Short Communications

Ba$_4$Cr$_2$US$_9$: The First Chalcogenide Analogue of the Perovskite-related (A$_3$A′BO$_6$)$_m$(A$_3$B$_3$O$_9$)$_n$ Family

Jiyong Yao and James A. Ibers*

Evanston, IL/USA, Northwestern University, Department of Chemistry

Abstract. The compound Ba$_4$Cr$_2$US$_9$, which crystallizes in space group *P*321, consists of one-dimensional $^1_\infty$[Cr$_2$US$_9{}^{8-}$] chains separated by Ba^{2+} cations. Each one-dimensional chain comprises face-sharing CrS$_6$ octahedra and US$_6$ trigonal prisms in the sequence *oct oct tp oct oct tp* with the U and Cr centers in a linear chain parallel to [001].

Keywords: Perovskite analogues; Solid-state chemistry; Barium chromium uranium sulfide

Low-dimensional inorganic structures are of great interest in solid-state chemistry and material sciences because of their physical properties. One of the structure types heavily studied in recent years is the (A$_3$A′BO$_6$)$_m$(A$_3$B$_3$O$_9$)$_n$ homologous series whose structures are related to the 2H-hexagonal perovskites. Here A is usually an alkaline-earth cation, A′ (which can be the same element as A or B) is a cation in a trigonal prismatic environment, and B is a cation in an octahedral environment. A 2H-hexagonal perovskite is often thought of as a pseudo-hexagonal closest-packed stack of AO$_3$ layers with the transition metal B occupying the octahedral holes between the layers to give the stoichiometry ABO$_3$ (sometimes more conveniently written as A$_3$B$_3$O$_9$). An A$_3$O$_6$ layer can be formed by the ordered removal of three O^{2-} anions from an A$_3$O$_9$ layer to create holes inside trigonal prisms of O^{2-} anions. When these holes are occupied by A′ cations, the stoichiometry of the layers becomes A$_3$A′O$_6$. If the stacking sequence of the A$_3$A′O$_6$ and the A$_3$O$_9$ layers is allowed to vary, a series of compounds can be formed with the general formula (A$_3$A′BO$_6$)$_m$(A$_3$B$_3$O$_9$)$_n$ ($m \geq 1$, $n \geq 0$). The structure features one-dimensional chains of ordered arrays of A′O$_6$ trigonal prisms and BO$_6$ octahedra, separated by A^{2+} cations. Many compounds have been synthesized in this homologous series, including Sr$_4$PtO$_6$ (A = A′, $m = \infty$) [1], Ba$_6$Ni$_5$O$_{15}$ (A′ = B, $m = 1$. $n = 1$) [2], Sr$_9$Ni$_{6.64}$O$_{21}$ (A′ = B, $m = 2$. $n = 1$) [3], Ca$_3$Co$_2$O$_6$ (A′ = B, $m = \infty$) [4], and Sr$_4$Mn$_2$MO$_9$ (M = Zn, Cu) (A′ = B, $m = 3$. $n = 1$) [5]. Some of these compounds exhibit interesting magnetic properties. For example, Ca$_3$Co$_2$O$_6$ [4] exhibits intrachain and interchain magnetic ordering at 24 K and 12 K, respectively; Sr$_4$Ir$_2$MO$_9$ (M = Zn, Cu) ($m = 1$, $n = 1$) [6] and Ba$_6$Mn$_4$MO$_{15}$ (M = Zn, Cu) [7] show three-dimensional antiferromagnetic ordering at 1.6 K and 6 K, respectively.

All the compounds reported in this homologous series are oxides. No related chalcogenides are known. Yet these would be interesting because the increased covalency of the metal-chalcogen bond compared to the metal-oxygen bond will likely lead to compounds with electronic structures and physical properties different from the oxides.

oct oct tp oct oct tp with the U and Cr centers in a linear chain parallel to [001].

During our exploration of the Ba/M/U/S system (M = transition metal), we have found the new compound Ba$_4$Cr$_2$US$_9$. It represents the first example of a chalcogenide in the (A$_3$A′BQ$_6$)$_m$(A$_3$B$_3$Q$_9$)$_n$ homologous series with (Q = S rather than O). It comprises A = Ba, A′ = U, B = Cr, $m = 3$, and $n = 1$.

2 Results and Discussion

Black needles of Ba$_4$Cr$_2$US$_9$ were first found accidentally in a two-step solid-state reaction that involved BaS, Cu$_2$S, and US$_2$. It turned out that Cr was an impurity in this reaction. A powder of Ba$_4$Cr$_2$US$_9$ was obtained in a rational manner from the stoichiometric reaction of BaS, Cr$_2$S$_3$, and US$_2$.

Ba$_4$Cr$_2$US$_9$ crystallizes in the non-centrosymmetric trigonal space group *P*321 [10]. The structure consists of one-dimensional $^1_\infty$[Cr$_2$US$_9{}^{8-}$] chains separated by Ba^{2+} cations (Figure 1). There are two crystallographically unique one-dimensional chains each composed of face-sharing CrS$_6$ octahedra and US$_6$ trigonal prisms in the sequence *oct oct tp oct oct tp* with the U and Cr cations in a linear arrangement parallel to [001]. The site symmetries of U and Cr are 32 and 3, respectively. The distances between neighboring Cr and U cations are 3.256(6) Å, 3.398 (5) Å, and 3.352(5) Å and those between neighboring Cr cations are 2.990(7) Å and 2.941(9) Å (Figure 2). The shortest S···S distance is 3.264(3) Å. Thus there are no S−S bonds and formal oxidation states of 2+, 4+, 3+, and 2− may be assigned to Ba, U, Cr, and S, respectively. In this way charge balance is achieved.

Selected interatomic distances and angles may be found in Table 1. The U-S distances, which range from 2.688(5) Å to 2.764(4) Å, are similar to those in other U^{4+} sulfides, for example, BaUS$_3$ (2.680(5)−2.709(5) Å) [8, 9]; the Cr−S distances range from 2.390(6) Å to 2.486(5) Å, consistent with those of 2.352−2.503 Å in TlCr$_5$S$_8$ [10]; and the Ba−S distances range from 3.093(4) Å to 3.510(5) Å, comparable to those of 3.118(2)−3.230(1) Å in BaLaCuS$_3$ [11]. The Cr−Cr distances of 2.990(7) and 2.941(9) Å may be compared with the shortest such distances of 2.959(2) Å in TlCr$_5$S$_8$ [10] and 2.97(2) Å in CsCr$_5$S$_8$ [12].

Preliminary measurement on the magnetic properties of the Ba$_4$Cr$_2$US$_9$ powder indicate complicated behavior. Further studies on single crystals are needed to elucidate the magnetic properties.

* Prof. Dr. James A. Ibers
Department Chemistry, Northwestern University
Evanston, IL / USA
E-mail: ibers@chem.northwestern.edu
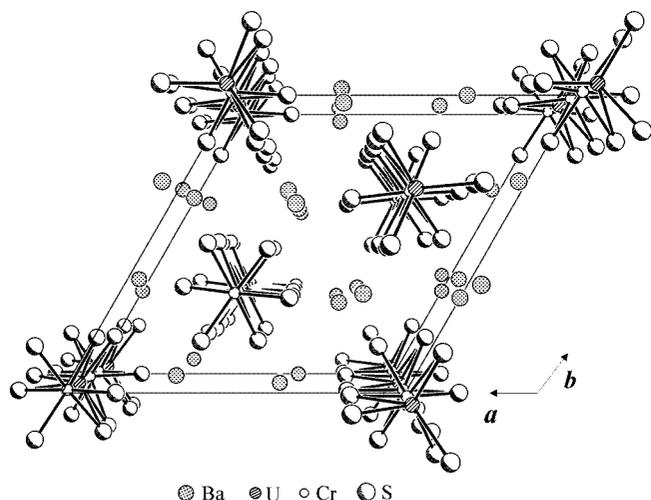
Figure 1 View along [001] of the unit cell of $Ba_4Cr_2US_9$.
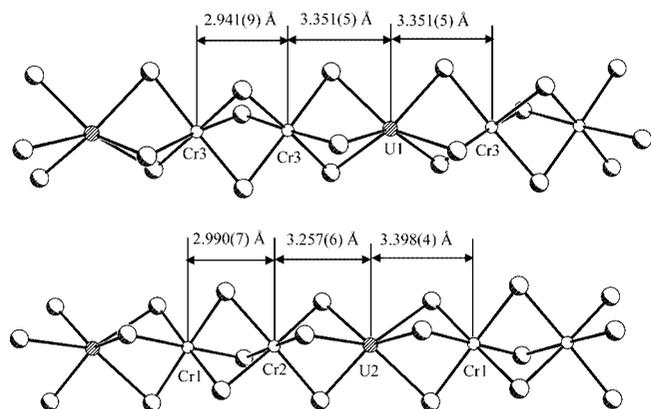
Figure 2 The $^1_\infty[Cr_2US_9{}^{8-}]$ chains in $Ba_4Cr_2US_9$.

Experimental Section

The following reagents were used as obtained: BaS (Aldrich, 98+%), Cr_2S_3 (Aldrich, 99.5 %), Cu_2S (Aldrich, 99.999 %), U (depleted, ORNL), and NaBr (Alfa Aesar, 99.99 %) as a flux. A few black needles of $Ba_4Cr_2US_9$ were first found accidentally during the exploration of the Ba/Cu/U/S system. Analyses of these needles with an EDX-equipped Hitachi S-3500 SEM showed the presence of Ba, Cr, U, and S, but not of Cu. The presence of Cr in the compound was confirmed by comparing the EDX pattern of a needle with that of Cr_2S_3, and by the successful refinement of the structure. The source of Cr is probably from contamination of the vacuum line from loadings of previous reactions. The compound is moderately stable in air.

Preparation of $Ba_4Cr_2US_9$

$Ba_4Cr_2US_9$ powder was obtained from the stoichiometric reaction of BaS, Cr_2S_3, and US_2 in the molar ratio 4:1:1. The reactants were ground in a glove box and then loaded into a carbon-coated fused-silica tube. The tube was sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace where it was heated

Table 1 Selected interatomic distances/Å and angles/deg for $Ba_4Cr_2US_9$

Ba1−S1 × 2	3.120(4)	Ba3−S1 × 2	3.492(5)
Ba1−S2 × 4	3.312(4)	Ba3−S3 × 2	3.184(5)
Ba1−S3 × 2	3.134(5)	Ba3−S4 × 2	3.321(2)
Ba2−S1	3.290(5)	Ba3−S5 × 2	3.400(5)
Ba2−S1	3.462(5)	U1−S1 × 6	2.727(4)
Ba2−S2	3.185(4)	U2−S5 × 3	2.688(5)
Ba2−S2	3.352(4)	U2−S2 × 3	2.764(4)
Ba2−S3	3.231(5)	Cr1−S2 × 3	2.486(5)
Ba2−S3	3.238(5)	Cr1−S3 × 3	2.434(5)
Ba2−S4	3.122(4)	Cr2−S3 × 3	2.441(6)
Ba2−S5	3.093(4)	Cr2−S5 × 3	2.426(5)
Ba2−S5	3.510(5)	Cr3−S1 × 3	2.485(5)
S1−U1−S1 × 6	78.4(1)	Cr3−S4 × 3	2.390(6)
S1−U1−S1 × 3	86.6(2)	S2−Cr1−S3 × 3	178.9(2)
S1−U1−S1 × 3	131.7(2)	S3−Cr1−S3 × 3	86.5(2)
S1−U1−S1 × 3	142.8(2)	S3−Cr2−S3 × 3	86.2(2)
S2−U2−S2 × 3	77.3(1)	S3−Cr2−S5 × 3	91.2 (2)
S2−U2−S5 × 3	86.0(1)	S3−Cr2−S5 × 3	93.5(2)
S2−U2−S5 × 3	135.7(2)	S3−Cr2−S5 × 3	177.4(2)
S2−U2−S5 × 3	139.1(2)	S5−Cr2−S5 × 3	89.1(2)
S5−U2−S5 × 3	78.6(1)	S3−Cr2−S3 × 3	86.2(2)
S2−Cr1−S2 × 3	88.0(2	S1−Cr3−S1 × 3	87.9(2)
S2−Cr1−S3 × 3	92.6(2)	S1−Cr3−S4 × 3	90.8(1)
S2−Cr1−S3 × 3	93.0(2)	S1−Cr3−S4 × 3	95.3(1)
S3−Cr1−S3 × 3	86.5(2)	S1−Cr3−S4 × 3	176.5(1)
S3−Cr1−S2 × 3	178.9(2)	S4−Cr3−S4 × 3	86.1(2)

to 1323 K at 50 K/h and held there for 5 days, and then the furnace was quickly cooled to 293 K at 100 K/h. X-ray diffraction analysis of the powder was performed at 298 K in the angular range $2\theta = 10°−70°$ (CuKα) The experimental diffraction pattern of the powder was in agreement with the pattern simulated from the single-crystal data.

Crystal structure determination

$Ba_4Cr_2US_9$ (1179.93 g mol^{-1}); trigonal system, space group $P321$, $a = 12.010(3)$ Å, $c = 9.644(5)$ Å, $V = 1204.7(8)$ Å^3, $Z = 3$, $T = 153(2)$ K, $\rho_c = 4.879$ g/cm^3; $\mu = 221.25$ cm^{-1}; diffractometer Bruker Smart-1000 CCD; Mo Kα radiation ($\lambda = 0.71073$ Å); 0.3° ω scans in groups of 606 frames at Φ settings of 0°, 90°, 180°, and 270°; 15 s/frame; $2\Theta_{max} = 57.6°$; 10444 reflections; face-indexed absorption correction, crystal size 0.19 mm x 0.02 mm x 0.02 mm, transmission factors 0.156−0.665. The structure was solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL [13]. The crystal was a racemic merohedral twin in space $P321$. The fractional contributions of the domains were 0.404, 0.072 (twofold operation about c); 0.448 (inversion center); 0.076 (twofold and inversion center). $R_1 = 0.040$, $wR_2 = 0.098$ for 1950 independent reflections and 78 variables. The program TIDY [14] was employed to standardize the atomic coordinates.

The crystallographic file in cif format for $Ba_4Cr_2US_9$ has been deposited with FIZ Karlsruhe as CSD number 419086. These data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysdata@fiz-karlsruhe.de (email).

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