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Dilithium barium diphosphate

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The crystal structure of the novel title diphosphate, $Li_2BaP_2O_7$, exists with a three-dimensional lattice composed of BaO_9 polyhedra linked to corner- and edge-sharing P_2O_7 diphosphate groups, forming layers parallel to the (010) plane, the layers being linked by P—O—Ba bridges. Tunnels thus created between the layers are occupied by Li^+ cations, two of which lie on twofold axes.

Comment

In recent years, structures of the formulation $A^{I}{}_2B^{II}P_2O_7$ (with $A^{I} = Li^+$, Na^+ or K^+, and where B^{II} is a bivalent ion; Spirlet *et al.*, 1993; Laligant, 1992*a*,*b*; Liebertz & Stahr, 1983; Huang & Hwu, 1998; Erragh *et al.*, 1991, 1995, 1998; Belharouak *et al.*, 2000; Dridi *et al.*, 2000; Bennazha *et al.*, 1999; El Maadi *et al.*, 1994, 1995*a*,*b*; Trunov *et al.*, 1991; Faggiani & Calvo, 1976) have been the object of structural investigation as single crystals. Except for $Na_2PdP_2O_7$ (Laligant, 1992*a*) and β-$Na_2CuP_2O_7$ (Erragh *et al.*, 1995), which crystallize with similar cell dimensions in space group *C*2/*c*, there are no isotypical relationships within the group. However, few of these structures exist with $A^{I} = Li^+$. Only the structures of $Li_2CuP_2O_7$ (Spirlet *et al.*, 1993) and $Li_2PdP_2O_7$ (Laligant, 1992*b*) have been reported in the literature with full structural details. $Li_2BaP_2O_7$ was first reported by Liebertz & Stahr (1983), who described the chemical preparation of the material. From precession photographs, they observed the systematic absences *hkl* with $h + k = 2n$ and *h*0*l* with $l = 2n$, and thus reported the cell parameters $a = 7.078$ (4), $b = 12.164$ (6) and $c = 13.856$ (6) Å, and space group *Cmcm* with $Z = 8$, for this compound. Neither positional parameters nor an *R* factor were published.

In this paper, we describe the synthesis and solid-state crystal structure redetermination of $Li_2BaP_2O_7$, a member of this little-known family of lithium-containing materials. We have refined the structure in monoclinic space group *C*2/*c* with $\beta = 90.49$ (7)°. Both the previously reported orthorhombic space group and *C*2/*c* share the same absences. Accommodating $Li_2BaP_2O_7$ with $Z = 8$ in space group *Cmcm* with $Z = 16$ requires the placing of Ba and the P_2O_7 group on a mirror, twofold or $\overline{1}$ symmetry element. A projection view of the P_2O_7 group refined in *C*2/*c* shows it to be staggered, with P1—O14—P2 = 123.3 (4)° and O—P···P—O torsion angles averaging 28.97°, significantly distorted from eclipsed (O—P···P—O = 0°) or ideally staggered symmetry (O—P···P—O = 60°), and thus the phosphate O atoms are not refinable except as disordered positions in orthorhombic space group *Cmcm*.

A projection view of $Li_2BaP_2O_7$ on to the (100) plane is shown in Fig. 1. The structure may be regarded as a three-dimensional packing of BaO_9 polyhedra sharing edges and corners with P_2O_7 diphosphate groups and thus forming layers parallel to [010], which are held together by P2—O21—Ba bridges. This arrangement gives rise to tunnels within the layers. The Li^+ cations are located in these tunnels.

The coordination sphere of the Ba^{2+} cations is composed of nine O^{2-} anions in an irregular geometry, located at Ba—O distances of between 2.714 (7) and 3.132 (8) Å. Each BaO_9 polyhedron is surrounded by nine PO_4 tetrahedra belonging to five different P_2O_7 groups. These values are comparable with those observed in various barium phosphate compounds, such as $CdBaP_2O_7$, $BaCuP_2O_7$ and σ-$Ba_2P_2O_7$ (Moqine *et al.*, 1991; Alaoui ElBelghiti *et al.*, 1991, 1995). Bond-valence

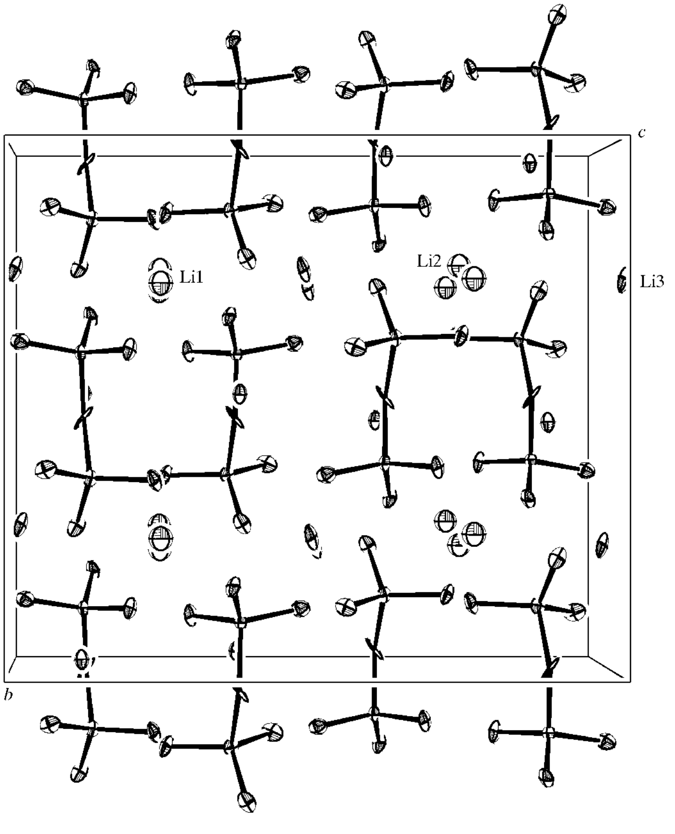

Figure 1
A projection view of $Li_2BaP_2O_7$ on to the (100) plane. Displacement ellipsoids are shown at the 50% probability level.

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calculations (Brown, 1981) show a total effective cationic charge of 1.877 for Ba^{+2} in this environment.

The Li^+ ions are seen in three different sites. Atom Li1, on a twofold axis, is surrounded by six O atoms in a distorted octahedral geometry, with an average Li1—O distance of 2.26 (2) Å. Atom Li2, also on a twofold axis, displays tetrahedral geometry, with an average Li2—O distance of 1.98 (2) Å. Atom Li3, in a general position, has five O-atom neighbors at distances in the range 1.932 (15)–2.41 (2) Å, with an average Li3—O distance of 2.10 (2) Å.

Bond-valence calculations total 0.849, 0.989 and 0.975 for Li1, Li2 and Li3, respectively. Bond-valence calculations which reveal an effective charge significantly less than the theoretical ionic charge frequently signal ion mobility in the site. Support for this point of view comes from the obvious elongation of the displacement ellipsoid of Li3 in the direction of the tunnel parallel to the (100) direction. On this basis, $Li_2BaP_2O_7$ may be suspected to have potentially exploitable physical properties, such as conductivity (Ba and Li1) and luminescence (with doping of small quantities of Ln^{3+} into the non-centrosymmetric Ba^{2+} site).

Experimental

Crystals of $Li_2BaP_2O_7$ were prepared by fusion of Li_2CO_3, $BaCO_3$ and $NH_4H_2PO_4$ in the proportions 1:1:2. The mixture was heated slowly to the fusion temperature (1100 K), was maintained at this temperature for 2 h and was then cooled slowly (5 K h^{-1}) to 650 K; the furnace power was then switched off. Single crystals of $Li_2BaP_2O_7$ were obtained.

Crystal data

$Li_2BaP_2O_7$
$M_r = 325.16$
Monoclinic, $C2/c$
$a = 7.147$ (8) Å
$b = 12.283$ (14) Å
$c = 14.016$ (16) Å
$\beta = 90.49$ (7)°
$V = 1230$ (2) Å^3
$Z = 8$

$D_x = 3.511$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 6.4$–10.5°
$\mu = 6.96$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, colorless
0.1 × 0.1 × 0.1 mm

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1991)
$T_{min} = 0.447$, $T_{max} = 0.499$
2324 measured reflections
1355 independent reflections
1231 reflections with $I > 2\sigma(I)$

$R_{int} = 0.091$
$\theta_{max} = 30°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -19 \rightarrow 19$
3 standard reflections every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.062$
$wR(F^2) = 0.189$
$S = 1.49$
1355 reflections
111 parameters

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.06$ e Å^{-3}
$\Delta\rho_{min} = -0.09$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ba1—O13^{i}	2.714 (7)	P2—O21	1.527 (7)
Ba1—O12^{ii}	2.747 (7)	P2—O23	1.542 (6)
Ba1—O23^{i}	2.788 (7)	P2—O14	1.656 (7)
Ba1—O22^{ii}	2.842 (8)	Li1—O13^{i}	2.05 (2)
Ba1—O22^{iii}	2.886 (7)	Li1—O21^{iv}	2.116 (10)
Ba1—O11	2.924 (7)	Li1—O23^{v}	2.61 (2)
Ba1—O14	2.957 (7)	Li2—O11^{vi}	1.966 (15)
Ba1—O13^{iii}	2.965 (6)	Li2—O23^{vii}	2.002 (17)
Ba1—O21^{iv}	3.132 (8)	Li3—O21^{iv}	1.932 (15)
P1—O12	1.526 (7)	Li3—O22^{ii}	2.00 (2)
P1—O11	1.530 (6)	Li3—O12^{iii}	2.066 (16)
P1—O13	1.538 (5)	Li3—O11^{viii}	2.101 (16)
P1—O14	1.647 (7)	Li3—O12^{viii}	2.41 (2)
P2—O22	1.522 (6)		
O12—P1—O11	110.5 (4)	O22—P2—O23	114.4 (4)
O12—P1—O13	112.6 (3)	O21—P2—O23	110.8 (4)
O11—P1—O13	115.8 (4)	O22—P2—O14	103.6 (4)
O12—P1—O14	109.2 (4)	O21—P2—O14	105.0 (3)
O11—P1—O14	101.5 (4)	O23—P2—O14	106.0 (4)
O13—P1—O14	106.4 (4)	P1—O14—P2	123.3 (4)
O22—P2—O21	115.9 (4)		

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

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1355). Services for accessing these data are described at the back of the journal.

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