

Figure 1. Polyhedral diagrams of T3 and T4 supertetrahedral clusters. The metal site is located at the center of each small red tetrahedron.

Supertetrahedral Clusters

Three-Dimensional Frameworks of Gallium Selenide Supertetrahedral Clusters**

Xianhui Bu, Nanfeng Zheng, Xiqing Wang, Bing Wang, and Pingyun Feng*

Dense chalcogenides of Ga, In, and Tl have been extensively studied because of their intriguing stoichiometry and because many of them are semiconductors, photoconductors, or light emitters. On the other hand, while crystalline porous oxides have been known for a long time,^[1] the development of crystalline porous chalcogenides, especially selenides and tellurides, is still in its early stages.^[2–4] Compared to porous oxides, which are usually insulators, crystalline porous chalcogenides can have substantially higher electrical conductivity, which in combination with uniform porosity could lead to new applications in areas such as shape- and size-selective sensors and high-surface-area photocatalysts and photoelectrodes.^[5]

One promising approach for the creation of crystalline porous chalcogenides is the directed assembly of chalcogenide clusters into three-dimensional (3D) frameworks.^[3,4] Among the most common chalcogenide clusters are a series of supertetrahedral clusters denoted as T n . These clusters are regular tetrahedrally shaped fragments of the cubic ZnS-type lattice.^[4] Here, n is the number of metal sites on each edge of the cluster (Figure 1). The large size of the supertetrahedral clusters usually leads to a highly open framework, particularly when the interpenetration of multiple sublattices is avoided.

[*] N. Zheng, X. Wang, B. Wang, Prof. P. Feng
Department of Chemistry
University of California
Riverside, CA 92521 (USA)
Fax: (+1) 909-787-4713
E-mail: pingyun.feng@ucr.edu

Prof. X. Bu
Department of Chemistry and Biochemistry
California State University
1250 Bellflower Blvd., Long Beach, CA 90840 (USA)

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Substantial success has recently been achieved with sulfides,^[6–8] but the progress with selenides is much slower. Not only are there few 3D open-framework selenides, the types of supertetrahedral selenide clusters are also limited.^[9–11] For example, although T5 sulfide clusters with as many as 35 metal atoms (e.g., Cu₅In₃₀S₅₆^{17–}) are known,^[12] the largest supertetrahedral selenide cluster prior to this work has only ten metal atoms (T3, In₁₀Se₂₀^{10–}).^[13] Larger clusters are desirable because they can be useful for studying the quantum size effect and can also serve as building blocks for constructing crystalline porous frameworks.^[14] The gallium selenides are particularly challenging. Thus far, neither T3 (e.g., Ga₁₀Se₂₀^{10–}) nor T4 (e.g., Zn₄Ga₁₆Se₃₅^{14–}) clusters are known. To our knowledge, no 3D gallium selenide open frameworks were known prior to this work.

Here we report a series of 3D gallium selenide superlattices built up of supertetrahedral T3 and T4 clusters. Three 3D framework types (denoted as OCF-1ZnGaSe, OCF-6GaSe, and OCF-13GaSe, respectively; OCF = organically directed chalcogenide framework) were realized (Table 1). Similar to the synthesis of zeolites, the preparation of chalcogenide open frameworks is performed in an alkaline environment under hydrothermal conditions at 200 °C or below.^[15] However, unlike the synthesis of zeolites, the self-assembly process in the chalcogenide system is usually preceded by redox reactions because one or more starting materials (e.g., S, Se, In) are in the elemental form.^[16]

One of the most important advances reported here is the synthesis of the selenide T4 cluster Zn₄Ga₁₆Se₃₅^{14–} in OCF-1ZnGaSe. This is the largest selenide supertetrahedral cluster made so far. Prior to this work, the largest selenide supertetrahedral clusters were the indium selenide T3 cluster In₁₀Se₂₀^{10–} and ligand-terminated T3 clusters such as [(CH₃)₄N]₄[Cd₁₀Se₄(SPh)₁₆].^[13,17] The increase in the cluster size from T3 to T4 represents a significant advance towards the synthesis of large selenide supertetrahedral clusters such as T5 (M₃₅X₅₆) or T6 (M₅₆X₈₄).^[7] Because of their uniform size and well-defined chemical composition, these supertetrahedral clusters could provide a unique opportunity for the study of quantum-confinement effects.^[18]

Surprisingly, all three gallium selenide phases reported here are noncentrosymmetric, and none of them consists of two or more of the interpenetrating lattices that are common for these types of materials. This structural feature is also in contrast with the corresponding Ga–S system, in which all

Table 1: A summary of crystallographic data^[a] for selected structures synthesized in this study.

Name ^[b]	Composition	Space group	<i>a</i> [Å]	<i>c</i> [Å]	<i>R</i> (<i>F</i>) [%]	<i>wR</i> 2 [%] (all data)
OCF-1ZnGaSe-TMDP	Zn ₄ Ga ₁₆ Se ₃₃ ¹⁰⁻	<i>I</i> 4̄2 <i>d</i>	41.311(7)	16.891(4)	8.33	28.9
OCF-6GaSe-TMDP	Ga ₁₀ Se ₁₈ ⁶⁻	<i>I</i> 4̄2 <i>d</i>	17.064(3)	32.320(7)	5.66	20.5
OCF-13GaSe-DPM	Ga ₁₀ Se ₁₈ ⁶⁻	<i>I</i> 4̄ <i>m</i> 2	35.052(8)	17.402(6)	7.96	24.9
OCF-13GaSe-TMDP	Ga ₁₀ Se ₁₈ ⁶⁻	<i>I</i> 4̄ <i>m</i> 2	34.978(6)	17.212(4)	7.83	27.7
(C ₄ H ₁₁ N ₂)GaSe ₂	GaSe ₂ ⁻	<i>P</i> 2 ₁ / <i>c</i>	6.3025(9)	8.408(1)	2.55	6.25

[a] $R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, where $F_o > 4.0\sigma(F)$. For GaSe₂-PPZ, $b = 16.660(2)$ Å, $\beta = 105.144(3)^\circ$. Crystal structures were solved from single-crystal data collected at 298 K on a SMART 1000 CCD diffractometer with MoK α radiation. The number of parameters and independent reflections were 241 and 4567 for OCF-1, 65 and 3070 for OCF-6, 132 and 3852 for OCF-13GaSe-DPM, 132 and 5151 for OCF-13GaSe-TMDP, and 95 and 1500 for (C₄H₁₁N₂)GaSe₂. CCDC 219205–219209 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[b] TMDP = 4,4'-trimethylenedipiperidine, C₁₃H₂₆N₂; DPM = dipiperidinomethane, C₁₁H₂₂N₂.

four known structure types are interpenetrating and centrosymmetric.^[19]

Synthetically, there is a major difference between gallium selenides and gallium sulfides. While the presence of water promotes the crystal growth of the gallium selenides reported here, the synthesis of gallium sulfide superlattices is successful only in a nonaqueous system.^[19] This difference between gallium selenides and gallium sulfides might be related to the relative hydrothermal stability of Ga–S and Ga–Se bonds.

The large cluster size and the absence of framework intergrowth help to generate a highly open architecture for these gallium selenides. The framework density, defined as the number of metal sites per 1000 Å³, is 5.6, 4.3, and 3.7 for OCF-1ZnGaSe, OCF-6GaSe, and OCF-13GaSe, respectively. The percentage of the crystal volume occupied by extra-framework species is as high as 63, 70, and 73%, respectively.^[20] These 3D selenides are by far the most open frameworks among known selenides.

All three phases also have large ring sizes, defined as the number of metal sites forming the window of the channel. OCF-1ZnGaSe contains windows of eight and four super-tetrahedral T4 clusters with a ring size of 32 (Figure 2C). To our knowledge, the topological type of OCF-1ZnGaSe is not known in dense inorganic compounds. OCF-6GaSe has a diamond-type structure in which T3 clusters occupy tetrahedral sites (Figure 2A). Only windows of six T3 clusters are present in OCF-6GaSe, giving rise to a ring size of 18. The framework topology of OCF-13GaSe is derived from the CrB₄-type network in which tetrahedral boron sites are replaced by T3 clusters (Figure 2B).^[21] In OCF-13GaSe, windows with four, six, and eight T3 clusters are all present, giving rise to a maximum ring size of 24.

A notable synthetic feature here is that either Ga₂O₃ or Ga can be used as the source for Ga³⁺ cations. Prior to this work, elemental metals (In or Ga) were usually used as reagents in the synthesis of indium or gallium sulfides. Here, open-framework gallium selenides can be obtained from gallium oxide in the presence of Se and organic amines. This indicates that the reducing property of elemental metals is not essential for activating Se. It is likely that Se disproportionated into SeO₃²⁻ and Se²⁻ ions in aqueous solution.^[22]

When attempts were made to synthesize centrosymmetric 3D framework selenides by employing nonaqueous conditions similar to those used for the preparation of gallium sulfides, an infinite chain structure (denoted as GaSe₂-PPZ, PPZ = piperazine) similar to that of fibrous SiS₂ is formed (Figure 2D). 1-(2-Aminoethyl)piperazine or piperazine can be used as the solvent. The chain consists of edge-sharing tetrahedral GaSe₄⁵⁻ units. Despite its simple structure, the GaSe₂⁻ chain has not been observed before. However, a fragment of this chain with six gallium atoms (Ga₆Se₁₄¹⁰⁻) is known.^[11]

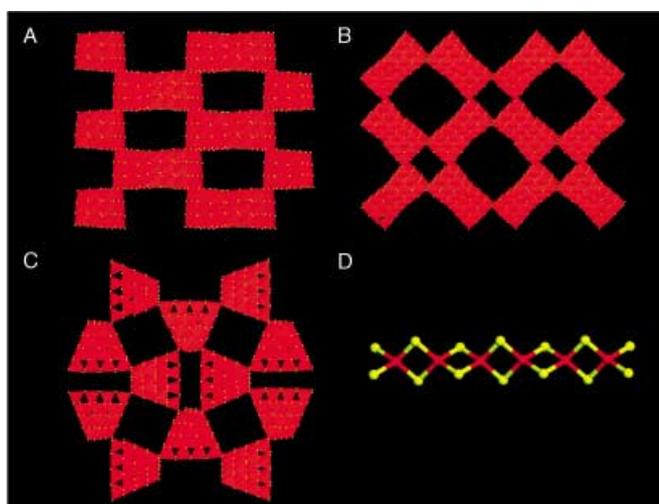


Figure 2. The 3D open frameworks of A) OCF-6GaSe, B) OCF-13GaSe, and C) OCF-1ZnGaSe, and D) the one-dimensional infinite chain in GaSe₂-PPZ.

Extra-framework species in the materials reported here are disordered, and their atomic positions could not be determined. Amines encapsulated in 3D chalcogenides are generally disordered, while those in lower-dimensional (i.e., 2D, 1D, and 0D) phases are ordered. In GaSe₂-PPZ, the negative charge of the GaSe₂⁻ chain is balanced by monoprotonated piperazine molecules. The piperazine molecules are so well ordered that even the position of the additional proton can be located from single-crystal diffraction data, and this suggests that protonation occurs on a particular nitrogen atom, instead of being statistically distributed over two nitrogen atoms.

Alternating-current impedance measurements on a single crystal of OCF-6GaSe shows a humidity-dependent behavior of the electrical conductivity (Figure 3). With increasing relative humidity (RH), the specific conductivity σ increases by over two orders of magnitude and ranges from $1.32 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at 84.9% RH to $5.37 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 100%

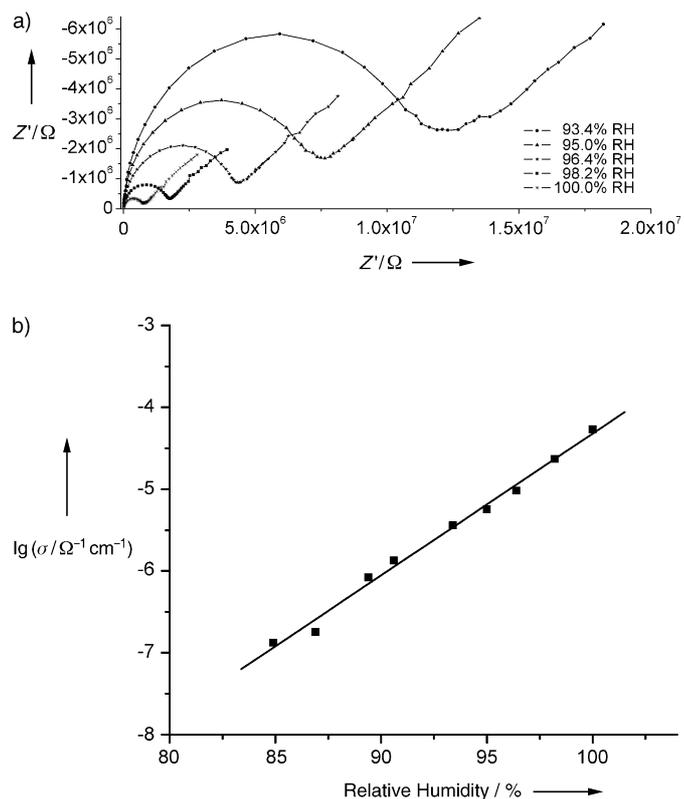


Figure 3. a) Alternating-current impedance plots at different humidities showing decreasing resistance with increasing RH for OCF-6GaSe-TMDP. b) Plot of electrical conductivity versus RH. The impedance plots were measured on a single-crystal sample by the ac impedance method using a Solartron 1260 frequency response analyzer.

RH. This property may have potential applications in electrochemical sensors.

The optical properties of the gallium selenides were studied by solid-state diffuse-reflectance UV/Vis/NIR spectroscopy. All phases show optical transitions with band gaps between 1.4 and 1.7 eV (Figure 4). The transition is likely to result from charge transfer from the Se^{2-} -dominated valence band to the Ga^{3+} -dominated conduction band. The similar values for the band gaps are consistent with the similar chemical compositions of the three phases. However, these band gaps are considerably smaller than those of corresponding gallium sulfides, which are about twice as large (2.6–2.8 eV).^[19] Clearly, the framework anions have a much more dramatic impact on the band gap than framework cations.

In conclusion, the first 3D gallium selenide open frameworks have been synthesized, and their unique structural, optical, and electrical properties characterized. The T4 selenide cluster is the largest selenide supertetrahedral cluster synthesized so far. These gallium selenides are distinctly different from known gallium sulfide open frameworks in nearly every respect, including synthesis conditions and structural and optical properties. This work represents an important step in the synthetic development of heavy chalcogenide clusters and open-framework materials.

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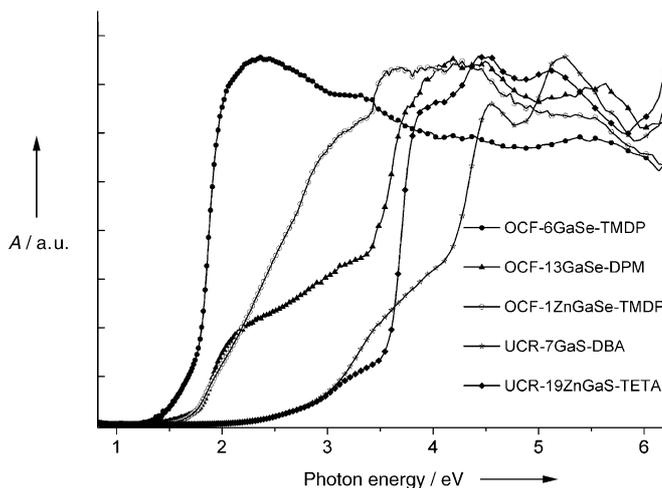


Figure 4. Optical absorption spectra of gallium sulfide and gallium selenide open-framework solids. Band gaps are 1.71 eV for OCF-12ZnGaSe-TMDP, 1.43 eV for OCF-6GaSe-TMDP, 1.76 eV for OCF-13GaSe-DPM, 2.60 eV for UCR-19ZnGaSe-TETA (TETA = triethylenetetramine), and 2.84 eV for UCR-7GaSe-DBA (DBA = di-*n*-butylamine). The absorption data were calculated from reflectance data by using the Kubelka–Munk function. BaSO_4 powder was used as reference (100% reflectance). UV/Vis/NIR diffuse reflectance spectra were measured on a Shimadzu UV 3101PC double-beam, double-monochromator spectrophotometer.

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with H₂O (4.0212 g) in a 23-mL teflon-lined stainless steel autoclave and stirred for 30 min. The vessel was sealed and heated to 200 °C for 8 days. After cooling to room temperature, pale-yellow crystals were obtained in a yield of about 66%. OCF-6GaSe-TMDP, (C₁₃H₂₆N₂H₂)₃(Ga₁₀Se₁₈): an autoclave containing Ga₂O₃ (101.1 mg), Se (213.4 mg), TMDP (1.1067 g), and H₂O (2.9683 g) was heated to 200 °C for 28 days, and pale-yellow octahedral crystals were obtained in a yield of about 77%. UCR-13GaSe-DPM, (C₁₁H₂₂N₂H₂)₃(Ga₁₀Se₁₈): an autoclave containing Ga₂O₃ (101.1 mg), Se (211.3 mg), DPM (dipiperidinomethane; 1.0230 g), and H₂O (4.0288 g) was heated to 200 °C for 19 days, and pale-yellow crystals were obtained in a yield of about 84%. (C₄H₁₁N₂)GaSe₂: an autoclave containing Ga (110.0 mg), Se (218.0 mg), piperazine (0.9508 g), and H₂O (3.1506 g) was heated to 200 °C for 8 days, and pale-yellow crystals were obtained in a yield of about 92%.

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