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Abstract
The synthesis and structure of the thiogermanic acids H4Ge4S10 and H2Ge4S9 are reported. A novel preparation method consisting of reacting germanium oxide with liquid hydrogen sulfide containing a trace amount of water is used to form Ge4S104- ions. Evaporating the hydrogen sulfide solution at room temperature leaves an unstable H4Ge4S10·xH2O product. The stoichiometry and structure of the thermally stable anhydrous phase are dependent on reaction time. An H4Ge4S10 product with an adamantane-like cage structure is obtained at shorter reaction times. Longer reaction times produce an H2Ge4S9 product with a more complex cage unit, a higher symmetry unit cell, and increased thermal stability. Raman, infrared, powder X-ray diffraction, and thermogravimetric data are reported for both structures.

Disciplines
Materials Science and Engineering | Physical Chemistry

Comments
Synthesis and Characterization of the Thiogermanic Acids H₄GeS₁₀ and H₂GeS₉

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The synthesis and structure of the thiogermanic acids H₄GeS₁₀ and H₂GeS₉ are reported. A novel preparation method consisting of reacting germanium oxide with liquid hydrogen sulfide containing a trace amount of water is used to form GeS₄²⁻ ions. Evaporating the hydrogen sulfide solution at room temperature leaves an unstable H₂Ge₂S₅·xH₂O product. The stoichiometry and structure of the thermally stable anhydrous phase are dependent on reaction time. An H₂Ge₂S₅ product with an adamantane-like cage structure is obtained at shorter reaction times. Longer reaction times produce an H₂GeS₃ product with a more complex cage unit, a higher symmetry unit cell, and increased thermal stability. Raman, infrared, powder X-ray diffraction, and thermogravimetric data are reported for both structures.

1. Introduction

Current and past efforts to produce protonated germanium sulfide complexes using hydrogen sulfide have resulted in the stoichiometric compound H₂GeS₅. The existence of a Ge₂S₅⁻ unit cage was first reported as a Ge₂S₅⁻·2H₂O product. The stoichiometry and structure of the thermally stable anhydrous phase were also reported to decompose slowly at 0 °C and was extremely soluble in water. This synthesis route proved to be inadequate for obtaining very pure samples without oxide contamination.

In the present study, a reaction medium consisting of liquid H₂S with a trace amount of water is implemented at room temperature. Under these conditions, it is possible to produce Ge₂S₅⁻ ions starting from quartz-type GeO₂ or glassy GeS₂. This new preparation method is simple and functional, producing a structural evolution of the Ge₂S₅⁻ cage unit over time. In this article, the stoichiometry and structure of the resulting thiogermanic acid starting from GeO₂ as a precursor are characterized as functions of the reaction time.

There have been two reported structural isomers for the Ge₂S₅⁻ complex: adamantane and “double-decker.” Figure 1 shows the structures of the adamantane and double-decker Ge₂S₅⁻ complex anions. An adamantane-like unit was recently determined for the H₂Ge₂S₅ phase.7 Adamantane units have also been determined for the phases of M₄Ge₂S₅ (M = Na, K, Rb, Cs, and Tl).1–6 and Ba₂Ge₂S₅.7 The adamantane unit is composed of four corner-shared GeS₄⁻ tetrahedra. This structural unit was reported to be synthesized from solid-state reactions in evacuated silica tubes. Aqueous solution reactions were also reported for Cs₂GeS₅·3H₂O, which was synthesized by adding GeS₂ to a concentrated aqueous solution of Cs₂S where upon crystallization of the adduct was observed on standing.8 These units are usually highly symmetric with point symmetry group of Tₐ.9 Hence, the vibrational modes of the adamantane Ge₂S₅⁻ unit are distributed among the following Raman (R) and infrared (IR) fundamental vibrations: Γ(Tₐ) = 3A₁(R) + 3E(R) + 3F₁(inactive) + 6F₂(IR, R). A triclinic unit cell with space group P1 is observed for the adamantane H₂Ge₂S₅ phase.2 Orthorhombic and monoclinic crystal systems with space groups Cmcm, C2/c, and C12/a/1 have been revealed for the M₄Ge₂S₅ adamantane compounds.4–6,10 A cubic unit cell with space group Fd3 or Fd3m has been reported for Ba₂Ge₂S₅.7

Although germanium oxide-based complexes are known to form higher homologous structures, the only additional reported structure for Ge₂S₅⁻ based complexes is the double-decker.11 This isomer has been previously reported for organo-substituted germanium sesquisulfides, R₄Ge₂S₅, where R represents an organic group.11,12 From a ring-strain perspective, the double-decker isomer is less favorable, having two sets of edge-shared tetrahedral units linked together. Structural solutions from X-ray diffraction (XRD) of R₄Ge₂S₅ indicate S-S distances in the shared edges of 3.30 Å, which is less than the sum of the van der Waals radii of 3.60 Å. Additionally, ⁷⁷Se NMR distinguishes two distinct selenium environments for R₄Ge₂S₅ and R₄Si₄Se₆ double-decker complexes.12 The double-decker Ge₄S₁₀⁻⁻ unit has a point symmetry group of D₂h and the vibrational modes are distributed among the following fundamental vibrations: Γ(D₂h) = 4A₁g (inactive) + 4B₁g (IR) + 4B₁u (IR) + 4B₂u (IR) + 2A₂g (IR) + 2B₂g (IR). Cubic and monoclinic crystal systems with space groups I23 and C2/c, respectively, have been revealed for the organo-substituted R₄Ge₂S₆ double-decker compounds.11,12

2. Experimental Section

2.1. Sample Preparation. A typical reaction consisted of placing 500 mg (± 1 mg) of commercial quartz-type GeO₂ powder (Cerac 99.999%, ~325 mesh) in an alumina tube, which in turn was placed inside a type 316 stainless steel reaction vessel. The total free volume inside the reaction vessel was ~72 mL. The reactor was sealed with a Teflon O-ring gasket and a Swagelok type 316 stainless steel needle valve. The assembled...
A 20 mL/min flow of N2 was used as the sample purge to prevent any oxidation reactions. About 25 mg of each sample was placed inside an aluminum sample pan. A heating rate of 10 °C/min was used for all TGA experiments.

3. Results and Discussion

3.1. Mass Change. Sample masses were recorded for all reactions as a function of reaction time. There was minimal water content in the GeO2 as can be seen in the mid-IR spectra in Figure 3; the initial H2O contamination was accredited to the impurity water content of the H2S. Hydroxyl group formation is also in agreement with the observation that hydrated GeO2 was necessary for the reaction to proceed.1 A white-to-beige colored product was collected for reaction times longer than 1 week. Two-week reactions produced stabilized sample masses consistent with ~92 wt % H4Ge4S10 with the balance as GeO2; this is in agreement with the mid-IR spectra in Figure 3. Stabilized masses from 3- and 4-week reaction times suggest mixed-phase products, whereas 8-week reactions indicated an H2GeS6 phase. As an example, a complete conversion to the stoichiometric compound H4Ge4S10 from 500 ± 1 mg of GeO2 would yield 694 ± 2 mg of product. A mixed oxy-sulfide phase of H2GeS6O2 would yield a similar mass, but no evidence for this type of phase is present in the corresponding vibrational spectra. Immediately after opening the reactors, the recorded sample masses were much higher. This is consistent with hydrous H4Ge4S10\(\times\)H2O phases stabilized by the cooler temperature resulting from endothermic boiling-off of H2S during rapid removal. For the 2- and 8-week reaction products, the decomposition reaction upon warming to room temperature may be written as

\[
\text{H}_4\text{Ge}_4\text{S}_{10}\times\text{H}_2\text{O}(s) \to \text{H}_4\text{Ge}_4\text{S}_{10}(s) + x\text{H}_2\text{O}(g) \quad (2a)
\]

and

\[
\text{H}_4\text{Ge}_4\text{S}_{10}\times\text{H}_2\text{O}(s) \to \text{H}_2\text{Ge}_6\text{S}_6(s) + x\text{H}_2\text{O}(g) \quad (2b)
\]

respectively. About 1 day after removing the liquid H2S, all intercalated H2O was evaporated and the decomposition reaction was complete.

3.2. Raman Scattering. Figure 2 presents the unpolarized Raman spectra of the stabilized products as a function of reaction time in liquid H2S at room temperature. The vibrational frequencies in the spectra are time independent after opening the reactor; for reaction times greater than one week, this implies the GeS10\(^{4-}\) structural cage unit is present in both the hydrous and anhydrous phases. For 1 week of reaction time, the vibrational bands assigned to quartz-type GeO2 are still present and the strongest band located at ~443 cm\(^{-1}\) can be assigned to Ge–O–Ge symmetric stretching.13 For 2 weeks of reaction time, new vibrational bands appear, suggesting a structure that is consistent with adamantane-like GeS10\(^{4-}\) units. Table 1
TABLE 1: Raman and IR Mode Assignments for the 2-Week Reaction Product H$_4$Ge$_4$S$_{10}$

<table>
<thead>
<tr>
<th></th>
<th>H$_4$Ge$<em>4$S$</em>{10}$ and H$_4$Ge$<em>4$S$</em>{10}$·H$_2$O adamantane</th>
<th>Cs$_4$Ge$<em>4$S$</em>{10}$ adamantane$^a$</th>
<th>Na$_4$Ge$<em>4$S$</em>{10}$ adamantane$^b$</th>
<th>lithium dithiogermaine glass$^{14}$</th>
<th>silver dithiogermaine glass$^{14}$</th>
<th>Raman</th>
<th>IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(F$_2$)</td>
<td>107</td>
<td>116</td>
<td>121</td>
<td></td>
<td></td>
<td>IR</td>
<td></td>
</tr>
<tr>
<td>$\nu$(F$_2$)</td>
<td>145</td>
<td>144</td>
<td>148</td>
<td></td>
<td></td>
<td>Raman</td>
<td></td>
</tr>
<tr>
<td>$\nu$(A$_1$)</td>
<td>187</td>
<td>193</td>
<td>200</td>
<td></td>
<td></td>
<td>IR</td>
<td></td>
</tr>
<tr>
<td>$\nu$(Ge–S–Ge)</td>
<td>355</td>
<td>340</td>
<td>354</td>
<td>350</td>
<td>339</td>
<td>330</td>
<td></td>
</tr>
<tr>
<td>$\nu$(A$_1$)($\nu$(Ge–S–Ge))</td>
<td>407, 416, 414</td>
<td>462</td>
<td>470</td>
<td>425</td>
<td>415</td>
<td>412</td>
<td></td>
</tr>
<tr>
<td>$\nu$(S–H)</td>
<td>2484, 2515, 2479, 2511</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $T_d$ point group symmetry is assumed for the adamantane Ge$_4$S$_{10}$+† unit cage. Assignments for comparable reference systems are also presented. All units are in wavenumbers (cm$^{-1}$).

TABLE 2: Raman and IR Mode Assignments for the 8-Week Reaction Product H$_2$Ge$_4$S$_9$

<table>
<thead>
<tr>
<th></th>
<th>H$_2$Ge$_4$S$_9$ and H$_2$Ge$_4$S$_9$·H$_2$O</th>
<th>Glassy GeS$_2$</th>
<th>High Temp 2D phase (β–GeS$_2$)</th>
<th>Low Temp 3D phase (α–GeS$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman</td>
<td>IR</td>
<td>Raman</td>
<td>IR</td>
</tr>
<tr>
<td>bond-bending</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E and low F$_2$</td>
<td>106, 127, 152, 172, 197, 240</td>
<td>105$^{19}$, 112$^{16}$, 110, 150$^{18}$</td>
<td>140$^{19}$, 147$^{16}$, 115, 153$^{18}$</td>
<td>356$^{19}$, 361$^{20}$, 342$^{20}$, 363$^{20}$, 363$^{15}$, 383$^{22}$, 340–450, exc. A$_1^{20}$, 350–450$^{20}$</td>
</tr>
<tr>
<td>A$_1$ corner-shared ($\nu$(Ge–S–Ge))</td>
<td>344</td>
<td>338</td>
<td>342$^{18}$, 343$^{16}$, 340$^{16}$</td>
<td>347$^{14}$, 342$^{20}$, 339$^{20}$</td>
</tr>
<tr>
<td>A$_1$ edge-shared ($\nu$(Ge–S–Ge))</td>
<td>352</td>
<td>374$^{14}$, 370$^{16}$</td>
<td>371$^{15}$, 390$^{16}$, 368$^{18}$</td>
<td>367$^{19}$, 395$^{16}$, 377$^{18}$</td>
</tr>
<tr>
<td>F$_2$ ($\nu$(Ge–S–Ge))</td>
<td>363</td>
<td>370</td>
<td>372$^{16}$</td>
<td>377$^{18}$, 409$^{19}$</td>
</tr>
<tr>
<td>bond-stretching</td>
<td>380</td>
<td>386</td>
<td>367$^{19}$, 395$^{16}$, 377$^{18}$</td>
<td>409$^{19}$</td>
</tr>
<tr>
<td>A$_1$ and high F$_2$</td>
<td>401</td>
<td>403</td>
<td>411</td>
<td>411</td>
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<tr>
<td></td>
<td>409</td>
<td>411</td>
<td>435</td>
<td>434</td>
</tr>
<tr>
<td></td>
<td>2520</td>
<td>2517</td>
<td>2525$^{23}$</td>
<td>2525$^{23}$</td>
</tr>
</tbody>
</table>

$^a$ Local $T_d$ point group symmetry is assumed for isolated GeS$_4$ units. Assignments for comparable reference systems are also presented. All units are in wavenumbers (cm$^{-1}$). $^b$Although controversial, in glassy GeS$_2$ the A$_1$ companion band is often attributed to edge shared tetrahedral units.

Figure 2. Raman spectra of GeO$_2$ reacted with liquid H$_2$S at room temperature as a function of time. No reaction is noted for 1 week; 2-week reaction time produces a highly vibrational symmetric adamantane H$_4$Ge$_4$S$_{10}$ phase; 3- and 4-week reaction times produce mixed phases, whereas 8 weeks of reaction time appears to produce an H$_2$Ge$_4$S$_9$ phase with a more complex cage unit. presents select Raman and IR vibrational mode assignments for the adamantane H$_4$Ge$_4$S$_{10}$ phase and representative reference systems assuming $T_d$ point group symmetry. In a polarized Raman spectrum, the strongest bands may be assigned to the 3A$_1$ vibrations for the adamantane structural unit.$^9$ In the unpolarized spectrum obtained for 2 weeks of reaction time, the strongest intensity band observed at ~355 cm$^{-1}$ is assigned to Ge–S–Ge symmetrical bridge-stretching mode $\nu_2$(A$_1$). This value is within resolution for that reported for Na$_4$Ge$_4$S$_{10}$.$^3$ The band observed at ~187 cm$^{-1}$ may be assigned to Ge–S–Ge symmetrical bridge bending mode $\nu_3$(A$_1$). The two overlapping bands centered around ~407 and ~416 cm$^{-1}$ may be attributed to Ge–S–Ge nonbridging or symmetrical terminal stretching mode $\nu_1$(A$_1$). This is consistent with two broad bands with peak intensities located around ~2484 and ~2515 cm$^{-1}$ assigned to S–H bond stretching. Two distinct bands indicate two unique hydrogen environments for the H$_4$Ge$_4$S$_{10}$ phase.

The products associated with 3 and 4 weeks of reaction time suggest mixed phases, whereas the product from 8 weeks of reaction time indicates a different structure altogether. Although it is not possible to fully resolve this new structure from the unpolarized Raman spectrum alone, inferences may be drawn from comparisons with established systems. Without knowing the structure, one may consider the individual GeS$_4$ units possessing $T_d$ symmetry to suggest mode assignments using crystalline and glassy GeS$_2$ as references. Table 2 presents Raman and IR suggested vibrational mode assignments of the H$_2$Ge$_4$S$_9$ phase for 8 weeks of reaction time. In the spectrum, medium-intensity vibrational bands at ~106, ~127, ~152, and ~172 cm$^{-1}$ and weak-intensity bands at ~197 and ~240 cm$^{-1}$ are located in the frequency region consistent with translational, rotational, and bond-bending E and lower frequency F$_2$ modes.$^{14–19}$ The strongest bands with peak intensity values at ~344, ~352, and ~363 cm$^{-1}$ may be attributed to Ge–S–Ge stretching modes. Specifically, the bands at ~344 and ~352 cm$^{-1}$ may be attributed to A$_1$ symmetric stretching due to weak
IR activity. In contrast, the band at ~363 cm\(^{-1}\) may be attributed to F\(_2\) asymmetric stretching due to strong IR activity. The ratio of the band intensities at ~344 and ~352 cm\(^{-1}\) are roughly consistent with corner-shared and edge-shared tetrahedral units, respectively, associated within the double-decker isomer. Note, the ~344 cm\(^{-1}\) band intensity was observed to increase after the mass of the reaction product stabilized, indicating bridging of discrete units into rings and/or chains. The medium-intensity vibrational bands with peak intensities located at ~380, ~401, ~409, ~435, and ~445 cm\(^{-1}\) may be generally attributed to A\(_1\) terminal stretching mode and higher F\(_2\) stretching modes. Specifically, the broad band located at ~409 cm\(^{-1}\) is close to the Ge\(^{-}\)–S\(^{-}\) nonbridging mode for the 2-week reaction time. The S–H bond stretching mode for the 8-week reaction time has a high intensity peak located ~2520 cm\(^{-1}\); this peak is narrower in frequency and half the integrated area of the S–H stretching mode for the 2-week reaction. This indicates one unique hydrogen environment for the H\(_2\)GeS\(_4\) phase.

The Raman spectrum resulting from 8 weeks of reaction time is more consistent with an isomer having reduced vibrational symmetry and a more complex cage unit. Again, it is suggested that intact Ge\(_4\)S\(_{10}\) units are linked together to form rings and/or chains. The possible formation of a double-decker isomer of Ge\(_4\)S\(_{10}\) units may be the result of extensive reaction time with hydrostatic pressure equal to that of the vapor pressure of H\(_2\)S at room temperature, i.e., 267 psia (1.8 MPa).

3.3 Infrared Spectra. Figure 3 presents the mid-IR spectra of the stabilized products as a function of reaction time in liquid H\(_2\)S at room temperature. For 1 week of reaction time, the resulting spectrum looks very similar to that of the starting GeO\(_2\) compound. The broad bands located around ~877 and ~553 cm\(^{-1}\) may be assigned to Ge–O–Ge asymmetric stretching modes \(v_\text{as}\) (860, 894, 989 cm\(^{-1}\)) and Ge–O–Ge symmetric stretching modes \(v_s\) (464, 569 cm\(^{-1}\)), respectively. Additionally, a weak O–H stretching mode centered around ~3400 cm\(^{-1}\) is present and is consistent with the hydration process as the first step of the total reaction. For a reaction time of 2 weeks, the corresponding mid-IR spectrum shows a reduction in the intensity of Ge–O–Ge asymmetric stretching and symmetric stretching modes. Two overlapping S–H stretching modes centered around ~2479 and ~2511 cm\(^{-1}\) are also present. As noted from the corresponding Raman spectrum, the presence of two distinct bands indicates two unique hydrogen environments.

The far-IR spectra of GeO\(_2\) reacted with liquid H\(_2\)S at room temperature as a function of time. Two and three-week reaction times produce IR active Ge–S\(^{-}\) terminal stretching modes at ~414 cm\(^{-1}\). Eight-week reaction time produces additional IR active modes including the strong asymmetric stretching mode at ~370 cm\(^{-1}\).
of reaction time; thus the existence of a double-decker complex isomer remains unresolved.

3.5. Thermal Analysis. Figure 6 presents the TGA spectra of the stabilized products of 2- and 8-week reaction times in liquid H$_2$S at room temperature. Decomposition onset temperatures corresponding to the 2-week reaction product H$_4$Ge$_4$S$_{10}$ and the 8-week reaction product H$_2$Ge$_4$S$_9$ were observed at $\sim$250 °C and $\sim$360 °C, respectively. Theoretical decomposition of pure phases of H$_4$Ge$_4$S$_{10}$ and H$_2$Ge$_4$S$_9$ into GeS$_2$ would produce final mass fractions of 0.89 and 0.94, respectively. Thermal relaxation of the 8-week reaction product converting to the adamantane structural unit before decomposition was not observed in the corresponding Raman spectra; initial decomposition of both phases formed a glassy GeS$_2$ product. After decomposition at 500 °C, the observed Raman spectra of both isomers exhibited a strong Ge$-$S$-$Ge symmetrical bridge stretching mode at $\sim$360 cm$^{-1}$; upon further heating ($\sim$700 °C), this band grew in intensity producing Raman spectra which were consistent with that reported for the high temperature 2-D crystalline GeS$_2$ (denoted as $\beta$-GeS$_2$ in this article).$^{15}$

4. Conclusions

Novel reactions of liquid H$_2$S with GeO$_2$ produce Ge$_4$S$_{10}^{4-}$ ions in solution. These reactions involve kinetic processes including hydroxide to hydrosulfide group transformation, adamantane cage formation, and cage restructuring. Evaporating the H$_2$O$-$H$_2$S solution leaves thermally unstable H$_4$Ge$_4$S$_{10}^-$ $\cdot$H$_2$O units that decompose into the thermally stable anhydrous H$_2$Ge$_4$S$_9$ or H$_2$Ge$_4$S$_7$ phases. In general, the adamantane H$_2$Ge$_4$S$_9$ phase is obtained from shorter reaction times, whereas an H$_2$Ge$_4$S$_7$ phase with a more complex cage unit and a more symmetric unit cell is suggested for longer reaction times. The Raman, IR, and XRD structural evolution as a function of reaction time indicates a strongly kinetically controlled formation rate with presumably the hydrostatic pressure of liquid H$_2$S as the driving force. Ultimately, this H$_2$Ge$_4$S$_9$ phase realized from longer reaction times is approximately 110 °C more thermally stable than that of the adamantane H$_2$Ge$_4$S$_9$ phase. For both thiogermainic acids, however, the thermal decomposition product is determined to be glassy GeS$_2$ from corresponding Raman spectra.

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