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Synthesis, structure, and magnetic properties of $Ba_2Cu_2US_5$

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Abstract

The alkaline-earth uranium chalcogenide $Ba_2Cu_2US_5$ was obtained in a two-step reaction from BaS, Cu_2S, and US_2. $Ba_2Cu_2US_5$ crystallizes in a new structure type in space group $C2/m$ of the monoclinic system with two formula units in a cell of dimensions $a = 13.606(3)$ Å, $b = 4.0825(8)$ Å, $c = 9.3217(19)$ Å, and $\beta = 116.32(3)^\circ$ (153 K). The structure consists of $^2_\infty[Cu_2US_5^{4-}]$ layers separated by Ba atoms in bicapped trigonal-prismatic coordination. The two-dimensional $^2_\infty[Cu_2US_5^{4-}]$ layer is built from US_6 octahedra and CuS_4 tetrahedra. The connectivity of the MS_n polyhedra within the layer in the [001] direction is *oct tet tet oct tet tet*. A μ_{eff} value of 2.69(2) μ_B/U was obtained from the magnetic susceptibility data. No magnetic transition was observed for $Ba_2Cu_2US_5$ down to 2 K.

Keywords: Uranium; Alkaline-earth; Crystal structure; Magnetism; Synthesis; Layered structure

1. Introduction

Interest in actinide chalcogenides stems not only from their varied structures but also from their magnetic and electrical properties that are associated with the more diffuse 5*f* orbitals vs. the 4*f* orbitals of the rare-earths. Many alkali-metal ternary and quaternary actinide (poly)chalcogenides have been synthesized [1–12] with the use of the reactive flux method [13]. However, only a few ternary and no quaternary alkaline-earth actinide chalcogenides have been reported [6,14–20]. Here we present the synthesis, structure, and magnetic properties of $Ba_2Cu_2US_5$, the first example of a quaternary alkaline-earth actinide chalcogenide.

2. Experimental

2.1. Syntheses

The following reagents were used as obtained: U (depleted, ORNL), Cu_2S (Alfa, 99.95%), BaS (Alfa, 99.7%), NaBr (Alfa, 99.99%), S (Aldrich, 99.5%). $Ba_2Cu_2US_5$ was prepared by a two-step reaction. In the first step, a mixture of 0.3 mmol US_2 (prepared from the stoichiometric reaction of U and S at 1223 K for 10 days) and 0.1 mmol Cu_2S were ground thoroughly in an Ar-filled glove box, pressed into a pellet, and then loaded into a fused-silica tube. The tube was sealed under a 10^{-4} Torr atmosphere and placed in a computer-controlled furnace. The sample was heated to 1323 K in 60 h, kept at 1323 K for 90 h, and then the furnace was turned off. In the second step, the tube was opened in a glove box and the resultant product was mixed with 0.1 mmol BaS and 2.4 mmol NaBr (to aid in crystal growth) and reground. The mixture was then loaded into a fused-silica tube. The tube was sealed under a 10^{-4} Torr atmosphere and heated to 1123 K in 60 h, kept at 1123 K for 240 h, slowly cooled at 3 K/h to 853 K, and then the furnace was turned off. After the product was washed with deionized water and dried with acetone, some black needles were found. Analyses of these needles with an EDX-equipped Hitachi S-3500 SEM showed the presence of Ba, Cu, U, and S. There was no indication of the presence of Na or Br. The compound is moderately stable in air.

A powder phase of $Ba_2Cu_2US_5$ was then obtained from the stoichiometric reaction of BaS, Cu_2S, and US_2 in a molar ratio of 2:1:1. 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 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.

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X-ray powder diffraction analysis of the powder was performed at 293 K in the angular range of $2\theta = 10$–70° (Cu$K\alpha$ radiation, $\lambda = 1.5418$ Å) with a step scan width of 0.02° and a fixed counting time of 3 s/step. The experimental diffraction pattern of the sample was in agreement with that calculated from the single-crystal data. No obvious impurity could be found in the pattern.

2.2. Structure determination

Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer [21]. The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606, 606, 606, and 606 frames at ϕ settings of 0°, 90°, 180°, and 270° with an exposure time of 15 s/frame. The collection of the intensity data was carried out with the program SMART [21]. Cell refinement and data reduction were carried out with the use of the program SAINT [21], and a face-indexed absorption correction was performed numerically with the use of the program XPREP [22]. Then the program SADABS [21] was employed to make incident beam and decay corrections.

The structure was solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL of the SHELXTL suite of programs [22]. The final refinement included anisotropic displacement parameters and a secondary extinction correction. The program TIDY [23] was then employed to standardize the atomic coordinates. Additional experimental details are given in Table 1 and in "Supporting material". Selected metrical details are presented in Table 2.

2.3. Magnetic susceptibility measurement

Magnetic susceptibility as a function of temperature was measured on an 11.3 mg powder sample of $Ba_2Cu_2US_5$ with the use of a Quantum Design SQUID magnetometer (MPMS5 Quantum Design). The sample was loaded into a gelatin capsule. Both zero-field cooled (ZFC) and field-cooled (FC) susceptibility data were collected between 2 and 300 K at applied fields of both 1000 and 2000 G. The susceptibility data in the temperature range 180–300 K were fit by a least-squares procedure to the Curie–Weiss equation $\chi = C/(T-\theta_p)$, where C is the Curie constant and θ_p is the Weiss constant. The effective moment (μ_{eff}) was calculated from the equation $\mu_{eff} = (7.997C)^{1/2}\,\mu_B$ [24].

3. Results and discussion

3.1. Synthesis

A two-step reaction afforded a few black crystals of $Ba_2Cu_2US_5$. In the first step, US_2 and Cu_2S were reacted at 1323 K. In the second step, the product of the first step was ground with BaS and NaBr (to aid in crystal growth) and the reaction was carried out at 1123 K. A rational stoichiometric synthesis involving BaS, Cu_2S, and US_2 at 1323 K in a molar ratio of 2:1:1 afforded a pure powder phase but no single crystals.

Table 1
Crystal data and structure refinement for $Ba_2Cu_2US_5$

fw	800.09
Space group	$C2/m$
Z	2
a (Å)	13.606(3)
b (Å)	4.0825(8)
c (Å)	9.3217(19)
β (°)	116.32(3)
V (Å^3)	464.11(16)
T (K)	153(2)
λ (Å)	0.71073
ρ_c (g cm^{-3})	5.725
μ (cm^{-1})	312.94
$R(F)$[a]	0.0228
$R_w(F_o^2)$[b]	0.0572

[a] $R(F) = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.
[b] $R_w(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma F_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (0.03P)^2$, where $P = (F_o^2 + 2F_c^2)/3$ for $F_o^2 > 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leqslant 0$.

Table 2
Selected interatomic distances (Å) and angles (°) for $Ba_2Cu_2US_5$

Ba–S1 × 2	3.180(2)
Ba–S1	3.496(2)
Ba–S2	3.322(2)
Ba–S2 × 2	3.393(2)
Ba–S3 × 2	3.067(1)
U–S1 × 2	2.673(2)
U–S2 × 4	2.770(1)
Cu–S1 × 2	2.381(1)
Cu–S2	2.368(2)
Cu–S3	2.305(1)
S1–U–S1	180
S1–U–S2	89.87(5)
S2–U–S2	180
S2–U–S2	85.07(6)
S1–Cu–S1	118.01(9)
S1–Cu–S2	108.11(6)
S1–Cu–S3	109.07(5)
S2–Cu–S3	103.49(6)

3.2. Structure

$Ba_2Cu_2US_5$ crystallizes in a new structure type. In the asymmetric unit, there is one crystallographically unique Ba atom at a site with m symmetry, one unique Cu atom at a site with m symmetry, and one unique U atom at a site with $2/m$ symmetry. The structure consists of $^2_\infty[Cu_2US_5^{4-}]$ layers separated by Ba atoms in bicapped trigonal-prismatic coordination (Fig. 1). The two-dimensional $^2_\infty[Cu_2US_5^{4-}]$ layer is built from US_6 octahedra and CuS_4

tetrahedra (Fig. 2). The edge-sharing US_6 octahedra form one-dimensional $^1_\infty[US_4^{4-}]$ chains along the [010] direction. A pair of CuS_4 tetrahedra are connected by corner sharing, forming a double Cu_2S_7 unit with a linear Cu–S–Cu arrangement. These double units are connected into a $^1_\infty[Cu_2S_5^{8-}]$ chain along the [010] direction by corner sharing. The $^1_\infty[US_4^{4-}]$ and $^1_\infty[Cu_2S_5^{8-}]$ chains are further connected by edge sharing to form the $^2_\infty[Cu_2US_5^{4-}]$ layer. The connectivity of the MS_n polyhedra in the [001] direction of the layer is *oct tet tet oct tet tet*. This connectivity is similar to that in the $^2_\infty[Cu_2ZrS_4^{2-}]$ layer in $Na_2Cu_2ZrS_4$ [25]. However, in $Na_2Cu_2ZrS_4$ the CuS_4 tetrahedra are connected to each other by both corner sharing and edge sharing, whereas in $Ba_2Cu_2US_5$ the CuS_4 tetrahedra are connected to each other only by corner sharing.

The shortest S···S distance is 3.670(2) Å. Thus, there are no S–S bonds and formal oxidation states of 2+, 4+, 1+, and 2− may be assigned to Ba, U, Cu, and S, respectively. In this way charge balance is achieved.

Selected bond distances are listed in Table 2. The U–S distances, which range from 2.673(2) to 2.770(1) Å, are similar to those in other U^{4+} sulfides, for example $BaUS_3$ (2.680(5)–2.709(5) Å) [15,16]; the Cu–S distances range from 2.305(1) to 2.381(1) Å, consistent with those of 2.3386(9)–2.3464(8) Å in KY_2CuS_4 [26]; and the Ba–S distances range from 3.0673(8) to 3.496 (2) Å, comparable to those of 3.118(2)–3.230(1) Å in $BaLaCuS_3$ [27].

3.3. Magnetism

The inverse molar magnetic susceptibility $1/\chi_m$ as a function of temperature for $Ba_2Cu_2US_5$ is shown in Fig. 3. The ZFC and FC data are essentially superimposable. The plot of $1/\chi_m$ vs. T has a continually changing slope, especially at low temperatures. There is no obvious magnetic ordering. For $T>180$ K, the data can be fit to the Curie–Weiss law $\chi_m^{-1}=(T-\theta_p)/C$, although such an approach it not without its pitfalls [28]. The values of the Curie constant C, the Weiss constant θ_p, and the effective magnetic moment μ_{eff} are 0.907(2) emu K mol^{-1}, −92.9(4) K, and 2.69(2) μ_B/U, respectively. The value of μ_{eff} is smaller than the theoretical one for U^{4+} (3.58 μ_B) [29]. However, it is comparable to the value of 2.5 μ_B/U for $Cu_2U_3S_7$ [30]. The value of θ_p may indicate local antiferromagnetic ordering. The rapidly changing slope of the data at low temperatures possibly results from crystal field effects. Because of the diffuse nature of the 5*f* electrons, U^{4+} exhibits pronounced crystal-field effects in some paramagnetic salts with small μ_{eff} values (2.60–2.91 μ_B) [31].

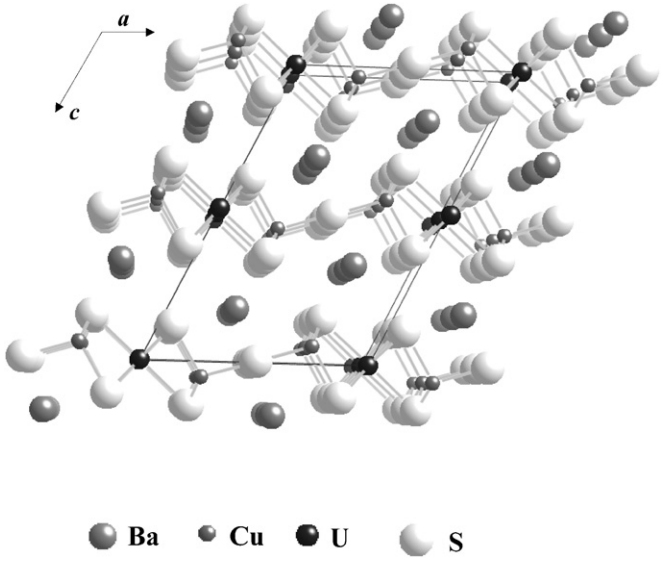

Fig. 1. Unit cell of $Ba_2Cu_2US_5$ viewed down [010].

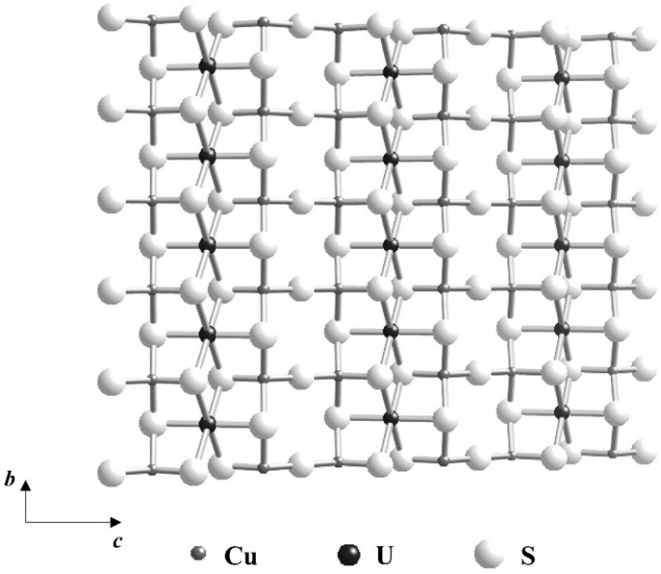

Fig. 2. The $^2_\infty[Cu_2US_5^{4-}]$ layer in $Ba_2Cu_2US_5$.

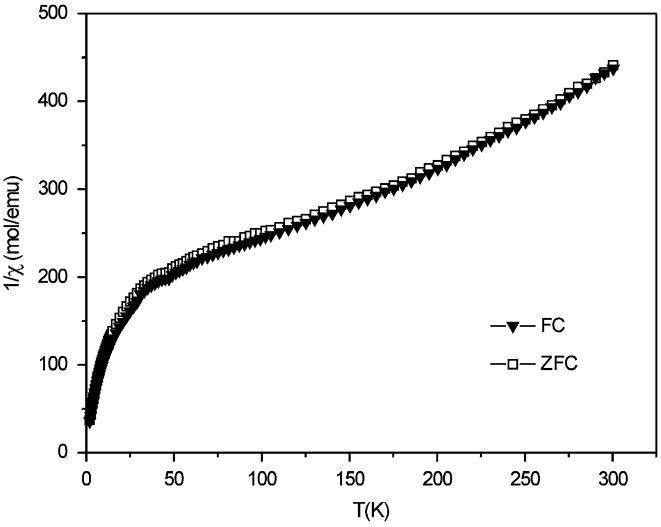

Fig. 3. $1/\chi_m$ (ZFC and FC) vs. T for $Ba_2Cu_2US_5$, in an applied field of 1000 G.

Supporting material

The crystallographic file in cif format for $Ba_2Cu_2US_5$ has been deposited with FIZ Karlsruhe as CSD number 418464. These data may be obtained free of charge by contacting FIZ Karlsruhe at +49 7247 808 666 (fax) or crysdata@fix-karlsruhe.de (e-mail).

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