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Preparation and crystal structure of chromium silicon selenide containing a B_{12} icosahedron with a tunnel structure

Masato Sugimori, Hiroshi Fukuoka [1], Hideo Imoto *[,2], Taro Saito [3]

Department of Chemistry, School of Science, University of Tokyo, Hongo, Tokyo, 113-0033, Japan

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Abstract

Chromium silicon boron selenide has been prepared by the reaction of chromium diboride and selenium in an evacuated silica tube at a high temperature. The compound is obtained as single crystals in a low yield. The X-ray studies have shown that the structure consists of the three-dimensional framework with a large tunnel and the filling component in the tunnels. The former is made of Si coordinated by four silicon atoms, chromium atoms coordinated by six selenium atoms, and B_{12} icosahedra. The filling component has a strongly disordered structure and estimated to be a chain of B_2Se_3. Analysis of the occupational factors of the filling component has indicated that the composition of the compound is $CrSi_3(B_{12})Se_{12}\cdot(B_2Se_3)_{1.33}$. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Selenide; Silicon; B_{12}-Icosahedron; Tunnel structure

1. Introduction

The linkage of SiO_4 tetrahedra makes a variety of network structures as observed in many silicate minerals, and some of the compounds containing SiO_4 tetrahedra, especially those of the zeolite group, have been found to be very useful in many chemical applications. It is expected that sulfide and selenide analogues of these SiO_4 network compounds may have different useful functions. However, much fewer compounds with SiS_4 or $SiSe_4$ tetrahedra have been reported. One of the problems of compounds with SiS_4 or $SiSe_4$ tetrahedra is that they are often moisture sensitive. In contrast to the very stable phases of SiO_2, both SiS_2 and $SiSe_2$ are easily decomposed by moisture. Stabilization with appropriate elements may be necessary to obtain SiS_4 or $SiSe_4$ networks stable in the atmosphere. In this article, we report a new chromium silicon boron selenide, which was accidentally obtained during the study of chromium chalcogenide. It has two conspicuous structural features. First, it has a large tunnel. Second, it has a B_{12} icosahedron in the $SiSe_4$ network.

2. Experimental

2.1. Preparation of $CrSi_3(B_{12})Se_{12}\cdot(B_2Se_3)_{1.33}$ (**1**)

The mixture of CrB_2(0.22 g, 3 mmol) and selenium (0.24 g, 3 mmol) was sealed in a silica tube (inner diameter 8–10 mm, length ca. 20 cm) under a reduced pressure. The mixture was placed at the high-temperature end of the silica tube, which was heated in a temperature gradient of 900–1100°C. After 4 days, the silica tube was cooled to ambient temperature. Usually 5–50 needle crystals of **1** were observed on the wall of the tube with a large amount of B_2Se_3 and other compounds. Because the main products of the reaction are quickly decomposed by the moisture of the atmo-

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* Corresponding author. Present address: Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan. Fax: + 81-28-6896009.

E-mail address: imoto@cc.utsunomiya-u.ac.jp (H. Imoto).

[1] Present address: Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8527, Japan

[2] Present address: Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, Yoto, Utsunomiya 321-8585, Japan

[3] Present address: Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka 259-1293, Japan

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sphere, which has evolved a poisonous hydrogen selenide, the following procedure must be performed in a hood. The silica tube was broken and immediately dropped into an aqueous solution of sodium hydrogen carbonate. After the gas evolution stopped, the solution was removed, and the residue was washed with a solution of sodium hydrogen carbonate, water, and ethanol, successively, and dried. Black needle crystals were picked up under a microscope for X-ray studies. The crystals were stable in ambient atmosphere. The amount of the crystals was too small to be weighed. The composition of the compound was determined by the single-crystal X-ray structure determination. The origin of silicon in **1** is the silica tube used as the reaction container. The silica tube was apparently eroded especially at the areas where the single crystals of **1** grew.

2.2. *X-ray studies of* **1**

The intensities of all reflections in the 2θ range 5.6–60° with a non-negative h index were measured on a Rigaku AFC5R diffractometer with graphite-monochromated Mo–K_α radiation in the 2θ–ω scan mode. The reflection data were empirically corrected for absorption by the method described in [1]. Relative transmission factors were in the range 0.899–0.952. The observed systematic absences (l odd for $00l$) indicated a unique space group ($P6_322$). Since the number of the observed absences was small, we tried to solve the structure assuming other possible hexagonal space groups. However, only the space group $P6_322$ led to the successful solution of the structure. The positions of Cr, Se1, and Se2 were determined by the direct method (SHELXS-86 [2]). Other atoms were located by the Fourier method. As the refinements proceeded, the difference Fourier map showed many peaks in the tunnel along the c-axis, and these peaks were assumed to be disordered Se atoms. The composition of these disordered components is discussed later. Final full-matrix refinement was performed on F^2 with the program ANYBLK [3], where all averaged reflections including those with negative intensities were used. A summary of crystallographic data follows. Crystal system: hexagonal. Space group: $P6_322$ (no. 182). Cell parameters: $a = 12.9772(6)$ Å, $c = 9.5322(10)$ Å, $V = 1390.2(2)$ Å^3. Chemical formula: $CrSi_3(B_{12})Se_{12}{\cdot}(B_2Se_3)_{1.33}$. Number of units per cell: $Z = 2$. Number of refined parameters: 65. Number of reflections used for the refinements: 1377. R (defined as $\Sigma||F_o|^2 - |F_c|^2|/\Sigma|F_o|^2) = 0.0482$, R_w^2 (defined as $[\Sigma w(|F_o|^2 - |F_c|^2)^2/(\Sigma w|F_o|^4)]^{1/2} = 0.0487$.

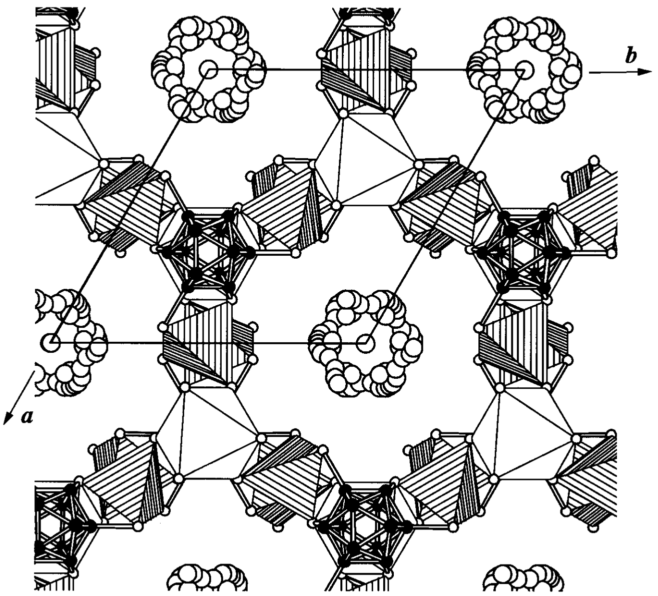


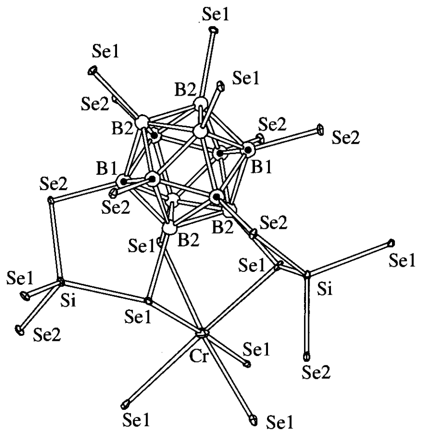
Fig. 1. Structure of $CrSi_3(B_{12})Se_{12}(B_2Se_3)_{1.33}$ projected along the c axis. Hatched tetrahedra are $SiSe_4$ units while octahedra without hatching are $CrSe_6$ units. Filled circles are boron atoms. The aggregations of unfilled circles around the centers of tunnels are disordered selenium atoms.

3. Results and discussion

3.1. *Structure of the framework*

The X-ray structure determination has revealed that the compound consists of a three-dimensional framework with large tunnels running along the c-axis and filling component of the tunnels (Fig. 1, Table 1). The framework is constructed from $SiSe_4$ tetrahedra, $CrSe_6$ octahedra, and B_{12} icosahedra, and the composition is $CrSi_3(B_{12})Se_{12}$. The B_{12} icosahedron which is connected to twelve selenium atoms was recently reported in $Cs_8[B_{12}(BSe_3)_6]$ [4]. The B–Se distances in **1** (1.98 and 2.00 Å) are similar to those reported for the cesium salt (1.98–2.01 Å). The observed B–B distances in **1** (1.76–1.81, average 1.772 Å) are also in a similar range as reported for the cesium salt (1.75–1.80, average 1.783 Å) and other B_{12} icosahedra (1.775 in $K_2B_{12}H_{12}$ [5]; 1.760 in $ZrB_{12}H_{12}$ [6]; 1.806 Å in tetragonal boron [7]). The $SiSe_4$ tetrahedra on the ab plane are arranged in the kagome pattern [8], and the layers are stacked along the c direction. Chromium atoms and B_{12} units are alternately aligned along the c-axis in the triangular column of the stacked kagome-pattern layers (Fig. 2). The tunnel running through the hexagonal hole of kagome-pattern layers are occupied by a filling component that is discussed later. All of the selenium atoms are connected to a silicon atom and a boron atom in the B_{12} unit (Fig. 3). Half of the selenium atoms coordinate further to a chromium atom.

Though the structure is complex, we can deduce the charge of the framework part. If we regard the bonding between the selenium atom and the chromium atom as the donation of the lone-pair electrons to the chromium



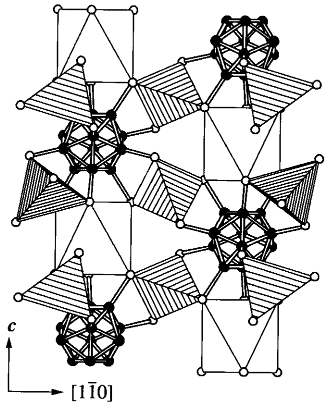


Fig. 3. ORTEP drawing of the framework part $CrSi_3(B_{12})Se_{12}$ with thermal ellipsoids drawn at the 80% probability level. Some of the boron atoms in the B_{12} icosahedron are not labeled for clarity. In the B_{12} icosahedron, circles with small filled circle at the center are the B1 atoms, and others are the B2 atoms.

atom, all selenium atoms have two bonds, one to a boron atom and another to a silicon atom, and, therefore, have no formal charge. The silicon atom has four bonds with selenium atoms and also no formal charge. Since each boron atom in a B_{12} unit is connected to a selenium atom, the B_{12} unit is electronically equivalent to the $B_{12}H_{12}^{2-}$ unit, and, therefore, has the formal charge of -2. The oxidation state of the chromium in the sulfides and selenides is generally between two and three [9–11]. The observed Cr–Se distance 2.83 Å is too long for a Cr(III)–Se distance, and we can tentatively assign the oxidation state of the chromium as $+2$. Then, the charge of the framework part is zero because the framework contains the same number of of Cr^{2+} ions and B_{12}^{2-} units. Therefore, both framework and filling component have no charge, and this conclusion is consistent with the observed disorder that indicates that the interaction between the two is too weak to fix the positions of the filling components.

3.2. Filling component

The difference Fourier maps have shown several peaks with a complex structure in the tunnel. Because the distances between the neighboring peaks are mostly less than 1 Å, they can be only partially occupied. The structural refinements have shown that heavier atoms, Cr and Se, are possible candidates for these peaks. The observation that **1** is heavier than diiodomethane (density 3.33 g cm^{-3}) is consistent with this X-ray results since the density of empty framework is calculated to be only 2.90 g cm^{-3}. We tentatively put Se atoms with a variable occupational factor at the observed peaks for the refinements (Fig. 4). The sites Se3–Se6 are arranged along the three spiral lines, and the sum of the occupations in these sites is 53% of the total. The site Se8 is just inside the spirals and has the largest occupation (34%). The site Se7 is along the central line of the tunnel, having 13% of the total occupation in the tunnel.

Because the component in the tunnel is neutral, it must be $SiSe_2$, CrSe, or B_2Se_3. The reported structure of $SiSe_2$ is a linear chain of Si atoms bridged by a pair of sulfur atoms [12]. If the filling component is $SiSe_2$, it will have the same structure as in the compound $SiSe_2$. However, the simple linear structure cannot fit to the complex peaks observed in the tunnel. It is also difficult

Table 1
Selected bond distances (Å) and angles (°) [a]

Bond distances	
Se1–Cr	2.8274(6)
Se1–Si^{ii}	2.3498(15)
Se1–B2^{iv}	2.004(5)
Se2–Si^{iii}	2.2508(16)
Se2–B1	1.984(5)
B1–B1^{v}	1.756(12)
B1–B1^{vi}	1.803(12)
B1–B2	1.777(7)
B1–B2^{v}	1.777(8)
B1–B2^{vi}	1.760(8)
B2–B2^{i}	1.766(9)
Bond angles	
Cr–Se1–Si^{ii}	118.80(5)
Cr–Se1–B2^{iv}	94.05(16)
Si^{ii}–Se1–B2^{iv}	93.6(2)
Si^{iii}–Se2–B1	94.90(18)
Se1–Cr–Se1^{i}	83.832(17)
Se1–Cr–Se1^{v}	92.28(2)
Se1–Cr–Se1^{vi}	100.41(2)
Se1–Cr–Se1^{vii}	173.94(2)
Se1^{i}–Si–Se1^{iv}	106.27(10)
Se1^{i}–Si–Se2^{iii}	109.460(19)
Se1^{i}–Si–Se2^{vi}	113.71(2)
Se2^{iii}–Si–Se2^{vi}	104.42(10)

[a] Symmetry codes. $^{i}-y, x-y, z$; $^{ii}-x+y, -x, z$; $^{iii}-x, -y, z+1/2$; $^{iv}-x, -x+y, -z$; $^{v}-y, -x, -z+1/2$; $^{vi}-x+y, y, -z+1/2$; $^{vii}x, x-y, -z+1/2$.

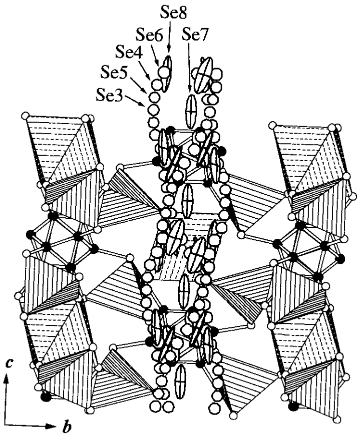


Fig. 4. Disordered selenium atoms with surrounding framework structure. Thermal ellipsoids are drawn at the 50% probability level.

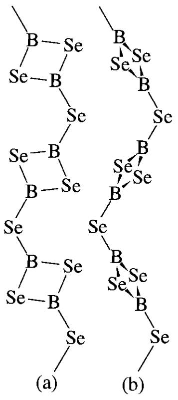


Fig. 5. Estimated structure of B_2Se_3 in the tunnel of **1**. (a) The four-membered B_2Se_3 rings are parallel to the sheet. (b) The four-membered B_2Se_3 rings are perpendicular to the sheet.

to construct a linear chain made of CrSe in the tunnel because the chromium atom requires six-fold coordination. Therefore, the only possible component in the tunnel is B_2Se_3. Since the electron densities due to the disordered boron sites are too small to be observed in disordered sites, the observed peaks are due to Se atoms only. Then, the composition of the compound calculated from the sum of the refined occupational factors (3.98) is $CrSi_3(B_{12})Se_{12}\cdot(B_2Se_3)_{1.33}$. The calculated density for this formula ($3.72\ g\ cm^{-1}$) is much heavier than that of diiodomethane.

Since the structure of the compound B_2Se_3 has not been reported so far as can be established, we estimated the structure of the filling component B_2Se_3 from the structure of the compound B_2S_3 [13]. The compound B_2S_3 has a layer structure, and the layer consists of six-membered B_3S_3 rings, four-membered B_2S_2 rings, and bridging selenium atoms. The six-membered B_3Se_3 ring with three selenium atoms connected to the boron atoms in the ring is too large to be accommodated in the tunnel. Then, the structure in the tunnel may be the chain of four-membered B_2Se_2 rings and bridging Se atoms as shown in Fig. 5. Because the bond angle of the selenium atom is 90–120°, the chain cannot be completely linear at the bridging selenium atom and has a zigzag shape. This complex configuration is consistent with the observed complicated disordered structure.

4. Supplementary material

Further details of the crystal structure determination can be ordered from Fachinformationszentrum Karlsruhe, 76344, Eggenstein-Leopoldshafen, Germany under the depository number CSD-411160.

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