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Journal of Alloys and Compounds 279 (1998) 215–219

Journal of
ALLOYS
AND COMPOUNDS

Preparation and crystal structure of a new compound Cu_2HfS_3

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Received 28 February 1998

Abstract

A new copper hafnium sulfide Cu_2HfS_3 has been prepared from solid state reaction at 600–1300°C. The compound of Cu_2HfS_3 crystallizes in the trigonal system, space group $P\bar{3}1c$(No. 163) with $a=6.4588(4)$ Å and $c=12.1943(5)$Å. The measured density is 6.10 gcm^{-3}, which is consistent with $Z=4$ for the formula unit. The crystal structure of Cu_2HfS_3 was determined from four-circle X-ray diffractometer data, and refined to a reliability factor $R=5.9\%$ for 541 independent reflections. Hf and Cu atoms are coordinated by six, four and three S atoms to form HfS_6 octahedra, CuS_4 tetrahedra and CuS_3 triangles, respectively. The structural feature of Cu_2HfS_3 is the alternative packing of layers of HfS_6 octahedra and the composite layers of CuS_3 and CuS_4 tetrahedra along the *c* direction.

Keywords: Crystal structure; Copper hafnium sulfides

1. Introduction

Ternary or quaternary group IV transition metal chalcogenides with copper have received much attention in view of their crystal structures and physical properties [1–9]. Extensive studies have been made of the compounds of Cu_2MTe_3 (M = Ti, Zr, Hf) [1–3], Cu_4TiS_4 [4], $ACuMX_3$ (A = K, Na, Tl; M = Zr, Hf; X = S, Se) [5–7] and $Tl_2Cu_2M_3X_8$ (M = Zr, Hf; X = S, Se) [8]. Except for Cu_4TiS_4, common structural feature of these compounds is the existence of MX_6 octahedra and CuX_4 tetrahedra. Contribution of both units is different in compounds depending on composition so that there has been some variation in their crystal structures. Double chains of edge sharing octahedra are observed in the compounds of Cu_2HfTe_3 [1], $NaCuZrSe_3$ [5], $Tl_2Cu_2Hf_3Se_8$ [8], $TlCuTiTe_3$ [9] and Tl_2ZrSe_3 [10]. Trans chains exist in $KCuZrS_3$ [6]. The similar octahedral chalcogen coordination of the group IV metal is also noted for compounds in the Ag–Hf–S systems. The edge sharing $[HfS_3]$ octahedral layers exist in Ag_2HfS_3 [11] and the three dimensional edge sharing HfS_6 octahedra are observed in $Ag_4Hf_3S_8$ [12,13]. It appeared of special interest to compare crystal structures of silver hafnium sulfides with that of analogous copper one from the view point of the crystal chemistry of coinage element containing chalcogenides. However, information on copper IV metal sulfides is rather scarce except for the thio-spinel of CuM_2S_4 (M = Zr, Hf) [14,15]. Little is known about the phase relations of the ternary compounds in the Cu–M–S (M = Zr, Hf) system.

In the course of an investigation of the copper hafnium sulfides we have recently discovered the new ternary compound Cu_2HfS_3 with hexagonal cell, $a \sim 6.549$ Å, $c \sim 12.194$ Å. In this paper we report its preparation and crystal structure of Cu_2HfS_3.

2. Experimental

For the preparation of copper hafnium sulfides, copper (99.9%), hafnium (99.9%), S powder (99.9999%), obtained from Rare Metallic Co. Ltd., were used as starting materials. Initially, CuS and HfS_2 powders were prepared from the elements at 600°C, respectively. Mixtures of CuS, HfS_2 and Cu with proper ratios were ground in an agate mortar under an N_2 atmosphere, pressed into pellets (radius 7 mm), and sealed in an evacuated silica tube ($P<10^{-3}$ Torr). The heat treatments were carried out at 600–1300°C for 0.33–7 days, followed by quenching. Density measurements were carried out using CCl_4.

The X-ray powder diffraction method was used mainly for the phase identification of samples. In the case of single crystals both Buerger-precession camera and four-circle

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0925-8388/98/$ – see front matter
PII: S0925-8388(98)00672-0

X-ray methods were applied to examine their crystal symmetry. Intesity data were collected with Mo Kα radiation ($\lambda = 0.7107$ Å) on an Enlaf–Nonius CAD4 diffractometer equipped with a graphite crystal incident beam monochrometor. The $\omega - 2\theta$ scan mode was applied. Three standard reflections monitored every 2h showed no signifcant change. The lattice parameters were calculated by a least-squares method.

3. Results and discussion

Several kinds of copper sulfides with different compositions were prepared in the subsolidus region with the system of Cu_2S and HfS_2. It was found that there exists the new compound Cu_2HfS_3 as a stable phase above 900°C. X-ray powder diffraction pattern for Cu_2HfS_3 can be indexed with hexagonal–trigonal cell. The unit cell parameters obtained are $a = 6.456$ Å and $c = 12.188$ Å, which are related to those of trigonal $Cd(OH)_2$-type HfS_2 (a_o,c_o) [16] by $a \sim \sqrt{3}a_o$ and $c \sim 2c_o$. The measured density 6.10 gcm^{-3} indicates Z = 4 as a nominal composition Cu_2HfS_3. In order to determine the crystal symmetry of the copper hafnium sulfides precession photographs were taken and intensity measurements were carried out using four-circle X-ray diffractometers.

The structure of Cu_2HfS_3 was determined using a single crystal which had grown on the surface of aggregates within sintered starting powders after the heating for 8h at 1300°C. A small thin crystal showing metallic luster with dimensions $0.05 \times 0.03 \times 0.12$ mm^3 was mounted at the tip of a quartz fiber. The precession photographs showed the Laue symmetry to be $\bar{3}m$. It was found that the systematic absences (hhl:$l = 2n$) are consistent with the possible trigonal space groups, $P\bar{3}1c$ (No.163) and $P31c$ (No.159).

The crystallographic data are summarized in Table 1. Cell constants, $a = 6.4588(4)$ Å, $c = 12.1943(5)$ Å, were derived from least squares refinement with 23 reflections. Reflections with $0 \leq h \leq 9$, $0 \leq k \leq 9$ and $-18 \leq l \leq 18$ were measured. The intensities of a total 1655 reflections were corrected for Lorentz polarization and Gaussian absorption correction. After averaging over equivalent reflections, 541 independent reflections with $I > 3\sigma(I)$ were obtained and used for refinement of the structure. First the starting structure model of Cu_2HfS_3 was constructed by analogy with Ag_2HfS_3, based on the assumption that Hf atoms form similar HfS_6 octahedra. The initial atomic coordinates were estimated approximately in such way that Hf and S sites were fully occupied whereas two Cu sites were half-occupied for the compositional requirement. The corresponding X-ray diffraction intensities were checked by the program pprg [17]. The centrosymmetric space group $P\bar{3}1c$ (No.163) was chosen as a most plausible one. At the same time the crystal structure of Cu_2HfS_3 was solved independently by dirrect methods with program SIR92 [18]. Comparison was made between them and the initial atomic coordinates were modified. Then the struc-

Table 1
Crystallographic data of Cu_2HfS_3

Chemical formula	Cu_2HfS_3
Formula weight (g)	401.76
Space group	$P\bar{3}1c$ (No. 163)
Cell parameters	
a(Å)	6.4588(4)
c(Å)	12.1943(5)
Volume ($Å^3$)	440.55(8)
Z	4
Calculated density (gcm^{-3})	6.06
Measured density (gcm^{-3})	6.10
Temperature of data collection (°C)	24
Radiation monochromated	
λ (Mo K_α) (Å)	0.71073
Crystal shape	plate
Crystal color	grey–black
Crystal size (mm)	$0.03 \times 0.06 \times 0.10$
Linear absorption coefficient (cm^{-1})	340.69
Transmission factors	0.187–0.219
Scan type	$\omega - 2\ \theta$
Scan speed	variable
Scan range	$(0.8 + 0.35 \tan\ \theta)$
$2\ \theta$ (max)	70 deg.
Data collected	$0 \leq h \leq 9, 0 \leq k \leq 9, -18 \leq l \leq 18$
No. of reflections measured	1655
No. of variables	46
No. of independent reflections with $I_o > 3\sigma(I_o)$	541
$R(F)$	0.059
$R_w(F)$	0.065

Table 2
Atomic coordinates for Cu_2HfS_3

Atom	Position	X	Y	Z	B_{eq} (Å^2)
Hf1	2d	0.3333	0.6667	0.2500	0.93 (1)
Hf2	2a	0.00	0.00	0.2500	0.90 (2)
Cu1	12i	0.6711 (6)	−0.0009 (6)	0.4464 (4)	2.05 (7)
Cu2	4f	0.6667	0.3333	0.3650 (8)	2.2 (1)
S	12i	0.0133 (5)	0.3345 (5)	0.3681 (3)	1.27 (5)

Table 4
Representative bond lengths and angles

Interatomic distances	(Å)
Hf1–S	2.552 (3) (×6)
HF2–S	2.562 (4) (×6)
Cu1–S	2.388 (4), 2.418 (4)
	2.262 (4), 2.263 (4)
Cu2–S	2.235 (4) (×3)
Cu1–Cu2	2.389 (6)

Angles	(deg.)
Cu2–Cu1–S	55.8 (1)
Cu1–Cu2–S	62.1 (1)
Hf1–S–Hf2	93.6 (1)
Hf1–S–Cu1	169.0 (2)
Hf1–S–Cu2	112.5 (2)
Hf2–S–Cu1	80.5 (1)
Hf2–S–Cu2	112.1 (2)
Cu1–S–Cu2	62.1 (2)
S–Hf1–S	176.9 (1), 86.6 (1), 90.9 (1), 91.3 (1)
S–Hf2–S	176.7 (1), 86.2 (1), 90.9 (1), 91.5 (1)

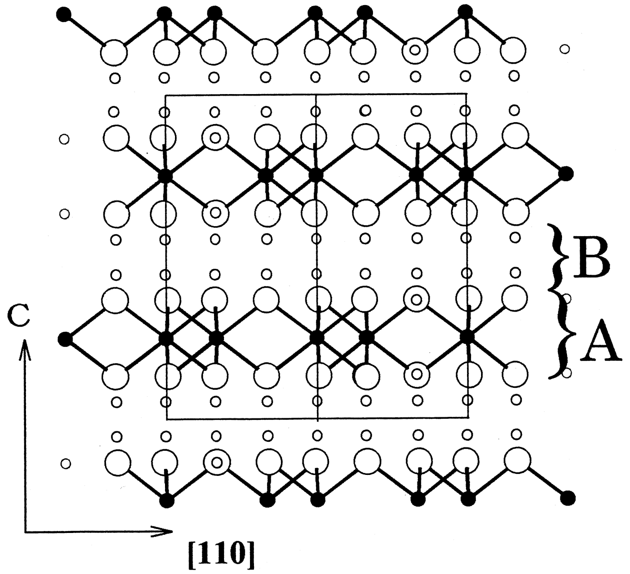

Fig. 1. View of the Cu_2HfS_3 structure projected on the (110) plane, where Hf–S bonds are drawn. Hf, Cu and S atoms are illustrated by black full, small and large circles, respectively.

ture was refined successfully from CAD4 intensity data using SDP [19] in full-matrix least squares with all atoms anisotropic. The final conventional reliability factors were $R(F)=5.9\%$ and $Rw(F)=6.5\%$. The atomic coordinates, isotropic and anistropic thermal parameters are given in Tables 2 and 3. The representative bond lengths and angles are summarized in Table 4. Figs. 1 and 2 show the projection of the structure of Cu_2HfS_3 on the (110) and the (100) planes respectively. The structure of Cu_2HfS_3 is built up as a combination of slabs A and slabs B which correspond to two-dimentional ${}^{2}_{\infty}[HfS_3]$ and Cu–S tetrahedral layers respectively. Fig. 3 shows an isolated ${}^{2}_{\infty}[HfS_3]$ layer viewed along c axis. This layer structure is very similar to that of Ag_2HfS_3 except for the presence of Cu in trigonal planar coordination. The Hf atoms lie in the 2a and 2d position and are surrounded by six S atoms with octahedral coordination. These octahedra are interconnected horizontally to produce the hexagonal rings. The alignment of Hf atoms is -Hf–Hf–vacancy–Hf–Hf- in the [110] direction. Vacancy positions are shifted by 1/3 distances along [110] direction between two repeating units of slab A, so that the zigzag chains of vacancies are running in the c direction. Stacking sequence of the Hf hexagonal rings is slightly different between Cu_2HfS_3 and Ag_2HfS_3. Overlapping hexagonal rings of Cu_2HfS_3 are shifted by a distance of nearest neighbor Hf–Hf bond in the direction parallel to a line connected beween ring center and one apex, whereas those of Ag_2HfS_3 are shifted by 3/2 times of Hf–Hf bond. Slab B is composed of S tetrahedra produced by sulfur stacking of the type of hexagonal close packing along the c direction and is sandwiched by two slabs of type A.

The HfS_6 octahedra are of regular type. As listed in Table 2, the Hf–S distances in the Hf octahedra are 2.552 Å in Hf1–S and 2.562 Å in Hf2S which is very close to the corresponding distances for Ag_2HfS_3 of 2.549Å [11] and $Ag_4Hf_3S_8$ of 2.541Å [12]. However, the Hf–S distances of binary phases are slightly longer than those of copper hafnium sulfides, being 2.63 Å in Hf_2S [20] and 2.622 Å in HfS_3 [21]. With respect to Cu–S tetrahedra, the

Table 3
Thermal parameters for Cu_2HfS_3

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hf1	0.0102 (2)	U_{11}	0.0171 (6)	$U_{11}/2$	0	0
Hf2	0.0106 (2)	U_{11}	0.0167 (6)	$U_{11}/2$	0	0
Cu1	0.0201 (1)	0.0197 (1)	0.0252 (2)	0.0117 (1)	−0.002 (2)	−0.002 (2)
Cu2	0.0199 (2)	U_{11}	0.0355 (5)	$U_{11}/2$	0	0
S	0.0120 (1)	0.0081 (1)	0.0191 (1)	0.0046 (8)	0.004 (1)	0.001 (1)

The form of the anisotropic thermal parameter is $\exp[-2^2\{h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2kha^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}\}]$.

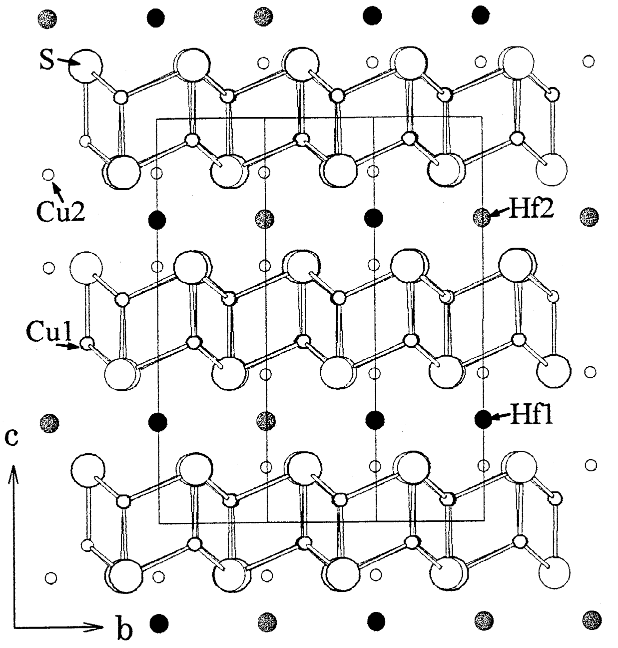

Fig. 2. Crystal structure of Cu_2HfS_3 projected on (100) plane. The Cu1–S bonds are indicated. Hf atoms are distingushed from each other by half-tone full circle as Hf2 and black full one as Hf1.

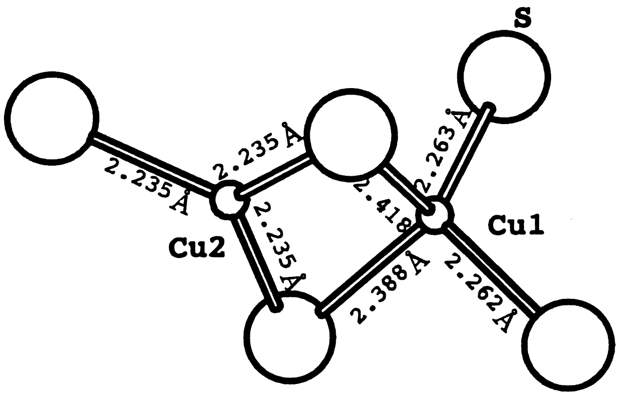

Fig. 4. Triangular $Cu2–S_3$ coordination and an isolated $Cu1–S_4$ tetrahedra.

Cu1–S distance is 2.388 Å which is slightly longer than the values of 2.333–2.357 Å in Cu_4TiS_4 and Cu_2WS_4 [22]. Fig. 4 shows the triangular coordination of Cu2 and the isolated Cu1 tetrahedra. The Cu1 zigzag chains run straight parallel to [110] direction. The Cu1 tetrahedra are connected to the Hf octahedra by sharing edges and one corner. The alighnment of Cu1 and S atoms makes a chain of –S–Cu1–S–Cu1– in the *c* direction. The Cu2–S distance in trigonal planar coordination is 2.235 Å which is in good agreement with that of Cu–S in Cu_2S [23,24]. The closest interlayer and intralayer S–S distances of 3.500 Å and 3.670 Å indicate that there is no significant S–S interaction. Formal oxidation states of this compound can be assigned as Cu(+1), Hf(+4) and S(−2). Further works on physical properties of this compound are now in progress.

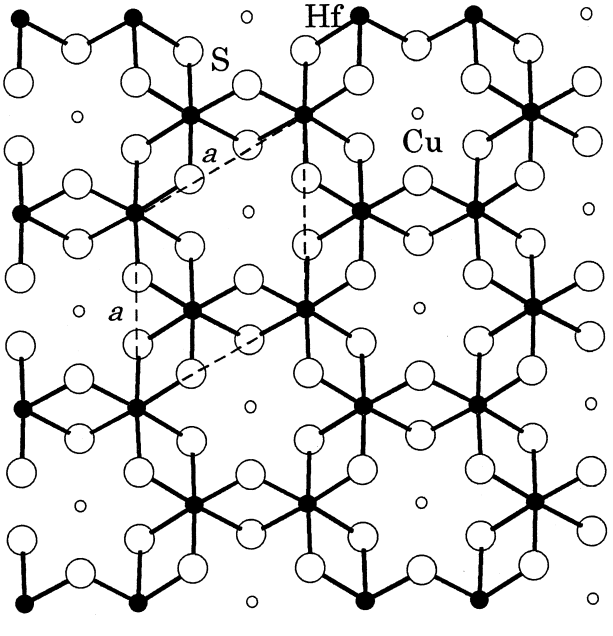

Fig. 3. Linkage of Hf-octahedra: the (001) projection of an isolated $^2_\infty[HfS_3^{2-}]$ layer of Cu_2HfS_3. Unit cell is designated as dotted line.

In summary the new compound Cu_2HfS_3 has been prepared and determined to crystallize in the triganal system of $P\,\bar{3}1c$ (No. 163) with the cell dimensions of $a=6.4588(4)$ Å and $c=12.1943(5)$ Å. The crystal structure analysis revealed the existence of infinite two-dimensional $^2_\infty[HfS_3]$ layers similar to those of Ag_2HfS_3. It was found that the structure of Cu_2HfS_3 is composed of the alternative layer packing of HfS_6 octahedra and a combination of CuS_3 triangles and CuS_4 tetrahedra along the *c* direction.

References

[1] P.M. Keane, J.A. Ibers, J. Solid State Chem. 93 (1991) 291.
[2] W. Bensch, P. Dürichen, Z. Krist. 209 (1994) 684.
[3] A.G. Kleyn, M.A. Pell, J.A. Ibers, Z. Krist. 212 (1997) 93.
[4] K.O. Klepp, D. Gurtner, J. Alloys Comp. 243 (1996) 19.
[5] M.F. Mansuetto, P.M. Keane, J.A. Ibers, J. Solid State Chem. 105 (1993) 580.
[6] M.F. Mansuetto, P.M. Keane, J.A. Ibers, J. Solid State Chem. 102 (1992) 257.
[7] K.O. Klepp, D. Gurtner, J. Alloys Comp. 243 (1996) 6.
[8] K.O. Klepp, D. Grurtner, J. Alloys Comp. 239 (1996) 1.
[9] M.A. Pell, J.A. Ibers, J. Alloys Comp. 240 (1996) 37.
[10] K.O. Klepp, D. Mayr, in: Proceedings of the 11th International Conference on Solid Compounds of Transition Elements, Wroclaw, 1994, collection abstract, p. 57.
[11] H. Wada, O. Amiel, A. Sato, J. Alloys Comp. 219 (1995) 55.
[12] O. Amiel, H. Wada, J. Solid State Chem. 115 (1995) 112.
[13] H. Wada, O. Amiel, A. Sato, Solid State Ionics 70 (1995) 129.
[14] L. Trichet, J. Rouxel, C.R. Acad. Sci. C267 (1968) 1322.
[15] C. Moreau, M. Spieer, J. Rouxel, C.R. Acad. Sci. C280 (1975) 1203.
[16] F.K. McTaggart, A.D. Wadsley, Australian J. Chem. 11 (1958) 445.

[17] K. Kato, personal communication, 1976.
[18] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Cryst. 26 (1993) 343.
[19] B.A. Frenz & Associates, Inc., SDP for windows reference manual, College Station, Tx, 1995.
[20] H.F. Franzen, J. Graham, Z. Kristallogr. 123 (1996) 133.
[21] S. Furuseth, L. Brattas, A. Kjekshus, Acta Chem. Scand. A29 (1975) 623.
[22] E.A. Pruss, B.S. Snyder, A.M. Stacy, Angew. Chem. 105 (1993) 279.
[23] H.T. Evans Jr., J.A. Konnert, Am. Mineral. 61 (1976) 996.
[24] H. Fjellvåg, F. Grønvold, S. Stølen, A.F. Andresen, R. Müller-Käfer, A. Simon, Z. Kristallogr. 184 (1988) 111.