Synthesis and Crystal Structure of Ca(VO)₂(PO₄)₂

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A new phosphate, Ca(VO)₂(PO₄)₂, was synthesized hydrothermally and its structure was determined from single-crystal X-ray diffraction data. It crystallizes in the noncentrosymmetric orthorhombic space group *Fdd*2 with $a = 11.795(4)$, $b = 15.784(6)$, $c = 7.190(4)$ Å, $Z = 8$, and $R = 0.0346$. The structure consists of infinite chains of *trans*-corner-sharing VO₆ octahedra cross-linked by phosphate groups to form a 3-dimensional network. These chains have alternating short and long V–O bonds. The network contains intersecting channels where the Ca²⁺ cations are located. The structure is compared with those of the AVOPO₄ (A = alkali metal) family. © 1992 Academic Press, Inc.

Introduction

Phosphates of stoichiometry $AMOPO_4$ (A = alkali metal, M = V and Ti) exhibit a few structure types. For example, KVOPO₄ (*1, 2*) and RbTiOPO₄ (*1*) are isostructural with the superior second-harmonic generation (SHG) crystal KTiOPO₄ (KTP) (*3*). With respect to SHG, the crystals of interest are confined to the 20 noncentrosymmetric crystal classes. KTP belongs to the orthorhombic space group $Pna2_1$ and is characterized by infinite chains of TiO₆ octahedra linked at two corners by alternating short and long Ti–O bonds (*4–6*). NaVOPO₄ (*7*) and α-NaTiOPO₄ (*8*) are structurally related to the naturally occurring mineral CaTiOSiO₄ (*9*), which is monoclinic with the space group $P2_1/c$. The polymorph of NaTiOPO₄ isomorphous with KTP, β-NaTiOPO₄, can

be prepared by the ion exchange method (*8*). The α- and β-polymorph of LiVOPO₄ were prepared by the high-temperature solid-state reaction and the hydrothermal method, respectively (*10, 11*). Both polymorphs are centrosymmetric ($P\bar{1}$ and $Pnma$) and are structurally related to Na VOPO₄. Interestingly, LiTiOPO₄ (*12*), which was prepared by the solid-state method, is isostructural with β-LiVOPO₄. To our knowledge, compounds RbVOPO₄, CsVOPO₄, and CsTiOPO₄ have not been reported.

We have also attempted the synthesis of new compounds of stoichiometry A'(VO)₂(PO₄)₂, where A' is an alkaline earth metal. These searches were motivated by the expectation that new structure types would result and in the hope that useful physical phenomena would be discovered.

In this work we report the synthesis and structural characterization of the noncentrosymmetric compound Ca(VO)$_2$(PO$_4$)$_2$.

Experimental

Synthesis

Reagent grade chemicals were used. A mixture of 0.1777 g Ca(OH)$_2$, 0.4010 g VO$_2$, 0.2058 g V$_2$O$_5$, 1.5 mL 85% H$_3$PO$_4$, and 10.5 mL H$_2$O was heated in a 23-mL Teflon-lined autoclave at 230°C for 5 days followed by slow cooling to room temperature at 5°C/hr. Visual microscopic inspection showed that the product contained many green prismatic crystals. It was found that the addition of V$_2$O$_5$ facilitated crystal growth of Ca(VO)$_2$(PO$_4$)$_2$. A single phase polycrystalline product of Ca(VO)$_2$(PO$_4$)$_2$ was obtained by heating a mixture of 0.1820 g Ca(OH)$_2$, 0.4031 g VO$_2$, 1.5 mL 85% H$_3$PO$_4$, and 10.5 mL H$_2$O under a similar reaction condition. The X-ray powder pattern of the product compared well with that calculated from the single-crystal data. The amounts of Ca, V, and P were determined by using an ICP-AE spectrometer after dissolving a sample in dilute aqua regia. Anal. Calcd for Ca(VO)$_2$(PO$_4$)$_2$: Ca, 11.01%; V, 28.00%; P, 17.02%. Found: Ca, 11.0%; V, 27.2%; P, 16.8%. The solid-state reaction of Ca$_3$(PO$_4$)$_2$, VO$_2$, and P$_2$O$_5$ (molar ratio 1 : 6 : 2) in an alumina crucible, which was sealed in a quartz glass tube, at 750°C for 3 days with an intermediate grinding, also led to a single-phase polycrystalline product.

Magnetic Measurements

Magnetization data were obtained from 4 to 300 K in a magnetic field of 5 kG using a SQUID magnetometer on 165.17 mg of polycrystalline sample. Observed susceptibilities were corrected for diamagnetism according to Selwood (13). The data between 20 and 300 K were described very well by a Curie–Weiss behavior: $\chi_M = C/(T - \theta)$,

where $C = 0.351$ cm$^3 \cdot$ K/mol and $\theta = 0.18$ K. From the relation $C = N\mu_{eff}^2/3k_B$ one obtains the effective magnetic moment $\mu_{eff} = 1.68$ per vanadium. The deviation of $1/\chi_M$ to larger values with decreasing temperature below ~15 K may arise from antiferromagnetic interaction.

Single-Crystal X-ray Diffraction

Peak profile analysis (ω scan) of the green crystals of Ca(VO)$_2$(PO$_4$)$_2$ using a Nicolet R3m/V diffractometer indicated that most of them were not single crystals. Many had to be selected before a satisfactory crystal was obtained. Finally a small prism of dimensions 0.02 × 0.03 × 0.16 mm was used for indexing and intensity data collection using graphite-monochromated MoKα radiation. Unit cell parameters and orientation matrices were determined by a least-squares fit of 14 peak maxima with 2θ ranging from 13 to 28°. Of the 453 reflections collected ($2\theta_{max} = 55°$, scan mode $2\theta/\theta$), 322 unique reflections were considered observed ($I > 3\sigma(I)$) after Lp and empirical absorption corrections ($T_{max/min} = 0.896/0.825$). On the basis of systematic absences and successful solution and refinement of the structure, the space group was determined to be $Fdd2$.

The structure was solved by direct methods and successive Fourier syntheses, and was refined by full-matrix least-squares refinement based on F values. The oxygen atoms were not refined with anisotropic temperature factors in order to increase the data-to-parameter ratio. The occupancy factor for the Ca atom was initially refined but did not deviate significantly from full occupancy. The final cycle of refinement gave R, R_w, and GOF values of 3.46, 3.46, and 0.931. The final difference map was flat to less than ±0.72/Å^3. Calculations were performed on a DEC MicroVAX II computer system using SHELXTL-Plus programs (14). Neutral-atom scattering factors and corrections for anomalous dispersion were taken from Cromer and Weber (15). Lists of observed

CRYSTAL DATA FOR $Ca(VO)_2(PO_4)_2$

Crystal system	orthorhombic
Space group	$Fdd2$ (No. 43)
Cell constants	$a = 11.795(4)$, $b = 15.784(6)$,
	$c = 7.190(4)$ Å,
	$V = 1338.5(9)$ Å^3
Z	8
Density	3.612 g/cm^3
Abs. coeff. ($MoK\alpha$)	39.74 cm^{-1}
$\lambda(MoK\alpha)$	0.71073 Å
Maximum 2θ	55°
Unique reflections measured	416
Reflection included	322 ($I > 3\sigma(I)$)
Parameters refined	44
Agreement factors[a]	$R = 0.0346$, $R_w = 0.0346$
GOF	0.931
$(\Delta\rho)_{max}$; $(\Delta\rho)_{min}$	0.72 e/Å^3; -0.70 e/Å^3

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w^{-1} = \sigma^2(F) + 0.001F^2$.

and calculated structure factors, anisotropic temperature factors, and magnetic data are available as supplementary material.

Results and Discussion

Table I lists the crystallographic data. Final atomic coordinates and thermal parameters are listed in Table II. Selected bond

TABLE III

SELECTED BOND DISTANCES (Å) FOR $Ca(VO)_2(PO_4)_2$

Ca–O(1)	2.405(8) (2×)[a]	Ca–O(2)	2.665(7) (2×)
Ca–O(4)	2.647(8) (2×)	Ca–O(5)	2.393(8) (2×)
V–O(1)	2.026(7)	V–O(2)	2.022(8)
V–O(3)	2.123(8)	V–O(3)	1.597(8)
V–O(4)	2.046(9)	V–O(5)	2.056(8)
P–O(1)	1.547(8)	P–O(2)	1.535(10)
P–O(4)	1.531(10)	P–O(5)	1.541(7)

[a] Number of times the distance occurs.

distances are given in Table III. Motif of mutual adjunction (16), coordination number (C.N.), and bond-valence sums (17) are given in Table IV. The Ca atom sits on the 2-fold axis, and all other atoms are at general positions. The C.N. of Ca^{2+} is determined on the basis of the maximum gap in the Ca–O distances ranked in increasing order. The ninth Ca–O bond length is at 3.5 Å. Bond-valence sums for the V, P, and O atoms are in good accordance with their formal oxidation states. The value for Ca is somewhat lower, suggesting that the Ca atom is not tightly bound, which is also indicated by its relatively high thermal parameters. Four of the five distinct oxygens are involved in V–O–P links, and the remaining one, O(3), participates in V–O–V bonds.

TABLE II

ATOMIC COORDINATES AND THERMAL PARAMETERS (Å^2 × 100) FOR $Ca(VO)_2(PO_4)_2$

Atom	x	y	z	U_{eq}[a,b]
Ca	$\frac{1}{4}$	$\frac{1}{4}$	0.5	0.83(8)
V	0.1102(1)	0.1182(1)	0.8540(6)	0.44(4)
P	−0.0007(2)	0.2923(1)	0.7469(9)	0.53(6)
O(1)	0.1033(6)	0.2332(4)	0.729(1)	0.6(1)
O(2)	0.2361(6)	0.0998(4)	0.668(1)	0.5(2)
O(3)	0.2529(6)	0.1688(3)	0.995(1)	0.4(1)
O(4)	0.0124(5)	0.1483(4)	0.080(1)	0.8(2)
O(5)	0.1427(6)	0.0134(4)	0.015(1)	0.5(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonallized U_{ij} tensor.

[b] The oxygen atoms were refined isotropically.

TABLE IV

MOTIF OF MUTUAL ADJUNCTION, COORDINATION NUMBER (C.N.), AND
BOND-VALENCE SUMS (Σs) IN Ca(VO)$_2$(PO$_4$)$_2$

	O(1)	O(2)	O(3)	O(4)	O(5)	C.N.	Σs
V	1/1	1/1	2/2	1/1	1/1	6	4.08
P	1/1	1/1		1/1	1/1	4	4.95
Ca	2/1	2/1		2/1	2/1	8	1.87
C.N.	3	3	2	3	3		
Σs	2.03	1.93	2.06	1.91	2.02		

All of the oxygen atoms except O(3) also coordinate to the Ca atoms. The VO$_6$ octahedron is distorted as a result from the displacement of the V atom toward one of the apical oxygen atoms. This kind of deformation is characteristic of most vanadyl(IV) compounds. The magnetic data also indicate the presence of V^{4+} (d^1) ions with spin $\frac{1}{2}$. The phosphate tetrahedron is quite regular with the average P–O bond length at 1.538 Å, which agrees well with the sum of the ionic radii (1.53 Å) (18).

As shown in Fig. 1, the structure of Ca (VO)$_2$(PO$_4$)$_2$ consists of infinite chains of trans-corner-sharing VO$_6$ octahedra cross-linked by phosphate groups to form a 3-dimensional network. These infinite chains have alternating short and long V–O bonds. The bond angle at the shared O atom, O(3), between two V atoms is 136.4(3)°. The extent of short–long bond length alternation in Ca(VO)$_2$(PO$_4$)$_2$ is considerably greater than that in KTP. The 8-coordinate Ca atoms occupy intersecting channels parallel to [100] and [001] with the average Ca–O bond length at 2.528 Å, which is a little longer than the sum of the radii for Ca^{2+} (C.N. = 8) and O^{2-} (C.N. = 3), 2.48 Å. Oxygen atoms O(1) and O(5) are bonded to the V atoms within a chain (O^i). Oxygen O(2) and O(4) of a phosphate group coordinate to the V atoms in different chains (O^a). Individual
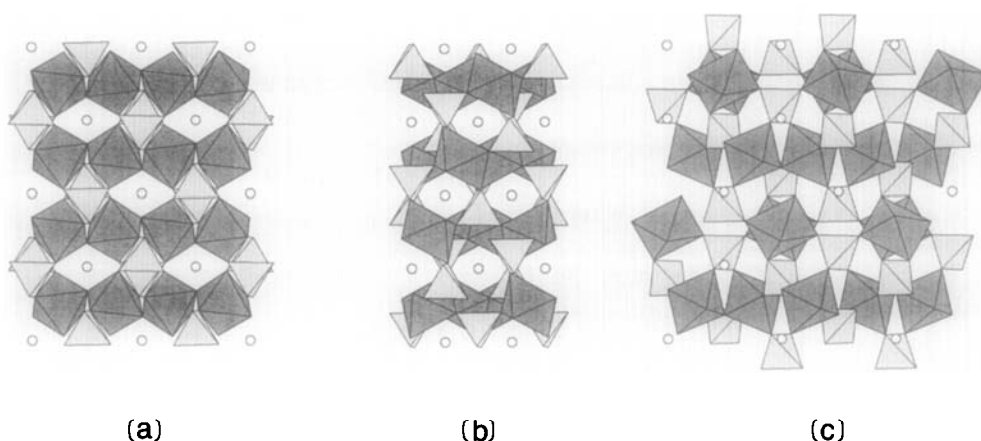

(a)   (b)   (c)

FIG. 1. View of the Ca(VO)$_2$(PO$_4$)$_2$ structure along (a) [001], (b) [100], and (c) [101]. In these representations, the corners of octahedra and tetrahedra are O^{2-} ions; the V and P ions are at the center of each octahedron and tetrahedron, respectively. Open circles are Ca^{2+} ions.
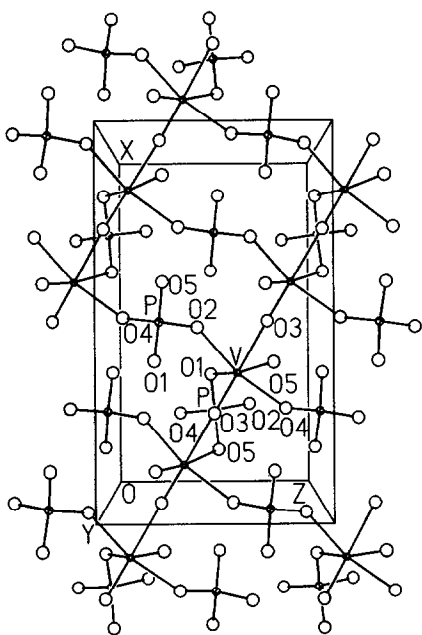
FIG. 2. Section of the $Ca(VO)_2(PO_4)_2$ structure showing the connectivity between infinite chains.

chains are linterlinked in the ac plane by $V–O^a–P–O^a–V$ bonding to form layers (Fig. 2). In the stacking of these layers along the b axis the infinite chains are directed alternately along the [101] and [10$\bar{1}$] directions in successive layers. The infinite chains in a layer are bound to those in layers above and below by $V–O^a–P–O^i–V$ crosslinking. Each phosphate group bonds to two adjacent octahedra in one chain, and two octahedra in two neighboring chains in an adjacent layer. The connectivity formula can be represented as $^3_\infty Ca[VO_{2/2}(PO_2^iO_2^q)_{4/4}]_2$, where the two numbers in superscript are used to indicate, in their order of appearance, the dimensionality of the substructure in square brackets and the dimensionality of the total structure, respectively (19). The infinite chains in $Ca(VO)_2(PO_4)_2$ appear similar to those found in $NaVOPO_4$, α-, and β-Li $VOPO_4$. However, adjacent VO_6 octahedra in the chains of $Ca(VO)_2(PO_4)_2$, $NaVOPO_4$, and α-LiVOPO$_4$ have a staggered configu-

ration in contrast to the eclipsed configuration in β-LiVOPO$_4$. The chains in KVOPO$_4$ (KVP) are rather different. As in KTP, there are two crystallographically distinct V atoms in KVP. Around V(1), the oxygen atoms in the V–O–V chain are in cis configuration; around V(2), the same two oxygen atoms are $trans$. The V–O–V bond angle in the Ca compound is smaller than those in the Li and Na compounds (136.6–142.9°), but greater than those in KVP (131.9, 134.0°). The short–long bond length alternation around V(1) in KVP is to the smallest extent (2.089, 1.673 Å). In β-LiVOPO$_4$, the alternation is to the greatest extent (2.342, 1.628 Å). While KVP remains paramagnetic at 5 K, β-LiVOPO$_4$, NaVOPO$_4$, and Ca (VO)$_2$(PO$_4$)$_2$ shows antiferromagnetic interaction at ~40, ~20, and ~10 K, respectively. The superexchange overlap of vanadium d and oxygen p orbitals depends not only on the V–O bond length alternation but also on the configuration of adjacent VO$_6$ octahedra in the chains.

Further investigation on Ca(VO)$_2$(PO$_4$)$_2$ and the titanium analogue would be interesting. Since the synthesis of new materials often leads to novel phenomena and applications, and the structural analysis of inorganic crystals plays an important part in the quest of new nonlinear optical materials, further research on the synthesis and structural chemistry of $AMOPO_4$ and $A'(MO)_2(PO_4)_2$ is in progress.

Acknowledgments

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