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Representatives of the structure type $MgCu_4Sn$ in the {Zr,Hf}–Cu–Ag systems

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Two ternary intermetallides, $ZrCu_4Ag$ and $HfCu_4Ag$, were synthesized by arc melting and annealed at 600°C; their crystal structures were studied by X-ray powder diffraction. The structures belong to the family of Friauf-Laves phases and are isotypic to $MgCu_4Sn$: Pearson symbol *cF*24, space group *F*-43*m*, $a = 6.9597(1)$ Å for $ZrCu_4Ag$ (refined composition $ZrCu_{4.05(2)}Ag_{0.95(2)}$), and $a = 6.9133(1)$ Å for $HfCu_4Ag$. The refinement indicated significant off-stoichiometry for the latter, $HfCu_{4.22(1)}Ag_{0.78(1)}$. No deviation from cubic symmetry was detected.

Zirconium / Hafnium / Copper / Silver / X-ray powder diffraction / Crystal structure / Friauf-Laves phase

1. Introduction

According to Pearson's Crystal Data [1], more than 140 ternary compounds have been reported to crystallize with structures that belong to the type $MgCu_4Sn$. The majority of these (87 %) contain rare-earth metals, but, as can be seen from Table 1, complete rows of isotypic compounds with each of the rare-earth elements, are not known. The maximum number of compounds, 14 representatives, is observed in the *R*–Ni–Cd and *R*–Ni–In systems, where *R* = Sc, Y, Ce-Sm, Gd-Lu). Up to date, the most "active" rare-earth metal is ytterbium, which forms 13 ternary compounds isotypic to $MgCu_4Sn$, whereas europium forms only one ternary compound, $EuPt_4In$.

Other ternary compounds isotypic to $MgCu_4Sn$ (13 %) form in systems with uranium (ten compounds: U–Cu–Au, U–Co–{In,Sn}, U–Ni–{Zn,Al,In,Sn}, and U–Pt–{Ir,Pd,Au}), magnesium (two compounds: Mg–Ca–Ni and Mg–Cu–In), calcium (two compounds: Ca–Cu–In and Ca–Au–Bi), zirconium (two compounds: Zr–Ni–{Zn,Sn}), potassium (one compound: K–Pb–Bi), and manganese (one compound: Mn–Cu–Sn).

The structure type $MgCu_4Sn$ (Pearson symbol *cF*24, space group *F*-43*m*) [2] belongs to the family of Friauf-Laves phases and is the second, in chronologic order of discovery, ternary phase of this class of structures. It can be derived from the binary structure type $MgCu_2$ (*cF*24, *Fd*-3*m*) [3] *via* ordered replacement of half of the Mg atoms by Sn atoms, or from $AuBe_5$ (*cF*24, *F*-43*m*) [4] *via* ordered substitution for 1/5 of the Be atoms.

The aim of the present work was to determine the structure of the ternary compound $ZrCu_4Ag$, for which a tetragonal unit cell was reported during an investigation of the phase diagram [5]. We also looked for a compound of the same stoichiometry in the closely related system Hf–Cu–Sn, where the existence of a $MgCu_4Sn$-type compound has been suspected but not yet experimentally proven.

2. Experimental

Samples of nominal compositions $Zr_{16.7}Cu_{66.6}Ag_{16.7}$ and $Hf_{16.7}Cu_{66.6}Ag_{16.7}$ were synthesized from the elements (purity for Zr ≥ 99.9 mass%, for Hf ≥ 99.9 mass%, for Cu ≥ 99.99 mass%, and for Ag ≥ 99.999 mass%) by arc-melting in a water-cooled copper crucible under a purified argon atmosphere (Ti getter), using a tungsten electrode. To achieve high efficiency of the interaction between the components, the sample was melted twice. The ingots were annealed at 600°C in quartz ampoules under vacuum for 1 month and subsequently quenched in cold water. The mass losses during the preparation of the samples were less than 1 % of the total mass, which was 1 g for each alloy.

Table 1 Ternary compounds with $MgCu_4Sn$-type structures in the systems R–{Cu,Co,Ni,Pt}–M (R = Sc, Y, La-Lu, M = Be, Mg, Ag, Au, Cd, Mn, Ni, Pd, In, Tl, Sn) [1].

M*/*R	**Sc**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
R–Cu–M																
Be														+		
Mg		+													+	
Ag					+	+	+		+	+	+	+	+	+	+	
Au									+	+	+	+	+		+	
Cd												+	+	+	+	
Ni																+
Pd						+	+		+	+	+	+	+		+	
In	+	+				+	+		+	+	+	+	+	+	+	+
Tl															+	
Sn	+														+	
R–Co–M																
Mg				+												
In											+	+	+	+		+
R–Ni–M																
Mg	+	+	+	+	+	+	+		+	+	+	+	+	+	+	+
Au	+	+							+	+	+	+	+	+	+	+
Cd	+	+		+	+	+	+		+	+	+	+	+	+	+	+
Mn				+						+						
In	+	+		+	+	+	+		+	+	+	+	+	+	+	+
Sn	+														+	+
R–Pt–M																
In			+	+	+	+	+	+	+	+	+	+	+			

Phase and structural analyses were performed based on X-ray powder diffraction data collected on a diffractometer of the model STOE Stadi P (Cu $K\alpha_1$ radiation, wavelength $\lambda = 1.5406$ Å) in the angular range $10 \leq 2\theta \leq 110.625°$ with a step of 0.015° and a scan time of 350 s. The profile and structural parameters were refined by the Rietveld method, using the program DBWS-9708 [6]. The structure drawings were made with the program ATOMS [7].

3. Results and discussion

The phase analysis by X-ray powder diffraction of the alloys $Zr_{16.7}Cu_{66.6}Ag_{16.7}$ and $Hf_{16.7}Cu_{66.6}Ag_{16.7}$ showed that both were two-phase samples. They contained as main phase the compounds $ZrCu_4Ag$ and $HfCu_4Ag$, respectively, together with small amounts of elementary silver.

The initial model used to refine the crystal structures of the studied compounds was the structure type $AuBe_5$. During the refinement the model was changed from the binary structure type $AuBe_5$ to its ternary derivative $MgCu_4Sn$. In the prototype $MgCu_4Sn$, each kind of atom occupies a distinct Wyckoff position of space group F-43m: Mg – 4a, Cu – 16e, Sn – 4c. In the structures of the investigated compounds the Wyckoff positions 4a and 16e are also occupied by one kind of atom, Zr or Hf, and Cu, respectively, but the position 4c was found to be occupied by a mixture of Ag and Cu atoms, with a majority of Ag atoms. The compositions from the Rietveld refinements were $ZrCu_{4.05(2)}Ag_{0.95(2)}$ and $HfCu_{4.22(1)}Ag_{0.78(1)}$. Possible partial substitution of Ag for Zr or Hf could be excluded.

Experimental details of the structural refinement of the compounds $ZrCu_4Ag$ and $HfCu_4Ag$, and their crystallographic data are presented in Table 2. The atom coordinates and isotropic displacement parameters are listed in Table 3, and interatomic distances and coordination numbers are given in Table 4. The observed and calculated diffraction diagrams are shown in Fig. 1. The content of one unit cell for the compound $ZrCu_4Ag$ and the coordination polyhedra of the three sites are presented in Fig. 2.

A binary phase of composition $ZrCu_5$ with $AuBe_5$ type structure was reported in [8]. Later, doubts appeared concerning the exact composition and the structure, and the same authors reported the result of a study on single-crystal diffraction data [9], where a more complicated structure, in agreement was revealed. The composition was found to be close to Zr_2Cu_9 and the structure a tetragonal derivative of the cubic $AuBe_5$ type, with $a_0 = 6.856(2)$, $c_0 = 6.882(2)$ Å. Weak reflections indicated a possible superstructure with $c = 10c_0$, explained by partial replacement of Cu atoms by Zr atoms. The composition Zr_2Cu_9 was later confirmed by electron probe microanalysis (EPMA) [10], and is in the generally accepted phase diagram of the Zr–Cu system [11] assigned to the Cu-richest phase, for which peritectic melting at 1012°C has been reported.

Table 2 Details of the structural refinements for $ZrCu_4Ag$ and $HfCu_4Ag$.

Compound	$ZrCu_{4.05(2)}Ag_{0.95(2)}$	$HfCu_{4.22(1)}Ag_{0.78(1)}$
Content, mass%	98.6(7)	97.7(3)
Space group	F-43m	
Cell parameter a, Å	6.9597(1)	6.9133(1)
Cell volume V, Å^3	337.11(1)	330.41(1)
Formula units per cell Z	4	
Density D_X, Mg m^{-3}	8.956	10.691
FWHM parameters U, V, W	0.190(9), -0.122(7), 0.048(3)	0.048(5), 0.016(6), 0.009(1)
Mixing parameter η	1.087(7)	1.103(9)
Asymmetry parameter C_M	-0.005(3)	-0.004(4)
Texture parameter G [direction]	0.989(5) [111]	0.966(6) [111]
Number of reflections	23	
Number of refined parameters	13	
Reliability factors R_B, R_p, R_{wp}	0.0139, 0.0770, 0.1093	0.0257, 0.0834, 0.1178

Table 3 Atom coordinates and isotropic displacement parameters for $ZrCu_4Ag$ and $HfCu_4Ag$: structure type $MgCu_4Sn$, $cF24$, F-43m.

Site	Wyckoff position	$ZrCu_4Ag$, a = 6.9597(1) Å, M = 0.95(2)Ag + 0.05(2)Cu				$HfCu_4Ag$, a = 6.9133(1) Å, M = 0.78(1)Ag + 0.22(1)Cu			
		x	y	z	B_{iso}, Å^2	x	y	z	B_{iso}, Å^2
Zr/Hf	4a	0	0	0	1.43(4)	0	0	0	1.05(3)
Cu	16e	0.6244(2)	0.6244(2)	0.6244(2)	1.73(5)	0.6248(2)	0.6248(2)	0.6248(2)	1.16(4)
M	4c	¼	¼	¼	1.73(5)	¼	¼	¼	1.16(4)

Table 4 Interatomic distances for $ZrCu_4Ag$ and $HfCu_4Ag$.

Atoms		δ, Å	Atoms		δ, Å	Coordination number
Zr	- 12 Cu	2.887(1)	Hf	- 12 Cu	2.867(1)	16
	- 4 M	3.014(1)		- 4 M	2.994(1)	
Cu	- 3 Cu	2.449(2)	Cu	- 3 Cu	2.440(2)	12
	- 3 Cu	2.472(2)		- 3 Cu	2.448(2)	
	- 3 M	2.884(1)		- 3 M	2.866(1)	
	- 3 Zr	2.887(1)		- 3 Hf	2.867(1)	
M [a]	- 12 Cu	2.884(1)	M [b]	- 12 Cu	2.866(1)	16
	- 4 Zr	3.014(1)		- 4 Hf	2.994(1)	

[a] M = 0.95(2)Ag + 0.05(2)Cu; [b] M = 0.78(1)Ag + 0.22(1)Cu.

One ternary phase, called "m", was found in the isothermal section of the phase diagram of the ternary Zr–Cu–Ag system at room temperature [5]. A certain homogeneity range was observed, in particular for Ag and Cu (16.4-17.6 at.% Zr, 64.4-70.6 at.% Cu, 13-18 at.% Ag). A slightly larger homogeneity range was found during an investigation of the isothermal section of the same system at 1023 K [12] (15.2-17.2 at.% Zr, 67.7-75.2 at.% Cu, 9.2-15.4 at.% Ag). The composition obtained from the Rietveld refinement in this work ($Zr_{16.7}Cu_{67.5}Ag_{15.8}$) is in good agreement with the Ag-rich limit of the homogeneity range reported at 1023 K. In both phase diagram studies, the m-phase was found to be in equilibrium with elementary silver on the Ag-rich side. The phase relations on the Ag-poor side were tentatively assigned and included a pseudo-binary equilibrium with the Cu_9Zr_2 phase reported with a structure derived from $AuBe_5$. An EPMA analysis of a sample containing both these phases [12] showed a significantly lower Zr content, close to 16.7 at.%, in the m-phase, whereas the Zr content in the Cu_9Zr_2 phase remained near 18.2 at.%, also after dissolution of some Ag.

The Zr–Cu system has attracted interest, among others because of its glass-forming properties, however, less information is available on the Hf–Cu system. The phase diagram on the Cu-rich side is similar to the phase diagram of the Zr–Cu system, before reconsideration of the $ZrCu_5$ phase. An $HfCu_5$ compound of unknown structure has been reported with a peritectic temperature of 1055°C [11].

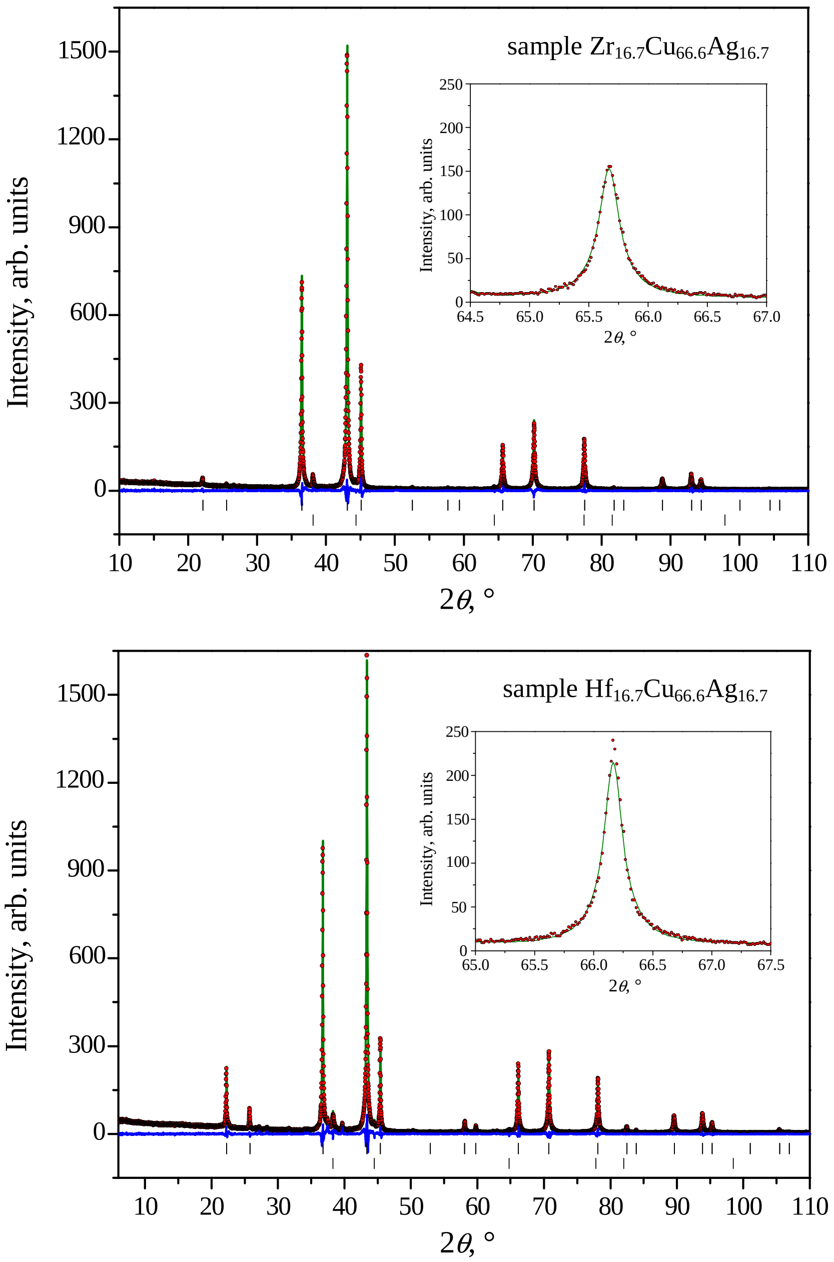

Fig. 1 Observed (dots), calculated (line) and difference (bottom) X-ray powder diffraction patterns (Cu $K\alpha_1$ radiation) for the samples $Zr_{16.7}Cu_{66.6}Ag_{16.7}$ and $Hf_{16.7}Cu_{66.6}Ag_{16.7}$; vertical bars indicate the peak positions of the compounds $ZrCu_4Ag$ and $HfCu_4Ag$ (upper row) and elementary Ag (bottom row). The insets show enlargements of the 224 peaks.

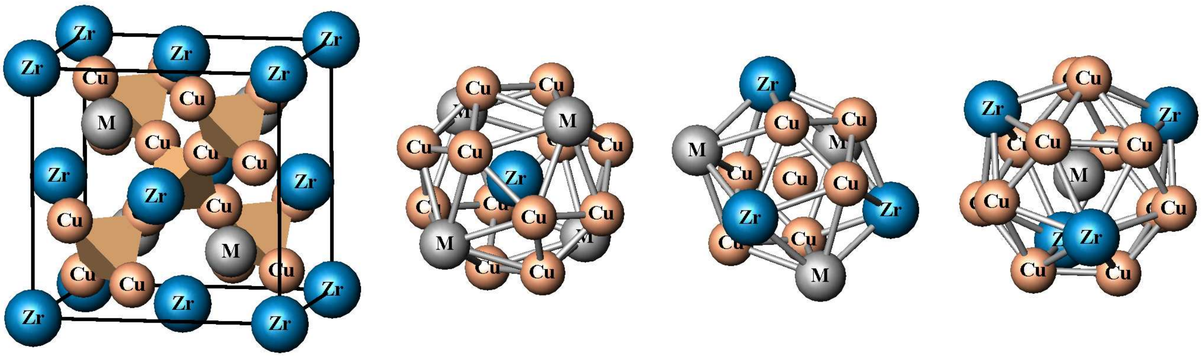

Fig. 2 Unit cell content and coordination polyhedra for $ZrCu_4Ag$.

The $AuBe_5$ type is considered as one of the plausible types adopted by this compound, and an optimized cell parameter of 6.892 Å was used in a recent computational study of the Hf–Cu system [13]. To our knowledge, no information is available on the Hf–Cu–Ag system.

A body-centered tetragonal unit cell was assigned to the ternary m-phase during the investigation of the Ag–Cu–Zr system [5]. The cell parameters, $a = 4.921$, $c = 6.917$ Å, reveal a clear relation to the cubic $MgCu_4Sn$ type cell, the parameters of the F-centered tetragonal unit cell being $\sqrt{2}a = 6.959 \approx c = 6.917$ Å. These values are clearly larger than those reported for Zr_2Cu_9 and the c/a ratio is in this case < 1 instead of > 1 for the binary compound. The average cell parameter, 6.945 Å, is, however, in good agreement with the cell parameter obtained here, 6.9597(1) Å. The latter was obtained at the Ag-rich boundary, *i.e.* it is expected to be the largest value within the homogeneity range, whereas the exact composition for the former is not known. It can be seen from Fig. 1 that the diffraction pattern is well explained by the presence of cubic $ZrCu_4Ag$ and small amounts of elementary silver (1.4(7) mass%). No significant line broadening was detected. The situation is similar for $HfCu_4Ag$, even if the refined composition ($HfCu_{4.22(1)}Ag_{0.78(1)}$) is here quite off the stoichiometric composition – the Rietveld refinement is satisfactory and no line broadening was observed. A certain deviation from cubic symmetry can of course not be excluded under other conditions.

Among the RCu_4Ag phases, off-stoichiometry has been studied for the Yb-containing phase [14], where a homogeneity range between $Yb_{1.1}Ag_{0.9}Cu_4$ and $Yb_{0.8}Ag_{1.2}Cu_4$ was found. In this case the Cu content remains constant at 66.7 at.% and the Ag atoms presumably substitute for Yb atoms. It may be noted that the binary RCu_5 phases crystallize with the hexagonal structure type $CaCu_5$, and the isoelectronic substitution by larger Ag atoms stabilizes the cubic Laves phase.

The replacement of Cu atoms by Ag atoms with a larger radius ($r_{Cu} = 1.278$, $r_{Ag} = 1.445$ Å [15]) causes an increase of the cell parameter for the ternary phases $ZrCu_4Ag$ and $HfCu_4Ag$. The cell parameter of the hafnium-containing compound is smaller than that of the zirconium-containing compound because of the lower content of Ag and the smaller atomic radii of Hf ($r_{Hf} = 1.580$, $r_{Zr} = 1.602$ Å [15]), due to the lanthanide contraction.

The structures of the two compounds studied here belong to the family of Friauf-Laves phases and the Cu atoms from the site in Wyckoff position 16*e* form empty tetrahedra. The interatomic distances $\delta_{Cu\text{-}Cu}$ within the tetrahedra are similar in the two compounds ($\delta_{Cu\text{-}Cu} = 2.449(2)$ and 2.472(2) Å for $ZrCu_4Ag$ and $\delta_{Cu\text{-}Cu} = 2.440(2)$ and 2.448(2) Å for $HfCu_4Ag$). In both compounds the $\delta_{Cu\text{-}Cu}$ distances are shorter than the $\delta_{Cu\text{-}M}$ distances ($\delta_{Cu\text{-}M} = 2.884(1)$ Å for $ZrCu_4Ag$ and $\delta_{Cu\text{-}M} = 2.866(1)$ Å for $HfCu_4Ag$), which is related to the high content of Ag on the M site.

For the Zr/Hf atoms and for the mixture of Ag and Cu atoms the coordination polyhedra are 16-vertex Frank-Kasper polyhedra. The Cu atoms are smaller and are situated inside icosahedra. The coordination polyhedron of the Zr/Hf site consists of four (Ag,Cu) atoms from the M site, which form a tetrahedron, and twelve Cu atoms, which form a truncated tetrahedron. A similar polyhedron is observed for the M site, occupied mainly by Ag atoms: four Zr/Hf atoms form the tetrahedron and twelve Cu atoms the truncated tetrahedron. The icosahedra around the Cu atoms are built up of three Zr/Hf atoms, six Cu atoms, and three Ag or Cu atoms from the mixed site.

Conclusions

The structures of $ZrCu_4Ag$ and $HfCu_4Ag$ at 600°C belong to the family of Friauf-Laves phases and are isotypic to cubic $MgCu_4Sn$ (space group F-43m). Contrary to literature reports, no deviation from cubic symmetry was detected. The former compound is close to the stoichiometric composition ($ZrCu_{4.05(2)}Ag_{0.95(2)}$), whereas the latter is off-stoichiometric ($HfCu_{4.22(1)}Ag_{0.78(1)}$). A mixture of Ag and Cu atoms (with a majority of Ag atoms) was found only on one site (Wyckoff position 4*c*), the two others (4*a* and 16*e*) being occupied by one kind of atom (Zr or Hf, and Cu, respectively).

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