

Al_{0.5}Nb_{1.5}(PO₄)₃

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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 × 0.05 × 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).

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

References

- Aatiq, A. & Bakri, R. (2007). *Powder Diffr.* **22**, 47–54.
Benmokhtar, S., El Jazouli, A., Aatiq, A., Chaminade, J. P., Gravereau, P., Wattiaux, A., Fournes, L. & Grenier, J. C. (2007). *J. Solid State Chem.* **180**, 2004–2012.
Boilot, J. P., Collin, G. & Colombari, Ph. (1987). *Mater. Res. Bull.* **22**, 669–676.
Brandenburg, K. (2004). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Brochu, R., Louer, M., Alami, M., Alqaraoui, M. & Louer, D. (1997). *Mater. Res. Bull.* **32**, 113–122.
Bruker (1997). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Chakir, M., El Jazouli, A. & de Waal, D. (2006). *J. Solid State Chem.* **179**, 1883–1891.
Hong, H. Y. P. (1976). *Mater. Res. Bull.* **11**, 173–182.
Leclaire, A., Borel, M.-M., Grandin, A. & Raveau, B. (1989). *Acta Cryst.* **C45**, 699–701.
Masquelier, C., Wurm, C., Rodriguez-Carvajal, J., Gaubicher, J. & Nazar, L. (2000). *Chem. Mater.* **12**, 525–532.
Rodrigo, J. L., Carrasco, M. P. & Alamo, J. (1989). *Mater. Res. Bull.* **24**, 611–618.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Trubach, I. G., Orlova, A. I., Beskrovnyi, A. I., Koryttseva, A. K., Zharinova, M. V., Kurazhkovskaya, V. S. & Lipatova, E. V. (2004). *Crystallogr. Rep.* **49**, 396–400.
Zatonvskii, I. V., Ushchapovskaya, T. I., Slobodyanik, N. S. & Ogorodnik, I. V. (2006). *Zh. Neorg. Khim.* **51**, 41–46.
Zhao, D., Xie, Z., Hu, J. M., Zhang, H., Zhang, W. L., Yang, S. L. & Cheng, W. D. (2009). *J. Mol. Struct.* **922**, 127–134.

supplementary materials

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Al_{0.5}Nb_{1.5}(PO₄)₃

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Comment

The mixed phosphates $AM_2(PO_4)_3$ family (A = alkali metals; M = Ti, Zr, Ge, Sn) which usually belong to the NASICON (Na₃Zr₂Si₂PO₁₂; Boilot, *et al.*, 1987) or the NZP (NaZr₂(PO₄)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 PO₄ tetrahedra sharing corners with MO₆ 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 Na₃MgZr(PO₄)₃ (Chakir, *et al.*, 2006), Na₃Fe₂(PO₄)₃ (Masquelier, *et al.*, 2000), NaFeNb(PO₄)₃ (Zatovskii, *et al.*, 2006), NaTi₂(PO₄)₃ (Rodrigo, *et al.*, 1989) and NaGe₂P₃O₁₂ (Zhao *et al.*, 2009). The three-dimensional network consisting of PO₄ and MO₆ 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 Fe_{0.5}Nb_{1.5}(PO₄)₃ (Trubach, *et al.*, 2004) and Fe_{0.5}Sb_{1.5}(PO₄)₃ (Aatiq & Bakri, 2007), Nb₂(PO₄)₃ (Leclaire, *et al.*, 1989) and Fe_{0.5}Ti₂(PO₄)₃ (Benmokhtar, *et al.*, 2007), *etc.* In order to enrich this type of compounds, we synthesis the compound Al_{0.5}Nb_{1.5}(PO₄)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 Al_{0.5}Nb_{1.5}(PO₄)₃ contains a single P and Al/Nb atoms. The P atom is four coordinated by four oxygen atoms, forming isolated PO₄ 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 PO₄ tetrahedra are further interconnected *via* corner-sharing O atoms to form the three-dimensional framework of Al_{0.5}Nb_{1.5}(PO₄)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 PO₄ 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)^o, 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 $Zr^{4+} \rightarrow 0.25 A l^{3+} + 0.73 N b^{5+}$.

Experimental

The finely ground reagents K₂CO₃, Al₂O₃, Nb₂O₅ and NH₄H₂PO₄ 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.

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.

Figures

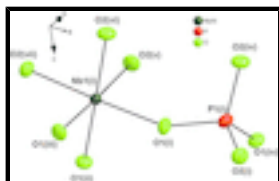


Fig. 1. The expanded asymmetric unit of $\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ showing the coordination environments of the P and Al/Nb atoms. The displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) x, y, z ; (ii) $-x + y, -x, z$; (iii) $-y, x - y, z$; (iv) $0.66667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

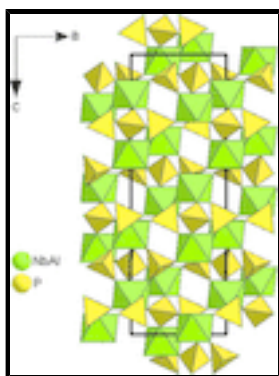


Fig. 2. View of the crystal structure of $\text{Al}_{0.5}\text{Nb}_{1.5}(\text{PO}_4)_3$ along $[010]$. PO_4 and Al/NbO_6 units are given in the polyhedral representation.

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: $-R\ 3\ 2''c$

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

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

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

$Z = 6$

$F(000) = 1254$

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

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

Radiation source: fine-focus sealed tube graphite

ω scans

302 independent reflections

298 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\text{max}} = 25.7^\circ$, $\theta_{\text{min}} = 3.3^\circ$

Absorption correction: multi-scan
(*SADABS*; Bruker, 1997) $h = -7 \rightarrow 10$
 $T_{\min} = 0.704$, $T_{\max} = 0.885$ $k = -10 \rightarrow 8$
2295 measured reflections $l = -26 \rightarrow 21$

Refinement

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

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)

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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) $-x+y+1/3, y+2/3, z+1/6$.

Fig. 1

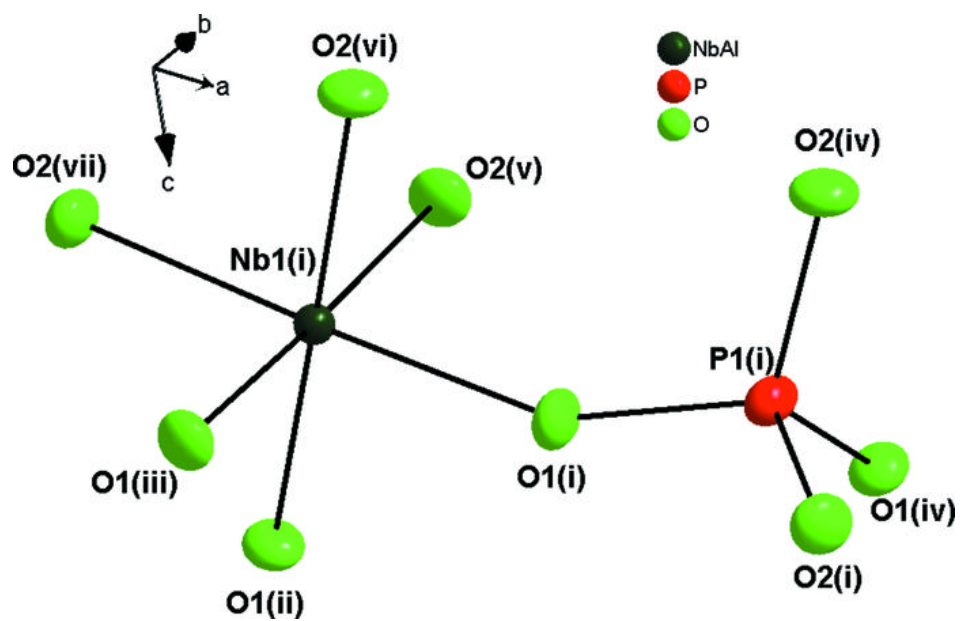


Fig. 2

