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A quaternary germanium(II) phosphate, $Na[Ge_4(PO_4)_3]$

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Key indicators: single-crystal X-ray study; T = 298 K; mean σ(Ge–O) = 0.013 Å; R factor = 0.058; wR factor = 0.133; data-to-parameter ratio = 10.3.

A new germanium(II) phosphate, sodium tetragermanium tris(phosphate), $Na[Ge_4(PO_4)_3]$, has been synthesized by a solid-state reaction. The compound is isotypic with $A[Sn_4(PO_4)_3]$ (A = Na, K, NH_4). It features a $[Ge_4(PO_4)_3]^-$ framework made up of GeO_3 pyramids and PO_4 tetrahedra, which are linked by shared corners, yielding a three-dimensional structure. The crystal studied showed partial inversion twinning.

Related literature

Open–framework series of isotypic tin(II) phosphates with general formula $A[Sn_4(PO_4)_3]$ (A = Na, K, NH_4) were synthesized by hydrothermal methods (Ayyappan *et al.*, 2000; Bontchev & Moore, 2004; Deng *et al.*, 2004; Mao *et al.*, 2004). For related literature, see: Brown & Altermatt (1985); Cheetham *et al.* (1999); Weakley & Watt (1979).

Experimental

Crystal data

$Na[Ge_4(PO_4)_3]$
M_r = 598.26
Trigonal, $R3c$
a = 9.377 (8) Å
c = 23.48 (3) Å
V = 1788 (3) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 10.49 mm^{-1}
T = 298 (2) K
0.2 × 0.13 × 0.1 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.488, T_{max} = 1
(expected range = 0.171–0.350)
2164 measured reflections
639 independent reflections
567 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.133
S = 1.09
639 reflections
62 parameters
1 restraint
$\Delta\rho_{max}$ = 1.71 e Å^{-3}
$\Delta\rho_{min}$ = −1.06 e Å^{-3}
Absolute structure: Flack (1983), 146 Friedel pairs
Flack parameter: 0.23 (8)

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Dowty, 2005); 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: FI2055).

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supplementary materials

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A quaternary germanium(II) phosphate, $Na[Ge_4(PO_4)_3]$

C.-S. Lee and S.-F. Weng

Comment

Open-framework metal phosphates exhibit interesting structural types and physical properties that have been the subject of intensive research due to their potential applications in the areas of catalysis, ion–exchange and phase separation (Cheetham *et al.*, 1999). Among these compounds, germanium phosphates are rare compared to other phosphate compounds. Most of reported germanophosphate contain germanium (IV) with octahedral coordination environment to oxygen atoms. To the best of our knowledge, germanophosphate with Ge(II) are very rare. Our group has demonstrated that A_2HPO_4 and metal can serve as reducing and oxidizing reagents to synthesize metal phosphates. In an attempt to synthesize compounds in the system using A_2HPO_4 as the precursor, we obtained a new quaternary compound $Na[Ge_4(PO_4)_3]$. As confirmed by measurements on single crystals, the synthesis of $Na[Ge_4(PO_4)_3]$ is presented as follows:

$$4Na_2HPO_4+17Ge+15GeO_2+10P_2O_5\rightarrow 8Na[Ge_4(PO_4)_3]+2H_2$$

The structure of $Na[Ge_4(PO_4)_3]$ is shown in Figure 1. The asymmetric unit contains two germanium, one phosphorus, four oxygen and one sodium atom (Figure 2). The Ge atoms occupy two different crystallographic sites and each site being coordinated by three O atoms to form distorted pyramids with Ge—O distances ranging from 1.87 (1) to 1.92 (1) Å, which agrees well with bond valence sum calculations (Brown & Altermatt, 1985). Similar Ge—O distances are reported in $GeCl(H_2PO_2)$ (Weakley & Watt, 1979). The coordination environment of the Ge^{2+} atoms is similar to Sn^{2+} in $A[Sn_4(PO_4)_3]$ (A=Na, K, NH_4) (Ayyappan *et al.*, 2000, Bontchev & Moore, 2004, Deng *et al.*, 2004, Mao *et al.*, 2004).. The phosphorus atoms is tetrahedrally coordinated with P—O distances in a range 1.53 (1) to 1.54 (1) Å, which agrees with literature values. The structure of the title compound contains $[PO_4]^{3-}$ layers stacked along the c–axis with a repeat sequence of six layers. The $[PO_4]^{3-}$ units on the *ab* plane form 6 membered–ring with corner–shared $[PO_4]$ and $Ge(2)O_3$ units, which are connected by $Ge(1)O_3$ pyramids to construct the two–dimensional framework. The two-dimensional layers are additionally connected to each other by out of plane$Ge(1)O_3$ groups to form a three–dimensional framework. Each sodium atom is coordinated by nine oxygen atoms with Na—O distances ranging between 2.46 (1) and 2.71 (1) Å in a basket–like cage.

Experimental

$Na[Ge_4(PO_4)_3]$ were synthesized from mixtures of Na_2HPO_4 (99%, Riedel-de Haën), Ge (99.999%, Alfa), GeO_2 (99.999%, Cerac), and P_2O_5 (99.999%, J·T·Baker) in stoichiometric proportions according to the solid state method. Initially, all reagents were mixed in an Ar-filled glove box (total weight≃0.5 g), placed in a silica tube, sealed under vacuum (P≃10^{-4} torr), and heated slowly to 600 °C over 48 h, followed by furnace cooling to room temperature on simply terminating the power. The length of the reaction tube was kept about 7~8 cm to avoid the prospective explosion due to the formation of gaseous hydrogen. The product contains hydrogen gas and brittle, colorless, transparent rod-shape crystals. The crystalline product

was confirmed to be pure $Na[Ge_4(PO_4)_3]$ by powder X-ray diffraction. Attempts to synthesize the analogue $K[Ge_4(PO_4)_3]$ with the precursor K_2HPO_4 failed.

Refinement

The structures were solved by direct methods and refined by full matrix least–squares techniques with the *SHELXTL* software package. Analysis of single-crystal *X*–ray diffraction data revealed four unique sites for Na, Ge and P and four unique sites for O atoms. The structural analysis yielded a charge–balanced formula $Na[Ge_4(PO_4)_3]$. All atomic positions were refined with anisotropic displacement parameters. The highest peak in the difference map is 1.67 e/Å^3 and 0.96 Å from Ge1, while the minimum peak is −1.08 e/Å^3 and 1.51 Å from O3.

Figures

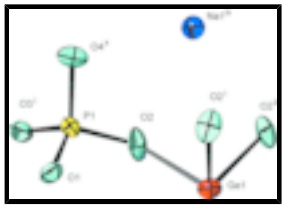

Fig. 1. The framework of $Na[Ge_4(PO_4)_3]$ [Symmetry codes: (i)-*y*,*x*-*y*,*z* (ii)-*x* + *y*, −*x*, *z* (ix)-*y* + 2/3, −*x* + 1/3, *z* + 5/6 (*x*)-*x* + *y*+2/3, *y* + 1/3, *z* + 5/6. Displacement ellipsoids are drawn at the 50% probability level.

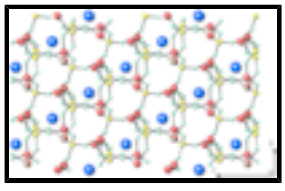

Fig. 2. The alternating full/empty sequence of channels running parallel to the a– and b–axes.

sodium tetragermanium tris(phosphate)

Crystal data

$Na[Ge_4(PO_4)_3]$	$Z = 6$
$M_r = 598.26$	$F_{000} = 1680$
Trigonal, *R*3*c*	$D_x = 3.334$ Mg m^{-3}
Hall symbol: R 3 -2" c	Mo *K*α radiation λ = 0.71073 Å
a = 9.377 (8) Å	Cell parameters from 2164 reflections
b = 9.377 (8) Å	θ = 3.1–28.3º
c = 23.48 (3) Å	μ = 10.49 mm^{-1}
α = 90º	*T* = 298 (2) K
β = 90º	Rod, colourless
γ = 120º	0.2 × 0.13 × 0.1 mm
V = 1788 (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	567 reflections with $I > 2\sigma(I)$

Monochromator: graphite
T = 298(2) K
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.488, T_{max} = 1
2164 measured reflections
639 independent reflections

R_{int} = 0.068
θ_{max} = 28.3º
θ_{min} = 3.1º
h = −11→6
k = −12→10
l = −14→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.133
S = 1.09
639 reflections
62 parameters
1 restraint
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 1.71 e Å^{-3}
$\Delta\rho_{min}$ = −1.06 e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 146 Friedel pairs
Flack parameter: 0.23 (8)

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ge1	1.0000	1.0000	0.07489 (10)	0.0243 (6)
Ge2	1.41201 (19)	1.47337 (17)	0.10322 (6)	0.0214 (4)
P1	1.3317 (4)	1.1233 (4)	0.14139 (17)	0.0190 (7)
Na1	0.6667	0.3333	0.0506 (4)	0.025 (2)
O1	1.4071 (13)	1.2667 (13)	0.0985 (4)	0.024 (2)
O2	1.1603 (13)	0.9917 (13)	0.1226 (5)	0.032 (2)
O3	1.6040 (13)	1.5600 (13)	0.1466 (4)	0.027 (2)
O4	1.5371 (12)	1.5216 (13)	0.0335 (4)	0.026 (2)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ge1	0.0271 (9)	0.0271 (9)	0.0187 (11)	0.0136 (4)	0.000	0.000
Ge2	0.0170 (8)	0.0212 (8)	0.0242 (6)	0.0083 (6)	−0.0022 (5)	−0.0022 (6)
P1	0.0169 (17)	0.0186 (17)	0.0205 (14)	0.0082 (14)	0.0026 (12)	0.0008 (12)
Na1	0.025 (3)	0.025 (3)	0.026 (5)	0.0125 (16)	0.000	0.000
O1	0.025 (5)	0.027 (6)	0.019 (4)	0.012 (5)	−0.005 (4)	0.000 (4)
O2	0.019 (5)	0.031 (6)	0.050 (6)	0.016 (5)	0.002 (4)	0.010 (5)
O3	0.027 (6)	0.028 (5)	0.020 (4)	0.009 (5)	0.000 (4)	−0.004 (4)
O4	0.018 (5)	0.024 (6)	0.019 (4)	−0.001 (4)	0.002 (4)	0.008 (4)

Geometric parameters (Å, °)

Ge1—O2	1.908 (10)	Na1—O1^{viii}	2.462 (11)
Ge1—O2^{i}	1.908 (10)	Na1—O4^{vii}	2.627 (11)
Ge1—O2^{ii}	1.908 (10)	Na1—O4^{ii}	2.627 (11)
Ge1—Na1^{iii}	3.343 (11)	Na1—O4^{viii}	2.627 (11)
Ge2—O3	1.864 (10)	Na1—O2^{ix}	2.705 (13)
Ge2—O1	1.918 (11)	Na1—O2^{x}	2.705 (13)
Ge2—O4	1.931 (10)	Na1—O2^{xi}	2.705 (13)
Ge2—Na1^{iv}	3.477 (5)	Na1—P1^{ix}	3.254 (7)
P1—O2	1.522 (12)	Na1—P1^{x}	3.254 (7)
P1—O3^{v}	1.534 (11)	Na1—P1^{xi}	3.254 (7)
P1—O1	1.540 (11)	O1—Na1^{iv}	2.462 (11)
P1—O4^{vi}	1.540 (9)	O2—Na1^{iii}	2.705 (13)
P1—Na1^{iii}	3.254 (7)	O3—P1^{xii}	1.534 (11)
Na1—O1^{vii}	2.462 (11)	O4—P1^{xiii}	1.540 (9)
Na1—O1^{ii}	2.462 (11)	O4—Na1^{iv}	2.627 (11)
O2—Ge1—O2^{i}	89.0 (5)	O2^{ix}—Na1—O2^{x}	59.2 (4)
O2—Ge1—O2^{ii}	89.0 (5)	O1^{vii}—Na1—O2^{xi}	135.5 (4)
O2^{i}—Ge1—O2^{ii}	89.0 (5)	O1^{ii}—Na1—O2^{xi}	122.3 (4)
O2—Ge1—Na1^{iii}	54.0 (3)	O1^{viii}—Na1—O2^{xi}	83.0 (3)
O2^{i}—Ge1—Na1^{iii}	54.0 (3)	O4^{vii}—Na1—O2^{xi}	77.9 (4)
O2^{ii}—Ge1—Na1^{iii}	54.0 (3)	O4^{ii}—Na1—O2^{xi}	113.5 (4)
O3—Ge2—O1	90.1 (5)	O4^{viii}—Na1—O2^{xi}	55.5 (3)
O3—Ge2—O4	91.2 (4)	O2^{ix}—Na1—O2^{xi}	59.2 (4)
O1—Ge2—O4	83.8 (4)	O2^{x}—Na1—O2^{xi}	59.2 (4)
O3—Ge2—Na1^{iv}	70.3 (3)	O1^{vii}—Na1—P1^{ix}	69.3 (2)
O1—Ge2—Na1^{iv}	43.3 (3)	O1^{ii}—Na1—P1^{ix}	158.4 (3)
O4—Ge2—Na1^{iv}	48.4 (3)	O1^{viii}—Na1—P1^{ix}	100.0 (3)
O2—P1—O3^{v}	108.5 (6)	O4^{vii}—Na1—P1^{ix}	27.8 (2)

O2—P1—O1	110.8 (6)	O4^{ii}—Na1—P1^{ix}	97.9 (3)
O3^{v}—P1—O1	110.5 (6)	O4^{viii}—Na1—P1^{ix}	119.8 (3)
O2—P1—O4^{vi}	108.4 (6)	O2^{ix}—Na1—P1^{ix}	27.7 (2)
O3^{v}—P1—O4^{vi}	109.1 (6)	O2^{x}—Na1—P1^{ix}	86.4 (3)
O1—P1—O4^{vi}	109.5 (6)	O2^{xi}—Na1—P1^{ix}	66.4 (3)
O2—P1—Na1^{iii}	55.7 (4)	O1^{vii}—Na1—P1^{x}	100.0 (3)
O3^{v}—P1—Na1^{iii}	122.1 (4)	O1^{ii}—Na1—P1^{x}	69.3 (2)
O1—P1—Na1^{iii}	127.4 (4)	O1^{viii}—Na1—P1^{x}	158.4 (3)
O4^{vi}—P1—Na1^{iii}	52.8 (4)	O4^{vii}—Na1—P1^{x}	119.8 (3)
O1^{vii}—Na1—O1^{ii}	100.8 (4)	O4^{ii}—Na1—P1^{x}	27.8 (2)
O1^{vii}—Na1—O1^{viii}	100.8 (4)	O4^{viii}—Na1—P1^{x}	97.9 (3)
O1^{ii}—Na1—O1^{viii}	100.8 (4)	O2^{ix}—Na1—P1^{x}	66.4 (3)
O1^{vii}—Na1—O4^{vii}	60.6 (3)	O2^{x}—Na1—P1^{x}	27.7 (2)
O1^{ii}—Na1—O4^{vii}	159.5 (5)	O2^{xi}—Na1—P1^{x}	86.4 (3)
O1^{viii}—Na1—O4^{vii}	76.3 (3)	P1^{ix}—Na1—P1^{x}	92.9 (2)
O1^{vii}—Na1—O4^{ii}	76.3 (3)	O1^{vii}—Na1—P1^{xi}	158.4 (3)
O1^{ii}—Na1—O4^{ii}	60.6 (3)	O1^{ii}—Na1—P1^{xi}	100.0 (3)
O1^{viii}—Na1—O4^{ii}	159.5 (5)	O1^{viii}—Na1—P1^{xi}	69.3 (2)
O4^{vii}—Na1—O4^{ii}	117.71 (15)	O4^{vii}—Na1—P1^{xi}	97.9 (3)
O1^{vii}—Na1—O4^{viii}	159.5 (5)	O4^{ii}—Na1—P1^{xi}	119.8 (3)
O1^{ii}—Na1—O4^{viii}	76.3 (3)	O4^{viii}—Na1—P1^{xi}	27.8 (2)
O1^{viii}—Na1—O4^{viii}	60.6 (3)	O2^{ix}—Na1—P1^{xi}	86.4 (3)
O4^{vii}—Na1—O4^{viii}	117.71 (15)	O2^{x}—Na1—P1^{xi}	66.4 (3)
O4^{ii}—Na1—O4^{viii}	117.71 (15)	O2^{xi}—Na1—P1^{xi}	27.7 (2)
O1^{vii}—Na1—O2^{ix}	83.0 (3)	P1^{ix}—Na1—P1^{xi}	92.9 (2)
O1^{ii}—Na1—O2^{ix}	135.5 (4)	P1^{x}—Na1—P1^{xi}	92.9 (2)
O1^{viii}—Na1—O2^{ix}	122.3 (4)	P1—O1—Ge2	127.8 (6)
O4^{vii}—Na1—O2^{ix}	55.5 (3)	P1—O1—Na1^{iv}	118.9 (6)
O4^{ii}—Na1—O2^{ix}	77.9 (4)	Ge2—O1—Na1^{iv}	104.4 (5)
O4^{viii}—Na1—O2^{ix}	113.5 (4)	P1—O2—Ge1	132.2 (6)
O1^{vii}—Na1—O2^{x}	122.3 (4)	P1—O2—Na1^{iii}	96.7 (5)
O1^{ii}—Na1—O2^{x}	83.0 (3)	Ge1—O2—Na1^{iii}	91.2 (4)
O1^{viii}—Na1—O2^{x}	135.5 (4)	P1^{xii}—O3—Ge2	141.5 (7)
O4^{vii}—Na1—O2^{x}	113.5 (4)	P1^{xiii}—O4—Ge2	123.5 (6)
O4^{ii}—Na1—O2^{x}	55.5 (3)	P1^{xiii}—O4—Na1^{iv}	99.4 (6)
O4^{viii}—Na1—O2^{x}	77.9 (4)	Ge2—O4—Na1^{iv}	98.3 (4)

Symmetry codes: (i) −*y*+2, *x*−*y*+1, *z*; (ii) −*x*+*y*+1, −*x*+2, *z*; (iii) −*y*+4/3, −*x*+5/3, *z*+1/6; (iv) *x*+1, *y*+1, *z*; (v) −*y*+3, *x*−*y*+1, *z*; (vi) −*x*+*y*+4/3, *y*−1/3, *z*+1/6; (vii) −*y*+2, *x*−*y*, *z*; (viii) *x*−1, *y*−1, *z*; (ix) −*y*+5/3, −*x*+4/3, *z*−1/6; (x) *x*−1/3, *x*−*y*+1/3, *z*−1/6; (xi) −*x*+*y*+2/3, *y*−2/3, *z*−1/6; (xii) −*x*+*y*+2, −*x*+3, *z*; (xiii) −*x*+*y*+5/3, *y*+1/3, *z*−1/6.

Fig. 1

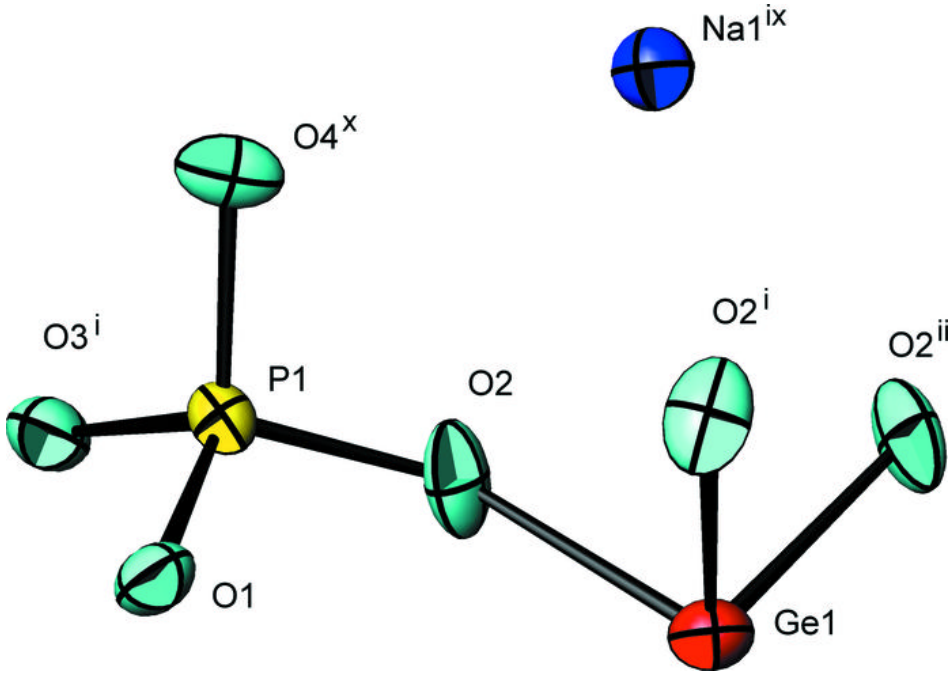

Fig. 2