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Crystal Structure of $LiPbPO_4$ with "Li_4O_{13}" Cluster

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The structure of $LiPbPO_4$ was solved at 173 K in the orthorhombic space group $Pna2_1$ and unit cell parameters a = 7.969(3), b = 18.591(5), and c = 4.926(1) Å, V = 730(1)Å^3, $F(000)$ = 1056, μ = 469 cm^{-1}, D_m = 5.55 g · cm^{-3}, D_c = 5.63 g · cm^{-3}, and Z = 8. The structure was refined to a final R = 0.0295 for 1872 independent reflections. It consists of PO_4 and LiO_4 distorted tetrahedra which are linked together in such a way that wide tunnels are formed where the lead cations are located.

1. Introduction

Most of the mixed orthophosphates with the formula $A^IB^{II}PO_4$ (A^I = monovalent cation, B^{II} = divalent cation) undergo phase transitions between room temperature and the melting point (*1–4*). Furthermore, ferroic properties have been recognized in some of these compounds (*2–5*). The present work on $LiPbPO_4$ is part of our broad program on crystal structure investigations, carried out in order to establish the structural filiations of this phosphate family and, consequently, to understand the origin of their transitions and ferroic properties. Single crystals of $LiPbPO_4$ were grown for the first time by Brixner and Foris ((*6*), see also (*7*)) who reported the unit cell parameters but did not determine the crystal structure. We report here the crystal structure of this compound.

2. Experimental

$LiPbPO_4$ single crystals were grown according to the method reported by Brixner and Foris (*6*). A suitable transparent single crystal (0.17 × 0.07 × 0.05 mm) was selected to record Weissenberg and precession photographs which showed orthorhombic symmetry with the reflection conditions $h0l$: $h = 2n$ ($h00$: $h = 2n$); $0kl$: $k + l = 2n$, ($0k0$: $k = 2n$) and ($00l$: $l = 2n$). These conditions are compatible with both space groups $Pna2_1$ and $Pnam$. Centering 25 independent reflections, the lattice parameters were refined to the following values: a = 7.969(3), b = 18.591(5), and c = 4.926(1) Å.

Reflections (8494) were collected (ω-scan) for $4.5° \leq 2\theta 60°$, $-12 \leq h \leq 12$, $-27 \leq k \leq 27$, $-7 \leq l \leq 7$ on an automated Syntex-Diffractometer R3 using

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graphite monochromatized Mo$K\alpha$ radiation (λ = 0.7107 Å). Two reflections (200) and (004) were measured periodically after every 200 reflections in order to control the stability of the intensity during the period of the data collection; no significant change was observed. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was made using "azimuthal data" (ψ-scan). Unique reflections (2123) were obtained after merging ($R_{\mathrm{int.}}$ = 0.0329).

The structure was solved using Patterson methods with 1872 independent reflections for which $I \geq 3\sigma$ (I). Statistical tests and a positive second harmonic generation signal favored strongly $Pna2_1$ over $Pnam$. Therefore, the former space group was used and this choice was confirmed by the successful refinement. Scattering factors for neutral atoms, including f' and f'' terms, were used from "International Tables for X-ray crystallography" (*8*). Oxygen and lithium atoms were localized after several least-squares cycles with isotropic displacement parameters and calculation of difference Fourier maps with the SHELXTL program (*9*); the R value was then 0.0503. The introduction of anisotropic displacement parameters reduced this value further to 0.0295 for 1872 independent reflections; $R(w)$ = 0.0270 with $w = (\sigma^2(F_o) + 0.0001\ F_o^2)^{-1}$.[1] extinction was corrected by an empirical parameter according to (*9*). Final atomic coordinates and displacement parameter coefficients are listed in Tables I and II, respectively. Bond lengths and bond angles are reported in Table III.

TABLE I

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS (Å^2)

Atom	x	y	z	U^a
Pb(1)	1742(1)	5539(1)	2500(0)	16(1)
Pb(2)	299(1)	7718(1)	2305(2)	18(1)
P(1)	2114(3)	6796(2)	6924(6)	14(1)
P(2)	−2673(4)	5715(2)	1950(7)	15(1)
O(1)	2297(11)	7578(5)	5770(17)	17(2)
O(2)	553(10)	6460(5)	5570(20)	20(3)
O(3)	1907(11)	6825(5)	10000(21)	23(3)
O(4)	3636(11)	6347(5)	6165(18)	18(2)
O(5)	−2833(10)	5735(5)	5062(18)	15(2)
O(6)	−4158(11)	5331(5)	658(18)	18(2)
O(7)	−1035(10)	5264(5)	1156(18)	18(2)
O(8)	−2474(12)	6482(4)	802(18)	17(2)
Li(1)	−94(22)	10575(10)	1945(43)	17(4)
Li(2)	−1787(21)	6520(9)	6873(36)	12(4)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

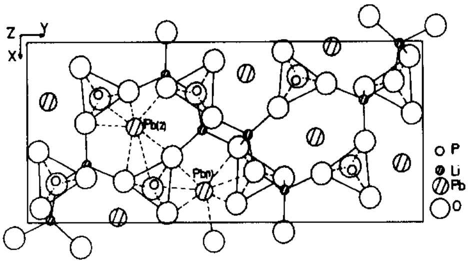

FIG. 1. The projection of $LiPbPO_4$ structure onto (001) showing PO_4 and LiO_4 tetrahedra and a tunnel where Pb atoms are located.

3. Discussion

Figure 1 shows the projection of crystal structure along [001]. The structure consists of almost regular PO_4 tetrahedra, with the P atoms off center giving nonequal P–O distances and O–P–O angles. These PO_4 are linked to distorted LiO_4 tetrahedra via common corners. LiO_4 shares its four corners with PO_4 but PO_4 shares only three corners. The heavy distortion of the polyhedra becomes noticeable by inspection of the bond lengths and angles listed in Table III. The arrangement of PO_4 and LiO_4 tetrahedra results in the formation of large tun-

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[1] F_{ON}–F_{C} to be deposited with NAPS. See NAPS Document No. 04607 for 13 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

TABLE II

ANISOTROPIC TEMPERATURE FACTORS (Å^2 × 10^3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	17(1)	15(1)	16(1)	−0(1)	1(1)	0(1)
Pb(2)	17(1)	19(1)	17(1)	−0(1)	−1(1)	2(1)
P(1)	15(1)	14(1)	15(2)	−0(1)	0(1)	−1(1)
P(2)	15(1)	14(1)	15(2)	−0(1)	2(1)	2(1)
O(1)	21(4)	14(4)	15(4)	1(3)	−3(3)	−6(3)
O(2)	12(4)	21(5)	27(5)	−2(4)	3(3)	−0(3)
O(3)	19(4)	24(5)	26(5)	−2(4)	3(3)	−1(4)
O(4)	20(4)	18(4)	18(4)	−0(3)	−2(3)	11(3)
O(5)	10(3)	15(4)	21(4)	4(3)	−2(3)	−5(3)
O(6)	21(4)	16(4)	16(4)	−2(3)	1(3)	−1(3)
O(7)	10(3)	18(4)	25(4)	−9(3)	−1(3)	5(3)
O(8)	26(4)	10(4)	17(4)	1(3)	−1(3)	2(3)

Note. The anisotropic temperature factor exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \ldots + 2hka^*b^*U_{12})$.

nels running along [100] and [001]. The two symmetrically independent lead cations are located at the intersection of the two tunnels (coordination number seven). The LiO_4 tetrahedra share one (Li(2)) or two (Li(1)) O atoms and build a cluster "Li_4O_{13}" with Li . . . Li distances varying in the range 2.993 to 3.299 Å (see Fig. 2). $LiPbPO_4$ is the first compound in the $A^{I}B^{II}PO_4$ family with such a cluster. The lead polyhedra are also heavily distorted with Pb–O distances varying between 2.349 and 3.053 Å. For each Pb cation three Pb–O bonds are conspicuously shortened and the four remaining ones seem to be more in accordance with a big cation-like Pb. Clearly the observed distortion around Pb is due to the well-known $6s^2$ lone pair effect of this atomic species. The lead polyhedra can be described as being formed by four almost coplanar atoms at $z \approx 0.56$ and three others, also coplanar at $z \approx 0$ (see Table I).

The structure of $LiPbPO_4$ is different from all other $A^{I}B^{II}PO_4$ structures known so

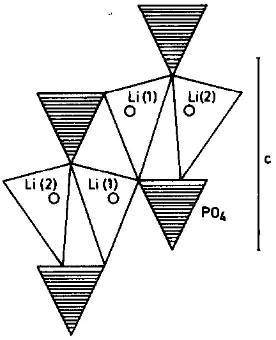

FIG. 2. Schematic drawing of the "Li_4O_{13}" cluster, viewed approximately along [210]. Empty and latched triangles represent LiO_4 and PO_4 tetrahedra, respectively.

TABLE III

BOND LENGTHS (Å) AND BOND ANGLES (°) OF DIFFERENT POLYHEDRA

	$P(1)O_4$ tetrahedron		
P(1)–O(1)	1.567(9)	O(1)–P(1)–O(2)	107.1(5)
P(1)–O(2)	1.544(9)	O(1)–P(1)–O(3)	109.8(5)
P(1)–O(3)	1.525(11)	O(1)–P(1)–O(4)	110.3(5)
P(1)–O(4)	1.519(9)	O(2)–P(1)–O(3)	110.8(5)
		O(2)–P(1)–O(4)	108.3(5)
		O(3)–P(1)–O(4)	110.5(5)
	$P(2)O_4$ tetrahedron		
P(2)–O(5)	1.539(10)	O(5)–P(2)–O(6)	111.3(5)
P(2)–O(6)	1.522(9)	O(5)–P(2)–O(7)	108.9(5)
P(2)–O(7)	1.600(9)	O(5)–P(2)–O(8)	110.6(5)
P(2)–O(8)	1.541(9)	O(6)–P(2)–O(7)	106.6(5)
		O(6)–P(2)–O(8)	111.1(5)
		O(7)–P(2)–O(8)	108.1(5)
	$Li(1)O_4$ tetrahedron		
Li(1)–O(4a)	1.887(20)	O(4a)–Li(1)–O(5a)	108.3(10)
Li(1)–O(5a)	1.918(20)	O(4a)–Li(1)–O(6a)	123.3(11)
Li(1)–O(6a)	1.976(22)	O(4a)–Li(1)–O(6b)	110.8(10)
Li(1)–O(6b)	1.947(20)	O(5a)–Li(1)–O(6a)	102.9(9)
		O(5a)–Li(1)–O(6b)	107.9(10)
		O(6a)–Li(1)–O(6b)	102.6(9)
	$Li(2)O_4$ tetrahedron		
Li(2)–O(1a)	1.908(19)	O(2)–Li(2)–O(1a)	108.6(9)
Li(2)–O(2)	1.975(19)	O(2)–Li(2)–O(5)	102.6(9)
Li(2)–O(5)	1.903(19)	O(2)–Li(2)–O(8a)	124.6(9)
Li(2)–O(8a)	2.013(20)	O(5)–Li(2)–O(1a)	111.9(9)
		O(5)–Li(2)–O(8a)	107.7(9)
		O(1a)–Li(2)–O(8a)	101.6(9)
	Pb–O distances		
Pb(1)–O(2)	2.475(9)	Pb(2)–O(1)	2.334(9)
Pb(1)–O(3a)	2.693(10)	Pb(2)–O(1a)	2.990(9)
Pb(1)–O(4)	2.792(9)	Pb(2)–O(2)	2.845(9)
Pb(1)–O(5b)	2.794(9)	Pb(2)–O(3a)	2.385(10)
Pb(1)–O(6c)	2.956(9)	Pb(2)–O(3b)	3.053(9)
Pb(1)–O(7)	2.366(8)	Pb(2)–O(4b)	2.897(9)
Pb(1)–O(7a)	2.406(9)	Pb(2)–O(8b)	2.431(9)

far. Its peculiarities seem to be due to the presence of Pb atoms with the polarizable $6s^2$ lone pair. The space group of $LiPbPO_4$ is a polar one and one might expect interesting pyroelectric properties. Due to the atomic arrangement in this structure it can be believed that switching of the spontaneous polarization vector requires such important atomic displacements that it could not be achieved experimentally without disrupting the crystal structure. The value of polarization can be estimated from the positional parameters assuming full ionization of the atoms (Li^+, Pb^{2+}, P^{5+}, O^{2-}) and using the relation $P = V^{-1} \Sigma q_i z_i = 0.486 \text{ C} \cdot \text{m}^{-2}$ where V is the unit cell volume, q_i the electric charge, and z_i the positional parameter in the polar direction. The summation is taken over all atoms in the unit cell.

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