Inorg. Chem. **2003**, *42*, 1794–1796

Inorganic Chemistry
Communication

Synthesis and Characterization of an Open Framework Gallium Selenide: $Ga_4Se_7(en)_2{\cdot}(enH)_2$

Yajie Dong, Qing Peng, Ruji Wang, and Yadong Li*

Department of Chemistry, Tsinghua University, Beijing 100084, Peoples' Republic of China

Received December 11, 2002

An open framework gallium selenide, $Ga_4Se_7(en)_2{\cdot}(enH)_2$, has been prepared by the direct reaction of gallium (Ga) and selenium (Se) in ethylenediamine (en), in which both covalent and hydrogen bonds have been employed to combine the inorganic structures and organic spacers to build layers with micropores. Its structure has been determined by X-ray diffraction. Its thermal and optical properties have been characterized by TGA and UV–vis, Raman, and IR spectroscopies, respectively.

Open frameworks, especially porous materials, have been of intensive research interest for decades because of their ability to interact with atoms, ions, and molecules throughout the bulk of the materials.[1] Their application range has been extended from traditional use as catalysts and absorbents to areas ranging from microelectronics to medical diagnosis.[2] In order to combine "porous properties" like catalysis or adsorption with "semiconductor properties" such as those found in chalcogenide materials, efforts have been made to substitute the oxygen atoms with other chalcogens such as S, Se, and Te. A series of open framework chalcogenides of metal germanium,[3,4] tin,[5] antimony,[6] and indium[7−9] have been successfully synthesized. However, unlike those open framework metal phosphates[10] or selenites[11] in which amines might play dual role of a metal ligand as well as a structure-directing agent, the organic components in metal chalcogenides simply enter the inorganic structures through either ionic bonding or relatively weak H-bonding and van der Waals interactions. Recently, several covalent organic−inorganic networks of hybrid chalcogenides such as ZnTe,[12] ZnSe, MnSe,[13] and CdSe[14] have been found. Herein, we report the synthesis,[15] crystal structure,[16] and some thermal and optical properties[17] of $Ga_4Se_7(en)_2{\cdot}(enH)_2$, in which both covalent and hydrogen bonds have been employed to

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* To whom correspondence should be addressed. E-mail: ydli@tsinghua.edu.cn.

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(15) Details of the synthesis follow: Gallium (Ga), selenium (Se), and ethylenediamine (en) were added into a Teflon-lined stainless steel autoclave with a molar ratio of 4:7:50 and heated at 140 °C for 5−7 days. Reddish platelike crystals (yield > 90%) were collected after cooling the autoclave naturally, washed with deionized water to remove organic residues, and dried in air at 50 °C for 3−4 h.

(16) Details of the structure determination follow: A single crystal of $Ga_4Se_7(en)_2{\cdot}(enH)_2$ with dimensions $0.3 \times 0.15 \times 0.05$ mm^3 was selected for data collection on a Bruker SMART APEX-CCD diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, $T = 300$ K). An absorption correction based on symmetry-equivalent reflections was applied using SADABS.[28] The structure was solved by direct methods using SHELXS.[29] Direct phase determination yielded the positions of Ga and the most Se atoms, and the N and C atoms were located in successive difference Fourier syntheses. Hydrogen atoms were generated geometrically. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix least-squares refinement on F^2 converged with R1 = 0.0576 and wR2 = 0.1091 for 5116 observed reflections [$I \geq 2\sigma(I)$]. Crystal data: $Ga_4Se_7(en)_2{\cdot}(enH)_2$, $M_r = 1074.03$, monoclinic, space group $P2_1/c$ (No.14), $a = 13.4928(9)$ Å, $b = 10.9203(7)$ Å, $c = 18.1866(13)$ Å, $\beta = 93.282(2)°$, $V = 2675.3(3)$ Å^3, $Z = 4$, $\mu = 13.522$ mm^{-1}, $\rho_{calcd} = 2.667$ g/cm^3, $F(000) = 2000$. The X-ray powder data for the $Ga_4Se_7(en)_2{\cdot}(enH)_2$ was in excellent agreement with its simulated pattern based on single-crystal data, indicating phase purity and high crystallinity. Selected bond lengths (Å) follow:

Ga(1)−Se(2)	2.3982(11)	Ga(3)−Se(2)	2.4111(12)
Ga(1)−Se(4)	2.4016(12)	Ga(3)−Se(6)	2.4162(11)
Ga(1)−Se(3)	2.4076(12)	Ga(4)−N(3)	2.006(7)
Ga(1)−Se(1)	2.4303(12)	Ga(4)−Se(7)	2.3732(12)
Ga(2)−N(1)	2.029(8)	Ga(4)−Se(6)	2.3744(13)
Ga(2)−Se(5)	2.3571(11)	Ga(4)−Se(4)	2.3749(12)
Ga(2)−Se(1)	2.3692(11)	Se(2)−Ga(3)	2.4111(12)
Ga(2)−Se(3)	2.3721(11)	Se(3)−Ga(2)	2.3721(11)
Ga(3)−Se(7)	2.3856(13)	Se(6)−Ga(4)	2.3744(13)
Ga(3)−Se(5)	2.4104(11)	Se(7)−Ga(4)	2.3732(12)

10.1021/ic0262536 CCC: $25.00

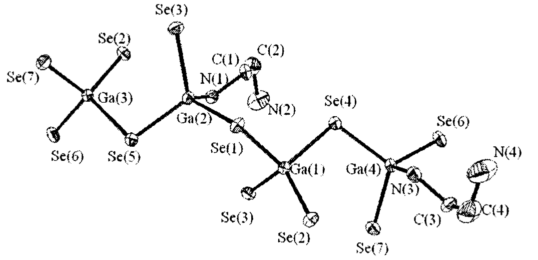

Figure 1. ORTEP drawing for $[Ga_4Se_7(NH_2C_2H_4NH_2)_2]^{2-}$ with 50% probability ellipsoids, showing the atomic numbering scheme.

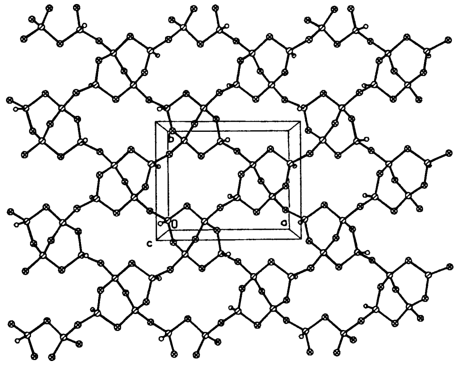

Figure 2. View down [001] of the sheet topology of $Ga_4Se_7(en)_2{\cdot}(enH)_2$. ⊖, Ga atom; ⊗, Se atom; ○, N atom; For clarity, all the C, H, and uncovalently bonded N have been omitted.

combine the inorganic structures and organic spacers to build layers with micropores. The unique structure of this compound offers great opportunity to study the structure−property correlation in open framework chalcogenides.

Single crystal characterization shows that this selenide is built up from two kinds of tetrahedra: $GaSe_4$ and $GaSe_3N$. The nitrogen atom in $GaSe_3N$ tetrahedron comes from the amine (en) covalently bonded to the inorganic framework. As depicted in Figure 1, $GaSe_4$ and $GaSe_3N$ tetrahedra share corners alternately through Ga−Se−Ga bondings to form infinite zigzag chains. These chains are cross-linked into a 2-D layer with 8-ring micropores (i.e., micropores built up from 8 tetrahedral building blocks, four $GaSe_4$ and four $GaSe_3N$ groups) (Figure 2). The other nitrogen atom of the en is connected through hydrogen bonding (N−H···N) to another en which resides between the layers (Figure 3). All these en molecules cooperate to separate and stabilize the semiconducting inorganic $Ga_4Se_7^{2-}$ layer.

The most prominent structural feature of this selenide is the coexistence of these two types of bondings. TGA analysis further evidences this result. The first sharp weight loss in Figure 4 might be due to the loss of the two en molecules residing between the inorganic sheets which are loosely connected to N atoms via hydrogen bonds, while the second

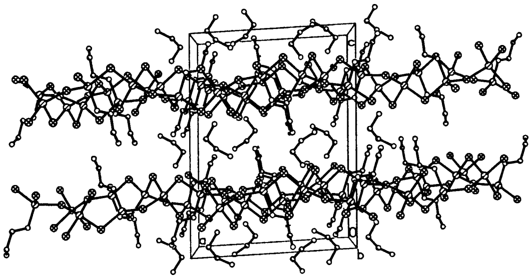

Figure 3. View down [010] of the $Ga_4Se_7(en)_2{\cdot}(enH)_2$ structures showing the sandwich motif of alternating semiconducting inorganic and insulating organic layers (inorganic plot scheme as for Figure 2).

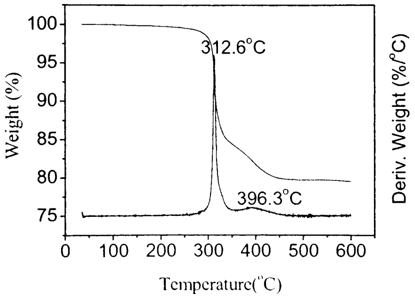

Figure 4. Thermogravimetric analysis data showing weight loss of $Ga_4Se_7(en)_2{\cdot}(enH)_2$ between 35 and 600 °C. The negative of the first derivative (%/°C) is also plotted as a function of temperature.

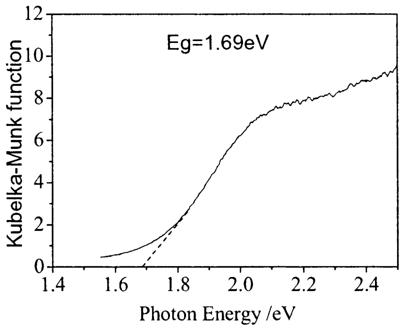

Figure 5. UV−vis absorbance of $Ga_4Se_7(en)_2{\cdot}(enH)_2$.

gradual slope corresponds to the loss of the other two en molecules covalently bonded to Ga atoms. Powder X-ray diffraction analysis following the TGA experiments showed that the residues were Ga_2Se_3 (see Supporting Information).

Another characteristic of this structure is that the Ga−Se−Ga angles vary from 98.66° to 109.39°. This is a range of up to 10°. Although this range is small compared to the range of T−O−T angles (T = tetrahedral atom) in zeolites and that of T−X−T angles in indium chalcogenides,[9] it is considerably greater than the 5° range (i.e., 103−108°) of T−S−T angles in some Ge−S compounds.[3a] The diversity of both bonding types and bonding angles suggests that there could be a rich structural diversity in gallium selenide open frameworks. For example, it can be imagined that one could substitute the en residing between the sheets with other amines of different lengths or different functional groups while keeping the en covalently bonded to Ga untouched.

The optical absorption spectrum of this compound, measured by diffuse reflectance experiments, is depicted in Figure 5. One absorption edge of 1.69 eV was found for it, compared to the value of 2.1 eV reported for bulk Ga_2Se_3 [18]

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(17) Details of characterization follow: Thermogravimetric analysis/differential thermal analysis (TGA/DTA) (ramp at 10 °K min^{-1} to 600 °C under the protection of N_2) for this product reveals that it is thermally stable up to 250 °C, above which there is a multistage 21% weight loss corresponding to the loss of four en molecules (calcd 22.6%). Optical diffuse reflectance of the samples was recorded on a Shimadzu UV-2100S spectrophotometer, Raman shifts were recorded on a Renishaw RM1000 Raman spectrometer with the excitation wavelength of 514 nm, and the infrared spectrum was measured on a Nicolet 560 FTIR Spectrometer.

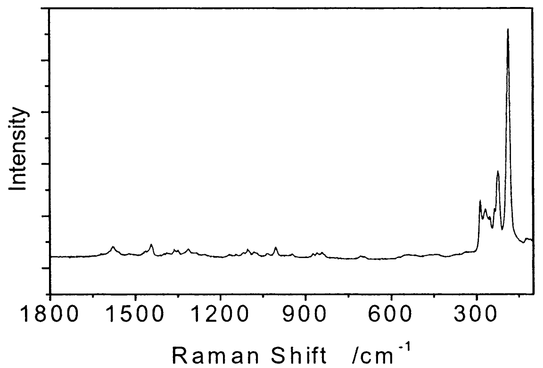

Figure 6. Raman spectrum of $Ga_4Se_7(en)_2\cdot(enH)_2$. The spectrum between 1800 and 400 cm^{-1} was enlarged in Figure 7.

or GaSe,[19] indicating a red shift (-0.4 eV) of the absorption edge. This result is interesting and surprising since at a first glance one would expect the energy gap to increase due to quantum confinement. However, similar to the red shift predicted for GaSe nanotubes,[20] this phenomenon might also be due to the pressure dependence of the electronic states in this compound. The fundamental energy gap in the bulk is from Γ to M with the conduction states at K. In comparison with the normal $GaSe_4$ tetrahadra, the $GaSe_3N$ tetrahedra are compressed obviously since the bond length of Ga−N is much shorter than that of Ga−Se.[16] The states at M and K thus come down in energy with respect to the valence state at Γ whereas the direct gap is roughly constant. The K states come down faster than the M states so that the fundamental gap becomes from Γ to K and thus a red shift of energy gap appears.

A symmetry analysis of $Ga_4Se_7(en)_2\cdot(enH)_2$ indicated that the Raman and IR spectra would be very complex. For example, a total of over 100 modes are to be expected in the Raman spectrum, which makes the assignment of all the experimental bands very difficult (Figure 6). Nevertheless, a comparison of the Raman spectrum with that of similar cadmium selenide (CdSe0.5en) open framework[14] and Ga_2Se_3 [21] allowed a tentative assignment of the strongest feature: The strongest peaks between 350 and 100 cm^{-1} may be attributed to the vibrational modes of the inorganic frameworks ($GaSe_4$ and $GaSe_3N$), whereas the relatively weak peaks between 1600 and 400 cm^{-1} (shown in Figure 7) may be attributed to the vibrational modes of the organic components (NH_2, CN, CH_2, CC, etc.). Because of the presence of too many different forms of amine groups, its IR spectrum (Figure 7) is also much more complicated than that of pure en or complexes of en with Zn^{2+}, Cd^{2+}, Hg^{2+} [22] and difficult to assign.

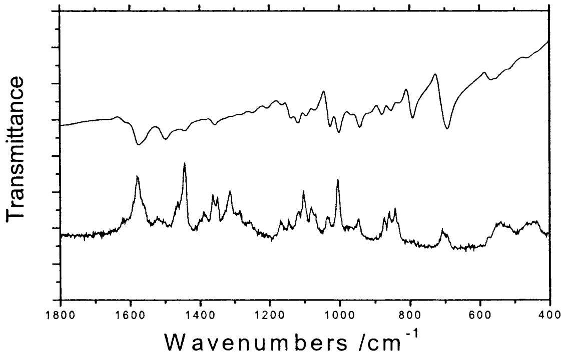

Figure 7. Infrared (above) and Raman (below) spectra of $Ga_4Se_7(en)_2\cdot(enH)_2$.

It is supposed that substances possessing layered structures might be able to form one-dimensional nanostructures under favorable conditions. Recently, we have proved that lamellar structures could be employed to prepare Bi nanotubes,[23] WS_2 nanotubes,[24] W nanowires,[25] MnO_2 nanowires,[26] CdS and CdSe nanorods,[14] and ZnS and ZnSe nanobelts.[27] In a theoretical study, Cote et al. proposed that the GaSe layered compound be explored to form nanotubes.[20] Therefore, it is safe to envision that the $Ga_4Se_7(en)_2\cdot(enH)_2$ with layered structure might also lead to one kind of gallium selenide nanotube. If that is possible, this compound might be the ideal candidate for the study of both 2-D and 1-D semiconductor quantum structures.

In conclusion, we have shown that one novel open framework $Ga_4Se_7(en)_2\cdot(enH)_2$ has been synthesized and structurally, thermally, and optically characterized. The diversity of both bonding types and bonding angles of this compound suggests that there could be a rich structural diversity in gallium selenide open frameworks which might lead to novel optical and electronic properties of corresponding chalcogenides.

Acknowledgment. This work was supported by the NSFC (20025102, 50028201, 20151001), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China, and the State Key Project of Fundamental Research for nanomaterials and nanostructures.

Supporting Information Available: Crystallographic data in CIF format, experimental and simulated X-ray powder pattern for $Ga_4Se_7(en)_2\cdot(enH)_2$. PXRD of the residue of TGA. This material is available free of charge via the Internet at http://pubs.acs.org.

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