

Lithium zincopyrophosphate,  
 $\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$ Lina Ji,<sup>a</sup> Hongwei Ma<sup>b\*</sup> and Jingkui Liang<sup>a,c</sup>

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The title compound, dilithium(I) trizinc(II) bis[diphosphate(4−)], is the first quaternary lithium zincopyrophosphate in the Li–Zn–P–O system. It features zigzag chains running along *c*, which are built up from edge-sharing  $[\text{ZnO}_5]$  trigonal bipyramids. One of the two independent Zn sites is fully occupied, whereas the other is statistically disordered by  $\text{Zn}^{2+}$  and  $\text{Li}^+$  cations, although the two Zn sites have similar coordination environments.  $\text{Li}^+$  cations occupy a four-coordinated independent site with an occupancy factor of 0.5, as well as being disordered on the partially occupied five-coordinated Zn site with a  $\text{Zn}^{2+}/\text{Li}^+$  ratio of 1:1.

## Comment

High-quality II–VI semiconductor zinc oxide (ZnO) crystals have various applications in functional devices (Look, 2001; Tsukazaki *et al.*, 2005). Due to the high melting point (2248 K) and serious volatilization of ZnO at high temperature, a suitable flux is needed for growing high-quality ZnO crystals at a lower temperature. The subsolidus phase relations of the ternary system  $A_2\text{O–ZnO–P}_2\text{O}_5$  (*A* = Li, Na or K) were systematically investigated to find such a flux. The title compound,  $\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$ , is a possible new phase in this system and  $\text{Zn}_2\text{P}_2\text{O}_7$  and  $\text{Li}_4\text{P}_2\text{O}_7$  were used for the synthesis. The X-ray powder diffraction pattern was measured on the reaction products and all peaks were indexed using *TREOR* (Werner *et al.*, 1985), with an orthorhombic unit cell *a* = 5.191 (1), *b* = 13.226 (4) and *c* = 16.166 (5) Å [*M*(20) = 17 and *F*(20) = 27], which indicates that the product is a single phase. This unit cell, being in good agreement with that from single-crystal diffraction, is similar but not identical to the cell parameters of  $\gamma\text{-Zn}_2\text{P}_2\text{O}_7$  (Bataille *et al.*, 1998). Also, the measured powder diffraction pattern did not match PDF entry 49–1240 (ICDD, 2004) for  $\gamma\text{-Zn}_2\text{P}_2\text{O}_7$  very well. In addition, the warming, heating and cooling scheme guaranteed that the volatilization of Li, Zn and P was avoided, hence the composition of the product was not significantly different from

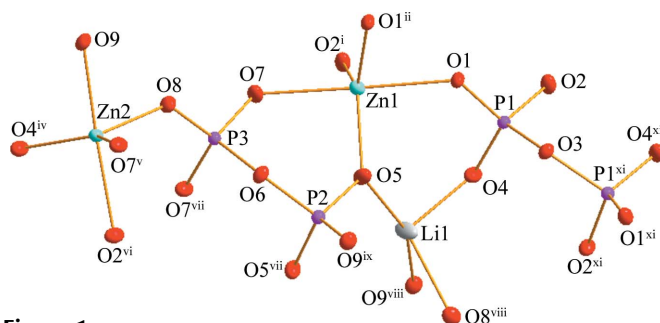
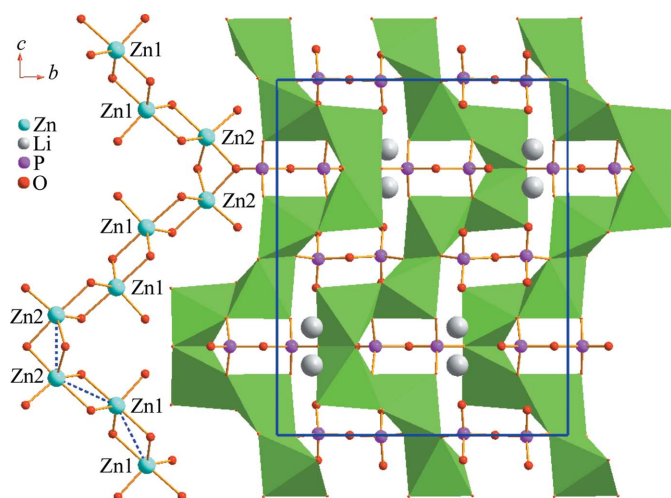


Figure 1

The atom-labelling scheme and coordination environments of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Li cations disordered on the Zn sites have been omitted for clarity. [Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $x - 1, y, -z + \frac{3}{2}$ ; (iv)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (v)  $x + 1, y, -z + \frac{3}{2}$ ; (vi)  $-x + 1, -y + 1, z + \frac{1}{2}$ ; (vii)  $x, y, -z + \frac{3}{2}$ ; (viii)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ix)  $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$ .]

the starting materials. Therefore, the product was believed to be  $\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$  and single-crystal structure analysis was performed to determine the structure and verify this new phase. We hereby report the structure of this compound from single-crystal diffraction analysis.

The title compound has two symmetry-independent sites for Zn atoms. One is fully occupied with a trace amount ( $\sim 0.9\%$ ) of  $\text{Li}^+$  contamination, whereas the other is disordered by  $\text{Zn}^{2+}$  and  $\text{Li}^+$  cations in a  $\text{Zn}^{2+}/\text{Li}^+$  ratio of 1:1. As shown in Fig. 1, Zn atoms are coordinated by five O atoms, three of which are in the equatorial plane, while the other two are in axial positions. For the fully occupied Zn sites, the average Zn–O bond length in the equatorial plane is 1.97 (2) Å, while the average Zn–O distance between Zn and the axial O atoms is 2.16 (1) Å. The corresponding values for the partially occupied Zn site are 2.01 (6) and 2.09 (7) Å, respectively. Two fully occupied Zn1–O trigonal bipyramids are connected by sharing one edge to form a  $[\text{Zn}_2\text{O}_8]$  dimer, and the partially occupied Zn2–O polyhedra build up  $[\text{Zn}_2\text{O}_8]$  dimers in the same fashion (Fig. 2). Fully and partially occupied  $[\text{Zn}_2\text{O}_8]$  dimers share edges alternately to form chains of  $[\text{ZnO}_5]$  trigonal bipyramids running along the *c* axis. The Zn1 $\cdots$ Zn1 interatomic distance between the centres of two adjacent fully occupied  $[\text{ZnO}_5]$  polyhedra is 3.1995 (4) Å, whereas the corresponding Zn2 $\cdots$ Zn2 distance for the partially occupied  $[\text{ZnO}_5]$  polyhedra is 2.857 (1) Å. The Zn1 $\cdots$ Zn2 distance between the centres of neighbouring fully and partially occupied  $[\text{ZnO}_5]$  pyramids is 3.2500 (7) Å. The difference between the Zn1 $\cdots$ Zn1 and Zn2 $\cdots$ Zn2 distances leads to  $\text{Zn}^{2+}/\text{Li}^+$  disordering on the Zn2 site rather than on both Zn1 and Zn2 sites. The shorter Zn2 $\cdots$ Zn2 distance favours lower charges on the Zn2 sites, produced by replacing half of the  $\text{Zn}^{2+}$  cations with the same number of  $\text{Li}^+$  cations, whereas the Zn1 site needs a fully occupied  $\text{Zn}^{2+}$  ion to stabilize the structure. The infinite chains are crosslinked by sharing tetrahedra vertices with  $[\text{P}_2\text{O}_7]^{4-}$  pyrophosphate groups to build up the three-dimensional framework structure of  $\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$  (Fig. 2). Half of the  $\text{Li}^+$  cations are disordered with  $\text{Zn}^{2+}$  on the partially occupied Zn2 positions and the other half are situated in the interstitial positions of the framework, with an occupancy



**Figure 2**  
The structure of the title compound viewed along  $a$ , showing the chains of  $[\text{ZnO}_5]$  trigonal bipyramids and the linkage of the polyhedra. Generic labels are used to depict symmetry-related positions of atoms Zn1 and Zn2.

factor of 0.5, coordinated by four O atoms, with an average Li–O distance of 2.0 (1) Å.

The basic structural features of the title compound are very similar to those of  $\gamma\text{-Zn}_2(\text{P}_2\text{O}_7)$  (Bataille *et al.*, 1998). The latter compound also consists of infinite corrugated chains of Zn–O trigonal bipyramids running along  $c$ , which are cross-linked by pyrophosphate groups to form the crystal structure. The title compound is essentially an Li-doped variant of  $\gamma\text{-Zn}_2(\text{P}_2\text{O}_7)$ . The  $\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$  phase can be derived from  $\gamma\text{-Zn}_2(\text{P}_2\text{O}_7)$  by replacing half of the  $\text{Zn}^{2+}$  cations on one of the two symmetry-independent Zn sites with  $\text{Li}^+$  cations, and by doping the same number of  $\text{Li}^+$  cations in the interstitial positions of the structure to balance the net charge due to  $\text{Zn}^{2+}\text{-Li}^+$  substitution. Similar to the title compound, the Zn···Zn distances in the  $\gamma\text{-Zn}_2(\text{P}_2\text{O}_7)$  structure also fall into two groups, *viz.* 3.084 and 3.242/3.252 Å. The former distance (3.084 Å) is significantly longer than the corresponding distance [2.857 (1) Å] in the title compound, whereas the values in the latter group are comparable with their counterparts in the  $\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$  structure. In the  $\gamma\text{-Zn}_2(\text{P}_2\text{O}_7)$  structure, it is the  $\text{Zn}^{2+}$  cations on the Zn sites involving shorter Zn···Zn distances (3.084 Å) that are partially substituted by  $\text{Li}^+$  cations to form the  $\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$  phase.

The structures of several Li–Zn–P–O quaternary compounds have been reported, examples being  $\alpha\text{-LiZnPO}_4$  (Elammari & Elouadi, 1989),  $\delta_1\text{-LiZnPO}_4$  (Jensen *et al.*, 1995),  $\varepsilon\text{-LiZnPO}_4$  (Bu *et al.*, 1996),  $\text{LiZnPO}_4\text{-CR1}$  (Bu *et al.*, 1998), and  $\alpha\text{-Li}_4\text{Zn}(\text{PO}_4)_2$  and  $\beta\text{-Li}_4\text{Zn}(\text{PO}_4)_2$  (Jensen *et al.*, 2002). All these compounds are orthophosphates and all the Zn atoms in these structures are tetrahedrally coordinated by O atoms, with an average Zn–O distance of 1.95 (1) Å. This indicates that the  $\text{Zn}^{2+}$  cation has a strong preference for tetrahedral coordination in the Li–Zn–P–O system. However, under the conditions reported in this paper, the  $\text{Zn}^{2+}$  cations are coordinated by five O atoms to form trigonal bipyramids, and these polyhedra build up infinite chains by sharing edges.

Pyrophosphate groups,  $[\text{P}_2\text{O}_7]^{4-}$ , rather than orthophosphate groups,  $[\text{PO}_4]^{3-}$ , are observed in the structure and crosslink the chains of  $[\text{ZnO}_5]$  trigonal bipyramids.

The  $\text{Li}^+$  cations in all the reported structures are tetrahedrally coordinated by four O atoms, whether they are situated in the walls of channels ( $\varepsilon\text{-LiZnPO}_4$ ), in negatively charged cages ( $\text{LiZnPO}_4\text{-CR1}$ ), or disordered with  $\text{Zn}^{2+}$  cations to a minor degree [ $\delta_1\text{-LiZnPO}_4$ ,  $\alpha\text{-Li}_4\text{Zn}(\text{PO}_4)_2$  and  $\beta\text{-Li}_4\text{Zn}(\text{PO}_4)_2$ ]. In contrast, the coordination of the  $\text{Li}^+$  cations in the title compound is rather complicated. The interstitial  $\text{Li}^+$  cations are tetrahedrally coordinated, whereas the  $\text{Li}^+$  cations disordered on the Zn sites are five-coordinated. Due to the similarity in the coordination radii of  $\text{Li}^+$  and  $\text{Zn}^{2+}$  cations (Shannon, 1976), statistical disorder of  $\text{Li}^+$  and  $\text{Zn}^{2+}$  is possible in principle. In fact, the mean Li–O and Zn–O distances calculated from the reported Li–Zn–P–O compounds are 1.97 (5) and 1.95 (1) Å, respectively. A minor degree of disorder was proposed in  $\beta\text{-Li}_4\text{Zn}(\text{PO}_4)_2$  (prepared from supercritical water at 875 K) and  $\delta_1\text{-LiZnPO}_4$  (obtained from solution at 365 K), but in the compounds synthesized by high-temperature solid-state reactions at 973–1275 K, a much higher degree of  $\text{Li}^+/\text{Zn}^{2+}$  statistical disorder ( $\text{Li}^+/\text{Zn}^{2+} = 1:1$ ) was reported in compounds such as  $\text{NaLiZnP}_2\text{O}_7$  (Shepelev *et al.*, 2005). Similarly, the title compound was prepared at 1123 K and a consequent 1:1  $\text{Li}^+/\text{Zn}^{2+}$  disorder is found. All  $\text{Li}^+$  cations in  $\text{NaLiZnP}_2\text{O}_7$  are disordered with  $\text{Zn}^{2+}$  cations, but only half of the  $\text{Li}^+$  cations in the title compound are disordered on the  $\text{Zn}^{2+}$  sites.

## Experimental

Pure  $\text{Zn}_2\text{P}_2\text{O}_7$  and  $\text{Li}_4\text{P}_2\text{O}_7$  were first prepared from analytically pure ZnO,  $\text{Li}_2\text{CO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ .  $\text{Zn}_2\text{P}_2\text{O}_7$  was synthesized from ZnO and  $\text{NH}_4\text{H}_2\text{PO}_4$ . The starting materials were first mixed in a molar ratio of 1:1, ground in an agate mortar and warmed at 773 K for 10 h. The powders were then pressed into a 1–2 mm thick pellet (diameter of around 12 mm), heated to 1173 K and sintered at this temperature for 48 h.  $\text{Li}_4\text{P}_2\text{O}_7$  was obtained in a similar manner by mixing  $\text{Li}_2\text{CO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  in a 2:1 molar ratio, but the sintering temperature and time were 1073 K and 96 h, respectively. These two compounds were then weighed and mixed in a molar ratio of 3:1 and ground in an agate mortar. The mixture was heated to 1193 K in a platinum crucible and held at this temperature for 30 min to make the melt homogeneous. The melt was then cooled to 1093 K at a rate of 1 K  $\text{h}^{-1}$ , followed by cooling to 693 K at a rate of 20 K  $\text{h}^{-1}$ , and finally quenching to room temperature by switching off the furnace. A suitable single crystal of size  $0.30 \times 0.28 \times 0.25$  mm was selected and mounted on a glass fibre for structure determination, and the remaining products were ground into a powder for phase identification by X-ray powder diffraction and for physical property measurements such as second harmonic generation (SHG). No observable SHG signal was detected.

### Crystal data

$\text{Li}_2\text{Zn}_3(\text{P}_2\text{O}_7)_2$	$V = 1098.48$ (11) Å <sup>3</sup>
$M_r = 557.87$	$Z = 4$
Orthorhombic, $Pbcm$	Mo $K\alpha$ radiation
$a = 5.1733$ (3) Å	$\mu = 7.17$ mm <sup>−1</sup>
$b = 13.1797$ (7) Å	$T = 298$ K
$c = 16.1108$ (9) Å	$0.30 \times 0.28 \times 0.25$ mm

**Table 1**  
Selected bond lengths (Å).

Zn1—O1	2.1532 (11)	Li2—O2 <sup>iii</sup>	1.958 (14)
Zn1—O1 <sup>i</sup>	1.9935 (11)	Li2—O4 <sup>iv</sup>	1.942 (15)
Zn1—O2 <sup>ii</sup>	1.9799 (11)	Li2—O7 <sup>v</sup>	1.876 (15)
Zn1—O5	1.9401 (11)	Li2—O9	2.257 (12)
Zn1—O7	2.1796 (11)	Li2—O8	2.381 (14)
Zn2—O2 <sup>iii</sup>	2.1694 (13)	Li1—O4	1.944 (8)
Zn2—O4 <sup>iv</sup>	1.9402 (14)	Li1—O5	1.929 (7)
Zn2—O7 <sup>v</sup>	2.0883 (14)	Li1—O9 <sup>vi</sup>	1.975 (7)
Zn2—O8	2.0230 (12)	Li1—O8 <sup>vi</sup>	2.180 (9)
Zn2—O9	2.0132 (12)		

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

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.115, T_{\max} = 0.165$

9756 measured reflections  
2135 independent reflections  
1994 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.022$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$   
 $wR(F^2) = 0.063$   
 $S = 1.05$   
2135 reflections

126 parameters  
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.46 \text{ e } \text{Å}^{-3}$

Refinement of the site-occupancy factors of Zn1 and Zn2 shows that the Zn1 site is contaminated with a trace amount (~0.9%) of Li<sup>+</sup> and the Zn2 site is statistically disordered by Li<sup>+</sup> and Zn<sup>2+</sup> in a Zn<sup>2+</sup>/Li<sup>+</sup> ratio of around 1:1. The refined site-occupancy factor of Li1 is also around 0.5. These refined values agree well with the expected composition of the title compound. In the final refinement, the site-occupancy factors of Zn1, Zn2, Li1 and Li2 were fixed due to the weak scattering power and partial occupancy of the Li<sup>+</sup> cations. A

small change in the Li<sup>+</sup> occupancy factor does not affect the structure features or refinement results significantly.

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: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3007). Services for accessing these data are described at the back of the journal.

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