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The crystal structure of HfZrP

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Abstract

The crystal structure of HfZrP has been determined using single crystal X-ray diffraction data. This compound crystallizes in the orthorhombic space group Cmmm (No.65), with $a=19.004(3)$, $b=29.372(4)$, $c=3.565(1)$ Å and the Zr_2P structure type. The Hf and Zr atoms are disordered on one site with total occupancy of 1.0. X-ray powder patterns indicate that $(Hf_xZr_{1-x})_2P$ alloys consist of single phase (Zr_2P-type),two phases and single phase (Hf_2P-type) corresponding to $0\leq x\leq0.5$, $0.5<x<0.8$ and $0.8\leq x\leq1.0$, respectively.

Keywords: Hafnium; Phosphorus; Zirconium; Crystal structure

1. Introduction

The binary Zr–P and Hf–P systems have been investigated extensively. In the Zr–P system the compounds Zr_3P [1], Zr_2P [2], Zr_7P_4 [3], $Zr_{14}P_9$ [4], ZrP [5,6] and ZrP_2 [7] have been reported and in the Hf–P system, there are known phases with the chemical formulas Hf_3P [8], Hf_2P [9], HfP [10], HfP_2 [11] and Hf_3P_2 [12]. Comparing the compounds in these two systems, we find there are significant differences in their compositions and their crystal structures. For example there are no Hf analogues of α-ZrP, Zr_7P_4 and $Zr_{14}P_9$ and Hf_3P_2 has no Zr counterpart as well. On the other hand, Hf_2P crystallizes in the Ta_2P-type, whereas Zr_2P crystallizes in Zr_2P-type. In order to add to our understanding of the behavior of Hf and Zr, we studied a series of $(Hf_xZr_{1-x})_2P$ alloys ($0\leq x\leq1.0$) and report the crystal structure of HfZrP and the homogeneity ranges of the solid solution phases.

2. Experimental details

The starting materials used in this experiment were red phosphorus (powder, −100 mesh, 99%, Alfa), hafnium (powder, −325 mesh, 99.6%, Alfa) and zirconium (powder, −60 mesh, 99.7%, Alfa). The preparation of $(Hf_xZr_{1-x})_2P$ samples ($x=0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0) involved three major steps. In the first, ZrP and HfP were prepared using the sealed tube method described previously [13]. Mixtures of ZrP, Zr and Hf (or HfP, Zr and Hf) in the different ratios were pelletized under a pressure of 10 000 psi, and then arc melted three to five times under an argon atmosphere. In the last step, these alloys were encased in Ta foil and then sealed in a evacuated fused silica tube and annealed at 1050°C for 30 days.

The identification of the various phases present in each sample was accomplished by examination of the X-ray powder patterns (Guinier FR552 camera using Cu Kα radiation). A needle-like single crystal from the sample $(Hf_{0.5}Zr_{0.5})_2P$ was selected and mounted on a glass fiber for the structure determination. The crystal quality was checked with a Weissenberg camera. The single-crystal diffraction data were collected on a four-circle-diffractometer with a rotating anode (Rigaku AFC6R), using monochromated Mo Kα radiation and the $\omega/2\theta$ scan technique. Three standard reflections monitored every 150 reflections showed no significant variation in intensity throughout the data collection. The details of data collection are given in Table 1.

The determination of the Laue group and the refinement of the unit cell parameters were performed using MSCIAFC diffractometer control software [14]. The crystal structure was solved using the direct method with the SHELXS program [15]. The structure was refined by

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Table 1
Crystal Data and Structure Refinement for HfZrP

Formula	HfZrP
Formula mass	299.81
space group	Cmmm (No.65)
a (Å)	19.004(3)
b (Å)	29.372(4)
c (Å)	3.565(1)
Z	36
T (K)	296
Diffractometer	Rigaku AFC6R
d_{calc} (g cm^{-3})	9.033
Crystal dimensions (mm)	0.03×0.035×0.19
Radiation (monochromated in incident beam)	(Mo Kα 0.71069 Å)
Absorption factors	514.35 mm^{-1} (Mo Kα)
2θ limits	$30° \leq 2\theta \leq 60°$
Data collected	$-10 \leq h \leq 26$, $0 \leq k \leq 40$, $-5 \leq l \leq 5$
No. of Data collected	4576
No. of reflections	1233
No. of variables	104
R[a]	0.028
R_w[b]	0.027
Goodness of fit[c]	1.850

[a] $R = \Sigma\ F_o - F_c\ /\Sigma F_o$.
[b] $R_w = [\Sigma\omega(\ F_o - F_c\ )^2/\Sigma w\ F_o\ ^2]^{1/2}$; $w = 1/\sigma^2(\ F_o\ )$.
[c] $\mathrm{GOF} = \Sigma[(\ F_o - F_c\ )/\sigma_i]/(N_{obs} - N_{parameters})$.

full-matrix, least-squares techniques with the TEXSAN software [16].

3. Results and discussion

The crystal belongs to orthorhombic system, mmm Laue group and C lattice type. The unit cell parameters were $a = 19.004(3)$, $b = 29.372(4)$, $c = 3.565(1)$ Å. The Laue group and systematic extinction of the crystal indicate the most probable space group is Cmmm (No. 65). Refinement indicates that all of the thirteen strongest electron density peaks correspond to Hf and Zr atoms disordered on each position with total occupancy of 1.0. A refinement with this model leads to $R = 0.028$, and $R_w = 0.027$.

Table 2 lists final values of the positional parameters, occupancies and temperature factors and Table 3 gives interatomic distances shorter than 3.6 Å. The structure of

Table 2
Atomic coordinates and temperature factors [Å^2] for HfZrP

Atom	Wyckoff position	x	y	z	occ.	B_{eq}	$U11$	$U22$	$U33$	$U12$	$U13$	$U23$
M1	4i	0	0.22046(3)	0	1.0	0.51(5)	0.0064(6)	0.0035(7)	0.0093(7)	0	0	0
M2	4j	0	0.30734(4)	1/2	1.0	0.65(7)	0.0073(7)	0.006(1)	0.011(1)	0	0	0
M3	8q	0.18910(6)	0.32868(3)	1/2	1.0	0.67(6)	0.0067(5)	0.0065(8)	0.0122(9)	−0.0009(6)	0	0
M4	8q	0.12914(6)	0.21561(3)	1/2	1.0	0.63(6)	0.0064(5)	0.0051(9)	0.013(1)	0.0014(7)	0	0
M5	4j	0	0.05596(4)	1/2	1.0	0.80(6)	0.0054(7)	0.0038(8)	0.021(1)	0	0	0
M6	8p	0.08105(5)	0.38014(2)	0	1.0	0.65(4)	0.0063(4)	0.0034(4)	0.0151(5)	0.0000(4)	0	0
M7	4g	0.89009(8)	0	0	1.0	0.64(6)	0.0120(8)	0.0025(8)	0.0098(9)	0	0	0
M8	4e	1/4	1/4	0	1.0	0.46(5)	0.0048(6)	0.0013(6)	0.0113(7)	−0.0007(6)	0	0
M9	4h	0.74915(8)	0	1/2	1.0	0.49(5)	0.0059(6)	0.0018(7)	0.0108(8)	0	0	0
M10	4j	0	0.44787(4)	1/2	1.0	0.90(6)	0.0050(7)	0.0154(8)	0.0139(8)	0	0	0
M11	4g	0.61482(8)	0	0	1.0	0.57(7)	0.0085(8)	0.004(1)	0.010(1)	0	0	0
M12	8p	0.08988(5)	0.12143(3)	0	1.0	0.59(4)	0.0064(5)	0.0048(6)	0.0114(6)	0.0001(5)	0	0
M13	8p	0.25077(6)	0.41633(3)	0	1.0	0.51(4)	0.0062(4)	0.0023(6)	0.0107(6)	0.0006(5)	0	0
P1	8q	0.1483(2)	0.4316(1)	1/2	1.0	0.9(2)	0.013(2)	0.012(2)	0.009(2)	−0.001(2)	0	0
P2	8q	0.3542(2)	0.4363(1)	1/2	1.0	0.7(2)	0.006(2)	0.009(2)	0.011(2)	−0.002(2)	0	0
P3	4j	0	0.1549(2)	1/2	1.0	0.6(2)	0.010(3)	0.002(2)	0.012(3)	0	0	0
P4	8p	0.2052(2)	0.1671(1)	0	1.0	0.6(1)	0.006(2)	0.006(2)	0.010(2)	−0.001(1)	0	0
P5	8p	0.1063(2)	0.2845(1)	0	1.0	0.7(1)	0.008(2)	0.009(2)	0.010(2)	−0.002(2)	0	0

M1=61%Zr+39%Hf, M2=44%Zr+56%Hf, M3=36%Zr+64%Hf, M4=34%Zr+66%Hf, M5=58%Zr+42%Hf, M6=63%Zr+36%Hf, M7=52%Zr+48%Hf, M8=59%Zr+41%Hf, M9=54%Zr+46%Hf, M10=63%Zr+37%Hf, M11=43%Zr+57%Hf, M12=49%Zr+51%Hf, M13=45%Zr+55%Hf.

Table 3
Interatomic distances (Å) shorter than 3.6 Å for HfZrP

M1	2 M1	3.5647(5)	M10	4 M6	3.083(1)
	2 M2	3.113(1)		2 M10	3.5647(5)
	4 M4	3.0364(9)		1 M10	3.062(2)
	2 M12	3.373(1)		4 M11	3.207(1)
	2 P3	2.624(4)		2 P1	2.859(5)
	2 P5	2.760(4)			
M2	2 M1	3.113(1)	M11	2 M6	3.5785(9)
	2 M2	3.5647(5)		2 M9	3.113(2)
	4 M6	3.182(1)		4 M10	3.207(1)
	4 P5	2.777(3)		2 M11	3.5647(5)
				2 M13	3.566(2)
M3	2 M3	3.5647(5)		4 P1	2.761(3)
	1 M4	3.511(1)			
	2 M6	3.111(1)			
	2 M8	3.1395(8)			
	2 M13	3.344(1)			
	1 P1	3.120(4)			
	2 P4	2.689(3)			
	2 P5	2.709(3)	M12	1 M1	3.373(1)
				2 M4	3.374(1)
M4	2 M1	3.0364(9)		2 M5	3.129(1)
	1 M3	3.511(1)		1 M7	3.587(1)
	2 M4	3.5647(5)		2 M12	3.5647(5)
	2 M8	3.0778(9)		1 M12	3.416(2)
	2 M12	3.374(1)		1 M13	3.225(2)
	1 P3	3.034(3)		2 P2	2.680(3)
	2 P4	2.701(3)		2 P3	2.657(2)
	2 P5	2.730(3)		1 P4	2.569(4)
M5	1 M5	3.287(2)	M13	2 M3	3.344(1)
	2 M5	3.5647(5)		1 M6	3.396(1)
	4 M7	3.200(1)		2 M9	3.0359(7)
	4 M12	3.129(1)		1 M11	3.566(2)
	2 P2	2.781(4)		1 M12	3.225(2)
	1 P3	2.906(5)		2 M13	3.5647(5)
				2 P1	2.677(4)
M6	2 M2	3.182(1)		2 P2	2.717(3)
	2 M3	3.111(1)		1 P4	2.590(4)
	1 M6	3.081(2)			
	2 M6	3.5647(5)	P1	1 M3	3.120(4)
	2 M10	3.083(1)		2 M6	2.663(3)
	1 M11	3.5785(9)		1 M9	2.777(4)
	1 M13	3.396(1)		1 M10	2.859(5)
	2 P1	2.663(3)		2 M11	2.761(3)
	1 P5	2.851(4)		2 M13	2.677(4)
				2 P1	3.5647(5)
M7	4 M5	3.200(1)			
	2 M7	3.5647(5)	P2	1 M5	2.781(4)
	2 M9	3.217(2)		2 M7	2.673(3)
	2 M12	3.587(1)		1 M9	2.735(4)
	4 P2	2.673(3)		2 M12	2.680(3)
				2 M13	2.717(3)
				2 P2	3.5647(5)
M8	4 M3	3.1395(8)			
	4 M4	3.0778(9)			
	2 M8	3.5647(5)	P3	2 M1	2.624(4)
	2 P4	2.580(4)		2 M4	3.034(3)
	2 P5	2.912(4)		1 M5	2.906(5)
				4 M12	2.657(2)
M9	2 M7	3.217(2)		2 P3	3.5647(5)
	2 M9	3.5647(5)			
	2 M11	3.113(2)	P4	2 M3	2.689(3)
	4 M13	3.0359(7)		2 M4	2.701(3)
	2 P1	2.777(4)		1 M8	2.580(4)
	2 P2	2.735(4)		1 M12	2.569(4)
				1 M13	2.590(4)
				2 P4	3.5647(5)
P5	1 M1	2.760(4)			
	2 M2	2.777(3)			
	2 M3	2.709(3)			
	2 M4	2.730(3)			
	1 M6	2.851(4)			
	1 M8	2.912(4)			
	2 P5	3.5647(5)			

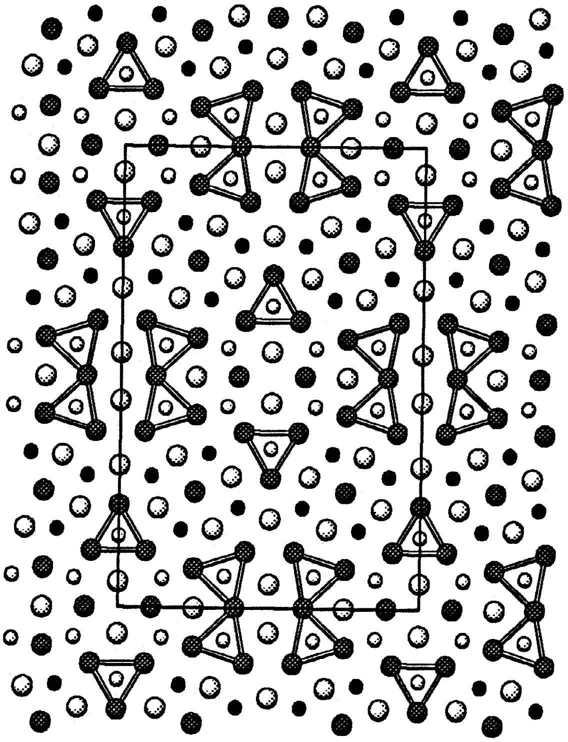

Fig. 1. Projection of HfZrP structure on [001] (large circles, M; small circles, P black circles, $z=0$; other circles, $z=1/2$).

HfZrP is similar to that of Zr_2P. Fig. 1 shows the projection of the HfZrP structure on [001]. Each position occupied by Zr atoms in Zr_2P was substituted by a mixture of Hf and Zr atoms with a different percentage occupation. Each P atom is surrounded by 7–9 mixed Hf and Zr atoms at distances between 2.569(4) and 3.120(4) Å and by two P atoms at a distance of 3.5647(5) Å. Each mixed atom M has coordination number 12–16 and is surrounded by three to five P atoms at distances between 2.569(4) and 3.120(4) Å, and from eight to twelve M neighbors at distances between 3.0359(7) and 3.566(2) Å.

Because Hf_2P and Zr_2P have different crystal structures, they can not form a continuous solid solution. From X-ray powder patterns of $(Hf_xZr_{1-x})_2P$ alloys, we found that if $0 \leq x \leq 0.5$, the compounds were solid solutions with the Zr_2P-type structure; if $0.8 \leq x \leq 1.0$, the compounds were the solid solutions with the Hf_2P-type structure, and if $0.5 < x < 0.8$, the samples consisted of these two phases.

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