

The Stannide Zr_5CuSn_3

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Zr_5CuSn_3 was prepared from the elements in an arc-melting furnace and investigated by X-ray diffraction of powders as well as of single crystals. The crystal structure was refined from four-circle diffractometer data: $P6_3/mcm$, $a = 860.04(7)$ pm, $c = 586.80(5)$ pm, $V = 0.3759(1)$ nm³, $Z = 2$, $wR2 = 0.0402$ for 371 F^2 values and 15 variables. A refinement of the occupancy parameters revealed that the copper position is occupied to only 95.3(8)% in the crystal used for the X-ray investigation. Zr_5CuSn_3 crystallizes in the Hf_5CuSn_3 type structure, a filled variant of the Mn_5Si_3 type. The main features of the Zr_5CuSn_3 structure are condensed Zr_6 octahedra that are centered by copper atoms.

Introduction

We recently started a systematic investigation on crystal structures and physical properties of ternary compounds R_2T_2X ($R = Ti, Zr, Hf$; $T =$ transition metal; $X = In, Sn$) [1,2]. These intermetallics belong to a large family of compounds which adopt the ordered U_3Si_2 or ordered Zr_3Al_2 structure [3, 4 and ref. therein]. Attempts to prepare “ Zr_2Cu_2Sn ” by arc-melting always resulted in considerable amounts of Zr_5CuSn_3 in very well crystallized form. Zr_5CuSn_3 is known since a long time [5–7], however, it was only characterized from X-ray powder data. Single crystal data for compounds with filled Mn_5Si_3 structure are desirable in order to determine the exact occupancy of the octahedral voids. The structure refinement from single crystal X-ray data for Zr_5CuSn_3 is reported in the present note.

Sample Preparation and Lattice Constants

Starting materials for the preparation of Zr_5CuSn_3 were zirconium foil (Johnson Matthey, 0.2 mm thick), copper wire (Johnson Matthey, \varnothing 1 mm) and tin granules (Merck), all with stated purities better 99.9%. In a first reaction step, the zirconium foil was arc-melted under argon (about 600 mbar) in order to obtain a compact button

(about 500 mg). The argon was purified over molecular sieves, titanium sponge (900 K) and an oxidant catalyst [8]. The zirconium pellet was then mixed with copper wire and tin granules in the ideal 5:1:3 atomic ratio and the elemental components were reacted in an arc-melting furnace. The product pellet was melted three times on each side to ensure homogeneity. The button was subsequently sealed in an evacuated quartz glass ampoule and annealed at 970 K for two weeks.

Guinier powder patterns were recorded with $CuK\alpha_1$ radiation using α -quartz ($a = 540.46$ pm, $c = 491.30$ pm) as an internal standard. The powder pattern could easily be indexed on the basis of a hexagonal cell with the lattice constants listed in Table I. To assure correct indexing, the observed pattern was compared with a calculated one [9] taking the atomic positions of the structure refinement.

Table I. Lattice constants of the hexagonal stannides Zr_5Sn_3 , Zr_5CuSn_3 , and Zr_5Sn_4 .

Comp.	a (pm)	c (pm)	c/a	V (nm ³)	Ref.
Zr_5Sn_3	845.60(7)	577.9(1)	0.683	0.35786(9)	[10]
Zr_5Sn_4	876.56(7)	593.7(1)	0.677	0.39506(9)	[10]
Zr_5CuSn_3	875	590	0.674	0.3912	[6]
Zr_5CuSn_3	860.0	586.8	0.682	0.3759	[5]
Zr_5CuSn_3	862.49(7)	587.7(1)	0.681	0.37861(9)	[7]
Zr_5CuSn_3	860.04(7)	586.80(5)	0.682	0.3759(1)	this work
Zr_5CuSn_3	859.4(1)	587.1(1)	0.683	0.3755(1)	this work ^a

^a Lattice constants of the single crystal determined on the four-circle diffractometer with $MoK\alpha$ radiation.

Structure Refinement

Irregular shaped single crystals of Zr_5CuSn_3 were isolated from the annealed sample by mechanical fragmentation and were examined by use of a Buerger camera. The precession photographs showed hexagonal symmetry, and the systematic extinctions ($h0l$ only observed with $l = 2n$) led to the space groups $P6_3cm$, $P6c2$, and $P6_3/mcm$, of which the centrosymmetric group $P6_3/mcm$ (No. 193) was found to be correct during structure refinement. All relevant crystallographic data and experimental details for the data collection are listed in Table II.

Single crystal intensity data were collected by use of a four-circle diffractometer (Enraf-Nonius, CAD4) with graphite monochromatized $MoK\alpha$ radiation and a scintillation counter with pulse height discrimination.



Table II. Crystal data and structure refinement for Zr_5CuSn_3 .

Empirical formula	Zr_5CuSn_3
Refined composition	$Zr_5Cu_{0.953(8)}Sn_3$
Formula weight	875.7 g/mol
Temperature	293(2) K
Wavelength	71.073 pm
Crystal system	hexagonal
Space group	$P6_3/mcm$ (No. 193)
Unit cell dimensions	see Table I
Formula units per cell	$Z = 2$
Calculated density	7.74 g/cm ³
Crystal size	20·20·45 μm ³
Absorption correction	from ψ -scan data
Transmission ratio (max:min)	0.998:0.774
Absorption coefficient	19.1 mm ⁻¹
F (000)	758
θ range for data collection	2 to 38°
Range in hkl	$\pm 17, \pm 17, +11$
Scan mode	$\omega / 2\theta$
Total no. reflections	4373
Independent reflections	388 ($R_{int} = 0.0562$)
Reflections with $I > 2\sigma(I)$	344
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	371 / 0 / 15
Goodness-of-fit on F^2	1.254
R indices [$I > 2\sigma(I)$]	$R1 = 0.0194, wR2 = 0.0338$
R indices (all data)	$R1 = 0.0291, wR2 = 0.0402$
Extinction coefficient	0.0013(1)
Largest diff. peak and hole	2054 and - 1556 e/nm ³

Starting atomic parameters were deduced from an automatic interpretation of direct methods with SHELX-86 [11] and the structure was refined using SHELXL-93 [12] with anisotropic atomic displacement parameters for all atoms. The equivalent isotropic displacement parameter for the copper position was somewhat high, indicating some defects on this position. A refinement of the occupancy parameters shows no significant deviations from full occupancies for the zirconium and tin positions, while some defects were found for the copper position. In the final cycles ideal occupancies were assumed with the exception of that for the copper position. The refinement resulted in lower residuals and smaller atomic displacement parameters for the copper position. The composition for the crystal investigated was refined to $Zr_5Cu_{0.953(8)}Sn_3$. Within the refinement 17 reflections with $F_o^2 < -2\sigma(F_o^2)$ were treated as unobserved [12]. A final difference Fourier synthesis revealed no significant residual peaks. The positional parameters and interatomic distances are listed in Tables III and IV. A listing of the observed and calculated structure factors is available.*

Discussion

The present structure refinement from single crystal X-ray data for Zr_5CuSn_3 clearly shows that this stannide adopts the Hf_5CuSn_3 structure [5], a ternary filled variant of Mn_5Si_3 [13,14]. A refinement of the occupancy parameters indicates small defects for the copper site and resulted in the composition $Zr_5Cu_{0.953(8)}Sn_3$ for the crystal investigated. Although the copper position is fully occupied within six standard deviations, the small defects cannot be neglected. Nevertheless we as-

Table III. Atomic coordinates and anisotropic displacement parameters (pm²) for Zr_5CuSn_3 . U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]. U_{13} = U_{23} = 0.$$

Atom	Wyckoff site	occ.	x	y	z
Zr1	6g	1	0.26598(8)	0	1/4
Zr2	4d	1	1/3	2/3	0
Cu	2b	0.953(8)	0	0	0
Sn	6g	1	0.61472(5)	0	1/4

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Zr1	150(2)	79(3)	109(2)	39(1)	120(1)
Zr2	53(2)	U_{11}	44(2)	26(1)	50(1)
Cu	128(5)	U_{11}	410(13)	64(3)	222(6)
Sn	98(1)	48(2)	82(2)	24(1)	82(1)

Table IV. Interatomic distances (pm) in the structure of Zr_5CuSn_3 , calculated with the lattice constants obtained from Guinier powder data. All distances shorter than 490 pm (Zr-Zr, Zr-Cu, Zr-Sn, Cu-Cu, Cu-Sn) and 440 pm (Sn-Sn) are listed. Standard deviations are all equal or less than 0.1 pm.

Zr1:	2 Cu	271.8	Cu:	6 Zr1	271.8
	2 Sn	293.8		2 Cu	293.4
	1 Sn	299.9		6 Sn	362.4
	2 Sn	310.8			
	4 Zr2	351.7	Sn:	2 Zr1	293.8
	4 Zr1	372.0		1 Zr1	299.9
	2 Zr1	396.2		4 Zr2	304.8
				2 Zr1	310.8
Zr2:	2 Zr2	293.4		2 Sn	353.6
	6 Sn	304.8		2 Cu	362.4
	6 Zr1	351.7			

* Details may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-405793.

sume essentially full occupancy of the octahedral voids for the bulk sample as can also be concluded from our quantitative synthesis as well as the results reported by Kwon and Corbett [7].

Two different sets of lattice constants (see Table I) have been reported for Zr_5CuSn_3 in the literature. The present lattice constants from Guinier powder data are in good agreement with the lattice constants determined on the four-circle diffractometer. These values are also close to the data given by Kwon and Corbett [7]. Rieger, Nowotny, and Benesovsky reported similar lattice constants [5], but they also gave much larger values in another paper [6]. These data are much closer to the lattice constants of Zr_5Sn_4 [10], where the octahedral void is filled by a tin atom. It is possible, that the latter data from Rieger *et al.* [6] correspond to a compound $Zr_5Cu_xSn_{4-x}$. Such a mixed occupancy can definitely be excluded for the present single crystal investigation, since Cu/Sn mixing would result in an occupancy parameter of more than 100% for the copper position.

Zr_5CuSn_3 belongs to a large family of compounds with structures derived from the well known Mn_5Si_3 type [13,14]. Those compounds of this family with filled octahedral void are called filled $D8_8$ or Nowotny phases [15]. Today more than 300 compounds [16] with unfilled, filled or partially filled Mn_5Si_3 structure are known. An overview of the different atomic combinations observed up to now is given in ref. 17.

A projection of the Zr_5CuSn_3 structure is shown in Fig. 1. The most remarkable structural feature of the Zr_5CuSn_3 structure are $[Zr1_6]$ octahedra, centered by copper atoms. These $[Zr1_6]$ octahedra are face-shared along the c -axis forming one-dimensionally infinite chains. A monomeric unit of these chains is shown in Fig. 2. Together with the two adjacent copper atoms (along the c -axis) and the six tin atoms, the coordination of each copper atom is very similar to that of the well known M_6X_8 cluster [19,20]. In Zr_5CuSn_3 these clusters have the composition $[Cu(Zr1_6Cu_2Sn_6)]$. They are condensed along the c -axis via common triangular $Zr1_3$ faces.

The Zr1-Cu distances within the octahedral units amount to 271.8 pm. They are only slightly larger than the sum of Paulings single-bond radii [21] for zirconium and copper of 262.7 pm indicating some bonding character for these interactions.

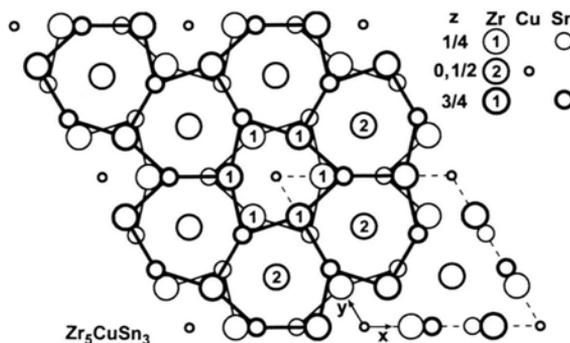


Fig. 1. Projection of the crystal structure of Zr_5CuSn_3 along the c -axis [18]. Atoms connected by thin and thick lines are at $z = 1/4$ and $z = 3/4$, respectively. Unconnected atoms are superimposed at $z = 0$ and $z = 1/2$. The two crystallographically different zirconium positions are indicated.

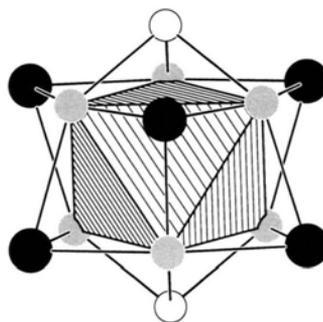


Fig. 2. Cutout of the one-dimensionally infinite chain of condensed $[CuZr1_6]$ octahedra in Zr_5CuSn_3 . Shown is one $[CuZr1_6]$ octahedron together with the adjacent tin and copper atoms forming a monomeric $[Cu(Zr1_6Cu_2Sn_6)]$ unit with the same atomic arrangement as in the well known M_6X_8 type clusters. The zirconium, copper, and tin atoms are shown as light grey, unfilled, and filled black circles, respectively.

The Cu-Cu distances between two adjacent octahedra of 293.4 pm are much longer than in *fcc* copper (255.6 pm [22]), and there are most likely no bonding interactions between the copper atoms.

The Zr-Zr distances in Zr_5CuSn_3 cover the wide range from 293.4 to 396.2 pm and deserve some comment. In the octahedral unit the Zr1-Zr1 distances amount to 396.2 pm (in the $Zr1_3$ triangular plane perpendicular to the c -axis) and 372.0 pm (between the triangular planes). Both of these distances are considerably larger than the average Zr-Zr distance of 320.6 pm for the twelve nearest

neighbors in *hcp* zirconium [22]. In contrast, the Zr₂-Zr₂ distances of 293.4 pm (half the translation period *c*) agree well with the sum of Paulings single bond radii of 290.8 pm. The Zr₂ atoms form one-dimensional infinite chains with a considerable degree of Zr-Zr bonding. A detailed study of chemical bonding on the basis of an extended Hückel band calculation was given recently for Zr₅Sb₃ and Zr₅Sb₃S by Corbett *et al.* [19].

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- [1] R. Pöttgen, G. Kotzyba, *Z. Naturforsch.* **51b**, 1248 (1996).
- [2] R. Pöttgen, R. Dronskowski, *J. Solid State Chem.*, in press.
- [3] R. Pöttgen, R. Dronskowski, *Z. Anorg. Allg. Chem.* **622**, 355 (1996).
- [4] F. Fourgeot, P. Gravereau, B. Chevalier, L. Fournès, J. Etourneau, *J. Alloys Comp.* **238**, 102 (1996).
- [5] W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.* **96**, 98 (1965).
- [6] W. Rieger, H. Nowotny, F. Benesovsky, *Monatsh. Chem.* **96**, 232 (1965).
- [7] Y.-U. Kwon, J. D. Corbett, *Chem. Mater.* **4**, 1348 (1992).
- [8] H. L. Krauss, H. Stach, *Z. Anorg. Allg. Chem.* **366**, 34 (1969).
- [9] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **10**, 73 (1977).
- [10] Y.-U. Kwon, J. D. Corbett, *Chem. Mater.* **2**, 27 (1990).
- [11] G. M. Sheldrick, SHELXS-86, Program for the Solution of Crystal Structures, University of Göttingen, Germany (1986).
- [12] G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, University of Göttingen, Germany (1993).
- [13] K. Åmark, B. Boren, A. Westgren, *Svensk Kem. Tidskr.* **48**, 273 (1936).
- [14] B. Aronsson, *Acta Chem. Scand.* **14**, 1414 (1960).
- [15] R. Kieffer, F. Benesovsky, *B. Lux, Planseeber.* **4**, 30 (1956).
- [16] P. Villars, L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*; American Society for Metals, Metals Park, OH, USA (1991).
- [17] M. Brylak, W. Jeitschko, *Z. Naturforsch.* **49b**, 747 (1994).
- [18] E. Keller, SCHAKAL92, Kristallographisches Institut, Universität Freiburg (1993).
- [19] A. Simon, *Angew. Chem.* **93**, 23 (1981).
- [20] J. D. Corbett, E. Garcia, Y.-U. Kwon, A. Guloy, *Pure Appl. Chem.* **62**, 103 (1990).
- [21] L. Pauling, *Die Natur der Chemischen Bindung*, p. 245, VCH, Weinheim (1973).
- [22] J. Donohue, *The Structures of the Elements*, Wiley, New York (1974).