

Na₃V⁴⁺O(PO₄)(HPO₄), a New Phase in the Na/V/P/H₂O System under Hydrothermal Conditions at 473 K

Michael Schindler,^{*} Werner Joswig,[†] and Werner H. Baur[‡]

^{*}Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada; [†]Institut für Mineralogie, Senckenberganlage 30, 60054 Frankfurt am Main, Germany; and [‡]Department of the Geophysical Sciences, University of Chicago, Illinois 60637

Received September 17, 1998; in revised form December 2, 1998; accepted December 14, 1998

A new examination of the Na/V/P/H₂O systems at 473 K under hydrothermal conditions yielded in a pH range between 6.5 and 7.6 and at synthesis times longer than 10 days a new blue Na₃VO(PO₄)(HPO₄) phase. It crystallizes in space group *P2₁/m* with $a = 9.6402(7)$ Å, $b = 6.4075(5)$ Å, $c = 6.2637(6)$ Å, and $\beta = 104.861(7)^\circ$. The crystal structure is composed of VOPO₄ layers, with additional HPO₄ tetrahedra between the layers. A symmetry supergroup/subgroup examination of all compounds containing VOXO₄ layers shows that all space groups of these compounds can be derived by reducing the symmetry elements of the aristotypic space group *I4/mmm*. The Na⁺ cations occupy every second possible position between the vanadium and the phosphate polyhedra of the VOPO₄ layers. This is in contrast to the class of *MVOPO₄ · nH₂O* ($M = \text{Na, K, Rb, Ca, Sr, Pb, Ba}$) ($n = 3-4$) compounds, where only every fourth possible position is occupied. © 1999 Academic Press

INTRODUCTION

In 1933 Jander and Jahr (1) pointed out the correlation of the polymerization of VO_x polyhedra in vanadates with the pH values employed in their synthesis. This observation proved to be useful for the synthesis of vanadium compounds from aqueous solutions as shown by Kiehl and Manfredo (2), Menzel and Müller (3), and Lelong (4) who studied the Na/V⁵⁺/H₂O system. Crystallizations under mildly reducing conditions in aqueous solutions yielded compounds containing reduced vanadium clusters as demonstrated more recently by Müller and Döring (5). All these studies showed clearly that under weakly acid or basic conditions the vanadium coordination polyhedra can polymerize into finite clusters, while at lower pH values, they form chains and sheets of polyhedra. A study of the ore deposits of the Colorado Plateau by Evans and Garrels (6) confirmed this relationship for vanadium-containing mineral assemblages.

¹To whom correspondence should be addressed.

Beltrán-Porter *et al.* (7) indicated in a review paper several methods for the crystallization of vanadium phosphate phases. Numerous studies in the last five years concern the synthesis of vanadium phosphate phases under hydrothermal conditions (for references see the Discussion section below, specifically (16–19, 22–24, 27–38, 40, 41)). We examined the occurrence of vanadium phosphate phases in several *M/V/P/(tEA)/H₂O* systems ($M = \text{Na, K, NH}_4^+$) (tEA = triethylamine = N(C₂H₅)₃) under hydrothermal conditions at 473 K (8,9) as a function of the pH value. In particular a detailed examination of the K/V/P/(tEA)/H₂O and NH₄/V/P/H₂O systems (9) showed that the type and the concentration of monovalent cations in the system have a strong influence on the crystallized vanadium phosphate phases. An examination of the KOH/V/H₃PO₄/(tEA)/H₂O system yielded the mixed valence V⁴⁺/V⁵⁺ phase K_{0.5}VOPO₄ · 1.5 H₂O at pH values lower than those at which the tetravalent KVOPO₄ phase occurred. This indicated that other parameters, such as the KOH content have a strong influence on the crystallization of vanadium phosphate compounds. This consideration prompted us to study in detail the phases occurring in the NaOH/V/P/(tEA)/H₂O system.

The structural topology of the title compound Na₃VO(PO₄)(HPO₄) is similar to that found in numerous other layered vanadium phosphate compounds. Roca *et al.* (10) recently published a very detailed description of the phases of *M(VOPO₄)₂ · nH₂O* ($M = \text{Ca, Sr, Ba, Pb, Ni, Na, K, Rb}$) ($n = 3-4$) composition. The Na₃VO(PO₄)(HPO₄) crystal structure and all these compounds share the same type of VOPO₄ layer as a fundamental building unit. We describe in the following the symmetry relationships of all phases containing this kind of VOPO₄ layer.

EXPERIMENTAL

Synthesis

We examined the Na/V/P/(tEA)/H₂O system under hydrothermal conditions at 473 K in the pH range between 1.5



and 12. As reported in Ref. (8), we adjust the pH value in the NaOH/V/H₃PO₄/(tEA)/H₂O runs by adding NaOH. In addition to the reexamination of this system, we also investigated the NaOH/V/H₃PO₄/H₂O system in a similar fashion. For every starting composition, the V/H₃PO₄/(tEA)/H₂O ratio was held constant at 1/4/(1.75)/700. The compounds used as a source of vanadium were either V⁴⁺OSO₄ or V₂⁵⁺O₅. The synthesis time was varied between 2.5 and 12 days. We measured the pH value before synthesis with a WTW pH meter with an accuracy of ± 0.1 .

When two phases are observed in the same pH-range, e.g., Na_{0.5}VOPO₄·H₂O/VOHPO₄·0.5H₂O or NaVOPO₄/Na₃VO(PO₄)(HPO₄), then the first mentioned compound occurs as a major phase in batches with a synthesis time of less than 4 days. The purities of the single phases listed in Table 4 are approximately 95% and the yield of a phase depends on pH value, stoichiometric ratio, and synthesis time. The maximal yield for Na₃VO(PO₄)(HPO₄) was 40% based on the total vanadium introduced into the reaction and was found in the batch: V₂O₅/H₃PO₄/NaOH/H₂O = 1/8/14/1400, pH value 6.5, 10 days. Other batches yielding a pure Na₃VO(PO₄)(HPO₄) phase (95%) are VOSO₄/H₃PO₄/NaOH/H₂O = 1/4/7/700, pH 6.4, 12 days, and 1/4/8/700, pH 6.9, 12 days. All three batches consist exclusively of aggregates of rather large single crystals which can be easily separated from each other.

Data Collection and Solution of the Crystal Structure

The new blue Na₃VO(PO₄)(HPO₄) phase is bounded by (100), (010), and (001) faces. The maximal size of the (100) face is 200 × 200 μm. One crystal from the batch with VOSO₄/H₃PO₄/NaOH/H₂O = 1/4/7/700, pH value 6.4, 12 days synthesis time, was used for single crystal diffraction data collection on an Enraf-Nonius CAD-4 diffractometer. The selected crystal had a size of 150 × 60 × 20 μm. The lattice cell refinement was based on 25 reflections in the range $\theta = 1\text{--}20^\circ$. Na₃VO(PO₄)(HPO₄) crystallizes in space group *P*2₁/*m* with $a = 9.6402(7)$ Å, $b = 6.4075(5)$ Å, $c = 6.2637(6)$ Å, and $\beta = 104.861(7)^\circ$.

The crystal structure was solved using direct methods (SHELXTS PC PLUS system, Ref. (11)). The crystal structure refinement with XTAL93 (12) yielded an *R* value of 0.096 and an *R*_w value of 0.123, respectively. At this point of the refinement we realized that the diffraction groups with $l = -5, 0, \text{ and } 5$ had *R* values of 0.26, 0.16, and 0.25, while the average discrepancy factor for all other diffractions was 0.07. Leaving out these reflections from the refinement yielded *R* values of 0.037 (*R*) and 0.041 (*R*_w). We assumed that we had encountered a sample consisting of two twinned crystals, where because of the peculiarity of the metric of the unit cell, not only the zero layer of diffractions, but also the layers with $l = -5$ and 5 were superposed. An analogous case was observed in the crystal structure determination of

Li_{3.75}Si_{0.75}P_{0.25}O₄ (13). We made an additional refinement using the least-squares routine from the SHELXTS PC PLUS program system (11). The *F*²(obs) for the *hkl* with $l = -5, 0, \text{ and } 5$ were marked as contributions from two twin components. The refinement with all reflections yielded an *R* value of 0.073 and a refined twin component factor of 0.59(1). In the end, the atom positions from both refinements were similar, but the calculated standard deviations of the refinement with all observed diffractions were twice as large. Crystal data, data collection parameters, and *R* values for both refinements are listed in Table 1, the coordinates obtained from the refinement with 944 *F*_{obs} (XTAL 3.0) are listed in Table 2. The bond lengths were calculated using SADIAN90 (14) and are listed in Table 3. The crystal structure diagrams were produced using STRUPLO90 (15) and the SHELXTS PC PLUS program system (11).

RESULTS

The Na/V/P/(tEA)/H₂O System

Table 4 shows a more detailed listing of all phases occurring in the Na/V/P/(tEA)/H₂O system as originally described in (8). However, in contrast to our earlier paper, we now distinguish between different Na/V/P/(tEA)/H₂O systems depending on whether the source of vanadium was VOSO₄ or V₂O₅. The majority of the listed phases, Na-FVP-1, Na₇(V⁵⁺O)₄(HPO₄)₅(PO₄)₃·2.4H₂O, Na_{0.5}VOPO₄·2H₂O, VOHPO₄·0.5H₂O, and NaVOPO₄, are well known

TABLE 1
Crystal Data, Data Collection Parameters, and *R* Values
for Na₃VO(PO₄)(HPO₄)

Crystal system	monoclinic		
Space group	<i>P</i> 2 ₁ / <i>m</i> (No. 11)		
Lattice constants	$a = 9.6402(7)$ Å, $b = 6.4075(5)$ Å, $c = 6.2637(6)$ Å, $\beta = 104.861(7)^\circ$		
Lattice cell refinement with 25 reflexes (range of $\theta = 1$ to 20°)			
Cell volume	373.965(1) Å ³	Measured <i>hkl</i> 1243	
Formula weight	327.86 g	Range of <i>hkl</i> 2.2–30.0 in <i>I</i>	
Density	2.893 g/cm ³	sin $\theta/\lambda_{\text{max}}$ 0.7025	
Scan mode	ω scan	range of <i>h</i> 0 to +13	
Scan width	1.8°	range of <i>k</i> 0 to +8	
Scan time	max. 200 s	range of <i>l</i> -7 to +8	
Absorption factor	36.1 cm ⁻¹		
Crystal size	150 × 60 × 20 μm		
XTAL 3.0		SHELXS93	
Unique <i>F</i> _{obs}	1178	<i>F</i> _{obs} ²	1243
Unique <i>F</i> _{obs} with $l = -5, 0, 5$	234	<i>R</i>	0.073
Remaining <i>F</i> _{obs}	944	<i>R</i> _w ($w = 1/F$)	0.161
<i>R</i> _w	0.041	Twin component factor	0.59(1)
<i>R</i>	0.037		

TABLE 2

Atomic Positions, Equivalent Isotropic Temperature Factors, and Wyckoff Positions (Wy.) with Symmetry (Sy.) of the Na₃VO(PO₄)(HPO₄) Phase

Atom	x	y	z	U[<i>equi</i>]	Wy. Sy.
V1	0.43699(8)	-1/4	0.2317(1)	0.0057(3)	2e m
P1	0.5021(1)	-1/4	0.7533(2)	0.0056(5)	2e m
P2	0.0794(1)	-1/4	0.2572(2)	0.0088(5)	2e m
O1	0.3986(4)	-1/4	0.9031(5)	0.010(1)	2e m
O2	0.3972(2)	0.0596(4)	0.2023(4)	0.010(1)	4f 1
O3	0.3886(4)	1/4	0.7077(6)	0.010(1)	2e m
O4	0.5961(4)	1/4	0.4775(5)	0.012(1)	2e m
O5	0.8092(3)	1/4	0.8768(5)	0.009(1)	2e m
O6	0.0738(4)	1/4	0.8846(6)	0.015(2)	2e m
O7	0.8988(3)	0.0517(4)	0.5871(4)	0.015(2)	4f 1
Na1	0.7740(2)	0.0020(3)	0.1736(3)	0.0217(8)	4f 1
Na2	0.8046(2)	-1/4	0.7232(3)	0.021(1)	2e m

and have been described in several papers (8, 16–19). Na-FVP-1 stands for Sodium Frankfurt Vanadium Phosphate one with the following chemical compositions: Na_v[(V_{4⁺}⁺_wV_{1⁺}⁵⁺_wO₉)(PO₄)₂](PO₄)_x(OH)_y·zH₂O (with $v = 2.8$ to 4.0 , $w = -0.1$ to 1.1 , $x = 0$ to 0.2 , $y = 0$ to 2.1 , and $z = 7$ to 10). The new Na₃VO(PO₄)(HPO₄) phase could only be synthesized in runs without tEA in a pH range between 6.5 and 7.6 and a synthesis time of 10 days or more.

The Na₃VO(PO₄)(HPO₄) Phase

Table 3 shows selected bond distances in the crystal structure of Na₃VO(PO₄)(HPO₄). The vanadium atoms are in a 4 + 1 + 1 coordination against oxygen. The planar bond lengths within the distorted octahedra have an average bond length of 1.991(1) Å which is a typical planar bond distance for V⁴⁺-O as opposed to V⁵⁺-O which measures about 1.880(8) Å (8). The vanadium octahedra are connected through the oxygen atoms of the planar four coordina-

TABLE 3

Selected Bond Distances in Na₃VO(PO₄)(HPO₄) (in Å)

V1–O3	1.626(3)	P1–O4	1.511(3)	P2–O6	1.516(3)
V1–O4	1.928(3)	P1–O1	1.535(3)	P2–O5	1.523(3)
V1–O1	1.996(3)	P1–O2	1.539(2)	P2–O7	1.583(3)
V1–O2	2.020(3)	P1–O2	1.539(2)	P2–O7	1.583(3)
V1–O2	2.020(3)				
V1–O5	2.295(2)	Na1–O1	2.262(3)	Na2–O7	2.384(3)
		Na1–O6	2.273(3)	Na2–O7	2.384(3)
		Na1–O3	2.493(3)	Na2–O2	2.441(2)
		Na1–O5	2.534(3)	Na2–O2	2.441(2)
		Na1–O2	2.536(3)	Na2–O3	2.859(4)
		Na1–O7	2.581(3)	Na2–O6	2.436(4)

tion around V to four P1 tetrahedra. The vanadium octahedra are connected also to the HPO₄ group via the long V1–O5 bond.

The hydrogen positions of the HPO₄ group could not be located in the difference Fourier maps. A comparison of the P2–O7 bond distance (1.583(3) Å) with the mean observed P–O distance of P–OH groups (1.590 Å according to Baur (20)) indicates clearly that a hydrogen atom has to be bonded to the O7 atom. Atom O7 occurs twice in the P2 coordination tetrahedron (the O7 atoms are related by a mirror plane), but there is only one hydrogen atom available in the HPO₄ group, therefore it must be disordered over the two O7 sites. A bond strength calculation (21) for atom O7 supports this interpretation. It shows that O7 is the most underbonded of the phosphate oxygen atoms (1.58 valence units, v.u.) in this crystal structure, but at the same time it displays the longest P–O bond length of them all. Therefore, the hydrogen atom present in the compound must be bonded to O7, thus increasing the sum of the bond strengths received by this oxygen atom and explaining at the same time the long observed bond length P2–O7 of 1.583 Å.

The six sodium ions in the unit cell are distributed over two different crystallographic positions: Na1 in 4f and Na2 in 2e. Both Na atoms have sixfold coordinations and display the typical interatomic distances to the oxygen atoms expected for these bonds.

DISCUSSION

The Na/V/P/(tEA)/H₂O Systems

The concentrations of [Na⁺] in solution under acidic conditions influence primarily the occurrence of the various phases (Table 4). This is analogous to what we reported for the K/V/P/tEA/H₂O system (9): mixed valence phases such as Na_{0.5}V^{4.5+}OPO₄·2H₂O, which is structurally related to the corresponding K_{0.5}V^{4.5+}OPO₄·1.5H₂O phase, crystallized in batches with low [Na⁺] concentrations and V₂O₅ as the starting vanadium compound. Thus, the Na_{0.5}V^{4.5+}OPO₄·2H₂O phase probably crystallizes during the reduction of the pentavalent V₂⁵⁺O₅ compound in batches with Na/V ratios from 1 to 2, while the tetravalent NaVOPO₄ phase can be only found in batches with Na/V ≥ 2 (Table 4).

In fact, despite the presence of the reduction agent tEA, no trivalent vanadium phosphate phases do occur in this system. Currently only four vanadium(III) phosphate phases with monovalent cations are known: CsV₂(PO₄)(HPO₄)₂(H₂O)₂, α-Rb[V(HPO₄)]₂, β-Rb[V(HPO₄)], and NH₄[V(HPO₄)]₂ (22, 23). There is, however, nothing known about the synthesis of a sodium vanadium(III) phosphate phase.

In the neutral and low basic pH range the character of the phases formed is strongly influenced by (A) the capability for

TABLE 4
The Observed Phases in the NaOH/V/P/tEA/H₂O Systems after 4 Days^a

Examined systems	Na/V ratio	pH range	Observed phases
I V ₂ O ₅ /P ₂ O ₅ /TEA/NaOH/H ₂ O	1–2	2.4–2.9	Na _{0.5} VOPO ₄ · 2H ₂ O/VOHPO ₄ · 0.5H ₂ O
	3–4	5.4–6.2	NaVOPO ₄
	5	6.5	Na-FVP-1/NaVOPO ₄
	6–9	6.9–10.6	Na-FVP-1
	10–12	> 11.0	Na ₇ (V ⁵⁺ O) ₄ (HPO ₄) ₅ (PO ₄) ₃ · 2.4H ₂ O
II VOSO ₄ /P ₂ O ₅ /TEA/NaOH/H ₂ O	3–5	4.5– 6.3	NaVOPO ₄
	6–9	6.9–10.8	Na-FVP-1
	10–13	> 11.0	Na ₇ (V ⁵⁺ O) ₄ (HPO ₄) ₅ (PO ₄) ₃ · 2.4H ₂ O
III V ₂ O ₅ /P ₂ O ₅ /NaOH/H ₂ O	1	1.5	Na _{0.5} VOPO ₄ · 2H ₂ O/ VOHPO ₄ · 0.5H ₂ O
	2–3	1.8–2.3	Na _{0.5} VOPO ₄ · 2H ₂ O/NaVOPO ₄
	4–6	3.2–5.9	NaVOPO ₄
	7	6.5	NaVOPO ₄ /Na ₃ VO(PO ₄)(HPO ₄)
	8–14	> 6.5	—
	IV VOSO ₄ /P ₂ O ₅ /NaOH/H ₂ O	2–6	1.9–5.5
	7	6.4	NaVOPO ₄ /Na ₃ VO(PO ₄)(HPO ₄)
	8	6.9	Na-FVP-1/Na ₃ VO(PO ₄)(HPO ₄)
	9	7.6	Na-FVP-1
	10–12	> 7.6	—

^a When two phases are separated by a slash, the first is the major phase, and the second is a minor phase.

polymerization of the vanadium polyhedra, (B) the presence of the organic compound tEA, and (C) the synthesis time.

(A) *Polymerisation.* The condensation of vanadium polyhedra into groups under weak acidic, neutral and weak basic conditions is well known in synthetic and mineral vanadium chemistry: thus in a temperature range from 300 to 370 K at similar pH values as in the synthesis of Na-FVP-1 we find [V₁₈O₄₂] vanadium clusters in the form of extended Keggin molecules (5) and [V₁₀O₂₈] decavanadate polyanions (6)

(B) *The role of tEA.* In batches with V₂O₅ as the starting vanadium compound, Na-FVP-1 crystallizes only in the presence of tEA, while it occurs in all batches with VOSO₄ as the starting compound. On the other hand, Na₃VO(PO₄)(HPO₄) occurs only in batches without tEA. This influence of an organic compound is known from many other syntheses involving organic compounds in vanadium phosphate systems (24), but its function during crystallization is still unknown.

(C) *Synthesis time.* In the VOSO₄/P₂O₅/NaOH/H₂O system, Na₃VO(PO₄)(HPO₄), Na-FVP-1, and NaVOPO₄ occur together in a pH range between 6.4 and 6.9 (Table 4). Detailed examinations showed, that beside stoichiometric ratio and pH value the synthesis time is also an important factor. In batches with synthesis times between 2.5 and 4 days, Na₃VO(PO₄)(HPO₄) occurs only as a minor phase alongside NaVOPO₄ and Na-FVP-1, while it is observed as

a single phase (95%) at synthesis times longer than 10 days. A similar observation can be made in the V₂O₅/P₂O₅/NaOH/H₂O system, where Na₃VO(PO₄)(HPO₄) occurs only as a major phase in batches with a synthesis time of 12 days.

The Na₃VO(PO₄)(HPO₄) Phase. Topology

The crystal structure of Na₃VO(PO₄)(HPO₄) is composed of VOPO₄ layers. We define a VOXO₄ layer (X = P, S) as follows:

In a VOXO₄ layer, every coordination pyramid or octahedron around vanadium is connected to four X-tetrahedra and every X-tetrahedron is surrounded by four vanadium coordination octahedra or pyramids.

A VOXO₄ sheet has an arrangement similar to a checkerboard pattern and its highest possible space group symmetry is *I4/mmm*. The black squares are alternately the phosphate (or sulfate) coordination tetrahedra and the vanadium coordination octahedra or pyramids (Fig. 1). In addition a further characteristic of the VOXO₄ layer is that the vanadyl bonds, none of which participate in the bonding to the tetrahedral groups, alternate in the direction in which the V=O groups are pointing: the four neighbors of a central vanadium octahedron or pyramid point in the opposite direction compared to the central polyhedron (Fig. 2). The white squares of the checkerboard correspond to the unoccupied spaces between the coordination polyhedra (Fig. 1). The subgroup/supergroup symmetry relationships (25) of vanadium phosphate phases containing VOXO₄ layers are

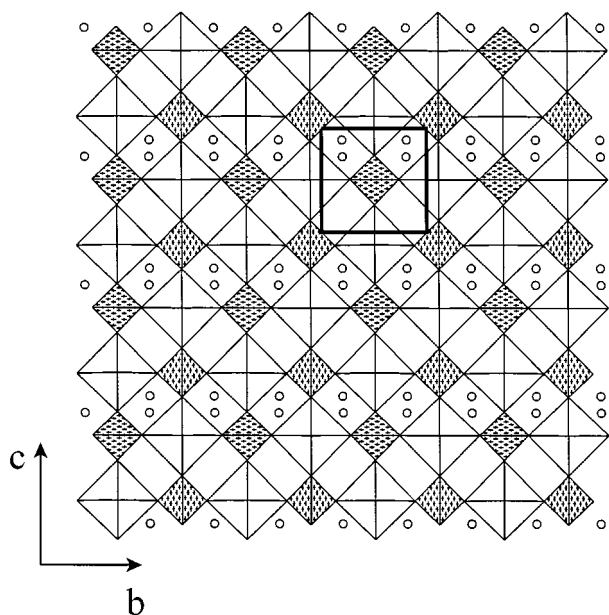


FIG. 1. The (VOPO₄) layer of Na₃VO(PO₄)(HPO₄) parallel to the plane (100). The sodium ions Na1 occupy every second nest of the VOPO₄ layer. In each occupied nest there are two Na1 ions, one above and one below the layer.

shown in Fig. 3. This Bärnighausen tree (26) usually illustrates the relationships of a family of one structure type with analogous chemical compositions. In the tree presented here all structures contain the VOXO₄ layer as a common

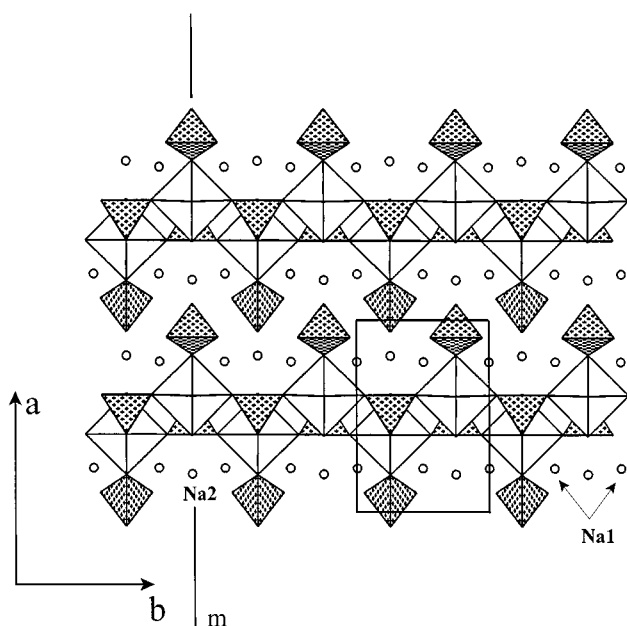


FIG. 2. The crystal structure of Na₃VO(PO₄)(HPO₄) viewed parallel to [001]. It is clearly visible how the VOPO₄ layers with their attached HPO₄ tetrahedra fit into each other like the teeth of a zipper.

fundamental building unit, but otherwise vary in their chemical make-up.

Similar layer arrangements are found in several MOXO₄ compounds ($M = \text{Mo, Ta, Nb}$). We do not take into consideration structures with defective VOXO₄ sheets (27), because they do not obey the previously given definition. Only the two lattice constants which define the two dimensional unit cell of a VOXO₄ sheet are important for the discussion of the symmetry group relationships and are indicated with bold letters in Fig. 3.

MVOPO₄ · nH₂O compounds

The class of MVOPO₄ · nH₂O compounds (with $M = \text{Ca, Sr, Pb, Ba, K, Na, Rb, Ni, Co, Cu, } n = 3-4$) have different space group symmetries, varying from the aristotype of the tree ($I4/mmm$) to the lowest symmetry of space group $P1$ (Fig. 3). The vanadium phosphates of the octahedrally coordinated d group elements Co and Ni (28, 29) crystallize in space group $I4/mmm$. They connect the VOXO₄ layers via V=O–Co(Ni)–O=V links. Roca *et al.* (10) called these positions “apices” and the positions in the cavities of the VOXO₄ layers “nests”. The different nest positions are occupied by spherical ions such as Na, K, Rb, Ca, Sr, Pb, and Ba (16, 30, 31, 10). The different crystallographic positions of the ions, the distortion of the VOXO₄ layers by differing sizes of the ions and varying nest positions of the ions and the shifts of the VOXO₄ layers relative to each other, cause symmetry reductions to different monoclinic and triclinic space groups.

The symmetry reduction in the monoclinic Cu_{0.5}[VOPO₄] · 2H₂O (32) phase is caused by the square planar coordination of copper against oxygen, in contrast to the octahedral coordinations of nickel and cobalt. A related Cu_{0.5}(OH)_{0.5}[VOPO₄] · 2H₂O (33) phase crystallizes in $P\bar{1}$ with unit cell constants of ca. 6.3 and 12.6 Å instead of the 8.9 and 9.0 Å lattice constant of the monoclinic phase.

VOXO₄ Layers with Additional Tetrahedra

If additional tetrahedra are inserted between the VOXO₄ layers, they are always linked via the longer V---O bonds of the distorted vanadium octahedra. In the VOSO₄ · 2H₂SO₄ structure (33), the tetrahedra link the VOXO₄ layers. The symmetry is reduced because of the symmetry of the tetrahedra to space group $P4_2/mnm$. In (VO₂)(PO₄)₂H₂PO₄ · N₂C₂H₄ (34) the additional organic molecule present causes the loss of the inversion center and of the 4-fold axes and also produces a doubling of a lattice constant parallel to the sheets. In contrast to the VOSO₄ · 2H₂SO₄ and (VO₂)(PO₄)₂H₂PO₄ · N₂C₂H₄ structures the HPO₄ tetrahedra in the Na₃VO(PO₄)(HPO₄) structure do not connect the VOXO₄ layers. The HPO₄ groups are opposite of the vanadyl bonds and are surrounded by the HPO₄

tetrahedra of the next VOXO₄ layer (Fig. 2). The layers fit snugly into each other, much like the teeth of a zipper. This results in a reduction of the symmetry to space group $P2_1/m$.

VOXO₄ Layers with Organic Molecules

The insertion of organic molecules as in VOPO₄·0.5 N₂C₄H₁₂ (34) and [(VO₂)₂(PO₄)₂]·(H₂NC₄H₈NH₂) (27) leads to the symmetry of space group $P2_1/c$. In the latter crystal structure the coordination around the vanadium atoms is trigonally bipyramidal, instead of octahedral, which likewise contributes to reducing the overall symmetry.

VOPO₄·2H₂O, α-VOXO₄, β-VOXO₄

Tietze (36) refined the crystal structure of VOPO₄·2H₂O in space group $P4/nmm$ with an R value of 5.3%. A reduction to space group $P4/n$ is seen in the α-VOXO₄ structures $X = P, S$ (37, 38), caused by the twisting of the vanadium pyramids and the phosphate tetrahedra. We can find a similar case in several natural zeolites of the natrolite group, where aluminosilicate chains of tetrahedra rotate in an opposite sense and lead to a symmetry reduction from $I4_1/amd$ to $Fdd2$ (39). Another type of tetrahedral orientation is illustrated by the β-VOXO₄ ($X = P, S$) (40, 41) structures where the symmetry is reduced to space group $Pnma$.

Positions of the Na⁺ Ions in Na₃VO(PO₄)(HPO₄)

Figure 1 shows that in every second nest inside the VOXO₄ layers there are two Na1 atoms, above and below the VOXO₄ layer. Roca *et al.* (10) described four different nest positions N1, N2, N3, and N4 for the MVOPO₄· n H₂O phases. N1 and N2 are enantiomorphic positions for undistorted VOXO₄ layers, while N3 and N4 are two different positions, which occurred in the distorted layers. In the undistorted VOXO₄ layer of the Na₃VO(PO₄)(HPO₄) structure, Na1 is at the nest positions of N1 and N2. It is slightly shifted to the underbonded O6 atom of the additional coordination tetrahedron around P2 and is not coordinated to one of the equatorial O atoms (O₄), which belong in the idealized nest positions of the MVOPO₄· n H₂O compounds to the M coordination sphere. The O6 atom receives a bond strength of 1.25 v.u from the central P atom (21), and it requires, therefore, for balancing an additional 0.75 v.u. from the Na atoms. This bond strength requirement can be only satisfied when every N1 and N2 nest position is occupied by Na atoms and thus, there are two Na1 (2.273(3) Å) and one Na2 (2.435(4) Å) atoms coordinated to O6. This is in contrast to the MVOPO₄· n H₂O compounds, where the additional phos-

phate tetrahedron is missing and only every fourth N1 or N2 position has to be occupied.

Figure 2 shows that the Na2 atom is on the mirror plane, in the straight line between the vanadyl bond and of one edge of the additional tetrahedron. The Na2 position is close to the ideal apical positions described by Roca *et al.* (10), which are normally occupied by regular octahedrally coordinated Ni and Co atoms. The octahedron around Na2 is elongated in the direction of the vanadyl bond (O3) with 2.859(4) Å, and the angles around Na2 are twisted (e.g. O3–Na2–O6 168.7(1)°, O7–Na2–O7 103.4(8)°). Figure 4 shows the coordination polyhedra around the Na atoms viewed parallel to [100]. The Na octahedra form Na₃O₈ layers, in which edge-sharing Na2 octahedra extend in chains parallel [010]. These chains are connected by Na1 octahedra parallel [001], where each Na1 octahedron shares edges with four Na2 octahedra. As Fig. 2 displays, there are two Na₃O₈ layers between each two [VOPO₄(HPO₄)] layers. Both Na₃O₈ layers are repeated by the 2-fold screw axes extending parallel to b , which shift the layers by $\frac{1}{2}b$ relative to each other and locate each Na2 octahedron once above and once below the Na1 octahedral chains (Figs. 2 and 4).

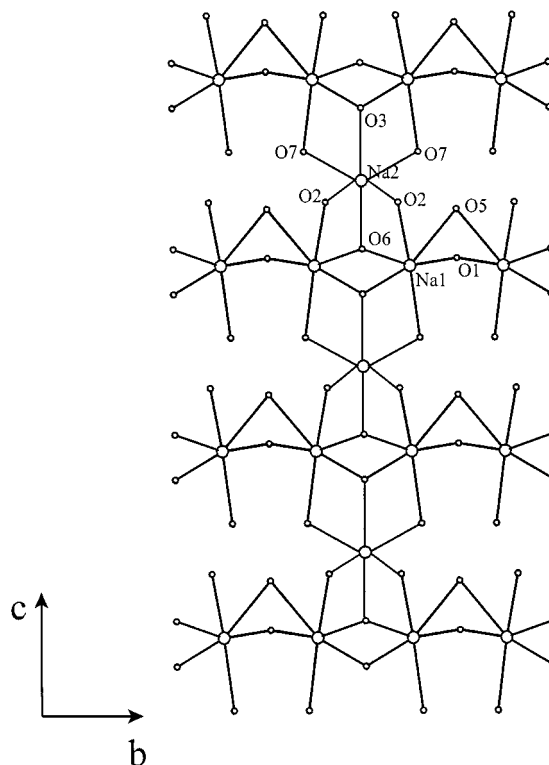


FIG. 4. One of the two interlayer (Na₃O₈)-layers parallel to (100). The Na atoms are presented as large and the O atoms as small circles. Chains of edge-sharing Na2 coordination polyhedra are extending parallel [010] and are linked by Na1 coordination octahedra in the [001] direction.

CONCLUSION

We synthesized the new phase $\text{Na}_3\text{VO}(\text{PO}_4)(\text{HPO}_4)$ examining in detail the $\text{NaOH}/\text{V}/\text{H}_3\text{PO}_4/\text{H}_2\text{O}$ systems. The crystal structure of $\text{Na}_3\text{VO}(\text{PO}_4)(\text{HPO}_4)$ contains a VOPO_4 layer which is a common fundamental building unit in many other vanadium phosphate and sulfate compounds. A symmetry tree illustrating the subgroup/supergroup relationships of all compounds containing this type of VOXO_4 layers ($X = \text{P}, \text{S}$) shows that we can derive all space groups of these different compounds by removing successively the symmetry elements from space group $I4/mmm$ of the aristotype down to Pn , $Pc2_1n$, and $P1$.

ACKNOWLEDGMENTS

We thank the anonymous reviewers for their comments and M. Cooper for discussions. The experimental part of this work was performed at the University of Frankfurt.

REFERENCES

- G. Jander and K. F. Jahr, *Z. Anorg. Chem.* **212**, 1 (1933).
- S. J. Kiehl and E. J. Manfredo, *J. Am. Chem. Soc.* **59**, 2118 (1937).
- H. Menzel and G. Müller, *Z. Anorg. Allg. Chem.* **272**, 6 (1953).
- M. Lelong, *Rev. Chim. Min.* **3**, 259 (1966).
- A. Müller and J. Döring, *Z. Anorg. Allg. Chem.* **595**, 251 (1991).
- H. T. Evans and R. M. Garrels, *Geochim. Cosmochim. Acta* **15**, 131 (1958).
- D. Beltrán-Porter, P. Amorós, R. Ibáñez, E. Martínez, and A. Beltrán-Porter, *Solid State Ionics* **32/33**, 57 (1989).
- M. Schindler, W. Joswig, and W. H. Baur, *Z. Anorg. Allg. Chem.* **623**, 45 (1997).
- M. Schindler, W. Joswig, and W. H. Baur, *J. Solid State Chem.* **134**, 286 (1997).
- M. Roca, M. Dolores Marcos, P. Amorós, J. Alamo, A. Beltrán-Porter, and D. Beltrán-Porter, *Inorg. Chem.* **36**, 3414 (1997).
- G. M. Sheldrick, "Crystallographic Computing Package," revision 4.1. Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
- S. R. Hall and J. M. Stewart, "XTAL3.0." Lamb Printers, Perth (1990).
- W. H. Baur and T. Ohta, *J. Solid State Chem.* **44**, 50 (1982).
- W. H. Baur and D. Kassner, *Z. Kristallogr. Suppl. Issue 3*, 15 (1991).
- R. X. Fischer, A. Le Lirzin, D. Kassner, and B. Rüdinger, *Z. Kristallogr. Suppl. Issue 3*, 75 (1991).
- S. L. Wang, H. Y. Kang, C. Y. Cheng, and K. H. Lii, *Inorg. Chem.* **30**, 3496 (1991).
- L. C. Torardi and J. C. Calabrese, *Inorg. Chem.* **23**, 1308 (1984).
- M. E. Leonowicz, J. W. Johnson, J. F. Brody, H. F. Shannon, and J. M. Newsam, *J. Solid State Chem.* **56**, 370 (1985).
- K. H. Lii, C. H. Lii, M. Chen, S. L. Wang, *Z. Kristallogr.* **197**, 67 (1991).
- W. H. Baur, *Acta Crystallogr.* **B30**, 1195 (1974).
- W. H. Baur, *Trans. Am. Crystallogr. Assoc.* **6**, 129 (1970).
- R. C. Haushalter, Z. Wang, M. E. Thompson, and J. Zubieta, *Inorg. Chem.* **32**, 3700 (1993).
- R. C. Haushalter, Z. Wang, M. E. Thompson, and J. Zubieta, *Inorg. Chim. Acta*, **232**, 83 (1995).
- M. I. Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta, and J. L. Dye, *Chem. Mater.* **8**, 43 (1996).
- "International Tables for Crystallography," Vol. A. Reidel, Dordrecht, 1983.
- H. Bärnighausen, *MATCH* **9**, 139 (1980).
- V. Soghomonian, R. C. Haushalter, Q. Chen, and J. Zubieta, *Inorg. Chem.* **33**, 1700 (1994).
- H. Y. Kang, W. C. Lee, S. L. Wang, and K. H. Lii, *Inorg. Chem.* **31**, 4743 (1992).
- R. C. Haushalter, V. Soghomonian, Q. Chen, and J. Zubieta, *J. Solid State Chem.* **105**, 512 (1993).
- D. Papoutsakis, J. E. Jackson, and D. G. Nocera, *Inorg. Chem.* **35**, 800 (1996).
- H. Y. Kang, W. C. Lee, S. L. Wang, and K. H. Lii, *Inorg. Chem.* **31**, 4743 (1992).
- Y. Zhang, A. Claerfeld, and R. C. Haushalter, *J. Solid State Chem.* **117**, 157 (1995).
- P. M. Tachez and F. Thébald, *Acta Crystallogr.* **B37**, 1978 (1981).
- W. T. A. Harrison, K. Hsu, and A. J. Jacobson, *Chem. Mater.* **7**, 2004 (1995).
- D. Riou and G. Férey, *Eur. J. Solid State Inorg. Chem.* **31**, 25 (1994).
- H. R. Tietze, *Aust. J. Chem.* **34**, 2035 (1981).
- B. Jordan and C. Calvo, *Can. J. Chem.* **51**, 2621 (1973).
- M. Longo and R. J. Arnott, *J. Solid State Chem.* **1**, 394 (1970).
- W. H. Baur, D. Kassner, C. H. Kim, and N. H. W. Sieber, *Eur. J. Min.* **2**, 761 (1990).
- R. Gopal and C. Calvo, *J. Solid State Chem.* **5**, 432 (1972).
- P. Kierkegaard and J. M. Longo, *Acta Chem. Scand.* **19**, 1906 (1965).