Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Synchrotron powder study of $Na_3V(PO_3)_3N$

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Received 1 March 2013; accepted 7 May 2013

Key indicators: powder synchrotron study; T = 298 K; mean σ(P–N) = 0.007 Å; R factor = 0.091; wR factor = 0.119; data-to-parameter ratio = 8.2.

Polycrystalline trisodium vanadium(III) nitridotriphosphate, $Na_3V(PO_3)_3N$, was prepared by thermal nitridation of a mixture of $NaPO_3$ and V_2O_5. The title compound is isotypic with $Na_3Al(PO_3)_3N$. In the crystal, the P-atom and the three O-atom sites are on general positions, whereas the Na-, V- and N-atom sites are located on threefold rotation axes. The P atom is coordinated by three O atoms and one N atom in form of a slightly distorted tetrahedron. Three PO_3N tetrahedra build up a nitridotriphosphate group, $(PO_3)_3N$, by sharing a common N atom. The V atom is coordinated by six O atoms in form of a slightly distorted octahedron. The Na^+ ions occupy three crystallographically distinct sites. One Na^+ ion is situated in an irregular polyhedral coordination environment composed of six O atoms and one N atom, while the other two Na^+ cations are surrounded by six and nine O atoms, respectively.

Related literature

For structure determination of the isotypic $Na_3Al(PO_3)_3N$, see: Conanec *et al.* (1994). For the preparation of various related materials, $A_3B(PO_3)_3N$ (A = Na, K; B = Al, Ga, Cr, Mn, Fe) and $A_2B_2(PO_3)_3N$ (A = Na; B = Mg, Mn, Fe, Co), see: Conanec *et al.* (1996); Feldmann (1987*a*,*b*). For studies focused on the ionic conductivity of $Na_2Mg_2(PO_3)_3N$, see: Lee *et al.* (2012). For a review of structural features of metal nitridophosphate compounds, see: Marchand & Laurent (1991); Marchand *et al.* (2000). For bond-valence-sum calculations, see: Brese & O'Keeffe (1991). For comparison of bond lengths in related structures, see: Conanec *et al.* (1994); Jacobs & Nymwegen (1997); Lee *et al.* (2012); Shannon (1976); Zatovsky (2010).

Experimental

Crystal data

$Na_3V(PO_3)_3N$
M_r = 370.83
Cubic, $P2_13$
a = 9.44783 (5) Å
V = 843.33 (1) Å^3
Z = 4
Synchrotron radiation, λ = 1.547400 Å
T = 298 K
Flat sheet, 20 × 20 mm

Data collection

Pohang Light Source 9B HRPD Beamline diffractometer
Specimen mounting: packed powder pellet
Data collection mode: reflection
Scan method: step
$2\theta_{min}$ = 10.060°, $2\theta_{max}$ = 130.500°, $2\theta_{step}$ = 0.010°

Refinement

R_p = 0.091
R_{wp} = 0.119
R_{exp} = 0.075
R_{Bragg} = 0.056
χ^2 = 2.519
12045 data points
288 parameters

Data collection: local software at 9B HRPD beamline; cell refinement: *DICVOL* (Boultif & Louër, 2004); data reduction: local software at 9B HRPD beamline; method used to solve structure: coordinates taken from an isotypic compound; program(s) used to refine structure: *FULLPROF* (Rodriguez-Carvajal, 2001); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *FULLPROF*.

This work was supported by the National Research Foundation of Korea (grant Nos. 2009-0094046 and 2010-0013089). The authors thank Dr Do-Cheon Ahn for his help in performing the sXRD experiment at the Pohang light source.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2731).

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supporting information

Acta Cryst. (2013). E**69**, i34   [doi:10.1107/S1600536813012427]

Synchrotron powder study of $Na_3V(PO_3)_3N$

Minwoong Kim and Seung-Joo Kim

S1. Comment

There has been growing interest in the area of mixed anionic systems for exploration of new functional materials. Synthesis in the area of mixed anionic systems allows for the tuning of numerous properties, including energy storage, photocatalytic, and dielectric properties. More than two decades ago, the synthesis of several isotypic compounds with the chemical formulae of $A_3B(PO_3)_3N$ (A = Na, K; B = Al, Ga, Cr, Mn, Fe) and $A_2B_2(PO_3)_3N$ (A = Na; B = Mg, Mn, Fe, Co) by versatile nitridation reactions have been reported (Conanec *et al.*, 1996; Feldmann, 1987*a,b*; Marchand & Laurent, 1991, Marchand *et al.*, 2000) The crystal structure of $Na_3Al(PO_3)_3N$ has been determined by X-ray diffraction from a single-crystal (Conanec *et al.*, 1994). For the other compounds, however, no information except their unit cell parameters are known. In this work, we report the synthesis of the new nitridophosphate compound, $Na_3V(PO_3)_3N$, and its crystal structure refined on baisi of the Rietveld method from synchrotron powder X-ray diffraction data.

The crystal structure of $Na_3V(PO_3)_3N$ is isotypic with that of $Na_3Al(PO_3)_3N$ (Conanec *et al.*, 1994). The lattice parameter of $Na_3V(PO_3)_3N$ (a = 9.44783 (5) Å) is slighty larger than that of $Na_3Al(PO_3)_3N$ (a = 9.274 (1) Å), which is attributed to the different sizes of the V(III) and Al(III) ions. In this structure, the P and the three O atoms lie on general positions (12*b*) while the other atoms lie on special positions related to threefold rotation axes (4*a*).

The P atom is coordinated by three O atoms and one N atom to form a PO_3N tetrahedron. The $(PO_3)_3N$ entity is formed by three PO_3N tetrahedra sharing the corner occupied by the nitrogen atom (Fig. 1). The range of P—O bond lengths (1.538 (6) - 1.541 (6) Å) in $Na_3V(PO_3)_3N$ is close to that found in compositionally related compounds such as $Na_3Al(PO_3)_3N$ (~1.50 - 1.53 Å); $Na_2Mg_2(PO_3)_3N$ (~1.53 - 1.55 Å); $Na_3V_2(PO_4)_3$ (~1.52 1.54 Å) (Conanec *et al.*, 1994; Lee *et al.*, 2012; Zatovsky, 2010). The P—N bond length (1.738 (7) Å) is similar to those observed for tricoordinating nitrogen atoms in nitrido-compounds such as $K_3P_6N_{11}$ (1.71 Å) (Jacobs & Nymwegen, 1997). Na, V and N atoms are arranged along the [111] direction in the sequence of Na2—V—Na3—Na1—N—Na2—V-··· (Fig. 2). The V atom is connected to six oxygen atoms located at the vertices of PO_3N tetrahedra, forming a slightly distorted octahedron. The average V—O distance is 2.005 (11) Å which is close to the sum of the ionic radii (2.02 Å) of V^{3+} and O^{2-} (Shannon, 1976). The Na atoms occupy three crystallographically distinct sites. Na1 is coordinated to six O atoms (mean Na—O is 2.58 Å) and one N atom (Na—N is 2.947 (7) Å) to form an irregular NaO_6N polyhedron. Na2 and Na3 are 6- and 9-coordinated, respectively, within distorted polyhedra elongated along the threefold axis. The bond valence sums (Brese & O'Keeffe, 1991) calculated from the bond lengths (valence units; Na1: 0.80, Na2: 1.29, Na3: 0.96, V: 2.96, P: 4.61, O1: 1.90, O2: 1.92, O3: 1.85, N: 2.80) are close to the expected valence states of respective atoms.

S2. Experimental

An appropriate amount of $NaPO_3$ and V_2O_5 was mixed thoroughly in an agate mortar and placed in an alumina crucible. The mixture was initially heated at 523 K for 6 h. The product was reground and heated again at 973 K for 8 h and furnace-cooled to room temperature. All the heat treatments were carried out in continuous flowing anhydrous ammonia gas (flow rate = 30 ml/min) in a tube furnace. The resultant powder sample was characterized by synchrotron X-ray diffraction (sXRD). The measurement was performed on beamline 9B-HRPD at Pohang Accelerator Laboratory, Pohang, Korea. The incident X-rays were vertically collimated by a mirror, and monochromated to the wavelength of 1.5474 Å by a double-crystal Si (111) monochromator. The datasets were collected in the range of $10° \leq 2\theta \leq 130°$ with a step size of 0.01° (2θ range).

S3. Refinement

Reflections were indexed using *DICVOL* (Boultif & Louër, 2004). The cubic symmetry was obviously obtained from sXRD data. Any additional peaks were not detected. The figures of merit were $M(20) = 277.6$ (19), $F(20) = 378$ (3). Systematic absences, $h = 2n + 1$ for $h00$ observed in the intensity data, suggested the space group $P2_13$. As an initial model for the Rietveld refinements, the structural parameters of $Na_3Al(PO_3)N$ from single crystal data (Conanec *et al.*, 1994) were used. Refinements of structural parameters were carried out using the Fullprof program package (Rodriguez-Carvajal, 2001). The shape of the diffraction peaks was modelled with the Thompson-Cox-Hastings pseudo-Voigt function. A manual background correction was used in the refinements; preferred orientation and absorption effects were not considered. In the final refinement run, the following parameters were refined: zero shift, peak width/shape/asymmetry, scale factor, and crystal structure parameters (lattice parameter, atomic positions, isotropic atomic displacement parameters). The final refinement plot is shown in Fig. 3.

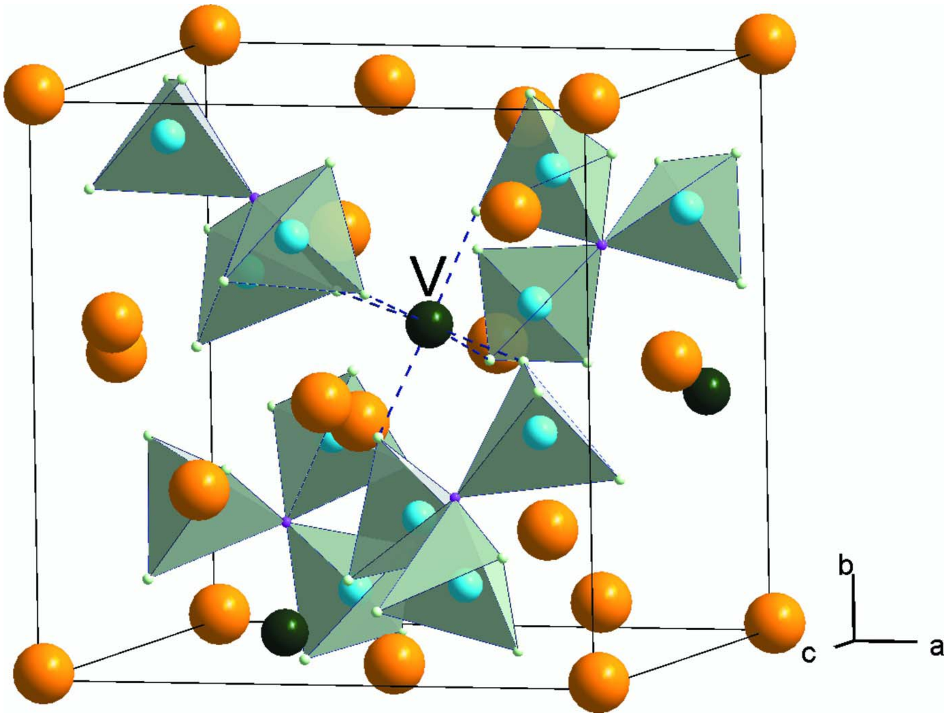

Figure 1

The crystal structure of $Na_3V(PO_3)_3N$. PO_4 tetrahedra are shown with gray shading; Na atoms are orange-colored spheres and V atoms are dark green spheres.

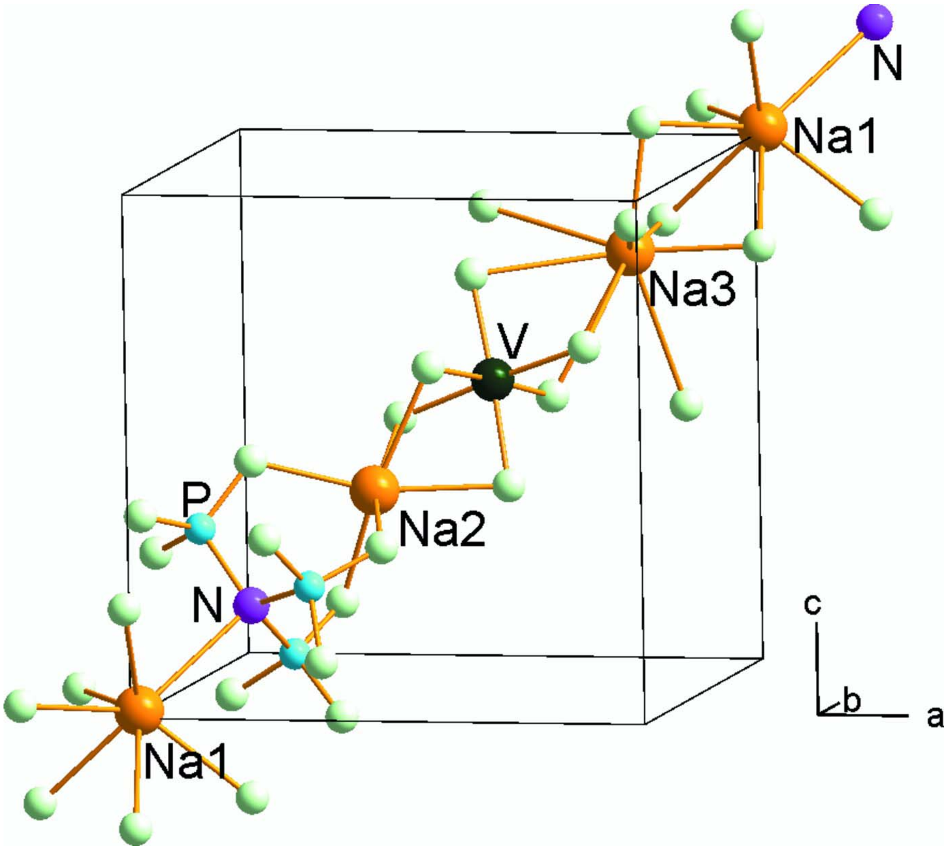

Figure 2

The local environments of Na, V and N atoms arranged along [111] in the structure of $Na_3V(PO_3)_3N$.

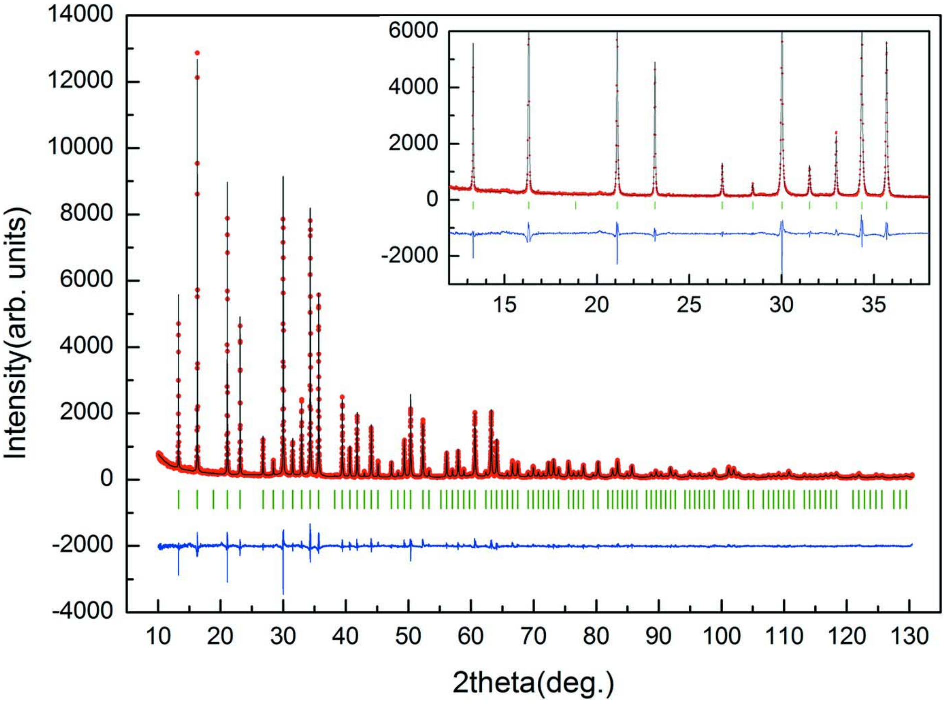

Figure 3

Rietveld refinement plot of $Na_3V(PO_3)_3N$ based on synchrotron X-ray powder diffraction data. The inset shows an enlarged section of the diffraction pattern.

Trisodium vanadium(III) nitridotriphosphate

Crystal data

$Na_3V(PO_3)_3N$
M_r = 370.83
Cubic, $P2_13$
Hall symbol: P 2ac 2ab 3
a = 9.44783 (5) Å
V = 843.33 (1) Å^3
Z = 4
D_x = 2.92 Mg m^{-3}
Synchrotron radiation, λ = 1.547400 Å
T = 298 K
Particle morphology: powder
green
flat sheet, 20 × 20 mm

Data collection

Pohang Light Source 9B HRPD Beamline diffractometer
Radiation source: synchrotron
Si 111 monochromator
Specimen mounting: packed powder pellet
Data collection mode: reflection
Scan method: step
$2\theta_{min}$ = 10.060°, $2\theta_{max}$ = 130.500°, $2\theta_{step}$ = 0.010°

Refinement

R_p = 0.091
R_{wp} = 0.119
R_{exp} = 0.075
R_{Bragg} = 0.056
χ^2 = 2.519
12045 data points
35 parameters
0 restraints
$(\Delta/\sigma)_{max}$ = 0.02

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
P1	0.3326 (3)	0.0844 (3)	0.2446 (3)	0.0143 (4)*
V1	0.08073 (17)	−0.08073 (17)	0.41927 (17)	0.0144 (6)*
Na1	0.0136 (3)	0.0136 (3)	0.0136 (3)	0.0278 (18)*
Na2	0.3913 (4)	0.3913 (4)	0.3913 (4)	0.0171 (18)*
Na3	0.6989 (5)	0.1989 (5)	0.3011 (5)	0.0310 (19)*
O1	0.2722 (6)	−0.0265 (6)	0.3479 (5)	0.0130 (14)*
O2	0.3727 (5)	0.0002 (6)	0.1109 (5)	0.0073 (15)*
O3	0.4543 (6)	0.1700 (6)	0.3106 (6)	0.0160 (18)*
N1	0.1937 (7)	0.1937 (7)	0.1937 (7)	0.012 (3)*

Geometric parameters (Å, º)

P1—O3	1.538 (6)	Na1—N1	2.947 (7)
P1—O2	1.540 (6)	Na2—O3$^{\mathrm{viii}}$	2.304 (7)
P1—O1	1.541 (6)	Na2—O3$^{\mathrm{v}}$	2.304 (7)
P1—N1	1.738 (7)	Na2—O3	2.304 (7)
V1—O1$^{\mathrm{i}}$	1.997 (6)	Na2—O2$^{\mathrm{ix}}$	2.456 (6)
V1—O1$^{\mathrm{ii}}$	1.997 (6)	Na2—O2$^{\mathrm{x}}$	2.456 (6)
V1—O1	1.997 (6)	Na2—O2$^{\mathrm{xi}}$	2.456 (6)
V1—O2$^{\mathrm{iii}}$	2.013 (5)	Na3—O3	2.329 (7)
V1—O2$^{\mathrm{iv}}$	2.013 (5)	Na3—O3$^{\mathrm{x}}$	2.329 (7)
V1—O2$^{\mathrm{v}}$	2.013 (5)	Na3—O3$^{\mathrm{xii}}$	2.329 (7)
Na1—O1$^{\mathrm{vi}}$	2.561 (6)	Na3—O1$^{\mathrm{xiii}}$	2.964 (7)
Na1—O1$^{\mathrm{vii}}$	2.561 (6)	Na3—O1$^{\mathrm{xiv}}$	2.964 (7)
Na1—O1$^{\mathrm{i}}$	2.561 (6)	Na3—O1$^{\mathrm{xi}}$	2.964 (7)
Na1—O3$^{\mathrm{vii}}$	2.604 (6)	N1—P1$^{\mathrm{viii}}$	1.738 (7)
Na1—O3$^{\mathrm{i}}$	2.604 (6)	N1—P1$^{\mathrm{v}}$	1.738 (7)
Na1—O3$^{\mathrm{vi}}$	2.604 (6)		
O3—P1—O2	114.9 (6)	O1—V1—O2$^{\mathrm{iii}}$	90.5 (4)
O3—P1—O1	112.2 (6)	O1$^{\mathrm{i}}$—V1—O2$^{\mathrm{iv}}$	92.2 (4)
O2—P1—O1	105.0 (5)	O1$^{\mathrm{ii}}$—V1—O2$^{\mathrm{iv}}$	90.5 (4)
O3—P1—N1	111.4 (6)	O1—V1—O2$^{\mathrm{iv}}$	176.8 (5)
O2—P1—N1	105.4 (6)	O2$^{\mathrm{iii}}$—V1—O2$^{\mathrm{iv}}$	86.5 (3)
O1—P1—N1	107.4 (6)	O1$^{\mathrm{i}}$—V1—O2$^{\mathrm{v}}$	90.5 (4)
O1$^{\mathrm{i}}$—V1—O1$^{\mathrm{ii}}$	90.8 (4)	O1$^{\mathrm{ii}}$—V1—O2$^{\mathrm{v}}$	176.8 (5)
O1$^{\mathrm{i}}$—V1—O1	90.8 (4)	O1—V1—O2$^{\mathrm{v}}$	92.2 (4)
O1$^{\mathrm{ii}}$—V1—O1	90.8 (4)	O2$^{\mathrm{iii}}$—V1—O2$^{\mathrm{v}}$	86.5 (3)
O1$^{\mathrm{i}}$—V1—O2$^{\mathrm{iii}}$	176.8 (5)	O2$^{\mathrm{iv}}$—V1—O2$^{\mathrm{v}}$	86.5 (3)
O1$^{\mathrm{ii}}$—V1—O2$^{\mathrm{iii}}$	92.2 (4)		

Symmetry codes: (i) −*y*, *z*−1/2, −*x*+1/2; (ii) −*z*+1/2, −*x*, *y*+1/2; (iii) −*x*+1/2, −*y*, *z*+1/2; (iv) −*z*, *x*−1/2, −*y*+1/2; (v) *y*, *z*, *x*; (vi) −*x*+1/2, −*y*, *z*−1/2; (vii) *z*−1/2, −*x*+1/2, −*y*; (viii) *z*, *x*, *y*; (ix) −*z*+1/2, −*x*+1, *y*+1/2; (x) *y*+1/2, −*z*+1/2, −*x*+1; (xi) −*x*+1, *y*+1/2, −*z*+1/2; (xii) −*z*+1, *x*−1/2, −*y*+1/2; (xiii) *y*+1, *z*, *x*; (xiv) *z*+1/2, −*x*+1/2, −*y*.