE ternary sulfide glasses under study here. The amount of bS can be calculated using the SRO atomic fraction model described in ref 18 and eq 6

\[ N_{gS}(x) = \sum_j f_j(x)N_{bSj} \]  

where \( f_j \) is the mole fraction of the various jth SRO structures and \( N_{bSj} \) is the number of bS associated with the jth SRO structural unit. Table 1 includes the number of bS associated with the various J’ species. Note that eq 6 is an alternate formalism of eq 1.

As described above, the relative amounts of Ge3B and Ge3M groups cannot be, at this time, uniquely determined from vibrational spectra alone of the glasses. In order to test our hypothesis that the formation of P0 and Ge3M units leads to a reduced glass network connectivity and hence to lower Tg’s of these ternary glasses, a method of quantifying \( f_{Ge3M} \), the fraction of Ge3 in Ge3S10−x molecular anions, is required. It is important to note that this is a fraction of Ge3 in the Ge3M environment, and it is not an absolute fraction of glass-forming cations in the Ge3M environment among all Ge SRO structures. For ease of comparison, scaled values of \( N_{bS} \), \( F_{bS} \), the number of bS and their fraction, are calculated using eq 7, and scaled Tg values, \( T_0' \), are calculated using eq 8.

<table>
<thead>
<tr>
<th>J’</th>
<th>bridging sulfur/J’</th>
<th>( N_{bS} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>P1</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>P2p</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>P2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ge4</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Ge3</td>
<td>1.5</td>
<td>0.75</td>
</tr>
<tr>
<td>Ge2</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*p2p* is considered to have 0.5 bridging sulfurs to account for its connectivity. \( N_{bS} \) values are on a 0.5 glass forming cation basis.

\[ F_{bS}(x) \equiv \sum_j f_j N_{bSj} = \sum_j f_j N_{bSj} = \frac{1}{4}(1 + x) \]  

\[ T_0'(x) = \frac{T_g(x)}{T_g(0)} \]  

In this SRO-adjusted bS model, we will assume that Ge3M groups decrease the connectivity of the glassy network, and thus, they are treated as having no bS, hence we hypothesize that the \( N_{bS} \) is reduced by the amount of S contained in the Ge3S10−x molecular anions. If, for example, there are 0.05 mols of Ge3S10−x molecular anions present in the glass, there would be \( 6 \times 0.05 = 0.3 \) mols of bS not available as network bS. Since Ge3M units do not contribute to the network connectivity, \( N_{bS,Ge3M} = 0 \) in eq 7 above. As a starting point, we will assume that \( f_{Ge3M} \) is constant for all ternary glass compositions and \( T_0' \) are plotted for \( f_{Ge3M} = 0 \), model 0; and \( f_{Ge3M} = 1 \), model 1, in Figure 7. Clearly, when \( f_{Ge3M} = 0 \), \( T_0'(x) \) is a linear interpolation of \( T_{bS}(0) \) and \( T_{bS}(1) \), and it fails to reproduce the composition dependence of \( T_g' \). At the other extreme, if we assume \( f_{Ge3M} = 1 \), that is all of the Ge3 units are in Ge3M structures that possess no contribution to the network bS, model 1, the number of bS is grossly underestimated and leads to a \( T_g' \) suppression far greater than that observed for the glasses. To show the trends in more realistic values of \( f_{Ge3M} \), \( F_{bS} \) and \( T_0' \) are plotted for a range of values between 0.05 ≤ \( f_{Ge3M} \) ≤ 0.1 in Figure 8, and these \( f_{Ge3M} \) values reproduce the overall trend in the composition dependence of \( T_g' \) especially for \( f_{Ge3M} = 0.07 \). For this reason, and as perhaps expected, we conclude...
that the formation of a small number of \( \text{Ge}^{3M} \) leads to the depressed \( T_g \) values of the ternary glasses, some \( \sim 93\% \) of the Ge are in normal Ge\(^{3B} \) sites. The strong effect that the small fraction of Ge\(^{3M} \), \( \sim 7\% \), has upon the \( T_g \) of these glasses presumably arises from the fact that a single Ge\( _{4S_{10}} \) unit contains 6 bS and as a result can remove a relatively large number of bS from the network structure of the glass with a relatively small fraction of Ge\( _{4S_{10}} \) units. Note that a single Ge\(^{3} \) unit only possesses 1.5 bS.

In order to further refine the structural model, \( f'_{\text{Ge}^{3M}}(x) \) values that more accurately reproduce the \( T_g \) behavior were calculated, Model 2, and a simple linear best-fit was determined excluding the \( T_g \) data point for the \( x = 0.6 \) glass, taken presently as an outlier in the data, and this is given in eq 9. Equation 9 is then used to quantify the extent of formation of Ge\(^{3M} \) groups, and Figure 9 shows \( T'_g \) calculated for Model 2. This model yields an excellent fit, where all calculated \( T'_g \) values are within 1\% of \( T_g \) derived from the data, with the exception of the \( x = 0.6 \) glass, which deviates by 2.27\%.

\[
f'_{\text{Ge}^{3M}}(x) = 0.0136 - 0.05118x
\]  

(9)

Using this model for the fraction of Ge\(^{3M} \) SRO structural units in the glasses, an improved SRO atomic fraction model of the SRO Ge\(^{a} \) species in these ternary glasses that now reflects the \( T_g \) considerations described above and derived using eq 9 is shown in Figure 10. The complete adjusted SRO atomic fraction model including all P\(^{a} \) and Ge\(^{a} \) species is shown in Figure 11. Note that all compositions and fractions were adjusted such that at a given composition the moles of P present in the glass equals 0.5(1 - \( x \)) and the moles of Ge present in the glass equals 0.5\( x \).

Molar Volume Model of the Density. Figure 3 shows that the density of the 0.5Na\(_2\)S + 0.5[xGe\(_2\)S\(_2\) + (1 - \( x \))PS\(_{5/2}\)] glasses increases as Ge\(_2\)S\(_2\) is exchanged for PS\(_{5/2}\) across the entire composition range. Interestingly, the densities of the ternary compositions do not deviate significantly from linear interpolation behavior between the end-member glasses only yielding a slight positive MGFE for most of the compositions. The molar volumes, Figure 12, were calculated using eq 1035–40.
from the density on a per atom basis, where the total moles of atoms at composition \( x \), \( Z(x) \), is calculated using eq 11,

\[
Z(x) = 3.25 - 0.25x
\]

in order to account for both the variable number of atoms in the SRO units and to see if a MGFE trend is apparent with the compositional atomic mass effects removed. \( \bar{V}(x) \) is the molar volume, \( \bar{M}(x) \) is the molar mass at composition \( x \), and \( \rho(x) \) is the experimental density.

Figure 12 reveals a negative MGFE in molar volume for all values of \( x \) except for the \( x = 0.2 \) composition, which shows a large positive deviation. Replicate density measurements were performed in order to verify that this behavior is real and not a measurement error and the behavior of this data at this point is not fully understood at this time, but studies are underway. The \( x = 0.5 \) composition exhibits the largest negative deviation from linear interpolation behavior at -1.31%, while the \( x = 0.2 \) glass deviates +0.93%.

In order to better understand the atomic level origin of this change in molar volume, we use the optimized SRO atomic fraction model, presented in Figure 11, to develop a molar volume model based on eq 12,

\[
\bar{V}(x) = \frac{\bar{M}(x)}{Z(x)\rho(x)} = \frac{\sum j f_j(x)\bar{M}_j}{Z(x)\rho(x)} = \sum j f_j(x)\bar{V}_j(x)
\]

where \( f_j \) is the mole fraction of the various \( j \)th SRO structure, \( \bar{M}_j \) is the molar mass of the \( j \)th SRO structure, and \( \bar{V}_j(x) \) is the molar volume of the various \( j \)th SRO structures. A priori, it is unknown if the various \( \bar{V}_j \) values are constant or varies with \( x \) or \( \bar{V}(x) \). Further, if \( \bar{V}_j(x) \) is variable, it is unknown initially how it varies with composition, \( x \).

To begin, the various molar volumes of the Ge SRO structural groups were determined by applying eq 12 to the molar volume data for the binary \( yNa_2S + (1-y)GeS_2 \) glasses, with the exception of \( \bar{V}_{PS^{5/2}} \), where the crystalline molar volume is used. In a similar manner, the molar volumes of the various \( P^i \) SRO groups were determined by applying eq 12 to molar volumes of the binary \( yNa_2S + (1-y)PS_{\text{5/2}} \) glasses where the various \( f_j(y) \) values were determined from \( ^{31}P \) MAS NMR as shown and previously reported by us. Since \( P^i \) and \( P^{1P} \) arise from the same stoichiometry, crystallographic data for analogous \( Ag^+ \) ion-containing materials were used. Literature values of density determined from crystallographic data for \( Ag_2P_2S_{\text{5/2}} \) analogous to the \( P^{1P} \) group, and \( Ag_2P_2S_7 \) analogous to \( P^i \) have molar volumes of 12.17 g/cm\(^3\) and 12.62 g/cm\(^3\), respectively. This corresponds to \( \bar{V}_{P^{1P}} = (12.17/12.62) \Rightarrow \bar{V}_{P^{1P}} = 0.9646 \bar{V}_{P^i} \). This relationship was inserted into eq 12, and the resulting volumes are \( \bar{V}_{P^{1P}} = 13.89 \text{ cm}^3/\text{mol} \) and \( \bar{V}_{P^i} = 14.42 \text{ cm}^3/\text{mol} \) were found. The densities of the binary glasses are shown in Figure 13, and the molar volumes determined for the \( Ge^0 \) and \( P^i \) SRO structures are listed in Table 2.

![Figure 12. Composition dependence of the molar volume, \( \bar{V}(x) \), of the 0.5Na\(_2\)S + 0.5[0.5GeS\(_2\) + (1-x)PS\(_{5/2}\)] glasses.](Image 79x554 to 281x706)

![Figure 13. Densities of the binary \( yNa_2S + (1-y)PS_{\text{5/2}} \) and \( yNa_2S + (1-y)GeS_2 \) glasses.](Image 360x449 to 529x604)

<table>
<thead>
<tr>
<th>( j )</th>
<th>( \bar{V}_j ) (cm(^3)/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P^i )</td>
<td>15.31</td>
</tr>
<tr>
<td>( P^i )</td>
<td>14.42</td>
</tr>
<tr>
<td>( P^{1P} )</td>
<td>13.89</td>
</tr>
<tr>
<td>( P^0 )</td>
<td>13.96</td>
</tr>
<tr>
<td>Ge(^4)</td>
<td>16.65</td>
</tr>
<tr>
<td>Ge(^{2B} )</td>
<td>14.95</td>
</tr>
<tr>
<td>Ge(^{3M} )</td>
<td>14.41</td>
</tr>
<tr>
<td>Ge(^2 )</td>
<td>14.49</td>
</tr>
</tbody>
</table>

To determine if the various \( \bar{V}_j \) values are constant or not with composition \( x \), we calculate the molar volume assuming that all \( \bar{V}_j \) remain constant for all \( x \) and this model, Model 3, is shown in Figure 14. Model 3 predicts a modest decrease in the molar volumes for all ternary glass compositions except for the \( x = 0.2 \) glass, which overlaps the linear interpolation of the molar volumes of the \( x = 0 \) and \( x = 1 \) glasses. The trend in the calculated, eq 12, molar volume values is consistent with the trend in the experimental molar volume data, but the magnitude of the negative deviation is significantly larger than that predicted by model 3, which suggests that the \( \bar{V}_j \) are not constant, as perhaps expected, in the ternary glasses.

To improve the agreement between the model calculated values and the experimental molar volume data, model 4 hypothesizes that as \( PS_{\text{5/2}} \) is exchanged for \( GeS_2 \), moving from \( x = 1 \) to \( x = 0 \), \( Ge^0 \)-based groups are terminated by the more abundant \( P^0 \) groups bonding to \( Ge^0 \) groups through a bS. If this is true, \( Ge^{2B} \) groups would become more isolated, and \( Ge^2 \)
chains would become shorter. It is plausible that limiting the size of Ge$^n$ networks would lead to increased packing efficiency of Ge$^n$ species which corresponds to smaller molar volumes. Crystalline values for the molar volume are used as boundary conditions as $x$ approaches 0, and $\bar{V}_{\text{Ge}^3}$ and $\bar{V}_{\text{Ge}^2}$ are decreased linearly from values determined from the $y\text{Na}_2\text{S}^+\left(1-y\right)\text{GeS}_2$ glasses. Model 4 results are shown in Figure 15. Model 4 predicts a decrease in the molar volume for all ternary glasses, and the calculated molar volumes show excellent agreement with measured values for all compositions except the $x=0.2$ glass. Densities calculated from model 4 are shown in Figure 16 and show excellent agreement with the measured values. Only the calculated density for the $x=0.2$ glass lies outside of experimental error. The excellent match of model 4 with the experimental data indicates that the Ge SRO groups experience increased packing efficiency with increasing concentration of PS$_{5/2}$ in the ternary glasses.

### CONCLUSIONS

The mixed glass former effect (MGFE) in $0.5\text{Na}_2\text{S} + 0.5\left[x\text{GeS}_2 + (1-x)\text{PS}_{5/2}\right]$ glasses manifests itself in a negative deviation from the linear interpolation of the properties of the binary end-member glasses, $x=0$ and $x=1$, of the $T_g$s, but not in the densities. Molar volumes of these MGF glasses reveal small deviations from a linear interpolation of the binary end-member glasses. A slight increase in density and corresponding decrease in molar volume is apparent in the $0.3 \leq x \leq 0.9$ compositions. It is found that the thiophosphate and thiogermaine SRO structural groups do not equally share Na$^+$ ions in the ternary compositions, the thiophosphate structural groups are found to possess more Na$^+$ than their base composition would suggest. To account for this, the dominant disproportionation reaction in the $0.5\text{Na}_2\text{S} + 0.5\left[x\text{GeS}_2 + (1-x)\text{PS}_{5/2}\right]$ glasses is suggested to be $\text{Na}_2\text{PS}_{7/2} + \text{Na}_2\text{GeS}_3 \rightarrow \text{Na}_3\text{PS}_4 + \text{NaGeS}_{5/2}$.

Formation of branching NaGeS$_{5/2}$ structures may be expected to cause a positive deviation from linear behavior of the $T_g$ of the glasses; however, the $T_g$ data reveals slight negative deviation from linearity in the $T_g$S. We proposed that this negative deviation is due to the formation of GeS$_{10}^{10-}$ molecular anions where the Ge$^+$ groups in this molecular anion do not contribute to the network connectivity of the glass. An adjusted SRO atomic fraction model was developed by investigating the MGFE on $T_g$, which allowed quantification of GeS$_{10}^{10-}$ molecular anion formation. This revised structural model was used to investigate the densities in the $0.5\text{Na}_2\text{S} + 0.5\left[x\text{GeS}_2 + (1-x)\text{PS}_{5/2}\right]$ glasses. The slight increase in density and corresponding decrease in molar volume is caused by increased packing efficiency of the germanium sulfide species in the ternary compositions due to smaller polymerized networks. These results will be used to analyze the MGFE on
ionic conductivity in the 0.5Na2S + 0.5[xGeS4 + (1 − x)PS4/S2] glasses.

■ AUTHOR INFORMATION

Corresponding Author
* (S.W.M.) E-mail: swmartin@iastate.edu.

Present Address
† (C.B.) Primary researcher and author. Present address: Missouri University of Science & Technology, Rolla, MO, 65409

Notes
The authors declare no competing financial interest.

‡ (K.S.) Undergraduate research assistant

§ (S.W.M.) Principal investigator.

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