

## Three-Dimensional Open Framework Built from Cu–S Icosahedral Clusters and Its Photocatalytic Property

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Open framework materials have been widely studied for applications in various technological areas such as gas separation and catalysis.<sup>1</sup> Since 1989, open framework chalcogenides have attracted increasing attention because they can integrate porosity with semiconductivity and are promising for applications ranging from photoelectrochemistry to visible-light photocatalysis.<sup>2–8</sup>

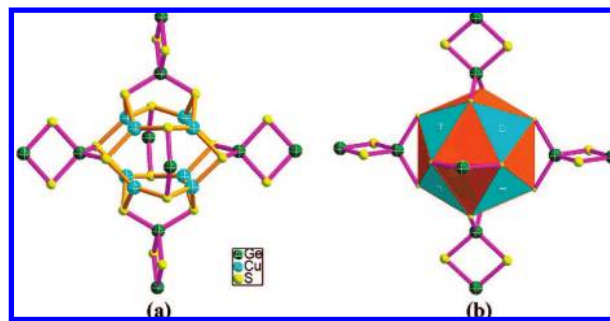
We have recently reported a family of chalcogenide clusters and open-framework materials based on tetrahedral clusters such as supertetrahedral T4 and T5 clusters (e.g., Zn<sub>4</sub>In<sub>16</sub>S<sub>35</sub><sup>14–</sup>, [Cu<sub>5</sub>In<sub>30</sub>S<sub>56</sub>]<sup>17–</sup>, [Zn<sub>13</sub>In<sub>22</sub>S<sub>56</sub>]<sup>20–</sup>) and capped supertetrahedral clusters (e.g., Cd<sub>54</sub>S<sub>32</sub>(SPh)<sub>48</sub>(H<sub>2</sub>O)<sub>4</sub><sup>4–</sup>).<sup>9</sup> In our continual efforts to explore the rich synthetic and structural chemistry of chalcogenides, we are increasingly interested in developing materials with new bonding patterns and from building blocks other than those based on tetrahedral clusters. This would allow an additional level of control in their topological features as well as optical and photocatalytic properties.

It is generally observed that, for the construction of open-framework chalcogenides with purely inorganic framework compositions (i.e., without surface organic ligands such as thiophenyl), tetra- or trivalent cations such as Ge<sup>4+</sup> and In<sup>3+</sup> are usually needed to prevent an excessively high negative charge on the framework. However, sulfides based on such high valent metal cations (e.g., GeS<sub>2</sub>) tend to have a large electronic band gap, making them less suitable for applications such as solar energy conversion. We are therefore interested in searching for new chalcogenide compositions that show a greater promise for applications such as visible-light photocatalysis.

One of the most interesting elements in chalcogenide chemistry and applications is copper, as evidenced by the importance of CuInS<sub>2</sub> and CuInSe<sub>2</sub> in photovoltaic applications. In our own work, we found that incorporation of Cu(I) into In–S supertetrahedral clusters led to a significant red shift in the electronic band gap and the resulting material showed active visible-light-driven photocatalytic properties for the reduction of H<sub>2</sub>O into H<sub>2</sub> even in the absence of a cocatalyst such as Pt.<sup>9f</sup>

Here we report a Ge–Cu–S open framework (denoted GeCuS-1) based on icosahedral [Cu<sub>8</sub>S<sub>12</sub>]<sup>16–</sup> clusters linked by GeS<sub>4</sub><sup>4–</sup> and Ge<sub>2</sub>S<sub>6</sub><sup>4–</sup> units. Among unusual features is the high concentration of low-valent Cu<sup>+</sup> sites as shown by the high Cu/Ge molar ratio (Cu/Ge = 1.6).

Prior to this work, three organic-templated Cu–Ge–S phases were reported.<sup>10</sup> They are based on Ge<sub>4</sub>S<sub>10</sub><sup>4–</sup> tetrahedral clusters linked by either monomeric Cu<sup>+</sup> or dimeric (Cu–Cu)<sup>2+</sup> units. As a result, their properties are dominated by Ge<sup>4+</sup> cations that are major building units of the framework. In comparison, GeCuS-1 has significantly more Cu<sup>+</sup> sites than Ge<sup>4+</sup> sites, which would have



**Figure 1.** View of the icosahedral [Cu<sub>8</sub>S<sub>12</sub>]<sup>16–</sup> cluster and its connectivity with the Ge<sup>IV</sup> and Ge<sup>IV</sup>S<sub>2</sub> units in GeCuS-1: (a) Ball and stick mode and (b) polyhedral mode.

a dramatic effect on its electronic and optical properties, because of the significant contribution of 3d, 4s, and 4p orbitals from Cu(I) to the valence and conduction bands. From the viewpoint of both compositional and structural features, GeCuS-1 represents a new type of material.

Solvothermal assembly of Cu(Ac)<sub>2</sub>·H<sub>2</sub>O, GeO<sub>2</sub>, S, and ethylenediamine at 190 °C for 7 days gave pale-yellow crystals of GeCuS-1.<sup>11</sup> Its structure was determined by single crystal X-ray diffraction.<sup>12</sup> The phase purity was supported by powder X-ray diffraction (Figure S1).

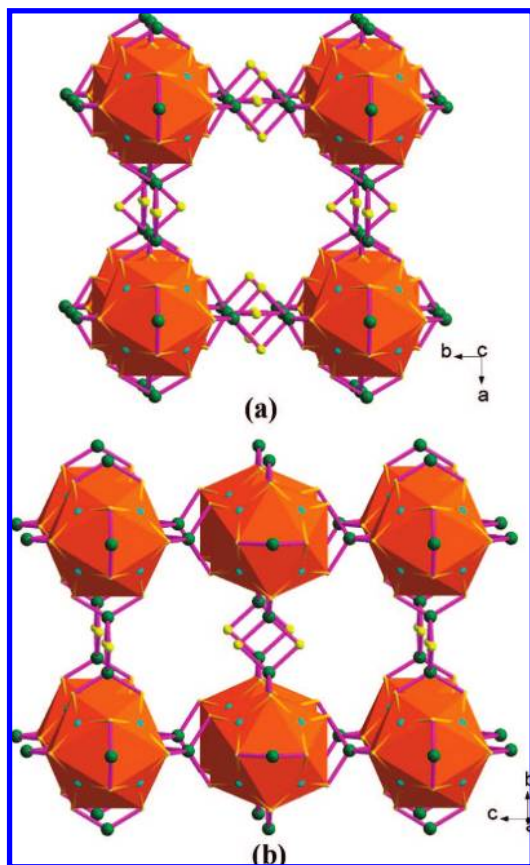
In GeCuS-1, each Cu(I) is trigonally coordinated to three S<sup>2–</sup> ions with Cu–S distances ranging from 2.243 to 2.252 Å, and each Ge(IV) adopts a tetrahedral coordination geometry and bonds to four S<sup>2–</sup> ions with Ge–S distances ranging from 2.191 to 2.264 Å (Figure 1). Sulfide ions adopt two different kinds of bridging modes: μ<sub>2</sub> and μ<sub>3</sub> in the ratio 1:3. Each Cu(I) is coordinated by three μ<sub>3</sub>–S<sup>2–</sup>, and each μ<sub>3</sub>–S<sup>2–</sup> bridges two Cu(I) sites and one Ge center.

The most interesting structural feature of GeCuS-1 is the presence of the anionic [Cu<sub>8</sub>S<sub>12</sub>]<sup>16–</sup> cluster consisting of a cubic array of Cu(I) sites with the adjacent Cu···Cu distances from 3.103 to 3.212 Å (Figure 1a). Each edge of the Cu<sub>8</sub> cube is bridged by a S<sup>2–</sup> ion. The shape of the [Cu<sub>8</sub>S<sub>12</sub>]<sup>16–</sup> cluster defined by 12 S sites is icosahedral (Figure 1b). However, it behaves as a superoctahedral unit based on its bonding pattern, because the 12 S<sup>2–</sup> vertices can be divided into six pairs, each of which is bonded to a single Ge<sup>4+</sup> site located between two adjacent icosahedra. Sulfur-based icosahedra are also known in some other structures; however, these structures with the formula such as Cu<sub>14</sub>S(SPh)<sub>12</sub>(PPh<sub>3</sub>)<sub>6</sub> bear no similarities to the 3-D open-framework GeCuS-1 semiconductor reported here.<sup>13</sup>

The overall 3-D structure can be viewed as simple cubic packing of icosahedral [Cu<sub>8</sub>S<sub>12</sub>]<sup>16–</sup> clusters. The [Cu<sub>8</sub>S<sub>12</sub>]<sup>16–</sup> clusters are extended in six directions into a six-connected 3-D framework via two types of Ge<sup>IV</sup>–S connectivity: the dimeric [Ge<sub>2</sub>S<sub>2</sub>]<sup>4+</sup> units

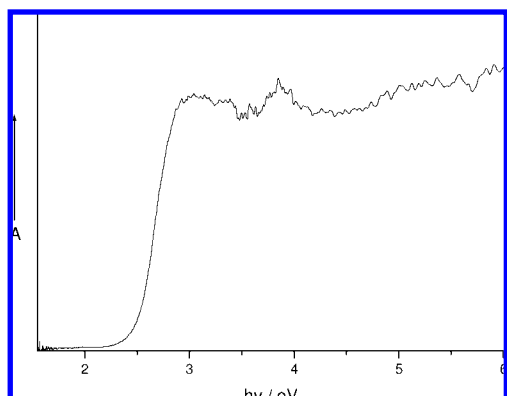
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**Figure 2.** Polyhedral views of 3-D framework of GeCuS-1 along the *c* axis (a) and the *a* axis (b).

along the *a* and *b* directions, and tetrahedral Ge<sup>IV</sup> centers along the *c* axis (Figure 2). Such a mixed mode of intercluster connectivity explains the tetragonal symmetry of the crystal and the framework formula of (Cu<sub>8</sub>S<sub>12</sub>)(Ge<sub>2</sub>S<sub>2</sub>)<sub>4</sub>×<sub>1/2</sub>(Ge)<sub>2</sub>×<sub>1/2</sub> (or rewritten as Cu<sub>8</sub>Ge<sub>5</sub>S<sub>16</sub><sup>4-</sup>). The resulting 3-D framework exhibits 3-D channels, and the biggest cylindrical channel along the *c* axis has a diameter of 16.4 Å. Disordered protonated amine molecules are located within such 3-D channels. The nitrogen adsorption measurement, however, did not reveal internal porosity, even after ion exchange with ions such as Li<sup>+</sup>, suggesting the blocking of pores by charge-balancing cations.



**Figure 3.** UV/vis diffuse reflectance spectrum of GeCuS-1.

The UV/vis diffuse reflectance spectrum of GeCuS-1 shows that the band gap of this compound is 2.5 eV (Figure 3). The photocatalytic reaction was performed in a quartz cell with GeCuS-1

(0.5 g) suspended in 270 mL of 1 M Na<sub>2</sub>SO<sub>3</sub> aqueous solution. The catalyst suspension was irradiated with a 300 W Xe lamp. ~20.6 μmol·h<sup>-1</sup>·g<sup>-1</sup> of H<sub>2</sub> could be generated without any cocatalyst such as Pt. The visible light photocatalytic activity was also measured by the addition of an optical cutoff filter (>400 nm) to the Xe lamp. ~2.64 μmol·h<sup>-1</sup>·g<sup>-1</sup> of H<sub>2</sub> were generated without any cocatalyst under visible light irradiation.

In conclusion, reported here is a novel metal sulfide containing icosahedral [Cu<sub>8</sub>S<sub>12</sub>]<sup>16-</sup> cluster cross-linked by two monomeric GeS<sub>4</sub><sup>4-</sup> in the tetragonal *c* direction and four dimeric Ge<sub>2</sub>S<sub>6</sub><sup>4-</sup> in the *a* and *b* directions into a 3-D open framework. The icosahedral cluster behaves like a pseudo-octahedral unit in its bonding geometry to adjacent tetrahedral Ge<sup>4+</sup> sites. Its large Cu to Ge ratio is highly unusual in 3-D open-framework sulfides and contributes to the low electronic band gap and visible light photocatalytic activity of this material.

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**Supporting Information Available:** XRD patterns and CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Typical synthesis of [Cu<sub>8</sub>Ge<sub>5</sub>S<sub>16</sub>]·x(solvent): Cu(Ac)<sub>2</sub>·H<sub>2</sub>O (254 mg, 1.27 mmol), GeO<sub>2</sub> (100 mg, 0.956 mmol), and S (174 mg, 5.42 mmol) were mixed with ethylenediamine (2.0688 g) in a 23 mL Teflon-lined stainless steel autoclave and stirred for 30 min. The vessel was sealed and heated to 190 °C for 7 days. After cooling to room temperature, pale-yellow crystals were obtained.
- (12) Crystal data: tetragonal, *P4<sub>2</sub>/mmc*, *a* = *b* = 11.5517(1) Å, *c* = 17.5999(4) Å, *V* = 2348.56(6) Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 2.184 g cm<sup>-3</sup>, *T* = 150 K, 7661 measured reflections, *R<sub>1</sub>* = 0.0428 for 831 reflections (*I* > 2σ(*I*)), *GOF* = 1.094. The structure was solved by direct methods, and the structure refinements were based on |*F*<sup>2</sup>|. All non-hydrogen atoms were refined with anisotropic displacement parameters, except the atoms of disordered amine molecules.
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