The crystals were kindly supplied by John J. Neumeier, Physics Department, Ludwig-Maximilian University, Munich.

References

Izumi, F., Asano, H., Ishigaki, T., Takayama-Muromachi, E., Matsui, Y. & Uchida, Y. (1987). *Jpn J. Appl. Phys.* **26**, L1153–L1155.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Norrestam, R. (1976). *CADABS. Program for CAD-4 Absorption Correction*. Technical University of Denmark, Denmark.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Torardi, C. C., McCarron, E. M., Subramanian, M. A., Sleight, A. W. & Cox, D. E. (1987). *Mater. Res. Bull.* **22**, 1563–1571.

A New Form of Lithium Zinc Phosphate with an Ordered Phenakite Structure, LiZnPO4

Xianhui Bu, Thurman E. Gier and Galen D. Stucky

Chemistry Department, University of California, Santa Barbara, CA 93106, USA. E-mail: xianhui@sbxray.ucsb.edu

Abstract

A new form of LiZnPO4 with an ordered non-centrosymmetric phenakite-type structure is reported.

Comment

A variety of framework topologies have been found for open-framework zincophosphates based on tetrahedral ZnO_2^{2-} and PO_2^{+} units. In addition to about a dozen novel zincophosphate open-framework structures (Feng, Bu & Stucky, 1995), structural analogs of some natural zeolites such as sodalite and zeolite X have been reported in the zincophosphate system (Gier & Stucky, 1991). Since there are many structure types based on tetrahedral T^{3+}/T^{4+} atoms, such as for the aluminosilicates, it is of interest to investigate to what extent these structure types exist in T^{2+}/T^{5+} systems such as the zin-cophosphates. The difficulties in working with T^{2+}/T^{5+} systems include the large difference in the ionic radii of T^{2+} and T^{5+}, especially in the zincophosphate system, and the increased tendency for divalent metals such as Zn^{2+} and Co^{2+} to assume non-tetrahedral coordination geometry. Here we report the discovery of a new zincophosphate in another structural family, phenakite. This is the first report of a phenakite-type structure in the T^{2+}/T^{5+} system.

The mineral phenakite, Be_2SiO_4, is rhombohedral and contains continuous six-ring channels parallel to the c axis. Derivatives of the phenakite structure include Zn_2SiO_4, Li_2BeF_4, Li_2SeO_4, Li_2WO_4 and α-$LiABO_4$ (where A = Al, Ga and B = Si, Ge) (Fleet, 1987). All have the space group $R\bar{3}$ except for α-$LiGaSiO_4$.

The centrosymmetric $R\bar{3}$ phenakite structure has seven atom positions, three of which are different tetrahedral sites and four of which are O-atom sites. The site which contains Si in phenakite may be labeled $T1$ and the other tetrahedral sites, which contain Be in phenakite, may be labeled $T2$ and $T3$. The key structural feature of the phenakite structure is that all the O atoms are bonded to three tetrahedrally coordinated atoms and there are no edge-sharing tetrahedra.

In the non-centrosymmetric title compound, LiZnPO4, there are fourteen unique atom positions, six of which are tetrahedral sites. Each O atom is bonded to one Li, one Zn and one P cation. The two divalent Zn cations occupy the two Si positions ($T1$) which are related by an inversion center in the $R\bar{3}$ structure. One Li cation and one P cation occupy the $T2$ positions that in $R\bar{3}$ would be related by a center of symmetry, and the other Li and P cations occupy the corresponding $T3$ positions. This reduces the lattice symmetry from $R\bar{3}$ to $R3$.

As expected for tetrahedral zincophosphates, there is a strict alternation of the ZnO_2^{2-} and PO_2^{+} units. The
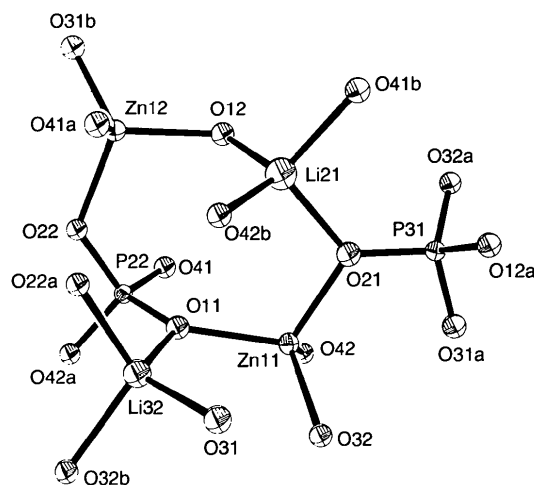

Fig. 1. A view of the Zn, P and Li tetrahedra showing the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

three different tetrahedral atoms, Li, Zn and P, form columns along the c axis in an alternating fashion.

The crystal structures of two other forms of LiZnPO₄ have been reported. They are α-LiZnPO₄ (Elammari & Elouadi, 1989; Elfakir, Souron, Robert & Quarton, 1989) and δ_1-LiZnPO₄ (Jensen, Norby & Stein, 1995; Harrison, Gier, Nicol & Stucky, 1995). Like the phenakite form of LiZnPO₄, these two forms have noncentrosymmetric tetrahedral frameworks with O atoms coordinated to three different tetrahedral cations (Li, Zn and P). In the phenakite form of LiZnPO₄, all three different tetrahedra are oriented with one vertex in the c direction, which results in columns of alternating tetrahedra. In α-LiZnPO₄, only one of the three tetrahedra is oriented in this way. δ_1-LiZnPO₄ has been described as having a cristobalite-type structure with four-coordinate Li cations in the six-ring channels. This is in contrast with the phenakite form, in which the Li cations are located in the walls of the channels.
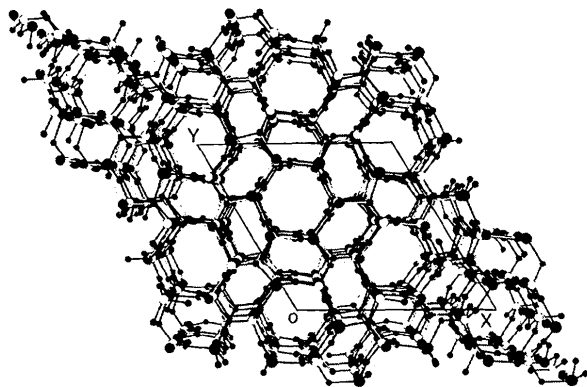

Fig. 2. A projection down the c axis showing the continuous six-ring channels. The smaller dark circles are O atoms, the larger dark circles are Zn atoms, the open circles are P atoms and the grey circles are Li atoms.

Experimental

To synthesize LiZnPO₄ crystals with the phenakite structure, 7.71 g of $2M$ Zn(NO₃)₂, 4.19 g of $4M$ H₃PO₄ and 7.64 g of $4M$ LiOH were sealed in a Teflon FEP film pouch. The gel slurry was then heated in an autoclave containing water as the support fluid at 468 K and 1.38 × 10⁷ Pa for three days. Upon cooling and recovery of the pouch contents *via* standard filtration and washing techniques, the yield of crystals (up to 1 mm in size) was 1.393 g (*ca.* 70% based on Zn). The pH of the crystallizing fluid was about 1.5.

Crystal data

LiZnPO₄	Mo $K\alpha$ radiation
$M_r = 167.29$	$\lambda = 0.71073$ Å
Trigonal	Cell parameters from 23
$R3$	reflections
$a = 13.628\,(3)$ Å	$\theta = 5.00\text{--}11.00°$
$c = 9.096\,(2)$ Å	$\mu = 8.06$ mm⁻¹

$V = 1463.0\,(5)$ Å³	$T = 293$ K
$Z = 18$	Translucent rhombohedron
$D_x = 3.418$ Mg m⁻³	0.47 × 0.33 × 0.33 mm
	Clear

Data collection

Huber four-circle diffractom-	424 observed reflections
eter	$[I_{net} > 2.0\sigma(I_{net})]$
$\theta/2\theta$ scans	$R_{int} = 0.041$
Absorption correction:	$\theta_{max} = 22.45°$
empirical using ψ scans	$h = -11 \rightarrow 12$
(North, Phillips &	$k = 0 \rightarrow 14$
Mathews, 1968)	$l = 0 \rightarrow 9$
$T_{min} = 0.105$, $T_{max} =$	3 standard reflections
0.260	monitored every 97
481 measured reflections	reflections
428 independent reflections	intensity decay: none

Refinement

Refinement on F	Extinction correction:
$R = 0.024$	Larson (1970)
$wR = 0.034$	Extinction coefficient: 6.3 (3)
$S = 1.75$	Atomic scattering factors
424 reflections	from *International Tables*
77 parameters	*for X-ray Crystallography*
$w = 1/\sigma^2(F)$	(1974, Vol. IV, Table
$(\Delta/\sigma)_{max} = 0.009$	2.2B)
$\Delta\rho_{max} = 0.54$ e Å⁻³	
$\Delta\rho_{min} = -0.99$ e Å⁻³	

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\mathring{A}^2$)*

U_{iso} for Li and O. $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for Zn and P.

	x	y	z	U_{eq}/U_{iso}
Zn11	0.45329 (9)	0.13974 (8)	0.08343	0.0143 (8)
Zn12	0.54174 (9)	−0.13951 (8)	−0.08554 (11)	0.0143 (8)
Li21	0.3484 (15)	−0.1273 (17)	0.081 (5)	0.029 (6)
P22	0.65327 (15)	0.12304 (19)	−0.0845 (4)	0.0118 (15)
P31	0.1976 (2)	−0.01292 (17)	0.0844 (4)	0.0123 (19)
Li32	0.6459 (13)	0.1202 (12)	0.243 (4)	0.022 (5)
O11	0.5884 (5)	0.1252 (5)	0.0528 (7)	0.0171 (14)
O12	0.4050 (4)	−0.1304 (5)	−0.1092 (7)	0.0169 (14)
O21	0.3136 (5)	−0.0067 (5)	0.0844 (7)	0.0184 (15)
O22	0.6640 (5)	0.0156 (5)	−0.0818 (8)	0.0140 (15)
O31	0.5573 (5)	0.1136 (5)	0.4159 (7)	0.0185 (14)
O32	0.4605 (4)	0.2038 (5)	0.2795 (7)	0.0153 (14)
O41	0.5925 (5)	0.1278 (5)	−0.2235 (7)	0.0171 (15)
O42	0.4521 (5)	0.2259 (5)	−0.0836 (6)	0.0147 (13)

Table 2. *Selected geometric parameters ($\mathring{A}$, °)*

Zn11—O11	1.968 (6)	P22—O11	1.538 (7)
Zn11—O21	1.951 (6)	P22—O22	1.543 (6)
Zn11—O32	1.967 (6)	P22—O41	1.531 (7)
Zn11—O42	1.925 (6)	P22—O42ⁱᵛ	1.541 (3)
Zn12—O12	1.940 (5)	P31—O12ⁱⁱⁱ	1.534 (6)
Zn12—O22	1.930 (6)	P31—O21	1.541 (6)
Zn12—O31ⁱ	1.936 (11)	P31—O31ˣ	1.552 (13)
Zn12—O41ⁱⁱ	1.962 (9)	P31—O32ˣ	1.545 (6)
Li21—O12	1.90 (4)	Li32—O11	1.91 (4)
Li21—O21	1.925 (19)	Li32—O22ⁱⁱ	1.93 (2)
Li21—O41ⁱⁱⁱ	1.92 (2)	Li32—O31	1.96 (3)
Li21—O42ⁱⁱⁱ	1.95 (4)	Li32—O32ⁱᵛ	1.989 (16)
O11—Zn11—O21	112.4 (3)	O11—P22—O22	109.5 (4)
O11—Zn11—O32	109.4 (2)	O11—P22—O41	110.0 (3)
O11—Zn11—O42	104.1 (2)	O11—P22—O42ⁱᵛ	109.9 (5)
O21—Zn11—O32	104.9 (2)	O22—P22—O41	111.3 (4)

O21—Zn11—O42	109.0 (3)	O22—P22—O42^{iv}	107.5 (6)
O32—Zn11—O42	117.3 (2)	O41—P22—O42^{iv}	108.7 (4)
O12—Zn12—O22	105.2 (2)	O12^{iii}—P31—O21	110.5 (6)
O12—Zn12—O31^{i}	108.2 (3)	O12^{iii}—P31—O31^{v}	108.6 (5)
O12—Zn12—O41^{iii}	108.4 (4)	O12^{iii}—P31—O32^{v}	110.4 (3)
O22—Zn12—O31^{i}	112.2 (2)	O21—P31—O31^{v}	107.6 (4)
O22—Zn12—O41^{iii}	106.1 (3)	O21—P31—O32^{v}	110.0 (5)
O31^{i}—Zn12—O41^{iii}	116.0 (5)	O31^{v}—P31—O32^{v}	109.7 (6)
O12—Li21—O21	107.9 (18)	O11—Li32—O22^{ii}	106.8 (15)
O12—Li21—O41^{iii}	110.2 (16)	O11—Li32—O31	118.3 (8)
O12—Li21—O42^{iii}	117.5 (9)	O11—Li32—O32^{iv}	111.6 (14)
O21—Li21—O41^{iii}	102.2 (9)	O22^{ii}—Li32—O31	104.2 (14)
O21—Li21—O42^{iii}	111.3 (17)	O22^{ii}—Li32—O32^{iv}	112.6 (9)
O41^{iii}—Li21—O42^{iii}	106.6 (18)	O31—Li32—O32^{iv}	103.3 (15)

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

A measurement of the second harmonic generation gave a value 0.9 times that of quartz, confirming the non-centrosymmetric nature of the space group.

The structure refinement was based on the model for α-LiGaSiO$_4$. Only the Zn and P atoms were refined anisotropically, as the loss of centrosymmetry led to an unfavorable reflection-to-parameter ratio. The chirality parameter was not refined as the structure deviates only slightly from centrosymmetry.

Data collection: *UCLA CCP* (Strouse, 1991). Cell refinement: *UCLA CCP*. Data reduction: *UCLA CCP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Molecular graphics: *ATOMS* (Dowty, 1994). Software used to prepare material for publication: *NRCVAX*.

We thank V. I. Srdanov for recording the second harmonic generation data.

References

Dowty, E. (1994). *ATOMS. A Computer Program for Displaying Atomic Structures.* Macintosh version 3.1. Shape Software, Kingsport, USA.
Elammari, L. & Elouadi, B. (1989). *Acta Cryst.* C45, 1864–1867.
Elfakir, A., Souron, J. P., Robert, F. & Quarton, M. (1989). *C. R. Acad. Sci. Ser. II*, 309, 199–203.
Feng, P., Bu, X. & Stucky, G. D. (1995). *Angew. Chem.* 34, 1745.
Fleet, M. E. (1987). *Z. Kristallogr.* 180, 63.
Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* 22, 384–387.
Gier, T. E. & Stucky, G. D. (1991). *Nature*, 349, 508.
Harrison, W. T. A., Gier, T. E., Nicol, J. M. & Stucky, G. D. (1995). *J. Solid State Chem.* 114, 249–257.
Jensen, T. R., Norby, P. & Stein, P. (1995). *J. Solid State Chem.* 117, 39–47.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber. Copenhagen: Munksgaard.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.
Strouse, C. E. (1991). *UCLA Crystallographic Computing Package.* Department of Chemistry, UCLA, Los Angeles, California, USA.

NiHP$_5$O$_{14}$ Ultraphosphate

Annett Olbertz,^{a} Dörte Stachel,^{a} Ingrid Svoboda^b and Hartmut Fuess^b

^{a}*Otto-Schott-Institut, Chemische Fakultät, Friedrich-Schiller-Universität Jena, Fraunhoferstrasse 6, 07743 Jena, Germany, and ^{b}Strukturforschung, FB Materialwissenschaft, Technische Hochschule Darmstadt, Petersenstrasse 20, 64287 Darmstadt, Germany. E-mail: de0s@hrzpub.th-darmstadt.de*

Abstract

The structure of the title compound, NiHP$_5$O$_{14}$, is built of two parallel chains interconnected to form a ribbon. The polyphosphate ribbons are coupled by hydrogen bonds.

Comment

The ratio between tetrahedra that are bridged *via* two O atoms (Q^2) and three O atoms (Q^3) is 2:3. These types of double chains and ribbons, respectively, are similar to those in ultraphophates with trivalent cations. Within the ribbons unusual distances are observed for P1—O11 and P5—O14. These bond lengths are long compared with typical values for unbridged O atoms. This can be explained by an additional H atom situated between the O atoms O11 and O14, belonging to Q^2 tetrahedra, and not coordinated to Ni. This assumption was confirmed by a difference Fourier map, which revealed an H atom covalently bonded to O11 and forming a hydrogen bond with O14. The O11$\cdots$O14 and O14$\cdots$H11 distance are 2.412 (1) and 1.402 (1) Å, respectively. The Ni—O distances are in the range 2.031 (2) to 2.080 (2) Å and
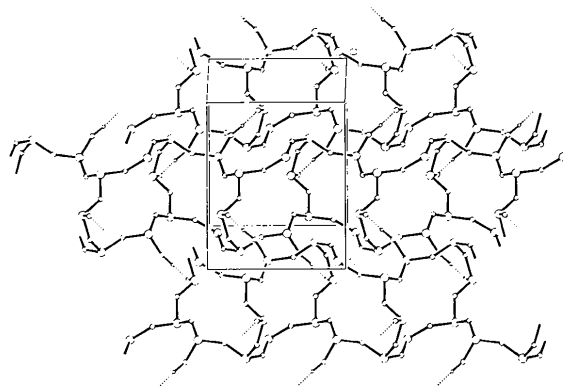

Fig. 1. The structure of NiHP$_5$O$_{14}$ as viewed along [010]. The atoms are drawn as circles of arbitrary radii: P large, O medium and H small. Only the bonding O, P and H atoms are shown.