

The Hydrothermal $\text{NH}_4/\text{V}/\text{P}/\text{H}_2\text{O}$ and $\text{K}/\text{V}/\text{P}/\text{N}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$ Systems at 473 K and the Crystal Structures of NH_4VOPO_4 and $(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$

Michael Schindler,^{1,2} Werner Joswig, and Werner H. Baur³

Institut für Mineralogie, Senckenberganlage 30, D-60054 Frankfurt am Main, Germany

Received February 10, 1997; accepted July 16, 1997

An examination of the $\text{NH}_4/\text{VO}_5/\text{P}/\text{H}_2\text{O}$ system at 473 K under hydrothermal conditions yielded the $(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$ and NH_4VOPO_4 phases. The crystal structure of the first compound is isotypical with the corresponding Ti^+ and K^+ phases. The cations NH_4^+ and Ti^+ have similar coordinations against oxygen. The investigation of the crystal structure of the second compound (space group $Pn2n$) shows it to be related to other $ABOTO_4$ phases of the potassium titanil phosphate type with $A = \text{Na}^+, \text{Ag}^+, \text{NH}_4^+, \text{Rb}^+, \text{K}^+$, and Ti^+ , and $B = \text{Ti}^{4+}, \text{V}^{4+}, \text{Sn}^{4+}, \text{Fe}^{4+}, \text{Ge}^{4+}, \text{Ga}^{3+}, \text{Zr}^{4+}, \text{Sb}^{5+}$, and Nb^{5+} , and $T = \text{P}^{5+}, \text{Ge}^{4+}, \text{Si}^{4+}$, and As^{5+} , but none of them crystallize in space group $Pn2n$. In the $\text{K}/\text{V}/\text{P}/\text{N}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$ system, three different K phases were found: $\text{K}_{0.5}\text{VOPO}_4 \cdot 1.5\text{H}_2\text{O}$, KVOPO_4 , and K-FVP-1 (Frankfurt vanadium phosphate, one, or for short, FVP-1). The microporous K-FVP-1 compound was synthesized in a similar pH range as the isotypic Na-FVP-1 phase. The $\text{V}^{4+}/\text{V}^{5+}$ ratio of K-FVP-1 varies from 3.5(1)/1.5(1) to 1.6(1)/3.4(1) and the corresponding lattice constants range from 16.0013(6) to 15.7665(4) Å. © 1997 Academic Press

INTRODUCTION

Most microporous frameworks are based on variously connected coordination tetrahedra of oxygen atoms around aluminum, phosphorus, or silicon. Much of the current synthetic work is devoted to incorporating into these frameworks reactive transition elements which may show varied coordinations around the cations (1,2). In the case of vanadium, the coordination number depends on the valence of the central cations, which again is influenced by the redox potentials and the pH values during synthesis. Studies of vanadium phosphate systems (3,4) showed that the chemi-

cal and physical parameters also regulate the condensation reactions of VO_5 square-pyramidal coordinations into V_5O_9 groups.

Recently, three compounds were synthesized containing the V_5O_9 group. They have a reasonable thermal stability, re- and dehydrate reversibly, are capable of exchanging cations located in the pore space, and have the most open microporous frameworks described so far: $\text{Na}_v[(\text{V}_4^{4+}\text{V}_1^{5+})\text{O}_9](\text{PO}_4)_2 \cdot (\text{PO}_4)_x \cdot (\text{OH})_y \cdot z\text{H}_2\text{O}$ (1) (with $v = 2.8\text{--}4.0$, $w = -0.1$ to $+1.1$, $x = 0\text{--}0.2$, $y = 0\text{--}2.1$, and $z = 7\text{--}10$) (ref 3), $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}]\text{K}_{1.35}[\text{V}_5\text{O}_9(\text{PO}_4)_2] \cdot x\text{H}_2\text{O}$ (2) (ref 4), and $\text{Cs}_3[\text{V}_5\text{O}_9(\text{PO}_4)_2] \cdot x\text{H}_2\text{O}$ (3) (ref 4). Each of these V_5O_9 groups comprises five square pyramidally coordinated V atoms and is surrounded by four PO_4 groups, thus yielding a pentameric $\text{V}_5\text{O}_9(\text{PO}_4)_{4/2}$ grouping. In terms of bonding topology, the active parts of the $\text{V}_5\text{O}_9(\text{PO}_4)_{4/2}$ groups are the PO_4 tetrahedra which connect the plane square groups at their corners with each other after rotations of 60 and 90°. This kind of connection is similar to the arrangement of planar single-four-rings (S4R) in several aluminosilicate frameworks (5). In the crystal structures of 1 and 3 the S4R are arranged in the same manner as in the zeolite sodalite (αSOD type) and in framework 2 as in zeolite rho (αRHO type) (5). Structure 1 (FVP-1, for Frankfurt vanadium phosphate, one) crystallizes in space group $Im\bar{3}m$. The $\text{V}_5\text{O}_9(\text{PO}_4)_{4/2}$ groups show a variable $\text{V}^{4+}/\text{V}^{5+}$ ratio ranging from 4.1/0.9 to 2.9/2.1 and are disordered around a mirror plane. In structure 3 (space group $Fd\bar{3}m$) the V_5O_9 groups are ordered but there is no information about any variation in the observed $\text{V}^{4+}/\text{V}^{5+}$ ratio: it is reported as constant at 4:1 (4). The order/disorder of the V_5O_9 pentamers depends on the kind of exchangeable cation present (with Na^+ and K^+ disordered FVP-1 is formed and with Cs^+ and Rb^+ the ordered structure 3 is formed) (3). We are trying to understand the conditions of formation of such microporous compounds and to compare the chemistry of the monovalent cations M in the $\text{V}/\text{P}/(\text{tEA})/\text{H}_2\text{O}$ (tEA = triethylamine = $\text{N}(\text{C}_2\text{H}_5)_3$) systems. Therefore it is necessary to study

¹ To whom correspondence should be addressed.

² Current address: Department of Geological Sciences, University of Manitoba, Winnipeg, MB R3T 2N2, Canada.

³ Current address: Department of Geophysical Sciences, University of Chicago, Chicago, IL 60637.

additional related systems. We show here that even though K^+ and NH_4^+ often form isostructural compounds, their influence on the V/P/(tEA)/H₂O systems differs.

EXPERIMENTAL

Synthesis

In the K/V/P/(tEA)/H₂O system we varied the pH value from pH 2.3 to pH 9.9 and in the NH₄/V/P/H₂O system from pH 2.7 to pH 8.8. In the K-containing system we used four acid–base complexes: K₃PO₄/K₂HPO₄, K₂HPO₄/KH₂PO₄, tEA/H₃PO₄/KOH, and H₃PO₄/KOH. In the NH₄-containing system the buffer (NH₄)₃PO₄/(NH₄)₂HPO₄/(NH₄)H₂PO₄ was employed. The vanadium sources were either VOSO₄ or V₂O₅. In both systems the V:P:(tEA):H₂O ratio was held at 1:4:(3.5):700 (tEA was not used in all the syntheses). The pH values were adjusted by using either KOH or by varying the ratios of K₃PO₄/K₂HPO₄/KH₂PO₄ or (NH₄)₃PO₄/(NH₄)₂HPO₄/(NH₄)H₂PO₄. The synthesis times were varied from 2.5 to 10 days. The pH values were measured before synthesis with a WTW pH meter and should be accurate within ± 0.1 .

Chemical Analysis

Chemical analyses were carried out by inductively coupled plasma emission spectroscopy (ICP-ES). The contents of V⁴⁺ ions were analyzed by potentiometric titrations with Ce⁴⁺(SO₄)₂·4H₂O solutions. The loss of water was determined by thermogravimetry.

Data Collection

The single-crystal measurements were carried out using an Enraf Nonius diffractometer and the X-ray powder diffraction patterns using a D500 Siemens diffractometer. The XTAL package (6) was used in the refinement of the single-crystal diffraction data. The lattice constant refinements employed the Rietveld refinement computer program RERIET (7). Distances were calculated with SADIAN90 (8) and the crystal structure diagrams were produced with STRUPLO90 (9).

RESULTS

The NH₄/V/P/H₂O System

All compounds encountered in the syntheses are listed in Table 1. The examination of the NH₄/V/P/H₂O system did not yield an NH₄-FVP-1 phase. The question mark indicates a green phase which could not be identified. The compound crystallizes in very small plates with a maximum size of 20 × 10 × 10 μm. We showed by simulating a powder diagram that the unknown phase is neither the trivalent NH₄[V(HPO₄)₂] phase nor the pentavalent α-NH₄(VO₂)

TABLE 1
Survey of the Phases Appearing in the K/V/P/(tEA)/H₂O and NH₄/V/P/H₂O Systems at 473 K

System	pH value	Phase
V ₂ O ₅ /(NH ₄) ₃ PO ₄ /(NH ₄) ₂ HPO ₄ /(NH ₄) ₂ H ₂ PO ₄ /H ₂ O	4.0–5.25	(NH ₄) ₃ V ₂ O ₃ (VO)(PO ₄) ₂ (HPO ₄)
VOSO ₄ /(NH ₄) ₃ PO ₄ /(NH ₄) ₂ HPO ₄ /(NH ₄) ₂ H ₂ PO ₄ /H ₂ O	5.8–8.7	NH ₄ VOPO ₄
VOSO ₄ /(NH ₄) ₃ PO ₄ /(NH ₄) ₂ HPO ₄ /(NH ₄) ₂ H ₂ PO ₄ /H ₂ O	3.2–3.4	NH ₄ VOPO ₄ /?
VOSO ₄ /(NH ₄) ₃ PO ₄ /(NH ₄) ₂ HPO ₄ /(NH ₄) ₂ H ₂ PO ₄ /H ₂ O	4.2–8.7	NH ₄ VOPO ₄
KOH/V ₂ O ₅ /H ₃ PO ₄ /tEA/H ₂ O	2.8–4.6	K _{0.5} VOPO ₄ ·1.5H ₂ O/KVOPO ₄
KOH/V ₂ O ₅ /H ₃ PO ₄ /H ₂ O	6.1–7.2	KVOPO ₄
KOH/V ₂ O ₅ /H ₃ PO ₄ /H ₂ O	7.7–9.3	K-FVP-1
KOH/V ₂ O ₅ /H ₃ PO ₄ /H ₂ O	2.2–3.8	K _{0.5} VOPO ₄ ·1.5H ₂ O
KOH/V ₂ O ₅ /H ₃ PO ₄ /H ₂ O	5.8–6.8	KVOPO ₄
KOH/V ₂ O ₅ /H ₃ PO ₄ /H ₂ O	> 6.8	—
KOH/VOSO ₄ /H ₃ PO ₄ /tEA/H ₂ O	2.3–2.6	KVOPO ₄ /VOHPO ₄ ·0.5H ₂ O
KOH/VOSO ₄ /H ₃ PO ₄ /tEA/H ₂ O	3.0–6.3	KVOPO ₄
KOH/VOSO ₄ /H ₃ PO ₄ /tEA/H ₂ O	6.9–9.9	K-FVP-1
KOH/VOSO ₄ /H ₃ PO ₄ /H ₂ O	1.8–2.6	KVOPO ₄ /VOHPO ₄ ·0.5H ₂ O
KOH/VOSO ₄ /H ₃ PO ₄ /H ₂ O	4.6–7.2	KVOPO ₄
KOH/VOSO ₄ /H ₃ PO ₄ /H ₂ O	7.4–7.9	KVOPO ₄ /K-FVP-1
KOH/VOSO ₄ /H ₃ PO ₄ /H ₂ O	> 7.9	—
(VOSO ₄ /KH ₂ PO ₄ /K ₂ HPO ₄ /K ₃ PO ₄)	2.7–7.3	KVOPO ₄
(VOSO ₄ /KH ₂ PO ₄ /K ₂ HPO ₄ /K ₃ PO ₄)	7.4–7.9	KVOPO ₄ /K-FVP-1
(VOSO ₄ /KH ₂ PO ₄ /K ₂ HPO ₄ /K ₃ PO ₄)	7.9–8.8	K-FVP-1

(HPO₄) phase, which can be also synthesized under hydrothermal conditions (10, 11).

The (NH₄)₃V₂O₃(VO)(PO₄)₂(HPO₄) Phase

The phase occurs only in the acidic pH range using V₂O₅ as the source of vanadium. The compound crystallizes as large brown plates up to 1 mm in their longest dimension and they show a pronounced pleochroism.

(NH₄)₃V₂O₃(VO)(PO₄)₂(HPO₄) is isostructural with Tl₃V₂O₃(VO)(PO₄)₂(HPO₄) (12) and K₃V₂O₃(VO)(PO₄)₂(HPO₄) (13). Table 2 lists the crystal data and data collection parameters, Table 3 the positional parameters and displacement factors, and Table 4 bond distances and angles. In (NH₄)₃V₂O₃(VO)(PO₄)₂(HPO₄) there are two differently coordinated vanadium atoms. Atom V2 is surrounded by six oxygen atoms in a distorted octahedral coordination while V1 is 5-coordinated by oxygen in the shape of a tetragonal square pyramid. The V2 octahedra are arranged in VO(PO₄)₂ chains parallel to [100] with alternating short and long bonds: –V=O–V=O–V (Fig. 1). The bond valence sum calculations (12, 13) indicated that V2 is tetravalent, while V1 has an average valence of 4.5.

Two V1 pyramids and one phosphate tetrahedron form a dimeric V₂O₃(PO₄) unit located on a mirror plane. The phosphate group of this dimer is even more disordered than it is in the Tl and K analogs. We refined three statistically occupied phosphorus atom positions with population factors of 0.45 for P2, 0.15 for P2a, and 0.4 for P2b. The sum of the population factors of these three phosphorus atom positions was constrained to 1.0, because the distances between

TABLE 2
Crystal Data, Diffraction Data Collection Parameters, and *R* Values for NH_4VOPO_4 and $(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$

	NH_4VOPO_4	$(\text{NH}_4)_3\text{V}_2\text{O}_3\text{VO}(\text{PO}_4)_2(\text{HPO}_4)$
Space group	<i>Pn</i> 2 <i>n</i> (No. 34)	<i>Pnma</i> (No. 62)
Cell parameters	<i>a</i> = 12.916(2) Å <i>b</i> = 6.4561(7) Å <i>c</i> = 10.491(1) Å	<i>a</i> = 7.143(2) Å <i>b</i> = 13.446(2) Å <i>c</i> = 14.458(2) Å
United cell refined from	25 reflections ($\theta = 1\text{--}20^\circ$)	25 reflections ($\theta = 1\text{--}20^\circ$)
Volume	874.9 Å ³	1388.6 Å ³
Formula weight	163.952 g/mol	443.852 g/mol
Crystal size	(200 × 375 × 50) μm	(200 × 200 × 100) μm
Scan mode	ω scan	ω scan
Scan width	1.2–1.4°	1.2–1.4°
Scan time	Max 300 s	Max 300 s
Wavelength (graphite monochromator)	MoK α = 0.71069 Å	MoK α = 0.71069 Å
Absorption factor	24.8 cm ⁻¹	15.1 cm ⁻¹
Measured <i>hkl</i>	3245	2776
Unique <i>F</i> _{obs}	837	1276
> 3 σ	837	1249
< 3 σ	0	27
Range of measured <i>hkl</i>	2.5–25° θ	2.0–25° θ
Maximal sin θ/λ	0.594 Å ⁻¹	0.594 Å ⁻¹
Range of		
<i>h</i>	0–15	– 17 to + 17
<i>k</i>	– 8 to + 8	0–8
<i>l</i>	– 12 to + 12	0–15
<i>R</i> (= $\sum IF_o - F_c I / \sum IF_c I$)	0.037	0.054
<i>R</i> _w (= $\sum [w(IF_o I - IF_c I)^2 / \sum w IF_c I^2]^{1/2}$)	0.038	0.061

them range from 0.24 to 0.70 Å and they obviously correspond to three disordered locations of one site. The *z* coordinate of the P2a position was restrained to *z* = 0.25. The oxygen atom O8 is part of the disordered phosphate tetra-

TABLE 3
Atomic Coordinates, Equivalent Isotropic Displacement Factors (*U*[*equi*]), and Wyckoff Positions (*Wy*) with Symmetry (*Sy*) for $(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> [<i>equi</i>]	<i>Wy</i>	<i>Sy</i>
V1	0.1559(2)	0.12332(7)	0.92432(7)	0.0151(5)	8 <i>d</i>	1
V2	0.7445(2)	$\frac{1}{4}$	0.25854(9)	0.0097(7)	4 <i>c</i>	<i>m</i>
P1	0.4619(2)	0.1003(1)	0.3805(1)	0.0114(7)	8 <i>d</i>	1
P2	0.236(1)	$\frac{3}{4}$	0.2374(3)	0.002(2)	4 <i>c</i>	<i>m</i>
P2a	0.215(4)	$\frac{3}{4}$	0.25	0.02(1)	4 <i>c</i>	<i>m</i>
P2b	0.1525(8)	$\frac{3}{4}$	0.2622(3)	0.003(1)	4 <i>c</i>	<i>m</i>
O1	0.9543(8)	$\frac{1}{4}$	0.3002(4)	0.016(3)	4 <i>c</i>	<i>m</i>
O2	0.7829(6)	0.1447(6)	0.1634(3)	0.018(2)	8 <i>d</i>	1
O3	0.6381(6)	0.1459(3)	0.3376(3)	0.017(2)	8 <i>d</i>	1
O4	0.4544(6)	0.1196(3)	0.4858(3)	0.017(2)	8 <i>d</i>	1
O5	0.0284(6)	0.0123(3)	0.8599(3)	0.019(2)	8 <i>d</i>	1
O6	0.3218(7)	0.0651(3)	0.9730(3)	0.025(2)	8 <i>d</i>	1
O7	0.2156(9)	$\frac{1}{4}$	0.9573(4)	0.018(3)	4 <i>c</i>	<i>m</i>
O8	0.951(2)	$\frac{3}{4}$	0.3162(8)	0.022(7)	4 <i>c</i>	<i>m</i>
O9	0.401(1)	$\frac{1}{4}$	0.6576(5)	0.034(4)	4 <i>c</i>	<i>m</i>
O10	0.2621(7)	0.1505(3)	0.7985(3)	0.027(3)	8 <i>d</i>	1
N1	0.584(1)	0.0014(4)	0.8348(4)	0.031(5)	8 <i>d</i>	1
N2	0.121(1)	$\frac{1}{4}$	0.4974(6)	0.031(5)	4 <i>c</i>	<i>m</i>

hedron. We could find only a fraction of this fourth oxygen atom position in the difference Fourier synthesis, which we refined with an occupation factor of one-half. Both units, the dimer $\text{V}_2\text{O}_3(\text{PO}_4)$ and the $\text{VO}(\text{PO}_4)_2$ chain, are connected to each other via oxygen atoms O4 and O5, thus yielding a three-dimensional framework (Fig. 1).

The NH_4VOPO_4 Phase

This phase was originally described in the standard setting *Pnn*2 of that space group (14). We chose the nonstandard setting *Pn*2*n* for a simpler comparison with the related *ABOTO*₄ compounds with *A* = Na⁺, Ag⁺, NH₄⁺, Rb⁺,

TABLE 4
Selected Bond Distances [Å] of $(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$

V1–O6	1.585(5)	V2–O1	1.615(6)	P2–P2a	0.24(1)
V1–O7	1.820(2)	V2–O3 (2 ×)	1.960(4)	P2–P2b	0.696(8)
V1–O4	1.939(5)	V2–O2 (2 ×)	1.993(4)	P2–O9	1.513(9)
V1–O5	1.981(4)	V2–O1	2.240(6)	P2–O10 (2 ×)	1.603(5)
V1–O10	2.045(5)			P2–O8	1.72(1)
V1–O9	2.760(6)			P1–O3	1.531(5)
P2a–P2b	0.48(3)			P1–O4	1.545(5)
P2a–O10 (2 ×)	1.519(5)	P2b–O9	1.56(1)	P1–O5	1.544(4)
P2a–O9	1.57(1)	P2b–O10 (2 ×)	1.561(5)	P1–O2	1.547(5)
P2a–O8	1.94(2)	P2b–O8 (2 ×)	1.64(1)		

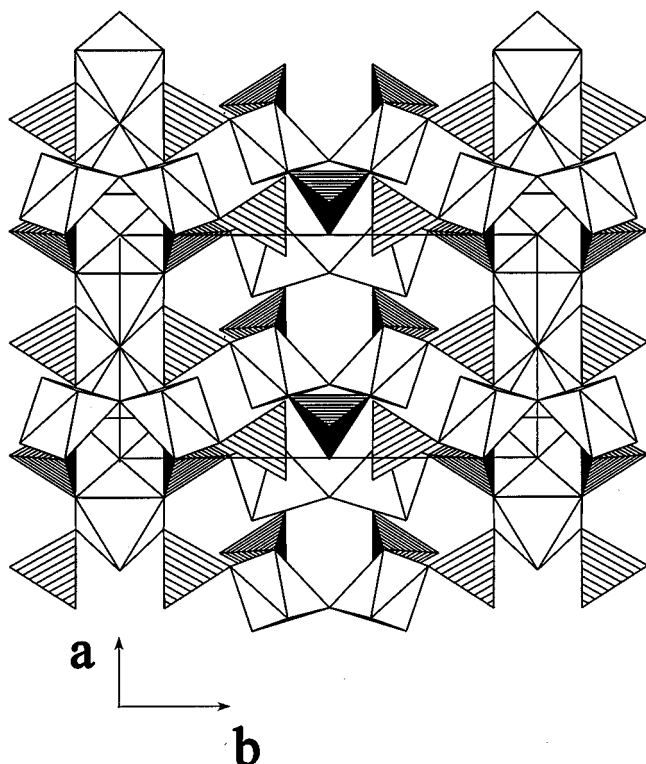


FIG. 1. View of the V=O–V=O–V chains and the V₂O₃ dimers in the *ab* plane of the crystal structure of (NH₄)₃V₂O₃(VO)(PO₄)₂(HPO₄).

K⁺, and Ti⁺, B = Ti⁴⁺, V⁴⁺, Sn⁴⁺, Fe³⁺, Ge⁴⁺, Ga³⁺, Zr⁴⁺, Sb⁵⁺, and Nb⁵⁺, and T = P⁵⁺, As⁵⁺, Si⁴⁺, and Ge⁴⁺ of the potassium titanil phosphate (or KTP) type with nonlinear optical properties (15, 16). Other AVOPO₄ or A(VOPO₄)₂ compounds with A = Na⁺, α-Li⁺, β-Li⁺, Rb⁺, and Cs⁺ (17–21) or Ca²⁺ and Ba²⁺ (22, 23) are not based on the same structure type. The brown crystals occur as hexagonal prisms, with maximum dimensions of 0.5 × 0.5 × 0.5 mm. The X-ray diffraction data show that *0kl* diffractions occur only with *k + l = 2n*, while the *hk0* diffractions occur only with *h + k = 2n*. Thus the presence of both *n* glide planes is established. On the other hand, systematic extinctions necessary to prove the presence of an *a* glide are absent. Thus space group *Pna2*₁ can be ruled out. The experimental data are listed in Table 2, positional parameters and displacement factors in Table 5, and bond distances and angles in Table 6.

The K/V/P/(tEA)/H₂O System

The K-FVP-1 phase was synthesized in a similar pH range as the isotypic Na-FVP-1 phase. We could not find other hydrothermal K phases such as K₂(VO)₃(HPO₄)₄, K₃(VO)(V₂O₃)(PO₄)₂(HPO₄), or K₃(VO)(HV₂O₃)(PO₄)₂(HPO₄) (13, 24) which were synthesized at 513 and 503 K, respectively. This shows how much phase stabilities can

TABLE 5
Atomic Coordinates, Equivalent Isotropic Displacement Factors (*U*[*equi*]), and Wyckoff Positions (*Wy*) with Symmetry (*Sy*) for NH₄VOPO₄

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> [<i>equi</i>]	<i>Wy</i>	<i>Sy</i>
V1	0.12469(8)	0.75	0.2402(1)	0.0082(5)	4 <i>c</i>	1
V2	0.2484(2)	0.9798(5)	0.4947(1)	0.0078(5)	4 <i>c</i>	1
P1	½	0.4223(8)	0	0.009(2)	2 <i>b</i>	2
P2	0.1819(1)	0.2572(6)	0.2590(2)	0.0084(8)	4 <i>c</i>	1
P3	0	0.5816(8)	0	0.008(2)	2 <i>b</i>	2
O1	0.1112(5)	0.445(1)	0.2855(6)	0.012(3)	4 <i>c</i>	1
O2	0.2570(6)	0.310(1)	0.1484(5)	0.011(3)	4 <i>c</i>	1
O3	0.1168(6)	0.066(1)	0.2248(6)	0.012(3)	4 <i>c</i>	1
O4	0.2513(6)	0.214(1)	0.3767(6)	0.012(3)	4 <i>c</i>	1
O5	0.5191(5)	0.284(1)	0.1163(5)	0.014(4)	4 <i>c</i>	1
O6	0.4010(6)	0.560(1)	0.0246(6)	0.013(3)	4 <i>c</i>	1
O7	0.0137(5)	0.724(1)	0.1184(5)	0.016(4)	4 <i>c</i>	1
O8	0.2198(5)	0.712(1)	0.1396(5)	0.011(3)	4 <i>c</i>	1
O9	0.2231(5)	0.801(1)	0.3902(5)	0.012(3)	4 <i>c</i>	1
O10	0.4038(5)	0.948(1)	0.4850(5)	0.012(2)	4 <i>c</i>	1
N1	0.3879(7)	0.976(1)	0.0767(9)	0.036(5)	4 <i>c</i>	1
N2	0.0948(6)	0.0730(1)	0.8284(8)	0.024(5)	4 <i>c</i>	1

change under hydrothermal conditions when the temperature varies by only 30 or 40 K.

The VOHPO₄ · 0.5H₂O Phase

The well-known VOHPO₄ · 0.5H₂O phase (25) was synthesized at low KOH contents and the crystals exhibit in some of the samples an unusual green color.

The K_{0.5}VOPO₄ · 1.5H₂O Phase

The mixed valence phase was prepared in the K/V/P/H₂O system with V₂O₅ as a source of vanadium and a

TABLE 6
Selected Bond Distances [Å] of NH₄VOPO₄

V1–O8	1.637(6)	V2–O9	1.624(6)	P1–O5 (2 ×)	1.531(6)
V1–O7	1.926(6)	V2–O2	1.950(6)	P1–O6 (2 ×)	1.578(8)
V1–O1	2.032(6)	V2–O4	1.954(7)		
V1–O5	2.042(6)	V2–O10	2.019(7)	P3–O10 (2 ×)	1.520(7)
V1–O3	2.048(7)	V2–O6	2.021(8)	P3–O7 (2 ×)	1.555(7)
V1–O9	2.049(6)	V2–O8	2.173(6)		
P2–O3	1.535(8)	N1–O5	2.64(1)	N2–O7	2.710(9)
P2–O1	1.542(7)	N1–O6	2.745(9)	N2–O3	2.79(1)
P2–O2	1.549(7)	N1–O8	2.84(1)	N2–O9	2.85(1)
P2–O4	1.550(7)	N1–O2	2.84(1)	N2–O10	2.924(9)
		N1–O1	3.06(1)	N2–O4	3.09(1)
		N1–O5	3.08(1)	N2–O2	3.18(1)
		N1–O9	3.21(1)	N2–O6	3.19(1)
		N1–O1	3.23(1)	N2–O8	3.23(1)
		N1–O4	3.24(1)	N2–O5	3.25(1)

low KOH content. The green crystals were synthesized with and without the presence of the reduction agent tEA and show the typical cleavage of a sheet structure. In the absence of tEA large crystals up to 2×2 mm in (001) could be prepared. The crystal structure contains layers of corner-sharing VO_6 octahedra and PO_4 tetrahedra (26) and is closely related to the structures of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ (27) and $A_{0.5}(\text{VO})(\text{PO}_4) \cdot 2\text{H}_2\text{O}$, with $A = \text{Na}, \text{Co}, \text{Ca}, \text{Sr}, \text{Pb}$, and Cu (26,28,29). The layered mixed-oxide hydrates $A_x\text{VOPO}_4 \cdot y\text{H}_2\text{O}$, with $A = \text{K}, \text{Na}, \text{Li}, \text{Rb}, \text{Cs}$, and $\text{N}(\text{CH}_3)_4$, were originally prepared by redox intercalation reactions of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ with iodides in aqueous solution (30).

The KVOPO_4 Phase

The KVOPO_4 phase is stable over the whole pH range. Exceptions are the syntheses with tEA or in the buffer system $\text{K}_2\text{HPO}_4/\text{K}_3\text{PO}_4$, where the K-FVP-1 phase occurs instead. The brown crystals have the same size and habit as the NH_4VOPO_4 crystals. KVOPO_4 is of the KTP structure type and was described in space group $Pna2_1$ (31, 32).

The K-FVP-1 Phase

The K-FVP-1 phase has the general formula $\text{K}_v[(\text{V}_4^{4+} + \text{V}_1^{5+} + \text{O}_9)(\text{PO}_4)](\text{PO}_4)_x(\text{OH})_y \cdot z\text{H}_2\text{O}$ (with $v = 2.48\text{--}2.55$, $w = 0.5\text{--}2.4$, $x = 0\text{--}0.06$, $y = 0\text{--}1.77$, and $z = 6.0\text{--}7.3$). The X-ray powder diffraction diagrams show the same peak distribution as the isotypic Na-FVP-1 phases. The additional Bragg peaks found for the supercells of the Rb^+ and Cs^+ phases in space group Fdm with $a \approx 32 \text{ \AA}$ do not occur here. Lattice constant refinements based on the Rietveld method of nine fully hydrated samples showed a variation of the lattice constants from 16.0013(6) to 15.7665(4) \AA . The redox titrations showed that with shorter lattice constants the corresponding $\text{V}^{4+}/\text{V}^{5+}$ ratios decreased from 3.5(1)/1.5(1) to 1.6(1):3.4(1) (Table 7). The results listed in Table 7 are representative of the compositions obtained for the stated starting chemical compositions. However, in any given run one may obtain deviations from these values.

DISCUSSION

The $\text{NH}_4/\text{V}/\text{P}/\text{H}_2\text{O}$ System

In the $\text{NH}_4/\text{V}/\text{P}/\text{H}_2\text{O}$ system we could not synthesize NH_4^+ -containing microporous materials with large pores as found in FVP-1. As far as we know, hydrothermal aluminosilicate syntheses do not yield microporous compounds containing NH_4^+ ions either.

$(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$

The isotypy of $(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$ and $\text{K}_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$ with $\text{Ti}_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$ is after $\text{K}/\text{NH}_4/\text{Rb}/\text{Tl}(\text{VO}_2)_2(\text{PO}_3\text{CH}_3)_2$ (33) and $\beta\text{-NH}_4/\text{K}/\text{Tl}/\text{Rb}(\text{VO}_2)(\text{HPO}_4)$ (12, 34) the third case in the structural chemistry of the vanadium phosphates. The substitution of NH_4^+ and K^+ ions for Ti^+ ions is generally rare, because Ti^+ has an inert lone pair of electrons, whereas the K^+ and NH_4^+ ions are approximately spherical. In all three crystal structures the oxygen atoms are more or less uniformly arranged around the cations with similar distances. The mean distances between A and the six or seven nearest oxygen atoms are 2.945 \AA for N1, 2.925 \AA for Tl1, 2.896 \AA for K1, 2.963 \AA for N2, 2.963 \AA for Tl2, and 2.908 \AA for K2 (Table 8). The lone pair of Ti^+ appears to have no stereochemical effect, and it must be assumed that it occupies a spherical orbital that lies closer to the nucleus than the orbitals occupied by the bonding electron pairs (35). Another example of the substitution $\text{NH}_4^+/\text{K}^+/\text{Ti}^+$ is the triplet $\text{TiTiOPO}_4/\text{KTiOPO}_4/\text{NH}_4\text{TiOPO}_4$ (36–38). All three crystallize in the KTP-type crystal structure in space group $Pna2_1$. However, in the crystal structure of TiTiOPO_4 the stereochemical effect of Ti^+ shows itself for the two crystallographically inequivalent Ti atoms by the four or three shorter bonds ranging from 2.67 to 2.86 \AA and the five or six $\text{Ti}\text{--}\text{O}$ distances ranging from 2.98 to 3.4 \AA .

The phosphate group around P2 has been identified previously as the HPO_4 group (12, 13). Its dimensions, however, do not fit the expected size of an acid phosphate tetrahedron, which should have three short $\text{P}\text{--}\text{O}$ distances of 1.522 \AA and a longer one of 1.590 \AA (37). This is due to the threefold disorder of the P2 atom itself and to the fact that the acid group OH either has a very high thermal motion

TABLE 7
Survey of Selected Syntheses with Chemical Composition, $\text{V}^{4+}/\text{V}^{5+}$ Ratios, and Lattice Constants of K-FVP-1

	Syntheses	pH	V/P	K/P	H_2O (wt %)	$\text{V}^{4+}/\text{V}^{5+}$	Lattice constant a (\AA)
I,	$\text{VOSO}_4:\text{K}_2\text{HPO}_4:\text{K}_3\text{PO}_4:\text{H}_2\text{O} = 1:2.5:1.5:700$, 473 K, 4 days	7.6	2.43	1.24	13	1.6(1)/3.4(1)	15.7665(4)
II,	$\text{V}_2\text{O}_5:\text{H}_3\text{PO}_4:\text{tEA}:\text{KOH}:\text{H}_2\text{O} = 1:8:3.5:16:700$, 473 K, 4 days	7.7	2.50	1.24	16	3.0(1)/2.0(1)	15.9893(3)
III,	$\text{V}_2\text{O}_5:\text{H}_3\text{PO}_4:\text{tEA}:\text{KOH}:\text{H}_2\text{O} = 1:8:3.5:18:700$, 473 K, 4 days	9.3	2.5	1.25	16	3.5(1)/1.5(1)	16.0013(6)

TABLE 8
Comparison of Ti–O, NH₄–O, and K–O Bond Lengths (Å) in Ti₃V₂O₃(VO)(PO₄)₂(HPO₄), (NH₄)₃V₂O₃(VO)(PO₄)₂(HPO₄), and K₃V₂O₃(VO)(PO₄)₂(HPO₄)

	A				A		
	NH ₄	Tl	K		NH ₄	Tl	K
A1–O3	2.804(8)	2.805(9)	2.723(6)	A2–O8	2.74(1)	2.81(1)	2.79(1)
A1–O5	2.847(7)	2.896(9)	2.807(5)	A2–O2 (2 ×)	2.957(9)	2.920(9)	2.834(5)
A1–O6	2.869(8)	2.89(1)	2.809(5)	A2–O4 (2 ×)	2.962(7)	2.928(9)	2.897(5)
A1–O6	2.995(7)	3.00(1)	3.015(5)	A2–O7	2.969(6)	3.01(1)	2.854(8)
A1–O10	3.058(8)	2.919(9)	2.943(5)	A2–O9	3.06(1)	3.10(1)	3.132(8)
A1–O10	3.095(8)	3.07(1)	2.958(6)	A2–O1	3.09(1)	3.02(1)	2.941(6)
A1–O5	3.198(8)	2.896(9)	3.019(5)	A2–O6	3.306(7)	3.377(9)	3.228(5)
A1–O2	3.275(8)	3.360(9)	3.308(5)				
A1–O8	3.362(7)	3.193(3)	3.222(3)				

(12, 13) or, as we observe in our ammonium compound, is heavily underpopulated. Even though the precision of locating the oxygen atoms in an ammonium compound is slightly higher than it is in the corresponding Tl and K compounds, it is still insufficient to disentangle the actual facts around atom P2.

The NH₄VOPO₄ and KVOPO₄ Phases

A detailed description of the different environments of the cations in the NH₄VOPO₄ and KVOPO₄ crystal structures was given in ref. 14. A thorough review of the ABOTO₄ phases of the KTP type as nonlinear optical materials and their synthesis, their chemical variation, and other physical properties was provided by Stucky *et al.* (15).

All frameworks of the KTP type can be described as intersecting tunnel structures related to the hexagonal tungsten bronzes (HTB) (31). The structures can be seen as composed of infinite BO₃ zigzag chains (where B are the octahedrally six-coordinated cations) along [011] (HTB chains) and connected by phosphate tetrahedra. The octahedra are alternately *cis* and *trans* linked. When a 4 + 1 + 1 coordination is present, as is the case for V⁴⁺ and Ti⁴⁺ environments, where one shorter and one longer bond alternate between the octahedra, the symmetries of the frameworks have to be noncentrosymmetric (space group *Pna2*₁ or *Pn2n*). In space group *Pna2*₁ neighboring BO₃ chains are related by two-fold rotational symmetry axes; thus all short V–O or Ti–O bonds point in the same direction (Fig. 2). In space group *Pn2n* neighboring VO₃ chains are repeated by two-fold axes normal to the chain direction thus the short V–O bonds point in different directions.

However, all crystal structures of ferroelectric KTP-type compounds, determined at room temperature and at higher temperatures, show space group symmetry *Pna2*₁. This includes also the crystal structures containing as the B atom Sb⁵⁺, Fe³⁺, Sn⁴⁺, or Ge⁴⁺ (40–43). Their octahedra are

less distorted than the [TiO₆]⁸⁻ or [VO₆]⁸⁻ octahedra. We can calculate the deviations of the framework from centrosymmetry by using the coordinates observed in space group *Pna2*₁ for calculating the interatomic distances of all framework atom positions in the symmetry of space group *Pnan*. These deviations are clearly larger than their standard deviations (σ) of ca. 0.01 Å. They measure for KGeOPO₄ 0.09/0.15 Å, KFeFPO₄ 0.13/0.19 Å (F instead of O), KSnOPO₄ 0.08/0.16 Å, and KSbOSiO₄ 0.13/0.22 Å (the first figure is the mean deviation of all the framework atoms from centrosymmetry, and the second figure gives the maximal deviation). For example, for KTP the corresponding values are twice as large (0.31/0.39 Å). The more distorted [TiO₆]⁸⁻ or [VO₆]⁸⁻ octahedra cause a more pronounced deviation of the framework from centrosymmetry.

The crystal structures of ASbOSiO₄ (A = Na⁺, K⁺) and ASbOGeO₄ (A = K⁺, Rb⁺) (16) were determined above the ferroelectric phase transition temperature *T*_c in space group *Pnan*. These transitions are characterized by large displacements of the cations Na⁺ and K⁺ in contrast to the aforementioned small deviations of the framework atoms from space group symmetry *Pnan*. KTP-type compounds with highly distorted octahedra such as [TiO₆]⁸⁻ show at the ferroelectric phase transition a 4 + 2 coordination, with two shorter bonds in *cis/trans* positions of the HTB chains (Fig. 2). This arrangement is also of space group symmetry *Pnan* and was reported for the high-temperature phase of TlTiOPO₄ (44) at 923 K. A smaller distortion of the coordination octahedron around Ti at higher temperatures and thus a trend toward space group *Pnan* are also reported for the compounds KTiOAsO₄ and Cs_{0.6}K_{0.4}TiOAsO₄ (45). The symmetries of the noncentrosymmetric space groups *Pna2*₁ and *Pn2n* are obtained from *Pnan* by a translationengleich reduction of symmetry of index 2 (Fig. 2) (46, 47).

We redetermined the crystal structure of NH₄VOPO₄ because it is the only one of all the KTP-type compounds crystallizing in space group *Pn2n*. This is a surprising result

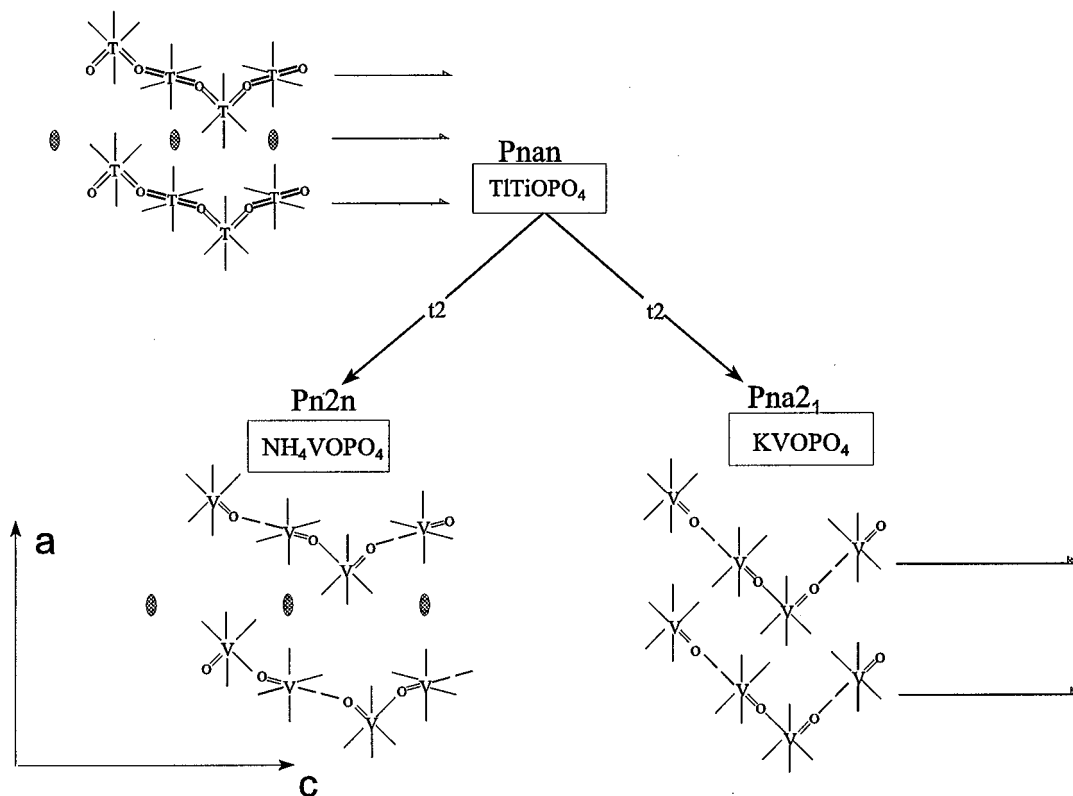


FIG. 2. KTP-type phases: lowering of the symmetry of the high-temperature TITiOPO_4 (30) phase with a 4 + 2 coordination around B to the two possible orientations of the 4 + 1 + 1 coordinations at room temperature. Shorter bonds in the distorted vanadium and titanium coordination octahedra of the schematically illustrated HTB chains are indicated as $\text{V}=\text{O}$ and $\text{T}=\text{O}$, respectively. In the NH_4VOPO_4 and KVOPO_4 structures $\text{V}(2)$ (in *trans* position) is in 4 + 1 + 1 coordination, while $\text{V}(1)$ (in *cis* position) shows approximately 5 + 1 coordination.

in view of the fact that all other KTP-type frameworks with $B = \text{V}$ or Ti , including reportedly even $\text{NH}_4\text{TiOPO}_4$ (38), crystallize at 293 K in space group $Pna2_1$. It might be worthwhile to recheck the space group of the latter compound.

The K-FVP-1 Phase

The synthesis of FVP-1 and the role of the tEA molecule during synthesis were discussed in ref. 3. The shrinking of the lattice constant from $a = 16.0013(6) \text{ \AA}$ with a $\text{V}^{4+}/\text{V}^{5+}$ ratio of 3.5(1)/1.5(1) (I) to $a = 15.7665(4) \text{ \AA}$ with $\text{V}^{4+}/\text{V}^{5+} = 1.6(1)/3.4(1)$ (II) (Table 7) could be caused by the shorter average basal $\text{V}^{5+}-\text{O}$ bond (1.880 \AA) in contrast to $\text{V}^{4+}-\text{O}$ (1.980 \AA) (3). This shrinking agrees very well with the results of a distance least-squares refinement (3) for a theoretical $\text{V}^{4+}/\text{V}^{5+}$ ratio of 0:5, yielding a unit cell constant a of 15.617 \AA . The chemical analyses show for I a K/P ratio of 1.25/1 and for II a K/P ratio of 1.24/1 (Table 7); thus there are 2.5 K^+ ions per V_5O_9 group. If we do not consider hydroxide ions, sample I is neutral and sample II has 1.77 positive charges. We assume that a minimum content of 2.5 cations per V_5O_9 group is present,

which would have to be balanced by a replacement of water molecules by hydroxide ions.

CONCLUSION

The appearance of the mixed-valence $\text{V}^{4+}/\text{V}^{5+}$ phases $(\text{NH}_4)_3\text{V}_2\text{O}_3(\text{VO})(\text{PO}_4)_2(\text{HPO}_4)$ and $\text{K}_{0.5}\text{VOPO}_4 \cdot 1.5\text{H}_2\text{O}$ at low pH values shows that other parameters such as the K^+ content have a strong influence on the crystallization. Normally one would expect in the acidic pH range phases without pentavalent vanadium. In the $\text{NH}_4/\text{V}/\text{P}/\text{H}_2\text{O}$ system the condensation of the VO_5 pyramids to larger units such as the pentameric V_5O_9 groups is not observed the way it is in similar systems containing Na, K, Rb, or Cs. The synthesis of a K-FVP-1 phase with only 1.6 V^{4+} per V_5O_9 pentamer shows that, given the proper conditions, it might even be possible to synthesize FVP-1 samples without any V^{4+} .

ACKNOWLEDGMENTS

We thank D. Büdel for the thermogravimetric measurements, J. Kühnel for the XRF analyses, and J. Kornatowski and H. Kollmann for discussions.

REFERENCES

1. J. Kornatowski, B. Wichterlova, M. Rozwadowski, and W. H. Baur, "Proceedings of the 10th IZC, Garmisch-Partenkirchen, 1994" (J. Weitkam *et al.*, Eds.). Elsevier, Amsterdam, 1994. *Stud. Surf. Sci. Catal.* **84**, 117 (1994).
2. J. Kornatowski, M. Sychev, S. Kuzenkov, K. Strnadova, W. Pilz, D. Kassner, G. Pieper, and W. H. Baur, *J. Chem. Soc., Faraday Trans.* **91**, 2217 (1995).
3. M. Schindler, W. Joswig, and W. H. Baur, *Z. Anorg. Allg. Chem.* **623**, 45 (1997).
4. M. I. Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta, and J. L. Dye, *Chem. Mater.* **8**, 43 (1996).
5. M. Schindler and W. H. Baur, *Angew. Chem.* **109**(1), 88 (1997).
6. S. R. Hall and J. M. Stewart, "XTAL3.0," Lamb Printers, Perth, 1990.
7. D. Kassner, "RERIET," University of Frankfurt, Frankfurt, Germany.
8. W. H. Baur and D. Kassner, *Z. Kristallogr. (Suppl. Issue 3)*, 15 (1991).
9. R. X. Fischer, A. Le Lirzin, D. Kassner, and B. Rüdinger, *Z. Kristallogr. (Suppl. Issue 3)*, 75 (1991).
10. R. C. Haushalter, Z. Wang, M. E. Thompson, and J. Zubieta, *Inorg. Chim. Acta* **232**, 82 (1995).
11. P. Amoros and A. Le Bail, *J. Solid State Chem.* **97**, 283 (1992).
12. G. Huan, J. W. Johnson, A. J. Jacobsen, E. W. Corcoran, Jr., and D. P. Goshorn, *J. Solid State Chem.* **93**, 514 (1991).
13. J. T. Vaughey, W. T. A. Harrison, and A. J. Jacobsen, *J. Solid State Chem.* **110**, 305 (1994).
14. R. C. Haushalter, Q. Chen, V. Soghomonian, J. Zubieta, and C. J. O'Connor, *J. Solid State Chem.* **108**, 128 (1994).
15. G. D. Stucky, M. L. F. Philips, and T. E. Gier, *Chem. Mater.* **1**(5), 492 (1989).
16. J. F. Favard, A. Verbaere, Y. Piffard, and M. Tournoux, *Eur. J. Solid State Inorg. Chem.* **31**(11), 995 (1994).
17. K. H. Lii, C. H. Li, T. M. Chen, and S. L. Wang, *Z. Kristallogr.* **197**, 67 (1991).
18. L. Benhamada, A. Grandin, M. M. Borel, A. Leclaire, and B. Raveau, *C. R. Acad. Sci. Paris II* **314**, 585 (1992).
19. A. V. Lavrov, V. P. Nikolaev, G. G. Sadiikov, and M. A. Porai-Koshits, *Sov. Phys.—Dokl. (Engl. Transl.)* **27**, 680 (1982).
20. K. H. Lii, C. H. Li, C. Y. Cheng, and S. L. Wang, *J. Solid State Chem.* **95**, 352 (1991).
21. K. H. Lii and W. C. Liu, *J. Solid State Chem.* **103**, 38 (1993).
22. K. H. Lii, B. R. Chueh, H. Y. Kang, and S. L. Wang, *J. Solid State Chem.* **99**, 72 (1992).
23. A. Grandin, J. Chardon, M. M. Borel, A. Leclaire, and B. Raveau, *J. Solid State Chem.* **99**, 297 (1992).
24. K. H. Lii and H. J. Tsai, *J. Solid State Chem.* **91**, 331 (1991).
25. L. C. Torardi and J. C. Calabrese, *Inorg. Chem.* **23**, 1308 (1984).
26. S. L. Wang, H. Y. Kang, C. Y. Cheng, and K. H. Lii, *Inorg. Chem.* **30**, 3496 (1991).
27. H. R. Tietze, *Aust. J. Chem.* **34**, 2035 (1981).
28. H. Y. Kang, W. C. Lee, S. L. Wang, and K. H. Lii, *Inorg. Chem.* **31**, 4743 (1992).
29. Y. Zhang, A. Clearfield, and R. C. Haushalter, *J. Solid State Chem.* **117**, 157 (1995).
30. J. W. Johnson and A. J. Jacobsen, *Angew. Chem.* **95**, 422 (1983).
31. L. Benhamada, A. Grandin, M. M. Borel, A. Leclaire, and B. Raveau, *Acta Crystallogr. Sect. C* **47**, 1138 (1991).
32. M. L. F. Philips, W. T. A. Harrison, T. E. Gier, G. D. Stucky, G. V. Kulkarni, and J. K. Burdett, *Inorg. Chem.* **19**, 2158 (1990).
33. W. T. A. Harrison, L. L. Dussack, and A. J. Jacobsen, *Inorg. Chem.* **35**, 1461 (1996).
34. P. Amoros, D. Beltrán-Porter, A. Le Bail, G. Férey, and G. Villeneuve, *Eur. J. Solid State Inorg. Chem.* **25**, 599 (1988).
35. R. J. Gillespie, "Molecular Geometry," Van Nostrand Reinhold Co., London, 1972.
36. W. T. A. Harrison, T. E. Gier, G. D. Stucky, and A. J. Schultz, *Mater. Res. Bull.* **30**, 1341 (1995).
37. I. Tordjman, R. Masse, and J. C. Guitel, *Z. Kristallogr.* **139**, 103 (1974).
38. M. M. Eddy, T. E. Gier, N. L. Keder, G. D. Stucky, D. E. Cox, J. D. Bierlein, and G. Jones, *Inorg. Chem.* **27**, 1856 (1988).
39. W. H. Baur, *Acta Crystallogr. Sect. B* **30**, 1195 (1974).
40. M. P. Crosnier, D. Guyomard, A. Verbaere, and Y. Piffard, *Eur. J. Solid State Inorg. Chem.* **27**, 845 (1990).
41. E. N. Matvienko, O. V. Yakubovich, M. A. Simonov, and N. V. Belov, *Dokl. Akad. Nauk SSSR* **246**, 875 (1979).
42. P. A. Thomas, A. M. Glazer, and B. E. Watts, *Acta Crystallogr. Sect. B* **46**, 333 (1990).
43. V. I. Voronkova, U. K. Yanovskii, N. I. Sorokina, I. A. Verin, and V. I. Simonov, *Crystallogr. Rep.* **38**, Issue 5 (1993).
44. W. T. A. Harrison, T. E. Gier, G. D. Stucky, and A. W. Schultz, *Chem. Commun.* 540 (1990).
45. P. A. Northrup, J. B. Parise, L. K. Cheng, L. T. Cheng, and E. M. McCarron, *Chem. Mater.* **6**, 434 (1994).
46. H. Bärnighausen, *Match* **9**, 139 (1980).
47. "International Tables for Crystallography," Vol. A. Reidel, Dordrecht, 1983.