

A new whitlockite, $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$

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Single crystals of a new complex phosphate, calcium sodium vanadium phosphate, $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$, have been grown from a melt under an inert atmosphere. The crystal structure has rhombohedral ($R\bar{3}c$) symmetry and belongs to the whitlockite structure type. Vanadium(III) ions occupy nearly regular octahedral sites ($M5$ with 3 point symmetry), which share corners with six PO_4 tetrahedra to form isolated units. The calcium ions occupy eight- and nine-coordinated sites. The sodium ions partially occupy one octahedral position and share one nine-coordinated position with a Ca atom.

Comment

The mineral whitlockite, $\text{Ca}_{18.19}(\text{Mg}_{1.17}\text{Fe}_{0.83})\text{H}_{1.62}(\text{PO}_4)_{14}$ (Calvo & Gopal, 1975), is isomorphous with $\beta\text{-Ca}_3(\text{PO}_4)_2$ (Dickens *et al.*, 1974). Some whitlockite-like phases, such as $M_9A(\text{XO}_4)_7$ ($M = \text{Ca}$ and Sr , A is a rare-earth or transition metal, and $X = \text{P}$, V and As), show ferroelectric phase transitions or non-linear optical properties, which make them potentially useful for practical applications. $\beta\text{-Ca}_3(\text{PO}_4)_2$ crystallizes in the rhombohedral space group $R\bar{3}c$, with unit-cell parameters $a = 10.439 \text{ \AA}$ and $c = 37.375 \text{ \AA}$. The structure contains six metal ($M1\text{--}M6$) and three phosphorus (P1--P3) positions; $M1\text{--}M3$, P2 and P3 are in general ($18b$) positions, while $M4\text{--}M6$ and P1 are in special ($6a$) positions with a 3 point symmetry. Different combinations of occupied and unoccupied $M1\text{--}M6$ positions provide the basis for the large number of compounds that belong to the whitlockite structure type.

In the rhombohedral $M_9A(\text{XO}_4)_7$ ($M = \text{Ca}$ and Sr) whitlockites, the $M1\text{--}M3$ positions have eightfold coordination, $M4$ has ninefold coordination and $M5$ has octahedral coordination. The Ca and Sr atoms occupy the $M1\text{--}M3$ positions, while the $M5$ position is usually occupied by a trivalent cation ($A = \text{Al}$, Sc , Ga , Cr , Fe , In , Y and rare-earth metals). All P atoms are located at the centres of the PO_4 phosphate

groups, and small cations, such as V^{5+} or As^{5+} , may also be accommodated in the P positions (Gopal & Calvo, 1971, 1973). In the case of $M = \text{Ca}$, all known compounds have non-centrosymmetric rhombohedral lattices (space group $R\bar{3}c$ or $R3$) with unit cells similar to that of $\beta\text{-Ca}_3(\text{PO}_4)_2$ (Belik *et al.*, 1997; Belik, Morozov, Kotov *et al.*, 2000; Belik, Morozov, Grechkin *et al.*, 2000; Belik, Grechkin *et al.*, 2000; Golubev & Lazoryak, 1990, 1991; Evans *et al.*, 2001; Lazoryak *et al.*, 1996). The $\text{Ca}_9A(\text{PO}_4)_7$ compounds ($A = \text{Fe}$ or In) exhibit a reversible phase transition to a high-temperature centrosymmetric phase (space group $R\bar{3}c$; Lazoryak *et al.*, 2003; Morozov *et al.*, 2002). The $\text{Sr}_9A(\text{PO}_4)_7$ compounds [$A = \text{Sc}$, Cr , Fe , Ga and In (Belik, Izumi, Ikeda, Okui *et al.*, 2002), or $A = \text{Y}$ and $\text{Gd}\text{--}\text{Lu}$ (Belik, Izumi, Ikeda, Lazoryak *et al.*, 2002)] reveal a monoclinic distortion of the whitlockite-like structure. The corresponding vanadates all have a rhombohedral symmetry (Belik *et al.*, 2005).

All of the $M_9A(\text{XO}_4)_7$ compounds mentioned above may be easily synthesized by annealing mixtures of the corresponding oxides and phosphates in air, since the A cation is always in its highest or most stable oxidation state. At the same time, the $M5$ position of the whitlockite structure may be occupied by other trivalent cations. In this work, we demonstrate that V^{3+} can be accommodated within the whitlockite structure if the synthetic conditions prevent the oxidation of vanadium. Initially, this compound was synthesized accidentally during our study of the vanadyl(IV) phosphates $\text{Na}_2M\text{VO}(\text{PO}_4)_2$ ($M = \text{Ca}$ and Sr ; Chernaya *et al.*, 2004), which melt incongruently with disproportionation of the V^{4+} cations.

The overall composition for the crystal investigated is $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$. Its crystal structure was found to be

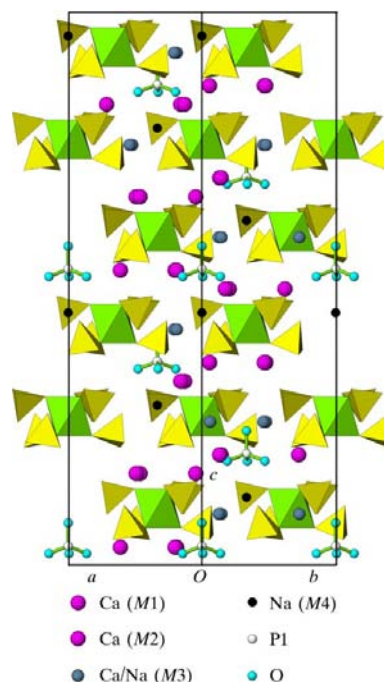


Figure 1

A projection of the $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$ structure along the $[110]$ direction.

similar to those of other $\text{Ca}_9\text{A}(\text{PO}_4)_7$ compounds (Fig. 1). The VO_6 octahedra share all six corners with PO_4 tetrahedra, forming isolated anionic groups. Additional isolated PVO_4 tetrahedra are also present in the structure. The Ca and Na cations randomly occupy interstices between the vanadium and phosphorus polyhedra.

The V—O distances are 2.0276 (16) and 2.0416 (16) Å. The V atom is situated in a nearly regular octahedron that is typical for V^{3+} . The calculated bond valence sum (BVS) of 2.89 is close to the estimated value of 3. The PO_4 tetrahedra are almost regular, with the P—O distances ranging from 1.5196 (16) to 1.5838 (16) Å (Table 1), and the BVS values are 4.99, 5.01 and 4.90 for atoms P1, P2 and P3, respectively. Atoms Ca1 and Ca2 have coordination number eight, while atom Ca3 has a ninth O-atom neighbour located at 2.9784 (16) Å. The BVS values for atoms Ca1–Ca3 are 2.12, 2.14 and 1.93, respectively. It should be remembered that the valence values estimated from the BVS calculations (Brown & Altermatt, 1985) are slightly conservative since the diffraction experiment was performed at low temperature. The lower BVS value for atom Ca3 may be caused by the presence of sodium in the *M3* position. The Na atom occupying the *M4* position is surrounded by six O atoms. However, the Na—O separations are significantly different, *viz.* three short distances of 2.4741 (16) Å and three long distances of 2.830 (3) Å.

As mentioned above, there are different possibilities for the distribution of the metal atoms among the *M1*–*M6* positions of the whitlockite structure. The filling of these positions in the $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$ structure is similar to that observed previously in other $\text{Ca}_9\text{MA}(\text{PO}_4)_7$ phosphates (*M* = Li, Na and K, and *A* = Mg, Ca, Mn and Co; Morozov *et al.*, 1997, 2000; Belik *et al.*, 1999, 2001) and in the $\text{Ca}_{10}\text{K}(\text{VO}_4)_7$ vanadate (Mueller-Buschbaum & Schrandt, 1996). In the latter structures, the alkali cations fully occupy the *M4* position and, therefore, the divalent cation may be accommodated in the *M5* position to keep electroneutrality of the compound. On the other hand, a monovalent cation can replace calcium in one of the *M1*–*M3* positions, similar to what is found in $\text{Ca}_{18}\text{Na}_3\text{Fe}(\text{PO}_4)_{14}$ (Strunenkova *et al.*, 1997). Thus, $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$ demonstrates a co-existence of both types of alkali cations incorporated into the whitlockite-type structure. The observed distribution is necessary to maintain the trivalent state of the V atoms.

We attempted to prepare an Na-free calcium vanadium phosphate, $\text{Ca}_9\text{V}(\text{PO}_4)_7$, by annealing a stoichiometric mixture of $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_2\text{P}_2\text{O}_7$ and V_2O_3 in an evacuated silica tube at different temperatures (1023–1473 K). These reactions always resulted in multi-phase mixtures containing a whitlockite-like phase along with minor (5% or less) amounts of unknown species. On the other hand, the addition of even small amounts of sodium pyrophosphate to the reaction mixture resulted in the formation of a pure whitlockite phase. The latter result suggests that, in the case of *A* = V^{III} , the presence of Na atoms causes the whitlockite-type structure to be more stable than in the case of the $\text{Ca}_9\text{A}(\text{PO}_4)_7$ phosphate.

Experimental

$\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ was synthesized from $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Ca}_2\text{P}_2\text{O}_7$ and VO_2 , as described previously (Chernaya *et al.*, 2004). Single crystals of $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$ were obtained by melting a single-phase powder sample of $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ in an argon atmosphere at 1013 K, followed by slow cooling (5 K min^{-1}). In addition to the brown crystals used for the present study, green crystals with unit-cell parameters close to those for $\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$ were also recovered. A refinement of the Na/Ca ratio in these crystals resulted in almost the same value (1.09/8.46) as for the brown crystals. The difference in colour may be attributed to structural defects or to an inhomogeneous distribution of Na atoms in the crystals.

Crystal data

$\text{Ca}_{8.42}\text{Na}_{1.16}\text{V}(\text{PO}_4)_7$	Mo $K\alpha$ radiation
$M_r = 1079.88$	Cell parameters from 9009 reflections
Trigonal, <i>R3c</i>	$\theta = 2.5\text{--}28.1^\circ$
$a = 10.3273$ (3) Å	$\mu = 2.97 \text{ mm}^{-1}$
$c = 37.098$ (2) Å	$T = 173 \text{ K}$
$V = 3426.5$ (2) Å ³	Irregular, brown
$Z = 6$	$0.18 \times 0.16 \times 0.06 \text{ mm}$
$D_x = 3.139 \text{ Mg m}^{-3}$	

Data collection

Bruker SMART APEX CCD diffractometer	1808 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.014$
Absorption correction: multi-scan (Bruker, 1997)	$\theta_{\text{max}} = 28.1^\circ$
$T_{\text{min}} = 0.615$, $T_{\text{max}} = 0.841$	$h = -13 \rightarrow 13$
9009 measured reflections	$k = -13 \rightarrow 13$
1818 independent reflections	$l = -49 \rightarrow 49$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.016$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
$wR(F^2) = 0.048$	$\Delta\rho_{\text{min}} = -0.67 \text{ e \AA}^{-3}$
$S = 1.12$	Extinction correction: <i>SHELXL97</i>
1818 reflections	Extinction coefficient: 0.00038 (4)
143 parameters	Absolute structure: Flack (1983), 875 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 2.3095P]$	Flack parameter: 0.47 (2)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1

Selected interatomic distances (Å).

V—O5	2.0276 (16)	Ca3—O3	2.4772 (13)
V—O2	2.0416 (16)	Ca3—O6 ^{ix}	2.4852 (14)
Ca1—O7 ⁱ	2.3131 (14)	Ca3—O1	2.5084 (8)
Ca1—O3 ⁱⁱ	2.3569 (16)	Ca3—O3 ^{viii}	2.5608 (13)
Ca1—O8 ⁱⁱ	2.4071 (15)	Ca3—O9 ^{iv}	2.6349 (16)
Ca1—O10 ⁱⁱⁱ	2.4681 (14)	Ca3—O7	2.6411 (15)
Ca1—O4	2.4694 (13)	Ca3—O8 ^{viii}	2.9784 (16)
Ca1—O5 ^{iv}	2.5135 (14)	P1—O1	1.528 (3)
Ca1—O5	2.5222 (14)	P1—O8	1.5399 (12)
Ca1—O6 ^{iv}	2.7679 (15)	P2—O3	1.5196 (16)
Ca2—O8 ^v	2.3215 (14)	P2—O7	1.5224 (15)
Ca2—O4 ^{vi}	2.3735 (13)	P2—O10	1.5323 (14)
Ca2—O9	2.4008 (15)	P2—O2 ^v	1.5674 (16)
Ca2—O6 ^{vii}	2.4515 (13)	P3—O9	1.5220 (15)
Ca2—O2 ⁱⁱ	2.4582 (13)	P3—O6	1.5233 (14)
Ca2—O2	2.4830 (13)	P3—O4	1.5399 (14)
Ca2—O10 ^{iv}	2.6080 (14)	P3—O5	1.5838 (16)
Ca2—O7 ⁱⁱ	2.6540 (15)	Na1—O9 ^x	2.4741 (16)
Ca3—O10 ^{viii}	2.3932 (14)	Na1—O8 ^{xi}	2.830 (3)
Ca3—O4 ^{iv}	2.4217 (13)		

Symmetry codes: (i) $-x + y + \frac{2}{3}, y + \frac{1}{3}, z - \frac{1}{6}$; (ii) $-y + 1, x - y + 1, z$; (iii) $-y + \frac{2}{3}, -x + \frac{2}{3}, z - \frac{1}{6}$; (iv) $-x + y, -x + 1, z$; (v) $-x + y + \frac{2}{3}, y + \frac{2}{3}, z + \frac{1}{6}$; (vi) $-x + y - \frac{2}{3}, y - \frac{1}{3}, z + \frac{1}{6}$; (vii) $x + \frac{1}{3}, x - y + \frac{2}{3}, z + \frac{1}{6}$; (viii) $-x + y + 1, -x + 1, z$; (ix) $x + 1, y, z$; (x) $x, y - 1, z$; (xi) $-y + \frac{1}{3}, -x + \frac{2}{3}, z + \frac{1}{6}$.

The atomic positions for the Ca, V, P and O atoms were determined by direct methods. Subsequent difference Fourier syntheses and least-square refinements resulted in the $\text{Ca}_9\text{V}(\text{PO}_4)_7$ composition, confirming that the structure belongs to the whitlockite type.

The isotropic displacement parameter for atom Ca3 (0.015 \AA^2) was found to be twice as large as those for atoms Ca1 and Ca2 (0.007 \AA^2), despite the fact that all three positions have similar O-atom coordination. The larger displacement parameter for atom Ca3 may be indicative of a partial occupancy or of the presence of a lighter atom in this position. Furthermore, a significant residual electron density (about 7.5 e \AA^{-3}) was detected near the M4 position. Both discrepancies have been attributed to Na atoms, which were present in the reaction mixture and thus may have entered the structure. A simple introduction of Na cations into the $\text{Ca}_9\text{Na}_x\text{V}(\text{PO}_4)_7$ structure should result in the reduction of vanadium. However, it is well known that a very strong reducing agent is required to reduce vanadium below the +3 oxidation state, whereas our synthetic conditions should not allow for that. The insertion of Na into the structure must be accompanied by a decrease in the Ca content in order to maintain the +3 oxidation state of vanadium. Thus, we have considered the following two models:

(i) Na randomly occupies the M4 position only, while the M3 position becomes partially occupied by Ca atoms, and the occupancy factors (g) for both cations are related by the equation $g_{\text{Na}}(M4) = 2[1 - g_{\text{Ca}}(M3)]$.

(ii) Na is located in both the M4 and M3 positions. The occupancies should therefore be expressed as $g_{\text{Na}}(M3) + g_{\text{Ca}}(M3) = 1$ and $g_{\text{Na}}(M3) = g_{\text{Na}}(M4)$.

Model (i) resulted in an R value of 0.025, while model (ii) led to an R value of 0.018. This value, however, is close to that (0.019) obtained for the structural model excluding Na atoms. Nevertheless, the similarity of the displacement parameters for the three Ca positions and the lower residual electron-density peaks observed in the difference Fourier map indirectly confirm the correctness of our structure solution using model (ii).

During the refinement, the Flack (1983) parameter was found to be 0.47 (3). This may indicate that either the structure is centrosymmetric or the crystal is twinned. The only possible space group having particular systematic extinctions is $R\bar{3}c$. Indeed, almost all cationic positions are placed in a centrosymmetric manner. However, this is not the case for the O-atom positions. The refinement in the $R\bar{3}c$ space group gave an R value of 0.30. Therefore, we considered the case of racemic twinning. This resulted in an R value of 0.016 and a BASF parameter of 0.47 (2). Thus, we conclude that the crystal used in this study is a racemic mixture of two twins with a non-centrosymmetric $R3c$ structure.

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ATOMS (Dowty, 1998); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1085). Services for accessing these data are described at the back of the journal.

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