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The system Hf–Ga–Sn at 600°C and the crystal structure of $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$

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The isothermal section at 600°C of the phase diagram of the ternary system Hf–Ga–Sn was constructed in the whole concentration range using X-ray diffraction and energy dispersive X-ray analysis. The binary gallides HfGa (structure type ThIn) and Hf_5Ga_3 (Mn_5Si_3) dissolve up to 17 at.% Sn, forming solid solutions characterized by constant Hf concentration. Based on the binary stannide Hf_5Sn_3 (Mn_5Si_3) an interstitial solid solution up to 11.1 at.% Ga is formed. Other binary compounds of the systems Hf–Ga and Hf–Sn do not dissolve noticeable amounts of the third component. One ternary compound, $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$, with homogeneity range 9 at.% Ga (Sn) is formed. Its crystal structure belongs to the structure type Nb_5SiSn_2 (Pearson symbol *tI*32, space group *I*4/*mcm*), which is a ternary variant of W_5Si_3. With increasing Sn content the unit-cell parameters within the homogeneity range increase from *a* = 10.9154(8), *c* = 5.51311(15) Å to *a* = 11.0203(7), *c* = 5.56591(16) Å. The structure is built up of two kinds of isolated column: face-sharing square antiprisms $\underline{Ga}Hf_8$ and edge-sharing tetrahedra $\underline{Hf}Sn_4$.

Hafnium / Gallium / Tin / Phase diagram / X-ray diffraction / Crystal structure / Solid solution

Introduction

Within the framework of systematic investigations of ternary alloys formed by transition metals with gallium and main-group elements, we decided to study the system Hf–Ga–Sn at 600°C. There are to our knowledge no literature data on this system. Among the ternary systems {Ti,Zr,Hf}–Ga–{Si,Ge,Sn}, {Nb,Ta}–Ga–Sn, and {Ti,Zr,Hf}–{Al,In}–Sn, the phase diagrams have been constructed only for the systems {Ti,Zr}–Ga–Si in the region 25-100 at.% Ti or Zr at 800°C [1]. Both systems are characterized by the formation of one ternary compound, $TiGa_{0.20-0.68}Si_{1.80-1.32}$ (structure type $ZrSi_2$) and $ZrGa_{0.66-0.90}Si_{0.34-0.10}$ (CrB), respectively. The latter represents a Si-stabilized high-temperature modification of the binary compound ZrGa [2]. Other systems have been investigated for the formation of ternary compounds: the silicide $HfGa_{0.33}Si_{0.67}$ (CrB) [3], germanides $TiGa_{0.3}Ge_{1.7}$ ($ZrSi_2$) [4], $TiGa_{0.5}Ge_{1.5}$ ($ZrSi_2$) [5], $ZrGa_{2.75}Ge_{0.25}$ ($TiAl_3$) [5], $Zr_{0.75}Ga_{0.90}Ge_{1.35}$ ($ZrSi_2$) [5], $ZrGa_{0.5}Ge_{1.5}$ ($ZrSi_2$) [6], $ZrGa_{0.1}Ge_{0.9}$ (CrB) [4], and the stannides Zr_5AlSn_3 (Hf_5CuSn_3) [7], Zr_5GaSn_3 (Hf_5CuSn_3) [7], Hf_5AlSn_2 (W_5Si_3) [8]. Ternary compounds crystallizing in the structure type W_5Si_3 [9] (or its ordered variant Nb_5SiSn_2 [10]) were also found in other related systems: Ti_5AlSn_2 [8], Zr_5AlSn_2 [8], Nb_5GaSn_2 [11], and Ta_5GaSn_2 [12]. Crystallographic data for the ternary compounds forming in the ternary systems {Ti,Zr,Hf}–Ga–{Si,Ge,Sn}, {Ti,Zr,Hf}–Al–Sn, and {Nb,Ta}–Ga–Sn are summarized in Table 1. It can be seen that most of the listed compounds crystallize with the binary structure types $ZrSi_2$, $TiAl_3$, CrB, W_5Si_3, and Ti_5Ga_4 (Hf_5CuSn_3). The first three structure types are common for ternary silicides and germanides containing Ga or Al, but not for stannides, whereas the last two are, in case of mixed gallide-tetrelides, formed exclusively by ternary stannides. This information gave us the possibility to expect new ternary intermetallic compounds with particular structure types in the ternary system Hf–Ga–Sn.

The binary systems that border the ternary system Hf–Ga–Sn have been studied in the whole concentration range and the corresponding phase diagrams are, at least partly, known [13]. Seven binary gallides were found in the system Hf–Ga. The compounds $Hf_{11}Ga_{10}$ and Hf_5Ga_3 melt congruently at 1700 and 1730°C, respectively; $HfGa_3$, Hf_2Ga_3, and HfGa form *via* peritectic reactions at 1400, 1480, and 1550°C, respectively; $HfGa_2$ and Hf_2Ga form *via* peritectoid reactions at 1100°C and 1200°C, respectively. The existence of four binary compounds was reported for the Hf–Sn system: Hf_5Sn_3 with

Table 1 Crystallographic data on ternary compounds of the systems {Ti,Zr,Hf}–Ga–{Si,Ge,Sn}, {Nb,Ta}–Ga–Sn, and {Ti,Zr,Hf}–{Al,In}–Sn.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Literature
				a	*b*	*c*	
$TiGa_{0.20-0.68}Si_{1.80-1.32}$	$ZrSi_2$	*oS*12	*Cmcm*	3.584	13.606	3.584	[1]
				at the composition $TiGa_{0.3}Si_{1.7}$			
$ZrGa_{0.66-0.90}Si_{0.34-0.10}$	CrB	*oS*8	*Cmcm*	3.908	10.197	3.824	[1]
				at the composition $ZrGa_{0.8}Si_{0.2}$			
$HfGa_{0.33}Si_{0.67}$	CrB	*oS*8	*Cmcm*	3.7338	9.889	3.7441	[3]
$TiGa_{0.3}Ge_{1.7}$	$ZrSi_2$	*oS*12	*Cmcm*	3.687	14.09	3.668	[4]
$TiGa_{0.5}Ge_{1.5}$	$ZrSi_2$	*oS*12	*Cmcm*	3.69	14.09	3.67	[5]
$Ti_5Ga_{1.5}Ge_{1.5}$	Mn_5Si_3	*hP*16	$P6_3/mcm$	7.5	–	5.2	[5]
$ZrGa_{2.75}Ge_{0.25}$	$TiAl_3$	*tI*8	*I*4/*mmm*	3.89	–	9.10	[5]
$Zr_{0.75}Ga_{0.90}Ge_{1.35}$	$ZrSi_2$	*oS*12	*Cmcm*	3.82	14.98	3.79	[5]
$ZrGa_{0.5}Ge_{1.5}$	$ZrSi_2$	*oS*12	*Cmcm*	3.804	14.975	3.765	[6]
$ZrGa_{0.1}Ge_{0.9}$	CrB	*oS*8	*Cmcm*	3.83	10.12	3.83	[4]
Zr_5AlSn_3	Hf_5CuSn_3	*hP*18	$P6_3/mcm$	5.655	–	5.871	[7]
Zr_5GaSn_3	Hf_5CuSn_3	*hP*18	$P6_3/mcm$	8.6599	–	5.8794	[7]
Hf_5AlSn_2	W_5Si_3	*tI*32	*I*4/*mcm*	11.014	–	5.542	[8]
Ti_5AlSn_2	W_5Si_3	*tI*32	*I*4/*mcm*	10.549	–	5.242	[8]
Zr_5AlSn_2	W_5Si_3	*tI*32	*I*4/*mcm*	11.181	–	5.538	[8]
Nb_5GaSn_2	W_5Si_3	*tI*32	*I*4/*mcm*	10.586	–	5.177	[11]
$Nb_3Ga_{0.52}Sn_{0.48}$	Cr_3Si	*cP*8	*Pm*-3*n*	5.257	–	–	[14]
Ta_5GaSn_2	W_5Si_3	*tI*32	*I*4/*mcm*	10.354	–	5.1795	[12]

congruent melting at 1900°C, $HfSn_2$, which forms peritectically, and two phases, Hf_5Sn_4 and HfSn, with undefined methods of formation. The system Ga–Sn is characterized by a eutectic reaction at 8.4 at.% Sn and 20.5°C. Maximal solubility of Ga in β-Sn is 6.4 at.% at 13°C. At the temperature of investigation (600ºC) both components are liquid, *i.e.* a continuous liquid region is observed on the Ga–Sn side of the isothermal section of phase diagram of the system Hf–Ga–Sn.

Experimental

The investigation was carried out on 13 two-component and 80 three-component alloys, which were synthesized from high-purity metals (Hf ≥ 99.9 wt.%, Ga ≥ 99.99 wt.%, Sn ≥ 99.99 wt.%) by arc melting under argon atmosphere, using a water-cooled copper hearth and a tungsten electrode. To purify the atmosphere inside the furnace Ti sponges were used as a getter. To achieve high efficiency of the interaction between the components the samples were melted twice. After the synthesis the alloys were wrapped into tantalum foil to ensure their isolation, sealed in quartz ampoules under vacuum and annealed at 600ºC for 720 hours. Finally the ampoules with the samples were rapidly quenched into cold water. The losses, which were controlled at all stages of synthesis, did not exceed 1 % of the total mass, which was approximately 1 g for each alloy. Additionally, induction melting was used to synthesize a sample of composition $Hf_{62.5}Sn_{37.5}$ (in at.%). The chemical composition of the single crystal $Hf_3Ga_{1.97}Sn_{1.03}$ was checked by energy dispersive X-ray analysis using a scanning electron microscope JEOL 5900LV.

Phase analysis and structure refinements were carried out using X-ray powder diffraction data collected on diffractometers DRON-2.0M (Fe *K*α-radiation, λ = 1.93801 Å, angular range $20° \leq 2\theta \leq 120°$, step 0.05°) and STOE Stadi P (Cu $K\alpha_1$-radiation, λ = 1.54056 Å, linear detector, range $6\text{-}10° \leq 2\theta \leq 110°$, step 0.010-0.015°). The profile and structural parameters were refined by the Rietveld method using the FullProf Suite program package [15]. Single crystals were extracted from selected alloys and were mounted on glass fibers. X-ray diffraction data were collected in the φ-oscillation scan mode at room temperature on a Stoe IPDS-IIT diffractometer (Mo *K*α-radiation, λ = 0.71073 Å, graphite monochromator, imaging plate detector). An analytical absorption correction was applied using X-Shape/X-Red software [16,17]. The structures were solved by direct methods using the program SHELXS-97 [18] and refined using the program SHELXL-97 [18] under the graphical user interface WinGX [19].

Results

Binary systems

The existence of nine compounds at 600ºC in the boundary binary systems Hf–Ga and Hf–Sn was confirmed: $HfGa_3$, $HfGa_2$, Hf_2Ga_3, HfGa, $Hf_{11}Ga_{10}$, Hf_5Ga_3, Hf_2Ga, $HfSn_2$, and Hf_5Sn_3. The binary phases HfSn and Hf_5Sn_4 do not form at the conditions of the

Table 2 Crystallographic data for the binary compounds of the systems Hf–Ga and Hf–Sn.

Compound	Structure type	Pearson symbol	Space group	Cell parameters, Å			Literature
				a	*b*	*c*	
$HfGa_3$	$TiAl_3$	*tI*8	*I*4/*mmm*	3.881	–	9.032	[20]
				3.87795(15)	–	9.0166(3)	this work
$HfGa_2$	$HfGa_2$	*tI*24	*I*4₁/*amd*	4.046	–	25.446	[20]
				4.0408(5)	–	25.438(6)	this work
Hf_2Ga_3	Zr_2Al_3	*oF*40	*Fdd*2	9.402	13.63	5.472	[20]
				9.4025(16)	13.632(3)	5.4696(8)	this work
HfGa	ThIn	*oP*24	*Pbcm*	9.171	8.503	5.648	[21]
				9.1609(10)	8.5097(8)	5.6384(6)	this work
$Hf_{11}Ga_{10}$	$Ho_{11}Ge_{10}$	*tI*84	*I*4/*mmm*	10.282	–	14.73	[22]
				10.2887(5)	–	14.7134(13)	this work
Hf_5Ga_3	Mn_5Si_3	*hP*16	*P*6₃/*mcm*	7.970	–	5.686	[20]
				7.9601(10)	–	5.6779(8)	this work
Hf_2Ga	$CuAl_2$	*tI*12	*I*4/*mcm*	6.690	–	5.294	[20]
				6.6815(19)	–	5.363(2)	this work
$HfSn_2$	$CrSi_2$	*hP*9	*P*6₂22	5.487	–	7.625	[23]
				5.4816(6)	–	7.6113(10)	this work
HfSn	FeSi	*cP*8	*P*2₁3	5.594	–	–	[24]
Hf_5Sn_4	Ti_5Ga_4	*hP*18	*P*6₃/*mcm*	8.740	–	5.910	[25]
Hf_5Sn_3	Mn_5Si_3	*hP*16	*P*6₃/*mcm*	8.376	–	5.737	[23]
				8.36562(6)	–	5.70775(4)	this work

Table 3 Crystallographic data for the phases in the ternary system Hf–Ga–Sn.

No.	Composition	Structure type	Pearson symbol	Space group	Cell parameters, Å		
					a	*b*	*c*
1	$Hf_3Ga_{3-1.97}Sn_{0-1.03}$	ThIn-Hf_3Ga_2Sn	*oP*24	*Pbcm*	9.1609(10)-9.3370(19)	8.5097(8)-8.6920(17)	5.6384(6)-5.6650(11)
2	$Hf_5Ga_{0-1}Sn_3$	Mn_5Si_3-Hf_5CuSn_3	*hP*16-*hP*18	*P*6₃/*mcm*	8.36562(6)-8.5564(12)	–	5.70775(4)-5.7859(12)
3	$Hf_5Ga_{3-1.64}Sn_{0-1.36}$	Mn_5Si_3	*hP*16	*P*6₃/*mcm*	7.9601(10)-8.1721(6)	–	5.6779(8)-5.7039(5)
4	$Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$	Nb_5SiSn_2	*tI*32	*I*4/*mcm*	10.9154(8)-11.0203(7)	–	5.51311(15)-5.56591(16)

investigation but, according to the X-ray phase analysis the samples in the concentration range $Hf_{33.3-62.5}Sn_{66.7-37.5}$ contained the binary compounds $HfSn_2$ and Hf_5Sn_3. Crystallographic data for the binary compounds of the systems Hf–Ga and Hf–Sn, including literature data and cell parameters refined in this work, are summarized in Table 2. At 600ºC alloys of the binary system Ga–Sn are liquid. The boundary of the liquid phase in the ternary system was extrapolated from its limits in the binary systems: 4 at.% in the system Hf–Ga and 3 at.% in the system Hf–Sn [13].

Isothermal section of the phase diagram of the system Hf–Ga–Sn at 600°C

The isothermal section of the phase diagram of the ternary system Hf–Ga–Sn at 600ºC is shown in Fig. 1. It is composed by 12 single-phase, 22 two-phase and 11 three-phase fields. The phase $HfGa_{1-x}Sn_x$ (x = 0-0.34) forms the highest number of equilibria (11). Two binary hafnium gallides, HfGa (structure type ThIn) and Hf_5Ga_3 (Mn_5Si_3), dissolve an appreciable amount of the third component, forming extended (up to 17 at.% Sn) solid solutions, which are characterized by constant Hf concentration. The formation of an interstitial solid solution $Hf_5Ga_xSn_3$ (x = 0-1) based on the binary compound Hf_5Sn_3 (Mn_5Si_3) was established (Table 3). The other binary compounds of the systems Hf–Ga and Hf–Sn do not dissolve noticeable amounts of the third component. One ternary compound, $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$, with homogeneity range 9 at.% Ga (Sn) is formed in the investigated system.

The cross-section between the two isostructural binary compounds Hf_5Ga_3 and Hf_5Sn_3 (structure type Mn_5Si_3) represents the only quasi-binary system in the investigated ternary system. The Hf_5Ga_3–Hf_5Sn_3 section consists of three single-phase ($Hf_5Ga_{3-x}Sn_x$ (x = 0-1.36), $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$, and Hf_5Sn_3) and two two-phase ($Hf_5Ga_{1.64}Sn_{1.36}$ +

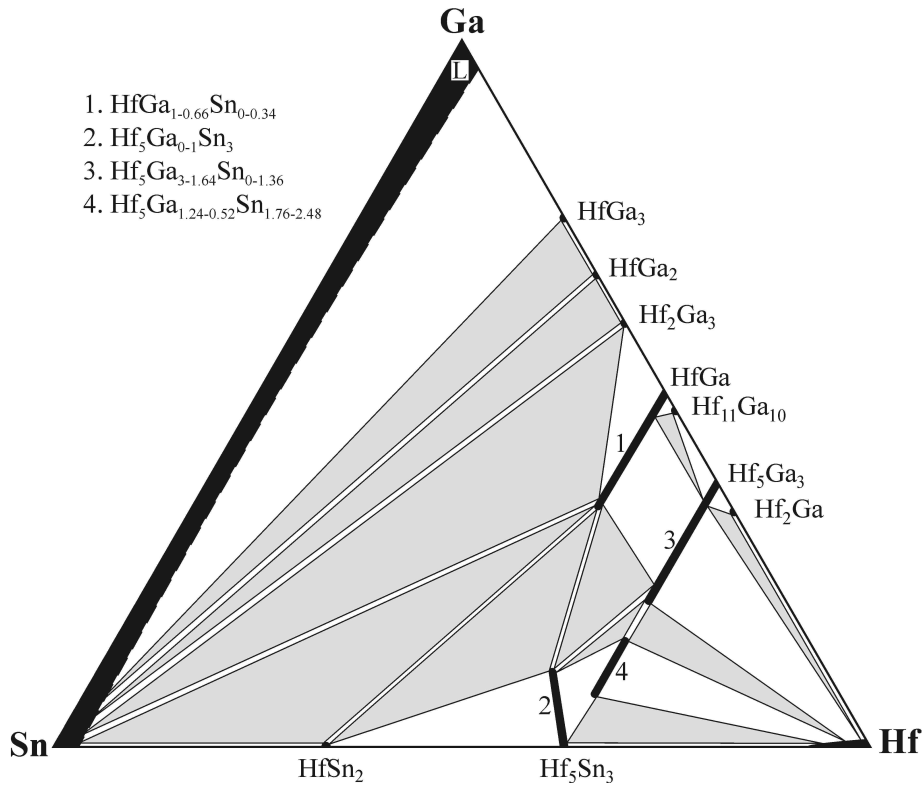

Fig. 1 Isothermal section of the phase diagram of the system Hf–Ga–Sn at 600ºC.

Table 4 Results of the X-ray spectral analysis of the single crystal $Hf_3Ga_{1.97}Sn_{1.03}$.

Element	Content, at.%	Accuracy of analysis, at.%
Hf	53.1	±6.3
Ga	34.2	±5.1
Sn	12.7	±4.6

$Hf_5Ga_{1.24}Sn_{1.76}$ and $Hf_5Ga_{0.52}Sn_{2.48}$ + Hf_5Sn_3) fields. Four out of seven binary gallides, or solid solutions based on them, are in equilibrium with the Ga–Sn liquid phase.

Substitutional solid solution $HfGa_{1-x}Sn_x$ (x = 0-0.34)

The crystal structure of the substitutional solid solution $HfGa_{1-x}Sn_x$ (x = 0-0.34) was refined from X-ray single-crystal and powder diffraction data (Pearson symbol *oP*24, space group *Pbcm*, a = 9.3370(19), b = 8.6920(17), c = 5.6650(11) Å for $Hf_3Ga_{1.97(2)}Sn_{1.03(2)}$) [26]. The obtained composition of the single crystal from X-ray spectral analysis agrees well with the nominal composition of the synthesized alloy (Table 4). The structure of the ideal limiting formula Hf_3Ga_2Sn, ignoring partial Ga/Sn disorder, represents the first ternary ordering derivative of the structure type ThIn. Atomic coordinates and displacement parameters for $Hf_3Ga_{2.16}Sn_{0.84}$ are listed in Table 5, the unit cell content and the coordination polyhedra of the atoms are shown in Fig. 2. The extent of this purely substitutional solid solution was confirmed from plots of the dependencies of the cell parameters from the compositions (Table 6, Fig. 3).

The cell parameters within the solid solution $HfGa_{1-x}Sn_x$ (x = 0-0.34) increase with increasing Sn content, which is in agreement with the larger atomic radius of Sn (r_{Sn} = 1.405 Å; r_{Ga} = 1.221 Å [27]). The a- and b-parameters increase by ~2%, the c-parameter ~0.5%. At the end of the solid solution the values of the cell parameters are slightly smaller than one would expect from their linear increase. This can be explained by ordering of Ga and Sn atoms at the limiting composition.

Substitutional solid solution $Hf_5Ga_{3-x}Sn_x$ (x = 0-1.36)

Formation of a substitutional solid solution $Hf_5Ga_{3-x}Sn_x$ (x = 0-1.36 at 600°C) based on the binary compound Hf_5Ga_3 (structure type Mn_5Si_3, Pearson symbol *hP*16, space group $P6_3/mcm$) was established. Its extent was confirmed from the plot of the dependence of the cell parameters on the composition (Table 7, Fig. 4). The a- and c-parameters increase by ~3% and ~0.5%, respectively, with increasing Sn content.

Table 5 Atomic coordinates and displacement parameters (Å^2) for $Hf_3Ga_{1.97}Sn_{1.03}$ (*oP*24, *Pbcm*, *a* = 9.3370(19), *b* = 8.6920(17), *c* = 5.6650(11) Å).

Site	Wyckoff position	Occupancy, %	*x*	*y*	*z*	U_{eq}
Hf1	4*d*	100	0.11272(8)	0.52840(7)	1/4	0.0072(2)
Hf2	4*d*	100	0.30446(8)	0.12864(8)	1/4	0.0086(2)
Hf3	4*c*	100	0.61864(8)	1/4	0	0.0098(2)
*M*1 (Sn)	4*d*	87(2)Sn/13(2)Ga	0.41493(13)	0.44960(13)	1/4	0.0077(5)
*M*2 (Ga1)	4*d*	90(2)Ga/10(2)Sn	0.1476(2)	0.8631(2)	1/4	0.0088(6)
*M*3 (Ga2)	4*c*	93(2)Ga/7(2)Sn	0.0704(2)	1/4	0	0.0085(7)

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hf1	0.0084(4)	0.0054(3)	0.0072(3)	-0.0006(3)	0	0
Hf2	0.0093(4)	0.0086(3)	0.0078(3)	0.0000(3)	0	0
Hf3	0.0108(4)	0.0112(4)	0.0075(3)	0	0	-0.0005(2)
*M*1 (Sn)	0.0080(8)	0.0066(7)	0.0086(6)	0.0010(4)	0	0
*M*2 (Ga1)	0.0083(11)	0.0090(10)	0.0092(9)	-0.0007(7)	0	0
*M*3 (Ga2)	0.0104(11)	0.0065(11)	0.0088(9)	0	0	0.0000(6)

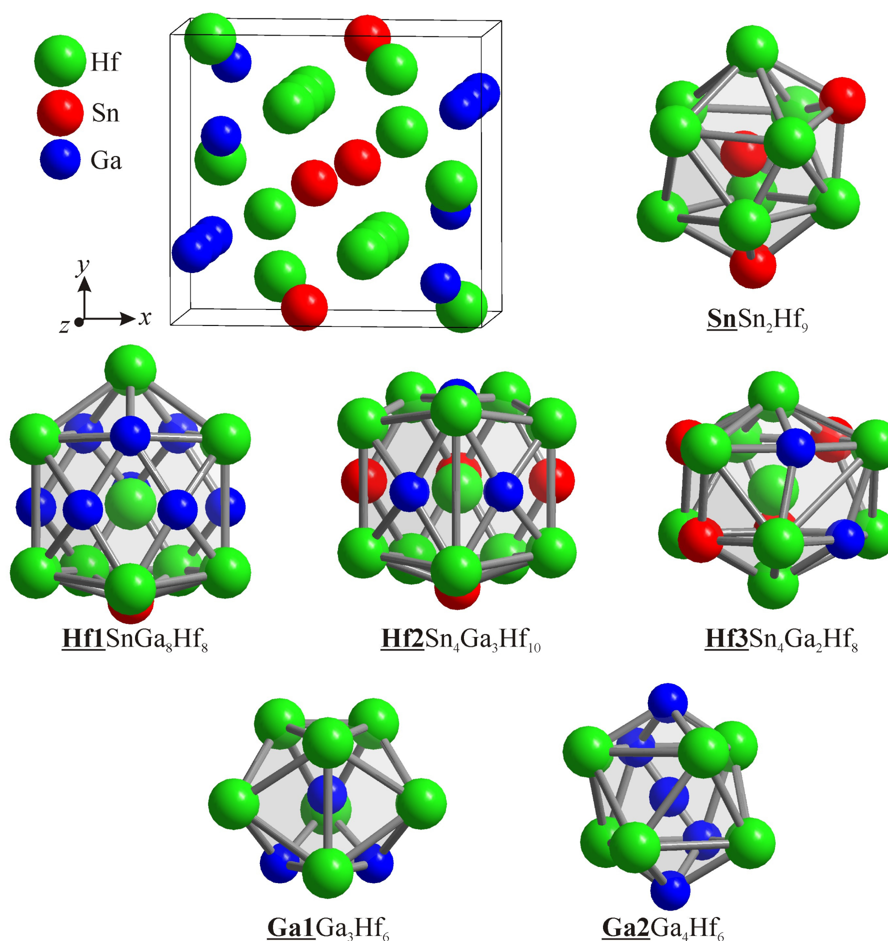

Fig. 2 Unit cell and coordination polyhedra of atoms in the structure of $Hf_3Ga_{1.97}Sn_{1.03}$.

Table 6 Unit-cell parameters of the solid solution $HfGa_{1-x}Sn_x$ (x = 0-0.34).

Nominal composition of the sample, at.%	x	a, Å	b, Å	c, Å	V, Å^3
$Hf_{50}Ga_{50}$	0	9.1609(10)	8.5097(8)	5.6384(6)	439.55(8)
$Hf_{50}Ga_{46}Sn_4$	0.08	9.2171(8)	8.5551(7)	5.651(5)	445.60(7)
$Hf_{50}Ga_{43}Sn_7$	0.14	9.2557(18)	8.5913(17)	5.6534(10)	449.40(15)
$Hf_{50}Ga_{39}Sn_{11}$	0.28	9.310(2)	8.647(2)	5.6670(12)	456.24(18)
$Hf_{50}Ga_{32}Sn_{18}$[a]	0.34(1)	9.3370(19)	8.6920(17)	5.6650(11)	459.76(16)
$Hf_{50}Ga_{30}Sn_{20}$	0.34	9.336(4)	8.693(4)	5.665(3)	459.74(3)

[a] Composition of the alloy from which the single crystal was extracted.

Table 7 Unit-cell parameters of the solid solution $Hf_5Ga_{3-x}Sn_x$ (x = 0-1.36).

Nominal composition of the sample, at.%	x	a, Å	c, Å	V, Å^3
$Hf_{62.5}Ga_{37.5}$	0	7.9601(10)	5.6779(8)	311.57(7)
$Hf_{62.5}Ga_{33.5}Sn_4$	0.32	8.0094(7)	5.6846(6)	315.8(5)
$Hf_{62.5}Ga_{27.5}Sn_{10}$	0.8	8.0804(7)	5.6935(7)	322.34(6)
$Hf_{62.5}Ga_{22.5}Sn_{11}$	1.2	8.1471(8)	5.7007(7)	326.89(7)
$Hf_{62.5}Ga_{17.5}Sn_{20}$	1.36[a]	8.1721(6)	5.7039(5)	329.42(5)

[a] Extrapolated from the plot of the unit-cell parameters (see Fig. 4).

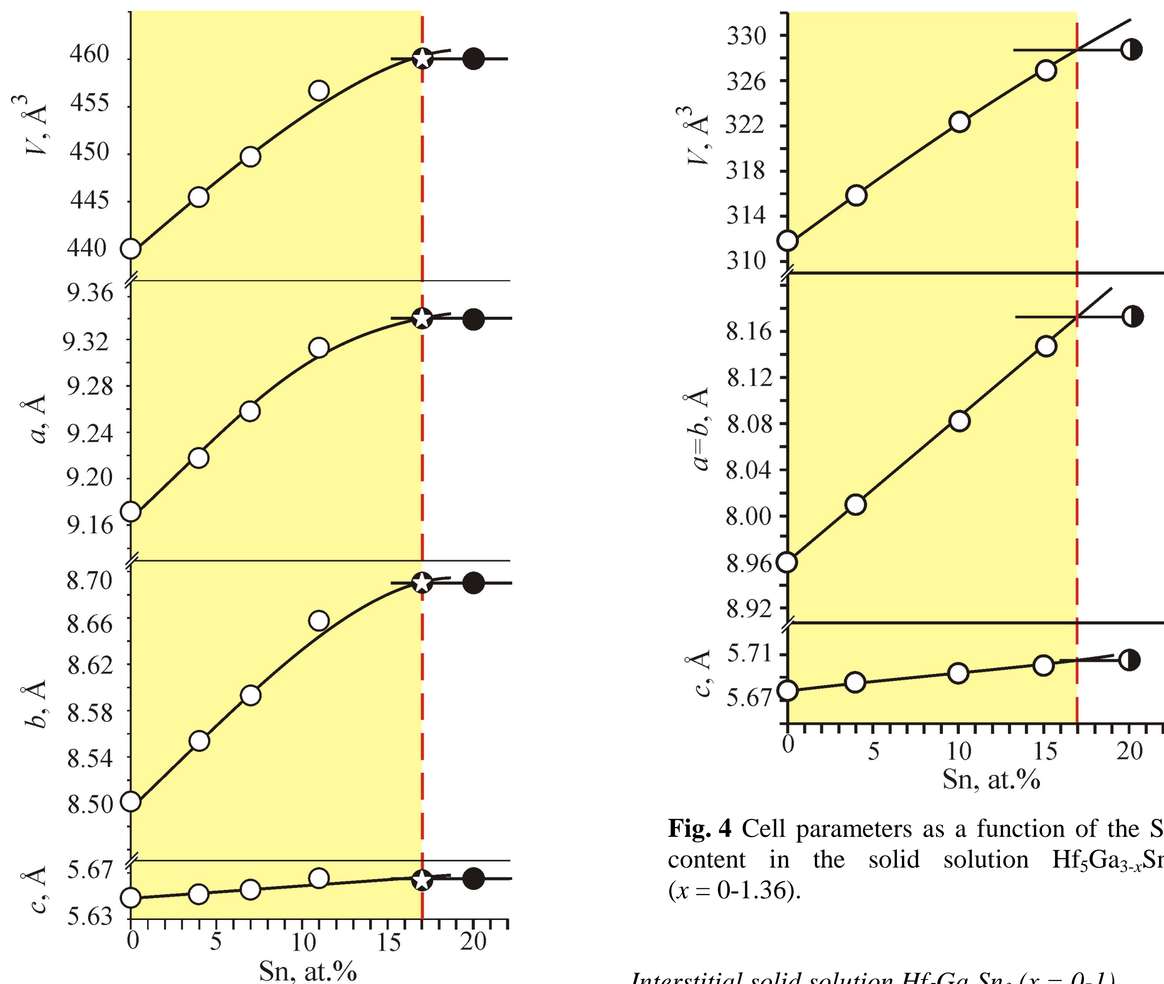

Fig. 3 Cell parameters as a function of the Sn content in the solid solution $HfGa_{1-x}Sn_x$ (x = 0-0.34). ✪ – single crystal data.

Fig. 4 Cell parameters as a function of the Sn content in the solid solution $Hf_5Ga_{3-x}Sn_x$ (x = 0-1.36).

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

Formation of an interstitial solid solution $Hf_5Ga_xSn_3$ (x = 0-1 at 600°C) based on the binary compound Hf_5Sn_3 (structure type Mn_5Si_3, Pearson symbol *hP*16,

Table 8 Atomic coordinates and displacement parameters (Å^2) for Hf_5GaSn_3 (structure type Hf_5CuSn_3, *hP*18, *P*6$_3$/*mcm*, *a* = 8.5564(12), *c* = 5.7859(12) Å).

Site	Wyckoff position	*x*	*y*	*z*	U_{eq}
Hf1	6*g*	0.26806(5)	0	1/4	0.00560(16)
Hf2	4*d*	1/3	2/3	0	0.00358(16)
Sn	6*g*	0.61101(8)	0	1/4	0.00411(19)
Ga	2*b*	0	0	0	0.0027(4)

Site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
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

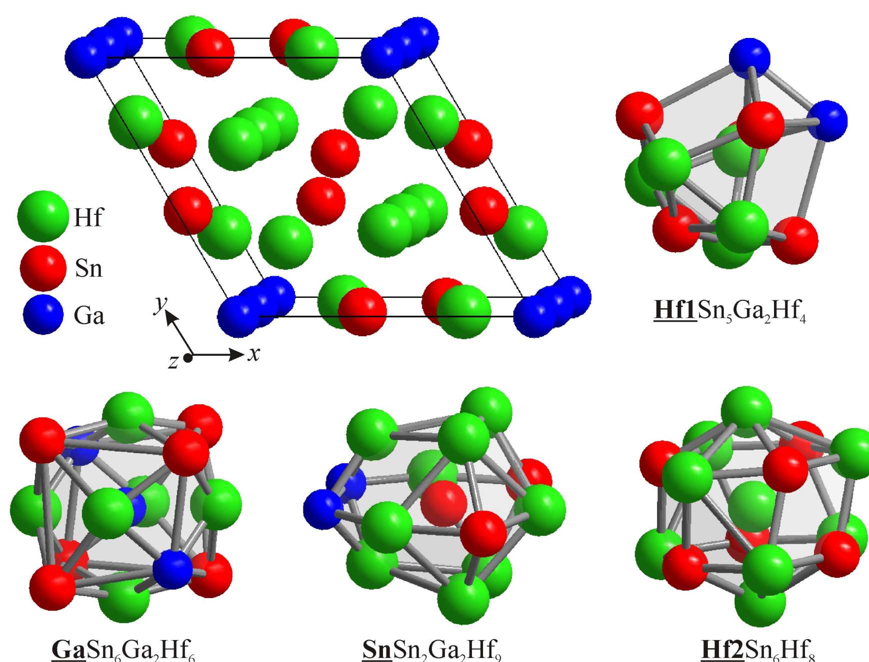

Fig. 5 Unit cell and coordination polyhedra of atoms in the structure of Hf_5GaSn_3.

space group *P*6$_3$/*mcm*, *a* = 8.36562(6), *c* = 5.70775(4) Å from X-ray powder diffraction) was established. The crystal structure (structure type Hf_5CuSn_3, ordered derivative of Ti_5Ga_4, *hP*18, *P*6$_3$/*mcm*) was refined from X-ray diffraction data for three single crystals, extracted from single-phase alloys: $Hf_5Ga_{0.16(3)}Sn_3$ (*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) [28]. The Ga atoms occupy Wyckoff position 2*b* at the centers of the Hf_6 octahedral interstices of the Mn_5Si_3-type structure. Atomic coordinates and displacement parameters for Hf_5GaSn_3 are listed in Table 8, the unit cell and coordination polyhedra of the atoms are shown in Fig. 5.

Ternary compound $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$

The crystal structure of the only ternary compound that forms in the system Hf–Ga–Sn at 600ºC (structure type Nb_5SiSn_2, Pearson symbol *tI*32, space group *I*4/*mcm*) was determined from X-ray powder diffraction data of three samples. The compound is characterized by a homogeneity range along the isoconcentrate 62.5 at.% Hf; it extends by 9 at.% Ga (Sn). X-ray powder diffraction patterns were obtained at room temperature on a STOE Stadi P diffractometer with Cu $K\alpha_1$-radiation. The structure was refined by the Rietveld method starting from the coordinates of the parent structure type Nb_5SiSn_2 [10]. From 3 to 7 wt.% of unreacted Hf was found in each sample. The secondary phase was modeled with scale factor and two cell parameters, while the profile

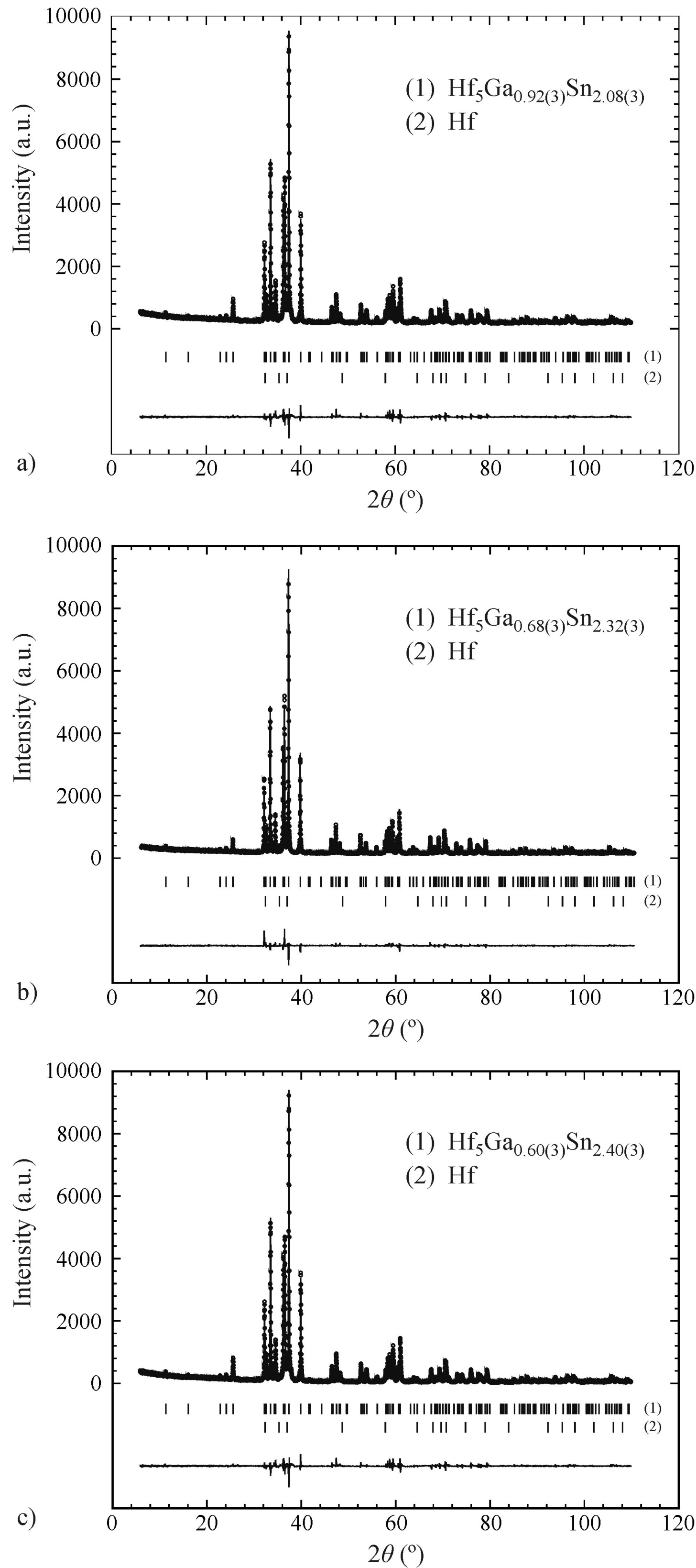

Fig. 6 Experimental (dots), calculated (line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the samples: a) $Hf_{62.5}Ga_{11.5}Sn_{26}$, b) $Hf_{62.5}Ga_{8.5}Sn_{29}$, c) $Hf_{62.5}Ga_{7.5}Sn_{30}$ (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of reflections for the ternary compound (1) and Hf (2).

Table 9 Experimental details and crystallographic data for three compositions from the homogeneity range of the ternary phase $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$.

Refined composition		$Hf_5Ga_{0.92(3)}Sn_{2.08(3)}$	$Hf_5Ga_{0.68(3)}Sn_{2.32(3)}$	$Hf_5Ga_{0.60(3)}Sn_{2.40(3)}$
Formula weight M_r		1203.51	1215.27	1219.19
Structure type		Nb_5SiSn_2, ordering derivative of W_5Si_3		
Pearson symbol		*tI*32		
Space group		*I*4/*mcm*		
Unit-cell parameters:	*a*, Å	10.9597(5)	10.9945(3)	11.0042(2)
	c, Å	5.5328(3)	5.55348(14)	5.55987(11)
Cell volume *V*, $Å^3$		664.58(5)	671.30(3)	673.26(2)
Formula units per cell *Z*		4		
Density D_X, g cm^{-3}		12.033	12.029	12.032
Preferred orientation: value / [direction]		1.006(4) / [110]	0.963(3) / [110]	0.955(3) / [110]
Scanning mode		$\theta/2\theta$		
Range 2θ, º		6-110		
Step size, °		0.015		
Scanning time per step, s		380		
Profile parameters:	*U*	0.059(7)	0.006(2)	0.0136(16)
	V	0.031(7)	0.002(2)	-0.0064(19)
	W	0.0059(16)	0.0106(6)	0.0121(5)
Shape parameter		0.584(7)	0.386(6)	0.570(6)
Asymmetry parameters		-0.003(6), -0.0366(13)	0.034(5), -0.0202(11)	0.050(4), -0.0083(10)
Reliability factors:	R_B	0.0375	0.0479	0.0425
	R_F	0.0429	0.0469	0.0317
	R_p [a]	0.1510, 0.0781	0.1500, 0.0818	0.1310, 0.0689
	R_{wp} [a]	0.1640, 0.1080	0.1630, 0.1130	0.1400, 0.0941
	χ^2	2.25	1.61	1.61

[a] Conventional and non-corrected for background.

Table 10 Atomic coordinates, site occupancies and isotropic displacement parameters for three compositions from the homogeneity range of the ternary phase $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$.

Site	Wyckoff position	Occupancy, %	*x*	*y*	*z*	B_{iso}, $Å^2$
$Hf_5Ga_{0.92(3)}Sn_{2.08(3)}$						
Hf1	16*k*	100	0.07635(9)	0.21842(9)	0	0.66(7)
Hf2	4*b*	100	0	1/2	1/4	0.61(5)
*M*1 (Sn)	8*h*	84.6(13)Sn/15.4(13)Ga	0.16473(13)	0.66473(13)	0	0.43(7)
*M*2 (Ga)	4*a*	61.2(16)Ga/38.8(16)Sn	0	0	1/4	0.73(13)
$Hf_5Ga_{0.68(3)}Sn_{2.32(3)}$						
Hf1	16*k*	100	0.07621(9)	0.22022(8)	0	0.95(3)
Hf2	4*b*	100	0	1/2	1/4	1.07(5)
*M*1 (Sn)	8*h*	92.0(13)Sn/8.0(13)Ga	0.16492(12)	0.66492(12)	0	0.93(7)
*M*2 (Ga)	4*a*	52.0(14)Ga/48.0(14)Sn	0	0	1/4	0.66(11)
$Hf_5Ga_{0.60(3)}Sn_{2.40(3)}$						
Hf1	16*k*	100	0.07628(8)	0.22061(7)	0	0.88(2)
Hf2	4*b*	100	0	1/2	1/4	0.86(4)
*M*1 (Sn)	8*h*	94.1(11)Sn/5.9(11)Ga	0.16443(10)	0.66443(10)	0	0.53(5)
*M*2 (Ga)	4*a*	48.2(14)Ga/51.8(14)Sn	0	0	1/4	0.70(9)

parameters were refined first and fixed in the final cycles of the refinement. Finally, 21 parameters were allowed to vary for both phases: the 2θ shift (with the $\sin(2\theta)$ dependence sample transparency coefficient), two scale factors, four cell parameters, six profile parameters (pseudo-Voigt profile), three positional parameters, four atomic displacements parameters and one texture parameter. The background was defined using the Fourier filtering technique. Experimental and calculated X-ray powder diffraction patterns and the difference between them for samples of nominal composition $Hf_{62.5}Ga_{11.5}Sn_{26}$,

Table 11 Interatomic distances and coordination numbers of atoms for the three compositions from the homogeneity range of the ternary phase $Hf_5Ga_{1.24\text{-}0.52}Sn_{1.76\text{-}2.48}$.

Atoms		*d*, Å			Coordination number
		$Hf_5Ga_{0.92(3)}Sn_{2.08(3)}$	$Hf_5Ga_{0.68(3)}Sn_{2.32(3)}$	$Hf_5Ga_{0.60(3)}Sn_{2.40(3)}$	
Hf1	– 2 *M*2	2.8886(10)	2.9141(9)	2.9206(8)	15
	– 1 *M*1	2.9362(18)	2.9104(17)	2.9195(15)	
	– 1 *M*1	2.8981(18)	2.9365(17)	2.9354(15)	
	– 1 Hf1	3.1809(16)	3.1652(14)	3.1609(12)	
	– 2 *M*1	3.1986(9)	3.2025(9)	3.2046(7)	
	– 2 Hf1	3.2332(8)	3.2432(7)	3.2475(6)	
	– 2 Hf2	3.4838(10)	3.4773(9)	3.4769(8)	
	– 2 Hf1	3.5358(10)	3.5671(9)	3.5739(8)	
	– 2 Hf1	3.5862(16)	3.6233(14)	3.6326(12)	
Hf2	– 2 Hf2	2.76640(15)	2.77674(7)	2.77994(6)	14
	– 4 *M*1	2.9038(13)	2.9160(13)	2.9120(11)	
	– 8 Hf1	3.4838(10)	3.4773(9)	3.4769(8)	
*M*1 (Sn)	– 2 Hf1	2.8981(18)	2.9104(17)	2.9195(15)	10
	– 2 Hf2	2.9038(13)	2.9160(13)	2.9120(11)	
	– 2 Hf1	2.9362(18)	2.9365(17)	2.9354(15)	
	– 4 Hf1	3.1986(9)	3.2025(9)	3.2046(7)	
*M*2 (Ga)	– 2 *M*2	2.76640(15)	2.77674(7)	2.77994(6)	10
	– 8 Hf1	2.8886(10)	2.9141(9)	2.9206(8)	

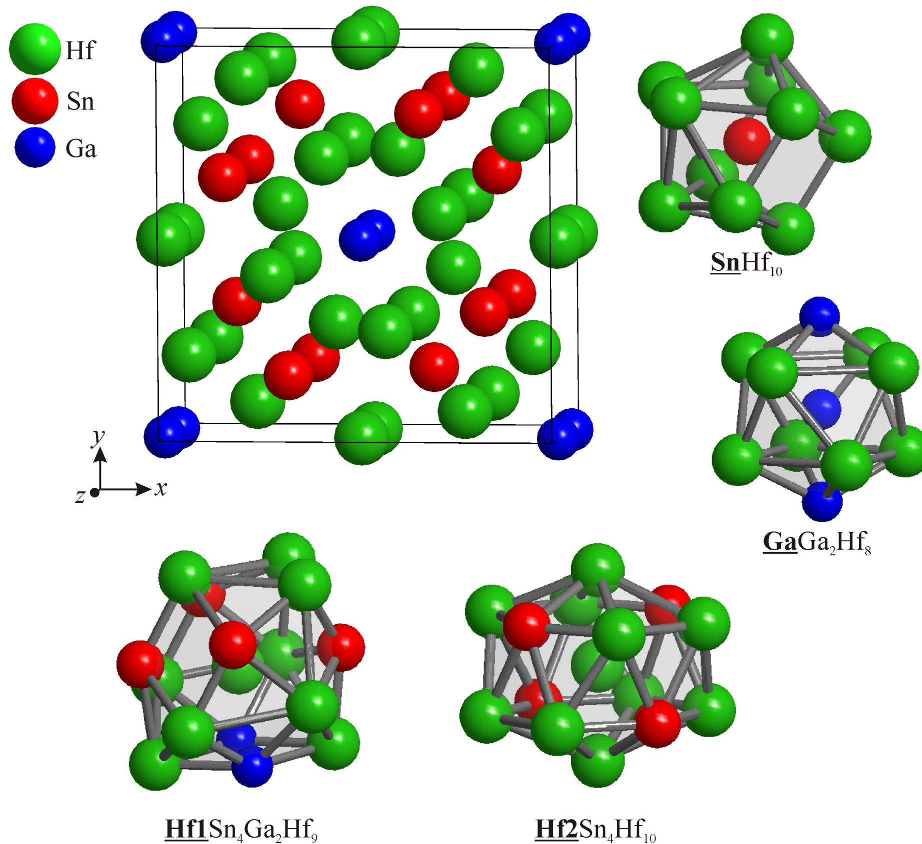

Fig. 7 Unit cell and coordination polyhedra of the atoms in the structure of $Hf_5Ga_{1.24\text{-}0.52}Sn_{1.76\text{-}2.48}$.

Table 12 Unit-cell parameters of the homogeneity range of the ternary compound $Hf_5Ga_{3-x}Sn_x$ (x = 1.76-2.48).

Nominal composition of the sample, at.%	x	a, Å	c, Å	V, Å^3
$Hf_{62.5}Ga_{17.8}Sn_{20}$	1.76[a]	10.9154(8)	5.51311(15)	656.86(10)
$Hf_{62.5}Ga_{11.5}Sn_{26}$	2.08(3)	10.9597(5)	5.5328(3)	664.58(5)
$Hf_{62.5}Ga_{8.5}Sn_{29}$	2.32(3)	10.9945(3)	5.55348(14)	671.30(3)
$Hf_{62.5}Ga_{7.5}Sn_{30}$	2.40(3)	11.0042(2)	5.55987(11)	673.26(2)
$Hf_{62.5}Ga_{4.5}Sn_{33}$	2.48[a]	11.0203(7)	5.56591(16)	675.96(8)

[a] Extrapolated from the plot of the unit-cell parameters (see Fig. 7).

$Hf_{62.5}Ga_{8.5}Sn_{29}$, and $Hf_{62.5}Ga_{7.5}Sn_{30}$ are shown in Fig. 6. Experimental details and crystallographic data for three compositions within the homogeneity range of the ternary phase $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$ are listed in Table 9. Atomic coordinates, site occupancies and isotropic displacement parameters are presented in Table 10.

The interatomic distances and coordination numbers of atoms for the three compositions from the homogeneity range of the ternary phase $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$ are listed in Table 11. The content of the unit cell and the coordination polyhedra of the different atom sites are shown in Fig. 7. Since the atomic sites *M*1 and *M*2 are occupied by considerably different proportions of Sn and Ga (see Table 10), we will in continuation refer to them as Sn and Ga, respectively.

The Hf atoms are coordinated by 15 and 14 atoms forming 15- and 14-vertex Frank-Kasper polyhedra of composition $\underline{Hf1}Sn_4Ga_2Hf_9$ and $\underline{Hf2}Sn_4Hf_{10}$, respectively. The atoms of the statistical mixture *M*1 (Sn) have ten Hf atoms in the closest environment forming a polyhedron of composition $\underline{Sn}Hf_{10}$, which can be described as a trigonal prism with four additional atoms in the equatorial plane. The atoms of the statistical mixture *M*2 (Ga) together with Hf atoms form centered two-capped square antiprisms of composition $\underline{Ga}Ga_2Hf_8$. The shortest distances in the structure are Hf2-Hf2 and *M*2-*M*2 distances (2.76640(15) Å, identical for both). A particular feature of the structure is the absence of Sn-Sn contacts. The shortest *M*1-*M*2 distance is 3.8262(14) Å, the same value as the shortest *M*1-*M*1 distance. The only homoatomic contacts between *p*-block elements are between atoms from site *M*2, *i.e.* mainly Ga-Ga contacts, and no Sn-Sn contacts, if we accept that the maximum proportion of Sn atoms on this site is 50 %.

The concentration range of the ternary compound at 600°C was confirmed from plots of the dependence of the cell parameters on the compositions. Unit-cell parameters of the homogeneity range of the ternary compound and their graphical representation are shown in Table 12 and Fig. 8, respectively.

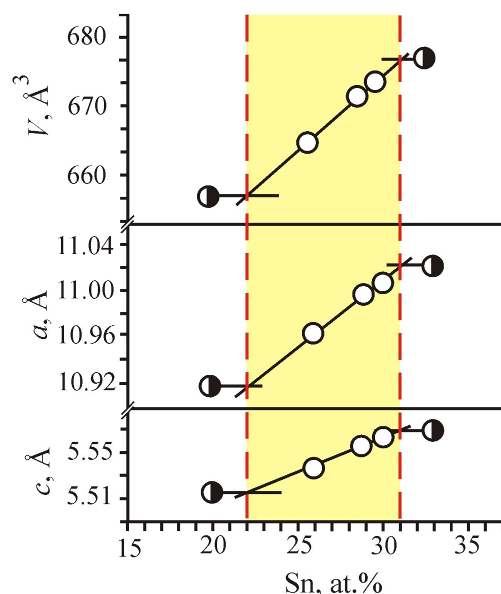

Fig. 8 Cell parameters as a function of the Sn content within the homogeneity range of the ternary compound $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$.

Discussion

The interaction of hafnium with two *p*-block elements in the investigated system Hf–Ga–Sn leads to the formation of only one ternary compound and solid solutions based on three binary compounds. Between the isostructural compounds Hf_5Ga_3 and Hf_5Sn_3 (structure type Mn_5Si_3) a continuous solid solution does not form. It should be noted that in the investigated system the ternary intermetallic compound and all solid solutions are formed in the Hf-rich region (> 50 at.%). A similar tendency is observed in related systems.

In comparison with the ternary systems containing Ge and Sb instead of Sn, there are similarities and differences in the interaction of the components along the isoconcentrate 62.5 at.% Hf. In the case of the quasibinary system Hf_5Ga_3–Hf_5Ge_3 a continuous solid solution is formed, whereas in the system Hf_5Ga_3–Hf_5Sb_3, similarly to the ternary stannide

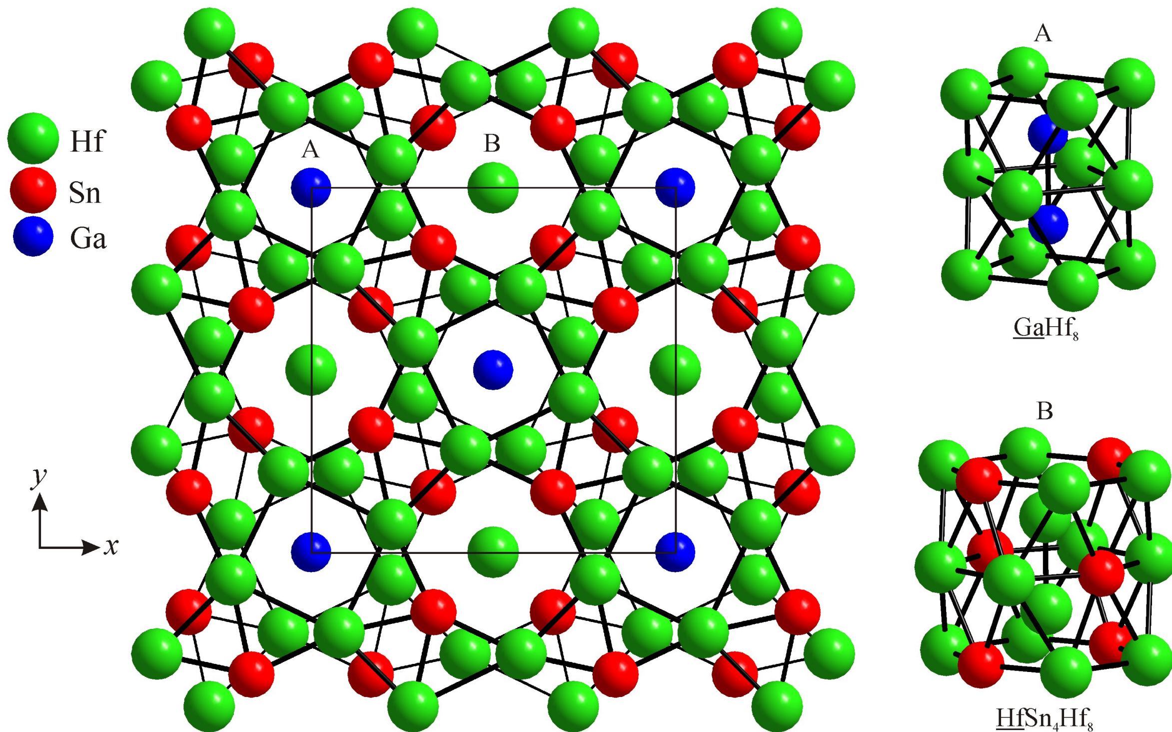

Fig. 9 Projection of the structure of $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$ along [001] and the square (A) and hexagonal (B) antiprisms that form channels containing linear chains of Ga/Sn and Hf atoms, respectively.

reported here, a compound $Hf_5Ga_{1.4-0.6}Sb_{1.6-2.4}$ (structure type Nb_5SiSn_2, Pearson symbol *tI*32, space group *I*4/*mcm*, $a = 10.8500(2)$-$10.9108(9)$, $c = 5.50169(11)$-$5.5434(5)$ Å) [29] is formed. The same tendency is confirmed by the formation of the compound $Zr_5Ga_{0.52(2)}Sn_{2.48(2)}$ ($a = 11.1656(4)$, $c = 5.5545(3)$ Å) with the same structure type [30].

Two of the four ternary structures in the investigated system can be considered as closely related. The structure of Hf_3Ga_2Sn (limiting composition of the substitutional solid solution $HfGa_{1-x}Sn_x$ (x = 0-0.34)), being an ordered derivative of the ThIn structure type, is closely related to the structure of Hf_5GaSn_3 (limiting composition of the interstitial solid solution $Hf_5Ga_xSn_3$ (x = 0-1), structure type Hf_5CuSn_3). Both structures can be conveniently described as being built from similar layers [26].

In the investigated and related systems, ternary compounds with the W_5Si_3 structure type or its ordered derivative Nb_5SiSn_2 are formed. Their compositions are usually rich in the *p*-block element which has larger atom size.

The structure of the compound $Hf_5Ga_{1.24-0.52}Sn_{1.76-2.48}$ is built up of two kinds of isolated column running infinitely along the [001] direction. The columns are constructed of centered square antiprisms $\underline{Ga}Hf_8$ (Hf atoms of the Wyckoff position 16*k*) and tetrahedra $\underline{Hf}Sn_4$ (Hf atoms of the Wyckoff position 4*b*). The square antiprisms share square faces, whereas the tetrahedra share edges. The composition of the compound is $Hf_5GaSn_2 \equiv GaHf_{8/2} + HfSn_{4/2}$. Adding Hf atoms to the tetrahedra $\underline{Hf}Sn_4$ hexagonal antiprisms $\underline{Hf}Sn_4Hf_8$ may be emphasized. In such a way square and hexagonal channels are formed and the atoms inside these channels (Ga/Sn and Hf, respectively) form linear chains that extend along [001] (Fig. 9).

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