

## Nonaqueous Synthesis and Selective Crystallization of Gallium Sulfide Clusters into Three-Dimensional Photoluminescent Superlattices

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Despite extensive research on chalcogenide clusters and open frameworks,<sup>1–8</sup> little is known about related gallium sulfides.<sup>9</sup> Most known gallium sulfides are made by high-temperature melt or solid-state reactions. As a result, few three-dimensional (3D) open-framework gallium sulfides are known.

We have now developed a low-temperature and nonaqueous synthesis approach and have successfully prepared a series of gallium sulfide and polysulfide open-framework materials built from binary Ga–S and ternary Zn–Ga–S clusters (Table 1).<sup>10</sup> These materials possess unprecedented structural properties, and their fluorescent emission wavelength fills the gap between open-framework oxides and indium chalcogenides.

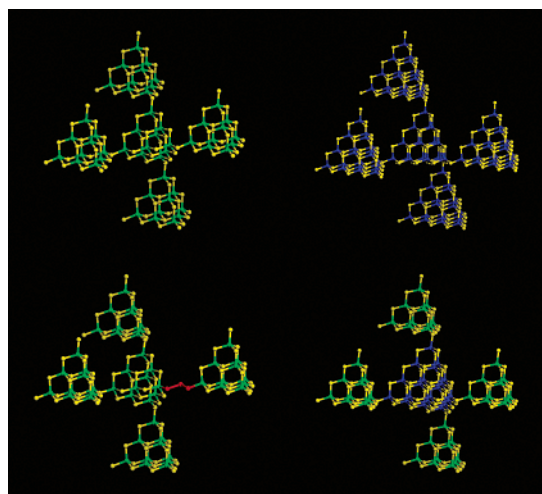
All new compounds contain supertetrahedral clusters that are tetrahedrally shaped fragments of the cubic ZnS-type lattice. They are denoted as *T<sub>n</sub>* by Yaghi, O’Keeffe et al.<sup>11,12</sup> With *T<sub>n</sub>* clusters as artificial tetrahedral atoms (T-atoms), it is possible to construct covalent superlattices with framework topology similar to that in zeolites. However, the ring size in terms of the number of T-atoms is increased by *n* times. An increase in the ring size is important because crystalline porous materials with a ring size larger than 12 T-atoms are scarce but highly desirable for applications involving large molecules.

In the absence of divalent cations, one of the superlattices formed is UCR-7GaS-TETA (Figure 1) built from T3 (Ga<sub>10</sub>S<sub>18</sub><sup>6-</sup>) clusters. All four corners of T3 clusters are shared through S<sup>2-</sup> bridges. The T3 cluster is known in both divalent metal thiolates (e.g., Cd<sub>10</sub>S<sub>4</sub>(SPh)<sub>16</sub><sup>4-</sup>) and boron or indium sulfides.<sup>1,11</sup> However, prior to this work, neither the molecular T3 cluster nor its covalent superlattice is known in the Ga–S system.

When divalent cations are introduced either directly through the addition of a salt (e.g., Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) or through the oxidation of the elemental form (e.g., Zn), the reaction system gains an extra capability to form T4 clusters (Zn<sub>4</sub>Ga<sub>16</sub>S<sub>33</sub><sup>10-</sup>), in addition to its inherent ability to form T3 clusters (Ga<sub>10</sub>S<sub>18</sub><sup>6-</sup>). This is because regular *T<sub>n</sub>* (*n* > 3) clusters can only be found in heterometallic compositions due to the local charge balance requirement around the four-coordinated core sulfur atoms.<sup>12–14</sup>

Therefore, both T3 and T4 clusters are likely present in the heterometallic sulfide solution. By using different structure-directing agents, one or both of them can be crystallized into a superlattice. In this work, several situations could be distinguished, leading to the synthesis of a number of superlattices built from binary and ternary sulfide clusters.

The first situation involves the use of 1-(2-aminoethyl)piperazine (AEP, C<sub>6</sub>H<sub>15</sub>N<sub>3</sub>). Only T3 clusters are formed in crystals (denoted as UCR-18GaS-AEP), even if various amounts of Zn<sup>2+</sup> cations are present. An unprecedented feature is the presence of the polysulfide linkage between T3 clusters. This is the first observation of



**Figure 1.** Four structure types made from T3 and T4 clusters. (Top left): the T3–T3 superlattice in UCR-7; (top right): the T4–T4 superlattice in UCR-5; (bottom left): the T3–T3 superlattice through mixed –S– and –S–S–S– bridges in UCR-18; (bottom right): the hybrid T3–T4 superlattice in UCR-19.

supertetrahedral clusters being linked through polysulfide bonds. Here, T3 clusters are connected at three corners through S<sup>2-</sup> bridges into a 3-connected sheet with 6-rings (six T3 clusters in a ring). These sheets are joined through –S–S–S– bridges into a 3D net.

In comparison, AEP gives a regular T3 superlattice in the In–S system with only S<sup>2-</sup> bridges (Table 1). In the Ga–S system, it appears that the lattice contraction caused by smaller Ga<sup>3+</sup> cations makes it less accommodating to AEP molecules. As a result, the introduction of longer S<sub>3</sub><sup>2-</sup> groups in UCR-18GaS-AEP further pushes the clusters apart to offset the contraction effect of Ga<sup>3+</sup> cations.

The selection of T4 clusters can be achieved with 1,4-bis(3-aminopropyl)piperazine (BAPP, C<sub>10</sub>H<sub>24</sub>N<sub>4</sub>). In this case, UCR-5ZnGaS-BAPP (Figure 1) built from T4 clusters is formed. Compared to AEP with 9 non-H atoms, BAPP has 14 non-H atoms. The large size of BAPP might be one reason for the preferential selection of large T4 clusters that once crystallized give a larger pore volume.

An interesting situation occurs when triethylenetetramine (TETA, C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>) (10 non-H atoms) is used. In the absence of Zn<sup>2+</sup>, it forms a regular T3 structure (UCR-7GaS-TETA). However, when Zn<sup>2+</sup> cations are introduced, UCR-19ZnGaS-TETA (Figure 2) with alternating T3 and T4 clusters is formed. UCR-19ZnGaS-TETA is the only known hybrid superlattice containing different regular supertetrahedral clusters. Prior to this work, the T3 cluster is known to connect with the coreless pseudo-T5 cluster into a superlattice.<sup>15</sup>

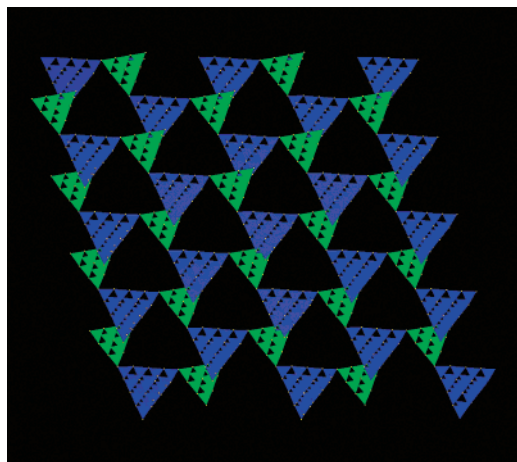
All materials reported here have a framework topology resembling that of the zinc blende when *T<sub>n</sub>* clusters are represented as

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**Table 1.** Summary of Important Data for Selected Structures Synthesized in This Study

| name <sup>a</sup>          | framework composition   | space group                      | a (Å)     | c (Å)     | R(F) <sup>b</sup> | λ <sub>em</sub> (nm) | λ <sub>ex</sub> (nm) |
|----------------------------|---|----------------------------------|-----------|-----------|-------------------|----------------------|----------------------|
| UCR-18GaS-AEP <sup>b</sup> | [Ga <sub>10</sub> S <sub>17.5</sub> (S <sub>3</sub> ) <sub>0.5</sub> ] <sup>6-</sup>                | C2/c                             | 35.903(5) | 21.183(3) | 6.41              | 500                  | 375                  |
| UCR-19ZnGaS-TETA           | [Ga <sub>10</sub> S <sub>18</sub> Zn <sub>4</sub> Ga <sub>16</sub> S <sub>33</sub> ] <sup>16-</sup> | I4 <sub>1</sub> /a               | 21.087(2) | 35.582(6) | 6.08              |                      |                      |
| UCR-5ZnGaS-BAPP            | [Zn <sub>4</sub> Ga <sub>16</sub> S <sub>33</sub> ] <sup>10-</sup>                                  | I4 <sub>1</sub> /acd             | 22.595(3) | 40.905(8) | 6.71              | 440                  | 368                  |
| UCR-7GaS-TETA              | [Ga <sub>10</sub> S <sub>18</sub> ] <sup>6-</sup>   | I4 <sub>1</sub> /acd             | 19.201(2) | 29.815(4) | 5.85              | 476                  | 370                  |
| UCR-7GaS-TAEA              | [Ga <sub>10</sub> S <sub>18</sub> ] <sup>6-</sup>   | I4 <sub>1</sub> /acd             | 19.220(3) | 29.866(6) | 5.80              |                      |                      |
| UCR-7GaS-DBA               | [Ga <sub>10</sub> S <sub>18</sub> ] <sup>6-</sup>   | P4 <sub>1</sub> 2 <sub>1</sub> 2 | 18.803(4) | 29.591(8) | 9.92              |                      |                      |
| UCR-7GaInS-TETA            | [Ga <sub>4.5</sub> In <sub>5.5</sub> S <sub>18</sub> ] <sup>6-</sup>                                | I4 <sub>1</sub> /acd             | 19.715(2) | 30.996(4) | 5.87              | 457                  | 367                  |
| UCR-7InS-AEP               | [In <sub>10</sub> S <sub>18</sub> ] <sup>6-</sup>   | I4 <sub>1</sub> /acd             | 20.318(2) | 31.994(5) | 4.74              |                      |                      |

<sup>a</sup> TAEA = Tris(2-aminoethyl)amine, C<sub>6</sub>H<sub>18</sub>N<sub>3</sub>; DBA = di-*n*-butylamine. In all compounds, framework atoms are located, and guest amine molecules are disordered. <sup>b</sup> R(F) = Σ||F<sub>o</sub>| - |F<sub>c</sub>||/Σ|F<sub>o</sub>| with F<sub>o</sub> > 4.0σ(F). For UCR-18GaS-AEP, b = 18.501(3) Å, β = 115.992(3)°.



**Figure 2.** 3D framework of the T3–T4 hybrid framework in UCR-19ZnGaS-TETA. Green: T3 clusters. Blue: T4 clusters. Only one set of superlattice is shown for clarity.

artificial T-atoms. Even though there are two interpenetrating lattices, the large size of T<sub>n</sub> clusters leads to a highly open framework. In all compounds, disordered extra-framework species occupy 56% of the crystal volume or more as calculated with PLATON.<sup>16</sup>

These gallium sulfide superlattices serve to bridge a previously observed gap in the emission wavelength of open-framework phosphors. It was reported earlier that open-framework oxides have an emission wavelength from 400 to 440 nm.<sup>17</sup> Later, open-framework indium sulfides were found to emit in the range from 520 to 570 nm.<sup>14,18</sup> Gallium sulfides reported here show strong photoluminescent emissions that can be varied from 440 to 500 nm (Table 1). For example, UCR-18GaS-AEP can be excited by a broad spectral range from 300 to 470 nm and emits at 500 nm (fwhm ≈ 100 nm).

Gallium sulfide superlattices reported here are more thermally stable than corresponding indium sulfides. For UCR-7GaS-TETA, after heating at 280 °C in flowing argon, over 49% of H and 63% of N were removed.<sup>10</sup> The XRD shows no deterioration in the sample crystallinity. UCR-7GaS-TETA remained crystalline after being heated at 300 °C in air, while UCR-7InS-AEP was found amorphous under the same condition.

During the direct calcination of UCR-7GaS-TETA, the amount of carbon was not reduced, likely because of the coke formation.<sup>10</sup> To help remove carbon and also to examine ion-exchange properties, UCR-7GaS-TETA was subject to ion exchange with 2 M NH<sub>4</sub>-Cl solution. The elemental analysis showed that over half of carbon

was removed after 6 d at room temperature.<sup>10</sup> The XRD showed that the ion-exchanged sample did not suffer a loss of crystallinity. Similar ion-exchange reactions were also observed for other mono- or divalent cations such as Na<sup>+</sup> and Ca<sup>2+</sup>.

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**Supporting Information Available:** Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) A typical synthesis is given below for the preparation of UCR-18GaS-AEP. Gallium metal (0.1266 g), sulfur (0.1921 g), 1-(2-aminoethyl)-piperazine (2.0246 g) were mixed in a 23-mL Teflon-lined stainless steel autoclave. The vessel was sealed and heated at 190 °C for 6 d. The autoclave was allowed to cool to room temperature. Light-yellow prismatic crystals were obtained in 86% yield. Elemental analysis (wt %) for UCR-18GaS-AEP: 15.25 C, 3.70 H, 9.35 N, calculated: 15.75 C, 3.64 H, 9.19 N based on the formula [Ga<sub>10</sub>S<sub>17.5</sub>(S<sub>3</sub>)<sub>0.5</sub>](C<sub>6</sub>H<sub>15</sub>N<sub>3</sub>H)<sub>2</sub>(C<sub>6</sub>H<sub>15</sub>N<sub>3</sub>H<sub>2</sub>)<sub>2</sub>. For UCR-7GaS-TETA: 10.90 C, 3.06 H, 8.83 N, calculated: 11.50 C, 3.26 H, 8.95 N based on the formula [Ga<sub>10</sub>S<sub>18</sub>](C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>H<sub>2</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>H<sub>3</sub>)<sub>2</sub>. For UCR-7GaS-TETA: after heating at 280 °C in Ar, 11.04 C, 1.57 H, 3.25 N; after ion exchange with 2 M NH<sub>4</sub>Cl, 4.47 C, 2.26 H, 4.44 N. The presence of Ga<sup>3+</sup> and Zn<sup>2+</sup> ions in T4-containing structures was verified by the energy-dispersive X-ray analysis.
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