

Three-Dimensional Frameworks of Cubic $(\text{NH}_4)_5\text{Ga}_4\text{SbS}_{10}$, $(\text{NH}_4)_4\text{Ga}_4\text{SbS}_9(\text{OH}) \cdot \text{H}_2\text{O}$, and $(\text{NH}_4)_3\text{Ga}_4\text{SbS}_9(\text{OH}_2) \cdot 2\text{H}_2\text{O}$

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Three new isostructural open-framework sulfides, $(\text{NH}_4)_5\text{Ga}_4\text{SbS}_{10}$ (**1**), $(\text{NH}_4)_4\text{Ga}_4\text{SbS}_9(\text{OH}) \cdot \text{H}_2\text{O}$ (**2a**), and $(\text{NH}_4)_3\text{Ga}_4\text{SbS}_9(\text{H}_2\text{O}) \cdot 2\text{H}_2\text{O}$ (**2b**), were synthesized under basic hydrothermal conditions using ammonium hydroxide as the structure-directing agent. The structures feature a three-dimensional open framework comprised of adamantane $[\text{Ga}_4\text{Q}_{10}]^{8-}$ clusters linked with Sb^{3+} centers. The compounds are wide gap semiconductors, crystallize in the chiral space group $P2_13$, and represent a new structure type. They exhibit nonlinear optical properties.

Open-framework metal chalcogenides have shown a remarkable array of structural, ion-exchange, and optical properties, many of which are not observed in oxides.^{1–4} Compounds that are built with chalcogenido clusters, such as the adamantane chalcogenido clusters of Ga, Ge, or Sn, exhibit a wide diversity in structure and porosity when synthesized with different structure-directing agents (SDAs). Many of these structures form from tetrahedral, supertetrahedral, or even pentasupertetrahedral clusters that can be linked and controlled in a variety of ways.^{2,3,5–10} Hydrothermal synthetic techniques are key to

synthesizing open-framework chalcogenides, and the process has opened the door to many new architectures.^{3,8–14}

Of particular interest are the several classes of materials that have been synthesized using SDAs to tune their properties. Often slight changes in an SDA can lead to large changes in the structure, while maintaining the general connectivity between clusters. Such compounds can thus be designed to selectively uptake ions through control of the pore size.¹⁵

The mode in which supertetrahedral clusters are bridged also affects properties. For instance, clusters known to have been linked via polysulfide bonds have interesting photoluminescence properties,¹⁶ while clusters linked with organic ligands have flexible pore sizes for optical tunability.⁵ In these cases, the mode of bridging is key to the properties of the material.¹⁷

Networks built from thioantimonates and linking group 13 metals are attractive because they can possess a variety of useful features such as porosity and selective ion-exchange properties.¹⁷ The group 15 elements are of specific interest, as the asymmetric coordination of ions such as As^{3+} and Sb^{3+} with stereochemically active lone pairs is known to induce noncentrosymmetric structures.^{18,19} The compounds presented herein are the first examples of sulfide networks with supertetrahedral gallium clusters linked by antimony atoms. Here, we describe the syntheses²⁰ and structures of new cubic

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(20) Compound **1** was synthesized hydrothermally in a 23 mL Teflon-lined autoclave using Ga, Sb, and S (1.0 mmol Ga, 1.0 mmol Sb, 10 mmol S) and a 6 mL 50% mixture of NH_4OH (30% in water) and triethylamine (TEA) (30% in water) at 160 °C for one week. There are at least three phases within the system that can be identified: Sb_2S_3 , $\text{NH}_4\text{Sb}_5\text{S}_8$, and $(\text{NH}_4)_5\text{Ga}_4\text{SbS}_{10}$ (**1**). Dark red crystals of **1** were removed manually and used for further analyses. $(\text{NH}_4)_4\text{Ga}_4\text{SbS}_9(\text{OH}) \cdot \text{H}_2\text{O}$ (**2a**) and $(\text{NH}_4)_3\text{Ga}_4\text{SbS}_9(\text{OH}_2) \cdot 2\text{H}_2\text{O}$ (**2b**) were synthesized hydrothermally using 8 mm o.d. pyrex tubes, to which was added Ga_2S_3 , Sb_2S_3 , S (0.4 mmol Ga_2S_3 , 0.1 mmol Sb_2S_3 , 0.9 mmol S), and 0.3 mL of NH_4OH (30% in water). These tubes were then sealed under a vacuum and kept in an oven at 160 °C for 7–10 days. Colorless crystals were collected manually from mixtures of unreacted starting materials.

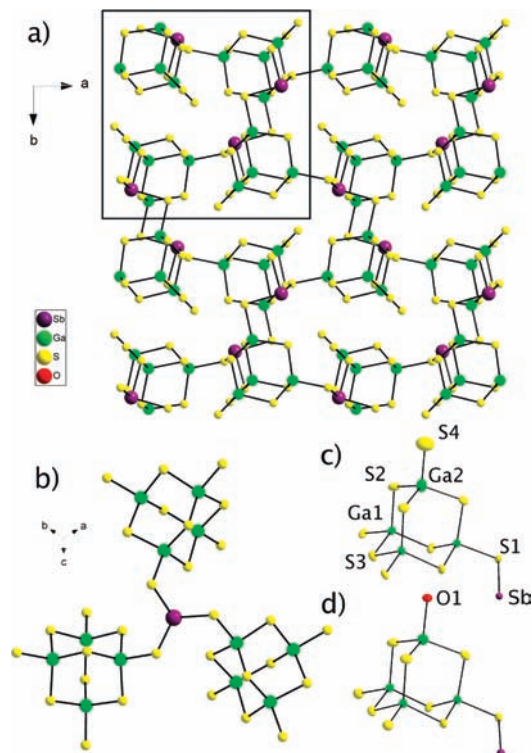


Figure 1. (a) The open-framework of **1**. Nitrogen atoms have been removed for clarity. (b) The three-coordinate bridging of T2 clusters by Sb. (c) The asymmetric unit of **1**. (d) The asymmetric unit of **2**.

compounds $(\text{NH}_4)_5\text{Ga}_4\text{SbS}_{10}$ (**1**), $(\text{NH}_4)_4\text{Ga}_4\text{SbS}_9(\text{OH})\cdot\text{H}_2\text{O}$ (**2a**), and $(\text{NH}_4)_3\text{Ga}_4\text{SbS}_9(\text{OH}_2)\cdot 2\text{H}_2\text{O}$ (**2b**), which feature an open framework resembling those of small pore zeolites. They possess thiogallate-based supertetrahedral T2 clusters linked by Sb^{3+} centers. Compounds **1**, **2a**, and **2b** are isostructural and present a new structure type.

The structure of **1** was solved in the noncentrosymmetric space group $P2_13$.²¹ The essential feature of the compound is the supertetrahedral T2 adamantane $[\text{Ga}_4\text{S}_{10}]^{8-}$ cluster, which is defined by four corner-sharing GaS_4 tetrahedra (Figure 1a). Three of the four apexes of the T2 supertetrahedral cluster are covalently bound to the Sb atoms, while a sulfur atom terminates the final apex. The Sb atoms bridge three separate T2 clusters, creating a three-fold axis of rotation around Sb (Figure 1b). There are four crystallographically distinct sulfur atoms within the structure: S1 is coordinated to Sb and Ga1, S3 is coordinated solely to two Ga1 atoms, S2 is coordinated to Ga1 and Ga2, and S4 exists as the terminal S at the “apex” of the T2 cluster (Figure 1c). The Ga–S bond distances are consistent with literature values, lying within the range of 2.201(8)–2.300(3) Å.⁷ The three equivalent Sb–S1 distances are 2.455(3) Å. The terminal atoms in **1** and **2** face toward the middle of the pores and are 3.37(2) Å away from an ammonium molecule located within the pore, suggesting $\text{NH}_4\cdots\text{S}\cdots\text{O}$ hydrogen-bonding.⁷ These terminal atoms thus constrict the pores to 1.67–1.77 Å.²²

(21) Crystals of **1** belong to the space group $P2_13$ (no. 198) with $a = 12.9000(5)$ Å and $V = 2146.69(14)$ Å³. Other crystal data: $Z = 4$; $D_c = 2.511$ g/cm³; $\mu = 7.165$ mm⁻¹; total reflections, 18 526; independent reflections, 2453; parameters, 61 ($R_{\text{int}} = 0.0644$); $R_1 = 0.0737$; $wR_2 = 0.1402$; GOF = 1.398.

(22) Pore sizes calculated by removing the atoms and calculating the void space in the crystal structure using PLATON software. See the Supporting Information.

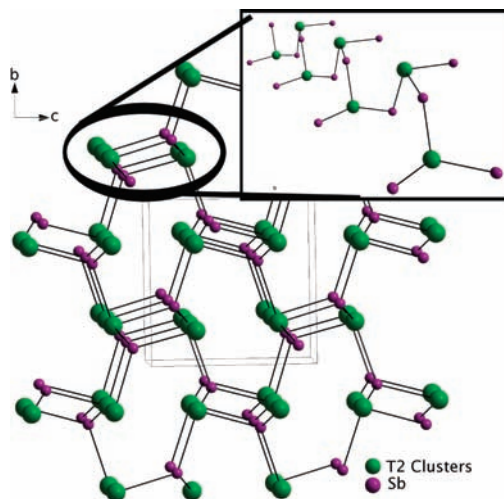


Figure 2. Representation of the T2 clusters as atoms, clearly showing the pores of the system. Typically, the apex atom (S4, O1) points toward the middle of these pores, reducing the average pore radii to between 1.67 and 1.77 Å, demonstrating a small zeolite-like pore system.

The crystal structures of compounds **2a** and **2b** were determined using synchrotron radiation and are isostructural to **1** and deviate solely at the terminal apex of the T2 cluster.²³ Instead of the terminal S4 atom at the apex of the $[\text{Ga}_4\text{S}_{10}]^{8-}$ cluster, **2a** and **2b** contain an oxygen atom from an –OH (**2a**) or –OH₂ (**2b**) ligand, giving rise to the new adamantane cluster $[\text{Ga}_4\text{S}_9(\text{OH})]^{7-}$ or $[\text{Ga}_4\text{S}_9(\text{OH}_2)]^{6-}$ (Figure 1d). The Ga2–O1 bond length is relatively long at 2.097(10) Å. To the best of our knowledge this is the first terminal Ga–OH example in supertetrahedral systems.

The three-dimensional structure can be simplified by representing the adamantane clusters as atoms (Figure 2). This simple representation shows the arrangement of the clusters in their chemical environments. When viewing down the a axis, it appears that the clusters are dimers, when in fact, they are helical chains of $[\text{T2}]\text{Sb}_3$. These helical chains are linked in all dimensions making up the complete three-dimensional structure. The helical formation reflects the chirality of the system and outlines a pore structure similar to the layered $(\text{Me}_2\text{NH}_2)_2\text{Ga}_2\text{Sb}_2\text{S}_7$ (Figure 2).²⁴

Interestingly, the syntheses of **2a** and **2b** are identical²⁰ and yet produce crystals of two different colors: orange-yellow and colorless. This is further verified by their energy bandgaps: the colorless crystals (**2a**) have a bandgap of 2.8 eV, and the yellow crystals (**2b**) exhibit 2.6 eV (Figure 3). Compounds **2a** and **2b** refine to the same structure, indicating that the color difference is due to a subtle change that cannot be determined through crystallography. To probe this color differentiation, crystals of **2a** were soaked in 0.2 M HCl. The crystals become yellow first and then take on their final orange hue as they interact with the acid. The crystal structure, refined after the acid treatment, remained essentially intact. This has led us to believe that the acid is protonating the inorganic framework either at the Ga–OH site to form a Ga–(OH₂) species where the terminal ligand is now water or at a sulfide Ga–S–Ga site to form

(23) Crystals of **2b** belong to the space group $P2_13$ (no. 198) with $a = 12.9098(4)$ Å and $V = 2151.58(12)$ Å³. Other crystal data: $Z = 4$; $D_c = 2.400$ Mg/m³; $\mu = 3.690$ mm⁻¹; total reflections, 16 614; independent reflections, 1036; parameters, 61 ($R_{\text{int}} = 0.060$); $R_1 = 0.046$; $wR_2 = 0.159$; GOF = 1.31.

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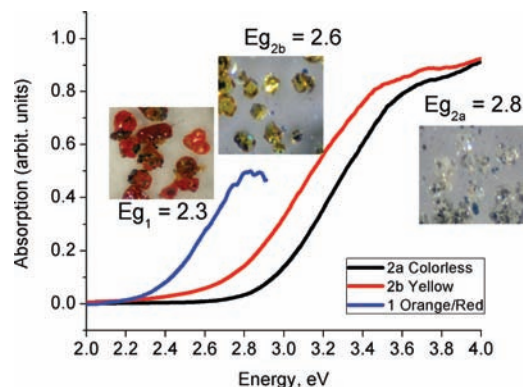


Figure 3. UV-vis optical absorption spectra of **1**, **2a**, and **2b**, showing their bandgaps. The bandgaps get wider as the colors change from red (**1**, 2.3 eV), to yellow (**2b**, 2.6 eV), to colorless (**2a**, 2.8 eV).

Ga-SH-Ga. Thus, differences in protonation appear to be the cause of the color change in the crystals, with minimal effect on the framework structure.

Mid-infrared (IR) spectroscopy of **1**, **2a**, and **2b** indicates a number of peaks between 3083 and 3267 cm^{-1} assigned to N-H and O-H stretches. We did not observe a peak at 2500 cm^{-1} , suggesting the absence of S-H bonds. This is consistent with the hypothesis that the color change of **2** is a product of protonation on the oxygen, rather than a sulfur atom. Thermogravimetric analyses (TGA) were performed on **1** and **2a**. The TGA of **1** showed a 3% weight loss from 130 to 217 $^{\circ}\text{C}$, and it is attributed to a loss of water physisorbed within the crystal. A weight loss of 17% from 220 to 333 $^{\circ}\text{C}$ is consistent with the losses of NH_3 and H_2S described in eqs 1 and 2. Further weight losses from 333 to 600 $^{\circ}\text{C}$ are attributed to the complete decomposition of the structure.



For **2a**, the analysis showed a near immediate loss of $\sim 2\%$, again caused by the loss of both physisorbed water and water located in the pores. From 195 to 364 $^{\circ}\text{C}$, a weight loss of 18% is also consistent with the theoretical losses described in eqs 3 and 4. The compound then undergoes a continuous weight loss until 600 $^{\circ}\text{C}$.



The noncentrosymmetric space group $P2_13$ can lead to a nonlinear optical second harmonic generation (SHG)

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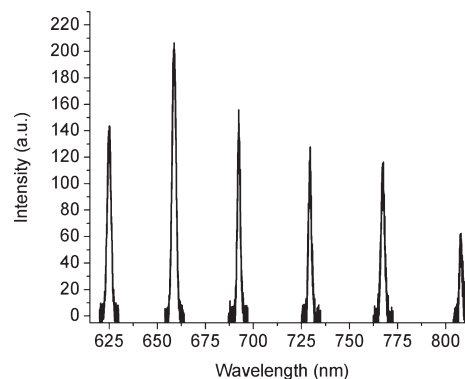


Figure 4. SHG response for $(\text{NH}_4)_5\text{Ga}_4\text{SbS}_{10}$. Maximum response observed at ~ 660 nm. The x axis is the converted wavelength ($\lambda/2$).

response.²⁵ We therefore performed SHG measurements on polycrystalline samples of **1** (Figure 4) and found its highest second-order nonlinear optical activity at 660 nm.²⁶

We have successfully synthesized the first 3-D gallium antimony sulfide framework motifs featuring a new three-coordinate bridging mode between supertetrahedral clusters. The use of pyramidal antimony ions as the linker induces the noncentrosymmetric space group. The compound undergoes protonation with strong acids that causes significant shifts in its optical absorption edge but preserves the framework, suggesting a topotactic process.

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Supporting Information Available: Details for the physical and analytical techniques used in the present work, crystallographic information files (CIF), TGA and mid-IR for compounds **1** and **2a,b** are available free of charge via the Internet at <http://pubs.acs.org>.