

Hf₃Ga_{1.97(2)}Sn_{1.03(2)}, a ternary derivative of the ThIn type

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The crystal structure of the substitutional solid solution HfGa_{1-x}Sn_x ($x = 0-0.34(1)$) was refined from X-ray single-crystal and powder diffraction data (space group *Pbcm*, Pearson symbol *oP24*, $a = 9.3370(19)$, $b = 8.6920(17)$, $c = 5.6650(11)$ Å for Hf₃Ga_{1.97(2)}Sn_{1.03(2)}). The structure of the ideal limiting formula Hf₃Ga₂Sn, ignoring partial Ga/Sn disorder, represents the first ternary ordering derivative of the structure type ThIn. The structure of Hf₃Ga₂Sn is closely related to that of Hf₅GaSn₃ (limiting composition of the interstitial solid solution Hf₅Ga_xSn₃ ($x = 0-1$), structure type Hf₅CuSn₃, space group *P6₃/mcm*) and can be derived from it applying group-subgroup relations between the space groups.

Hafnium / Gallium / Tin / Single-crystal X-ray diffraction / Crystal structure / Substitutional solid solution

Introduction

The phase diagram of the ternary system Hf–Ga–Sn has not yet been constructed. The formation and crystal structure of the interstitial solid solution Hf₅Ga_xSn₃ (structure type Mn₅Si₃ for $x = 0$ (Hf₅CuSn₃ for $0 < x \leq 1$), Pearson symbol *hP16* (*hP18*), space group *P6₃/mcm*, $a = 8.3656$ (8.5564), $c = 5.7077$ (5.7859) Å) and the ternary compound Hf₅Ga_{0.56}Sn_{2.44} (structure type Nb₅SiSn₂, *tI32*, *I4/mcm*, $a = 11.0023$, $c = 5.5582$ Å) have been reported in the Hf-rich part of the system [1,2]. The structure of the latter is characterized by partial ordering of atoms of *p*-block elements, which are statistically distributed over one of the two available atom sites (Wyckoff position *4a*), whereas the second site (*8h*) is occupied exclusively by Sn atoms. In the structure of Hf₅Ga_xSn₃ ($x = 0-1$) interstitial Ga atoms progressively fill Wyckoff position *2b*, whereas replacement of Sn atoms by Ga atoms, *i.e.* the formation of a substitutional solid solution, is not observed.

During a systematic investigation of the interaction of the components in the ternary system Hf–Ga–Sn at 600°C the formation of an extended solid solution based on the binary compound HfGa was established. Hafnium monogallide forms peritectically at 1550°C by the reaction Hf₁₁Ga₁₀ + L ↔ HfGa [3] and crystallizes in the orthorhombic structure type ThIn (*oP24*, *Pbcm*, $a = 9.171$, $b = 8503$, $c = 5648$ Å) [4]. The structure type ThIn [5] is not very common

among the structures of intermetallic compounds: in addition to ThIn and HfGa, the structures of three binary compounds (ThTl, UGe, USn) and four ternary phases (ZrAl_{0.3}Ga_{0.7}, Zr_{0.5}Nb_{0.5}Ga, Zr_{0.88}V_{0.12}Ga, Zr_{0.9}Ti_{0.1}Ga) have been reported with this type of structure [6]. The structure of the binary compound HfGa is characterized by three 4-fold sites occupied by Hf atoms and three 4-fold sites occupied by Ga atoms, implying possible ordering of Ga and Sn atoms in the structure of the solid solution HfGa_{1-x}Sn_x. Among the ternary phases crystallizing with ThIn-type structures, a complete structure determination was carried out only for ZrAl_{0.3}Ga_{0.7} and Zr_{0.88}V_{0.12}Ga, however, ordering of the atoms of the *p*- or *d*-block elements was not observed [4].

The aim of the present work was the investigation of the solid solution HfGa_{1-x}Sn_x by means of X-ray phase and structure analyses and a detailed determination of its crystal structure by single-crystal X-ray diffraction.

Experimental

Alloys were synthesized from the elements (purity > 99.9 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To ensure homogeneity the samples were remelted twice. The ingots were wrapped into tantalum foil, annealed at

600°C in quartz ampoules under vacuum for 1 month and subsequently quenched in cold water. The weight loss during the preparation of the samples was less than 1 % of the total mass, which was 1 g for each alloy.

A prism-like single crystal was extracted from the alloy of composition Hf₅₀Ga₃₂Sn₁₈ (in at.%), mounted on a glass fiber and 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, $\lambda = 0.71073$ Å, graphite monochromator) equipped with an imaging plate detector. An analytical absorption correction was applied using X-Shape/X-Red software [7,8]. No significant variation of the intensities was observed during the data collection. The structure was solved by direct methods in the centrosymmetric, orthorhombic space group *Pbcm*, using the program SHELXS-97 [9] and the program package WinGX [10]. It belongs to the ThIn structure type with cell parameters $a = 9.3370(19)$, $b = 8.6920(17)$, $c = 5.6650(11)$ Å. The cell parameters are larger than those of HfGa

($a = 9.171$, $b = 8.503$, $c = 5.648$ Å), which indicates the presence of Sn atoms in the structure, *i.e.* formation of a solid solution. Full-matrix least-squares refinements of the positional and anisotropic displacement parameters and the site occupancies were performed on F^2 using the program SHELXL-97 [9]. The three sites of atoms of *p*-block element were set to be occupied by statistical mixtures of Ga and Sn, but their relative occupancies were allowed to vary. The final refinement led to the composition Hf₃Ga_{1.97(2)}Sn_{1.03(2)}; the Sn atoms showed a clear preference for one of the sites, whereas the two other sites remained occupied almost exclusively by Ga atoms. Experimental details and results of the crystal structure determination are listed in Table 1.

The chemical composition of the single crystal was checked by energy dispersive X-ray analysis using a scanning electron microscope JEOL SEM 5900LV. The obtained composition agrees well with the nominal composition of the synthesized alloy (Table 2).

Table 1 Experimental details and crystallographic data for Hf₃Ga_{1.97(2)}Sn_{1.03(2)}.

Refined composition	Hf ₃ Ga _{1.97(2)} Sn _{1.03(2)}
Formula weight M_r	795.095
Structure type	Hf ₃ Ga ₂ Sn, ordering derivative of ThIn
Pearson symbol	<i>oP24</i>
Space group	<i>Pbcm</i>
Unit-cell parameters:	
a , Å	9.3370(19)
b , Å	8.6920(17)
c , Å	5.6650(11)
Cell volume V , Å ³	459.76(16)
Formula units per cell Z	4
Density D_x , g cm ⁻³	11.491
Diffractometer	Stoe IPDS-IIT
Radiation, wavelength λ , Å	Mo <i>K</i> α , 0.71073
Scanning mode	φ -oscillation
Absorption coefficient μ , mm ⁻¹	84.13
Crystal shape	plate
Crystal size, mm	0.080×0.060×0.005
Color	metallic grey
Number of reflections:	
measured	6591
independent	513
with $I > 2\sigma(I)$	410
Reliability factor R_{int}	0.0878
Range of h, k, l	$-12 \leq h \leq 12, -11 \leq k \leq 11, -7 \leq l \leq 7$
Range of θ , °	4.37-27.48
Reliability factors ($I > 2\sigma(I)$):	
R	0.0235
wR	0.0363
S	0.940
Number of reflections used in refinement	513
Number of refined parameters	39
Weighting scheme	
$(P = (F_o^2 + 2F_c^2)/3)$	$w = 1/[\sigma^2(F_o^2) + (0.0148P)^2]$
Extinction coefficient	0.00077(7)
Residual electron density: $\Delta\rho_{max}$, e Å ⁻³	1.643
$\Delta\rho_{min}$, e Å ⁻³	-2.242

Table 2 Results of the X-ray spectral analysis of the single crystal Hf₃Ga_{1.97(2)}Sn_{1.03(2)}.

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

Table 3 Unit-cell parameters of the solid solution HfGa_{1-x}Sn_x.

Sample composition, at. %	<i>x</i>	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , 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	0.22	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)

^a Composition of the alloy from which the single crystal was extracted (unit-cell parameters were refined from the single crystal data).

Table 4 Atomic coordinates and displacement parameters (Å²) for Hf₃Ga_{1.97(2)}Sn_{1.03(2)} (*oP24*, *Pbcm*, *a* = 9.3370(19), *b* = 8.6920(17), *c* = 5.6650(11) Å).

Site	Wyckoff position	Occupancy, %	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Hf1	4 <i>d</i>	100	0.11272(8)	0.52840(7)	1/4	0.0072(2)
Hf2	4 <i>d</i>	100	0.30446(8)	0.12864(8)	1/4	0.0086(2)
Hf3	4 <i>c</i>	100	0.61864(8)	1/4	0	0.0098(2)
M1 (Sn)	4 <i>d</i>	87(2)Sn/13(2)Ga	0.41493(13)	0.44960(13)	1/4	0.0077(5)
M2 (Ga1)	4 <i>d</i>	90(2)Ga/10(2)Sn	0.1476(2)	0.8631(2)	1/4	0.0088(6)
M3 (Ga2)	4 <i>c</i>	93(2)Ga/7(2)Sn	0.0704(2)	1/4	0	0.0085(7)

Site	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> 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)
M1 (Sn)	0.0080(8)	0.0066(7)	0.0086(6)	0.0010(4)	0	0
M2 (Ga1)	0.0083(11)	0.0090(10)	0.0092(9)	-0.0007(7)	0	0
M3 (Ga2)	0.0104(11)	0.0065(11)	0.0088(9)	0	0	0.0000(6)

In order to establish the range of Sn solubility in HfGa at 600°C and to analyze the evolution of the cell parameters within the solid solution HfGa_{1-x}Sn_x, four alloys containing 50 at.% Hf and different amounts of Ga and Sn (0, 4, 7, and 11 at.%) were examined by X-ray phase analysis. The analysis was carried out using X-ray powder diffraction data collected at room temperature on a diffractometer DRON-2.0M (Fe K α radiation, $\lambda = 1.93801$ Å) in the angular range $20^\circ \leq 2\theta \leq 140^\circ$ with the step 0.05° . Profile and structure parameters, including cell parameters were refined by the Rietveld method starting from the atomic coordinates of HfGa or Hf₃Ga_{1.97(2)}Sn_{1.03(2)} using the program package FullProf Suite [11]. The refined cell parameters for the samples of the solid solution HfGa_{1-x}Sn_x are listed in Table 3.

Results

The refined atomic coordinates and displacement parameters of the structure of Hf₃Ga_{1.97(2)}Sn_{1.03(2)} are listed in Table 4. This structure derives from the binary structure type ThIn by partial ordering of the atoms of the *p*-block elements on the three crystallographically independent sites (two sites in Wyckoff position 4*d* and one in 4*c*, space group *Pbcm*). Sn atoms replace Ga atoms in the structure of the binary compound HfGa on one of two 4*d* sites almost completely, whereas on the two other sites only small amounts of Sn atoms substitute for Ga atoms. The range of the substitutional solid solution extends up to 17 at.% Sn at 600°C, *i.e.* its composition can be presented as HfGa_{1-x}Sn_x ($x = 0-0.34(1)$). The

unit-cell parameters increase linearly with increasing Sn content and the dependencies can be described by Vegard's law. The ideal composition $\text{Hf}_3\text{Ga}_2\text{Sn}$ (16.7 at.% Sn) is reached at 600°C but without complete ordering of Ga and Sn atoms over the three atom sites.

The content of the unit cell and coordination polyhedra in the structure of $\text{Hf}_3\text{Ga}_{1.97(2)}\text{Sn}_{1.03(2)}$ are shown in Fig. 1, relevant interatomic distances and the coordination numbers of the atoms are listed in Table 5. Since the atomic sites $M1$, $M2$, and $M3$ are occupied by mainly one sort of atom (see Table 4), we will in continuation refer to them as Sn, Ga1, and Ga2, respectively.

The atoms of the closest coordination sphere of Hf1 form a 17-vertex polyhedron $\text{Hf1SnGa}_8\text{Hf}_8$, which can be considered as a pentagonal prism of composition Ga_3Hf_7 with five additional Ga atoms capping the side faces and one Sn and one Hf atom capping the base faces. The coordination polyhedron

of Hf2 is a 17-vertex polyhedron of composition $\text{Hf}_2\text{Sn}_4\text{Ga}_3\text{Hf}_{10}$, which can be represented as a pentagonal prism of composition Hf_{10} with three Ga and four Sn atoms capping the faces. A deformed 14-vertex Frank-Kasper polyhedron $\text{Hf}_3\text{Sn}_4\text{Ga}_2\text{Hf}_8$ (a hexagonal antiprism of composition $\text{Sn}_4\text{Ga}_2\text{Hf}_6$ with two additional Hf atoms capping the base faces) is formed around Hf3. The Sn site is surrounded by nine Hf atoms and two Sn atoms forming a pseudo Frank-Kasper 11-vertex polyhedron (defect icosahedron) of composition SnSn_2Hf_9 . The coordination polyhedra of the Ga sites are 9- and 10-vertex polyhedra $\text{Ga}_1\text{Ga}_2\text{Hf}_7$ and $\text{Ga}_2\text{Ga}_4\text{Hf}_6$, respectively. The former can be represented as a trigonal prism of composition Ga_2Hf_4 with three additional Hf atoms capping the rectangular faces, and the latter as a deformed tetragonal antiprism of composition Ga_2Hf_6 with two additional Ga atoms capping the base faces, or as a deformed defect icosahedron.

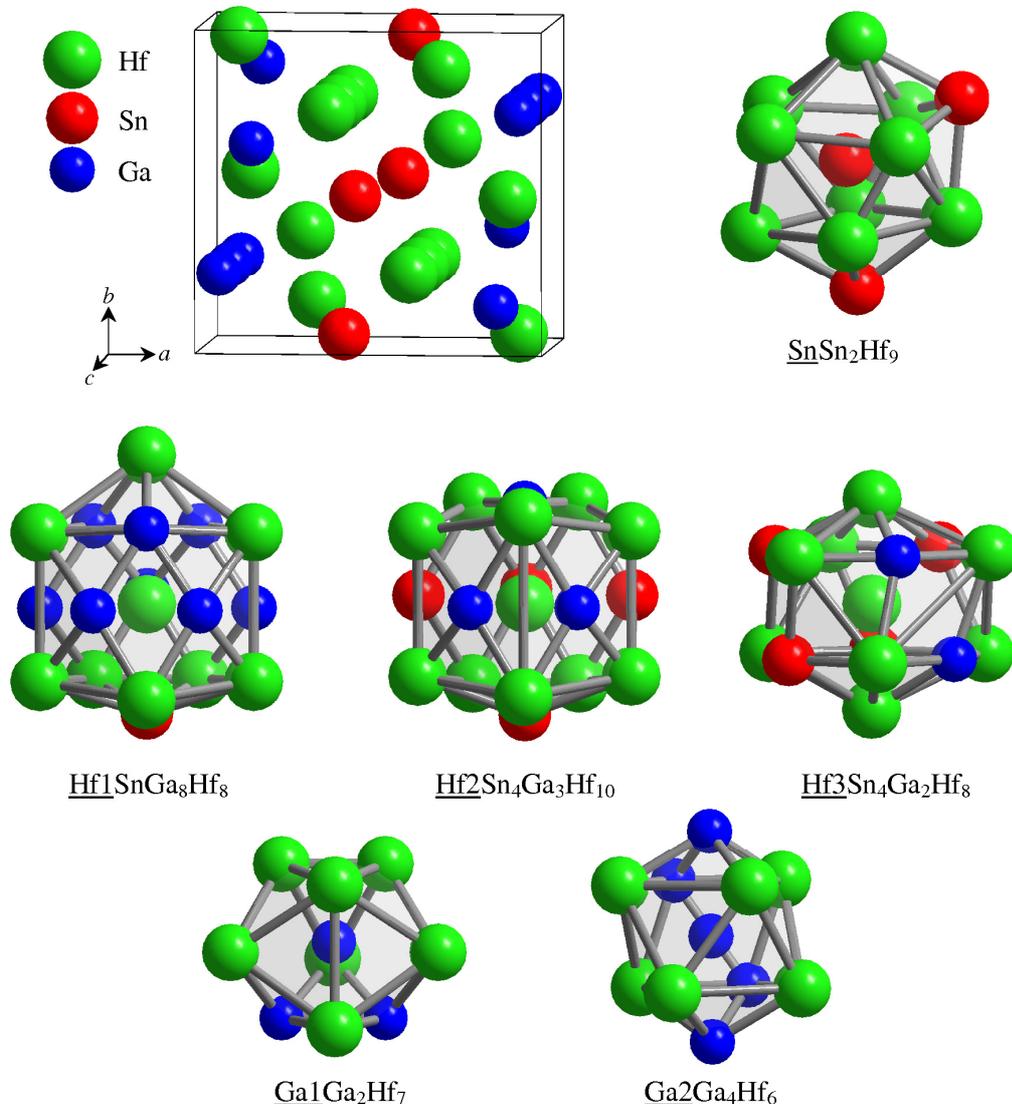


Fig. 1 Unit-cell content and coordination polyhedra of the atoms in the structure of $\text{Hf}_3\text{Ga}_{1.97(2)}\text{Sn}_{1.03(2)}$.

Table 5 Interatomic distances and coordination numbers (CN) of the atoms in the structure of Hf₃Ga_{1.97(2)}Sn_{1.03(2)} (*oP*24, *Pbcm*, *a* = 9.3370(19), *b* = 8.6920(17), *c* = 5.6650(11) Å).

Atoms		δ , Å	CN
Hf1	- 1 <i>M</i> 2	2.823(2)	17
	- 2 <i>M</i> 3	2.8315(7)	
	- 1 <i>M</i> 1	2.9036(16)	
	- 1 <i>M</i> 2	2.9273(18)	
	- 2 <i>M</i> 3	2.9392(13)	
	- 2 <i>M</i> 2	3.0032(8)	
	- 2 Hf1	3.5635(8)	
	- 2 Hf2	3.6183(8)	
	- 1 Hf2	3.9087(11)	
	- 1 Hf2	3.9915(13)	
	- 2 Hf3	3.4651(9)	
	Hf2	- 1 <i>M</i> 2	
- 2 <i>M</i> 3		2.8098(17)	
- 1 <i>M</i> 1		2.9743(14)	
- 1 <i>M</i> 1		3.0473(15)	
- 2 <i>M</i> 1		3.0903(8)	
- 2 Hf3		3.4240(11)	
- 2 Hf2		3.5318(8)	
- 2 Hf1		3.6183(8)	
- 2 Hf3		3.6541(9)	
- 1 Hf1		3.9087(11)	
- 1 Hf1		3.9915(13)	
Hf3		- 2 <i>M</i> 2	2.7814(17)
	- 2 Hf3	2.8326(5)	
	- 2 <i>M</i> 1	2.9383(12)	
	- 2 <i>M</i> 1	2.9868(11)	
	- 2 Hf2	3.4240(11)	
	- 2 Hf1	3.4651(9)	
	- 2 Hf2	3.6541(9)	

Atoms		δ , Å	CN
<i>M</i> 1	- 1 Hf1	2.9036(16)	11
	- 2 Hf3	2.9383(12)	
	- 1 Hf2	2.9743(14)	
	- 2 Hf3	2.9868(11)	
	- 1 Hf2	3.0473(15)	
	- 2 Hf2	3.0903(8)	
	- 2 <i>M</i> 1	3.3638(10)	
<i>M</i> 2	- 2 <i>M</i> 3	2.668(2)	9
	- 1 Hf2	2.7334(18)	
	- 2 Hf3	2.7814(17)	
	- 1 Hf1	2.823(2)	
	- 1 Hf1	2.9273(18)	
<i>M</i> 3	- 2 <i>M</i> 2	2.668(2)	10
	- 2 Hf2	2.8098(17)	
	- 2 Hf1	2.8315(7)	
	- 2 <i>M</i> 3	2.8326(5)	
	- 2 Hf1	2.9392(13)	
	- 2 Hf1	2.9392(13)	

Discussion

Complete ordering of the Sn atoms on one of the sites in Wyckoff position 4*d* would lead to the composition Hf₃Ga₂Sn. The structure of Hf₃Ga₂Sn, ignoring partial Ga/Sn disorder, represents a new structure type: a ternary ordering derivative of the structure type ThIn. A particular feature of the ordered structure is the absence of heteroatomic Sn-Ga contacts (the shortest Sn-Ga distance is 3.920(2) Å). The only homoatomic contacts between atoms of *p*-block elements are Ga-Ga distances (2.668(2) Å), which are the shortest interatomic distances in the structure and are similar to the average distance in the structure of pure gallium, which contains distances of three lengths: 2.43, 2.69, and 2.79 Å [12]. The interatomic distances Sn-Sn (3.3638(10) Å) are longer than the contact distances in the structure of Sn (3.024 Å) [13]. The hafnium atoms are connected to the atoms of both types of *p*-block element. The shortest distances from Hf atoms are observed to Ga atoms in position 4*d* (2.7334(18) Å). The interatomic distances in the structure of Hf₃Ga_{1.97(2)}Sn_{1.03(2)} correlate well with the sums of the atomic radii of the components ($r_{\text{Hf}} = 1.564$ Å, $r_{\text{Sn}} =$

1.405 Å and $r_{\text{Ga}} = 1.221$ Å [14]) and are in good agreement with the distances in the structures of binary hafnium stannides and gallides. The gradual replacement of smaller Ga atoms by larger Sn atoms within the solid solution HfGa_{1-x}Sn_x ($x = 0-0.34(1)$) leads to a linear increase of the cell parameters.

The coordination polyhedra of the atoms in the structure of Hf₃Ga_{1.97(2)}Sn_{1.03(2)} are similar to those in the structure of the binary compound HfGa, however, the replacement of Ga atoms by Sn atoms on preferentially one of the Ga sites leads to the deformation of some of the polyhedra.

The orthorhombic structure of Hf₃Ga₂Sn can be decomposed into two kinds of monoatomic layer stacked along the crystallographic direction [0 0 1] (Fig. 2). The translation unit contains four layers, two of each kind. Those at $z = \frac{1}{4}$ and $\frac{3}{4}$, composed by Hf, Ga and Sn atoms in the ratio 2:1:1, are hexagon-mesh layers (plane group *p*1). The hexagons have composition Hf₃Ga₂Sn or Hf₃GaSn₂ with only heteroatomic contacts. The Hf atoms are surrounded either by two Ga and one Sn atom or by one Ga and two Sn atoms, whereas the Ga and Sn atoms are surrounded by three Hf atoms. The layers at $z = 0$ and

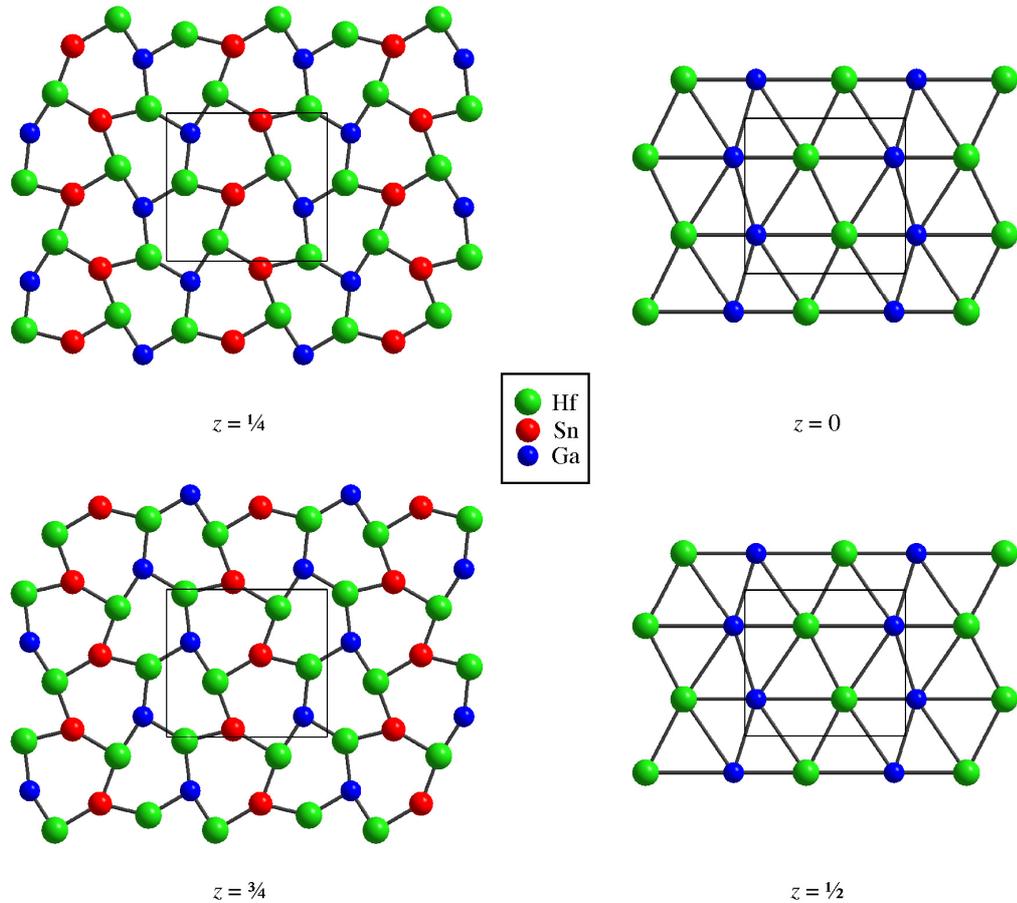
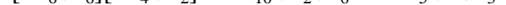
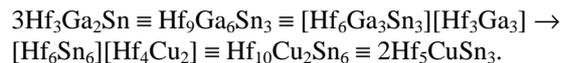


Fig. 2 Monoatomic layers in the structure of $\text{Hf}_3\text{Ga}_2\text{Sn}$.

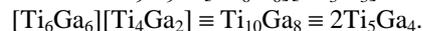
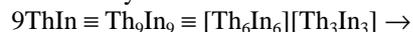
$1/2$, composed by Hf and Ga atoms in the ratio 1:1, have triangular mesh, *i.e.* possess the motif of close-packed layers (plane group $p2mg$). The composition of the triangles is Hf_2Ga or HfGa_2 , each atom having two homoatomic and four heteroatomic contacts. The atoms in the layers at $z = 0$ and $1/2$ are situated between two hexagons formed by the atoms in the layers at $z = 1/4$ and $3/4$.

Similar layers form the hexagonal structure of the compound Hf_5GaSn_3 [1], which belongs to the Hf_5CuSn_3 type, a ternary ordering variant of the Ti_5Ga_4 type (Fig. 3). The hexagon-mesh layers contain Hf and Sn atoms in the ratio 1:1, each atom being surrounded by three atoms of the other kind (plane group $p31m$). The remaining Hf and Cu atoms in the ratio 2:1 are situated in triangle-mesh layers (plane group $p6mm$). In these layers the Hf atoms form large hexagons centered by Cu atoms. Consequently each Hf atom is surrounded by three Hf and three Cu atoms, whereas each Cu atom has six neighboring Hf atoms. As in the structure of $\text{Hf}_3\text{Ga}_2\text{Sn}$, two kinds of layer alternate. The symmetry of the layers in Hf_5CuSn_3 is higher than in $\text{Hf}_3\text{Ga}_2\text{Sn}$ (plane group $p31m$ for the hexagon-mesh layer and $p6mm$ for the triangle-mesh layer), leading to overall hexagonal symmetry (space group $P6_3/mcm$). The two structures

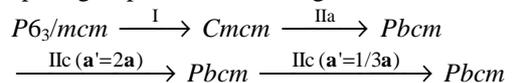
are thus closely related, but have different ordered distribution of atoms:



The relationship between the parent structure types, ThIn and Ti_5Ga_4 , respectively, can be presented in a similar way:



The group-subgroup relation for the corresponding space groups is the following:



(Table 6).

Conclusions

Partial replacement of Ga by Sn in the structure of HfGa leads to the formation of a substitutional solid solution $\text{HfGa}_{1-x}\text{Sn}_x$, which extends up to $x = 0.34(1)$ at 600°C . The refined composition of a Sn-rich crystal, $\text{Hf}_3\text{Ga}_{1.97(2)}\text{Sn}_{1.03(2)}$, is close to the ideal composition $\text{Hf}_3\text{Ga}_2\text{Sn}$. Sn preferentially occupies one of the Ga sites, which reduces the number of Sn-Ga

Table 6 Transformation from the structure of Hf₅GaSn₃ (Hf₅CuSn₃ type) to the structure of Hf₃Ga₂Sn (own type).

Model	I (Hf ₅ GaSn ₃)	II	III	IV	V (Hf ₃ Ga ₂ Sn)	
Transformation matrix		2 1 0 0 1 0 0 0 1	2 1 0 0 1 0 0 0 1	4 2 0 0 1 0 0 0 1	$\frac{4}{3}$ $\frac{2}{3}$ 0 0 1 0 0 0 1	
Space group	(193) <i>P6₃/mcm</i>	(63) <i>Cmcm</i>	(57) <i>Pbcm</i>	(57) <i>Pbcm</i>	(57) <i>Pbcm</i>	
Cell parameters, Å	$a_1 = 8.56$ ($b_1 = a_1 = 8.56$) $c_1 = 5.79$	$a_{II} = \sqrt{3}$ $a_1 = 14.83$ $b_{II} = a_1 = 8.56$ $c_{II} = c_1 = 5.79$	$a_{III} = \sqrt{3}$ $a_1 = 14.83$ $b_{III} = a_1 = 8.56$ $c_{III} = c_1 = 5.79$	$a_{IV} = 2\sqrt{3}$ $a_1 = 29.66$ $b_{IV} = a_1 = 8.56$ $c_{IV} = c_1 = 5.79$	$a_{V} = 2/\sqrt{3}$ $a_1 = 9.89$ $b_V = a_1 = 8.56$ $c_V = c_1 = 5.79$	
Site, Wyckoff position, coordinates	Hf1 6g 0.333,0,¼	Hf1 4c 0,0.667,¼	Hf1 4d 0.250,0.083,¼	Hf1 4d 0.375,0.083,¼	Hf1 4d 0.125,0.583,¼	
				Hf2 4d 0.125,0.583,¼	Hf2 4d 0.375,0.083,¼	
		Hf2 8g 0.167,0.167,¼	Hf2 4d 0.017,0.083,¼	Hf3 4d 0.542,0.083,¼	Hf2	
				Hf4 4d 0.042,0.083,¼	Hf1	
			Hf3 4d 0.583,0.083,¼	Hf5 4d 0.292,0.583,¼	Hf1	
				Hf6 4d 0.208,0.583,¼	Hf2	
		Hf2 4d ¼,¾,0	Hf3 8e 0.333,0,0	Hf4 4c 0.083,¼,0	Hf7 4c 0.958,¼,0	Ga2 4c 0.125,¼,0
					Hf8 4c 0.458,¼,0	Hf3 4c 0.625,¼,0
	Hf5 4c 0.417,¼,0		Hf9 4c 0.792,¼,0	Hf3		
			Hf10 4c 0.292,¼,0	Ga2		
	Ga 2b 0,0,0	Ga 4a 0,0,0	Ga 4c 0.749,¼,0	Ga1 4c 0.625,¼,0	Ga2	
				Ga2 4c 0.125,¼,0	Hf3	
	Sn 6g 0.667,0,¼	Sn1 8g 0,0.333,¼	Sn1 4d 0.249,0.417,¼	Sn1 4d 0.375,0.417,¼	Ga1 4d 0.125,0.917,¼	
				Sn2 4d 0.125,0.917,¼	Sn 4d 0.375,0.417,¼	
		Sn2 8g 0.333,0.333,¼	Sn2 4d 0.083,0.917,¼	Sn3 4d 0.042,0.417,¼	Ga1	
				Sn4 4d 0.542,0.417,¼	Sn	
Sn5 4d 0.208,0.417,¼				Sn		
Sn6 4d 0.708,0.417,¼				Ga1		
Origin shift ^a	0,0,0	0,0,½	0,½,0	0,0,0	0,½,0	

^a The atom coordinates were standardized by the program STRUCTURE TIDY [15].

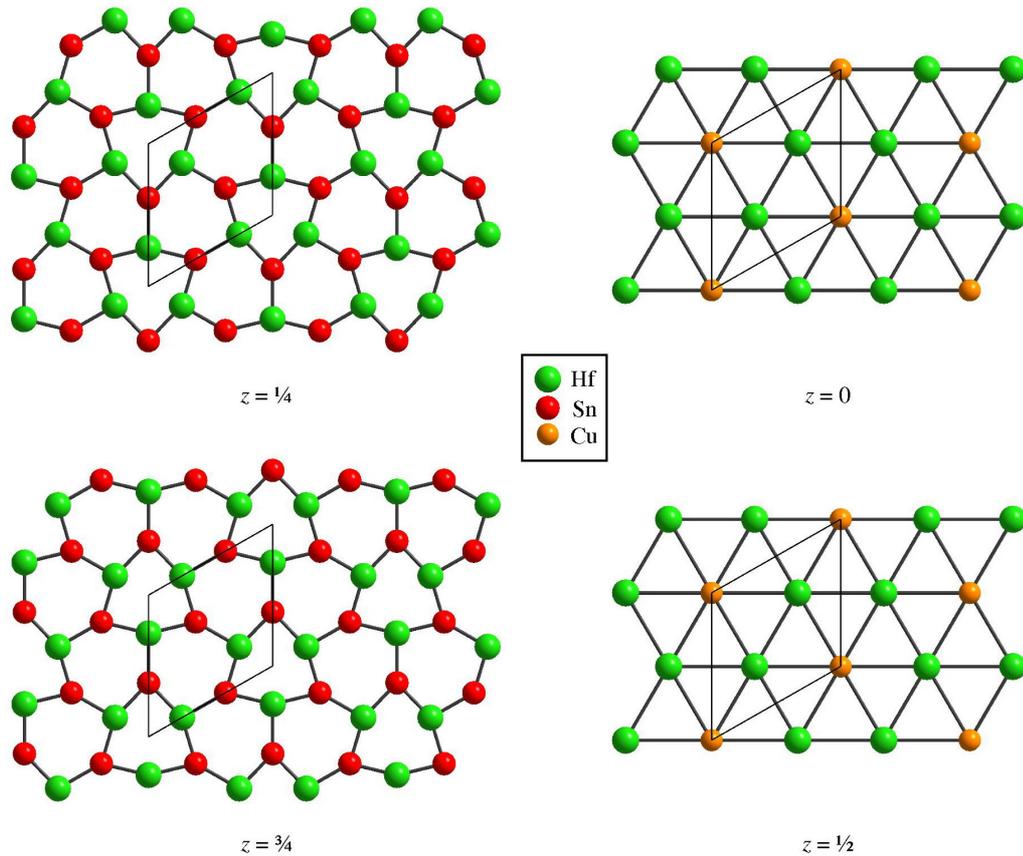


Fig. 3 Monoatomic layers in the structure of Hf_5CuSn_3 .

contacts in the structure. Complete ordering of Ga and Sn would represent a ternary ordering derivative of the ThIn type. Ordering may possibly be realized by annealing at a different temperature, or for a longer time. The structure of $\text{Hf}_3\text{Ga}_2\text{Sn}$ is closely related to that of the Hf_5CuSn_3 type, which is adopted by the interstitial solid solution $\text{Hf}_3\text{Ga}_x\text{Sn}_3$ ($x = 0-1$) in the same system. The structures can be derived from each other according to a scheme of substitutions that can be described by group-subgroup relations between their space groups.

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