

Complex Palladium Oxides. V. Crystal Structure of $\text{LiBiPd}_2\text{O}_4$: An Example of Three Different Fourfold Coordinations of Cations*

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The crystal structure of $\text{LiBiPd}_2\text{O}_4$ has been determined from X-ray powder diffraction data. This compound is tetragonal [space group $P4/nmm$ (No. 129) ($Z = 2$)] with $a = 6.9109(2)$ Å, $c = 4.3557(2)$ Å. The structure was solved ab initio from the X-ray powder data by direct methods and refined by the Rietveld profile technique. $\text{LiBiPd}_2\text{O}_4$ exhibits a completely new three-dimensional structure type with Li^+ , Bi^{3+} , and Pd^{2+} in tetrahedral, square pyramidal, and square planar coordinations, respectively. Oxygen atoms draw a $[4.8^2]$ plane net. The role of the lone pair is investigated and the subnetwork of Pd square planes is compared to corresponding ones in other structures. © 1989 Academic Press, Inc.

Introduction

Recent improvements in the techniques of ab initio structure determination from powder diffraction data [(1) and references therein] provide new opportunities to increase the knowledge of inorganic materials. This is particularly interesting for oxides whose crystal growth is often very difficult. It is the case of palladium oxides for which we have undertaken a general survey (2–5), in order to characterize the by-products which can appear during the synthesis of palladium substituted high- T_c superconductors. We describe here the structure of $\text{LiBiPd}_2\text{O}_4$.

Experimental

$\text{LiBiPd}_2\text{O}_4$ was obtained from elementary oxides as a black powder according to the following reaction:

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This mixture was heated in a silica crucible for 18 hr at 550°C, and then for 7 hr at 700°C.

The X-ray diffractograms used for the structure determination were recorded on a Siemens D501 diffractometer with back-monochromatized $\text{CuK}\alpha$. The sample was passed through a 63- μm sieve, and the method of filling the sample holder described in (6) was used in order to avoid possible preferential orientation.

Data Analysis

The X-ray powder pattern was indexed by the program TREOR (7). A probable tetragonal solution with figures of merit $M(14) = 24.1$, $F(14) = 10.9$ was obtained from the first 14 peaks. The observed reflection conditions are consistent with the space groups $P4/nmm$ (No. 129) and $P4/n$ (No. 85) (Table I).

TABLE I
d SPACINGS OF LiBiPd₂O₄ (INTERNAL STANDARD,
 W), CuK α RADIATION

<i>d</i> _{obs}	<i>d</i> _{calc}	<i>h</i>	<i>k</i>	<i>l</i>	<i>I</i> _{obs}
4.887	4.887	1	1	0	39
4.357	4.356	0	0	1	1
3.685	3.685	1	0	1	2
3.456	3.456	2	0	0	1
3.252	3.252	1	1	1	33
2.707	2.707	2	0	1	100
2.521	2.521	2	1	1	1
2.443	2.443	2	2	0	27
2.181	2.185	3	1	0	22
	2.178	0	0	2	
2.130	2.131	2	2	1	<1
2.078	2.077	1	0	2	<1
2.036	2.036	3	0	1	1
1.989	1.989	1	1	2	9
1.953	1.953	3	1	1	16
1.728	1.728	4	0	0	16
1.627	1.629	3	3	0	28
	1.626	2	2	2	
1.543	1.543	3	1	2	7
1.526	1.526	3	3	1	3
1.456	1.456	4	2	1	28
1.392	1.392	1	1	3	3

Assuming the *4/mmm* Laue symmetry group as first hypothesis, individual intensities were then extracted from the powder patterns by a profile fitting procedure which constrains the angular positions of the reflections to be consistent with the cell parameters. The method used here has been described elsewhere [(1) and refs. therein].

Intensities were converted into structure factor amplitudes and used as input for the SHELX76 program (8) after elimination of the strictly superimposed reflections [h_1k_1l and h_2k_2l with $h_1^2 + k_1^2 = h_2^2 + k_2^2$]. Atomic scattering factors and anomalous-dispersion corrections for Li⁺, Bi³⁺, and Pd²⁺ were taken from "International Tables for X-Ray Crystallography" (9) and for O²⁻ from (10).

Application of the fast automatic centrosymmetric direct methods facilities of the SHELX76 program gave one solution for

the position of bismuth. Successive least-squares refinements of this position and Fourier difference maps enabled the palladium and oxygen sites to be located, and a possible lithium position to be proposed. The final refinement of all the positions gave a conventional *R* value of 0.20.

At this stage, the modified Rietveld method was applied using this structural model. This is necessary because some of the intensities previously obtained are doubtful because of very close overlapping with others.

With anisotropic *B* factors on bismuth and palladium, isotropic *B* value for O²⁻, and fixed *B* value of 2.0 (Å²) for Li⁺, the conventional Rietveld reliability factors dropped to *R*_i = 4.12(%), *R*_p = 9.14(%), *R*_{wp} = 11.48(%). The final atomic coordinates and thermal parameters are reported in Table II, together with the profile parameters. Further refinements with the *P4/n* space group do not improve these results. The observed and calculated patterns are presented in Fig. 1.

Discussion

Figure 2 shows the (0 0 1) projection of the three-dimensional structure of LiBiPd₂O₄. The most striking feature concerns the coordination of the cations. All of them are fourfold coordinated with usual metal oxygen distances (Table III), but in three different ways: tetrahedra for Li⁺, square pyramids for Bi³⁺ [which occupy the top of the pyramid as in the Aurivillius phases (11)], square planes for Pd²⁺.

The three-dimensional network (Fig. 3, top) results from the stacking and the connection along *c* of two types of layers: one with Li and Bi polyhedra at $z = \frac{1}{2}$ (type I), the other only with Pd (type II) at $z = 0$. Layers (I) are built up from corner sharing of Li⁺ tetrahedra with Bi³⁺ square pyramids (Fig. 3, middle). Each tetrahedron is surrounded by four pyramids, and vice versa,

TABLE II
STRUCTURE AND PROFILE PARAMETERS FOR LiBiPd₂O₄

Cell parameters: $a = 6.9109(2)$ Å, $c = 4.3557(2)$ Å					
Space group: $P4/nmm$ (129)					
Volume (Å ³): 208.0(1)					
2θ range (°): 15–145					
Step scan (° 2θ): 0.02					
Time/step (sec): 44					
No. of reflections: 138					
No. of parameters (total): 23					
Zero point (° 2θ): 0.017(2)					
Profile parameters: $U_1 = 0.13(1)$, $V_1 = -0.13(2)$, $W_1 = 0.170(5)$					
for $a = 80$, $l = 39$: $U_2 = -0.14(4)$, $U_2 = 0.32(6)$, $W_2 = 1.36(2)$					
$C = 0.006(2)$, $D = -0.41(9)$					
Reliability factors (%): $R_i = 4.12$, $R_p = 9.14$, $R_{wp} = 11.48$, $R_{exp} = 2.77$					
Atom	Site	x	y	z	B (Å ²)
Bi	2c	$\frac{1}{4}$	$\frac{1}{4}$	0.4956(5)	0.28(1)
		$\beta_{11}: 209(14)$, $\beta_{12}: 0$,	$\beta_{22}: 209(14)$, $\beta_{13}: 0$,	$\beta_{33}: 656(55)$ $\beta_{23}: 0$	
Pd	4d	0	0	0	0.35(1)
		$\beta_{11}: 281(25)$, $\beta_{12}: -2(17)$,	$\beta_{22}: 281(25)$, $\beta_{13}: -90(70)$,	$\beta_{33}: 759(90)$ $\beta_{23}: -90(70)$	
O	8i	$\frac{1}{4}$	$\frac{1}{4}$	0.235(2)	1.4(1)
Li	2b	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{2}$	2.0 ^a

Note. The β and B values relate to the expressions: $\exp(-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl])$, $\exp(-B[\sin \theta/\lambda]^2)$. β are $\times 10^5$.

^a Fixed value.

in such a way that the diagonals of the basal plane of the pyramids are aligned with edges of the tetrahedra. Layers (II) (Fig. 3, bottom) contain exclusively square planes of Pd²⁺ which share all their corners with others, within the layer. The latter corresponds to a strong distortion of the perfectly planar arrangement of corner-sharing square planes which exist, for instance, in Nd₂CuO₄ (12). The “hills and valleys” Pd layers in LiBiPd₂O₄ can indeed be obtained from Nd₂CuO₄ planes by pulling alternatively up and down on the empty squares hatched in Fig. 4.

This type of arrangement for square planes is rather scarce, and, to our knowledge, it is the first time that it is obtained as a two-dimensional area. The “four square

planes unit” of Fig. 4b is however encountered as a part of the rhombicuboctahedron of Ag₇O₈NO₃ (13) and for the giant cluster in BaCuO₂ (14). We shall expand on the comparison between BaCuO₂ and LiBiPd₂O₄, but it can be already claimed that it is the peculiar arrangement of layer (II) which explains the building of the three-dimensional network. Indeed, layers (I) and (II) are connected together as shown in Fig. 3 (top). The basement of the square plane of oxygen of the Bi³⁺ pyramid corresponds to the square vacancy created by four square planes of palladium, while one edge of Li⁺ tetrahedra links two “four square planes units” of layer (II). This leads also to a tetrahedral coordination for oxygen atoms. In this way, LiBiPd₂O₄ is a unique example in

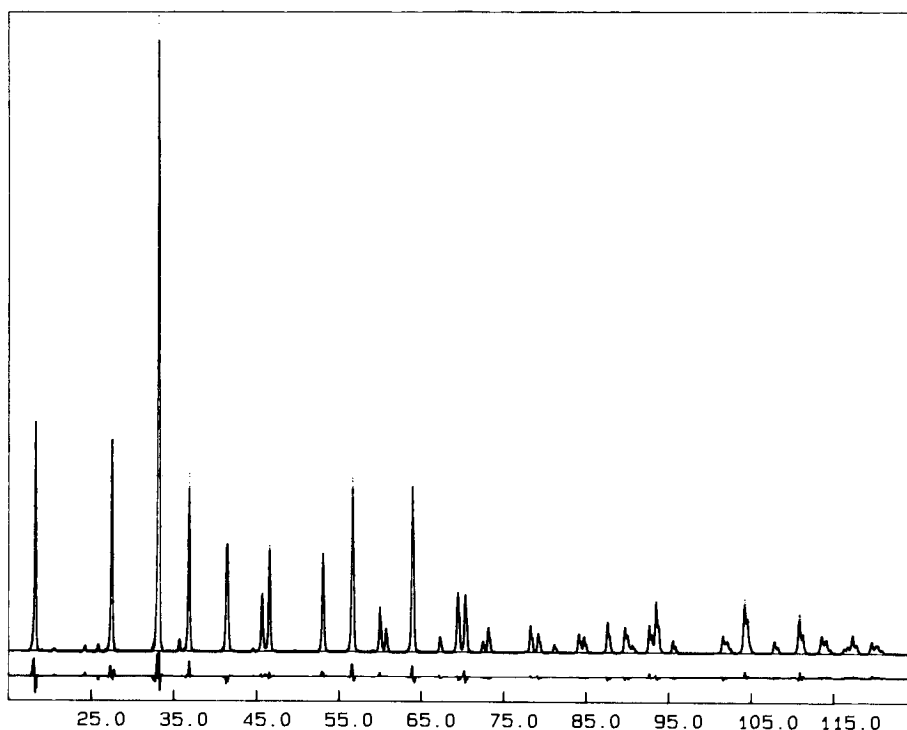


FIG. 1. Comparison of observed (· · ·) and calculated (—) intensities for $\text{LiBiPd}_2\text{O}_4$. The difference pattern appears below, at the same scale.

which all the ions (anions as well as cations) are fourfold coordinated, with three distinct types of polyhedra. Note that in the binary compounds Bi_2PdO_4 (15, 16) and Li_2PdO_2 (17) the coordinations were similar, but there are no obvious structural relations with $\text{LiBiPd}_2\text{O}_4$.

These coordinations can be illustrated using the subnetwork of oxygens in terms of plane nets [(18) and refs. therein, (19)] at $z = 0.23$ and 0.77 . Indeed, it provides a very nice example (Fig. 5) of two $[4.8^2]$ nets (A and B) [Schläfli symbolism (19)] translated by $a/\sqrt{2}$. The sequence of plane nets along c is ABABA Consequently, Bi^{3+} projects on the squares within the octagons, whereas lithium is situated at the crossing of nonoblique edges of the octagon; palladium lies between two squares of the net. The tetrahedral coordination of ox-

xygen (2 Pd, 1 Li, 1 Bi) becomes obvious. It is noteworthy that such plane nets, sometimes encountered in hydrogen-bonded organic molecules [such as caprolactam (18) and refs. therein] and in alloys [such as UB_{12} and Mg_2Ca_5 (19)], are very rare in ionic crystals except in some zeolites (A, for example) and in $\text{Ag}_7\text{O}_8\text{NO}_3$. For the latter compound, the sequence of plane nets is AABBA . . . instead of ABAB . . . in $\text{LiBiPd}_2\text{O}_4$.

The presence of octagonal vacancies in the oxygen subnetwork requires discussion about the role of the lone pair of Bi^{3+} . It is located between two "four square planes units" as indicated in Fig. 6. The large vacancy at $z = 0.77$ ($z(\text{Bi}^{3+}) \approx \frac{1}{2}$) provided by the crown of eight oxygens has a useful radius of 2.2 \AA (taking 1.38 \AA as the radius of O^{2-} in fourfold coordination (20)). This in-

TABLE III
INTERATOMIC DISTANCES (Å) IN $\text{LiBiPd}_2\text{O}_4$
(STANDARD DEVIATIONS ARE GIVEN IN
PARENTHESES)

Bi polyhedron		
Bi-O	$4 \times 2.197(5)$	d_{Shannon} : not defined
O-O	$2 \times 2.66(1)$ $3.76(2)$	
Pd polyhedron: Square plane		
Pd-O	$4 \times 2.014(6)$	$d_{\text{Shannon}} = 2.02$ (Ref. (20))
O-O	$2 \times 2.66(1)$ $2 \times 3.03(1)$ $2 \times 4.03(2)$	
Li polyhedron: Tetrahedron		
Li-O	$4 \times 1.952(6)$	$d_{\text{Shannon}} = 1.97$
O-O	$4 \times 3.21(2)$ $2 \times 3.15(2)$	
O polyhedron: Tetrahedron		
O-Li	$1.952(6)$	
O-Pd	$2 \times 2.014(6)$	
O-Bi	$2.197(5)$	
Metal-metal distances		
Bi-Pd	$4 \times 3.260(1)$ $4 \times 3.286(1)$	
Bi-Li	$4 \times 3.456(1)$	
Pd-Li	$4 \times 3.273(1)$	
Pd-Pd	$4 \times 3.455(1)$	

indicates a rather large activity of the lone pair E, as does the calculation of the average anionic volume (26.0 \AA^3 if the lone pair is not taken into account; 20.8 \AA^3 when it contributes to the calculation). The localization of the lone pair using the formalism of Galy and Andersson (21-24) at $\frac{1}{4}, \frac{1}{4}, 0.71$) confirms the previous assessment. The distance Bi-E (0.94 \AA), smaller than that calculated for the yellow variety of PbO (1.16 \AA), is in good agreement with the value of 0.98 \AA calculated by Galy *et al.* (24) for Bi-

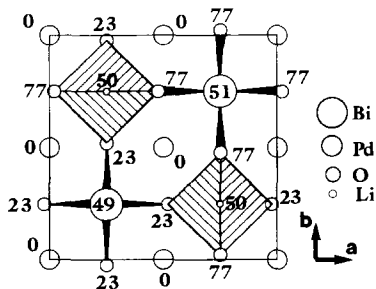


FIG. 2. (0 0 1) projection of $\text{LiBiPd}_2\text{O}_4$.

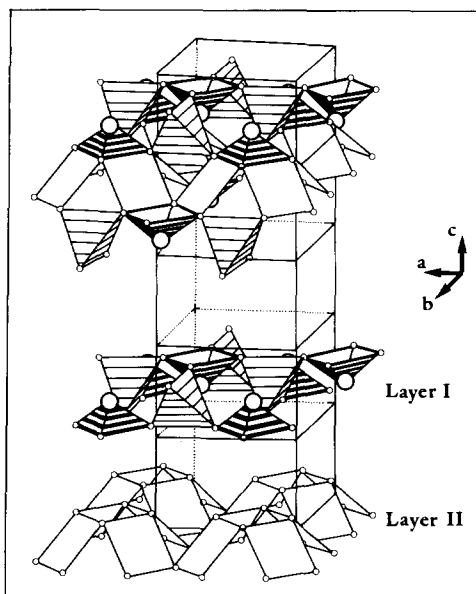


FIG. 3. Perspective view of (bottom) layer (II) (corrugated planes of Pd squares planes), (middle) layer (I) (lithium tetrahedra and bismuth pyramids), and (top) their three-dimensional linkage.

E distance, and indicates a strong activity of the lone pair in $\text{LiBiPd}_2\text{O}_4$.

One can therefore consider bismuth as inside a square pyramid O_4E and a more

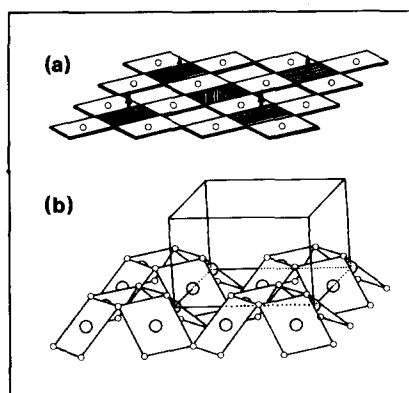


FIG. 4. The relation between (a) perfectly planar $[\text{CuO}_2]^{2-}$ layer in Nd_2CuO_4 (12) and (b) the corrugated $[\text{PdO}_2]^{2-}$ layer in $\text{LiBiPd}_2\text{O}_4$. Arrows in (a) indicate the direction of pulling (see text).

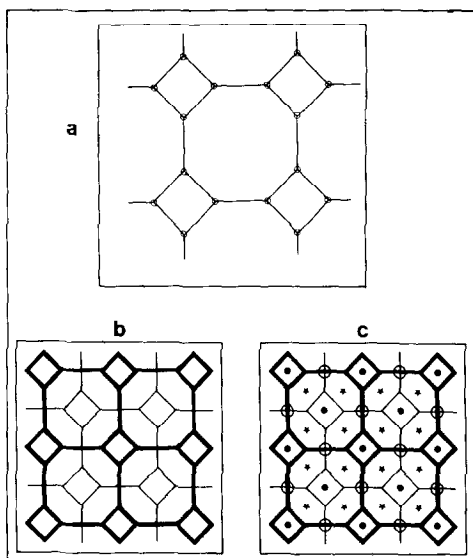


FIG. 5. The $[4.8^2]$ plane net (a); the two $a/\sqrt{2}$ translated $[4.8^2]$ nets (A, heavy; B, light) in $\text{LiBiPd}_2\text{O}_4$ (b); and the location of cations between these plane nets (c) (Bi^{3+} , filled circles; Li^+ , empty circles; Pd^{2+} , stars).

complete comparison with the giant cluster in BaCuO_2 (14) can be undertaken (Fig. 7). The latter is built up from two $([\text{Cu}_5][\text{O}_{13}])$ units (1 CuO_5 + 4 "CuO₂") related by a center of symmetry and connected one to the other by an octagonal crown of edge-sharing CuO_5 pyramids and Cu square planes. One finds the same structural unit

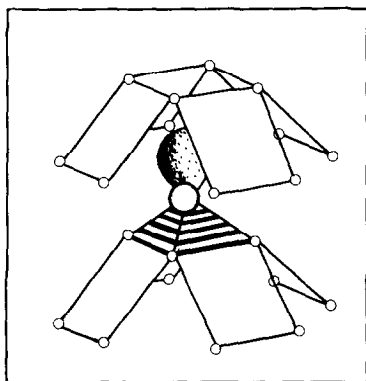


FIG. 6. Location of the lone pair of bismuth between two corrugated planes of Pd.

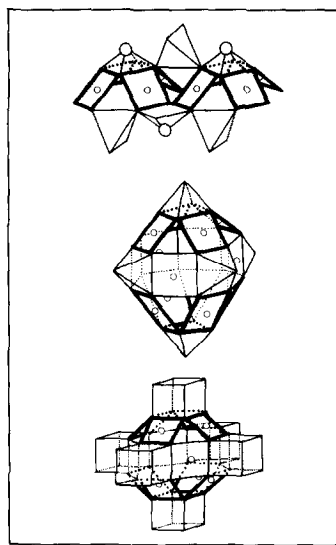


FIG. 7. The "hills and valleys" subnetwork in $\text{LiBiPd}_2\text{O}_4$ (top), BaCuO_2 (middle), and $\text{Ag}_7\text{O}_8\text{NO}_3$ (bottom).

$([\text{Pd}_4\text{Bi}][\text{O}_{12}\text{E}])$ in $\text{LiBiPd}_2\text{O}_4$ but the lone pair leads to their stacking along the c -axis.

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