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Short range order characterization of the $\text{Na}_2\text{S} + \text{SiS}_2$ glass system using Raman, infrared and ^{29}Si magic angle spinning nuclear magnetic resonance spectroscopies

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ABSTRACT

Sodium thiosilicate glasses are of interest in electrochemical applications as fast ion conducting solid state electrolyte materials. While some structural studies have been performed on this glass series, their short range order (SRO) structure has not been fully realized. Specifically the SiS_4 tetrahedra corner sharing behavior in these glasses appears to be less understood, particularly the existence and nature of the Si^3 , where the superscript describes the number of bridge bonds of the form $\equiv\text{Si}-\text{S}-\text{Si}\equiv$, structure in this glass system has not been fully examined. In this paper, glasses and polycrystals in the sodium thiosilicate system have been explored and characterized using a combination ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy, infrared (IR) spectroscopy and for the first time Raman spectroscopy. Raman and IR spectroscopy have been used to determine the composition dependence of the structural units in this system. Specifically, the Raman spectra were used to differentiate corner shared Si^3 , Si^2 , and Si^1 units and edge shared Si^2 structure units. ^{29}Si MAS NMR spectra were then deconvoluted to determine the composition dependence of the populations of these different structural units.

1. Introduction

1.1. Background

Electrochemical storage of grid level electrical energy has become important to the full implementation of renewable energy harvesters such as wind turbines and solar thermal and solar photovoltaic systems. In regions where adaptations of the existing fossil energy converters can no longer be adjusted either fast enough in real time to effectively manage the temporal nature of renewable energy, or enough in magnitude to effectively manage the large quantity of renewably sourced electrical energy, saturation levels of these renewable energy harvesters have been reached [1–5]. For these reasons, there is a renewed worldwide interest in developing effective means to “shave” and “shift” the electrical energy being harvested renewably [2]. One of the most efficient and cost effective means is to employ electrochemical battery-based systems. All-solid-state batteries based in part on glassy solid electrolytes, while in their early stages of development, none-the-less, have significant potential advantages over traditional liquid electrolyte based battery systems. Low cost, scalable, high conductivity and safe, solid glassy electrolytes are gaining renewed research interest, even

though such ion conducting glasses have been known and studied for more than a century [6–12].

Perhaps the most widely known and studied of all alkali ion conducting glasses are the simple binary alkali silicate glasses, of general composition $\text{M}_2\text{O} + \text{SiO}_2$ [7,13–15]. These glasses are relatively poor conductors of alkali ions, exhibiting room temperature conductivities of typically no more than $\sim 10^{-9} (\Omega \text{ cm})^{-1}$ [16]. However, these glasses are nonetheless exceptionally low cost, strong glass formers, easy to prepare, and chemically durable. For these reasons, binary alkali silicate glasses are often model glass systems used to study the many orders of magnitude decoupling of the mobile alkali ion motion from the viscous-structural relaxation motions of the host glassy silicate network structure [17–19].

More recent work on sulfide analogs of alkali oxide glasses have reported many orders of magnitude higher room temperature conductivities, in some cases reaching $\sim 10^{-2} (\Omega \text{ cm})^{-1}$ [20] which has spurred renewed interest in exploring them as solid electrolytes in a new class of all solid state alkali-based batteries. For example, binary $\text{Li}_2\text{S} + \text{P}_2\text{S}_5$ glasses (and glass ceramics) have received significant research interest by Tatsumisago et al. [21] [22–24]. Martin et al. have explored nearly all of the binary alkali thioborate glasses, $\text{M}_2\text{S} + \text{B}_2\text{S}_3$

Abbreviations: MAS NMR, magic angle spinning nuclear magnetic resonance; MIR, mid infrared; FIR, far infrared; BS, bridging sulfur; NBS, non-bridging sulfur; SRO, short range order

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[25–28], and have reported on them extensively. Quite surprisingly, the binary alkali thiosilicate glasses, $M_2S + SiS_2$, have received far less attention, although a few early reports on these glasses are available [29–31]. The binary lithium thiosilicate, $yLi_2S + (1 - y)SiS_2$, glasses have been more extensively investigated, likely due to the greater interest in lithium-based batteries and the known higher ionic conductivities of lithium-based solid electrolytes. However, glass formation in the binary lithium thiosilicate system is very limited and appears to lie only in a narrow composition range around the $y = 0.60$ composition for normal splat quenching methods. Presumably, a wider glass formation region could be achieved at more extreme quenching rates. For this reason, studies of the lithium thiosilicate system have focused more heavily on crystalline and partially crystalline glass ceramic materials and oxy-sulfide glass-ceramics [32–34].

In contrast, the sodium thiosilicates, $yNa_2S + (1 - y)SiS_2$, while being much less studied, interestingly appear to be much better glass formers. For example, using roller quenching techniques, Pradel et al. were able to prepare glasses in the low modifier range of $y = 0.1$ to $y = 0.33$ [31]. Martin et al. used splat quenching to prepare glasses from $y = 0.4$ to $y = 0.75$, a significantly wider glass forming range than that for the binary lithium thiosilicates [35]. The infrared (IR) spectra for all of these glasses were reported along with conductivities [35]. Eckert et al. has examined the ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) of these sodium thiosilicate glasses up to $y = 0.6$ [31]. So far, it seems that no Raman spectra have been reported for the binary $Na_2S + SiS_2$ glasses. Therefore, a unique opportunity exists to use a combination of vibrational and NMR spectroscopies to explore the atomic level structures of this glass family.

In this new report, the $Na_2S + SiS_2$ glass forming system has been revisited because it serves as the foundation of a larger study of ternary mixed glass former solid electrolytes that are based upon the mixing of two different glass formers, such as $Na_2S + SiS_2 + PS_{5/2}$. In the study of this latter ternary system, it has been found that there are significant gaps in the precise details of the atomic level structures of the binary sodium thiosilicate glasses and which has proven to be a significant barrier to the full understanding of ternary glasses.

For these reasons, the short-range order (SRO) structure for all of the silicon Si^i structures has been investigated, where i is the number of bridging sulfur (BS) atoms, $\equiv Si-S-Si \equiv$, to other Si atoms, see Table 1. The coordination sphere around the Si atom in the binary $yNa_2S + (1 - y)SiS_2$ glass forming system using IR, Raman, and NMR spectroscopies have all been examined. In particular, the full composition (y) dependence of the various SRO Si^i structures have been determined which exist in these glasses from the low alkali range, $yNa_2S < 0.5$, to the high alkali range, $yNa_2S > 0.5$. The number of non-bridging sulfur ions per Si, (NBSs), is $4-i$, and these are charge compensated by the mobile Na^+ ions, see Fig. 1 for the structure of these units. Glasses with high concentrations of Na_2S have received much more attention because it is these glasses that have the significantly higher Na^+ ion conductivities and are of more electrochemical interest. Hence, more is

Table 1

Number of BS, NBS_j, and NBS, N_{NBSj}, associated with each Qⁿ structural unit. P^{1P} is considered to have 0.5 bridging sulfurs to account for its connectivity. N_{NBSj} values are on a 0.5 glass forming cation basis.

Short range order units	Composition	Net bridging sulfur/Si ⁿ	Net non-bridging sulfur/Si ⁿ
Si ⁴	SiS ₂	2	0
Si ³	0.33Na ₂ S + 0.67SiS ₂	1.5	1
Si ²	0.50Na ₂ S + 0.50SiS ₂	1	2
Si ¹	0.60Na ₂ S + 0.40SiS ₂	0.5	3
Si ⁰	0.67Na ₂ S + 0.33SiS ₂	0	4

known of the structure of those glasses where the structure is based upon more depolymerized “salt-like” ions such as Si^1 and Si^0 groups, where $yNa_2S > 0.5$ and the number of NBS are relatively high, 3 and 4, and are the so-called molecular ions. In this study and for this reason, we have purposefully also examined the glass formation into the lower Na_2S content range (where it is possible to still prepare glasses) to explore the more network forming SRO groups, Si^4 , Si^3 , and Si^2 groups, that have received significantly less research attention.

It has been found that pure SiS_2 is a very high vapor pressure liquid and is a very poor glass former due to the strong preference of the Si^4 group to form edge-sharing groups, E^2Si^4 , Fig. 1, which form into long chain structures. Similarly, it has been reported that the Si^2 group, Fig. 1, also forms these edge-shared structures, E^1Si^2 , which in this case form molecular dimer anion $(NaS)_2Si(S_2)Si(NaS)_2$ units due to the fact that this unit must also carry two NBSs [30]. Unknown so far is whether the Si^3 SRO group forms these-edge shared units, E^1Si^3 , and if so, what is its structure.

Given the lack of detailed knowledge of the structures of these binary alkali thio-silicate glasses, we have begun to address this here and report here on the use of IR, Raman, and NMR spectroscopies to probe the atomic level structures of the binary $Na_2S + SiS_2$ glass system. The SRO structures of some of the crystalline phases that exist in this system have been explored and used to help interpret the SRO structure of the glasses. As seen in other studies of these glasses and unlike their analogous alkali oxide silicate glasses, it is found that the edge-sharing structural SRO plays an important role in the structures of these sodium thiosilicate glasses for $yNa_2S \leq 0.5$. This study combines IR, Raman, and ^{29}Si MAS NMR spectroscopies to determine both the concentration (Na_2S) dependence of the various Si^i SRO structural groups that exist in these glasses and the connectivity of different SRO groups.

2. Experimental methods

2.1. Sample preparation

2.1.1. Starting materials

Sodium sulfide (Na_2S) and silicon sulfide (SiS_2) were synthesized to obtain highest purity. Sodium sulfide was synthesized via thermal dehydration of sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$) (Sigma Aldrich) under vacuum over a temperature range of 25° to 200 °C for 35 h. The dehydrated crystals were then mechanically milled for 5 min in a stainless steel pot inside a N_2 glove box, and then heat treated at 200 °C for 10 min. The X-ray diffraction pattern (XRD) of the resulting sodium sulfide was obtained to determine phase purity. Silicon sulfide was synthesized by combining stoichiometric amounts of Si (Alfa Aesar 99.999% metals basis) and S (Alfa Aesar Puratronics 99.999% metals basis). To ensure thorough mixing, the Si and S were mechanically milled together before being placed in the silica ampoule. The ampoule was evacuated, placed in a tilted furnace and rotated at a 45° angle for a 48 h during which reactants were heated from 50 to 970 °C at 1 °C/min, followed by cooling to room temperature. The final product was then removed from the ampoule in a N_2 glove box and mechanically milled to obtain a fine powder for glass batching purposes. XRD was used to evaluate the phase purity of each batch.

2.1.2. Glass samples

Samples were prepared by mixing stoichiometric amounts of Na_2S and SiS_2 , melting these in vitreous carbon crucibles at temperatures between 770 and 800 °C for 6 to 7 min each in a tube furnace hermetically sealed to a nitrogen glove box. After the first melt, a weight of the melted charge was taken to ensure the composition was maintained. All batches exhibited a weight loss of < 2%. Samples were then melted a second time and splat quenched (SQ) between brass plates.

In some compositions, where glasses could not be prepared by splat quenching, mechanochemical or planetary milled (PM) glasses were

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