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Interstitial solid solution $Hf_5Ga_xSn_3$ ($x = 0–1$)

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ABSTRACT

Formation of an interstitial solid solution $Hf_5Ga_xSn_3$ ($x = 0–1$) based on the binary compound Hf_5Sn_3 (structure type Mn_5Si_3, Pearson symbol *hP*16, space group $P6_3/mcm$, $a = 8.36562(6)$, $c = 5.70775(4)$ Å from X-ray powder diffraction) was established at 600 °C. The crystal structure (structure type Hf_5CuSn_3, ordered derivative of Ti_5Ga_4, *hP*18, $P6_3/mcm$) was refined on X-ray single-crystal diffraction data for three compositions: $Hf_5Ga_{0.16(3)}Sn_3$ ($a = 8.3288(12)$, $c = 5.6988(11)$ Å), $Hf_5Ga_{0.53(2)}Sn_3$ ($a = 8.4205(12)$, $c = 5.7655(12)$ Å) and Hf_5GaSn_3 ($a = 8.5564(12)$, $c = 5.7859(12)$ Å). The Ga atoms occupy Wyckoff position 2*b* at the centres of Hf_6 octahedral interstices.

1. Introduction

The structure type Mn_5Si_3 (Pearson symbol *hP*16, space group $P6_3/mcm$) [1] is widespread among the structures of binary intermetallic compounds M_5X_3 formed by transition metals with *p*-block elements of group IV (Si, Ge, Sn) [2]. The main feature of this structure is the existence of octahedral interstices that can be occupied by interstitial atoms. The octahedra (trigonal antiprisms) share atoms and form columns along [0 0 1]. In the case when all the interstices are fully occupied, the structure type Ti_5Ga_4 (*hP*18, $P6_3/mcm$) [3,4], or its ordered derivative Hf_5CuSn_3 (*hP*18, $P6_3/mcm$) [5], is realized.

The binary system Hf–Sn is characterized by the formation of the phases Hf_5Sn_3 and Hf_5Sn_4 crystallizing with Mn_5Si_3 and Ti_5Ga_4 structure types, respectively. The Hf_5Sn_3 binary compound with Mn_5Si_3-type structure is formed incongruently at 1900 °C, whereas the type and temperature of the formation of Hf_5Sn_4 with Ti_5Ga_4-type structure was not established [6]. The crystal structure of Hf_5Sn_3 was first determined in [7] (*hP*16, $P6_3/mcm$, $a = 8.376$, $c = 5.737$ Å). The existence of the binary compound Hf_5Sn_4 was reported in [4,5] (*hP*18, $P6_3/mcm$, $a = 8.695$, $c = 5.875$ Å).

The interstitial chemistry of isostructural Zr_5Sn_3 (structure type Mn_5Si_3) was described in [8]. The formation and crystal structures of stoichiometric Zr_5XSn_3 phases (X = B, C, N, O, Al, Si, P, S, Cu, Zn, Ga, Ge, Sn, As, Se) have also been reported in [8]. The structure was discussed in terms of incorporation of X-atoms into the chains of cofacial Zr_6 octahedra in the parent Mn_5Si_3-type structure. The crystal structure of the Ga-containing phase was studied by X-ray single-crystal and powder diffraction. The variation of the cell parameters and refined interstitial occupancies indicate the formation of a solid solution. However, its range or the structure evolution within it was not investigated, since the authors focused on the stoichiometric composition Zr_5GaSn_3 observed at 1000 °C.

Due to the close similarity between hafnium and zirconium it seemed of interest to investigate the effect of the insertion of gallium atoms into the structure of the binary compound Hf_5Sn_3. The present article is devoted to the investigation of the solubility of Ga in Hf_5Sn_3 at 600 °C and a discussion of the structural changes occurring within the interstitial solid solution $Hf_5Ga_xSn_3$ ($x = 0–1$).

2. Experimental

Alloys of the binary system Hf–Sn and the ternary system Hf–Ga–Sn were synthesized from the elements (purity >99.9 wt.%) by arc melting in a water-cooled copper crucible under purified argon, using Ti as a getter and a tungsten electrode. The ingots were wrapped into Ta foil and annealed at 600 °C in quartz ampoules under vacuum for 1 month and subsequently quenched in cold water. The weight losses during the preparation of the samples were less than 1% of the total mass, which was 1g for each alloy. In addition a sample of composition $Hf_{62.5}Sn_{37.5}$ (in at.%) was synthesized by induction melting.

Phase analysis was carried out using X-ray powder diffraction data collected on a diffractometer DRON-2.0M (Fe Kα-radiation, $\lambda = 1.93801$ Å) in the angular range $20° \le 2\theta \le 120°$ with the step 0.05°. X-ray powder diffraction data for $Hf_{62.5}Sn_{37.5}$ were collected at room temperature on a STOE Stadi P diffractometer equipped with a linear detector (Cu $K\alpha_1$ radiation, $\lambda = 1.54056$ Å, range $10° \le 2\theta \le 110°$, step

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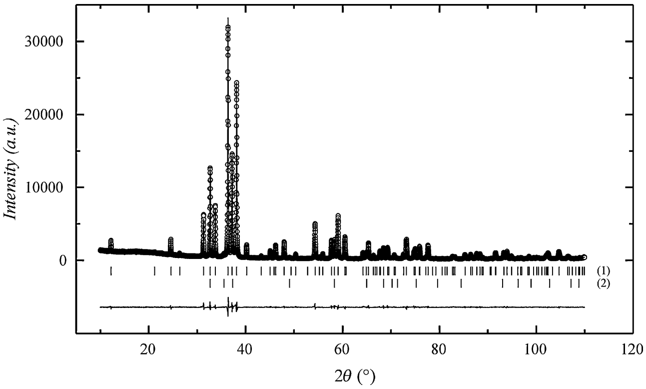


Fig. 1. Experimental (dots), calculated (line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Hf_{62.5}Sn_{37.5}$ (Cu Kα-radiation). Vertical bars indicate the positions of reflections for the Hf_5Sn_3 compound (1) and Hf (2).

0.01°). The crystal structure of the binary compound Hf_5Sn_3 was refined by the Rietveld method, starting from coordinates reported in [7]. The profile and structural parameters were refined using the FullProf Suite program package [9]. In the final refinement cycles 16 parameters were allowed to vary: sample shift, scale factor, two cell parameters, six profile parameters (pseudo-Voigt profile), two positional parameters, three atomic displacement parameters and one texture parameter. The Hf_5Sn_3 sample contained, in addition, 3.29(5) wt.% of a secondary phase, Hf, for which only the scale factor was included in the final refinement. The profile parameters for Hf were first refined and then kept fixed in the final cycles of the refinement. The background was defined using the Fourier filtering technique. Experimental, calculated and difference powder diffraction patterns of the sample of composition $Hf_{62.5}Sn_{37.5}$ are shown in Fig. 1. Experimental details and crystallographic data for Hf_5Sn_3 are listed in Table 1.

Single crystals were extracted from alloys of nominal compositions $Hf_{61}Ga_2Sn_{37}$, $Hf_{59}Ga_6Sn_{35}$ and $Hf_{55.6}Ga_{11.1}Sn_{33.3}$. They were mounted on glass fibers and X-ray diffraction data were collected in oscillation mode at room temperature on a Stoe IPDS-IIT diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Numerical absorption corrections were applied using X-Shape/X-Red software [10]. No significant variations of the intensities were observed during the data collections. Full-matrix least-squares refinements of the positional and anisotropic displacement parameters were performed on F^2 using the SHELXL-97 program [11]. For the single crystal of composition Hf_5GaSn_3 the occupancy of the Ga site was first refined (1.00(2)) and then fixed in the final refinement cycles to 1, whereas the occupancy parameters for other two compositions were allowed to vary. Experimental details and crystallographic data for the three single crystals from the interstitial solid solution $Hf_5Ga_xSn_3$ (x = 0–1) are listed in Table 2.

Table 1
Experimental details and crystallographic data for Hf_5Sn_3.

Formula weight M_r	1248.58
Structure type	Mn_5Si_3
Pearson symbol	*hP*16
Space group	$P6_3/mcm$
Unit-cell parameters	
a, Å	8.36562(6)
c, Å	5.70775(4)
Cell volume V, $Å^3$	345.933(4)
Formula units per cell Z	2
Density D_X, g cm^{-3}	11.987
Preferred orientation: value/[direction]	0.9872(8)/[0 0 1]
Scanning mode	$\theta/2\theta$
Range 2θ,°	10–110
Step size,°	0.01
Scanning time per step, s	20
Profile parameters	
U	0.0597(17)
V	0.000(2)
W	0.0078(4)
Shape parameter	0.765(3)
Asymmetry parameters	0.015(5), 0.0125(6)
Reliability factors	
R_B	0.019
R_F	0.0203
R_p	0.0448
R_{wp}	0.0583
χ^2	2.41

3. Results and discussion

X-ray phase analysis of the binary alloys of the Hf–Sn system showed the formation of only one binary compound, Hf_5Sn_3, as a single phase in the concentration range 37.5–50 at.% Sn at 600 °C. The two-phase alloy of nominal composition $Hf_{62.5}Sn_{37.5}$ contained the hexagonal phase with cell parameters a = 8.36562(6), c = 5.70775(4) Å and very small amounts of Hf, whereas all the samples with higher Sn content contained, in addition to the main phase Hf_5Sn_3, the binary compound $HfSn_2$ ($CrSi_2$ structure type, *hP*9, $P6_222$ [7]). The refined cell parameters of the phase Hf_5Sn_3 are

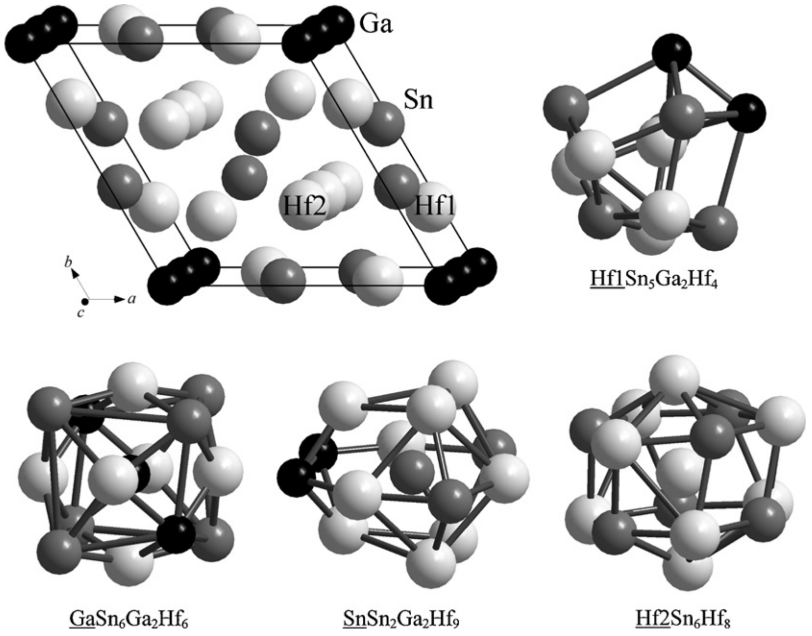


Fig. 2. Unit cell of Hf_5GaSn_3 and coordination polyhedra of the atoms.

Table 2
Experimental details and crystallographic data for three single crystals from the interstitial solid solution $Hf_5Ga_xSn_3$ ($x = 0–1$).

Refined composition	$Hf_5Ga_{0.16(3)}Sn_3$	$Hf_5Ga_{0.53(2)}Sn_3$	Hf_5GaSn_3
Formula weight M_r	1259.75	1285.55	1318.32
Structure type	Hf_5CuSn_3 (ordered derivative of Ti_5Ga_4)		
Pearson symbol	*hP*18		
Space group	$P6_3/mcm$		
Cell parameters			
a, Å	8.3288(12)	8.4205(12)	8.5564(12)
c, Å	5.6988(11)	5.7655(12)	5.7859(12)
Cell volume *V*, $Å^3$	342.36(10)	354.03(10)	366.85(11)
Formula units per cell *Z*	2		
Density D_X, g cm^{-3}	12.143	11.985	11.934
Absorption coefficient μ, mm^{-1}	43.323	42.603	41.960
Scanning mode	φ-Oscillation		
Absorption correction	Analytical method		
No. of reflections			
Measured	5005	3495	4612
Independent	162	145	175
With $F > 2\sigma(F)$	162	145	175
Reliability factor R_{int}	0.0812	0.0446	0.0422
Range of *h*, *k*, *l*	$-10 \le h \le 10$, $-10 \le k \le 10$, $-7 \le l \le 7$	$-10 \le h \le 9$, $-10 \le k \le 10$, $-6 \le l \le 6$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-7 \le l \le 6$
θ_{max},°	27.43	25.94	27.49
Reliability factors			
R	0.0184	0.0206	0.0163
wR	0.0406	0.0436	0.0259
S	1.494	1.600	1.412
No. of reflections used in refinement	162	145	175
No. of refined parameters	15	15	14
Weighting scheme ($P = (F_o^2 + 2F_c^2)/3$)	$w = 1/[\sigma^2(F_o^2) + (0.0064P)^2 + 8.8221P]$	$w = 1/[\sigma^2(F_o^2) + 12.8295P]$	$w = 1/[\sigma^2(F_o^2) + (0.0102P)2 + 1.3790P]$
Residual electron density			
$\Delta\rho_{max}$, e$Å^{-3}$	1.256	1.608	1.061
$\Delta\rho_{min}$, e$Å^{-3}$	−1.729	−1.138	−1.515
Extinction coefficient	0.0041(3)	0.0030(3)	0.0059(2)

slightly smaller than those reported in [7]. Similar cell parameters were reported in [12] ($a = 8.36$, $c = 5.71$ Å). It was concluded that a phase with Mn_5Si_3-type structure exists at 600 °C, whereas the formation of a compound Hf_5Sn_4 (Ti_5Ga_4 structure type) was not observed at this temperature. The compound HfSn (FeSi structure type, *cP*8, $P2_13$), reported previously [13], was also not observed.

The investigation of the interstitial solid solution $Hf_5Ga_xSn_3$ ($x = 0–1$) was started from the refinement of the structural parameters for the Hf_5Sn_3 binary compound based on X-ray powder diffraction data. It was confirmed that it crystallizes with the hexagonal Mn_5Si_3 structure type. Atomic coordinates and isotropic (equivalent) displacement parameters in the structure of the binary Hf_5Sn_3 and for three compositions from the $Hf_5Ga_xSn_3$ solid solution ($x = 0.16$, 0.53, 1) are listed in Tables 3 and 4. Anisotropic displacement parameters refined from X-ray single-crystal diffraction data are listed in Table 5.

The Ga atoms occupy Wyckoff position 2*b*, which is empty in the Mn_5Si_3 structure type, leading to the realization of the Hf_5CuSn_3 type of structure (ordered derivative of Ti_5Ga_4). The latter represents a filled-up variant of the Mn_5Si_3 type. A gradual increase of the Ga content in the samples leads to an increase of the occupancy of the position 2*b*, i.e. an interstitial solid solution is formed. Such inclusion of Ga atoms takes place up to the composition Hf_5GaSn_3 characterizing by full occupancy of the position 2*b*. Mutual replacement of Sn atoms and Ga atoms, i.e. the formation of substitution solid solution, was not observed. The cell parameters and the cell volume increase with increasing gallium content in the phase.

The content of the unit cell of Hf_5GaSn_3 and the coordination polyhedra of the different atom sites are shown in Fig. 2. The atoms of site Hf1 are coordinated by eleven atoms forming a defect anticubooctahedron of composition $\underline{Hf1}Sn_5Ga_2Hf_4$, which can also be represented as a deformed pentagonal bipyramid of composition $[Sn_5Ga_2]$ with four additional Hf atoms, or as a tricapped trigonal prism of composition $[Sn_5Hf_4]$ with two additional Ga atoms. The atoms from the closest environment of sites Hf2 and Ga form Frank-Kasper polyhedra consisting of 14 atoms, $\underline{Hf2}Sn_6Hf_8$ and $\underline{Ga}Sn_6Ga_2Hf_6$, respectively. $\underline{Hf2}Sn_6Hf_8$ can be described as a deformed hexagonal prism of composition $[Sn_6Hf_6]$ with two Hf atoms capping the base faces. $\underline{Ga}Sn_6Ga_2Hf_6$ is a deformed rhombododecahedron formed by a $[Sn_6Ga_2]$ cube and a $[Hf_6]$ octahedron. The Sn atoms are coordinated by nine Hf atoms, two Sn and two Ga atoms forming a Frank-Kasper 13-vertex polyhedron of composition $\underline{Sn}Sn_2Ga_2Hf_9$. It can be represented as a deformed anticubooctahedron with one additional atom, or as a tricapped trigonal prism of composition $[Hf_9]$ with four additional atoms. The coordination polyhedron for Sn atoms in the structure of Hf_5Sn_3 is pseudo Frank-Kasper 11-vertex polyhedron of composition $\underline{Sn}Sn_2Hf_9$, which can be represented as defect icosahedron.

Interatomic distances and coordination numbers for each of the structures are listed in Table 6. The interatomic distances correlate with the sums of the atomic radii of the components ($r_{Hf} = 1.564$, $r_{Sn} = 1.405$ and $r_{Ga} = 1.221$ Å [14]) and are in good agreement with the distances in the structures of binary hafnium stannides and gallides. For all of the $Hf_5Ga_xSn_3$ compositions the shortest

Table 3
Atomic coordinates and isotropic displacement parameters for Hf_5Sn_3 (X-ray powder diffraction data).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, $Å^2$
Hf1	6*g*	0.24167(6)	0	1/4	0.890(12)
Hf2	4*d*	1/3	2/3	0	0.564(15)
Sn	6*g*	0.60627(8)	0	1/4	0.588(15)

Table 4
Atomic coordinates, site occupancies and equivalent displacement parameters for $Hf_5Ga_xSn_3$ (X-ray single-crystal diffraction data).

Site	Wyckoff position	Occupancy	x	y	z	U_{eq}, Å^2
$Hf_5Ga_{0.16(3)}Sn_3$						
Hf1	6*g*	1	0.23603(9)	0	1/4	0.0090(3)
Hf2	4*d*	1	1/3	2/3	0	0.0062(3)
Sn	6*g*	1	0.60380(14)	0	1/4	0.0073(3)
Ga	2*b*	0.16(3)	0	0	0	0.08(3)
$Hf_5Ga_{0.53(2)}Sn_3$						
Hf1	6*g*	1	0.25522(15)	0	1/4	0.0185(4)
Hf2	4*d*	1	1/3	2/3	0	0.0086(4)
Sn	6*g*	1	0.60882(19)	0	1/4	0.0119(4)
Ga	2*b*	0.53(2)	0	0	0	0.011(3)
Hf_5GaSn_3						
Hf1	6*g*	1	0.26806(5)	0	1/4	0.00560(16)
Hf2	4*d*	1	1/3	2/3	0	0.00358(16)
Sn	6*g*	1	0.61101(8)	0	1/4	0.00411(19)
Ga	2*b*	1	0	0	0	0.0027(4)

Table 5
Anisotropic displacement parameters (Å^2) for $Hf_5Ga_xSn_3$.

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
$Hf_5Ga_{0.16(3)}Sn_3$						
Hf1	0.0092(3)	0.0057(4)	0.0107(4)	0.0029(2)	0	0
Hf2	0.0076(3)	0.0076(3)	0.0034(4)	0.00380(17)	0	0
Sn	0.0062(4)	0.0063(6)	0.0094(5)	0.0032(3)	0	0
Ga	0.09(3)	0.09(3)	0.05(3)	0.045(16)	0	0
$Hf_5Ga_{0.53(2)}Sn_3$						
Hf1	0.0270(5)	0.0114(5)	0.0118(5)	0.0057(3)	0	0
Hf2	0.0106(4)	0.0106(4)	0.0045(5)	0.0053(2)	0	0
Sn	0.0140(6)	0.0100(8)	0.0105(7)	0.0050(4)	0	0
Ga	0.011(3)	0.011(3)	0.011(4)	0.0057(17)	0	0
Hf_5GaSn_3						
Hf1	0.00553(19)	0.0051(2)	0.0060(2)	0.00254(12)	0	0
Hf2	0.00391(18)	0.00391(18)	0.0029(3)	0.00195(9)	0	0
Sn	0.0036(3)	0.0029(4)	0.0056(3)	0.00145(18)	0	0
Ga	0.0018(5)	0.0018(5)	0.0047(9)	0.0009(2)	0	0

distances are between Hf1 and Ga (2.428 Å for $Hf_5Ga_{0.16(3)}Sn_3$). They are shorter than in the binary gallide Hf_5Ga_3 (2.725 Å), which also crystallizes with a Mn_5Si_3-type structure [15]. However, these distances increase with increasing Ga content within the solid solution and at the composition Hf_5GaSn_3 (2.712 Å) they become similar to those in Hf_5Ga_3.

The increase of the Ga content within the solid solution $Hf_5Ga_xSn_3$ has an influence on the interatomic distances and the coordination polyhedra. Insertion of Ga atoms into [$Hf1_6$] octahedra (Fig. 3) leads to an expansion of the latter (the distances from the centre of the octahedron to the Hf1 vertices increase from 2.475 to 2.712 Å). The chain of $GaHf_6$ octahedra exhibits strong Hf1–Sn interactions, whereas the interatomic distances Hf2–Sn increase. Similar behavior was reported for the isostructural phase Zr_5GaSn_3 [8]. The coordination number and polyhedron of the Hf1 site change when Ga is inserted. In the structure of binary Hf_5Sn_3 the coordination polyhedron is a 14-vertex deformed pentagonal prisms [Hf_{10}] with five additional Sn atoms capping two bases and three side faces, while in the structure of Hf_5GaSn_3 it is, as discussed above, an 11-vertex polyhedron (Fig. 4). The coordination numbers and polyhedron types of the other atoms do not change.

The structure of Hf_5GaSn_3 can also be described in terms of atom layers. The atoms are located in layers A at $z = 0$ and 1/2, and layers

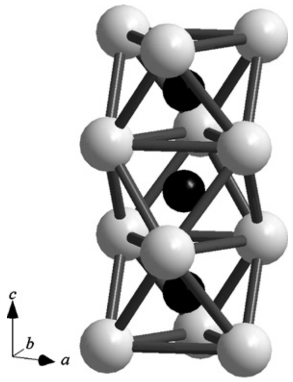


Fig. 3. Columns of face-linked $GaHf_6$ octahedra running along [0 0 1].

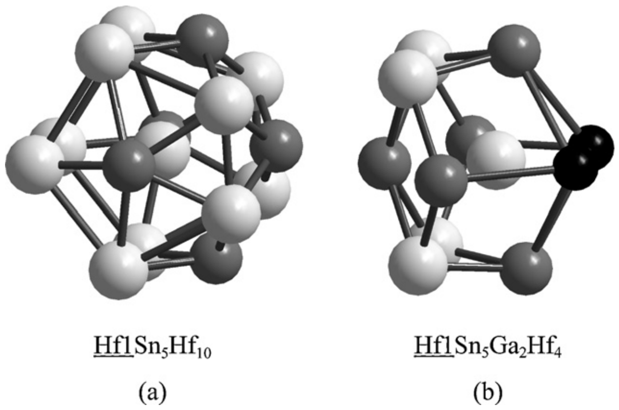
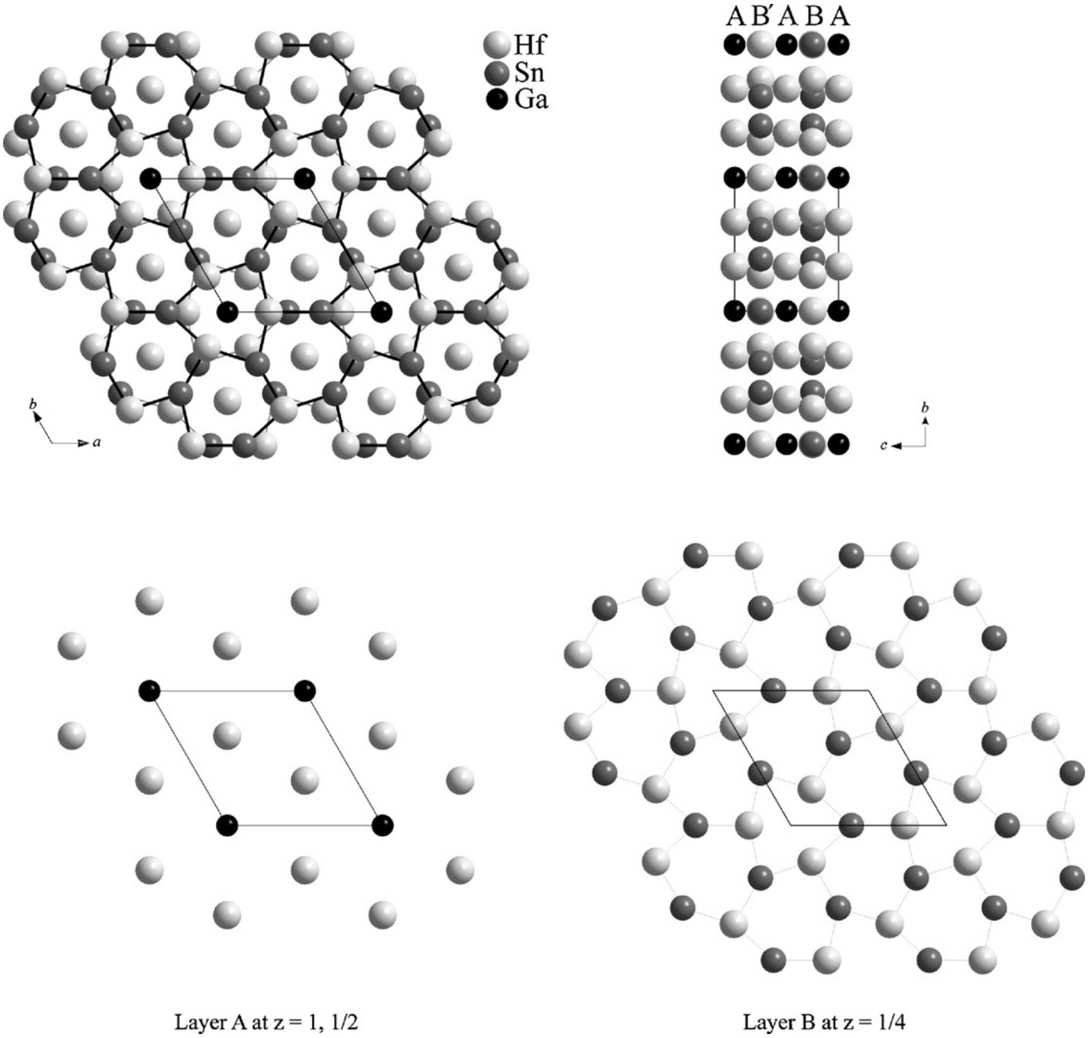

$\underline{\mathrm{Hf1}}\mathrm{Sn_5Hf_{10}}$
(a)
$\underline{\mathrm{Hf1}}\mathrm{Sn_5Ga_2Hf_4}$
(b)

Fig. 4. Coordination polyhedra of the site Hf1 in the structures of Hf_5Sn_3 (a) and Hf_5GaSn_3 (b).

Table 6
Interatomic distances (d) and coordination numbers (CN) of atoms for $Hf_5Ga_xSn_3$.

Atoms		d, Å				Coordination number
		Hf_5Sn_3	$Hf_5Ga_{0.16(3)}Sn_3$	$Hf_5Ga_{0.53(2)}Sn_3$	Hf_5GaSn_3	
Hf1	–2Ga	–	2.4278(7)	2.5877(11)	2.7116(5)	11–15
	–Sn	3.0501(9)	3.0631(15)	2.977(2)	2.9344(9)	
	–2Sn	2.87703(12)	2.8752(10)	2.8965(13)	2.9504(7)	
	–2Sn	3.1245(4)	3.1462(8)	3.1018(10)	3.0724(6)	
	–2Hf1	3.5017(6)	3.4049(14)	3.7223(16)[a]	3.9727(6)[a]	
	–4Hf1	3.4974(2)	3.4617(7)	3.5957(9)[a]	3.6919(6)[a]	
	–4Hf2	3.5409(3)	3.5562(8)[a]	3.4978(9)	3.4831(5)	
Hf2	–2Hf2	2.8539(2)	2.8494(5)	2.8828(6)	2.8929(6)	14
	–6Sn	2.9425(2)	2.9254(5)	2.9708(6)	3.0159(4)	
	–6Hf1	3.5409(3)	3.5559(7)	3.4978(9)	3.4831(5)	
Sn	–2Hf1	2.8770(7)	2.8752(10)	2.8965(13)	2.9504(7)	11–13
	–4Hf2	2.9425(2)	2.9254(5)	2.9708(6)	3.0159(4)	
	–2Hf1	3.1245(4)	3.1462(8)	3.1018(10)	3.0724(6)	
	–Hf1	3.0501(9)	3.0631(15)	2.977(2)	2.9344(9)	
	–2Sn	3.3624(6)	3.333(1)	3.4160(13)	3.4609(7)	
	–2Ga	–	3.5943(7)	3.5955(9)	3.6291(5)	
Ga	–6Hf1	–	2.4278(7)	2.5877(11)	2.7116(5)	14
	–2Ga	–	2.8494(5)	2.8828(6)	2.8929(6)	
	–6Sn	–	3.5943(7)	3.5955(9)	3.6291(5)	

[a] Not included in the coordination polyhedra.



Layer A at z = 1, 1/2

Layer B at z = 1/4

Fig. 5. Projection of the structure of Hf_5GaSn_3 along [0 0 1] (top left) and [1 0 0] (top right). The atoms of layer B lie in the mirror plane at $z = 1/4$ (thin lines), layer B′ at $z = 3/4$ (thick lines).

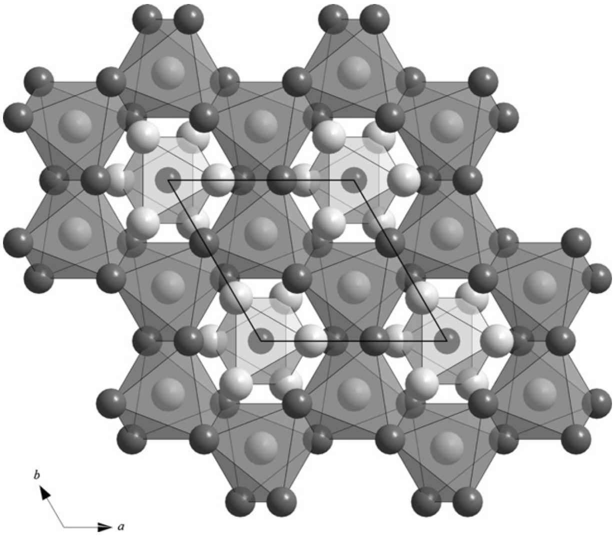


Fig. 6. View of the structure of Hf_5GaSn_3 along [0 0 1]. The $HfSn_6$ (dark) and $GaHf_6$ (light) octahedra are emphasized.

B (B′) at z = 1/4 and 3/4, resulting in the stacking sequence ABAB′ along the c axis (Fig. 5). The layers B and B′ are identical, but B′ is rotated by 60° (6-fold screw axis) with respect to B. The layer A contains regular hexagons of Hf atoms centred by Ga atoms, "Hf_2Ga", while the layer B contains distorted hexagons of Hf and Sn atoms and has the composition "Hf_3Sn_3". The atoms of the layers B and B' form octahedra around the atoms of the layer A: distorted $HfSn_6$ octahedra share edges in the plane (0 0 1), forming cavities in which the $GaHf_6$ octahedra are situated (Fig. 6). Along the direction [0 0 1] the $HfSn_6$ as well as the $GaHf_6$ octahedra are connected by common faces and form a 3D-framework and 1D-rods, respectively. Interestingly, atoms of the *d*-block element (Hf) centre octahedra formed by atoms of a *p*-block element (Sn) and *vice versa*, Ga atoms (*p*-block element) centre octahedra formed by Hf atoms (*d*-block element).

4. Conclusions

The binary compound Hf_5Sn_3 dissolves 11.1 at.% Ga forming an interstitial solid solution $Hf_5Ga_xSn_3$ (x = 0–1). The Ga atoms occupy [Hf_6] octahedral interstices (Wyckoff position 2*b*) up to the composition Hf_5GaSn_3, which represents a Hf_5CuSn_3-type structure (ordered derivative of Ti_5Ga_4). The cell parameters and cell volume increase with increasing gallium content. The coordination number of the hafnium atoms in Wyckoff position 6*g* is reduced from 15 ($Hf1Sn_5Hf_{10}$ for Hf_5Sn_3) to 11 ($Hf1Sn_5Ga_2Hf_4$ for Hf_5GaSn_3).

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References

[1] K. Åmark, B. Borén, A. Westgren, Metallwirtsch. Metallwiss. Metalltech. 15 (1936) 835–836.
[2] P. Villars, K. Cenzual (Eds.), Pearson's Crystal Data, Crystal Structure Database for Inorganic Compounds (Release 2010/11), ASM International, Materials Park, OH, 2010.
[3] M. Pötzschke, K. Schubert, Z. Metallkd. 53 (1962) 474–488.
[4] K. Schubert, H.G. Meissner, M. Pötzschke, W. Rossteutscher, E. Stolz, Naturwissenschaften 49 (1962) 57.
[5] W. Rieger, H. Nowotny, F. Benesovsky, Monatsh. Chem. 96 (1965) 232–241.
[6] T.B. Massalski (Ed.), Binary Alloy Phase Diagrams, ASM International, Ohio, 1990.
[7] H. Boller, H. Nowotny, A. Wittmann, Monatsh. Chem. 91 (1960) 1174–1184.
[8] Y.U. Kwon, J.D. Corbett, Chem. Mater. 4 (1992) 1348–1355.
[9] J. Rodriguez-Carvajal, Newsletter 26 (2001) 12–19.
[10] X-Shape (Version 2.05), X-Red (Version 1.26) and IPDS Software (Version 2.92), Stoe & Cie, Darmstadt, 2000.
[11] G.M. Sheldrick, SHELXS-97 and SHELXL-97, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, 1997;
G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112–122.
[12] I.A. Tsyganova, M.A. Tylkina, E.M. Savitskii, Russ. Metall. 3 (1971) 129–130.
[13] O. Schob, E. Parthé, Acta Crystallogr. 17 (1964) 452–453.
[14] J. Emsley, The Elements, Oxford University Press, 1997.
[15] H. Boller, E. Parthé, Monatsh. Chem. 94 (1963) 225–226.