Journal of Alloys and Compounds 317–318 (2001) 217–221

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Preparation and crystal structures of Cu_2HfS_3

H. Wada*, A. Sato, H. Nozaki

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

Abstract

The phase relations of the compound Cu_2HfS_3 have been studied by XRD and DSC methods. The following three types were found to exist in the temperature range from 500 to 1300°C: (a) monoclinic α-Cu_2HfS_3 phase with $a=12.271(3)$ Å, $b=11.162(3)$ Å, $c=6.429(2)$ Å, $\beta=100.04(2)°$ below 650°C, (b) monoclinic β-Cu_2HfS_3 phase with $a=9.611(2)$ Å, $b=6.444(1)$ Å, $c=7.127(3)$ Å, $\beta=98.05(2)°$ in the temperature range of 650–780°C, and (c) trigonal γ-Cu_2HfS_3 phase with $a=6.456$ Å and $c=12.188$ Å above 787°C. Structure determination of β-Cu_2HfS_3 phase was attempted using the Rietveld method. Electrical resistivity measurements were carried out for the trigonal γ-Cu_2HfS_3 phase. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper hafnium sulfide; Phase relation; Crystal structure; Phase transition; Electrical resistivity

1. Introduction

Recently we have reported the syntheses and structures of new ternary hafnium sulfides with the composition A_2HfS_3 (A=Ag, Cu) [1,2]. The common feature of crystal structures of these compounds is the existence of HfS_6 octahedra and AS_4 tetrahedra. These octahedra are interconnected horizontally to make the edge-sharing $[HfS_3]$ octahedral layers. The three-dimensional edge-sharing HfS_6 octahedra exist in $Ag_4Hf_3S_8$ [3,4]. Double chains of edge-sharing octahedra have been known for the compounds of Cu_2HfTe_3 [5], $TlCuHfS_3$ [6] and $Tl_2Cu_2Hf_3Se_8$ [7]. In spite of much knowledge of the structures concerning ternary and/or quaternary hafnium chalcogenides little is known about their phase relations. We studied the Cu–Hf–S system and found the new modifications of Cu_2HfS_3 prepared at temperatures ranging from 500 to 800°C.

In this work we report the preparation, the phase transition and the crystal structure determination from X-ray powder diffraction data by using the Rietveld method of the low-temperature phase of Cu_2HfS_3, and its resistivity measurement.

2. Experimental

Copper hafnium sulfides were prepared from the pure elements and the related binary compounds. The mixtures were ground in an agate mortar, pressed into pellets (diameter 7 mm), and sealed in evacuated silica tubes at a pressure of less than 10^{-3} Torr (1 Torr=133.322 Pa). Heat treatments were carried out at 550~1300°C for 5 h~45 d, followed by quenching.

In the case of high-temperature experiments above 900°C an alumina crucible was used as the sample container inside the silica tube to avoid the reaction of silica and pellet. Samples obtained were identified with X-ray powder and single crystal diffraction methods. The structure refinement of the compound was performed using the total pattern fit program RIETAN [8].

Differential thermal analysis was carried out using SETARAM DSC-111 instruments at a heating/cooling rate of 10°C min^{-1}. Less than 100 mg of powder samples was put into small quartz ampoules, sealed in vacuum and used.

Electrical resistivity measurements were taken on rectangular shaped, cold-pressed polycrystalline samples (2.1×2.4×5 mm). Electrical contacts were made by silver paste.

3. Results and discussion

3.1. Phase relations of Cu_2HfS_3

Several kinds of copper hafnium sulfides with different compositions were prepared in the subsolidus region.

---

*Corresponding author. Tel./fax: +81-298-58-5641.
E-mail address: wadah@nirim.go.jp (H. Wada).

PII: S0925-8388(00)01330-X

Representative powder X-ray diffraction (XRD) patterns of Cu_2HfS_3 obtained at 550, 650, 700 and 900°C are shown in Fig. 1. Patterns (a), (c) and (d) belong to the single phases with different structures. Pattern (a) is from the high-temperature phase of Cu_2HfS_3 with the space group of $P\bar{3}1c$ which has been reported before [2]. Patterns (c) and (d) are from the low-temperature phases of Cu_2HfS_3 which have been studied in this work. The structure difference between (a) and (c) is considered very small because both diffraction profiles resemble each other especially concerning strong main reflections. Pattern (b) represents the mixture of high- and low-temperature Cu_2HfS_3 phases. The unit cell parameters of the Cu_2HfS_3-related compounds are listed in Table 1. For the sake of convenience we designate here these modifications as γ-, β- and α-phases, respectively.

The differential thermal analyses of the α- and β-phases prepared were carried out in order to check the stability and phase relations of Cu_2HfS_3. Differential scanning calorimetry (DSC) curves are shown in Fig. 2. On heating the first endothermic peak appears at around 515°C. This probably corresponds to the decomposition of a small amount of coexisting CuS impurity ($1.8CuS \rightarrow Cu_{1.8}S + 0.8S$). The second endothermic peak with an enthalpy of 6.77 J g^{-1} appears at 658°C where the α-phase changes to β-phase owing to the irreversible phase transition. On subsequent heating up to the temperature limit of 830°C for the apparatus the third endothermic process with an

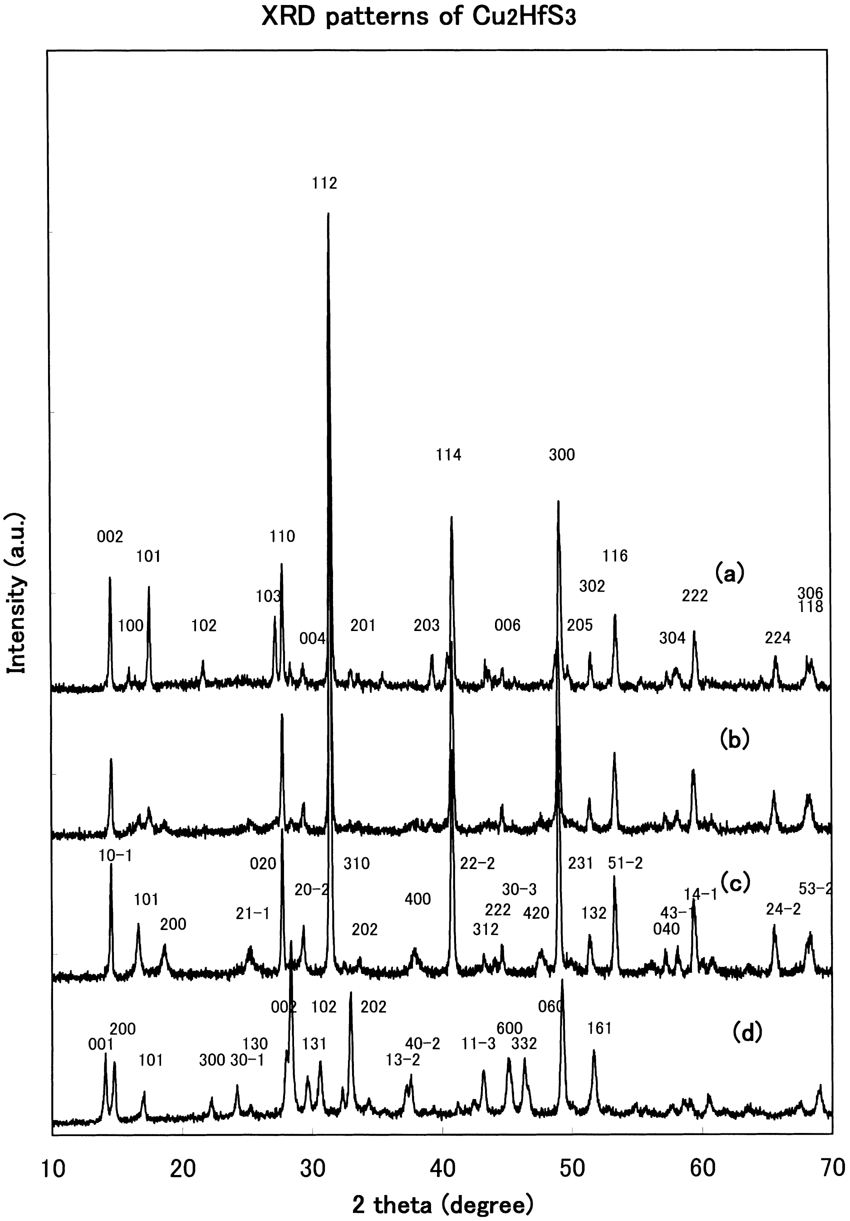

Fig. 1. Typical XRD patterns of Cu_2HfS_3: (a) prepared at 900°C, (b) prepared at 700°C, (c) prepared at 650°C and (d) prepared at 550°C.

Table 1
Summary of crystal structures of Cu_2HfS_3

Compound	Crystal system	Space group	*Z*	Lattice parameters	Comments	Ref.
α-Cu_2HfS_3	Monoclinic	–	8	a=12.271(3) Å b=11.162(3) Å c=6.429(2) Å β=100.04°	Stable below 650°C ρ_{calc}=6.15 g cm^{-3}	This work
β-Cu_2HfS_3	Monoclinic	$P2_1/n$	4	a=9.611(2) Å b=6.444(1) Å c=7.127(3) Å β=98.05°	Stable at 650~760°C ρ_{calc}=6.10 g cm^{-3}	This work
γ-Cu_2HfS_3	Trigonal	$P\bar{3}1c$	4	a=6.4588 Å c=12.1943 Å	Prepared above 800°C	[2]
HfS_2	Trigonal	$P\bar{3}m1$	1	a=3.625 Å c=5.846 Å		[9]

enthalpy of 4.69 J g^{-1} observed at 787°C where the phase transition of β- to γ-phase occurs. The final products after the DSC run were checked by X-ray powder diffraction and confirmed as γ-phase. In the case of the DSC curve of the β-phase prepared at 650°C for 14 days, however, no endothermic peaks appear at temperatures from 550°C to 760°C. There exists a similar phase transition from β- to γ-phase at 787°C as in the sample of 550°C. These results suggest that the α-phase is stable below 650°C, β-phase is stable in the range of temperature between 650 and 760°C and γ-phase is formed above 787°C.

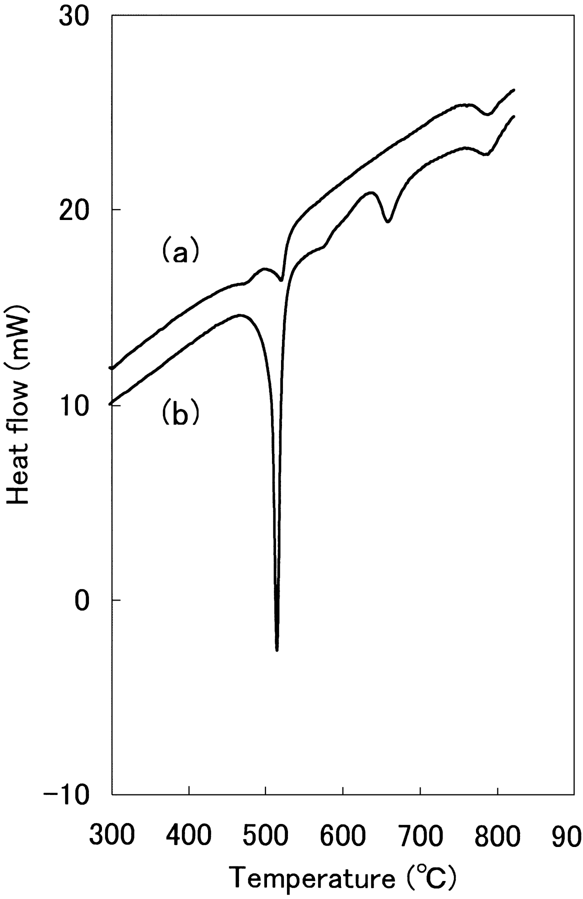

Fig. 2. DSC heating curves of Cu_2HfS_3: (a) β-phase prepared at 650°C and (b) α-phase prepared at 550°C.

3.2. Structure determination of β-Cu_2HfS_3

The X-ray diffraction intensity data were collected with a step scan procedure on a Rigaku diffractometer (Rint2000) using graphite-monochromated CuKα radiation. It was found that the systematic reflection conditions (hhl; $l=2n$, $0k0$; $k=2n$) are consistent with the possible monoclinic space group, $P2_1/c$ (No. 14). As a first step, a structure model of β-Cu_2HfS_3 was embodied on the basis of crystal structure of γ-Cu_2HfS_3 with a=6.456 Å and c=12.188 Å [2], which is related to those of trigonal $Cd(OH)_2$-type HfS_2 (a_0, c_0) [9] by $a_\gamma \sim \sqrt{3}a_0$ and $c_\gamma \sim \sqrt{3}c_0$. Lattice parameters of β-Cu_2HfS_3 are related to those of γ-Cu_2HfS_3 by $a_\beta \cong 2/3\times(a_\gamma - b_\gamma) - 1/2\times c_\gamma$, $b_\beta \cong a_\gamma + b_\gamma$, $c_\beta \cong 1/3\times(a_\gamma - b_\gamma) + 1/2\times c_\gamma$. As shown in Fig. 3, the starting structure was constructed on the basis of the assumption that Hf atoms form similar Hf layers as in γ-Cu_2HfS_3 and the stacking of atoms in the vertical direction against layer is –S–Hf–S–Cu–S–Hf–S–Cu– in order. The intensity data in the range of d-spacings from 8.855 to 1.3456 Å were used and 21 positional parameters, three isotropic thermal parameters, one occupation parameter and one scaling factor were refined from the initial parameters. The agreement of observed and calculated patterns was satisfactory: R_{wp}=16.3%, R_p=12.5%, R_I=9.8%, and R_F=6.3% for B(Hf)=1.5(0.2) $Å^2$, B(Cu)=4(1) $Å^2$, and B(S)=3(1) $Å^2$. The observed and calculated X-ray powder diffraction profiles of Cu_2HfS_3 are shown in Fig. 4, where the experimental data are plotted by dots and Bragg positions are indicated as vertical lines. Final values

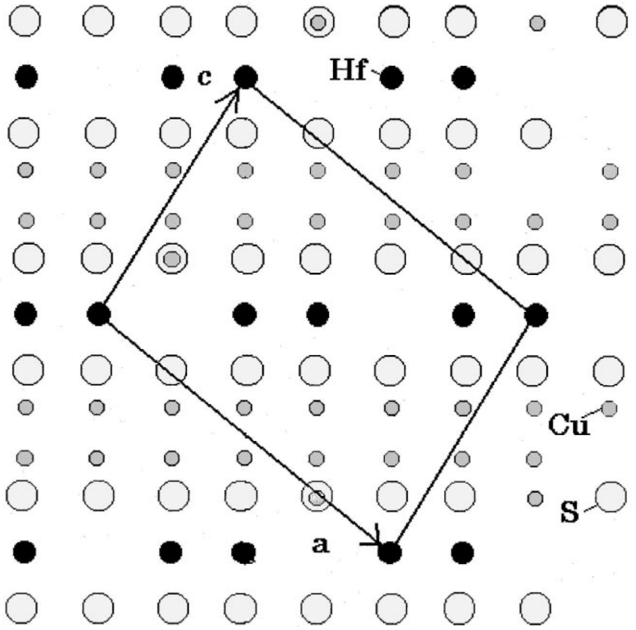

Fig. 3. Lattice relation of Cu_2HfS_3 between the γ- and β-phases. The section (110) plane of the γ-plane is presented. Arrows correspond to *a* and *c* axes of the β-phase.

of all structural parameters are given in Table 2. The observed and calculated *d*-spacings of reflection peaks are listed in Table 3, together with the observed intensity.

The HfS_6 octahedra are largely distorted when compared with high-temperature phase. The Hf–S distances are an average 2.78Å in Hf(1)–S and average 2.63 Å in Hf(2)–S which is slightly longer than the corresponding distances for Ag_2HfS_3 of 2.549 Å [1] and $Ag_4Hf_3S_8$ of 2.541 Å [3]. These values are rather close to those of binary phases, 2.63 Å in Hf_2S [10] and 2.622 Å in HfS_3 [11]. The Cu–S distances ranges from 2.15 to 2.84 Å. However, further work on single crystals would be absolutely necessary to clarify the details of the true crystal structure.

3.3. Electrical resistivity of γ-Cu_2HfS_3

The electrical resistivity of a sintered polycrystalline sample of γ-Cu_2HfS_3 was measured from liquid N_2 temperature to 300 K. The uncertainty of the resistivity was estimated to be ±1 in value owing to the experimental limitation. As shown in Fig. 5, a plot of ρ in Ω cm vs. T in K for γ-Cu_2HfS_3 reflects a resistivity anomaly behavior. On cooling from 298 to 78 K, the sample shows a resistivity hump around 252 K. The resistivity slightly increases from 21 to 28.4 Ω cm in the temperature range 298–252 K, and decreases gradually to 11.7 Ω cm of the minimum until 204 K, and again increases to 24.8 Ω cm with temperature up to 78 K in the semiconducting behavior. A similar resistivity anomaly has been reported in the compounds of $ACu_{7-x}S_4$ (A=Tl, K, Rb) [12].

4. Summary

The phase relations of Cu_2HfS_3 at 500–1300°C were determined by sealed silica tube experiments. There exist

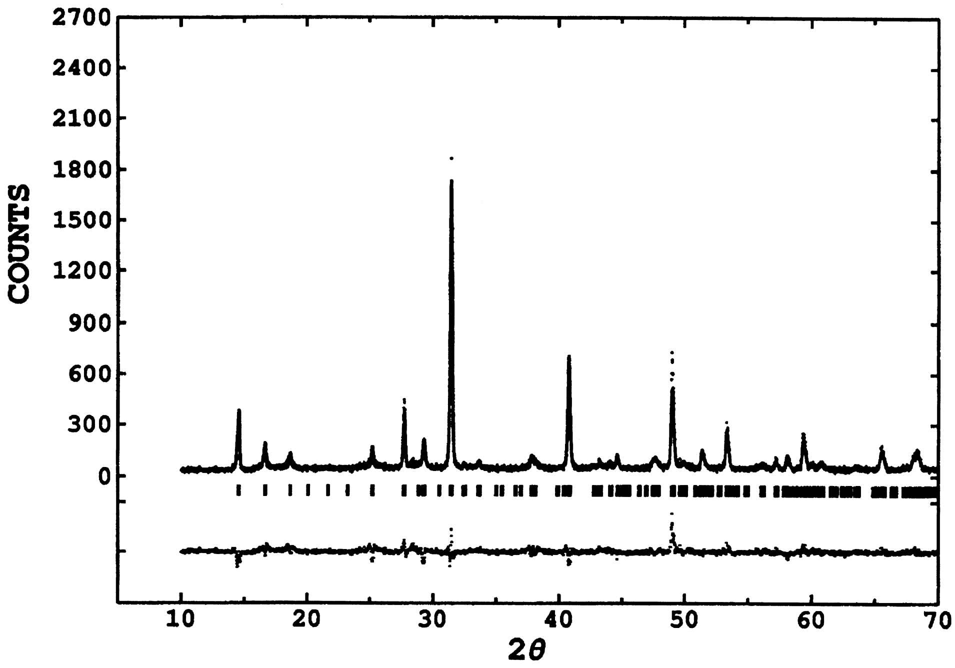

Fig. 4. The observed (dots) and calculated (solid line) XRD patterns of Cu_2HfS_3. The difference between the observed and calculated profiles is plotted below on the same scale.

Table 2
Structure parameters of β-Cu_2HfS_3

Space group: $P2_1/n$ (No. 14); a=9.611(2) Å, b=6.444(1) Å, c=7.127(3) Å, β=98.05(2)°

Atom	Position	Ocp	x	y	z	B_{eq} (Å^2)
Cu(1)	4e	0.39(4)	0.575(11)	0.480(28)	0.302(13)	4(1)
Cu(2)	4e	0.92	0.505(6)	0.262(5)	0.976(8)	–
Cu(3)	4e	0.69	0.207(8)	0.639(13)	0.523(10)	–
Hf(1)	2a	0.5	0	0	0	1.5(2)
Hf(2)	4e	0.75	0.339(2)	0.006(5)	0.328(4)	–
S(1)	4e	1.0	0.250(10)	0.853(15)	0.054(14)	3(1)
S(2)	4e	1.0	0.404(12)	0.845(17)	0.729(12)	–
S(3)	4e	1.0	0.929(10)	0.335(20)	0.180(12)	–

Table 3
X-Ray powder diffraction data of β-Cu_2HfS_3

h	k	l	d_0 (Å)	d_c (Å)	I_0
1	0	−1	6.087	6.090	18
1	0	1	5.323	5.323	7
2	0	0	4.751	4.758	5
2	1	−1	3.537	3.536	5
0	2	0	3.218	3.221	26
2	0	−2	3.046	3.045	8
3	1	0	2.847	2.846	100
2	0	2	2.662	2.661	4
4	0	0	2.3805	2.3791	5
2	2	−2	2.2130	2.2131	39
3	1	2	2.0888	2.0905	4
2	2	2	2.0527	2.0519	4
3	0	−3	2.0300	2.0302	7
4	2	0	1.9126	1.9138	5
2	3	1	1.8596	1.8591	41
1	3	2	1.7776	1.7776	9
5	1	−2	1.7179	1.7181	17
0	4	0	1.6112	1.6109	5
4	3	−1	1.5874	1.5874	5
1	4	−1	1.5571	1.5574	14
2	4	−2	1.4243	1.4240	8
6	1	−3	1.3775	1.3771	7
5	3	−2	1.3722	1.3717	9

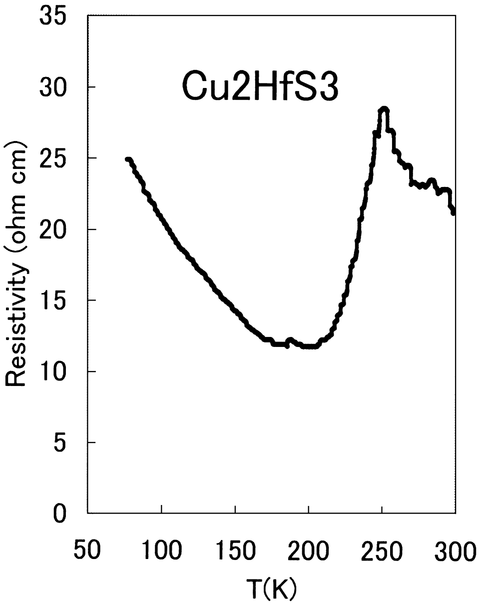

Fig. 5. Electrical resistivity of γ-Cu_2HfS_3.

three modifications: (a) monoclinic α-Cu_2HfS_3 phase below 650°C (b) monoclinic β-Cu_2HfS_3 phase in the temperature range of 650–780°C, and (c) trigonal γ-Cu_2HfS_3 phase above 787°C. The structure of the β-Cu_2HfS_3 phase was determined using the Rietveld method. The γ-Cu_2HfS_3 phase pellet showed a resistivity hump around at 252 K and became a semiconductor below 200 K.

References

[1] H. Wada, O. Amiel, A. Sato, J. Alloys Comp. 219 (1995) 55.
[2] H. Wada, A. Sato, J. Alloys Comp. 279 (1998) 215.
[3] O. Amiel, H. Wada, J. Solid State Chem. 115 (1995) 112.
[4] H. Wada, O. Amiel, A. Sato, Solid State Ionics 70 (1995) 129.
[5] P.M. Keane, J.A. Ibers, J. Solid State Chem. 93 (1991) 291.
[6] M.F. Mansuetto, P.M. Keane, J.A. Ibers, J. Solid State Chem. 105 (1993) 580.
[7] K.O. Klepp, D. Grurtner, J. Alloys Comp. 239 (1996) 1.
[8] F. Izumi, in: R.A. Young (Ed.), The Rietveld Method, Oxford University Press, Oxford, 1993, pp. 236–345, Chapter 13.
[9] F.K. McTaggart, A.D. Wadsley, Australian J. Chem. 11 (1958) 445.
[10] H.F. Franzen, J. Graham, Z. Kristallogr. 123 (1996) 133.
[11] S. Furuseth, L. Brattas, A. Kjekshus, Acta Chem. Scand. A29 (1975) 623.
[12] T. Ohtani, J. Ogura, H. Yoshihara, Y. Yokota, J. Solid State Chem. 115 (1995) 379.