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Journal of Solid State Chemistry 176 (2003) 206–212

JOURNAL OF  
SOLID STATE  
CHEMISTRY

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# High-pressure synthesis and structures of novel chromium sulfides, $\text{Ba}_3\text{CrS}_5$ and $\text{Ba}_3\text{Cr}_2\text{S}_6$ with one-dimensional chain structures

Hiroshi Fukuoka,\* Yuji Miyaki, and Shoji Yamanaka

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan

Received 21 April 2003; received in revised form 8 July 2003; accepted 12 July 2003

## Abstract

Two new ternary chromium sulfides,  $\text{Ba}_3\text{CrS}_5$ , and  $\text{Ba}_3\text{Cr}_2\text{S}_6$  were synthesized by the reaction of sulfur, barium sulfide, and chromium metal under a high pressure of 5 GPa at 1200°C.  $\text{Ba}_3\text{CrS}_5$  crystallized in the hexagonal space group  $P6_3cm$  (No. 185) with  $a = 9.1208(3)$  Å,  $c = 6.1930(3)$  Å,  $V = 446.17(3)$  Å<sup>3</sup>, and  $Z = 6$ . It had a column structure with one-dimensional chains of  $[\text{CrS}_3]_\infty$  composed of face-sharing  $\text{CrS}_6$  octahedra surrounded with  $\text{Ba}^{2+}$  ions. Additional S columns surrounded with Ba ions were running along with the  $\text{CrS}_6$  columns.  $\text{Ba}_3\text{Cr}_2\text{S}_6$  crystallized in the trigonal space group  $R\bar{3}c$  (No. 167) with  $a = 11.8179(7)$  Å,  $c = 12.796(1)$  Å,  $V = 1547.7(2)$  Å<sup>3</sup>, and  $Z = 6$ . The structure of  $\text{Ba}_3\text{Cr}_2\text{S}_6$  also contains  $[\text{CrS}_3]_\infty$  chains but the chains are composed of octahedral and trigonal prismatic  $\text{CrS}_6$  units, which are alternately stacked in a face-sharing manner. The formal charges of Cr ions in  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$  are 4+ and 3+, respectively.

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## 1. Introduction

Chromium sulfides show a variety of structures and have been extensively studied in the past few decades. Focusing on ternary  $A\text{--Cr--S}$  systems ( $A$ : metal elements), many compounds have been characterized, such as,  $ACr_2S_4$  spinel type compounds [1–5],  $ACrS_2$  [6–13] and  $ACr_2S_4$  [14] layered compounds,  $A_3Cr_{11}S_{18}$  [15],  $ACr_5S_8$  [16–19], and  $ACr_3S_5$  [20,21] tunnel type compounds, and so on. However, only a few sulfides have been reported in  $Ae\text{--Cr--S}$  systems, where  $Ae$  = alkaline earth metals. The poor line-up in the systems is due to the difficulty of preparation by conventional synthesis methods. In attempts to synthesize ternary chromium sulfides of alkaline earth metals in evacuated silica ampoules,  $\text{CrS}_x$  with  $0.96 < x < 1.5$  [22] is often obtained as a major product. New synthesis methods should be necessary for the synthesis of new compounds. We, therefore, tried to prepare new sulfides by using high-pressure and high-temperature (HPHT) conditions.

High-pressure synthesis of sulfides is getting common in the past few years [23,24]. In this method it is rather easy to maintain the composition and the homogenization of samples during the reaction. In the present

paper, we have tried to prepare new sulfides in the  $\text{Ba--Cr--S}$  system. There were only three sulfides in this system. They are  $\text{Ba}_{0.51}\text{Cr}_5\text{S}_8$  with a tunnel structure [17],  $\text{Ba}_{1-x}\text{Cr}_2\text{S}_{4-x}$  with an incommensurate column structure [25–28], and  $\text{BaCrS}_2$  with a layer structure [29]. We describe the HPHT synthesis and single crystal structure analysis of two new ternary chromium sulfides,  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$ . They had closely related column structures with one-dimensional chains of  $[\text{CrS}_3]_\infty$  surrounded with  $\text{Ba}^{2+}$  ions.

## 2. Experimental

### 2.1. Preparation and structural study for single crystals of $\text{Ba}_3\text{CrS}_5$ and $\text{Ba}_3\text{Cr}_2\text{S}_6$

Single crystals of  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$  were obtained from a mixture of barium sulfide (Alfa 99.7%), chromium (Katayama Chemical 200 mesh, 99%), and sulfur (Rare Metallic Co. Ltd. 99%) powders with a mole ratio of  $\text{Ba:Cr:S} = 2:1:3.2$ . About 0.3 g of the mixture was put in a BN cell. The cell was placed in a carbon tube heater, and was put in a pyrophyllite cube as a pressure media as shown in Fig. 1. The sample was pressed and heated in a multi-anvil assembly at 5 GPa

\*Corresponding author. Fax: +81-0824-24-5494.

E-mail address: [hfukuoka@hiroshima-u.ac.jp](mailto:hfukuoka@hiroshima-u.ac.jp) (H. Fukuoka).

and was heated at 1200°C for 30 min, and then quenched to the room temperature. Powder X-ray diffraction measurements revealed that the products were not well crystallized but contained two new chromium sulfides,  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$ . Black single crystals of  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$  were obtained together in the product.

The crystal structures of  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$  were determined by the single X-ray structure analysis using Rigaku RAXIS imaging plate area detector with graphite monochromated  $\text{MoK}\alpha$  radiation.  $\text{Ba}_3\text{CrS}_5$  crystallized in the hexagonal space group  $P6_3cm$

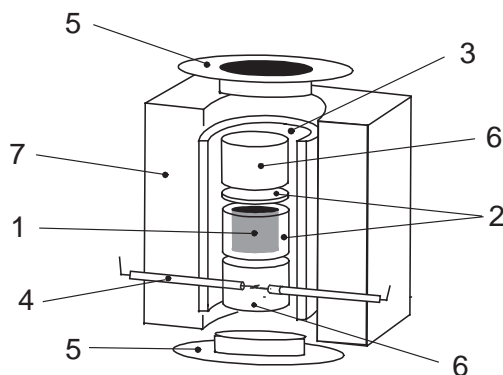


Fig. 1. An assembly of a high-pressure cell (a cross-section). (1) sample ~ 300 mg; (2) BN cell (5 mm of inner diameter, and 5 mm in depth); (3) carbon ring heater; (4) thermo-couple; (5) copper electrodes; (6) pyrophyllite rods; (7) pyrophyllite cube (20 × 20 × 20 mm<sup>3</sup>).

(No. 185) with  $a = 9.1208(3) \text{ \AA}$ ,  $c = 6.1930(3) \text{ \AA}$ ,  $V = 446.17(3) \text{ \AA}^3$  and  $Z = 2$ .  $\text{Ba}_3\text{Cr}_2\text{S}_6$  crystallized in the trigonal space group  $R\bar{3}c$  (No. 167) with  $a = 11.8179(7) \text{ \AA}$ ,  $c = 12.796(1) \text{ \AA}$ ,  $V = 1547.7(2) \text{ \AA}^3$  and  $Z = 6$ . The experimental conditions for data collection are listed in Table 1.

The structures were solved by direct methods and expanded using Fourier techniques using Rigaku CrystalStructure software [30]. All atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement based on the reflections with  $I > 3.0\sigma(I)$  and converged with  $R = 2.2\%$ ,  $R_w = 2.8\%$ , and  $R = 2.1\%$ ,  $R_w = 1.1\%$  for  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$ , respectively. Refined atomic parameters and anisotropic displacement parameters are listed in Tables 2 and 3. The selected bond distances and angles of  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$  are listed in Table 4.

### 3. Results and discussions

#### 3.1. Synthesis of $\text{Ba}_3\text{CrS}_5$ and $\text{Ba}_3\text{Cr}_2\text{S}_6$

We prepared some samples under 5 GPa at 1200°C by changing the nominal compositions of the starting mixtures from Ba:Cr:S = 2:1:3 to 2:1:4. BaS and  $\text{Ba}_3\text{Cr}_2\text{S}_6$  were obtained from the mixture of Ba:Cr:S = 2:1:3. As the S content increased, the main phase of the product changed from  $\text{Ba}_3\text{Cr}_2\text{S}_6$  to  $\text{Ba}_3\text{CrS}_5$ . The main product from the mixture of

Table 1  
Details of X-ray diffraction data collection for  $\text{Ba}_3\text{CrS}_5$  and  $\text{Ba}_3\text{Cr}_2\text{S}_6$

	$\text{Ba}_3\text{CrS}_5$	$\text{Ba}_3\text{Cr}_2\text{S}_6$
Formula	$\text{Ba}_3\text{CrS}_5$	$\text{Ba}_3\text{Cr}_2\text{S}_6$
Formula weight	624.29	708.34
Space group	$P6_3cm$ (No. 185)	$R\bar{3}c$ (No. 167)
$a$ (Å)	9.1208(3)	11.8179(7)
$c$ (Å)	6.1930(3)	12.796(1)
$V$ (Å <sup>3</sup> )	446.17(3)	1547.7(2)
$Z$	2	6
$F(000)$ , electrons	544	1872
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	4.647	4.559
$T$ (K) of data collection	296	296
Crystal size (mm)	0.016 × 0.016 × 0.048	0.016 × 0.016 × 0.040
Diffractometer	Rigaku Raxis-Rapid	Rigaku Raxis-Rapid
Radiation (graphite monochromated)	$\text{MoK}\alpha$	$\text{MoK}\alpha$
$2\theta$ limit	54.9	54.9
No. of measured reflections	3957	4259
No. of observed reflections	126	171
Linear absorption coeff. (cm <sup>-1</sup> )	153.2	144.56
Transmission factor (max/min)	1.348	1.476
No. of variables	19	21
$R$ , $R_w$ <sup>a</sup>	0.022, 0.028	0.021, 0.011
Godness of fit, $S$ <sup>b</sup>	1.09	0.53
Residual density (e Å <sup>-3</sup> )	1.00/−1.05	1.00/−0.75

<sup>a</sup>  $R(F_o) = \sum(|F_o| - |F_c|) / \sum|F_o|$ ,  $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$  ( $w = 1/\sigma(F_o)^2$ ).

<sup>b</sup>  $S = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$ ,  $N_o$  = number of observed reflections,  $N_v$  = number of valuables.

Table 2  
Atomic parameters and anisotropic displacement parameters of Ba<sub>3</sub>CrS<sub>5</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )		
Ba	0.3840(1)	0.0	−0.156(1)	1.78(2)		
Cr	0.0	0.0	0.103(3)	0.82(7)		
S1	0.66667	0.33333	0.039(1)	1.2(1)		
S2	0.0	−0.2122(5)	−0.144(4)	0.91(9)		
Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Ba	0.0170(5)	0.0440(9)	0.0155(5)	0.0220	0.001(2)	0.0
Cr1	0.011(2)	0.011	0.009(3)	0.0055	0.0	0.0
S1	0.007(2)	0.007	0.032(5)	0.0033	0.0	0.0
S2	0.020(2)	0.010(2)	0.008(3)	0.010	0.0	0.005(6)

Table 3  
Atomic parameters and anisotropic displacement parameters of Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )		
Ba	0.94815(7)	0.28145	0.4167	0.73(2)		
Cr1	0.0	0.0	0.25	1.16(8)		
Cr2	0.0	0.0	0.5	0.53(6)		
S	0.0306(2)	−0.1409(2)	0.3783(1)	0.82(5)		
Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Ba	0.0083(4)	0.0083	0.0117(5)	0.0045(6)	−0.0014	0.0014
Cr1	0.016(2)	0.016	0.013(3)	0.0078	0.0	0.0
Cr2	0.008(1)	0.008	0.004(2)	0.0040	0.0	0.0
S	0.010(1)	0.010	0.012(1)	0.006(1)	0.000(1)	−0.001(1)

Table 4  
Selected bond distances (Å) and angles (deg) of Ba<sub>3</sub>CrS<sub>5</sub> and Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub>

Ba <sub>3</sub> CrS <sub>5</sub>		Ba <sub>3</sub> Cr <sub>2</sub> S <sub>6</sub>	
Ba–S1	3.084(3) × 2, 3.408(5) × 2	Ba–S	3.175(2) × 2, 3.180(2)
Ba–S2	3.039(1) × 2, 3.41(2), 3.53(2)		3.181(2), 3.182(2), 3.183(3), 3.260(2) × 2
Ba–Ba	3.751(1)	Ba–Ba	4.246, 4.396
Cr–S2	2.47(2) × 3, 2.49(2) × 3	Cr1–S	2.490(2) × 6
		Cr2–S	2.436(2) × 6
S2–Cr–S2	85.6(8), 94.88(5)	S–Cr1–S	84.3(1), 81.27(7)
Cr–S2–Cr	77.3(1)	S–Cr2–S	96.52(7), 83.48(7)
		Cr1–S–Cr2	80.99(7)

Ba:Cr:S = 2:1:4 was Ba<sub>3</sub>CrS<sub>5</sub>. Single crystals of these new phases suitable for the single crystal X-ray analysis were obtained only in the reaction described in the experimental section.

### 3.2. Structure descriptions of Ba<sub>3</sub>CrS<sub>5</sub>

The crystal structure of Ba<sub>3</sub>CrS<sub>5</sub> is shown in Fig. 2. One-dimensional (1D) [CrS<sub>3</sub>]<sub>∞</sub> chains running along the *c*-axis are composed of face-sharing CrS<sub>6</sub> octahedra as shown in Fig. 2(a). The chains have the C<sub>3v</sub> symmetry and are mutually separated in 9.12 Å by surrounding Ba atoms as shown in Fig. 2(b). There are additional columns of S atoms. Each S atom in the columns is

surrounded with six Ba atoms. The Ba atoms are surrounded with eight S atoms with the distances of 3.039–3.53 Å.

The CrS<sub>6</sub> octahedron in the 1D-chain is not regular. The S–Cr–S bond angles of 85.6° and 94.9° given in Fig. 2(a) show that each CrS<sub>6</sub> octahedron is slightly elongated along the *c*-axis. The distance of 3.097 Å observed for the neighboring Cr–Cr distance is the same with that between the neighboring S<sub>3</sub>–S<sub>3</sub> planes composing the faces of the CrS<sub>6</sub> octahedron. If the CrS<sub>6</sub> octahedron is ideal, the value of  $2a/\sqrt{3}$  should be observed for the Cr–Cr distance, where *a* represents the Cr–S bond distance of the ideal octahedron. When the average Cr–S distance of 2.48 Å is used, the value of

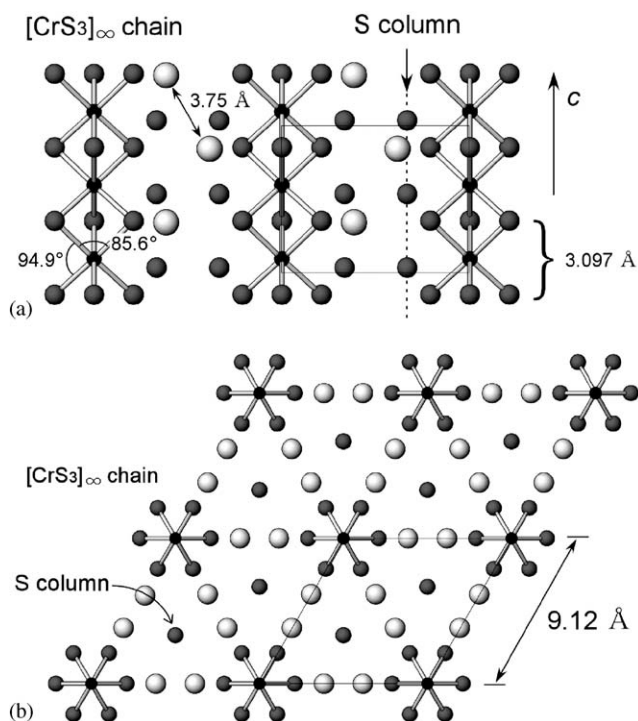


Fig. 2. Crystal structure of  $\text{Ba}_3\text{CrS}_5$ . Large open circles represent Ba atoms, and small gray and black circles represent S and Cr atoms, respectively. (a) Projection on the  $b$ - $c$  plane.  $[\text{CrS}_3]_\infty$  chains and S columns running along the  $c$ -axis are shown. (b) The structure projected along the  $c$ -axis.

2.86 Å is calculated for the Cr–Cr distance. Since the observed value is much larger than the calculated one, the Cr ions in the 1D chain would be subjected to the strong repulsion between the neighboring Cr ions.

The formal charge of Cr in  $\text{Ba}_3\text{CrS}_5$  is calculated to be 4+. In sulfides, Cr usually shows 2+ or 3+ oxidation states. The oxidation state of 4+ is rarely observed in sulfides and if any, it is only observed in III–IV mixed-valence compounds [14]. Even the disulfide  $\text{CrS}_2$ , which is the very Cr(IV) sulfide, has not been discovered. In the structure analysis, we carefully examined the possibility of the existence of any defects, but found no traces of them. Since the result of the structure analysis was well converged, we concluded the composition was  $\text{Ba}_3\text{CrS}_5$ . The quit high oxidation state of Cr in  $\text{Ba}_3\text{CrS}_5$  would arise from the HPHT condition, and could be a cause of the abnormal elongation of the  $\text{CrS}_6$  octahedra in the 1D-chain. In the HPHT synthesis, excessive amount of sulfur was maintained in the reaction system and it was very convenient to prepare sulfur-rich phases.

The Cr–S distances of 2.49 and 2.47 Å in  $\text{Ba}_3\text{CrS}_5$  are comparable with some known ternary chromium sulfides, e.g., 2.401–2.442 Å in  $\text{NiCr}_2\text{S}_4$ , 2.341–2.518 Å in  $\text{CsCr}_5\text{S}_8$ , 2.385–2.446 Å in  $\text{AgCrS}_2$ , 2.38 Å in  $\text{AuCrS}_2$ , and 2.374–2.495 Å in  $\text{LaCrS}_3$ . In all these sulfides, the oxidation state of chromium is  $\text{Cr}^{3+}$ . Though the

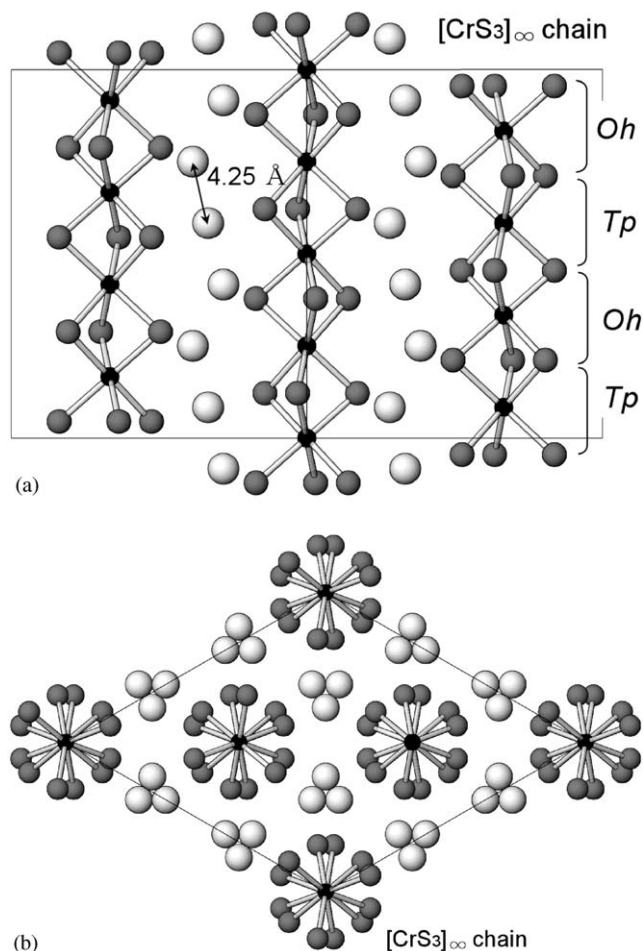


Fig. 3. Crystal structure of  $\text{Ba}_3\text{Cr}_2\text{S}_6$ . Large open circles represent Ba atoms, and small gray and black circles represent S and Cr atoms, respectively. (a) The structure projected along [110].  $[\text{CrS}_3]_\infty$  chains are composed of face-sharing octahedral (Oh) and trigonal prismatic (Tp)  $\text{CrS}_6$  units. (b) The structure projected along the  $c$ -axis.

oxidation state of Cr in  $\text{Ba}_3\text{CrS}_5$  is 4+, the bond distances are similar with those in the Cr(III) sulfides.

### 3.3. Structure description of $\text{Ba}_3\text{Cr}_2\text{S}_6$

The crystal structure of  $\text{Ba}_3\text{Cr}_2\text{S}_6$  is shown in Fig. 3. This compound also has a column structure composed of  $[\text{CrS}_3]_\infty$  chains like as in  $\text{Ba}_3\text{CrS}_5$  but the configurations of the chains in the both compounds are quite different. The chain in  $\text{Ba}_3\text{Cr}_2\text{S}_6$  is composed of two structural units, octahedral (Oh) and trigonal prismatic (Tp)  $\text{CrS}_6$ . The units are alternatively stacked to form the face-sharing 1D-  $[\text{CrS}_3]_\infty$  chains shown in Fig. 3(a). To the best of our knowledge, the trigonal prismatic configuration of  $\text{CrS}_6$  was first observed in chromium sulfides. The Tp- $\text{CrS}_6$  is a little bit distorted and the upper  $\text{S}_3$  plane twists about  $10^\circ$  against the bottom  $\text{S}_3$  plane as shown in Fig. 3(b). The chains are hexagonally surrounded with six helical columns of Ba atoms.

There are two crystallographically independent sites for Cr. The Cr1 site is at the center of the Tp–CrS<sub>6</sub> unit and the Cr2 site is on the inversion center of the Oh–CrS<sub>6</sub> unit. The Cr–S bond distances were 2.436 and 2.490 Å for the Oh- and Tp–CrS<sub>6</sub> part, respectively. Though the formal charge of the Cr is 3+ in this compound, the distances are quite similar with those in Ba<sub>3</sub>CrS<sub>5</sub>. The distances between the neighboring S<sub>3</sub> planes along the *c*-axis were 3.115 and 3.283 Å for the Oh- and Tp–CrS<sub>6</sub> part, respectively.

The detailed studies on X-ray diffraction images of the Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub> single crystal revealed that the crystal had a superstructure. The super cell was two times larger than the fundamental unit cell in the *c*-axis. Since the superspots were too weak to analyze the superstructure, only its fundamental structure was refined in the present analysis. There are two plausible reasons for the occurrence of the superstructure in the compound. One is a misfit between the two substructures of the 1D-chain and the Ba columns. If the repeat distances of them are different along the *c*-axis, the whole structure should have a superstructure. Some sulfides having related 1D-chain structures show this type of superstructures. We will discuss about those compounds in the following section. Second one is a disordering of the 1D-chain. The chain containing the relatively unstable Tp configuration may arise a disorder of S and/or Cr atoms around their regular positions. Such a disordering can be a cause of a superstructure. Single crystals with larger size and better quality should be needed for the further investigation of the superstructure.

### 3.4. Comparison with other 1D structures

Both structures of Ba<sub>3</sub>CrS<sub>5</sub> and Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub> have 1D-chains of face-sharing CrS<sub>6</sub> units. This type of structure is not so familiar in transition metal sulfides. This is often explained in according to the Pauling third rule,

that is, face-sharing octahedra become unstable by the effect of the electrostatic repulsion between two neighboring cations because these cations are situated much closer to each other in the face-sharing structure than in other structures such as edge- or corner-sharing octahedra. The formation of the 1D-structures in Ba<sub>3</sub>CrS<sub>5</sub> and Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub> would be owing to the effect of HPHT conditions, where dense structures become stable. Another advantage of HPHT synthesis is ‘locking effect’. Though Ba and S are easily evaporated at high temperature, HPHT conditions can hold these elements in reaction systems, and would make possible to prepare the Ba and S rich phases like as Ba<sub>3</sub>CrS<sub>5</sub> and Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub>.

The structures of the four ternary Ba–Cr–S compounds, Ba<sub>0.51</sub>Cr<sub>5</sub>S<sub>8</sub>, BaCrS<sub>2</sub>, Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub> and Ba<sub>3</sub>CrS<sub>5</sub> show an interesting implication. The Ba content in their chemical formula is getting increase in this order. As shown in Fig. 4, Ba<sub>0.51</sub>Cr<sub>5</sub>S<sub>8</sub> has a three dimensional Cr–S framework composed of face- and edge-sharing CrS<sub>6</sub> octahedra forming tunnels, where Ba atoms are situated [17]. There are four crystallographically independent S atoms in this structure and two of them are coordinated with three Cr atoms and the rest are coordinated with four and five Cr atoms. In BaCrS<sub>2</sub>, all Ba atoms are in the interlayer region between the CrS<sub>2</sub> layers composed of edge-sharing CrS<sub>5</sub> square pyramids [29]. There are two types of S sites in this compound, one is apical and another is basal sulfur atoms. The basal S atoms are coordinated with four Cr and two Ba atoms and the apical S atoms are coordinated with one Cr and five Ba atoms. In Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub> and Ba<sub>3</sub>CrS<sub>5</sub>, where much more Ba atoms are contained, S atoms are coordinated with only two Cr atoms and form the 1D-chain structure. These observations show that the increase of the Ba content resulted in the reduction of the dimensionality of the host Cr–S framework. The Ba atoms need not only large space but also connection

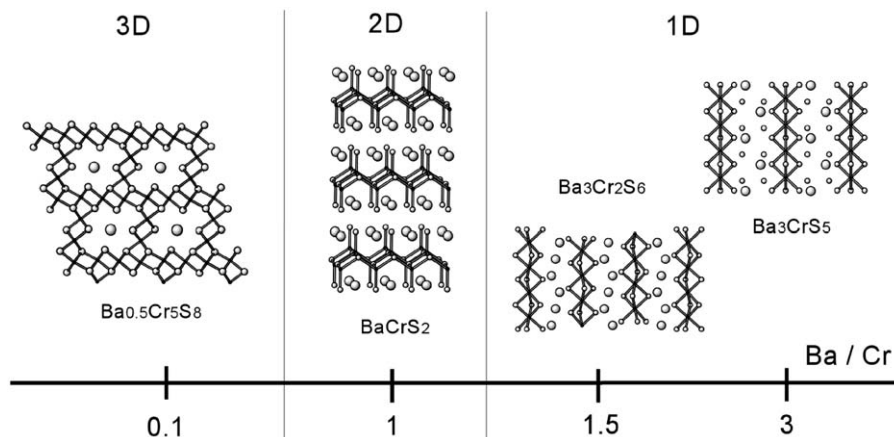


Fig. 4. Variation in the structure of the ternary Ba–Cr–S system. The relationship between the composition (molar ratio of Ba/Cr) and dimensionality of sulfides is schematically illustrated. Large and small open circles represent Ba and S atoms, respectively. Small black balls show Cr atoms. As the ratio increases, the dimensionality of the sulfide decreases.



with S atoms in the structure. The S atoms coordinated with many Ba atoms can coordinate with less number of Cr atoms. The low dimensional structures are preferred in such situations like in the ternary manganese oxides, where a similar structural series can be observed.

The lowering of the dimensionality of a large variety of compounds on incorporation of electropositive cations has been previously noted (see for instance the review of Tulsy et al. and references therein [31]). Especially, the dimensional reduction of certain chalcogenides was discussed by the group of Kanatzidis and Ibers [32,33]. The Ba–Cr–S system provides another example of the reduction of the dimensionality in sulfides.

The sulfides containing 1D-chains are rare even now.  $A_x\text{TiS}_3$ ;  $A = \text{Ba}$  ( $1.0 < x < 1.05$ ) [34,35] and  $\text{Sr}$  ( $1.05 < x < 1.22$ ) [36,37], and  $A_{1-x}\text{Cr}_2\text{S}_{4-x}$ ;  $A = \text{Ba}, \text{Sr}, \text{Sn}, \text{Pb},$  and  $\text{Eu}$  were the exceptions [25–28,38]. They contain  $[\text{TiS}_3]_\infty$  or  $[\text{CrS}_3]_\infty$  1D-chains in their structures as shown in Fig. 5. Especially, the structure of  $A_x\text{TiS}_3$  is closely related with that of  $\text{Ba}_3\text{Cr}_2\text{S}_6$  ( $\equiv \text{Ba}_{1.5}\text{CrS}_3$ ). In fact, the projections along the  $c$ -axis of these compounds show almost the same structural features, although their compositions are different (see Figs. 3 and 5). These structures are variations of the  $\text{BaNiO}_3$  structure [39–41]. They have 1D-chains composed of  $\text{MX}_3$  units surrounded by columns of large alkali earth ions. There are many oxides having structures related to  $\text{BaNiO}_3$  and they are often called as the hexagonal perovskite family [42–45].

The variation of the structures in those compounds comes from the positional relationships between the two columns. In the  $A_x\text{TiS}_3$  structure, the repeat distances of  $[\text{TiS}_3]_\infty$  and  $A$  columns along the  $c$ -axis, which are named as  $c_{\text{TiS}}$  and  $c_A$ , respectively, do not coincident. Furthermore, the ratio of  $c_{\text{TiS}}/c_A$  is not a rational. Therefore, any normal unit cell is not defined for this structure [35,36]. This type of structures is called as the vernier structure. The ratio of  $2c_{\text{TiS}}/c_{\text{Sr}}$  is 1.145 in  $\text{Sr}_{1.145}\text{TiS}_3$  and this non-integral number is not due to any defect structure but to the incommensurate structure. Since the structure cannot be described in the three-dimensional formalism, the structure analysis met with difficulties even though single crystals were obtained. The structure was solved first by Onoda et al.

for  $\text{Sr}_{1.145}\text{TiS}_3$  in a sophisticated way on the basis of the four-dimensional super space group [46].

The ternary chromium sulfides,  $A_{1-x}\text{Cr}_2\text{S}_{4-x}$ , are also incommensurate compounds. The structure of these compounds has not been solved completely because the structure is too complicated. Brouwer et al. revealed that it had three components; the main framework composed of edge and face-sharing  $\text{CrS}_6$  octahedra and two different kinds of columns running along the  $c$ -axis [27]. One of the columns is composed of 1D chains of face-sharing  $\text{CrS}_6$  octahedra and another is  $\text{AS}_3$  column as shown in Fig. 5(a). These three substructures have mutually incommensurate repeat distances along the  $c$ -axis.

The reason why those related compounds shows incommensurate or normal structure in case by case is not clear but we will point out an interesting structural difference among them. The difference is in the distortions of octahedra in the 1D-chains. If an  $\text{MX}_6$  octahedron is ideal, the thickness of it, which is corresponding to the distance between two parallel faces of the octahedron, is to be  $2a/\sqrt{3}$  as mentioned above. In the incommensurate sulfides,  $A_{1-x}\text{Cr}_2\text{S}_{4-x}$   $A = \text{Sn}, \text{Pb}, \text{Eu}, \text{Sr},$  and  $\text{Ba}$ , the thickness values of 2.865–2.903 Å were obtained for the  $\text{CrS}_6$  octahedra from the observation of electron diffraction measurements. Though the distances of Cr–S bonds in these compounds are not determined, if an averaged value of 2.405 Å for  $\text{Cr}^{3+}\text{–S}$  bond in octahedral coordination by Shannon [47] is used, the value of 2.78 Å is calculated with the equation. The octahedra are elongated by 3–5% along the  $c$ -axis and the elongation is not so much. This comes true in  $\text{Sr}_{1.145}\text{TiS}_3$ . The repetition distance of the  $\text{TiS}$  part, which corresponds to the average distance of two adjacent  $\text{S}_3$  planes, is ~6% larger than the ideal value obtained by using the average Ti–S distance of 2.44 Å. On the other hand, the  $\text{CrS}_6$  octahedra in  $\text{Ba}_3\text{Cr}_2\text{S}_6$  and  $\text{Ba}_3\text{CrS}_5$  are also much elongated along the  $c$ -axis. The observed values of 3.115 and 3.097 Å are 11% and 9% larger than the ideal values. Consequently, compounds having elongated octahedra have normal unit cells, and others having less elongated octahedra show superstructures or incommensurability. It is worth noting that the thickness of  $\text{NiO}_6$  octahedra in  $\text{BaNiO}_3$  is 2.41 Å, which is

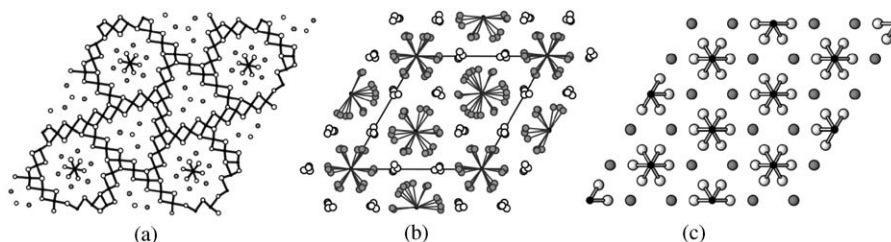


Fig. 5. Projections on the  $b$ - $c$  planes of three compounds having  $\text{Ba}_3\text{Cr}_2\text{S}_6$  related structures. (a)  $\text{Ba}_{1-x}\text{Cr}_2\text{S}_{4-x}$ , (b)  $\text{Sr}_{1.14}\text{CrS}_3$ , and (c)  $\text{BaNiO}_3$ .

quite larger than the calculated value of 2.154 Å. The NiO<sub>6</sub> octahedra are elongated by ~12% compared to the calculated value along the *c*-axis in order to fit to the repetition distance of the Ba column.

#### 4. Conclusions

Two new ternary chromium sulfides, Ba<sub>3</sub>CrS<sub>5</sub> and Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub> were prepared by the HPHT synthesis. These crystals have mutually related 1D-chain structures made of face-sharing [CrS<sub>3</sub>]<sub>∞</sub> chains running on a parallel with Ba columns. While the chains in Ba<sub>3</sub>CrS<sub>5</sub> are composed of CrS<sub>6</sub> octahedra, the chains in Ba<sub>3</sub>Cr<sub>2</sub>S<sub>6</sub> are composed of alternative stacking of octahedral and trigonal prismatic CrS<sub>6</sub> units.

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