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$Na_4Ni_5[(As_{1-x}P_x)O_4]_2[(As_{2y}P_{2-2y})O_7]_2$ (x = 0.27 and y = 0.295)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Ni–O) = 0.003 Å
Disorder in main residue
R factor = 0.024
wR factor = 0.065
Data-to-parameter ratio = 10.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Crystals of the title compound, tetrasodium pentanickel arsenic–phosphorus (2.64/3.36) docosaoxide, has been grown by a solid-state reaction and characterized by single-crystal X-ray diffraction. The structure is built up from corner- and edge-sharing $(AsP)O_4$ tetrahedra, $(AsP)_2O_7$ groups, NiO_6 octahedra and Ni_2O_9 units, giving rise to a polyhedral connectivity having tunnels running along the [001] direction. It is isostructural with $Na_4Ni_5(PO_4)_2(P_2O_7)_2$.

Comment

Phosphate and arsenate inorganic materials offer a considerable variety of structures, giving rise to various potential applications. In the course of our investigations of the Na_2O–NiO–As_2O_5 and K_2O–NiO–As_2O_5 ternary systems, in a search for new materials likely to exhibit interesting magnetic or ionic conductivity properties, we have previously isolated four compounds: $NaNi_4(AsO_4)_3$ (Ben Smail *et al.*, 2002), $Na_4Ni_7(AsO_4)_6$ (Ben Smail *et al.*, 2004), $K_4Ni_7(AsO_4)_6$ (Ben Smail *et al.*, 1999) and $K_3Ni(AsO_4)(As_2O_7)$ (Ben Smail & Jouini, 2000). Recently, during our investigation of the Na_2O–NiO–As_2O_5–P_2O_5 quaternary system, two compounds have been isolated in the same preparation: $Na_3Ni_2(As_{0.1}P_{0.9})O_4(As_{1.3}P_{0.7})O_7$ (Ben Smail & Jouini, 2004) and $Na_4Ni_5[(As_{0.73},P_{0.27})O_4]_2[(As_{0.59},P_{1.41})O_7]_2$.

This paper reports the crystal structure of the latter compound. The asymmetric unit is illustrated in Fig. 1. This structure is isomorphous with that of $Na_4Ni_5(PO_4)_2(P_2O_7)_2$ (Sanz *et al.*, 1999). The structures of these compounds have channels running along c, in which alkali metal ions are

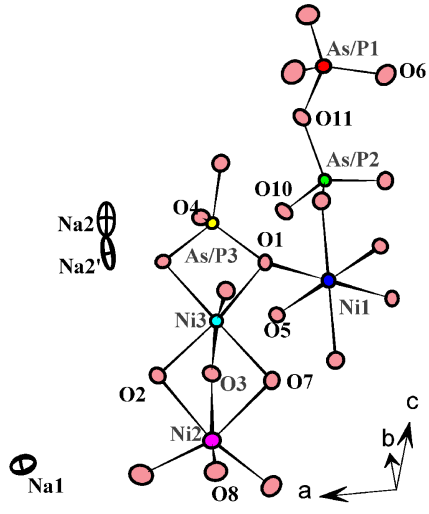

Figure 1
A plot (*DIAMOND*; Brandenburg, 1998) of the asymmetric unit with labeled atoms. Displacement ellipsoids are plotted at the 50% probability level.

located (Fig. 2). This solid solution phase differs from the phosphate-limiting phase $Na_4Ni_5(PO_4)_2(P_2O_7)_2$ by the splitting of Na2 over two distinct sites (Na2 and Na2′) separated by 0.82 (4) Å.

Bond valence calculations (Brown & Shannon, 1973; Brown & Altermatt, 1985) confirm the experimentally determined occupancies: 0.79 from bond valences (*cf.* 0.75 from X-ray experiment) for P1, 0.67 (*cf.* 0.66) for P2 and 0.21 (*cf.* 0.27) for P3.

This structure is determined with lower $R = 0.0241$ and $wR = 0.0653$ values than the isotypic phosphate structure form, $R = 0.0608$ and $wR = 0.1693$.

Experimental

The preparation of the title compound is described elsewhere (Ben Smail & Jouini, 2004).

Crystal data

$Na_4Ni_5[(As_{0.73}P_{0.27})O_4]_2[(As_{0.59}P_{1.41})O_7]_2$
$M_r = 1039.26$
Monoclinic, $P2_1/a$
$a = 10.676$ (2) Å
$b = 6.716$ (1) Å
$c = 12.812$ (2) Å
$\beta = 103.77$ (1)°
$V = 892.2$ (3) Å^3
$Z = 2$
$D_x = 3.868$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.4$–15°
$\mu = 10.56$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, brown
0.20 × 0.08 × 0.02 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.368$, $T_{max} = 0.784$
2051 measured reflections
1942 independent reflections
1672 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 27.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = -16 \rightarrow 15$
2 standard reflections
frequency: 120 min
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.065$
$S = 1.10$
1942 reflections
187 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 1.9015P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.032$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0013 (2)

Table 1
Selected geometric parameters (Å).

As/P1—O8^{i}	1.528 (3)	As/P3—O1	1.677 (3)
As/P1—O9^{ii}	1.554 (3)	As/P3—O5^{ii}	1.682 (3)
As/P1—O6^{iii}	1.555 (3)	Na1—O6^{vii}	2.287 (3)
As/P1—O11	1.666 (3)	Na1—O8^{v}	2.364 (4)
As/P2—O10^{iv}	1.556 (3)	Na1—O7^{v}	2.366 (3)
As/P2—O2^{v}	1.583 (3)	Na1—O4^{iv}	2.456 (3)
As/P2—O7^{vi}	1.587 (3)	Na1—O11^{iv}	2.523 (4)
As/P2—O11^{iv}	1.644 (3)	Na1—O2^{v}	2.805 (3)
As/P3—O4	1.633 (3)	Na1—O9^{iv}	2.968 (4)
As/P3—O3^{ii}	1.642 (3)		

Symmetry codes: (i) $x, y, 1+z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (iii) $x-1, y, z$; (iv) $1-x, -y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, z$; (vi) $1+x, y, z$; (vii) $\frac{3}{2}-x, y-\frac{1}{2}, 1-z$.

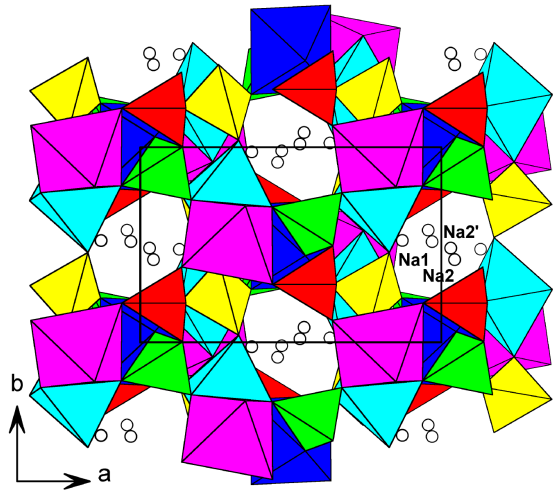

Figure 2
Shape and size of a section through the tunnel in the structure of $Na_4Ni_5[(As_{0.73}P_{0.27})O_4]_2[(As_{0.59}P_{1.41})O_7]_2$.

The occupation factors of the As/P atoms in the tetrahedral sites have been refined, the sum of the occupation factors being fixed at 1.0. Pairs of atoms at the same site were given the same coordinates and atomic displacement parameters. A residual Fourier peak (2.6 e Å^{-3}) still remained close to the Na2 site. It was refined as an alternative sodium position, the refinement of the occupancy factors of the neighboring Na^+ cations leading to a small improvement of reliability factors. Consequently, the Na2 sodium atom has been split into two positions (Na2 and Na2′), with different occupancies. They are separated by 0.82 (4) Å.

Data collection: *CAD*-4 *EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL*97.

References

Ben Smail, R., Driss, A. & Jouini, T. (1999). *Acta Cryst.* C**55**, 284–286.
Ben Smail, R. & Jouini, T. (2000). *Acta Cryst.* C**56**, 513–514.
Ben Smail, R. & Jouini, T. (2004). *Ann. Chim. Sci. Mat.* Accepted.
Ben Smail, R., Touati, A. & Jouini, T. (2004). In preparation.
Ben Smail, R., Zid, M. F. & Jouini, T. (2002). *J. Soc. Chim. Tunisie*, **4**, 1655–1673.
Brandenburg, K. (1998). *DIAMOND*. Version 2.0. University of Bonn, Germany.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Brown, I. D. & Shannon, R. D.. (1973). *Acta Cryst.* A**29**, 266–282.
Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Marburg, Germany.
Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sanz, F., Parade, C., Rojo, J. M. & Ruiz-Valero, C. (1999). *Chem. Mater.* **11**, 2673–2679.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.