

Al_{0.5}Nb_{1.5}(PO₄)₃

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Received 9 January 2011; accepted 31 January 2011

 Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{P-O}) = 0.004$ Å; some non-H atoms missing; disorder in main residue; R factor = 0.027; wR factor = 0.064; data-to-parameter ratio = 11.2.

Single crystals of the title compound, aluminium niobium triphosphate, Al_{0.5}Nb_{1.5}(PO₄)₃, have been synthesized by a high-temperature reaction in a platinum crucible. The Al^{III} and Nb^V atoms occupy the same site on the $\bar{3}$ axis, with disorder in the ratio of 1:3. The fundamental building units of the title structure are isolated Al/NbO₆ octahedra and PO₄ tetrahedra (. 2 symmetry), which are further interlocked by corner-sharing O atoms, leading to a three-dimensional framework structure with infinite channels along the a axis.

Related literature

For related structures, see: Aatiq & Bakri, (2007); Boilot *et al.* (1987); Chakir *et al.* (2006); Hong (1976); Masquelier *et al.* (2000); Trubach *et al.* (2004); Rodrigo *et al.* (1989); Zatonvskii *et al.* (2006); Zhao *et al.* (2009). For compounds with the same structure type, see: Benmokhtar *et al.* (2007); Leclaire *et al.* (1989). For related structures, see: Brochu *et al.* (1997).

Experimental

Crystal data

Al_{0.5}Nb_{1.5}(PO₄)₃
 $M_r = 437.76$
 Trigonal, $R\bar{3}c$
 $a = 8.5679$ (6) Å
 $c = 21.898$ (2) Å
 $V = 1392.14$ (19) Å³

$Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 2.51$ mm⁻¹
 $T = 293$ K
 $0.15 \times 0.05 \times 0.05$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1997)
 $T_{\min} = 0.704$, $T_{\max} = 0.885$
 2295 measured reflections
 302 independent reflections
 298 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.064$
 $S = 1.39$
 302 reflections
 27 parameters
 $\Delta\rho_{\max} = 0.45$ e Å⁻³
 $\Delta\rho_{\min} = -0.39$ e Å⁻³

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2004); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

The authors acknowledge the Doctoral Foundation of Henan Polytechnic University (B2010–92, 648483).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2384).

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supporting information

Acta Cryst. (2011). E67, i23 [doi:10.1107/S1600536811003886]

Al_{0.5}Nb_{1.5}(PO₄)₃**Dan Zhao, Peng Liang, Ling Su, Huan Chang and Shi Yan****S1. Comment**

The mixed phosphates $AM_2(\text{PO}_4)_3$ family (A = alkali metals; M = Ti, Zr, Ge, Sn) which usually belong to the NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$; Boilot, *et al.*, 1987) or the NZP ($\text{NaZr}_2(\text{PO}_4)_3$; Hong, 1976) structure-type have been extensively investigated for the low thermal expansion behavior of some members. The crystal structure that features a flexible three-dimensional framework of PO_4 tetrahedra sharing corners with MO_6 octahedra, is amenable to a wide variety of chemical substitutions at the various crystallographic positions, thus yielding a large number of closely related compounds, such as $\text{Na}_3\text{MgZr}(\text{PO}_4)_3$ (Chakir, *et al.*, 2006), $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ (Masquelier, *et al.*, 2000), $\text{NaFeNb}(\text{PO}_4)_3$ (Zatovskii, *et al.*, 2006), $\text{NaTi}_2(\text{PO}_4)_3$ (Rodrigo, *et al.*, 1989) and $\text{NaGe}_2\text{P}_3\text{O}_{12}$ (Zhao *et al.*, 2009). The three-dimensional network consisting of PO_4 and MO_6 octahedra delimit two different types of channels in which the A atoms are usually located to compensate the negative charges. It is reported that the A atoms can completely empty in some areas, such as $\text{Fe}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ (Trubach, *et al.*, 2004) and $\text{Fe}_{0.5}\text{Sb}_{1.5}(\text{PO}_4)_3$ (Aatiq & Bakri, 2007), $\text{Nb}_2(\text{PO}_4)_3$ (Leclaire, *et al.*, 1989) and $\text{Fe}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ (Benmokhtar, *et al.*, 2007), *etc.* In order to enrich this type of compounds, we synthesis the compound $\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ by a high-temperature reaction and determine the crystal structure from single-crystal X-ray diffraction analysis.

As shown in Fig. 1, the asymmetric unit of $\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ contains a single P and Al/Nb atoms. The P atom is four coordinated by four oxygen atoms, forming isolated PO_4 tetrahedron. Al and Nb atoms are in mixed occupancy disorder locating at the $\bar{3}$ axes with the molar ratio of 1: 3, being coordinated by six oxygen atoms to form Al/NbO₆ octahedra. Al/NbO₆ octahedra and PO_4 tetrahedra are further interconnected *via* corner-sharing O atoms to form the three-dimensional framework of $\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$, as shown in Fig. 2. The Al/Nb—O bonds have two groups of different distances, that is, 1.913 (3) and 1.949 (3) Å. The PO_4 tetrahedra are regular with two groups of P—O bond distances of 1.521 (3) and 1.529 (3) Å, and O—P—O bond angles weak dispersion from 107.91 (16) to 111.3 (2)°, which is about the ideal value of 109.48°. On the other hand, this structure can be viewed as a NZP structure, in which the Na atom sites empty and the Zr atoms site are replaced by Al and Nb atoms in disordered manner on the principle of aliovalent pair combination $\text{Zr}^{4+} \rightarrow 0.25 \text{ Al}^{3+} + 0.75 \text{ Nb}^{5+}$.

S2. Experimental

The finely ground reagents K_2CO_3 , Al_2O_3 , Nb_2O_5 and $\text{NH}_4\text{H}_2\text{PO}_4$ were mixed in the molar ratio K: Al: Nb: P = 1: 3: 10: 20, were placed in a Pt crucible, and heated at 573 K for 4 h. The mixture was then re-ground and heated at 1473 K for 20 h, then cooled to 973 K at a rate of 3 K h⁻¹, and finally quenched to room temperature. A few colorless crystals of the title compound with prismatic shape were obtained.

S3. Refinement

The structure contains substitutional disorder in which Al1 and Nb1 occupy the same position. The atomic positional and anisotropic displacement parameters of Al1 and Nb1 atoms were constrained to be identical by using EADP and EXYZ constraint instructions (*SHELXL97*; Sheldrick, 2008). The ratio of Al1 and Nb1 was fixed to 1: 3 to achieve charge balance.

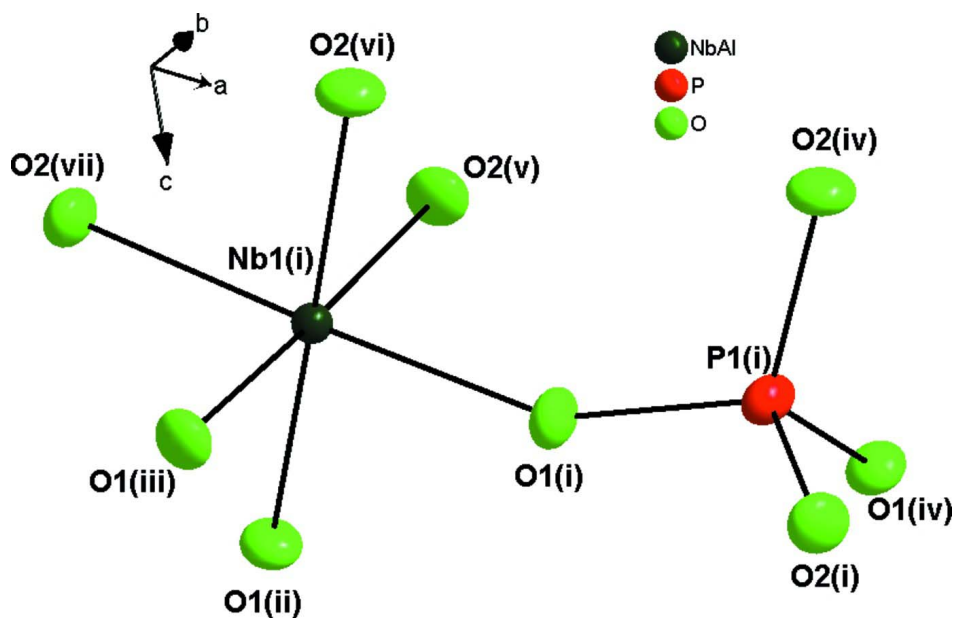
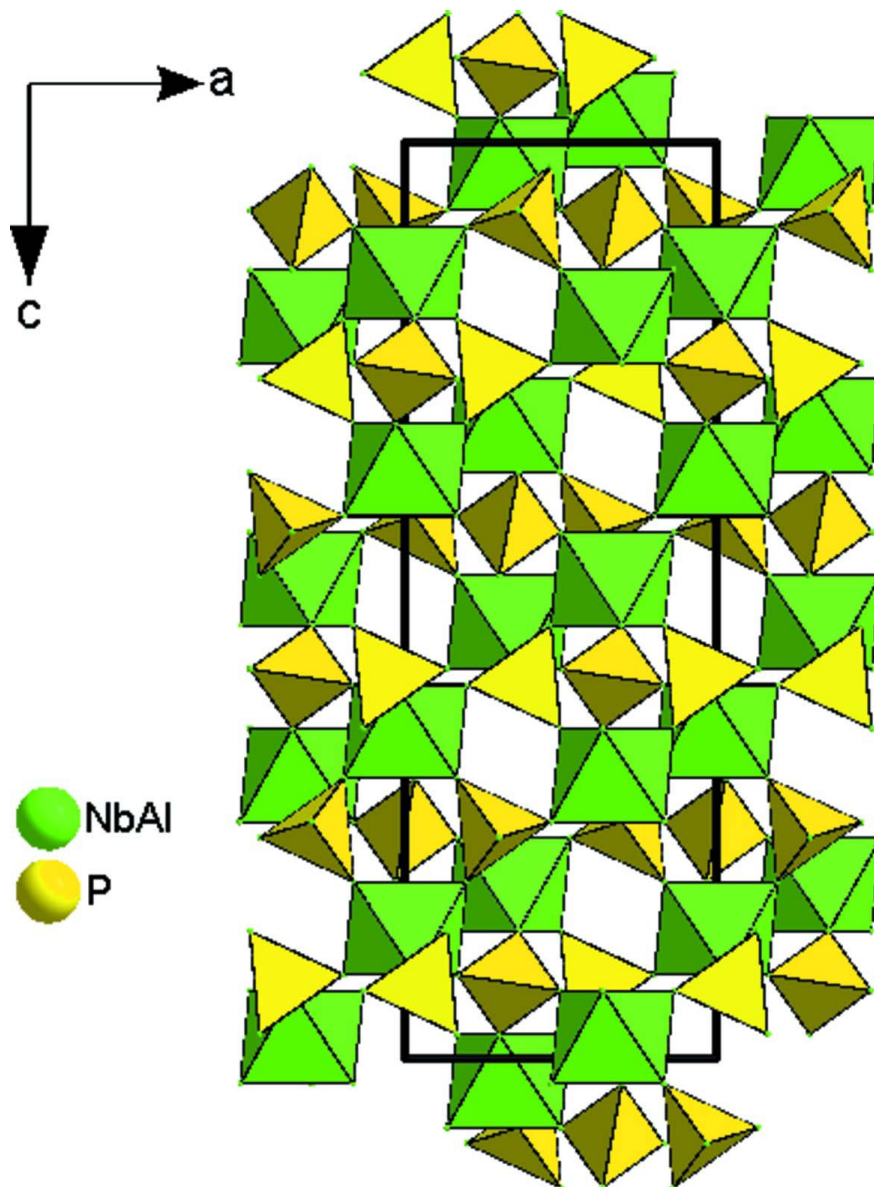


Figure 1

The expanded asymmetric unit of $\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ showing the coordination environments of the P and Al/Nb atoms. The displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) x, y, z ; (ii) $-x + y, -x, z$; (iii) $-y, x - y, z$; (iv) $0.66667 - x, 0.33333 - x + y, 0.83333 - z$; (v) $0.66667 - y, 0.33333 - x, -0.16667 + z$; (vi) $-1/3 + x, 1/3 + x - y, -0.16667 + z$; (vii) $-0.33333 - x + y, -2/3 + y, -0.16667 + z$.]

**Figure 2**

View of the crystal structure of $\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ along [010]. PO_4 and Al/NbO_6 units are given in the polyhedral representation.

aluminium(III) triniobium(V) phosphate(V)

Crystal data

$\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$

$M_r = 437.76$

Trigonal, $R\bar{3}c$

Hall symbol: $-\text{R } 3 \ 2''c$

$a = 8.5679 (6) \text{ \AA}$

$c = 21.898 (2) \text{ \AA}$

$V = 1392.14 (19) \text{ \AA}^3$

$Z = 6$

$F(000) = 1254$

$D_x = 3.133 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 247 reflections

$\theta = 2.6\text{--}25.0^\circ$

$\mu = 2.51 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism, colourless

$0.15 \times 0.05 \times 0.05 \text{ mm}$

Data collection

Bruker SMART 1K CCD area-detector diffractometer	2295 measured reflections
Radiation source: fine-focus sealed tube	302 independent reflections
Graphite monochromator	298 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.029$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$\theta_{\text{max}} = 25.7^\circ$, $\theta_{\text{min}} = 3.3^\circ$
$T_{\text{min}} = 0.704$, $T_{\text{max}} = 0.885$	$h = -7 \rightarrow 10$
	$k = -10 \rightarrow 8$
	$l = -26 \rightarrow 21$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.027$	$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 17.3988P]$
$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.39$	$(\Delta/\sigma)_{\text{max}} < 0.001$
302 reflections	$\Delta\rho_{\text{max}} = 0.45 \text{ e } \text{\AA}^{-3}$
27 parameters	$\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{\AA}^{-3}$
0 restraints	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Nb1	0.0000	0.0000	0.35896 (3)	0.0091 (2)	0.75
Al1	0.0000	0.0000	0.35896 (3)	0.0091 (2)	0.25
P1	0.3333	0.38482 (17)	0.4167	0.0143 (4)	
O1	0.1675 (4)	0.1984 (4)	0.40796 (12)	0.0173 (6)	
O2	0.3025 (4)	0.4696 (4)	0.47305 (12)	0.0194 (7)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nb1	0.0092 (3)	0.0092 (3)	0.0090 (4)	0.00460 (14)	0.000	0.000
Al1	0.0092 (3)	0.0092 (3)	0.0090 (4)	0.00460 (14)	0.000	0.000
P1	0.0179 (8)	0.0126 (5)	0.0141 (7)	0.0089 (4)	-0.0043 (6)	-0.0022 (3)
O1	0.0172 (15)	0.0132 (14)	0.0183 (14)	0.0053 (13)	-0.0039 (12)	-0.0051 (11)
O2	0.0253 (16)	0.0164 (15)	0.0162 (14)	0.0102 (14)	-0.0008 (12)	-0.0052 (11)

Geometric parameters (Å, °)

Nb1—O1	1.913 (3)	P1—O2	1.521 (3)
Nb1—O1 ⁱ	1.913 (3)	P1—O2 ^{vi}	1.521 (3)
Nb1—O1 ⁱⁱ	1.913 (3)	P1—O1 ^{vi}	1.529 (3)
Nb1—O2 ⁱⁱⁱ	1.949 (3)	P1—O1	1.529 (3)
Nb1—O2 ^{iv}	1.949 (3)	O2—Al1 ^{vii}	1.949 (3)
Nb1—O2 ^v	1.949 (3)	O2—Nb1 ^{vii}	1.949 (3)
O1—Nb1—O1 ⁱ	91.63 (12)	O1 ⁱⁱ —Nb1—O2 ^v	89.81 (12)
O1—Nb1—O1 ⁱⁱ	91.63 (12)	O2 ⁱⁱⁱ —Nb1—O2 ^v	88.66 (12)
O1 ⁱ —Nb1—O1 ⁱⁱ	91.63 (12)	O2 ^{iv} —Nb1—O2 ^v	88.66 (12)
O1—Nb1—O2 ⁱⁱⁱ	89.81 (12)	O2—P1—O2 ^{vi}	111.3 (2)
O1 ⁱ —Nb1—O2 ⁱⁱⁱ	89.86 (12)	O2—P1—O1 ^{vi}	110.32 (15)
O1 ⁱⁱ —Nb1—O2 ⁱⁱⁱ	177.90 (12)	O2 ^{vi} —P1—O1 ^{vi}	107.91 (16)
O1—Nb1—O2 ^{iv}	177.90 (12)	O2—P1—O1	107.91 (16)
O1 ⁱ —Nb1—O2 ^{iv}	89.81 (12)	O2 ^{vi} —P1—O1	110.32 (15)
O1 ⁱⁱ —Nb1—O2 ^{iv}	89.86 (12)	O1 ^{vi} —P1—O1	109.1 (2)
O2 ⁱⁱⁱ —Nb1—O2 ^{iv}	88.66 (12)	P1—O1—Nb1	152.96 (18)
O1—Nb1—O2 ^v	89.86 (12)	P1—O2—Al1 ^{vii}	155.8 (2)
O1 ⁱ —Nb1—O2 ^v	177.90 (12)	P1—O2—Nb1 ^{vii}	155.8 (2)

Symmetry codes: (i) $-x+y, -x, z$; (ii) $-y, x-y, z$; (iii) $-y+2/3, -x+1/3, z-1/6$; (iv) $-x+y-1/3, y-2/3, z-1/6$; (v) $x-1/3, x-y+1/3, z-1/6$; (vi) $-x+2/3, -x+y+1/3, -z+5/6$; (vii) $-x+y+1/3, y+2/3, z+1/6$.