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Crystal structure of Zr_5AlGe_3

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The new ternary intermetallic compound Zr_5AlGe_3 was synthesized and its crystal structure was determined by X-ray single-crystal diffraction (structure type Hf_5CuSn_3, Pearson symbol *hP*18, space group $P6_3/mcm$, $a = 8.104(3)$, $c = 5.654(2)$ Å, $Z = 2$). The structure type Hf_5CuSn_3 is a ternary variant of the structure type Ti_5Ga_4 and a filled-up variant of the Mn_5Si_3 type. $\underline{Zr}Ge_6$ and $\underline{Al}Zr_6$ octahedra are connected by common faces and form 1D-rods along the crystallographic direction [001], the former sharing edges to build up a 3D-framework with channels hosting the latter. At 600°C no solid solution was observed between the Mn_5Si_3-type binary compound Zr_5Ge_3 and the ternary compound Zr_5AlGe_3.

Zirconium / Aluminum / Germanium / X-ray single-crystal diffraction / Crystal structure

Introduction

The phase diagram of the ternary system Zr–Al–Ge has to our knowledge not yet been investigated. The structural evolution in the Al-rich alloys $ZrAl_{3-x}Ge_x$ (x = 0-0.8) at 600°C, when Al atoms are progressively replaced by Ge atoms, and the crystal structure of the ternary compound $ZrAl_{2.5}Ge_{0.5}$ (structure type $TiAl_3$, Pearson symbol *tI*8, space group $I4/mmm$: $a = 3.92395$, $c = 9.0476$ Å) were reported in [1]. Information on the phase relations in the Zr-rich part of the system Zr–Al–Ge is absent in the literature.

The aim of the present work was to refine the crystal structure of the new ternary compound Zr_5AlGe_3, discovered during an investigation of the Zr–Al–Ge system. The structure was identified as belonging to the structure type Hf_5CuSn_3 (Pearson symbol *hP*18, space group $P6_3/mcm$) [2], which is a ternary filled-up variant of the Mn_5Si_3 type (*hP*16, $P6_3/mcm$) [3]. Among the related ternary systems of Ti, Zr, or Hf with *p*-elements of group III, IV, or IV, isotypic ternary phases have only been reported for some of the systems {Zr,Hf}–{Al,Ga}–{Sn,Sb} (Table 1). However, in the binary systems Ti–{Ga,Sb}, Zr–{Al,Ga,Sn,Pb,Sb}, and Hf–Sn the existence of several compounds T_5M_4 adopting the binary variant of the Hf_5CuSn_3 type, the Ti_5Ga_4 type (*hP*18, $P6_3/mcm$) [10], has been reported. Like Hf_5CuSn_3, the structure type Ti_5Ga_4 is a filled-up derivative of the Mn_5Si_3 type. In the system Zr–Al–Ge three binary compounds have been reported with one of these types: Zr_5Al_3 (Mn_5Si_3, *hP*16, $P6_3/mcm$, $a = 8.184$, $c = 5.702$ Å) [11], Zr_5Al_4 (Ti_5Ga_4, *hP*18, $P6_3/mcm$, $a = 8.447$, $c = 5.810$ Å) [12], and Zr_5Ge_3 (Mn_5Si_3, *hP*16, $P6_3/mcm$, $a = 7.99$, $c = 5.54$ Å) [13]. It should be noted that the voids in Mn_5Si_3-type structures can sometimes be occupied by small atoms, easily overlooked, such as C, N, or O (structure type Hf_5CuSn_3), *e.g.* Zr_5Al_3C, Zr_5Al_3N, $Zr_5Al_3O_{0.17}$ [4].

Experimental

An alloy of nominal composition $Zr_{55.6}Al_{11.1}Ge_{33.3}$ was synthesized from high-purity metals (≥ 99.9 mass %) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using a tungsten electrode and Ti as a getter. To achieve homogeneity the sample was melted twice. After the synthesis the ingot was wrapped into tantalum foil, sealed in a quartz ampoule under vacuum and annealed at 600°C for 720 h. Finally the ampoule with the sample was quenched into cold water. The mass loss did not exceed 1 mass% of the total mass, which was approximately 1 g.

Table 1 Unit-cell parameters for ternary compounds with Hf_5CuSn_3-type structures (Pearson symbol *hP*18, space group $P6_3/mcm$) reported in the systems {Zr,Hf}–{Al,Ga}–{Sn,Sb} [4].

Compound	Unit-cell parameters, Å		Ref.
	a	*c*	
Zr_5AlSn_3	8.655	5.871	[5]
Zr_5GaSn_3	8.6599	5.8794	[5]
Hf_5GaSn_3 [a]	8.5564	5.7859	[6,7]
Zr_5AlSb_3	8.5802	5.8465	[8]
Hf_5GaSb_3	8.4747	5.7190	[9]

[a] limiting composition of the solid solution $Hf_5Ga_xSn_3$ (x = 0-1) of inclusion type

A prism-like single crystal was extracted from the alloy, mounted on a glass fiber and X-ray diffraction data were collected on a Rigaku AFC7 diffractometer, equipped with a Mercury CCD detector (graphite monochromator, Mo $K\alpha$ radiation, λ = 0.71073 Å) at room temperature. No significant variations of the intensities were observed during the data collection. An absorption correction was performed applying a multi-scan procedure.

The structure was solved by direct methods in the centrosymmetric hexagonal space group $P6_3/mcm$; the positional and anisotropic displacement parameters were refined by the full-matrix least-squares method, using the program package WinCSD [14]. Experimental details and crystallographic data for Zr_5AlGe_3 are listed in Table 2.

Results and discussion

The structure of the ternary compound Zr_5AlGe_3 belongs to the structure type Hf_5CuSn_3 (Pearson symbol *hP*18, space group $P6_3/mcm$), which represents a ternary ordered variant of the structure type Ti_5Ga_4, which is a filled up derivative of the structure type Mn_5Si_3 (*hP*16, $P6_3/mcm$). Atom coordinates and isotropic displacement parameters from the refinement are given in Table 3. The structure of Zr_5AlGe_3 is characterized by two sites occupied by Zr atoms, one site by Al atoms, and one site by Ge atoms. The Al atoms occupy Wyckoff position 2*b*, which is empty in the structure of the binary germanide Zr_5Ge_3 (structure type Mn_5Si_3). According to preliminary results of an investigation of the phase relations in the system Zr–Al–Ge, at 600°C Zr_5AlGe_3 is a distinct ternary compound, whereas the binary compound Zr_5Ge_3 dissolves up to 8 at.% Al forming a solid solution $Zr_5Al_xGe_{3-x}$ (x = 0-0.64) of the substitution type.

The interatomic distances and coordination numbers in the structure of Zr_5AlGe_3 are summarized in Table. 4. The interatomic distances correlate with the sums of the atomic radii of the elements (r_{Zr} = 1.60, r_{Al} = 1.431 and r_{Ge} = 1.225 Å [15]) and are also in good agreement with the distances in the structures of known binary zirconium aluminides and germanides.

Table 2 Experimental details and crystallographic data for Zr_5AlGe_3.

Compound composition		Zr_5AlGe_3
Formula weight		701.02
Structure type		Hf_5CuSn_3
Pearson symbol		*hP*18
Space group		$P6_3/mcm$
Unit-cell parameters:	*a*, Å	8.104(3)
	c, Å	5.654(2)
Cell volume V, $Å^3$		321.62(18)
Formula units per cell Z		2
Density D_X, g cm^{-3}		7.241
Absorption coefficient μ, mm^{-1}		22.2
Number of reflections:	measured	1558
	independent	248
	with $F > 3\sigma(F)$	248
Reliability factor	R_{eq}	0.0392
Range of h, k, l		$-10 \le h \le 9$, $-6 \le k \le 12$, $-8 \le l \le 8$
θ_{max}, °		33.4
Reliability factors:	R	0.0357
	wR	0.0375
	S	1.01

Table 3 Atomic coordinates, anisotropic and equivalent isotropic displacement parameters for Zr_5AlGe_3 (Hf_5CuSn_3, *hP*18, $P6_3/mcm$, a = 8.104(3), c = 5.654(2) Å, R = 0.0357, wR = 0.0375).

Site	Wyckoff position	x	y	z	B_{eq}, Å^2
Zr1	6*g*	0.2567(2)	0	¼	1.21(4)
Zr2	4*d*	⅓	⅔	0	0.87(3)
Al	2*b*	0	0	0	1.27(14)
Ge	6*g*	0.6100(2)	0	¼	1.05(4)

Site	B_{11}, Å^2	B_{22}, Å^2	B_{33}, Å^2	B_{12}, Å^2	B_{13}, Å^2	B_{23}, Å^2
Zr1	1.25(4)	0.87(5)	1.09(5)	0.43(2)	0	0
Zr2	0.86(3)	0.86(3)	0.59(5)	0.43(2)	0	0
Al	1.4(2)	1.4(2)	0.6(2)	0.69(9)	0	0
Ge	0.96(4)	0.94(5)	0.94(5)	0.47(3)	0	0

Table 4 Interatomic distances (δ) and coordination numbers (CN) in the structure of Zr_5AlGe_3 (Hf_5CuSn_3, *hP*18, $P6_3/mcm$, a = 8.104(3), c = 5.654(2) Å).

Atoms	δ, Å	CN
Zr1 – 2 Al	2.5151(8)	11
– 1 Ge	2.782(1)	
– 2 Ge	2.864(1)	
– 2 Ge	3.0261(8)	
– 4 Zr2	3.3702(9)	
Zr2 – 2 Zr2	2.8270(8)	14
– 6 Ge	2.8752(8)	
– 6 Zr1	3.3702(9)	

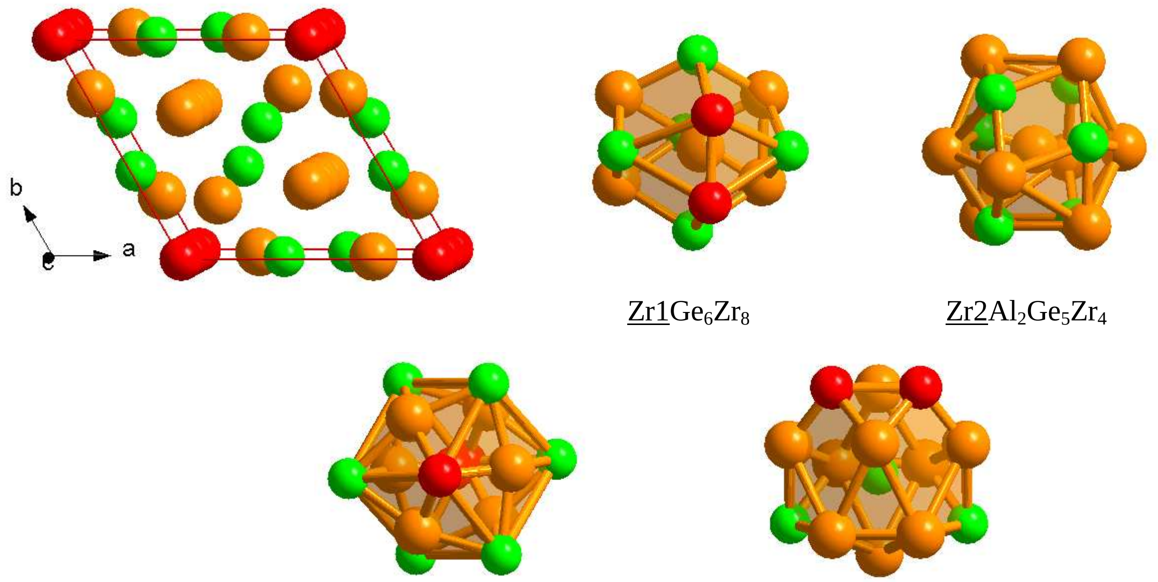
Atoms	δ, Å	CN
Al – 6 Zr1	2.5151(8)	14
– 2 Al	2.8270(8)	
– 6 Ge	3.4616(9)	
Ge – 2 Zr1	2.782(1)	13
– 2 Zr1	2.864(1)	
– 4 Zr2	2.8752(8)	
– 1 Zr1	3.0261(8)	
– 2 Ge	3.3430(9)	
– 2 Al	3.4616(9)	

The shortest distances in the structure are distances between the sites Zr1 and Al (2.515 Å). These are shorter than in the binary aluminide Zr_5Al_4 (2.849 Å) [12], which crystallizes with a Ti_5Ga_4-type structure. Insertion of Al atoms into $Zr1_6$ octahedra in the structure of Zr_5Ge_3 [13] leads to an expansion of these (the distance from the center of the octahedron to its vertices increases from 2.340 Å in Zr_5Ge_3 to 2.515 Å in Zr_5AlGe_3) and to an expansion of the hexagonal unit cell. Another feature of the structure of the title compound is the short Zr2-Zr2 distance (2.827 Å), indicating strong interaction between Zr atoms. Similar behavior has been reported for the isostructural phases listed in Table 1.

The content of the unit cell of Zr_5AlGe_3 and the coordination polyhedra of the atoms are shown in Fig. 1. The Zr atoms are coordinated by 11 (site Zr1) and 14 (site Zr2) atoms and form polyhedra of composition $\underline{Zr1}Al_2Ge_5Zr_4$ and $\underline{Zr2}Ge_6Zr_8$, respectively. The defect anticubooctahedron $\underline{Zr1}Al_2Ge_5Zr_4$ can also be seen as a deformed pentagonal bipyramid of composition Al_2Ge_5 with four additional Zr atoms, or as a tricapped trigonal prism of composition Ge_5Zr_4 with two additional Al atoms. The Frank-Kasper polyhedron $\underline{Zr2}Ge_6Zr_8$ can be described as a deformed hexagonal prism of composition Ge_6Zr_6 with two Zr atoms capping the hexagonal faces. The atoms belonging to the closest environment of the Al atoms also form Frank-Kasper polyhedra consisting of 14 atoms, $\underline{Al}Zr_6Al_2Ge_6$. These polyhedra are deformed rhombododecahedra formed by an Al_2Ge_6 cube and a Zr_6 octahedron. The Ge atoms are coordinated by nine Zr atoms, two Al and two Ge atoms forming a Frank-Kasper 13-vertex polyhedron of composition $\underline{Ge}Zr_9Ge_2Al_2$. It can be described as a deformed anticubooctahedron with one additional atom, or as a tricapped trigonal prism of composition Zr_9 with four additional atoms.

The coordination number and polyhedron of the Zr1 site changes when Al is inserted into the structure of the binary compound Zr_5Ge_3. The 15-vertex polyhedron in the structure of Zr_5Ge_3 (deformed pentagonal prism Zr_{10} with five additional Ge atoms capping the two bases and three lateral faces) transforms into an 11-vertex polyhedron in the structure of Zr_5AlGe_3. The coordination numbers and polyhedron types of the other atoms do not change.

In the structure of the ternary compound Zr_5AlGe_3 columns of simple polyhedra may be considered. Distorted $\underline{Zr}Ge_6$ octahedra share edges, forming cavities in which $\underline{Al}Zr_6$ octahedra are situated (Fig. 2). The $\underline{Zr}Ge_6$octahedra, as well as the $\underline{Al}Zr_6$ octahedra, are connected by common faces along the crystallographic direction [001] and form a 3D-framework and 1D-rods, respectively. It is interesting to note that, in the structure of Zr_5AlGe_3, as in the structures of the isotypic ternary phases listed in Table 1, atoms of a *d*-element (Zr) center octahedra formed by atoms of a *p*-element (Ge) and *vice versa*, Al atoms (*p*-element) center octahedra formed by Zr atoms (*d*-element).



$\underline{\mathrm{Zr1}}\mathrm{Ge_6Zr_8}$ $\underline{\mathrm{Zr2}}\mathrm{Al_2Ge_5Zr_4}$

$\underline{\mathrm{Al}}\mathrm{Zr_6Al_2Ge_6}$ $\underline{\mathrm{Ge}}\mathrm{Zr_9Al_2Ge_2}$

Fig. 1 Content of the unit cell and coordination polyhedra of the atoms in the structure of Zr_5AlGe_3 (yellow balls – Zr, red – Al, and green – Ge atoms).

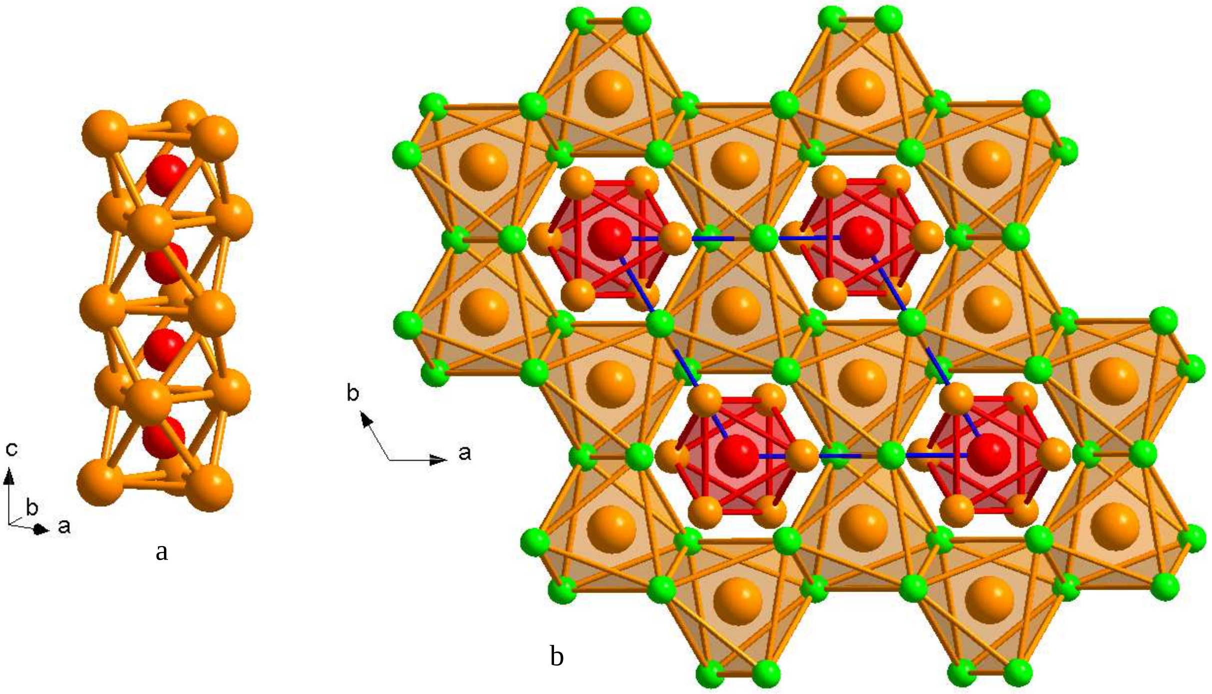


Fig. 2 Part of an infinite column of Al-centered Zr_6 octahedra along [001] (a) and 3D-framework of Zr-centered Ge_6 octahedra with Al-centered Zr_6 octahedra in channels (b) in the structure of Zr_5AlGe_3 (yellow balls – Zr, red – Al, and green – Ge atoms).

Conclusions

A new ternary compound, Zr_5AlGe_3, was synthesized and its crystal structure was determined by means of X-ray single-crystal diffraction. The structure belongs to the structure type Hf_5CuSn_3, which is a ternary ordered derivative of Ti_5Ga_4 and a filled-up variant of the Mn_5Si_3 type. The Al atoms occupy Wyckoff position 2*b* at the origin of the unit cell and center Zr_6 octahedra. The structure can be visualized as built up from columns of $\underline{Zr}Ge_6$ and $\underline{Al}Zr_6$ octahedra running along the crystallographic direction [001].

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