of Structural Chemistry and Fujian Province Natural Science Foundation.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Benbertal, D., Mosset, A. & Trombe, J. C. (1994). *Mater. Res. Bull.* **29**, 47–54.

Chen, J.-T., Guo, G.-C., Zhuang, H.-H., Huang, J.-S. & Zhang, Q.-E. (1995). *J. Solid State Chem.* **116**, 211–215.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Tables 2.2A and 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Enraf–Nonius (1977). *CAD-4 Operations Manual.* Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Wang, S. M. & Hwu, S.-J. (1992). *J. Am. Chem. Soc.* **114**, 6920–6922.

Acta Cryst. (1996). C**52**, 2127–2129

The Binary Hafnium Phosphide Hf_3P_2

Holger Kleinke and Hugo Fritz Franzen

Ames Laboratory - DOE, Iowa State University, Ames, IA 50011, USA. E-mail: kleinke@ameslab.gov

(*Received 28 February 1996; accepted 16 April 1996*)

Abstract

The structure of trihafnium diphosphide, Hf_3P_2, has been redetermined by single-crystal analysis. Hf_3P_2 crystallizes in the orthorhombic space group *Pnma* (No. 62), with $a = 10.128\,(2)$, $b = 3.5707\,(6)$, $c = 9.868\,(2)$ Å, $V = 356.87\,(12)$ Å^3, and the *anti*-Sb_2S_3 structure type. The P atoms are situated in singly capped and bicapped trigonal Hf prisms. In contrast to the structure of $Zr_{14}P_9$, no centered Hf cubes as observed in the bcc packing occur in the structure of Hf_3P_2.

Comment

Significant differences in composition and crystal structure occur in the binary Zr–P and Hf–P systems. The Hf analogues of α-ZrP (Schönberg, 1954), Zr_7P_4 (Ahlzén & Rundqvist, 1989) and $Zr_{14}P_9$ (Tergenius, Noläng & Lundström, 1981) were unknown until recently we were able to synthesize Hf_7P_4 (Kleinke & Franzen, 1996*a*). In order to confirm earlier reports of Hf_3P_2 (Lundström, 1968), which has no Zr counterpart, we reinvestigated its crystal structure. We determined the structure with higher precision than in 1968, using a four-circle diffractometer with a rotating anode.

Hf_3P_2 crystallizes in the *anti*-Sb_2S_3 structure type, consisting of singly capped and bicapped trigonal Hf_6P prisms. Whereas the Zr sublattice of $Zr_{14}P_9$ (Zr:P ratio = 3.11:2) can be described in terms of bcc packing, these structure motifs are not found in Hf_3P_2. The three crystallographically different Hf atoms have high coordination numbers, ranging from 14 to 16. Each Hf atom is surrounded by five P atoms at distances between 2.599 (4) and 3.077 (4) Å, and from nine to eleven Hf neighbors at distances between 3.052 (1) and 3.674 (1) Å.

No regular coordination polyhedra were found around the Hf atoms. Therefore, the structure is best described by the three-dimensional connection of Hf_6P prisms, *i.e.* the Hf_6P1 prisms are interconnected *via* opposite triangular faces forming chains running parallel to [010], and the Hf_6P2 prisms, lying perpendicular to the Hf_6P1 prisms, form infinite chains parallel to [010] and share common edges (Fig. 1). Two chains of the Hf_6P2 prisms form a double chain sharing one common edge. The two crystallographically different Hf_6P prisms are interconnected *via* a rectangular face in one direction and *via* one common edge in a second direction,

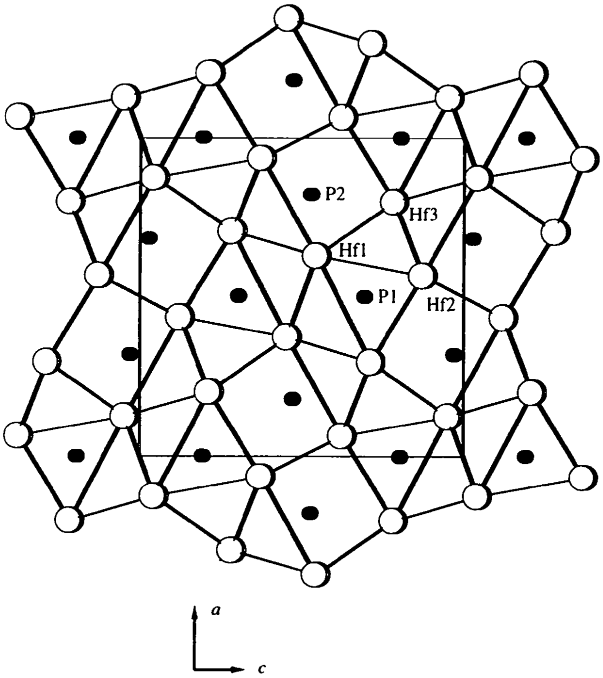

Fig. 1. Projection of the structure of Hf_3P_2 along [010]. Small filled circles represent P atoms and large open circles represent Hf atoms.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

resulting in a three-dimensional structure. From another point of view, the Hf atoms form a three-dimensional network with the P atoms in trigonal prismatic voids. Altogether, the structural differences between Zr and Hf phosphides are confirmed for the *M*:P ratio of *ca.* 3:2. Although it is generally understood that the 5*d* metals tend to form structures with a higher metal–metal bond order (Franzen & Köckerling, 1995), this generalization cannot totally explain the different behavior of Zr and Hf, which is observed in case of the phosphides with the approximate ratio of 3:2, but not for the ratio 7:4. Further investigations of the similarities and differences are currently in progress.

Experimental

HfP was synthesized in an evacuated fused silica tube at a reaction temperature of 1073 K, starting from the elements in the stoichiometric ratio [Hf: Alfa Products, powder, −325 mesh (<0.044 mm), purity 99.6% (2–3.5% Zr); P: Alfa, powder, −100 mesh (<0.149 mm), red amorphous, 99%]. Co was obtained from Alfa [powder, −50 + 150 mesh (0.100–0.297 mm), 99.9%]. Needle-like single crystals of Hf_3P_2 were obtained after arc-melting of HfP, Hf and Co in the ratio 3:2:1 and subsequent annealing in an induction furnace at 1673 K over a period of 6 h. The powder diagram, obtained from the ground bulk sample, contained only the reflections of Hf_3P_2 and $Hf_5Co_{1+x}P_{3-x}$ (Kleinke & Franzen, 1996*b*).

Crystal data

Hf_3P_2
$M_r = 597.41$
Orthorhombic
Pnma
$a = 10.128\,(2)$ Å
$b = 3.5707\,(6)$ Å
$c = 9.868\,(2)$ Å
$V = 356.87\,(12)$ Å^3
$Z = 4$
$D_x = 11.119$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 18 reflections
$\theta = 6.4–23.41°$
$\mu = 87.674$ mm^{-1}
$T = 293\,(2)$ K
Needle-like
0.1 × 0.01 × 0.01 mm
Black

Data collection

Rigaku AFC-6*R* diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (*TEXSAN*; Molecular Structure Corporation, 1989)
$T_{min} = 0.44$, $T_{max} = 0.99$
1457 measured reflections
548 independent reflections

443 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.077$
$\theta_{max} = 30.06°$
$h = 0 \rightarrow 12$
$k = -3 \rightarrow 5$
$l = -13 \rightarrow 13$
3 standard reflections monitored every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0293$
$wR(F^2) = 0.0574$
$S = 1.085$
548 reflections
32 parameters
$w = 1/[\sigma^2(F_o^2) + 1.3185P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.38$ e Å^{-3}
$\Delta\rho_{min} = -3.19$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00014 (11)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hf1	0.04686 (6)	1/4	0.12605 (6)	0.0032 (2)
Hf2	0.37636 (7)	1/4	0.06432 (5)	0.0033 (2)
Hf3	0.21585 (7)	1/4	0.79665 (6)	0.0038 (2)
P1	0.3066 (4)	1/4	0.4991 (4)	0.0059 (8)
P2	0.4729 (4)	1/4	0.8203 (4)	0.0039 (9)

Table 2. *Selected geometric parameters (Å)*

$Hf1—P2^{i,ii}$	2.627 (3)	$Hf2—Hf3^{viii}$	3.1016 (10)
$Hf1—P1^{i,ii}$	2.638 (3)	$Hf2—Hf2^{xi,xii}$	3.3274 (12)
$Hf1—P1^{iii}$	2.729 (4)	$Hf2—Hf1^{xiii}$	3.5097 (10)
$Hf1—Hf1^{iv,v}$	3.2057 (11)	Hf3—P2	2.614 (4)
$Hf1—Hf3^{vi,vii}$	3.2938 (9)	$Hf3—P1^{xiv,xv}$	2.689 (3)
Hf1—Hf2	3.3923 (12)	$Hf3—P2^{xvi}$	2.718 (4)
$Hf1—Hf3^{i,ii}$	3.4347 (8)	$Hf3—Hf2^{xiv,xv}$	3.0521 (8)
$Hf2—P2^{viii}$	2.599 (4)	Hf3—P1	3.077 (4)
$Hf2—P2^{ix,x}$	2.611 (3)	$Hf3—Hf2^{xvii}$	3.1016 (10)
$Hf2—P1^{i,ii}$	2.652 (3)	$Hf3—Hf1^{vi,vii}$	3.2938 (9)
$Hf2—Hf3^{i,ii}$	3.0521 (8)	$Hf3—Hf1^{xiv,xv}$	3.4347 (8)

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} - z$; (iv) $-x, -y, -z$; (v) $-x, 1 - y, -z$; (vi) $-x, -y, 1 - z$; (vii) $-x, 1 - y, 1 - z$; (viii) $x, y, z - 1$; (ix) $1 - x, 1 - y, 1 - z$; (x) $1 - x, -y, 1 - z$; (xi) $1 - x, 1 - y, -z$; (xii) $1 - x, -y, -z$; (xiii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (xiv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (xv) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (xvi) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{3}{2} - z$; (xvii) $x, y, 1 + z$; (xviii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS* (Dowty, 1991). Software used to prepare material for publication: *SHELXL*93.

HK thanks the Deutsche Forschungsgesellschaft for financial support of this work. The Ames Laboratory is operated for the US Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This research was also supported by the Office of the Basic Energy Sciences, Materials Science Division, Department of Energy.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1144). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahlzén, P.-J. & Rundqvist, P.-J. (1989). *Z. Kristallogr.* **189**, 149–153.
Dowty, E. (1991). *ATOMS*1.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Franzen, H. F. & Köckerling, M. (1995). *Prog. Solid State Chem.* **23**, 265-289.
Kleinke, H. & Franzen, H. F. (1996*a*). *Angew. Chem.* Submitted.
Kleinke, H. & Franzen, H. F. (1996*b*). *J. Alloys Compds.* In the press.
Lundström, T. (1968). *Acta Chem. Scand.* **22**, 2191–2199.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software.* Version 4.30. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Schönberg, N. (1954). *Acta Chem. Scand.* **8**, 226–239.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Tergenius, L.-E., Noläng, B. I. & Lundström, T. (1981). *Acta Chem. Scand. Ser. A*, **35**, 693–699.

Acta Cryst. (1996). C**52**, 2129-2132

Tricaesium Ditellurium Tetravanadium Chloride Tetradecaoxide

JEROME MARROT AND JEAN-MICHEL SAVARIAULT

Centre d'Elaboration de Materiaux et d'Etudes Structurales, CNRS, 29 Rue Jeanne Marvig, BP 4347, 31055 Toulouse CEDEX, France. E-mail: savariau@cemes.cemes.fr

(*Received 6 December 1995; accepted 5 March 1996*)

Abstract

The title compound, $(CsCl)Cs_2(TeV_2O_7)_2$, was obtained at 700 K during the crystallization of a mixed tellurium–caesium vanadate using tellurium tetrachloride as a transport agent. The structure consists of stacks of $[V_2TeO_7]$ sheets alternately separated by layers of caesium atoms and layers of caesium and chlorine atoms. Within the sheets, the V atoms are distributed over two sites: a tetrahedral site containing V^{5+} ions and a square pyramidal site containing V^{4+} ions. The Te^{4+} ion lies within a tetrahedron formed by three O atoms and a lone pair. A maximum in the electron density is observed at the expected position of the lone pair.

Comment

In our long-term research, we are particularly interested in mixed valence transition metal (*M*) oxides, among them the vanadium bronzes, $M'_xV^{5+}_{2-x}V^{4+}_xO_5$ (M'= Li, Na, K, Rb, Ag) (Galy, 1992; Savariault, Déramond & Galy, 1994; Déramond, Savariault & Galy, 1994; Hirschinger *et al.*, 1993; Savariault & Galy, 1992), and the so-called lone-pair elements, M^*, characterized by unusual stereochemical effects (M^* = As^{3+}, Se^{4+}, Sn^{2+}, Sb^{3+}, Te^{4+}, Pb^{2+}, Bi^{3+}) (Galy, Meunier, Andersson & Åström, 1975; Enjalbert, Savariault & Galy, 1980; Galy & Enjalbert, 1982; Castro, Enjalbert, Schnuriger & Galy, 1990). These oxides also give a rich series of double oxides, among which are the compounds $MV^{5+}Te^{4+}O_5$, which are related to the vanadium bronzes in formula but are completely different in structure and physical properties (Darriet, Guillaume, Wilhelmi & Galy, 1972). Several phases containing M and M^* metals have been synthesized, particularly for M = V, for example $Te_2V_2O_9$ and α- and β-$TeVO_4$ (Darriet & Galy, 1973; Meunier, Darriet & Galy, 1972, 1973), but with vanadium simultaneously present in two different valence states. During studies of the crystal growth of $CsVTeO_5$ by chemical transport using $TeCl_4$, the title compound was been discovered.

A projection of the structure of the title compound onto the [001] plane is given in Fig. 1, showing the presence of sheets of vanadium and tellurium oxide separated alternately by layers of caesium atoms and layers of caesium and chlorine atoms. The corresponding average distances between successive metal oxide layers are 5.68 and 6.12 Å, respectively. A view of a metal oxide sheet is given in Fig. 2. The V atoms lie in two types of site: atom V1 in a VO_5 square pyramid and atom V2 in a VO_4 tetrahedron. The Te^{4+} ion, bonded to three O atoms, has a lone pair (E), thus forming a TeO_3E tetrahedron. The VO_4 and TeO_3E tetrahedra share atom O4 [V2—O4—Te 132.2 (4)°] to form a pair of tetrahedra in a staggered conformation with an angle between the O-atom basal planes of 57.6 (1)°. The O atoms of each base, O2 and O3, are shared with the basal plane of the V1O5 pyramid. This leads to a sheet of formula

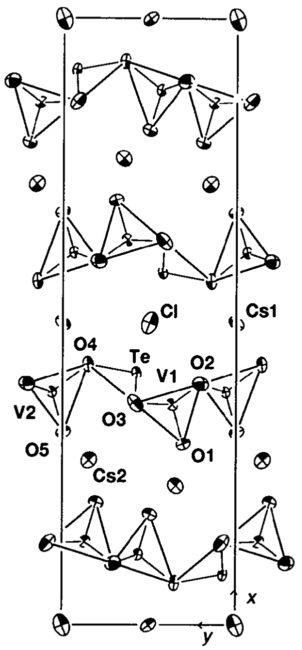

Fig. 1. A projection of the unit cell along the [001] direction. Displacement ellipsoids are drawn at the 75% probability level.