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Indium selenide superlattices from $(In_{10}Se_{18})^{6-}$ supertetrahedral clusters

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Three-dimensional open framework selenides and tellurides are rare despite the recent progress in the synthesis of indium sulfides with large pore sizes; here we report a family of amine-directed indium selenide superlattices constructed from T3 supertetrahedral $(In_{10}Se_{18})^{6-}$ clusters.

Since their discovery in 1989 by Bedard *et al.*, chalcogenide open framework materials have generated a lot of interest. [1,2] These host–guest framework materials could have applications as porous hosts similar to zeolites. In addition, because of their semiconducting properties, they may find applications in semiconductor technologies where their inorganic counterparts are currently being used.[3]

Thus far, a significant progress has been made in sulfides. The exploration of open framework sulfides started with the synthesis of germanium and tin sulfides,[1,2,4] in part because germanium and tin are in the same group as silicon that is a key element in zeolite frameworks. Subsequently, novel sulfides incorporating antimony or indium were also discovered.[5–9] Some of these materials consist of large cages comparable to or even larger than those found in aluminosilicate zeolites.[10,11]

In comparison with sulfides, very few three-dimensional open-framework selenides are known. One rare example is $[NMe_4]_2MGe_4Se_{10}$ (M = Fe, Mn) in which $(Ge_4Se_{10})^{4-}$ clusters are connected into a three-dimensional framework through divalent metal ions.[12] The development of heavy chalcogenides such as selenides and tellurides is desirable because these compositional variations allow electronic bandgap engineering and make it possible to tune the electronic, optical and electrooptic properties of the resulting materials. In addition, heavy chalcogenides tend to have higher electrical conductivity and lower thermal conductivity than sulfides, which make them suitable candidates for study as thermoelectric materials.[13]

Here we report a family of three-dimensional open framework indium selenides constructed from supertetrahedral T3 clusters (Fig. 1).† The T3 cluster is the third member of a series of clusters denoted as T*n* where *n* refers to the number of metal layers. A T1 cluster is a simple tetrahedron such as $(GeS_4)^{4-}$ whereas a T2 cluster refers to a small cage unit such as $(Ge_4S_{10})^{4-}$ that is structurally similar to the admantane cage. The stoichiometry of a discrete T3 cluster is $(M_{10}E_{20})^{10-}$. Because of the large size of the T3 cluster compared to an individual tetrahedral atom, the resulting frameworks can have a very open architecture.

To prepare crystals of UCR-7InSe-TETA, indium metal (Strem, 99.99%, 77 mg), selenium (Acros, 99.5%, 133 mg), triethylenetetramine (TETA) (TCI, 70%, 2.546 g), and distilled water (2.134 g) were mixed in a 23 ml Teflon-lined stainless steel autoclave and the mixture was stirred for 10 min. The vessel was then sealed and heated at 190 °C for 6 days. The autoclave was subsequently allowed to cool to room temperature. The yellow product was filtered off, washed with distilled H_2O and ethanol, and further purified by the ultrasonic technique. The yield was approximately 33%. Elemental analysis (in wt%, found: C, 7.38; H, 1.80; N, 5.25. Calc.: C, 7.17; H, 2.01; N, 5.58) showed that triethylenetetramine was incorporated in the diprotonated form, $[In_{10}Se_{18}](C_6H_{18}N_4H_2)_3$. Other members of UCR-7InSe (Table 1) were prepared under similar conditions, but with different organic guest molecules. When 2-(2-aminoethylaminoethanol) was used, a mixture of UCR-2InSe and UCR-7InSe was obtained.[14] Thermogravimetric analysis showed that under a nitrogen atmosphere, UCR-7InSe-TETA was stable up to 200 °C whilst between 200 and 400 °C, the total weight loss was 20.6%.

UCR-7InSe structures are formed from corner-sharing T3 supertetrahedral clusters. Supertetrahedral clusters such as T3 are regular fragments of the cubic ZnS type lattice (Fig. 1). In a T3 cluster, all metal sites are four-coordinate, but none of the selenium sites is tetrahedral. There are 12 bicoordinated Se^{2-} sites on six edges of the supertetrahedron and four tricoordinated Se^{2-} ions on each face of the supertetrahedron. In addition, there are four terminal Se^{2-} sites at each supertetrahedral corner. In the structures reported here, T3 clusters are connected through the Se^{2-} bridges into a three-dimensional covalent network. Each Se^{2-} bridge connects two T3 clusters so that the overall framework formula is $(In_{10}Se_{18})^{6-}$. If each T3 cluster is conceptually viewed as a pseudo-tetrahedral atom, a 3D 4-connected net similar to those found in zeolites is obtained.

In UCR-7InSe, the topological type resembles that of the cubic ZnS lattice with only six-membered rings (Fig. 2). In other words, inter- and intra-cluster connectivities are the same. In UCR-7InSe, there are two identical sublattices that interpenetrate each other (Fig. 3). However, the percentage of the crystal volume occupied by framework atoms in UCR-7InSe is still quite low (about 47%) as calculated by using the program PLATON.[15]

While all framework atoms can be unambiguously determined, guest amine molecules are disordered inside large

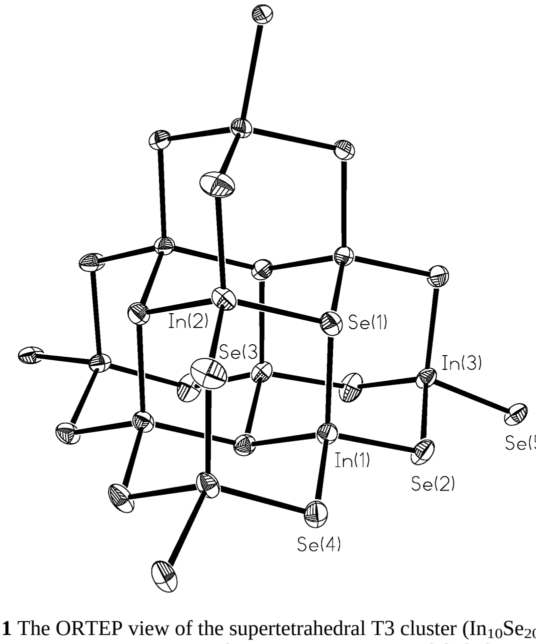

Fig. 1 The ORTEP view of the supertetrahedral T3 cluster $(In_{10}Se_{20})^{10-}$ in UCR-7InSe-TETA. Atoms in the asymmetric unit are labeled.

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Table 1 A summary of crystallographic data for open framework indium selenides synthesized in this study

Name[a]	Framework formula	Space group	a/Å	c/Å	$R(F)$[b]
UCR-7InSe-TETA	$(In_{10}Se_{18})^{6-}$	$I4_1/acd$	20.543(9)	33.160(24)	7.03
UCR-7InSe-PPZ	$(In_{10}Se_{18})^{6-}$	$I4_1/acd$	20.859(3)	33.177(6)	5.04
UCR-7InSe-DABCO	$(In_{10}Se_{18})^{6-}$	$I4_1/acd$	20.886(9)	33.154(16)	8.39
UCR-7InSe-AEAE	$(In_{10}Se_{18})^{6-}$	$P4_12_12$	20.541(6)	32.915(13)	7.00
UCR-7InSe-DMAPA	$(In_{10}Se_{18})^{6-}$	$P4_12_12$	20.096(3)	33.001(7)	6.68

[a] TETA = triethylenetetramine, $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, $C_6H_{18}N_4$; PPZ = piperazine, $C_4H_{10}N_2$; DABCO = 1,4-diazabicyclo[2.2.2]octane, $C_6H_{12}N_2$; AEAE = 2-(2-aminoethylaminoethanol), $H_2N(CH_2)_2NH(CH_2)_2OH$, $C_4H_{12}N_2O$; DMAPA = 3-dimethylaminopropylamine, $(CH_3)_2N(CH_2)_3NH_2$, $C_5H_{14}N_2$. [b] Structures were solved from single crystal data collected at 298 K on a SMART CCD diffractometer with Mo-Kα radiation, $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o > 4.0\sigma(F)$, $Z = 8$ and $2\theta_{max} = 45°$.

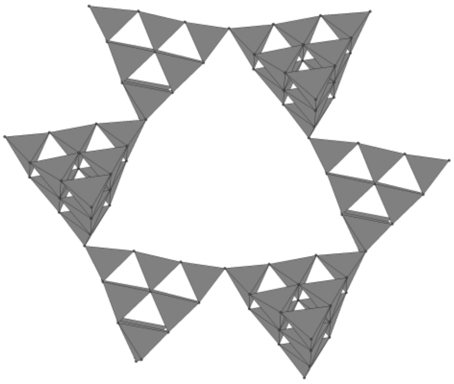

Fig. 2 The polyhedral view of T3 supertetrahedral clusters connected into a six-membered ring in UCR-7InSe-TETA.

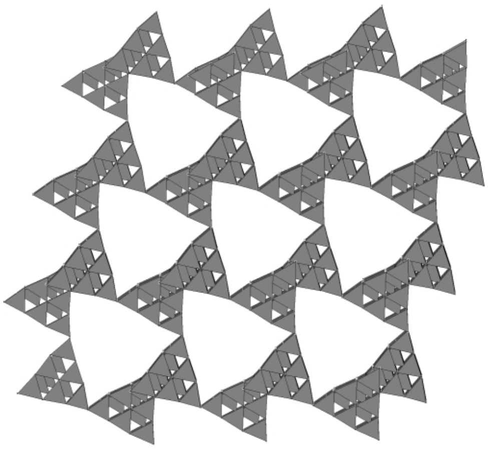

Fig. 3 The three-dimensional framework structure of UCR-7InSe-TETA. Only one set of sublattice is shown for clarity.

cavities. We have employed a number of different amine molecules including piperazine and diazabicyclo[2.2.2]octane. The purpose is to examine whether the host–guest interaction can be enhanced to induce structural ordering of guest molecules. However, all these amine molecules are similarly disordered. Such an observation is similar to that found for open framework sulfides,[10,14] but is in contrast with that found in oxides where some types of amine molecules such as piperazine have a strong structure-directing role and often remain ordered even at the cost of the framework symmetry.[16] The disorder of amine molecules in selenides is apparently due to the weak host–guest interaction. In particular, the N–H···Se type hydrogen bonding is considerably weaker than the N–H···O type that is often responsible for the ordering of guest amine molecules in oxides.[17]

The synthesis of open-framework indium selenides reported here is our first step towards the development of host–guest heavy chalcogenides with an emphasis towards creating nanoporous semiconductors for both semiconducting and porous applications. Future synthetic challenges include creating similar materials in tellurides and larger clusters and tunable pore sizes in both selenides and tellurides.

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Notes and references

† CCDC reference numbers 183232 and 185958–185961. See http://www.rsc.org/suppdata/cc/b2/b203253h/ for crystallographic data in CIF or other electronic format.

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