Synthesis and Characterization of Hydrated Rubidium Thio-hydroxosilicogermanates Using Mechanochemical Hydrothermal Synthesis

Carly R. Nelson
Iowa State University

Sarah Olson
Iowa State University

Steven A. Poling
Iowa State University

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

Follow this and additional works at: http://lib.dr.iastate.edu/mse_pubs

Part of the Ceramic Materials Commons, Inorganic Chemistry Commons, and the Materials Chemistry Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/mse_pubs/53. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Synthesis and Characterization of Hydrated Rubidium Thio-hydroxosilicogermanates Using Mechanochemical Hydrothermal Synthesis

Abstract
The synthesis, structure, and proton conductivity of the hydrated thio-hydroxosilicogermanates Rb<sub>z</sub>Ge<sub>x</sub>Si<sub>1-x</sub>(OH)<sub>4-z</sub>yH<sub>2</sub>O (2 ≤ z ≤ 3; 0 < y < 1.7) are reported. X-ray diffraction indicates that the z = 2 materials are amorphous and show no unreacted starting materials, which is consistent with the mechanochemical hydrothermal evaporation−precipitation synthesis method. Infrared spectroscopy shows a fully reacted system where both silicon and germanium central anions have vibrational modes at 950, 780, 667, and 450 cm<sup>-1</sup> associated with asymmetric modes for Si−O, Ge−O, Si−S, and Ge−S chemical bonds, respectively. O−H stretching and bending modes are present at 3370 and 1655 cm<sup>-1</sup>, respectively, with the intensities of both modes decreasing with the addition of SiO<sub>2</sub>. Raman spectroscopy reveals symmetric stretching modes of the Ge−S unit at 420 cm<sup>-1</sup>. A new peak appears at 460 cm<sup>-1</sup> with the substitution of Si<sup>4+</sup> for Ge<sup>4+</sup>. There are weak peaks above 460 cm<sup>-1</sup> that can be attributed to H<sub>2</sub>O and O−H libration modes. Thermogravimetric analysis shows that water loss begins above the synthesis temperature of 75 °C. All water is lost by 300 °C which is consistent with the onset of the loss of conductivity. Alternating current impedance spectroscopy measurements performed on low-pressure sealed pellets show conductivity values ranging from 10<sup>-5</sup> to 10<sup>-2.5</sup> S/cm from 100 to 260 °C, respectively. Maximum conductivity values of 10<sup>-4.5</sup> and 10<sup>-3.5</sup> S/cm at 120 °C are obtained for 2RbSH + 0.9GeO<sub>2</sub> + 0.1SiO<sub>2</sub> + 0.8H<sub>2</sub>O and 3RbSH + 0.9GeO<sub>2</sub> + 0.1SiO<sub>2</sub> + 1.1H<sub>2</sub>O, respectively. A.c. impedance experiments under humidified conditions resulted in large increases in the proton conductivity at low temperatures. For x = 0.9 and 0.8 for the 2RbSH + xGeO<sub>2</sub> + (1−x)SiO<sub>2</sub> +yH<sub>2</sub>O samples, the humidified d.c. conductivity was 10<sup>-4</sup> S/cm at 60 °C, up from 10<sup>-8</sup> S/cm for samples measured under dry nitrogen. The effects of water and SiO<sub>2</sub> content on the proton conductivity are also discussed.

Disciplines
Ceramic Materials | Inorganic Chemistry | Materials Chemistry | Materials Science and Engineering

Comments
Synthesis and Characterization of Hydrated Rubidium Thio-hydroxosilicogermanates Using Mechanochemical Hydrothermal Synthesis

Carly R. Nelson, Sarah Olson, Steven A. Poling, and Steve W. Martin*

Department of Materials Science and Engineering, 2220 Hoover Hall, Iowa State University of Science and Technology, Ames, Iowa 50011

Received August 9, 2006

The synthesis, structure, and proton conductivity of the hydrated thio-hydroxosilicogermanates Rb$_x$Ge$_y$Si$_{1-x-y}$O$_z$(OH)$_{1+z-y}$H$_2$O (2 \leq z \leq 3; 0 < y < 1.7) are reported. X-ray diffraction indicates that the $z = 2$ materials are amorphous and show no unreacted starting materials, which is consistent with the mechanochemical hydrothermal evaporation–precipitation synthesis method. Infrared spectroscopy shows a fully reacted system where both silicon and germanium central anions have vibrational modes at ~950, ~780, ~667, and ~450 cm$^{-1}$ associated with asymmetric modes for Si–O, Ge–O, Si–S, and Ge–S chemical bonds, respectively. O–H stretching and bending modes are present at ~3370 and 1655 cm$^{-1}$, respectively, with the intensities of both modes decreasing with the addition of SiO$_2$. Raman spectroscopy reveals symmetric stretching modes of the Ge–S unit at ~420 cm$^{-1}$. A new peak appears at ~460 cm$^{-1}$ with the substitution of Si$^{4+}$ for Ge$^{4+}$. There are weak peaks above ~460 cm$^{-1}$ that can be attributed to H$_2$O and O–H libration modes. Thermogravimetric analysis shows that water loss begins above the synthesis temperature of ~75 °C. All water is lost by ~300 °C which is consistent with the onset of the loss of conductivity. Alternating current impedance spectroscopy measurements performed on low-pressure sealed pellets show conductivity values ranging from 10$^{-5}$ to 10$^{-2.5}$ S/cm from ~100 to 260 °C, respectively. Maximum conductivity values of 10$^{-4.3}$ and 10$^{-3.3}$ S/cm at 120 °C are obtained for 2RbSH + 0.9GeO$_2$ + 0.1SiO$_2$ + 0.8H$_2$O and 3RbSH + 0.9GeO$_2$ + 0.1SiO$_2$ + 1.1H$_2$O, respectively. a.c. impedance experiments under humidified conditions resulted in large increases in the proton conductivity at low temperatures. For $x = 0.9$ and 0.8 for the 2RbSH + xGeO$_2$ + (1-x)SiO$_2$ + yH$_2$O samples, the humidified d.c. conductivity was ~10$^{-4}$ S/cm at 60 °C, up from ~10$^{-8}$ S/cm for samples measured under dry nitrogen. The effects of water and SiO$_2$ content on the proton conductivity are also discussed.

Introduction

The need for alternative energy sources has increased greatly over the past few years due to high gasoline prices and stricter pollution regulations. Research into H$_2$–O$_2$ fuel cells operating in the intermediate temperature range (~100–300 °C) provides possible solutions to these problems with H$_2$–O$_2$ fuel cells having zero emission and using hydrogen and oxygen as fuels. The heart of the H$_2$–O$_2$ fuel cell is the proton-exchange membrane (PEM) which works to transport protons species from the anode to the cathode, thus creating electricity. A common material for the PEM is Nafion, a proton species from the anode to the cathode, thus creating proton-exchange membrane (PEM) which works to transport protons.

Our work has been performed to develop a material for the PEM that does not rely on such high levels of hydration to have high proton conductivity.

* To whom correspondence should be addressed. E-mail: ssmartin@iastate.edu. Fax: (515) 294-5444.


Hydrated Rubidium Thio-hydroxosilicogermanates

Chem. Mater., Vol. 18, No. 26, 2006 6437

materials was \(10^{-3} \text{ S/cm} \) at \(300 \, ^\circ\text{C}\) for \(3\text{HGe}_{2}\text{O}_{16}\cdot4\text{H}_{2}\text{O}\).\(^{12}\)

To further increase the ionic conductivity, \(\text{Si}^{4+}\) was substituted for \(\text{Ge}^{4+}\) which was expected to weaken the electrostatic interaction between mobile cations, resulting in an increase in the cation conductivity. Materials of the form \(M_{x}\text{Si}_{y}\text{Ge}_{z}\text{O}_{16}\cdot\gamma\text{H}_{2}\text{O}\) where \(M = \text{K}, \text{Rb}, \text{Cs}\), \(0 < m < 3\) and \(x = 0-4\) were synthesized and were observed to show an increase in the cation conductivity and a decrease in the activation energy with increasing silicon content.\(^{13}\)

A mechanochemical hydrothermal reaction method has been used to promote reaction of the silicon dioxide in water. This method has previously been shown to work in the \(\text{MgO}–\text{SiO}_{2}\) and \(\text{Mg(OH)}_{2}–\text{SiO}_{2}\) system where amorphous products were obtained through hydrothermal reactions.\(^{14,15}\)

For example, Avvakumov et al. was able to show that hydrated oxides react faster mechanochemically than for anyhydrous oxide mixtures.\(^{16,17}\)

In this work, we expand on the previously synthesized alkali thio-hydroxosilicogermanates of the form \(M_{x}\text{Ge}_{2}\text{S}_{y}\text{(OH)}_{z}\cdot\gamma\text{H}_{2}\text{O}\). We have specifically focused on the rubidium system which was shown to have the best combination of proton conductivity and thermal stability. In an effort to improve the thermal stability and proton conductivity by substituting \(\text{Si}^{4+}\) for \(\text{Ge}^{4+}\), hydrothermal mechanochemical synthesis technique will be investigated to increase the reactivity of \(\text{SiO}_{2}\) in water.

**Experimental Section**

**Sample Preparation.** Samples of the form \(\text{Rb}_{x}\text{Ge}_{y}\text{Si}_{z}\text{(OH)}_{t}\cdot\gamma\text{H}_{2}\text{O}\) were prepared by placing 0.5 g batches of stoichiometric amounts of \(\text{RbSH}\),\(^{13}\)commercial quartz-type \(\text{GeO}_{2}\) (Cerac 99.999%, \(\sim 325 \text{ mesh}\)), and amorphous \(\text{SiO}_{2}\) (Alfa 99.9%) in 5 mL of deionized (DI) water in a Fritsch Pulverisette-6 planetary mono mill with 10 \(\text{ZrO}_{2}\) milling balls, 10 mm in size, in a \(\text{ZrO}_{2}\) bowl. Planetary milling was used to decrease the particle size, thus increasing the surface area available to increase the reaction rate. The corresponding reactions may be written as:

\[
c_{\text{RbSH}} + x\text{GeO}_{2} + (1-x)\text{SiO}_{2} + (y+2-x)\text{H}_{2}\text{O} \rightarrow \\
\text{Rb}_{x}\text{Ge}_{y}\text{Si}_{z}\text{(OH)}_{t} \cdot \gamma\text{H}_{2}\text{O}, 2 \leq x \leq 3, 0.5 \leq y \leq 1.0
\]

Samples were milled for 2 h at 200 rpm and then transferred to a polypropylene jar on a hot plate at \(75 \, ^\circ\text{C}\) to dry. A dried film was deposited after allowing the excess water to evaporate at \(75 \, ^\circ\text{C}\). Samples were then stored under a dry \(\text{N}_{2}\) atmosphere where preparations for sample characterizations were performed.

**Structural Characterizations.** Structural investigations were performed using X-ray diffraction (XRD), infrared (IR) absorption, Raman scattering, and scanning electron microscopy energy dispersive spectrometry (SEM-EDS). The powder XRD spectra were collected at 298 K with a Scintag XDS-2000 diffractometer using Cu K\(\alpha\) radiation (\(\lambda = 1.54178 \, \text{Å}\)). 40 kV, and 30 mA. Scans were performed between 20\(^{\circ}\) and 60\(^{\circ}\) using a 0.02\(^{\circ}\) step size and a 0.5 s dwell time. Powdered samples were packed into a recessed square polycarbonate sample holder and covered with 0.001 in. thick Kapton (Polyimide) tape to seal out atmospheric moisture. The IR absorption spectra were collected at 298 K with a Bruker IFS 66 v/S spectrometer using 32 scans and 4 cm\(^{-1}\) resolution in both the mid-IR and far-IR regions. Translucent \(\text{CsI}\) pellets were prepared for transmission by mixing \(\sim 1\%\) wt % of powder sample with \(\text{CsI}\) and pressing. The Raman scattering spectra were collected at 298 K with a Bruker FT-Raman RFS 100/S spectrometer using a 1064 nm Nd:YAG laser, 32 scans, 2 cm\(^{-1}\) resolution, and 300 mW of power focused on a \(\sim 0.1\) mm diameter spot size. SEM-EDS measurements were performed using a Jeol JSM-6060LV system with an Inca EDS-7582. The samples were pressed into pellets and sputtered in gold (\(\sim 5\) nm) in a \(\text{N}_{2}\) atmosphere.

**Thermal Characterizations.** Thermal mass loss measurements were performed with a Perkin-Elmer Thermogravimetric Analyzer TGA 7 (TGA). About 10 mg of sample was placed in an open aluminum sample pan. The sample was then heated at a rate of 10 \(\text{C/min}\) from 50 to 300 \(\text{C}\) using 20 mL/min flow of \(\text{N}_{2}\) as the purge gas.

**Conductivity Measurements.** a.c. impedance data were collected with a Gamry PC4/750 potentiostat in the frequency range of 0.2 Hz to 100 kHz using 0.5 V amplitude on compacted powder samples. Hardened steel blocking electrodes with a 6.35 mm o.d. were pressed inside an undersized Teflon sleeve containing \(\sim 60\) mg of sample. A pressure of \(\sim 562\) MPa was applied to produce an average pellet thickness of \(0.4\) mm. Constant pressure was maintained on the pellet during the measurement by the electrodes and an aluminum ‘O’-frame insulated from the electrodes with Teflon. The pellet/electrode/frame assembly was contained inside a mullite cell that maintained about 1 atm of \(\text{N}_{2}\). Hydrated impedance runs were performed by bubbling dry air (\(\sim 0\%\) R.H. at STP) through a controlled temperature water bath (\(T \sim 50\, ^\circ\text{C}\)). The bottom of the cell was placed into a custom-built crucible furnace and data were collected using increments of 10 \(\text{C}\) after allowing the sample temperature to stabilize for 20 min. The d.c. conductivity values were determined from the intersection of the observed depressed semicircle and the low-frequency polarization “tail” in the Nyquist plot of the complex impedance.

**Results and Discussion**

**Sample Preparation.** Amorphous products were obtained which are consistent with the evaporation—precipitation synthesis method used. The resulting dried material was in the form of a translucent film. At room temperature in humidified air, the rubidium thio-hydroxosilicogermanates readily absorb water and are very soluble in water, similar to alkali salts. This strong affinity for water affects the stoichiometry of the final product in that different amounts of intercalated water can be present in the sample with slightly different experimental conditions. Under nonhumidified (dry) conditions, the samples are very stable and easily pressed into powder pellets.

**Structural Characterizations.** XRD. The powder XRD diffractograms indicate that the substitution of small amounts of \(\text{Si}^{4+}\) for \(\text{Ge}^{4+}\) results in a noncrystalline material for the \(2\text{RbSH} + x\text{GeO}_{2} + (1-x)\text{SiO}_{2} + y\text{H}_{2}\text{O}\) samples which was observed for the previously synthesized alkali thio-hydroxosilicogermanates.\(^{5}\) Figure 1 shows the diffractograms for 2RbSH...
The samples were covered with a Polyimide tape to prevent sample hydration at room temperature. There were no observed peaks that were distinguishable from the polycarbonate holder background from 20° to 60° 2θ for the 2RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O samples. There was no evidence of unreacted RbSH, GeO 2, SiO 2, or ZrO 2 from the milling bowl and ball media. Weak peaks were present for the x = 0.8 and x = 0.6 composition of the 3RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O phase, perhaps indicating a semicrystalline structure. Crystalline β-SiO 2, 19 Si 3 S 2, 20 GeO 2, 21 and GeS 2 are shown for reference. It does appear that there is a small percentage of crystalline products in the 3RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O samples. The resulting XRD amorphous materials are consistent with the employed synthesis route of planetary milling and then evaporating—precipitating at ~75 °C. Crystalline products have been obtained for similar binary samples, NaGeS 2(OH) 2·2H 2 O and Na 2GeS 4(OH)·8H 2 O, by using large amounts of acetone at room temperature to isolate the crystalline phases. 22,23 The proposed structural model is a metal anion, either germanium or silicon, tetrahedrally coordinated by sulfur anions and hydroxide ions. The sulfur anions are terminated by rubidium cations.

**Structural Characterizations: IR.** The IR spectra indicate a mixed system with both germanium and silicon bonding to both oxygen and sulfur and the presence of hydrated water. Figures 2 and 3 show the spectra for samples of the form Rb 2(Ge, Si) x−y S y(OH) e−z+H 2 O and Rb 3(Ge, Si) x−y S y−z(OH) e+H 2 O. The intense asymmetric vibration associated with Ge−S bond stretching vibrations are observed at ~3370 and 1655 cm −1, respectively. H 2 O and O−H liberation modes are present as sharp bands between 1446 and 534 cm −1.

(22) Prewitt, C. T.; Young, H. S. Science 1965, 149, 535.

Figure 1. Powder XRD diffractograms for the as-prepared 2RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O and 3RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O (x = 1.0, 0.8, 0.6) samples. Scans were obtained from finely powdered samples covered with 0.001 in. thick Kapton (Polyimide) tape. An empty polycarbonate sample holder covered with tape is shown as a reference. Major peaks from crystalline β-SiO 2, Si 3 S 2, GeO 2, and GeS 2 are also shown for reference.

+ xGeO 2 + (1−x)SiO 2 + nH 2 O (x = 1.0, 0.8, 0.6) and 3RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O (x = 1.0, 0.8, 0.6). The samples were covered with a Polyimide tape to prevent sample hydration at room temperature. There were no observed peaks that were distinguishable from the polycarbonate holder background from 20° to 60° 2θ for the 2RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O samples. There was no evidence of unreacted RbSH, GeO 2, SiO 2, or ZrO 2 from the milling bowl and ball media. Weak peaks were present for the x = 0.8 and x = 0.6 composition of the 3RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O phase, perhaps indicating a semicrystalline structure. Crystalline β-SiO 2, 19 Si 3 S 2, 20 GeO 2, 21 and GeS 2 are shown for reference. It does appear that there is a small percentage of crystalline products in the 3RbSH + xGeO 2 + (1−x)SiO 2 + nH 2 O samples. The resulting XRD amorphous materials are consistent with the employed synthesis route of planetary milling and then evaporating—precipitating at ~75 °C. Crystalline products have been obtained for similar binary samples, NaGeS 2(OH) 2·2H 2 O and Na 2GeS 4(OH)·8H 2 O, by using large amounts of acetone at room temperature to isolate the crystalline phases. 22,23 The proposed structural model is a metal anion, either germanium or silicon, tetrahedrally coordinated by sulfur anions and hydroxide ions. The sulfur anions are terminated by rubidium cations.

**Structural Characterizations: IR.** The IR spectra indicate a mixed system with both germanium and silicon bonding to both oxygen and sulfur and the presence of hydrated water. Figures 2 and 3 show the spectra for samples of the form Rb 2(Ge, Si) x−y S y(OH) e−z+H 2 O and Rb 3(Ge, Si) x−y S y−z(OH) e+H 2 O. The intense asymmetric vibration associated with Ge−S bond stretching vibrations are observed at ~3370 and 1655 cm −1, respectively. H 2 O and O−H liberation modes are present as sharp bands between 1446 and 534 cm −1.

(22) Prewitt, C. T.; Young, H. S. Science 1965, 149, 535.
ated with Ge–S– is observed to decrease in intensity with the reduction of germanium in the sample. The mode at ~667 cm\(^{-1}\) has previously been reported as the stretching vibration for the Si–S\(^{-}\) bond.\(^{25}\) The addition of SiO\(_2\) also results in a decrease in the O–H stretching vibrations at ~3360 cm\(^{-1}\), perhaps indicating that the retention of water in the sample is due to the presence of germanium, not silicon. In agreement with this, there is a very weak O–H bending mode at ~1655 cm\(^{-1}\) for the x = 0.9 of 2RbSH + xGeO\(_2\) + (1–x)SiO\(_2\) + yH\(_2\)O, but it is observed to disappear with further additions of SiO\(_2\). The O–H bending mode is present at ~1655 cm\(^{-1}\) for x = 1.0 to x = 0.7 for the 3RbSH + xGeO\(_2\) + (1–x)SiO\(_2\) + yH\(_2\)O samples, which indicates that higher concentrations of alkali lead to larger amounts of intercalated water.

**Structural Characterizations: Raman.** Figure 3 shows the corresponding Raman spectra for the as-prepared xRbSH + xGeO\(_2\) + (1–x)SiO\(_2\) + yH\(_2\)O (\(z = 2\) and \(0.5 \leq x \leq 1.0\)) samples. The Raman spectra for 2RbSH + GeO\(_2\) + yH\(_2\)O and 3RbSH + GeO\(_2\) + yH\(_2\)O have been previously reported and show peaks between 483 and 358 cm\(^{-1}\) which are associated with stretching modes of terminal Ge–S\(^{-}\) and bridging Ge–O–Ge units and of nonbridging Ge–O\(^{-}\) (H\(^{+}\)) and Ge–O\(^{-}\) (M\(^{+}\)) units.\(^{3}\) The substitution of Si\(^{4+}\) for Ge\(^{4+}\) results in a new peak at ~460 cm\(^{-1}\). It has previously been reported that the substitution of Si for Ge in Ge\(_2\)S\(_2\) units results in additional Raman lines between 450 and 550 cm\(^{-1}\), perhaps explaining the evolution of the peak at ~460 cm\(^{-1}\).\(^{26}\) The intensity of the symmetric stretching Ge–S\(^{-}\) mode at ~420 cm\(^{-1}\) is observed to decrease in intensity as the concentration of Si\(^{4+}\) increases. There does not appear to be a vibrational mode associated with bridging Ge–S–Ge modes (~340 cm\(^{-1}\)), which supports our proposed structure.\(^{27}\)

**Compositional Characterizations: SEM-EDS.** Table 1 shows the results for the four samples investigated using X-ray diffraction, 2RbSH + 0.6GeO\(_2\) + 0.4SiO\(_2\), 2RbSH + 0.8GeO\(_2\) + 0.2SiO\(_2\), 3RbSH + 0.6GeO\(_2\) + 0.4SiO\(_2\), and 3RbSH + 0.8GeO\(_2\) + 0.2SiO\(_2\). The EDS results agree well with trends that are to be expected for the samples investigated. Within each system, the xRbSH + 0.8GeO\(_2\) + 0.2SiO\(_2\) sample was found to have more germanium and less silicon than the corresponding xRbSH + 0.6GeO\(_2\) + 0.4SiO\(_2\). Larger errors were observed for the silicon and oxygen contents which were to be expected. Silicon is very light and present in such small amounts that accuracy is difficult. Errors were observed for oxygen because the exact amount of intercalated water upon exposing the samples to air momentarily and then placing under high vacuum is not known so theoretical calculations were performed assuming a completely dehydrated sample which would be consistent with the full removal of water under high vacuum.

**Thermal Characterizations: TGA.** Figures 4 and 5 present the TGA thermograms for the as-prepared 2RbSH + xGeO\(_2\) + (1–x)SiO\(_2\) + yH\(_2\)O and 3RbSH + xGeO\(_2\) + (1–x)SiO\(_2\) + yH\(_2\)O, respectively. The calculations for the amount of water (~yH\(_2\)O) present in each sample were performed by assuming that all intercalated water was lost by the second inflection point. Continuous mass loss is observed above the preparation temperature of ~75 °C with open sample pans purged under a nitrogen atmosphere. Both

---

**Table 1. SEM-EDS Results Using a Febol JSM-6060LV System with an Inca EDS-7582**

<table>
<thead>
<tr>
<th>sample</th>
<th>Rb</th>
<th>Ge</th>
<th>Si</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>2RbSH + 0.6GeO(_2) + 0.4SiO(_2) theoretical weight %</td>
<td>52.8</td>
<td>13.5</td>
<td>3.47</td>
<td>19.8</td>
<td>9.88</td>
</tr>
<tr>
<td>EDS weight %</td>
<td>50.3</td>
<td>22.7</td>
<td>4.79</td>
<td>15</td>
<td>7.16</td>
</tr>
<tr>
<td>2RbSH + 0.8GeO(_2) + 0.2SiO(_2) theoretical weight %</td>
<td>51.4</td>
<td>17.5</td>
<td>1.69</td>
<td>19.3</td>
<td>9.61</td>
</tr>
<tr>
<td>EDS weight %</td>
<td>48.7</td>
<td>26.6</td>
<td>3.46</td>
<td>15.6</td>
<td>5.77</td>
</tr>
<tr>
<td>3RbSH + 0.6GeO(_2) + 0.4SiO(_2) theoretical weight %</td>
<td>60.4</td>
<td>10.3</td>
<td>2.65</td>
<td>22.7</td>
<td>3.77</td>
</tr>
<tr>
<td>EDS weight %</td>
<td>54.9</td>
<td>12.7</td>
<td>3.68</td>
<td>17.2</td>
<td>11.5</td>
</tr>
<tr>
<td>3RbSH + 0.8GeO(_2) + 0.2SiO(_2) theoretical weight %</td>
<td>59.2</td>
<td>13.4</td>
<td>1.3</td>
<td>22.2</td>
<td>3.69</td>
</tr>
<tr>
<td>EDS weight %</td>
<td>54.3</td>
<td>16.8</td>
<td>2.72</td>
<td>17.8</td>
<td>8.37</td>
</tr>
</tbody>
</table>

*Samples were pressed into 0.5 in. diameter pellets and sputtered in gold in a N\(_2\) atmosphere.

---

of the $x = 1$ samples for $2\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ and $3\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ have the highest amount of intercalated water. It was previously shown for the alkali thio-hydroxogermanates that the inflection point between 200 and 300 °C is attributed to the removal of molecular water associated with the hydrated cation shell. A second inflection point around 400–450 °C is attributed to the thermal decomposition of hydroxyl groups and the formation of bridging oxygens. A second inflection point is not easily observed for the $2\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ materials, indicating perhaps a higher temperature decomposition; however, an inflection point is observed for $3\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ samples around ~450 °C. The presence of this inflection point for the higher alkali content samples agrees with the conductivity data in that the thermal stability is less for these samples compared to the $2\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ samples. This decrease in thermal stability could be due to the fact that the $3\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ samples have more alkali modifier which acts to break up the structure, thereby reducing the thermal stability.

**Conductivity Measurements.** a.c. impedance measurements indicate that the substitution of $\text{Si}^{4+}$ for $\text{Ge}^{4+}$ reduces the proton conductivity for both the $2\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ and $3\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ amorphous materials. Figures 6 and 7 show the Arrhenius temperature-dependent plot of the d.c. conductivity for the as-prepared $2\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ and $3\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ materials, respectively. The conductivity drops over an order of magnitude at 120 °C from $\sim 10^{-3.4}$ S/cm for the undoped sample, $2\text{RbSH} + \text{GeO}_2 + 1.7\text{H}_2\text{O}$, to $\sim 10^{-4.5}$ S/cm for $2\text{RbSH} + 0.9\text{GeO}_2 + 0.1\text{SiO}_2 + 0.8\text{H}_2\text{O}$, respectively, using a low-pressure sealed holder for the pressed powder samples which helps to minimize effects from different thermal histories. A similar conductivity decrease was observed for the $3\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + y\text{H}_2\text{O}$ samples upon substitutions of $\text{Si}^{4+}$ for $\text{Ge}^{4+}$; see Figure 7. The proton conductivity at 120 °C for the undoped $3\text{RbSH} + \text{GeO}_2 + y\text{H}_2\text{O}$ sample was $\sim 10^{-2.6}$ S/cm and was $\sim 10^{-3.5}$ S/cm for the $3\text{RbSH} + 0.9\text{GeO}_2 + 0.1\text{SiO}_2 + 1.1\text{H}_2\text{O}$ sample. The conductivity was found to be highly dependent on both the amount of silicon and intercalated water present in the dry $\text{N}_2$ atmosphere. In general, as the concentration of germanium decreases, the amount of intercalated water present decreases, leading to a decrease in the proton conductivity. This result indicates that germanium plays a large role in the amount of intercalated water present in the materials which in turn plays an important role in the proton conductivities. So far, it appears that the highest proton conductivities were observed for the binary rubidium thio-hydroxogermanates, $\delta_{\text{pc}} > 10^{-3}$ S/cm.

Thermal cycling of the conductivity was performed to determine the ratio of proton to alkali conductivity. The first conductivity heating cycle was performed on the as-prepared material heated from $\sim 25$ to $\sim 280$ °C. The cell was then cooled back to room temperature and the second run was performed on the now dehydrated material, resulting in only alkali conductivity (here rubidium) as opposed to the first cycle where it is dominated by proton motion (with some rubidium motion). It is evident from the IR spectra in Figure 2 that the presence of vibrational modes associated with $\delta(\text{H}_2\text{O})$ modes leads to enhanced proton conductivity while samples without this peak in the IR spectra have no observable proton conductivity (i.e., their first and second cycle conductivity runs are the same). The two different possible proton conduction mechanisms are vehicle and free-proton types (Grotthuss). It is observed in these materials that as the amount of hydrated water is increased, the proton conductivity increases, indicating that the conduction method is due to this extrinsic water in a free-proton type mechanism.

a.c. impedance measurements were also performed in the presence of low levels of relative humidity (R.H.), $\sim 6\%$,

![Figure 6. Arrhenius temperature-dependent plot of d.c. conductivity for the as-prepared $2\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + n\text{H}_2\text{O}$, both first and second heating cycles. Measurements were performed using 10 °C steps and 20 min stabilization times on compacted powder pellets sealed in a Teflon sleeve by hardened steel electrodes.](Image 6)

![Figure 7. Arrhenius temperature-dependent plot of d.c. conductivity for the as-prepared $3\text{RbSH} + x\text{GeO}_2 + (1-x)\text{SiO}_2 + n\text{H}_2\text{O}$, both first and second heating cycles. Measurements were performed using 10 °C steps and 20 min stabilization times on compacted powder pellets sealed in a Teflon sleeve by hardened steel electrodes.](Image 7)
Summary and Conclusions

In summary, a series of novel amorphous hydrated alkali thio-hydroxosilicogermanates of the form $2RbSH + xGeO_2 + (1-x)SiO_2 + nH_2O$ where $2 \leq z \leq 3$ and $0.5 \leq x \leq 1.0$ were synthesized from hydrothermal reactions and characterized with respect to their structure, conductivity, and thermal properties. In general, the samples were found to be X-ray amorphous with high amounts of SiO$_2$, resulting in semi-crystalline materials for $3RbSH + xGeO_2 + (1-x)SiO_2 + nH_2O$, $x = 0.6$ sample. The amorphous nature is consistent with the mechanochemical hydrothermal evaporation–precipitation synthesis method used to prepare the materials. The vibrational spectra indicate the presence of a mixed system with both germanium and silicon bonded to non-bridging oxygen and sulfur anions. There is also extensive hydrogen bonding observed through O–H stretching modes and bending modes in some samples which leads to higher proton conductivities. Maximum d.c. conductivity values of $10^{-4.5}$ and $10^{-3.5}$ S/cm at $120^\circ$C were obtained for small SiO$_2$ doping amounts for $2RbSH + 0.9GeO_2 + 0.1SiO_2 + 0.8H_2O$ and $3RbSH + 0.9GeO_2 + 0.1SiO_2 + 1.1H_2O$, respectively. These conductivity values were an order of magnitude lower than that of the binary alkali thio-hydroxosilicogermanates previously synthesized, indicating that the addition of Si$^{4+}$ for Ge$^{4+}$ does not weaken the electrostatic interaction between mobile cations and framework anions, but instead acts as a barrier to proton conduction. However, the presence of humidity during the d.c. conductivity experiments for $2RbSH + xGeO_2 + (1-x)SiO_2 + nH_2O$ resulted in a 4 order of magnitude increase in the proton conductivity at $60^\circ$C to $10^{-4}$ S/cm and a smaller increase at $120^\circ$C to $10^{-3}$ S/cm.

Acknowledgment. This material is based on the work funded by the Honda Research Initiation Grant.

CM0618796