structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

This research was supported by the National Natural Science Foundation of China, State Key Laboratory 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: BR1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

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.

Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, University of Glasgow, Scotland.

Gravereau, P., Es-Sakhi, B. & Fouassier, C. (1988). *Acta Cryst.* C**44**, 1884–1887.

Gravereau, P., Es-Sakhi, B. & Fouassier, C. (1989). *Acta Cryst.* C**45**, 1677–1679.

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.

Siegrist, T., Petter, W. & Hulliger, F. (1982). *Acta Cryst.* B**38**, 2872–2874.

Acta Cryst. (1996). C**52**, 2125–2127

$Nd_4V_5Si_4O_{22}$

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Abstract

The title compound, tetraneodymium pentavanadium octaoxygen bis(pyrosilicate), has a quasi-two-dimensional chevkinite-type structure, consisting of rutile-like vanadium–oxygen layers with V—V distances of 2.794 (2) Å.

Comment

Lanthanide oxosilicates containing early transition metals are rare. Wang & Hwu (1992) first prepared $La_4Ti_9Si_4O_{30}$, which shows a perrierite-related structure; $La_2Ti_2SiO_9$ has also been reported (Benbertal, Mosset & Trombe, 1994). Recently, we prepared $Pr_4V_5Si_4O_{22}$ (Chen, Guo, Zhuang, Huang & Zhang, 1995) as the first praseodymium oxosilicate containing vanadium; it has a quasi-two-dimensional chevkinite-type structure.

$Nd_4V_5Si_4O_{22}$ is isostructural with $Pr_4V_5Si_4O_{22}$, consisting of rutile-like vanadium–oxygen layers and neodymium–oxygen layers formed by $[Nd_2O_{13}]$ dimers. In this compound, the V—V distance across the shared octahedral edges along the rutile-like vanadium–oxygen chains is 2.794 (2) Å, the Nd—Nd distance within the

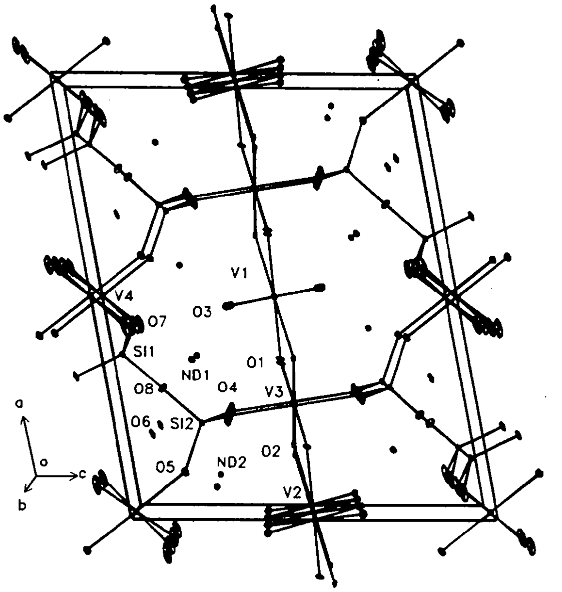

Fig. 1. The crystal structure of $Nd_4V_5Si_4O_{22}$ with displacement ellipsoids at the 50% probability level (all bonds to Nd atoms are omitted).

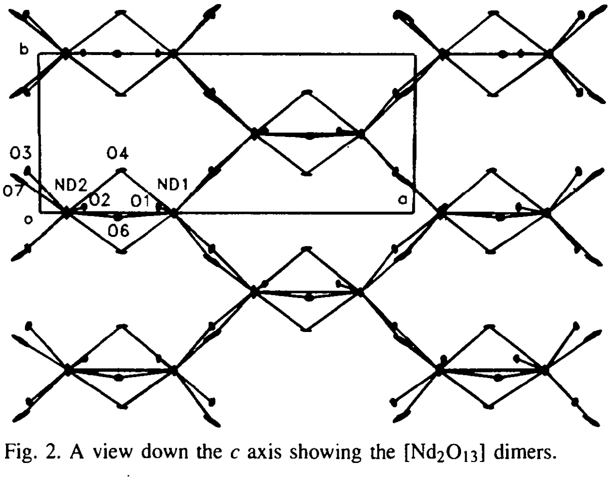

Fig. 2. A view down the *c* axis showing the $[Nd_2O_{13}]$ dimers.

$[Nd_2O_{13}]$ dimers is 3.823 (1) Å, the Nd1—V1 distance is 3.1047 (9) Å and the Nd2—V2 distance is 3.0773 (8) Å; these are almost identical to the corresponding distances in $Pr_4V_5Si_4O_{22}$ (Chen, Guo, Zhuang, Huang & Zhang, 1995).

Experimental

$Nd_4V_5Si_4O_{22}$ was prepared by solid-state reaction. A pressed pellet of 105 mg $NdCl_3$ [from dehydrating $NdCl_3.7H_2O$ (99.95%) at 473 K in vacuum; a trace amount of H_2O may be left], 43.6 mg vanadium powder (SP) and about 50 mg sulfur powder (99.999%) was sealed in an evacuated silica tube. The tube was heated at 473 K for 12 h, then slowly heated to 1273 K within 72 h, held at 1273 K for 240 h, then cooled to room temperature. Black prismatic crystals which are stable in air were found. The source of silicon is the reaction tube.

Crystal data

$Nd_4V_5Si_4O_{22}$
$M_r = 1296.00$
Monoclinic
$C2/m$
$a = 13.377\ (4)$ Å
$b = 5.589\ (4)$ Å
$c = 10.983\ (3)$ Å
$\beta = 100.61\ (2)°$
$V = 807\ (1)$ Å^3
$Z = 2$
$D_x = 5.33$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12–14°$
$\mu = 15.77$ mm^{-1}
$T = 293$ K
Needle
0.40 × 0.03 × 0.02 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: spherical and ψ scan (North, Phillips & Mathews, 1968)
$T_{\rm min} = 0.30$, $T_{\rm max} = 0.53$
2760 measured reflections
2594 independent reflections

2031 observed reflections $[I > 3.0\sigma(I)]$
$R_{\rm int} = 0.046$
$\theta_{\rm max} = 40.0°$
$h = 0 \rightarrow 24$
$k = 0 \rightarrow 10$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: 5.4%

Refinement

Refinement on F
$R = 0.0463$
$wR = 0.0585$
$S = 1.17$
2031 reflections
100 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\rm max} = 0.0043$
$\Delta\rho_{\rm max} = 4.94$ e Å^{-3}
$\Delta\rho_{\rm min} = -2.27$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

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

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

	x	y	z	$U_{\rm eq}$
Nd1	0.35659 (3)	0	0.24327 (4)	0.00894 (7)
Nd2	0.07178 (3)	0	0.24941 (4)	0.01245 (9)
V1	1/2	0	1/2	0.0071 (3)
V2	0	0	1/2	0.0062 (3)
V3	1/4	1/4	1/2	0.0038 (2)
V4	1/2	0	1	0.0043 (3)
Si1	0.2952 (2)	0	0.7703 (2)	0.0042 (4)
Si2	0.1372 (2)	0	0.9571 (2)	0.0040 (3)
O1	0.3501 (4)	0	0.4848 (6)	0.008 (1)
O2	0.1439 (4)	0	0.4775 (5)	0.0055 (9)
O3	0.0216 (3)	0.2498 (8)	0.6330 (4)	0.0086 (7)
O4	0.2743 (4)	0.2382 (8)	0.6863 (4)	0.0096 (7)
O5	0.4094 (5)	0	0.8423 (7)	0.025 (2)
O6	0.1887 (5)	0	0.0990 (5)	0.009 (1)
O7	0.0678 (5)	0.235 (1)	0.9130 (5)	0.029 (1)
O8	0.2153 (5)	0	0.8623 (7)	0.029 (2)

Table 2. *Selected geometric parameters (Å, °)*

Nd1—O1	2.670 (6)	V3—O2	1.975 (4)
Nd1—O3$^{\rm i}$	2.375 (4)	V3—O4	2.013 (4)
Nd1—O4$^{\rm i}$	2.511 (5)	V4—O5	1.922 (7)
Nd1—O6	2.498 (6)	V4—O7$^{\rm iii}$	2.063 (6)
Nd1—O7$^{\rm i}$	2.609 (6)	Si1—O4	1.615 (4)
Nd2—O2	2.513 (5)	Si1—O5	1.586 (7)
Nd2—O3$^{\rm ii}$	2.402 (5)	Si1—O8	1.599 (8)
Nd2—O4$^{\rm i}$	2.518 (4)	Si2—O6$^{\rm iv}$	1.583 (6)
Nd2—O6	2.476 (7)	Si2—O7	1.628 (6)
Nd2—O7$^{\rm ii}$	2.676 (6)	Si2—O8	1.606 (8)
V1—O1	1.982 (5)	Nd1—V1	3.1047 (9)
V1 O3$^{\rm iii}$	2.004 (4)	Nd2—V2	3.0773 (8)
V2—O2	1.985 (5)	V1—V2$^{\rm iii}$	2.794 (2)
V2—O3	2.003 (4)	V3—V3$^{\rm i}$	2.794 (2)
V3—O1	1.963 (4)		
O1—V1—O3$^{\rm iii}$	94.0 (2)	O2—V3—O4$^{\rm viii}$	85.3 (2)
O1—V1—O3$^{\rm i}$	86.0 (2)	O5—V4—O7$^{\rm iii}$	80.8 (2)
O3$^{\rm iii}$—V1—O3$^{\rm i}$	91.5 (2)	O5—V4—O7$^{\rm ix}$	99.2 (2)
O3$^{\rm iii}$—V1—O3$^{\rm v}$	88.5 (2)	O7$^{\rm iii}$—V4—O7$^{\rm ix}$	88.0 (2)
O2—V2—O3	94.5 (2)	O7$^{\rm iii}$—V4—O7$^{\rm v}$	92.0 (2)
O2—V2—O3$^{\rm ii}$	85.5 (2)	O4—Si1—O4$^{\rm vi}$	111.1 (2)
O2—V2—O3$^{\rm vi}$	94.5 (2)	O4—Si1—O5	109.5 (2)
O3—V2—O3$^{\rm ii}$	91.6 (2)	O4—Si1—O8	107.2 (2)
O3—V2—O3$^{\rm vi}$	88.4 (2)	O5—Si1—O8	112.3 (4)
O1—V3—O2	88.4 (2)	O6$^{\rm iv}$—Si2—O7	114.5 (2)
O1—V3—O2$^{\rm vii}$	91.6 (2)	O6$^{\rm iv}$—Si2—O8	114.9 (4)
O1—V3—O4	94.5 (2)	O7—Si2—O7$^{\rm vi}$	107.3 (3)
O1—V3—O4$^{\rm viii}$	85.5 (2)	O7—Si2—O8	102.1 (3)
O2—V3—O4	94.7 (2)		

Symmetry codes: (i) $\frac{1}{2}-x, y-\frac{1}{2}, 1-z$; (ii) $-x, y, 1-z$; (iii) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (iv) $x, y, 1+z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (vi) $x, -y, z$; (vii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (viii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (ix) $\frac{1}{2}-x, y-\frac{1}{2}, 2-z$.

The values of U_{22} for atoms O5 and O8 (which lie on the mirror plane) are almost six times larger than the values of U_{11} and U_{33}, suggesting that the y coordinate of these atoms is not zero and that the mirror plane may not be present. However, attempts to refine the structure in $C2$ were unsuccessful because of high correlations, which resulted in several atoms having non-positive definite values of U. O5 and O8 each form only two bonds, both of which lie in the mirror plane. This allows these atoms free movement perpendicular to this plane, as indicated by the displacement parameters.

In the final difference Fourier map, the highest and lowest peaks are 4.94 and −2.27 e Å^{-3}. There are seven peaks with density greater than 2.0 e Å^{-3}, but the distances between these peaks and the Nd1 or Nd2 atoms are less than 0.8 Å.

Data collection: CAD-4 software (Enraf–Nonius, 1977). Cell refinement: CAD-4 software. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

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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

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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,

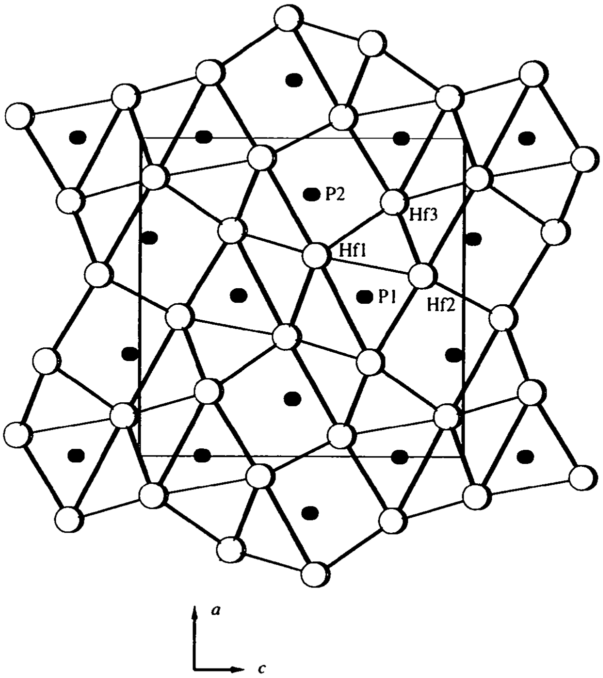

Fig. 1. Projection of the structure of Hf_3P_2 along [010]. Small filled circles represent P atoms and large open circles represent Hf atoms.