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Crystal structures of alloys in the $HfPt_xPd_{1-x}Ga$ ($0 \le x \le 1$) solid solution

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The paper presents crystal structure data for three samples from the partially ordered solid solution $HfPt_xPd_{1-x}Ga$, with x ranging from 0 to 1. Their crystal structures were determined by Rietveld refinements of powder X-ray diffraction patterns. The phase crystallizes with the HfRhSn type of structure (space group $P\bar{6}2c$; Z = 6; Pearson symbol $hP18$). Unit cell parameters for x = 0.24 are: a = 7.1502(2) Å and c = 6.9106(3) Å. Both a and c change approximately linearly with increasing Pt content.

Intermetallics / Crystal structure / X-ray diffraction

1. Introduction

Platinum- and palladium-containing materials possess valuable chemical and physical properties. Consequently, they play an important role in different industries (electronics, electrotechnology and radio engineering), chemistry (catalysis), biology, and medicine. In order to develop new materials, there is an increasing interest in the investigation of related alloys and intermetallic compounds.

Up to now, in the {Zr,Hf}-{Pt,Pd}-Ga systems, eleven intermetallic compounds are known from the literature, namely: $ZrPt_{0.45}Ga_{2.55}$ ($AuCu_3$ type) [1], $ZrPt_{0.62}Ga_{1.38}$ (Co_2Si type) [2], ZrPtGa (HfRhSn type) [3], $Zr_6Pt_7Ga_{16}$ ($Mg_6Cu_{16}Si_7$ type) [4], $ZrPd_{0.6}Ga_{2.4}$ ($AuCu_3$ type) [5], $ZrPd_{0.7}Ga_{1.3}$ (KHg_2 type) [5], ZrPdGa (LaNiAl type) [6], $Zr_6Pd_{6.41\text{-}9.89}Ga_{16.59\text{-}13.11}$ (Th_6Mn_{23} or $Mg_6Cu_{16}Si_7$ type) [4,7], HfPtGa (HfRhSn type) [8], $HfPd_{0.58}Ga_{2.42}$ ($AuCu_3$ type) [9], and HfPdGa (HfRhSn type) [8,10].

This work is the continuation of a systematic research of the above mentioned and related alloys. Here, we present the results of a crystal structure investigation of the $HfPt_xPd_{1-x}Ga$ ($0 \le x \le 1$) solid solution.

2. Experimental details

The samples were prepared by arc-melting the initial components under high purity argon on a water-cooled copper hearth. High-purity metals (>99.9 wt.%) in the form of pieces were used as starting materials. The samples were re-melted four times for a better homogeneity. The weight loss during the melting was smaller than 0.5 %. The ingots were afterwards sealed in evacuated quartz tubes and annealed at 800 °C for one week. After the heat treatment, the samples were quenched into cold water.

Phase analysis of the annealed samples was performed using X-ray diffraction patterns collected with an HZG-4a diffractometer (Cu Kα-radiation). All the synthesized specimens were single-phase. For the crystal structure determination of the ternary compounds, the following scanning parameters were used: 2θ region 20-130º, step-width 0.05º, counting time 20 s per step. Rietveld refinements were carried out with the program FullProf [11], using a pseudo-Voigt profile function. The background was refined with a polynomial function.

3. Results and discussion

Based on X-ray diffraction analysis we studied the crystal structures of three alloys from the $HfPt_xPd_{1-x}Ga$ solid solution; x was refined to 0.24(2), 0.34(5) and 0.53(2). Data on the crystal structures of the HfPdGa and HfPtGa intermetallics were published in an earlier work [8]. Tables 1 and 2 present the results of the refinements, unit cell dimensions and atom positions. Fig. 1 shows an example of the powder X-ray diffraction patterns, together with the corresponding Rietveld refinement profiles.

Table 1 Unit-cell parameters and details of the crystallographic study on $HfPt_xPd_{1-x}Ga$ samples.

x	0	0.24	0.34	0.53	1
a, Å	7.1543	7.1502(2)	7.1431(3)	7.1387(2)	7.1244
c, Å	6.8932	6.9106(3)	6.9282(4)	6.9457(2)	6.9891
V, Å^3	305.55	305.97(2)	306.15(2)	306.54(1)	307.22
R_B,%	–	6.54	6.82	9.79	–
R_p,%	–	2.37	2.77	2.37	–
R_{wp},%	–	3.21	3.67	3.21	–
Reference	[2]	this work	this work	this work	[2]

Table 2 Positional and displacement parameters of the $HfPt_xPd_{1-x}Ga$ solid solution.

x	0	0.24	0.34	0.53	1
Hf in 6*h* (x y ¼)	x=0.4068 y=0.3865	x=0.4112(4) y=0.3892(4)	x=0.4122(5) y=0.3886(5)	x=0.4152(5) y=0.3909(5)	x=0.4109 y=0.3871
B_{iso}, Å^2	–	0.93(6)	1.39(8)	1.03(7)	–
*M*1 in 4*f* (⅓ ⅔ z)	z=0.0333	z=0.0348(8)	z=0.0351(8)	z=0.0342(6)	z=0.0322
B_{iso}, Å^2	–	0.56(9)	0.66(11)	0.80(8)	–
Occ.	1Pd	0.36(3)Pt + 0.64(3)Pd	0.52(7)Pt + 0.48(7)Pd	0.76(3)Pt + 0.24(3)Pd	1Pt
*M*2 in 2*b* (0 0 ¼)					
B_{iso}, Å^2	–	0.74(11)	0.84(15)	0.44(16)	–
Occ.	1Pd	1Pd	1Pd	0.05(3)Pt + 0.95(3)Pd	1Pt
Ga in 6*g* (x 0 0)	x=0.2633	x=0.2669(6)	x=0.2643(8)	x=0.2619(8)	x=0.2625
B_{iso}, Å^2	–	0.42(11)	0.91(16)	1.02(15)	–

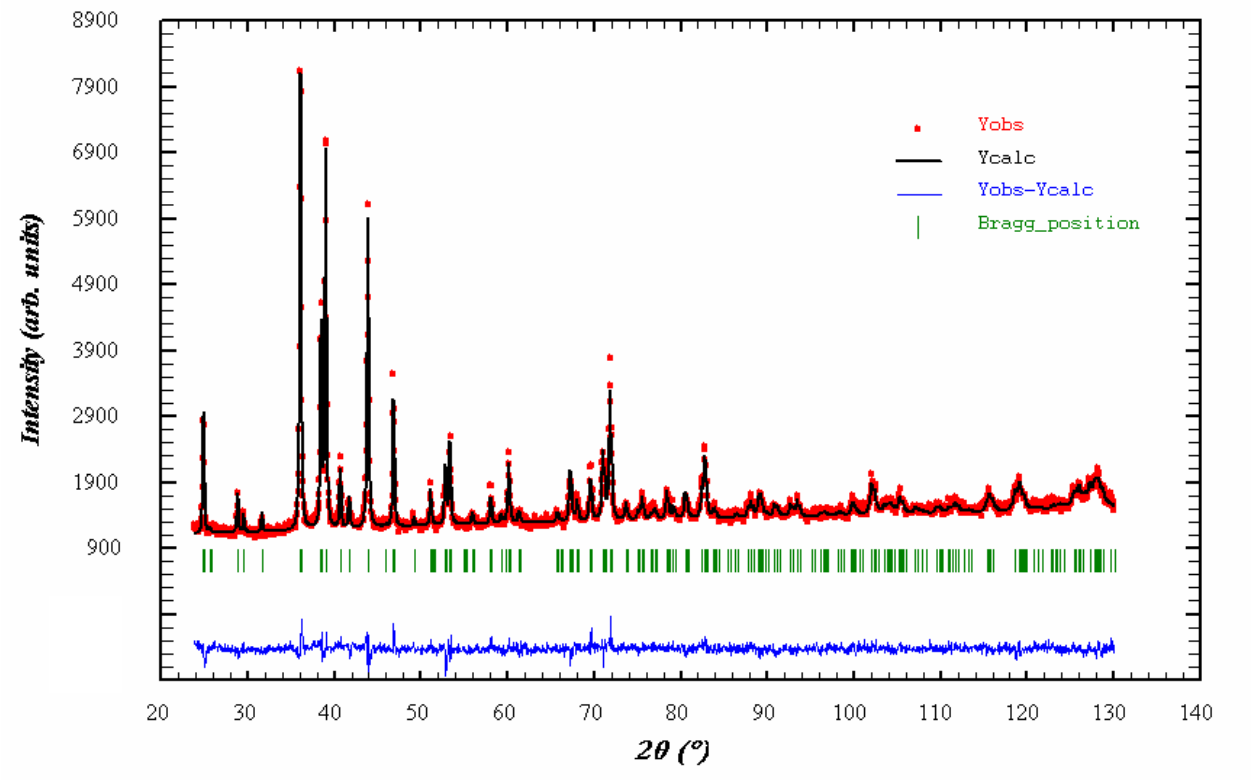

Fig. 1 Powder X-ray diffraction pattern and Rietveld refinement profiles for the $HfPt_xPd_{1-x}Ga$ solid solution with x = 0.34 at room temperature. Observed data (circles), calculated profile (upper line), difference profile (lower line), peak positions (bars).

The title ternary phase with $0 \le x \le 1$ crystallizes in the hexagonal space group $P\bar{6}2c$ (Pearson symbol *hP*18) with a partially ordered substituted variant of the HfRhSn type (a superstructure of the Mg_2Ga type) [12,13]. The atoms in the structure of $HfPt_xPd_{1-x}Ga$ are positioned in four crystallographic sites: Hf in 6*h*; a statistic mixture *M*1 (Pt and Pd atoms) in 4*f*; *M*2 (Pd) in 2*b* and Ga in 6*g*. From the refinements we concluded that in the phase with $x = 0.53$ the 2*b* site is occupied by a statistic mixture 95% Pd / 5% Pt.

The unit cell and coordination polyhedra of the atoms are presented in Fig. 2. The Hf atoms are surrounded by 13 neighbours. For the *M*1 and *M*2 atoms the coordination polyhedra are trigonal prisms with three extra atoms centring sides of the prisms. The Ga atoms are located in a 10-vertex polyhedron. The array of slightly distorted Hf_6 and regular Ga_6 trigonal prisms in the structure of $HfPt_xPd_{1-x}Ga$ is shown in Fig. 3. A different view of the structure, along the same direction, is shown in Fig. 4. Here, the stacking of 35_3 and 5_3 nets along the [001] direction is emphasized. These nets are formed by Pt (Pd) and Ga atoms. The hafnium atoms are embedded in voids of the network and form zig-zag chains within distorted channels.

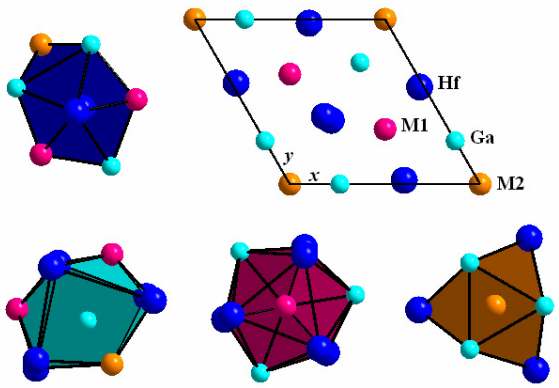

Fig. 2 Projection of the unit cell on the *xy* plane and coordination polyhedra of the atoms for the $HfPt_xPd_{1-x}Ga$ solid solution.

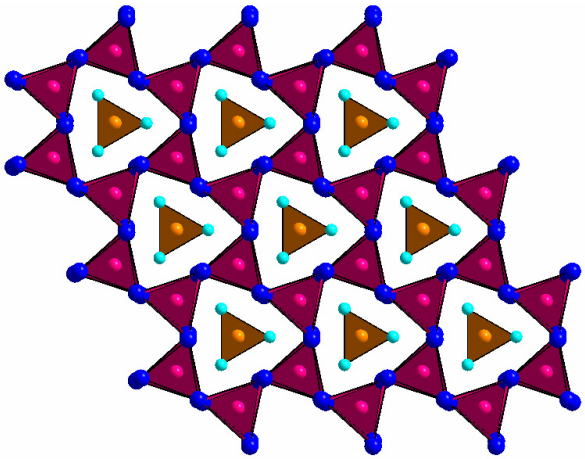

Fig. 3 Projection of the $HfPt_xPd_{1-x}Ga$ solid solution structure along the *z* axis.

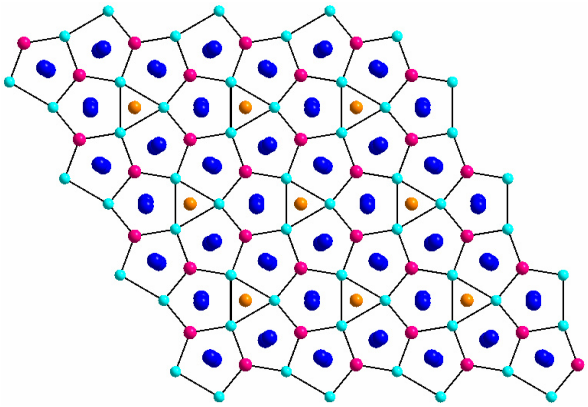

Fig. 4 Pentagonal-trigonal nets in the structure of $HfPt_xPd_{1-x}Ga$ viewed along the [001] direction.

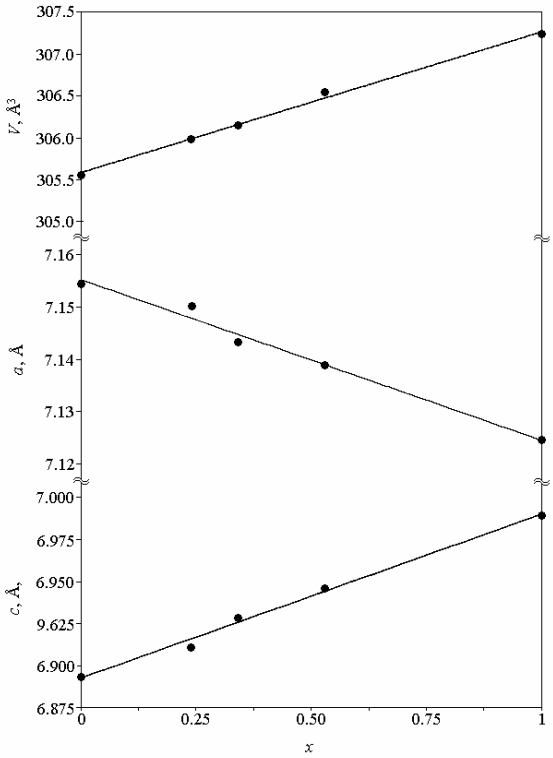

Fig. 5 Variation of the unit-cell parameters as a function of *x* in the $HfPt_xPd_{1-x}Ga$ solid solution.

The shortest interatomic distances present in $HfPt_xPd_{1-x}Ga$ are given in Table 3. These distances are close to the sums of the atomic radii of the respective atoms [14]. It should be noted that all Hf-Hf distances are longer than the shortest Hf-Hf contacts (3.18 Å) in hafnium metal. The Hf-*M*2 distances are longer than the Hf-*M*1 ones; however, both are slightly shorter than the sums of r_{Hf} and r_{Pt} (r_{Pd}). Hf-Ga contacts are observed near the sum of r_{Hf} and r_{Ga} [14]. The *M*1-*M*1 bonds are longer than the distances in *ccp* platinum or palladium. The distances between *M*1 or *M*2 and Ga atoms are shorter than the sum of r_{Ga} and r_{Pt} (r_{Pd}) based on data from [14].

Table 3 Shortest interatomic distances (Å) for the $HfPt_xPd_{1-x}Ga$ solid solution.

x	0	0.24	0.34	0.53	1
Hf-Hf	3.456	3.466	3.476	3.486	3.507
Hf-*M*1	2.753	2.750	2.757	2.760	2.774
Hf-*M*2	2.841	2.865	2.864	2.881	2.846
Hf-Ga	2.972	2.944	2.959	2.959	2.977
*M*1-*M*1	2.987	2.974	2.978	2.998	3.044
*M*1-Ga	2.680	2.663	2.673	2.681	2.672
*M*2-Ga	2.553	2.574	2.562	2.552	2.559

Standard deviations ≤0.001 Å.

Unit-cell dimensions of $HfPt_xPd_{1-x}Ga$ samples with various compositions are given in Fig. 5. Based on these data and previously published results, the unweighted fits yielded the following relations: a(Å) = 7.1551(12) – 0.031(2)x_{Pt} (R = 0.983), c(Å) = 6.8921(25) + 0.098(5)x_{Pt} (R = 0.993), V(Å^3) = 305.58(3) + 1.68(6)x_{Pt} (R = 0.995). It should be noted that substitution of Pt atoms for Pd atoms in HfPdGa leads to an unusual decrease of the a and increase of the c lattice parameters. The reason for this behaviour of the cell parameters in the $HfPt_xPd_{1-x}Ga$ solid solution is still unknown. But the unit-cell volume increases during the replacement of the smaller Pd atoms (r_{Pd} = 1.37 Å) by the slightly larger Pt atoms (r_{Pr} = 1.38 Å).

References

[1] Yu. Verbovytsky, K. Łątka, *J. Alloys Compd.* 428 (2007) 90-93.

[2] Yu. Verbovytsky, K. Łątka, *Visn. L'viv Univ., Ser. Khim.* 48(1) (2007) 179-182.

[3] M.F. Zumdick, R.-D. Hoffmann, R. Pöttgen, *Z. Naturforsch. B* 54 (1999) 45-53.

[4] V.Ya. Markiv, A.I. Storozhenko, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* (1973) 941-943.

[5] O.Ya. Myakush, I.R. Mokra, Z.M. Shpyrka, O.R. Myakush, *Coll. Abs. IX Int. Conf. Cryst. Chem. Intermet. Compd.*, Lviv, 2005, p. 59.

[6] R. Demchyna, Yu. Prots, U. Schwarz, Yu. Grin, *Z. Anorg. Allg. Chem.* 630 (2004) 1717.

[7] O.Ya. Myakush, I. Mokra, O.R. Myakush, A. Fedorchuk, *Coll. Abs. XII Int. Semin. Phys. Chem. Solids*, Lviv, 2006, p. 126.

[8] Yu. Verbovytsky, K. Łątka, *J. Alloys Compd.* 431 (2007) 130-135.

[9] Yu. Verbovytsky, K. Łątka, *J. Alloys Compd.* 438 (2007) L7-L11.

[10] R. Demchyna, Yu. Prots, U. Burkhardt, U. Schwarz, Yu. Grin. *Z. Kristallogr. New Cryst. Struct.* 221 (2006) 427-428.

[11] J. Rodriguez-Carvajal, *Physica B* 192 (1993) 55.

[12] E. Parthé, L. Gelato, B. Chabot, M. Penzo, K. Cenzual, R. Gladyshevskii, *TYPIX, Standardized Data and Crystal Chemical Characterization of Inorganic Structure Types*, Springer-Verlag, Berlin, 1994.

[13] M.F. Zumdick, R. Pöttgen, *Z. Kristallogr.* 214 (1999) 90-97.

[14] G.B. Bokiy, *Crystal Chemistry*, 3rd ed., Nauka, Moscow, 1971, 400 p. (in Russian).