atoms. The residual maximum and minimum electron densities are located at 0.78 and 0.71 Å from the Cs and Mo2 atoms, respectively.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *CADAK* (Savariault, 1991). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96 (Sheldrick, 1996). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*96.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1225). Services for accessing these data are described at the back of the journal.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Enraf–Nonius (1993). *CAD*-4 *EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.

Foerster, A., Kreusler, H. U. & Fuchs, J. (1985). *Z. Naturforsch. Teil B*, pp. 1139–1148.

Gatehouse, B. M. & Leverett, P. (1968). *J. Chem. Soc. A*, pp. 1398–1405.

Muetterties, E. L. & Guggenberger, L. J. (1974). *J. Am. Chem. Soc.* pp. 1748–1756.

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

Savariault, J. M. (1991). *CADAK. Program for CAD-*4 *Data Reduction*. CEMES, Toulouse, France.

Seleborg, M. (1966). *Acta Chem. Scand.* **20**, 2195–2201.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SHELXL*96. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). C**55**, 276–279

The vanadium oxide bronze η-$Na_xV_2O_5$ (x = 1.286)

Patrice Millet,[a] Jean-Yves Henry[b] and Jean Galy[a]

[a]*Centre d'Elaboration de Matériaux et d'Etudes Structurales, CNRS, 29 rue Jeanne Marvig, BP 4347, 31055 Toulouse CEDEX, France, and* [b]*Commissariat á l'Energie Atomique, DRFMC/SPSMS/MDN, 17 rue des Martyrs, 38054 Grenoble CEDEX 9, France. E-mail: millet@cemes.fr*

(*Received 8 July 1998; accepted 25 November 1998*)

Abstract

The vanadium oxide bronze η-$Na_xV_2O_5$ (x = 1.286) crystallizes in the monoclinic system with an original structure built up of layers formed by VO_5 square pyramids and VO_4 tetrahedra parallel to the (010) plane, with the Na atoms lying between these layers. To form the layer, the V atoms are distributed on seven different crystallographic sites: V1 and V2 are in oxygen tetrahedra connected in the layer *via* their corners to V3, V4, V5, V6 and V7 in oxygen square pyramids which share corners and edges. The general formula of the layer, with vanadium exhibiting mixed V^{5+}/V^{4+} valency, is $[V_{14}O_{35}]_n^{9n-}$, the electrical balance being assumed by $9n$ interleaved Na^+ cations.

Comment

Following the pioneer work by Wadsley (1955), with the synthesis and crystal structure determination of the β-$Na_xV_2O_5$ phase ($x \sim 0.3$), an original vanadium bronze with typical non-stoichiometry in sodium and mixed valency (V^{5+} and V^{4+}) of the vanadiums, an investigation was reported for the first time (Hardy *et al.*, 1965) of the $Na_xV_2O_5$ system with $0 \leq x \leq 1$. This study was then completed for x up to 2 (Pouchard *et al.*, 1967) and five phases were evidenced: (i) $0 \leq x \leq 0.02$, an α-$Na_xV_2O_5$ phase with an orthorhombic crystal structure analogous to V_2O_5, few Na atoms being intercalated between the layers; (ii) $0.22 \leq x \leq 0.40$, a β-$Na_xV_2O_5$ monoclinic phase with sodium inserted in tunnels as described by Wadsley (1955); (iii) $0.70 \leq x \leq 1$, an α'-$Na_xV_2O_5$ orthorhombic phase and an α-like phase with a high sodium concentration (Carpy & Galy, 1975); (iv) $1.28 \leq x \leq 1.45$, an η-$Na_xV_2O_5$ phase solely characterized by its powder pattern; (v) $1 \leq x \leq 2$, a χ-$Na_xV_2O_5$ phase crystallizing in the rhombohedral system [cell parameters a = 6.99 (1) Å and α = 101.7 (1)°] with eight formula units per unit cell ($\rho_{\rm exp}$ = 3.05 g cm^{-3}). Recently, another sodium vanadium bronze, τ-$Na_xV_2O_5$ with x = 0.64, has been isolated and characterized (Savariault *et al.*, 1996). Its layered monoclinic structure is constituted by a balanced packing of DZ and D4 $(V_2O_5)_n$ layers separated by a plane of Na atoms. D4 depicts $(V_2O_5)_n$ double layers built up by infinite quadruple chains of VO_6 octahedra sharing equatorial-plane edges and associated along the short b axis (*i.e.* 3.6 Å) by edges. D2 depicts a $(V_2O_5)_n$ layer obtained from a crosslinked double string of VO_6 octahedra sharing edges and corners.

Up to now, it had been impossible to obtain single crystals of the η-$Na_xV_2O_5$ phase due to its easy decomposition. New crystal-growth methods which will be reported in a forthcoming paper have been developed. They allowed us to isolate blue–black crystals of the η phase. Single-crystal X-ray analysis shows that η-$Na_xV_2O_5$ crystallizes in the monoclinic system and exhibits a typical layer structure with alternating $[V_{14}O_{35}]_n^{9n-}$ and sodium layers. Within the mixed-valence vanadium layers, V^{5+} and V^{4+} are clearly evidenced. For example, V1 sits in a $V1O_4$ tetrahedron of O atoms similar to V2, but this last $V2O_4$ tetrahedron shares an oxygen, on a twofold axis, with its symmetry equivalent resulting in a $[V2_2O_7]$ group. All the inter-

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

atomic distances are in good agreement with the already reported V^{5+}—O distances of a V^{5+} ion sitting in a tetrahedron. The V3, V4, V5 and V6 atoms are in square pyramids (SP) of O atoms with the characteristic V═O vanadyl group (~ 1.61 Å) directed towards their apices. The interatomic distances allow us to assume that such polyhedra welcome V^{4+}. To obtain a perfect electric balance it is then necessary to have an equal amount of V^{5+} and V^{4+} spread out onto the remaining vanadium crystallographic site. We retained for such a proposal the V7 site; as a matter of fact, this square pyramid is clearly smaller than the others, indicating the presence of V^{5+}. To confirm such a hypothesis, we performed bond-valence-sum analysis (Brown & Altermatt, 1985). The calculated valences were 5.08 for V1, 5.01 for V2, 4.02 for V3, 4.10 for V4, 4.04 for V5, 4.04 for V6 and 4.46 (V^{4+}, r_o = 1.784 Å) or 4.69 (V^{5+}, r_o = 1.803 Å) for V7; the mean value of 4.56 is consistent with a partial oxidation state $V^{4,5+}$ in the V7 site. The V3, V4, V5, V6 and V7 square pyramids point their apices in the [010] direction, share diagonally opposite corners, are quasi-aligned along the a axis and form a kind of string. The V3 pyramid in the centre has a symmetry centre on one of its sides repeating this string after pyramid reversal and making a double string of ten square pyramids sharing corners and edges (see Fig. 1). At the position of V7, a second symmetry centre repeats this double string after a little stair step, leading to an infinite puckered double string of these square pyramids in the [100] direction with their basal plane parallel to (010) at an average elevation of $y \sim 0\pm0.05$. This little stair step corresponds to a constrained region of the structure which could explain why the O18 atom located at the junction of the double string presents an elongated ellipsoid. The infinite double strings are repeated *via* a 2 axis and a c glide plane with a $c/2$ period. They are held together by $V1O_4$ tetrahedra sharing corners with the two V4 and one V5 square pyramid, and the $[V2_2O_7]$ groups sharing corners with the V3 and V6 square pyramids. The $[V_{14}O_{35}]_n^{9n-}$ layers are thus generated. Their charges are balanced by the Na atoms located between the layers which appear in the projection onto the (010) plane through a kind of tunnel running along the [010] direction. The Na2, Na3 and Na4 atoms sit in distorted octahedra, while the Na1 and Na5 atoms, with a coordination number of 8, are surrounded by O atoms situated at the apices of distorted archimedian square antiprisms. The formula derived from the structural data is $Na_{18}V_{28}O_{70}$ or formally $Na_{18}V_8^{5+}[V_2^{5+}V_2^{4+}]V_{16}^{4+}O_{70}$, *i.e.* in the simple formulation of the $Na_xV_2O_5$ vanadium bronze family, $Na_{1.286}V_2O_5$; this x = 1.286 value seems to be the upper limit for the homogeneity range of this phase.

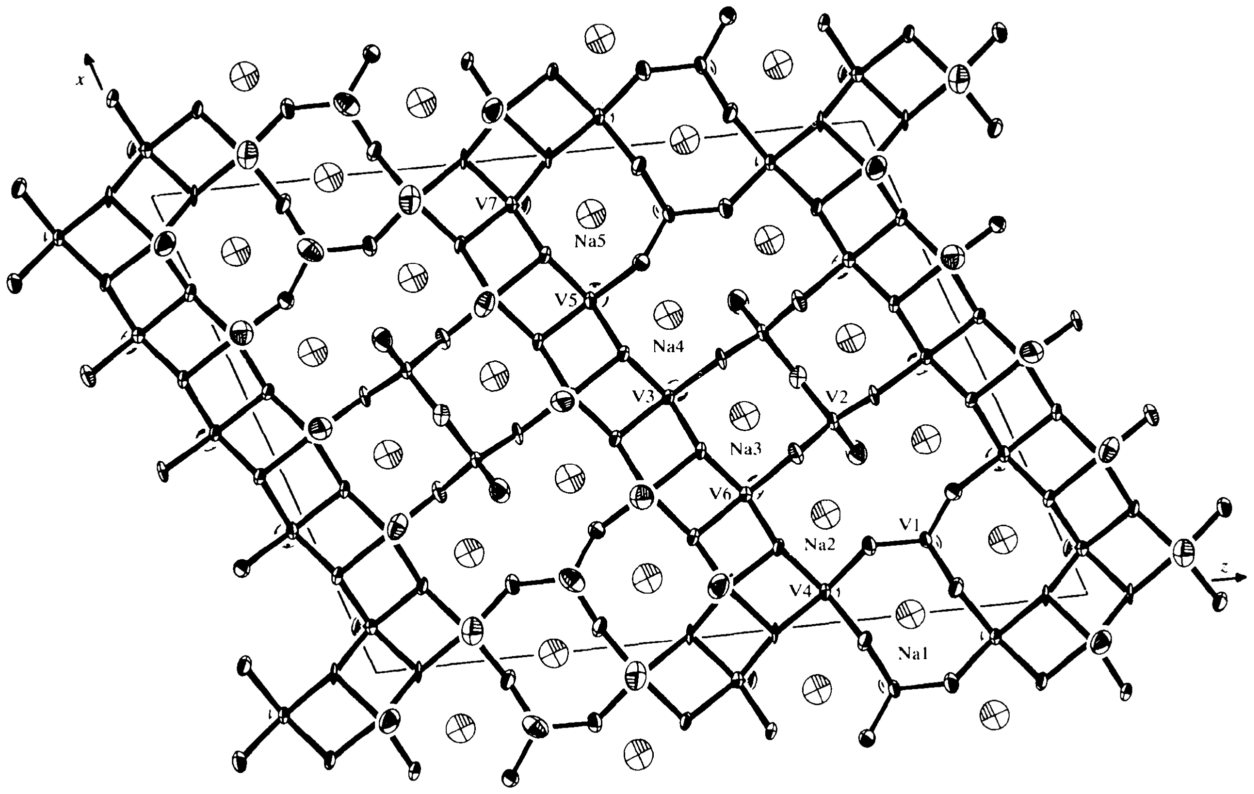

Fig. 1. Projection of the structure onto (010). Anisotropic displacement ellipsoids are plotted at the 95% probability level.

Experimental

High purity grade reagents were used for the synthesis, *i.e.* sodium carbonate (99.997%) and ammonium vanadium oxide (99.99%) used as a precurssor of V_2O_3, V_2O_4 and V_2O_5. Powders corresponding to a V^{4+}/V^{5+} ratio in the range 2±0.2 were prepared in a sealed quartz tube and heated in the temperature range 893–953 K. These powders were subsequently used for the growth of single crystals. A flux technique was used, details of which will be published elsewhere.

Crystal data

$Na_{4.5}V_7O_{17.5}$
$M_r = 740.03$
Monoclinic
$P2/c$
$a = 15.181\ (9)$ Å
$b = 5.0319\ (8)$ Å
$c = 20.760\ (4)$ Å
$\beta = 109.07\ (3)^\circ$
$V = 1498.8\ (1)$ Å^3
$Z = 4$
$D_x = 3.280$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.82$–26.07°
$\mu = 4.401$ mm^{-1}
$T = 293\ (2)$ K
Platelet
0.25 × 0.10 × 0.05 mm
Metallic dark blue

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.554$, $T_{\max} = 0.802$
4983 measured reflections
4354 independent reflections
2388 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\max} = 30^\circ$
$h = -21 \rightarrow 20$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 28$
6 standard reflections every 250 reflections frequency: 60 min intensity decay: 0.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.127$
$S = 0.963$
4983 reflections
264 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.471$ e Å^{-3} (at 0.79 Å from V2)
$\Delta\rho_{\min} = -1.301$ e Å^{-3} (at 0.72 Å from V3)
Extinction correction: *SHELXL*97
Extinction coefficient: $4\ (14) \times 10^{-5}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
V1	0.14470 (6)	0.91921 (18)	0.81807 (4)	0.00711 (19)
V2	0.40299 (6)	0.85641 (17)	0.76864 (4)	0.00720 (18)
V3	0.48782 (6)	0.90070 (19)	0.56437 (4)	0.00702 (19)
V4	0.06343 (6)	0.9129 (2)	0.65012 (4)	0.0073 (2)
V5	0.69879 (6)	0.8988 (2)	0.52283 (4)	0.00725 (19)
V6	0.27552 (6)	0.90049 (19)	0.60617 (4)	0.00723 (19)
V7	0.90714 (6)	0.8832 (2)	0.47782 (4)	0.0091 (2)
Na1	0	0.3997 (7)	3/4	0.0200 (7)
Na2	0.21797 (16)	0.3830 (5)	0.70038 (11)	0.0170 (5)
Na3	0.43315 (15)	0.3734 (5)	0.65425 (11)	0.0144 (5)
Na4	0.65359 (16)	0.3746 (5)	0.61796 (11)	0.0175 (5)
Na5	0.87129 (17)	0.3586 (5)	0.57850 (11)	0.0191 (5)
O1	0.1413 (3)	0.5918 (8)	0.82015 (19)	0.0154 (8)
O2	0.3359 (3)	0.6214 (8)	0.78080 (18)	0.0146 (8)
O3	0.4988 (3)	0.5845 (9)	0.57920 (18)	0.0159 (9)
O4	0.0620 (3)	0.5919 (9)	0.65514 (19)	0.0167 (9)
O5	0.7077 (3)	0.5817 (8)	0.53421 (19)	0.0149 (8)
O6	0.2862 (3)	0.5847 (8)	0.62073 (19)	0.0136 (8)
O7	0.9022 (3)	0.5698 (9)	0.48829 (19)	0.0167 (9)
O8	1/2	0.6910 (11)	3/4	0.0114 (11)
O9	0.7640 (2)	0.0423 (8)	0.61492 (17)	0.0093 (7)
O10	0.5534 (2)	0.0486 (8)	0.65941 (16)	0.0108 (8)
O11	0.3470 (2)	0.0485 (8)	0.69900 (17)	0.0097 (7)
O12	0.1453 (3)	0.0323 (8)	0.73845 (17)	0.0115 (8)
O13	0.0429 (2)	0.0421 (8)	0.82765 (17)	0.0119 (7)
O14	0.1622 (2)	0.0356 (8)	0.61619 (17)	0.0098 (7)
O15	0.3728 (2)	0.0330 (8)	0.57380 (16)	0.0095 (7)
O16	0.5841 (2)	0.0388 (8)	0.53233 (17)	0.0097 (7)
O17	0.7986 (2)	0.0301 (8)	0.49087 (17)	0.0085 (7)
O18	0.9921 (2)	0.0323 (8)	0.55719 (16)	0.0103 (8)

Table 2. *Selected bond lengths* (Å)

V1—O1	1.649 (4)	Na1—O13	2.361 (5)
V1—O9$^{\rm i}$	1.727 (4)	Na1—O1	2.370 (4)
V1—O13$^{\rm ii}$	1.736 (4)	Na1—O1$^{\rm vii}$	2.370 (4)
V1—O12$^{\rm ii}$	1.751 (4)	Na1—O4$^{\rm vii}$	2.629 (4)
V2—O2	1.634 (4)	Na1—O4	2.629 (4)
V2—O11$^{\rm ii}$	1.716 (4)	Na1—O12$^{\rm vii}$	2.947 (5)
V2—O10$^{\rm i}$	1.720 (4)	Na1—O12	2.947 (5)
V2—O8	1.840 (3)	Na2—O2	2.340 (4)
V3—O3	1.619 (5)	Na2—O12	2.351 (5)
V3—O16$^{\rm ii}$	1.922 (4)	Na2—O14	2.421 (4)
V3—O15$^{\rm ii}$	1.937 (4)	Na2—O6	2.440 (4)
V3—O16$^{\rm iii}$	1.970 (3)	Na2—O4	2.477 (5)
V3—O10$^{\rm ii}$	2.038 (4)	Na2—O11	2.590 (5)
V4—O4	1.619 (5)	Na3—O15	2.358 (4)
V4—O13$^{\rm iv}$	1.930 (4)	Na3—O3	2.359 (5)
V4—O12$^{\rm ii}$	1.944 (4)	Na3—O6	2.362 (5)
V4—O14$^{\rm ii}$	1.953 (4)	Na3—O10	2.427 (5)
V4—O18$^{\rm v}$	1.972 (3)	Na3—O11	2.457 (4)
V5—O5	1.612 (4)	Na3—O8	2.493 (4)
V5—O16$^{\rm ii}$	1.948 (4)	Na4—O9	2.383 (4)
V5—O17$^{\rm ii}$	1.957 (4)	Na4—O5	2.391 (5)
V5—O15$^{\rm iii}$	1.975 (3)	Na4—O2$^{\rm viii}$	2.401 (4)
V5—O9$^{\rm ii}$	1.980 (3)	Na4—O16	2.430 (4)
V6—O6	1.616 (4)	Na4—O3	2.459 (5)
V6—O14$^{\rm ii}$	1.923 (4)	Na4—O10	2.569 (5)
V6—O15$^{\rm ii}$	1.931 (4)	Na5—O7	2.331 (4)
V6—O17$^{\rm iii}$	1.991 (3)	Na5—O17	2.439 (4)
V6—O11$^{\rm ii}$	2.020 (4)	Na5—O1$^{\rm viii}$	2.470 (5)
V7—O7	1.597 (5)	Na5—O13$^{\rm viii}$	2.524 (4)
V7—O18$^{\rm ii}$	1.885 (4)	Na5—O9	2.562 (5)
V7—O17$^{\rm ii}$	1.904 (4)	Na5—O18	2.605 (5)
V7—O14$^{\rm iii}$	1.934 (3)	Na5—O5	2.604 (5)
V7—O18$^{\rm vi}$	1.943 (4)	Na5—O4$^{\rm ix}$	3.047 (1)
Na1—O13$^{\rm vii}$	2.361 (5)		

Symmetry codes: (i) $1-x, 1+y, \frac{3}{2}-z$; (ii) $x, 1+y, z$; (iii) $1-x, 1-y, 1-z$; (iv) $-x, 1+y, \frac{3}{2}-z$; (v) $x-1, 1+y, z$; (vi) $2-x, 1-y, 1-z$; (vii) $-x, y, \frac{3}{2}-z$; (viii) $1-x, y, \frac{3}{2}-z$; (ix) $1+x, y, z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *CRYSTALS* (Watkin *et al.*, 1985). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*97.

We thank CNRS and Région Midi–Pyrénées for their support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1224). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, C., Giacovazzo, A., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Carpy, A. & Galy, J. (1975). *Acta Cryst.* B**31**, 1481–1483.

Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 5.1. Enraf–Nonius, Delft, The Netherlands.

Hardy, A., Galy, J., Casalot, A. & Pouchard, M. (1965). *Bull. Chim. Soc. Fr.* **4**, 1056–1061.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–356.

Pouchard, M., Casalot, A., Galy, J. & Hagenmuller, P. (1967). *Bull. Chim. Soc. Fr.* **11**, 4343–4348.

Savariault, J. M., Parize, J. L., Ballivet-Tkatchenko, D. & Galy, J. (1996). *J. Solid State Chem.* **122**, 1–6.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Wadsley, A. D. (1955). *Acta Cryst.* **8**, 695–701.

Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide*. Chemical Crystallography Laboratory, University of Oxford, England.

Acta Cryst. (1999). C**55**, 279–281

Monoclinic $InPO_4 \cdot 2H_2O$

Kazumasa Sugiyama,[a] Jihong Yu,[b] Kenji Hiraga[a] and Osamu Terasaki[c]

[a]Institute for Materials Research (IMR), Tohoku University, Sendai 980-8577, Japan, [b]CREST, Japan Science and Technology Corporation (JST), and Department of Physics, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan, and [c]Department of Physics, Graduate School of Science, and Center for Interdisciplinary Research, Tohoku University, Sendai 980-8578, Japan. E-mail: kazumasa@imrtuns.imr.tohoku.ac.jp

(*Received 8 June 1998; accepted 5 October 1998*)

Abstract

A new monoclinic phase of indium phosphate dihydrate, $InPO_4 \cdot 2H_2O$, was prepared from a hydrothermal synthesis of H_3PO_4, $In(OH)_3$ and H_2O in the presence of HF and $C_7H_{13}N$ (quinuclidine). The structure is isostructural with $AlPO_4 \cdot 2H_2O$ (metavariscite). The geometry of the H atoms in the title compound is consistent with that of metavariscite.

Comment

The previously known structure of indium phosphate dihydrate, $InPO_4 \cdot 2H_2O$, is orthorhombic (*Pbca*, a = 10.187, b = 8.842 and c = 10.327 Å; Mooney-Slater, 1961; Xu *et al.*, 1995). We report here the structure of monoclinic $InPO_4 \cdot 2H_2O$. The title compound is isostructural with $AlPO_4 \cdot 2H_2O$ (metavariscite; $P2_1/n$, a = 5.178, b = 9.514, c = 8.454 Å and β = 90.35°; Borensztajn, 1966; Kniep & Mootz, 1973).

The a-axis projection of the crystal structure, formed by the linkage of PO_4 tetrahedra and $InO_4(H_2O)_2$ octahedra, is shown in Fig. 1. One-dimensional eight-membered-ring channels are formed along the a axis, which are intersected by six-membered-ring channels along the b and c axes.

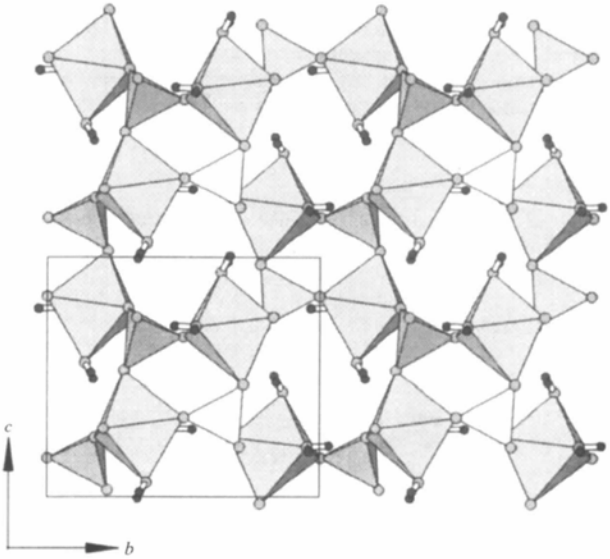

Fig. 1. The a-axis projection of the structure of monoclinic $InPO_4 \cdot 2H_2O$. Translation along the a axis produces a three-dimensional framework of eight-membered rings. Small circles indicate the H atoms.

The two distinct In—O*W*1 [2.128 (3) Å] and In—O*W*2 [2.174 (3) Å] distances are attributed to endothermic dehydration reactions at about 528 and 645 K, observed by common differential thermal analysis. In—O*W*2 is the longest among six In—O distances, whereas In—O*W*1 shows no appreciable difference from the In—O1, In—O3 and In—O4 distances. This feature of the indium coordination contrasts with the situation in orthorhombic $InPO_4 \cdot 2H_2O$ (Mooney-Slater, 1961; Xu *et al.*, 1995), where two In—O*W* distances are the first and second longest among six In—O distances. The large value of U^{33} for O*W*1 may suggest a possible disordered distribution of water molecules in the channels. Such features of the O*W*1 site are also seen in the structure of monoclinic $AlPO_4 \cdot 2H_2O$, including a relatively