

Synthesis and Crystal Structure of $\text{NaV}_3\text{P}_3\text{O}_{12}$: A Stuffed Structure of $\alpha\text{-CrPO}_4$

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A new vanadium phosphate containing sodium, $\text{NaV}_3\text{P}_3\text{O}_{12}$, was prepared under reducing conditions. The compound is a paramagnetic insulator, having a Curie constant coincident with the one calculated for the the chemical formula $\text{NaV}^{2+}\text{V}_2^{3+}\text{P}_3\text{O}_{12}$. The orthorhombic lattice constants are $a = 10.488(2)$, $b = 13.213(3)$, and $c = 6.455(1)$ Å with $z = 4$. The structure was solved with the space group *Imma*, composed of $-\text{O}-\text{P}-\text{O}-\text{V}-\text{O}-$ chains combined with $\text{V}_2\text{P}_2\text{O}_{14}$ units which are formed by edge-sharing of tetrahedra and octahedra. The sodium ions are located in a tunnel in a framework similar to $\alpha\text{-CrPO}_4$. © 1989 Academic Press, Inc.

Introduction

Under reducing conditions, many new phosphates containing transition metal ions with low valence states have been prepared (1-6). Their structures are built up from corner-sharing MO_6 ($M =$ transition metal) octahedra and PO_4 tetrahedra and, in the case of orthophosphates, structural units formed only by linkage of MO_6 octahedra via corner or edge sharing are often separated by the tetrahedra, as seen, for example, in MoOPO_4 , TiPO_4 , and VPO_4 . Such compounds are suitable for an examination of their physical properties, because the interaction between transition metal ions is simplified (7, 8).

By adding large ions, such as alkali metal ions, in these systems, structures are modified greatly to accommodate the large ions,

providing a variety of structural types with so-called cage or tunnel structure (9-12). Several structural types have been reported for MPO_4 (13, 14). Among them, the quartz modifications and $\alpha\text{-CrPO}_4$ (15) types have fairly large cavities in the structure; therefore, it is expected that a compound including alkali metal ions with a staffed structure derived from these structural types will be found. In the course of preparation of phosphates with low valence transition metals, a compound with the anticipated structure was prepared in the system $\text{Na}-\text{V}-\text{P}-\text{O}$. Its structure and properties are described here.

Experimental and Results

Sample Preparation

Powders of VCl_3 and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ with a molar ratio of 1:1 were mixed in a glove box filled with dry nitrogen. The mix-

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ture was put into a carbon or boron nitride crucible, dried at 300°C for 1 hr, and then sealed in an evacuated silica tube. The starting material was heated at 500°C for 2 hr and finally reacted at 900°C for 3 days. Products were washed with hot water to remove NaCl , one of the reaction products, and black needle-like crystals were isolated. At higher temperatures the compound crystallized in a plate form.

Chemical Composition and Lattice Constants

Amounts of Na, V, and P were analyzed by the atomic absorption method, volumetric titration, and chelatometric titration, respectively. The observed values coincided with the calculated ones for $\text{NaV}_3\text{P}_3\text{O}_{12}$ (found: Na, 6.0%; V, 32.2%; P, 20.8%; calc.: Na, 5.0%; V, 33.2%; P, 20.2%). Weight gain on oxidation was measured by heating the sample at 600°C in air for 2 hr several times until a constant weight was attained. The observed value of 12.3% was in good agreement with the calculated one accompanying the oxidation of V^{2+} and 2V^{3+} to 3V^{5+} (12.2%).

X-ray powder patterns (XRD) were recorded on a diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation. The lattice constants were determined by least-squares refinement of XRD taken with a scanning speed of $\frac{1}{4}^\circ/\text{min}$ and with silicon as an internal standard. The pattern was found to be similar to that for $\alpha\text{-CrPO}_4$ (15). Therefore, the pattern was indexed with an orthorhombic cell. The refinement gave the lattice parameters $a = 10.488(2)$, $b = 13.213(3)$, and $c = 6.455(1)$ Å; $\alpha\text{-CrPO}_4$: $a = 10.403$, $b = 12.898$, $c = 6.299$ Å. Observed density of 3.60 g/cm³ indicates four formula units in the cell. The similarity of powder pattern and lattice constants implies that the structure of $\text{NaV}_3\text{P}_3\text{O}_{12}$ is modified to accommodate the sodium and V^{2+} ions in the structure from $\alpha\text{-CrPO}_4$.

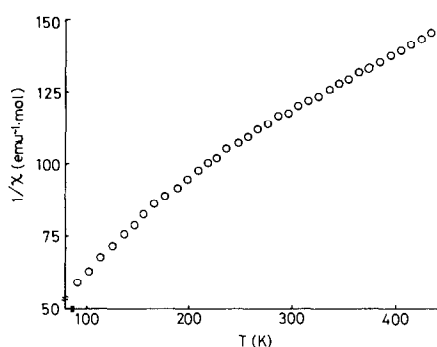


FIG. 1. Temperature dependence of reciprocal susceptibility of $\text{NaV}_3\text{P}_3\text{O}_{12}$.

Magnetic Measurement

Magnetic susceptibility was measured by using a Faraday balance from liquid nitrogen temperature to about 450 K. As shown in Fig. 1, the magnetic susceptibility of $\text{NaV}_3\text{P}_3\text{O}_{12}$ followed the Curie-Weiss law above approx 200 K, although downward deviation from the law was observed in the lower temperature region. A least-squares fitting of the data gave the Curie constant of $C = 5.02$ K/mole and the paramagnetic Curie temperature $\theta = -293$ K in the high-temperature region. The Curie constant agrees fairly well with the calculated value $C = 4.74$ K/mole on supposition that spins of one bivalent and two trivalent vanadium ions contribute to the susceptibility.

Measurements of the electric resistivity were performed on pressed pellets by the two-probe method and revealed the resistivity to be very high with an order of $\text{M}\Omega$.

Structure Determination

A rectangular crystal ($0.029 \times 0.037 \times 0.075$ mm) was selected for the structure determination. Weissenberg photographs confirmed the orthorhombic system and the systematic absences (hkl : $h + k + l = 2n$; $hk0$: $h = 2n$ and $k = 2n$; $0kl$: $k + l = 2n$; and $h0l$: $h + l = 2n$) indicate the space group of Imma or $\text{Ima}2$. The structure was solved

TABLE I
 ATOMIC PARAMETERS AND ANISOTROPIC TEMPERATURE FACTORS^a (×104) FOR NaV₃P₃O₁₂

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Na	4e	0	25	4005(12)	511(51)	483(48)	167(31)	0	0	0
V(1)	4a	0	0	0	28(5)	69(6)	71(6)	0	0	-0(6)
V(2)	8g	2500	6345(1)	2500	39(4)	66(4)	78(5)	0	-8(4)	0
P(1)	4e	0	2500	9167(5)	61(10)	97(10)	89(11)	0	0	0
P(2)	8g	2500	4264(1)	2500	67(6)	85(6)	94(7)	0	-10(6)	0
O(1)	8h	0	6544(4)	9538(9)	128(22)	45(18)	116(22)	0	0	6(17)
O(2)	8i	8817(6)	2500	7686(11)	83(20)	195(23)	125(26)	0	-42(20)	0
O(3)	16j	2841(6)	3639(3)	615(7)	111(14)	148(17)	132(16)	-11(14)	28(13)	40(15)
O(4)	16j	1394(3)	5054(3)	2017(6)	64(11)	101(13)	120(15)	-3(13)	-20(10)	-23(12)

^a Anisotropic temperature factors have the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

and refined in the centrosymmetric space group *Imma*.

The data were collected on a Rigaku automated four-circle diffractometer using graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å). The intensities were measured up to $2\theta = 90^\circ$ in the ω - 2θ scanning mode with scanning speed of 2.0°/min in ω , and the scan was repeated three times when the total counts were less than 10,000. A scan width was determined according to the formula $(1.8 + 0.4 \tan \theta)^\circ$. Of the 944 independent intensity data, 809 had $|F_o| > 3.0\sigma_F$ and were corrected for Lorentz and polarization effect but not absorption.

Atomic coordinates of the vanadium atoms, phosphorus atoms, and the oxygen atoms coordinating to them were deduced from the Patterson function and the position of the sodium atom was derived from subsequent Fourier synthesis by using the program UNICS (16). The positional and thermal parameters were refined with the full-matrix least-squares program LINUS (17). The atomic scattering factors for neutral atoms were taken from the "International Tables for X-Ray Crystallography" (18) and unit weights were allotted to all reflections. Anisotropic refinement yielded the final $R = 0.056$ and $R_w = 0.064$, respec-

tively. Final atomic and anisotropic thermal parameters are given in Table I. A similar refinement in *Ima2* was found to be less satisfactory.

Structure Description and Discussion

Figure 2 shows a view of the NaV₃P₃O₁₂ structure along the *a*-axis. The framework of this structure is composed of two structural units all of which are parallel to the *b*-axis. One is a zigzag chain of PO₄ tetrahedra and VO₆ octahedra linked alternatively by corner sharing at O₁, as seen in Fig. 3a. The other unit is a rigid rod-shaped block, consisting of two VO₆ octahedra and two

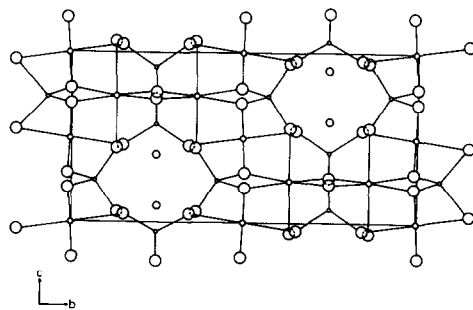


FIG. 2. Structure of NaV₃P₃O₁₂ projected along the *a*-axis. Half of V₂P₂O₁₄ units are omitted for clarity.

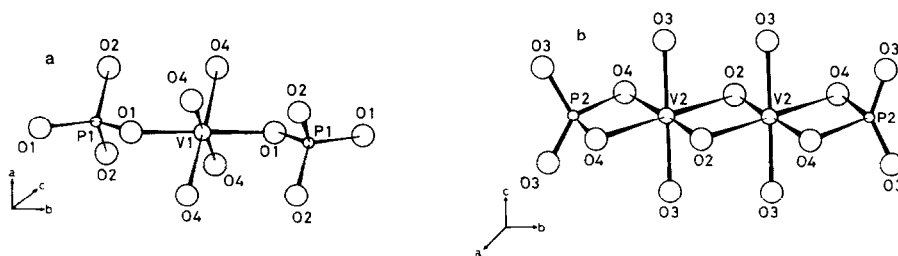


FIG. 3. Two structural units in $\text{NaV}_3\text{P}_3\text{O}_{12}$: (a) zigzag . . .O-P-O-V-O. . . chain; (b) $\text{V}_2\text{P}_2\text{O}_{14}$ cluster.

PO_4 tetrahedra, shown in Fig. 3b. In this structural unit with a formula of $\text{V}_2\text{P}_2\text{O}_{14}$, each VO_6 octahedron shares opposite edges with a VO_6 octahedron and a PO_4 tetrahedron. The two structural units share O_2 and O_4 , and the structural units of $\text{V}_2\text{P}_2\text{O}_{14}$ are attached to each other by sharing O_3 in such a way that O_3 at the corners of the tetrahedron and the octahedron on a cluster are linked to the corners of the octahedron and the tetrahedron on the other. Tunnels run through the framework along the a - and b -axes. The sodium atoms are located at the spaces where the two types of tunnels intercross. The feature of the framework of $\text{NaV}_3\text{P}_3\text{O}_{12}$ is very similar to that of $\alpha\text{-CrPO}_4$ (15) as expected from the powder pattern, but the counteranions are located in the tunnel.

The atomic distances and bond angles were calculated by the program UNICS (16) and are given in Table II. Polyhedra in the zigzag chain seem to be rather regular. The $\text{V}_1\text{-O}$ distances are 4×1.982 and 2×2.062 Å, and the $\text{P}_1\text{-O}$ distances are 2×1.515 and 2×1.566 Å. The P-O_2 distance is slightly longer than P-O_1 because O_2 is common to two VO_6 octahedra and one PO_4 tetrahedron. The bond angles in these polyhedra deviate only slightly from the ideal ones.

On the other hand, polyhedra in $\text{V}_2\text{P}_2\text{O}_{14}$ are deformed because of edge sharing of these polyhedra. The O-O distances range

TABLE II
SELECTED INTERATOMIC DISTANCES (IN Å)
AND ANGLES (IN DEGREES) FOR $\text{NaV}_3\text{P}_3\text{O}_{12}$
(ESD IN PARENTHESES)

[. . .O-P-O-V-O. . .] chain			
$\text{P}_1\text{-O}_1$	1.515(6)	$\text{O}_1\text{-P}_1\text{-O}_1$	112.9(2)
-O_2	1.566(7)	$\text{O}_1\text{-P}_1\text{-O}_2$	109.7(2)
$\text{O}_1\text{-O}_2$	2.519(8)	$\text{O}_2\text{-P}_1\text{-O}_2$	104.8(2)
$\text{O}_2\text{-O}_2$	2.481(9)		
$\text{V}_1\text{-O}_1$	2.062(4)	$\text{O}_{1,1}\text{-V}_1\text{-O}_{1,2}$	180.0
-O_4	1.982(4)	$\text{O}_{4,1}\text{-V}_1\text{-O}_{4,3}$	180.0
$\text{O}_{1,1}\text{-O}_{4,1}$	2.947(6)	$\text{O}_{1,1}\text{-V}_1\text{-O}_{4,1}$	93.5(2)
$\text{O}_{1,1}\text{-O}_{4,3}$	2.770(6)	$\text{O}_{1,1}\text{-V}_1\text{-O}_{4,3}$	86.4(2)
$\text{O}_{4,1}\text{-O}_{4,2}$	2.941(4)	$\text{O}_{4,1}\text{-V}_1\text{-O}_{4,2}$	95.8(2)
$\text{O}_{4,1}\text{-O}_{4,4}$	2.677(5)	$\text{O}_{4,1}\text{-V}_1\text{-O}_{4,4}$	85.0(2)
[$\text{V}_2\text{P}_2\text{O}_{14}$] cluster			
$\text{P}_2\text{-O}_3$	1.513(4)	$\text{O}_{3,1}\text{-P}_2\text{-O}_{3,2}$	113.9(2)
-O_4	1.585(4)	$\text{O}_{3,1}\text{-P}_2\text{-O}_{4,1}$	113.1(2)
$\text{O}_{3,1}\text{-O}_{3,2}$	2.536(6)	$\text{O}_{3,1}\text{-P}_2\text{-O}_{4,2}$	109.1(2)
$\text{O}_{3,1}\text{-O}_{4,1}$	2.585(6)	$\text{O}_{4,1}\text{-P}_2\text{-O}_{4,2}$	97.6(2)
$\text{O}_{3,1}\text{-O}_{4,2}$	2.524(5)		
$\text{O}_{4,1}\text{-O}_{4,2}$	2.385(5)		
$\text{V}_2\text{-O}_5$	2.062(4)	$\text{O}_{2,1}\text{-V}_2\text{-O}_{2,2}$	84.5(2)
-O_3	2.042(5)	$\text{O}_{2,1}\text{-V}_2\text{-O}_{3,3}$	86.1(2)
-O_4	2.081(4)	$\text{O}_{2,1}\text{-V}_2\text{-O}_{3,4}$	93.0(2)
$\text{O}_{2,1}\text{-O}_{2,2}$	2.773(9)	$\text{O}_{2,1}\text{-V}_2\text{-O}_{4,1}$	103.0(2)
$\text{O}_{2,1}\text{-O}_{3,3}$	2.802(7)	$\text{O}_{2,1}\text{-V}_2\text{-O}_{4,2}$	171.1(2)
$\text{O}_{2,1}\text{-O}_{3,4}$	2.977(6)	$\text{O}_{3,3}\text{-V}_2\text{-O}_{3,4}$	180.0
$\text{O}_{2,1}\text{-O}_{4,1}$	3.243(4)	$\text{O}_{3,3}\text{-V}_2\text{-O}_{4,1}$	92.4(2)
$\text{O}_{3,3}\text{-O}_{4,1}$	2.976(6)	$\text{O}_{4,1}\text{-V}_2\text{-O}_{4,2}$	69.9(2)
$\text{O}_{3,3}\text{-O}_{4,2}$	2.880(6)		
$\text{P}_2\text{-V}_2$	2.750(6)		
$\text{V}_2\text{-V}_2$	3.052(2)		

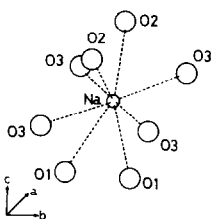


FIG. 4. Environment of sodium ion.

from 2.385 to 2.585 Å for the PO_4 tetrahedron, and from 2.385 to 3.243 Å for the VO_6 octahedron, the shared edges are shortened and the edge parallel to the V–V axis gives the greatest length. For the same reason, the $\text{P}_2\text{--O}_4$ and $\text{V}_2\text{--O}_4$ distances going to the shared edges are long, especially the $\text{P}_2\text{--O}_4$ distance of 1.585 Å. A similar structural unit is seen in $\alpha\text{-CrPO}_4$, but the distribution of metal–O and P–O distances is smaller than in $\text{NaV}_3\text{P}_3\text{O}_{12}$.

The sodium ion in the tunnel is surrounded by eight oxygen atoms with distances ranging from 2.613 to 2.730 Å (Fig. 4). Two PO_4 tetrahedra in the zigzag chains sandwich a sodium ion along the c -axis.

As the magnetic property of this compound indicates, direct bonding between the vanadium ions is not likely, although edge-sharing of VO_6 octahedra exists. In fact, the V–V distance of 3.052 Å is longer than the critical distances for $\text{V}^{2+}\text{--V}^{2+}$ and $\text{V}^{3+}\text{--V}^{3+}$ proposed by Goodenough (19). The mean V–O distances are 2.008 Å in the zigzag chain and 2.061 Å in the $\text{V}_2\text{P}_2\text{O}_{14}$ unit. From this difference, V^{2+} ions located randomly in one of the larger octahedra of the $\text{V}_2\text{P}_2\text{O}_{14}$ unit are highly probable.

As indicated by $\text{NaV}_3\text{P}_3\text{O}_{12}$, the framework of $\alpha\text{-CrPO}_4$ -type structure can accommodate small alkali metal ions in the tunnel. A variety of compounds having the framework and containing other alkali metal ions may be synthesized by a direct reaction, as with $\text{NaV}_3\text{P}_3\text{O}_{12}$, or by an indirect reaction, such as lithiation. In the cases of VPO_4 and

TiPO_4 which have linear chains of octahedra sharing edges, Ti–Ti bonding was observed but not V–V bonding (2). It is interesting to prepare the titanium phosphate corresponding to $\text{NaV}_3\text{P}_3\text{O}_{12}$ in which V–V bonding is not conceivable.

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