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# High-Pressure Synthesis and Structures of New Barium Chromium Sulfides, $BaCr_4S_7$ and $Ba_2Cr_5S_{10}$, with New Type Face-Sharing $CrS_6$ Structure Units

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Two new ternary barium chromium sulfides, $BaCr_4S_7$ and $Ba_2Cr_5S_{10}$, were synthesized by reactions of barium sulfide, sulfur, and chromium metal under high-pressure and high-temperature conditions. Single crystals of $BaCr_4S_7$ were obtained from a starting mixture with a molar ratio of Ba:Cr:S = 2:5:10 after reacting at 1200 °C and under a pressure of 5 GPa. It crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 6.739(4)$ Å, $b = 22.665(9)$ Å, $c = 5.907(3)$ Å, $\beta = 90.1(4)°$, $V = 902.2(7)$ Å$^3$, and $Z = 4$. It contains $CrS_2$ sheets composed of edge-sharing $CrS_6$ octahedra. The sheets are connected by wall-shaped subunits composed of face-sharing $CrS_6$ octahedra to form a tunnel structure. Ba atoms are situated in the tunnels. Single crystals of $Ba_2Cr_5S_{10}$ were synthesized by heating a mixture with a molar ratio of Ba:Cr:S = 1:1:3 under a pressure of 5 GPa at 1200 °C. It crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 5.940(4)$ Å, $b = 6.645(5)$ Å, $c = 17.39(2)$ Å, $\alpha = 95.19(3)°$, $\beta = 91.67(3)°$, $\gamma = 90.16(2)°$, $V = 683.1(9)$ Å$^3$, and $Z = 2$. The structure is composed of $CrS_2$ sheets and the wall-shaped subunits, like as in $BaCr_4S_7$, but the subunits do not connect the adjacent $CrS_2$ sheets. It has a two-dimensional structure, and Ba atoms are situated in interlayer regions.

Structural chemistry of ternary chromium sulfides is an attractive subject, because they show a variety of structures: one-dimensional (1-D) chain, two-dimensional (2-D) layer, and three-dimensional (3-D) networks.[1–8] Most of them contain $CrS_6$ octahedra as the smallest structural unit. The octahedra are linked together to form frameworks of sulfides in different ways by sharing corners, edges, or faces. The wide variations in structure among chromium sulfides arise from the difference in linkage of octahedra. For example, a $CrS_2$ sheet, which is one of the most important building blocks of chromium sulfides, is formed by sharing edges of $CrS_6$ octahedra as shown in Fig. 1b. This type of 2-D layer is found in the structure of $ACrS_2$ (A = Li, Na, K, Cu, Ag, and Au), where the A atoms are situated in the interlayer region.[9–15]

The $CrS_2$ sheet is contained in some 3-D chromium sulfides, such as $ACr_5S_8$, (A = K, Rb, Cs, Tl, In, and Ba), in which the adjacent sheets are connected through other building units composed of edge-sharing $CrS_6$ octahedra. These sulfides have a tunnel structure shown in Fig. 1c.[3,4,16,17] $K_3Cr_{11}S_{18}$ also contains the 2-D sheets, but has a different tunnel structure. It contains two different kinds of tunnels having different sizes, one of which is the same as that in $ACr_5S_8$.[17]

We have prepared two chromium sulfides with 1-D structures, $Ba_3CrS_5$, and $Ba_3Cr_2S_6$ at high pressures and high temperatures.[1] These sulfides, having structures that are closely related to $BaNiO_3$,[18–20] contain $CrS_3$ 1-D chains composed of face-sharing $CrS_6$ units as shown in Fig. 1a. They were the first examples of chromium sulfides having 1-D chain

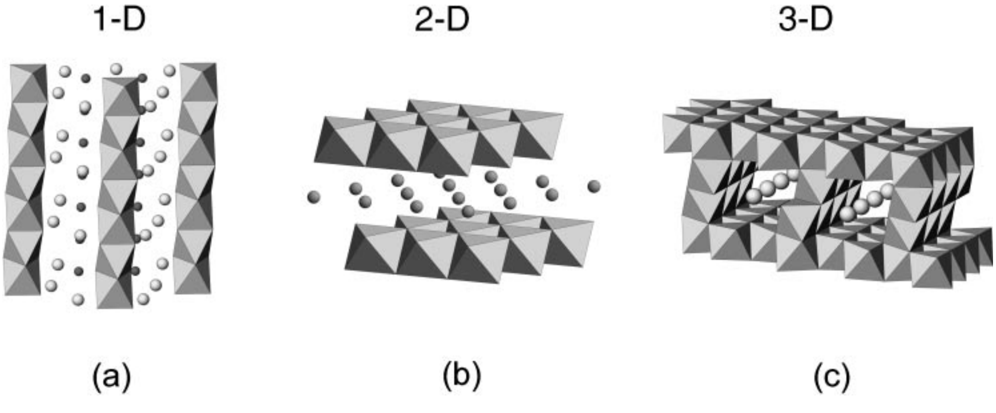

Fig. 1. Fundamental structures of ternary chromium sulfides: (a) 1-D chain structure composed of face-sharing $CrS_6$ octahedra in $Ba_3CrS_5$, (b) 2-D layer structure of edge-sharing octahedra in $AuCrS_2$, and (c) 3-D tunnel structure of $TlCr_5S_8$.

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structure and can be prepared only by high-pressure synthesis method.

Reaction conditions of the high-pressure synthesis method are completely different from any other conventional ones using evacuated ampoules or floating $CS_2$ or $H_2S$ gases. The method, therefore, has the potential for producing new $CrS_6$ linkages. Another advantage of this method in the synthesis of sulfides is that sulfur, which is a highly volatile component, can be easily kept in the reaction system even at high temperatures.

In the present study, we examined the reactions of Ba, Cr, and S at different pressures and temperature while varying the composition of the starting mixture of BaS, Cr, and S. Two new sulfides having new 2-D and 3-D host networks were obtained, and their structures were analyzed by single X-ray crystal analysis.

## Experimental

**Synthesis.** Barium sulfide (Alfa 99.7%), chromium (Katayama Chemical 200 mesh, 99%), and sulfur (Rare Metallic Co., Ltd. 99%) powders were mixed in various compositions in an Ar filled glove box. Each mixture was put in a BN container with 5 mm in inner diameter and 5 mm in depth. The container was placed in a graphite heater rod, and then the assembly packed in a cube ($20 \times 20 \times 20\,\mathrm{mm}^3$) made of pyrophyllite. The cube was compressed in a multi anvil press in order to react the sample mixture at 3–5 GPa and 1000–1200 °C for 30 min. Detailed information about the cell assembly and the process of the high-pressure synthesis is described elsewhere.[21]

**Characterization.** Powder X-ray diffraction measurements were carried out on a M18XHF diffractometer with monochromated Cu K$\alpha$ radiation. Single crystal analysis was performed using Rigaku R-AXIS diffractometers with graphite monochromated Mo K$\alpha$ radiation. The structures were determined by using CrystalStructure: crystal structure analysis packages.[22] Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the following depository numbers: CSD-418254 for $BaCr_4S_7$ and CSD-418255 for $Ba_2Cr_5S_{10}$.

## Results and Discussion

**Synthesis.** A new barium chromium sulfide $BaCr_4S_7$ was obtained as the main phase in the reaction of BaS, Cr, and S with an atomic ratio of Ba:Cr:S = 1:4:7 at 5 GPa and 1200 °C. Greenish black single crystals of $BaCr_4S_7$ were obtained in the product. When the same starting mixture was heated in a sealed silica ampoule at 1200 °C, $BaCr_4S_7$ was not obtained. This reaction yielded a composite crystal of $Ba_{1-p}Cr_2S_{4-p}$[5,6] as the main phase. Therefore, high pressures are required for the synthesis of this compound.

In order to determine the crystal structure of $BaCr_4S_7$, we examined many crystals, but their quality was not good enough for single crystal structure analysis. The poor crystallinity of the compound is due to the structural features as described below. The purest sample of $BaCr_4S_7$ was obtained from a reaction mixture with Ba:Cr:S = 2:5:10 at 5 GPa and 1200 °C. Single crystals were also obtained in this product. After examining many crystals again, a single crystal suitable for the analysis was selected.

A reaction mixture having the molar ratio of Ba:Cr:S = 1:1:3 reacted at 5 GPa and 1200 °C yielded a product with poor crystallinity that only gave a few broad X-ray diffraction peaks of $BaS_3$. A very small amount of greenish black single crystals of another new sulfide, $Ba_2Cr_5S_{10}$, were obtained. Owing to their small sizes and diffuse scattering lines, which indicate a disordered structure, it was extremely difficult to find a good single crystal. Finally, we selected a single crystal having relatively high quality; however, it showed disorder as described below. $Ba_2Cr_5S_{10}$ was always obtained in a mixture with other sulfides, such as $BaCr_4S_7$.

**Crystal Structure of $BaCr_4S_7$.** $BaCr_4S_7$ crystallizes in a monoclinic unit cell with $a = 6.739(4)$ Å, $b = 22.665(9)$ Å, $c = 5.907(3)$ Å, $\beta = 90.1(4)°$, $V = 902.2(7)$ Å$^3$, and $Z = 4$. The unit cell seems to show that the crystal is orthorhombic at first glance. The diffraction data, however, showed only two independent systematic absences of $h0l$ ($l =$ odd) and $0k0$ ($k =$ odd). There is no orthorhombic space group consistent with these extinction conditions. Furthermore, assuming orthorhombic symmetry, the $R$(int) parameter, which indicates the internal consistency of equivalent diffraction intensities, was about two times as large as that for monoclinic symmetry. These observations indicated that the space group of $BaCr_4S_7$ is the monoclinic $P2_1/c$.

The crystallographic data of $BaCr_4S_7$ are listed in Table 1. All atoms except S(4) were refined anisotropically. Since the anisotropic thermal parameters for S(4) became unreasonably small, the isotropic parameter was used in the refinement. The reason why S(4) had very small thermal parameters is discussed below. The final cycle of full-matrix least-squares refinement converged with $R = 4.6\%$, and $Rw = 5.3\%$. Refined

Table 1. Details of X-ray Diffraction Data Collection for $Ba_2Cr_5S_{10}$ and $BaCr_4S_7$

| Formula | $Ba_2Cr_5S_{10}$ | $BaCr_4S_7$ |
|---|---|---|
| Space group | $P\bar{1}$ (2) | $P2_1/c$ (14) |
| $a$/Å | 5.940(4) | 6.739(4) |
| $b$/Å | 6.645(5) | 22.665(9) |
| $c$/Å | 17.39(2) | 5.907(3) |
| $\alpha$/° | 95.19(3) | |
| $\beta$/° | 91.67(3) | 90.1(4) |
| $\gamma$/° | 90.16(2) | |
| $V$/Å$^3$ | 683.1(9) | 902.2(7) |
| $Z$ | 2 | 4 |
| $F(000)$, electrons | 784 | 1056 |
| $D_{\mathrm{calc}}$/g cm$^{-1}$ | 4.16 | 4.19 |
| $T$ (K) of data collection | 296 | 296 |
| Crystal size/mm$^3$ | $0.02 \times 0.02 \times 0.01$ | $0.02 \times 0.02 \times 0.01$ |
| Diffractometer | Rigaku Raxis-Rapid | Rigaku Raxis-Rapid |
| Radiation (graphite monochromated) | Mo K$\alpha$ | Mo K$\alpha$ |
| Scan range/degree | $2\theta < 55$ | $2\theta < 55$ |
| No. of unique reflections | 2844 | 2072 |
| No. of used reflections | 1485 ($>3\sigma(I)$) | 1182 ($>3\sigma(I)$) |
| No. of variables | 166 | 104 |
| $R$, $Rw$ | 0.057, 0.067 | 0.046, 0.053 |
| Godness of fit, $S$ | 1.77 | 1.06 |
| Residual density/e A$^{-3}$ | −2.03/2.14 | 3.33/−1.33 |

atomic parameters and thermal parameters are listed in Table 2. Selected bond lengths of $BaCr_4S_7$ are listed in Table 3.

$BaCr_4S_7$ has a tunnel structure as shown in Fig. 2a. The framework is composed of face- and edge-sharing $CrS_6$ octahedra. Ba ions are situated in the tunnels running along the *c*-axis. The framework has two building units. One is the flat $CrS_2$ sheet composed of edge-sharing $Cr(1)S_6$, and $Cr(2)S_6$ octahedra. This unit is commonly observed in chromium sulfides. For example, $ACrS_2$ ($A =$ Li, Na, K, Ag, and Au) contain the same kind of sheet in the structure as shown in Fig. 1b. The adjacent $CrS_2$ sheets of $BaCr_4S_7$ are connected through $Cr(3)S_6$ and $Cr(4)S_6$ octahedra. These octahedra share their faces to form another subunit in the shape of a wall separating interlayer spaces into small tunnels where Ba ions reside.

The wall-shaped subunit has a quite compact structure, in which each $Cr(4)S_6$ octahedron shares their three faces with two neighboring $Cr(4)S_6$ and one $Cr(3)S_6$ polyhedra. The whole linkage of those octahedra is shown in a ball and stick and polyhedral representations in Figs. 2b and 2c, respectively. Each $Cr(3)S_6$ octahedron shares a face with one $Cr(1)S_6$ in the $CrS_2$ sheet and one $Cr(4)S_6$ in the wall. These sheets and walls are, therefore, connected through the face-sharing $Cr(3)S_6$ and $Cr(1)S_6$ octahedra.

Table 2. Atomic Parameters for $BaCr_4S_7$

| Atom | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| Ba | 0.37221(16) | 0.32693(4) | 0.38927(17) | 1.716(18) |
| Cr(1) | 0.8755(3) | 0.50538(10) | 0.7562(3) | 0.70(4) |
| Cr(2) | 0.3759(3) | 0.50152(10) | 0.7693(3) | 0.71(4) |
| Cr(3) | 0.8719(3) | 0.37332(10) | 0.7403(3) | 0.98(4) |
| Cr(4) | 0.8708(3) | 0.24882(11) | 0.6209(3) | 1.02(4) |
| S(1) | 0.6261(5) | 0.44333(13) | 0.5861(5) | 0.72(5) |
| S(2) | 0.1073(5) | 0.29956(16) | 0.8678(5) | 1.02(6) |
| S(3) | 0.6351(5) | 0.29991(16) | 0.8664(5) | 0.94(6) |
| S(4) | 0.8736(4) | 0.32943(12) | 0.3845(5) | 0.22(4) |
| S(5) | 0.1253(5) | 0.44041(13) | 0.5936(5) | 0.79(5) |
| S(6) | 0.3759(5) | 0.43713(14) | 0.0794(5) | 0.88(6) |
| S(7) | 0.8732(5) | 0.43848(16) | 0.0668(5) | 0.75(6) |

The structure of $BaCr_4S_7$ is possibly disordered. The positional relationship of Ba ions and the wall-shaped units in the upper and lower interlayer spaces in Fig. 2a may be changeable. For example, the positions of Ba and wall-shaped units in the upper spaces can be mutually replaced. The resulting structure becomes one polytype of $BaCr_4S_7$. This is possibly the reason why most of the single crystals of $BaCr_4S_7$ were low quality. In polytype structures, some of the S(4) sites are replaced with the Ba sites, because, as shown in Fig. 2b, the *y*- and *z*-coordinates of these sites are almost the same. This

Table 3. Selected Bond Lengths (Å) of $BaCr_4S_7$

| Atom | Atom | Distance | Atom | Atom | Distance |
|---|---|---|---|---|---|
| Ba | S(1) | 3.352(3) | Ba | S(2) × 2 | 3.380(3),<br>3.402(3) |
| Ba | S(3) × 2 | 3.380(3),<br>3.383(3) | Ba | S(4) × 2 | 3.361(3),<br>3.380(3) |
| Ba | S(5) | 3.293(3) | Ba | S(6) | 3.097(3) |
| Cr(1) | S(1) | 2.410(4) | Cr(1) | S(5) × 2 | 2.404(3),<br>2.435(4) |
| Cr(1) | S(6) | 2.348(4) | Cr(1) | S(7) × 2 | 2.361(4),<br>2.380(4) |
| Cr(2) | S(1) × 2 | 2.400(4),<br>2.443(3) | Cr(2) | S(5) | 2.418(4) |
| Cr(2) | S(6) × 2 | 2.342(4),<br>2.351(4) | Cr(2) | S(7) | 2.368(4) |
| Cr(3) | S(1) | 2.467(4) | Cr(3) | S(2) | 2.424(4) |
| Cr(3) | S(3) | 2.424(4) | Cr(3) | S(4) | 2.325(3) |
| Cr(3) | S(5) | 2.446(4) | Cr(3) | S(7) | 2.429(4) |
| Cr(4) | S(2) × 2 | 2.446(4),<br>2.446(4) | Cr(4) | S(3) × 2 | 2.444(4),<br>2.449(4) |
| Cr(4) | S(4) × 2 | 2.300(3),<br>2.360(3) | | | |

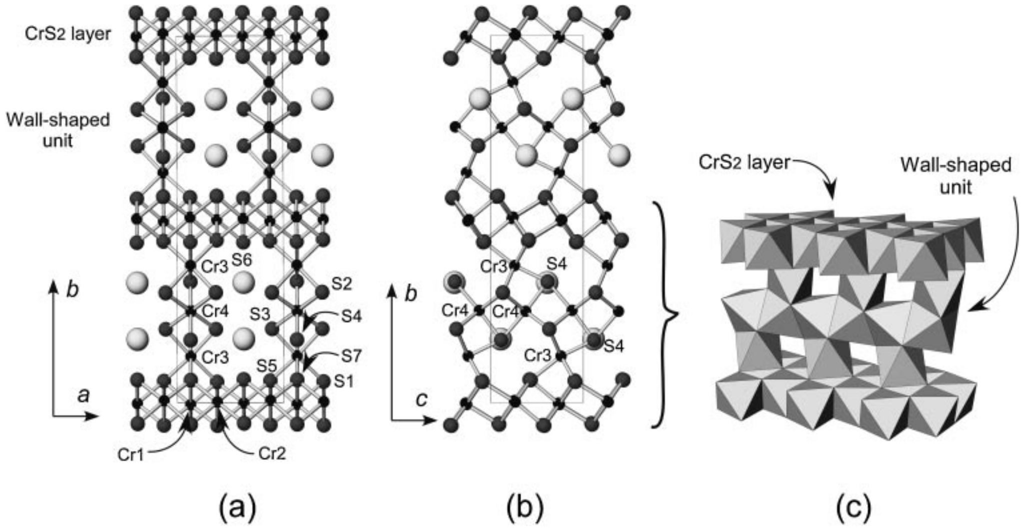

Fig. 2. Crystal structures of $BaCr_4S_7$ projected along the *c*-axis (a), and the *a*-axis (b). Small black, middle gray, and large white balls represent chromium, sulfur, and barium atoms, respectively. The linkage of $CrS_6$ octahedra is shown by a polyhedral representation in (c). The Cr(1) and Cr(2) octahedra share their edges to form 2-D $CrS_2$ layers. The $Cr(3)S_6$ octahedron has two faces shared with $Cr(3)S_6$ and $Cr(4)S_6$ octahedra. The Cr(4) octahedron shares three faces with one $Cr(3)S_6$ and two $Cr(4)S_6$ octahedra.

Table 4. Atomic Parameters for $Ba_2Cr_5S_{10}$

| Atom | *x* | *y* | *z* | $B_{eq}$ a) | ocp. |
|---|---|---|---|---|---|
| Ba(1) | 0.6324(2) | 0.6815(2) | 0.22552(9) | 1.73(3) | |
| Ba(2) | 0.2637(10) | 0.7378(4) | 0.4542(3) | 2.30(9) | 0.582(11) |
| Ba(3) | 0.1371(14) | 0.7339(5) | 0.4222(3) | 1.94(11) | 0.417(11) |
| Cr(1) | 0.7574(4) | 0.8791(4) | 0.00748(19) | 0.66(6) | |
| Cr(2) | 0.2304(4) | 0.6258(4) | −0.0024(2) | 0.86(6) | |
| Cr(3) | 0.2777(4) | 0.1687(4) | 0.16847(19) | 0.97(7) | |
| Cr(4) | 0.3961(5) | 0.2084(4) | 0.3306(2) | 1.48(7) | |
| Cr(5) | −0.0813(5) | 0.2085(5) | 0.3290(2) | 1.56(7) | |
| S(1) | 0.4224(7) | 0.3911(7) | 0.0744(2) | 0.73(10) | |
| S(2) | 0.4140(7) | 0.8942(7) | 0.0783(2) | 0.68(9) | |
| S(3) | −0.0576(7) | 0.1463(6) | 0.0822(3) | 0.87(10) | |
| S(4) | 0.9320(7) | 0.6434(7) | 0.0823(3) | 0.76(10) | |
| S(5) | 0.6376(7) | 0.1812(7) | 0.2238(2) | 0.81(10) | |
| S(6) | 0.1524(7) | 0.9540(7) | 0.2638(3) | 1.07(10) | |
| S(7) | 0.1568(8) | 0.4308(7) | 0.2629(3) | 1.11(10) | |
| S(8) | 0.1655(8) | 0.2331(8) | 0.4372(3) | 1.73(12) | |
| S(9) | 0.6663(10) | 0.4527(13) | 0.3901(4) | 4.89(19) | |
| S(10) | 0.6645(10) | 0.9926(16) | 0.3896(5) | 6.1(2) | |

a) $B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$.

would be the reason why the thermal parameter of S(4) site was too small. The single crystal examined in the present work probably contains a very small portion that has a polytype structure, and the heavy Ba atoms are partially superimposed on the S(4) site, and the small thermal parameters of the S(4) site probably are a result of this disordering.

The oxidation state of Cr atoms in $BaCr_4S_7$ was calculated to be 3+ from the composition. The bond length between Cr and S atoms is in the range from 2.300(3) to 2.467(4) Å, and the average is 2.401(4) Å. The averaged distances are 2.390(4), 2.387(4), 2.419(4), and 2.408(4) Å for Cr(1), Cr(2), Cr(3), and Cr(4), respectively. These values are comparable with those of other chromium sulfides containing octahedrally coordinated $Cr^{3+}$ ions: 2.38 Å ($AuCrS_2$), 2.40 Å ($TlCr_5S_8$), 2.41 Å ($AgCrS_2$, $TlCr_3S_5$,[23,24] $CsCr_5S_8$, and $RbCr_3S_5$), 2.43 Å ($KCrS_2$ and $NaCrS_2$), and 2.46 Å ($Ba_3Cr_2S_6$).

The face-sharing $CrS_6$ structure has short Cr–Cr distances of 2.995(3) Å (Cr(1)–Cr(3)), 2.908(3) Å (Cr(3)–Cr(4)), and 2.954(3) Å (Cr(4)–Cr(4)). These values are similar to those observed in other chromium sulfides having face sharing $CrS_6$ units. They are 2.992 Å ($TlCr_3S_5$), 2.917 Å ($RbCr_3S_5$), 2.958 Å ($TlCr_5S_8$), and 2.977 Å ($Ba_{0.51}Cr_5S_8$).

The coordination octahedra around the Cr(1) and Cr(2) atoms in the $CrS_2$ sheets are almost regular. The bond angles of S–Cr–S are in the range from 84.1(1) to 96.1(1)°. However, the Cr(3) and Cr(4) octahedra are more distorted. The S–Cr–S bond angles around Cr(3) and Cr(4) are in the range from 82.1(1) to 100.1(1)° and 81.1(1) to 99.0(1)°, respectively. This distortion around Cr(3) and Cr(4) is due to the structural strain arising from the compact face-sharing linkages of $CrS_6$ octahedra in this compound.

Each Ba atom is coordinated by nine S atoms. The Ba–S bond distances range from 3.097(3) to 3.402(3) Å. Only the S(7) atom has no bonding with any Ba atom. The bond distance between Ba and S(6) is remarkably short. Bond distances between Ba and S depend a lot on the coordination number of sulfur atoms. Whereas S(1) to S(5) atoms have five bonds with Ba and Cr atoms, S(6) has only four neighbors: one Ba and three Cr atoms. In general, a smaller coordination number often leads to shorter bond distances. This is a reason for the short Ba–S(6) bond distance.

There are a few sulfides that have similar structural features to $BaCr_4S_7$. For example, $ACr_5S_8$, where $A$ = Cs, Rb, K, Tl, and 0.5Ba, have a tunnel structure composed of $CrS_2$ sheets and wall-shaped units. The wall-shaped units in these compounds are, however, composed of edge-sharing octahedra as shown in Fig. 1c, whereas the unit of $BaCr_4S_7$ is composed of face-sharing $CrS_6$ octahedra. Another chromium sulfide $KCr_{3.67}S_6$ having a tunnel structure also contains only edge-sharing type units. It is often reported that structures containing face-sharing polyhedra are less stable than those containing only edge- or corner-sharing polyhedra due to the electrical repulsion between the central cations. The compact face-sharing structure in $BaCr_4S_7$ is, therefore, probably attributed to the effect of the high-pressure treatment.

**Crystal Structure of $Ba_2Cr_5S_{10}$.** $Ba_2Cr_5S_{10}$ crystallizes in triclinic space group $P\bar{1}$ (No. 2) with $a = 5.940(4)$ Å, $b = 6.645(5)$ Å, $c = 17.387(16)$ Å, $\alpha = 95.19(3)°$, $\beta = 91.67(3)°$, $\gamma = 90.16(2)°$, $V = 683.1(9)$ Å$^3$. The crystallographic data are listed in Table 1. The final cycle of full-matrix least-squares refinement converged with $R = 5.7\%$, and $Rw = 6.7\%$. The structure was found to have disorder in the barium sites (Ba(2) and Ba(3)). In the refinement, occupational parameters of them were refined using a constraint of Ocp(Ba(2)) + cp(Ba(3)) = 1. Refined atomic parameters and thermal parameters are listed in Table 4. Quite large equivalent thermal parameters for S(9) and S(10) were observed. This is clearly due to the disorder of barium, because S(9) and S(10) are the nearest neighbors of Ba(2) and Ba(3). These sulfur sites have elongated anisotropic thermal parameters as if they stand aside from barium atoms.

The crystal structure of $Ba_2Cr_5S_{10}$ is shown in Fig. 3. It has

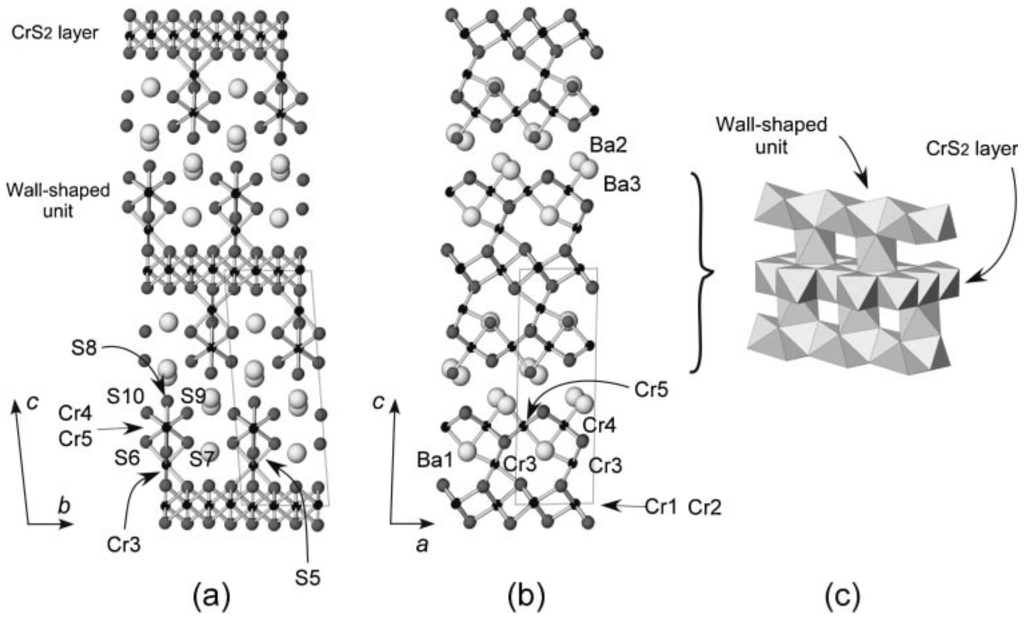

Fig. 3. Crystal structure of $Ba_2Cr_5S_{10}$ projected along the *a*- and *b*-axes ((a) and (b)). Small black, middle gray, and large white balls represent chromium, sulfur, and barium atoms, respectively. The linkage of $CrS_6$ octahedra is shown by a polyhedral representation in (c).

a novel layered structure. A projection along the *a*-axis, given in Fig. 3a, shows that barium ions are packed between layers composed of $CrS_6$ octahedra. The $Ba_2Cr_5S_{10}$ framework is composed of two structure units; flat $CrS_2$ sheets and wall-shaped units, like that in $BaCr_4S_7$.

The interconnection between these units is shown in Figs. 3b and 3c using ball and stick and polyhedral representations, respectively. $Cr(1)S_6$ and $Cr(2)S_6$ octahedra share their edges to form $CrS_2$ sheets, and $Cr(4)S_6$ and $Cr(5)S_6$ octahedra share their faces of both sides with each other as shown in Fig. 3b. Each $Cr(3)S_6$ octahedron shares two faces with $Cr(4)S_6$ and $Cr(1)S_6$ octahedra. The wall-shaped unit is composed of $Cr(3)S_6$, $Cr(4)S_6$, and $Cr(5)S_6$ octahedra and is connected to a $CrS_2$ sheet through the $Cr(3)S_6$ octahedra.

$Ba_2Cr_5S_{10}$ has a closely related structure to that of $BaCr_4S_7$. The similarity can be easily understood by comparing the images in Figs. 2 and 3. In fact, the layer of $Ba_2Cr_5S_{10}$ has a partial structure of 3-D $BaCr_4S_7$. In $BaCr_4S_7$, each wall-shaped unit connects two adjacent $CrS_2$ sheets on the both ends to make a 3-D tunnel structure, whereas the unit in $Ba_2Cr_5S_{10}$ is attached to only one $CrS_2$ sheet to form the 2-D layered structure.

Selected bond lengths of $Ba_2Cr_5S_{10}$ are given in Table 5. The bond distance of $Cr(1)S_6$ and $Cr(2)S_6$ octahedra in the $CrS_2$ sheet ranges from 2.333(5) to 2.441(5) Å. These octahedra are almost regular. On the other hand, $Cr(3)S_6$, $Cr(4)S_6$, and $Cr(5)S_6$ octahedra having more than two shared faces are rather distorted. The Cr–Cr distances between face-sharing octahedra are 3.048(5) Å for Cr(1)–Cr(3); 2.874(5) for Cr(3)–Cr(4); 2.835(5) and 3.105(5) for Cr(4)–Cr(5).

The average oxidation state of chromium was calculated to be 3.2+ from the composition of $Ba_2Cr_5S_{10}$. This shows that four $Cr^{3+}$ and one $Cr^{4+}$ ions are involved in the formula unit. The site distribution of these ions, however, could not be

Table 5. Selected Bond Lengths (Å) of $Ba_2Cr_5S_{10}$

| Atom | Atom | Distance | Atom | Atom | Distance |
|---|---|---|---|---|---|
| Ba(1) | S(1) | 3.326(4) | Ba(1) | S(2) | 3.273(5) |
| Ba(1) | S(4) | 3.095(5) | Ba(1) | S(5) × 2 | 3.322(5),<br>3.323(5) |
| Ba(1) | S(6) | 3.431(4) | Ba(1) | S(7) | 3.384(5) |
| Ba(1) | S(9) | 3.361(8) | Ba(1) | S(10) | 3.368(9) |
| Ba(2) | S(8) × 3 | 3.212(8),<br>3.382(6), | Ba(2) | S(9) × 2 | 3.108(10),<br>3.217(8) |
| | | 3.387(6) | Ba(2) | S(10) × 2 | 3.132(10),<br>3.205(10) |
| Ba(3) | S(6) | 3.236(8) | Ba(3) | S(7) | 3.280(7) |
| Ba(3) | S(8) × 3 | 3.069(9),<br>3.307(6), | Ba(3) | S(9) | 3.363(10) |
| | | 3.365(7) | Ba(3) | S(10) | 3.357(10) |
| Cr(1) | S(1) | 2.414(5) | Cr(1) | S(2) × 2 | 2.410(5),<br>2.419(5) |
| Cr(1) | S(3) × 2 | 2.353(5),<br>2.398(5) | Cr(1) | S(4) | 2.349(5) |
| Cr(2) | S(1) × 2 | 2.411(5),<br>2.441(5) | Cr(2) | S(2) | 2.405(5) |
| Cr(2) | S(3) | 2.362(6) | Cr(2) | S(4) × 2 | 2.333(5),<br>2.350(5) |
| Cr(3) | S(1) | 2.472(6) | Cr(3) | S(2) | 2.451(5) |
| Cr(3) | S(3) | 2.454(5) | Cr(3) | S(5) | 2.317(5) |
| Cr(3) | S(6) | 2.415(6) | Cr(3) | S(7) | 2.408(5) |
| Cr(4) | S(5) | 2.374(6) | Cr(4) | S(6) | 2.415(5) |
| Cr(4) | S(7) | 2.412(6) | Cr(4) | S(8) | 2.330(6) |
| Cr(4) | S(9) | 2.422(8) | Cr(4) | S(10) | 2.415(9) |
| Cr(5) | S(5) | 2.435(5) | Cr(5) | S(6) | 2.414(5) |
| Cr(5) | S(7) | 2.428(6) | Cr(5) | S(8) | 2.344(6) |
| Cr(5) | S(9) | 2.409(8) | Cr(5) | S(10) | 2.408(9) |

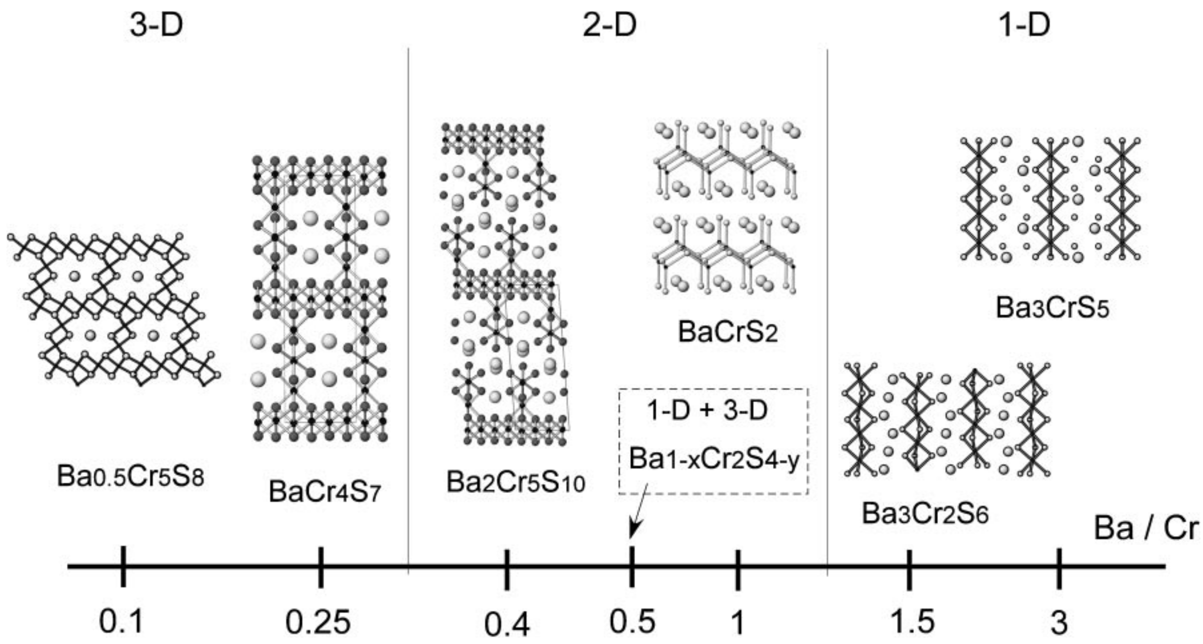

Fig. 4. Relationship between the dimension of structures and the molar ratio of Ba/Cr in the ternary Ba–Cr–S system. Large open and small filled bolls represent Ba and Cr atoms, respectively. As the Ba/Cr ratio increases, the structure type of frameworks is changing from 3-D to 1-D structure.

determined, because the averaged bond lengths of the Cr sites showed only subtle differences. However, only Cr(2)$S_6$ octahedra have no shared faces. They are connected with the edges of neighboring octahedra. Ions having a highly oxidized state do not preferably reside in face-sharing octahedra, because of stronger Coulomb repulsion. It is, therefore, reasonable to assume that the $Cr^{4+}$ ion is situated in the Cr(2) site. This assumption is supported by the fact that the averaged Cr–S bond distance for the Cr(2) site is shortest among those for the five chromium sites. They are 2.391, 2.384, 2.420, 2.395, and 2.406 Å for Cr(1) to Cr(5), respectively. Further investigation into the details about the site distribution of chromium ions is required.

**Comparison with Other Sulfides in the Ba–Cr–S System.** The relationship between the dimension of the structures and Ba/Cr ratios in the Ba–Cr–S system is illustrated in Fig. 4. All of the compounds, except for $BaCrS_2$, are composed of $CrS_6$ octahedra. Only $BaCrS_2$ is composed of $CrS_5$ trigonal bipyramids.[2] It is easily understood from this illustration that as the system contains more Ba atoms, the dimension of the structure is reduced. For example, the Ba/Cr ratios in $BaCr_4S_7$ and $Ba_2Cr_5S_{10}$ are 0.25 and 0.4, respectively, and they have a 3-D and 2-D structure, respectively. 1-D type structures are formed on the right side of the figure, whereas 3-D structures appear on the left side. This can be geometrically explained. Sulfur atoms in the 3-D structures can coordinate to more than two chromium atoms, like as in $BaCr_4S_7$. In the 1-D structures, however, all of the sulfur atoms should coordinate to only two chromium atoms. Therefore, more counter cations, which can coordinate with sulfur atoms, are necessary to stabilize the lower dimensional structure.

$Ba_{1-x}Cr_2S_{4-y}$, which is not shown in Fig. 4, is an interesting exception in the present system. This is not a spinel type compound, which has not yet been reported in this system. $Ba_{1-x}Cr_2S_{4-y}$ does not have a 2-D structure. Its framework is composed of edge-sharing $CrS_6$ octahedra and has a 3-D structure containing two different types of tunnels. In one of these tunnels, there are 1-D $CrS_3$ columns composed of face-sharing octahedra. The whole structure is a combination of 1-D and 3-D building blocks, and it is called a composite crystal. The position of this compound (Ba/Cr = 0.5) on the illustration is, therefore, quite reasonable, because it is intermediate between the compounds with only 3-D and 1-D structures.

## Conclusion

Two new ternary barium chromium sulfides, $BaCr_4S_7$ and $Ba_2Cr_5S_{10}$, were prepared by using high pressures and high temperatures. They have a 3-D tunnel and a complicated 2-D layered structures, respectively. Their structures are closely related and contain the same structural units: a wall-shaped unit composed of face-sharing $CrS_6$ octahedra and a $CrS_2$ sheet composed of edge-sharing octahedra. The formation of these complicated face-sharing linkages in these compounds could be ascribed to the effect of the high pressure.

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