

LiBiO₂: a Model for Bi³⁺ Co-ordination in High Temperature Superconductors

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The structure of LiBiO₂, determined by powder neutron diffraction, contains adjacent rocksalt-related BiO layers similar to those found in superconducting phases, but the simpler composition has allowed reliable determination of the Bi³⁺ co-ordination (pyramidal with Bi–O bonds of 2.038, 2.096, and 2.130 Å).

The high temperature superconductor Bi₂Sr₂CaCu₂O₈, $T_c = 85$ K, and related superconductors containing Bi³⁺, have layer structures containing pairs of adjacent BiO layers in a rocksalt type arrangement.^{1,2} Such regular co-ordination would be highly unusual for Bi³⁺ in an oxide environment and oxide ion displacements within these layers have been suggested.³ Unfortunately precise structural data are not available for Bi₂Sr₂CaCu₂O₈ owing to complications arising from an incommensurate superstructure, which has been attributed to such distortions, and ill-defined non-stoichiometry resulting in partial oxidation of Cu²⁺ to Cu³⁺. Since LiBiO₂ also contains similar twin BiO rocksalt layers, but has a much simpler chemistry and structure,⁴ this phase has been examined using powder neutron diffraction. In this case the rocksalt-related blocks are separated by an antiferrotype configuration of two O²⁻ ion layers which sandwich Li⁺ ions in all the tetrahedral sites. Whereas the previously reported structure⁴ [from single crystal X-ray diffraction (X.R.D.)] implied Bi in a distorted octahedral environment which does not satisfy bond length/strength requirements⁵ (bond strength sum 2.09 for Bi³⁺), the present study indicates O displacements to provide pyramidally co-ordinated Bi³⁺ (bond strength sum 3.07). Such co-ordination appears rare for Bi³⁺ and contrasts with the trigonal bipyramidal arrangement (equatorial lone pair) found in Bi^{III} oxides. Similar stereochemistry, however, occurs in Sb₂O₃ and As and Sb trihalides. It is felt that LiBiO₂ may therefore provide a realistic and useful structural model for the BiO layers in Bi₂Sr₂CaCu₂O₈ and related phases.

LiBiO₂ was synthesized from an intimate mixture of Li₂O and α-Bi₂O₃ by repeated heating at 500 °C for 12 hours in dry N₂. Powder X.R.D. data implied a body-centred orthorhombic unit cell [*Ibam*; $a = 17.976(4)$, $b = 5.179(1)$, $c = 4.972(1)$ Å] similar to that previously proposed.⁴ Neutron diffraction

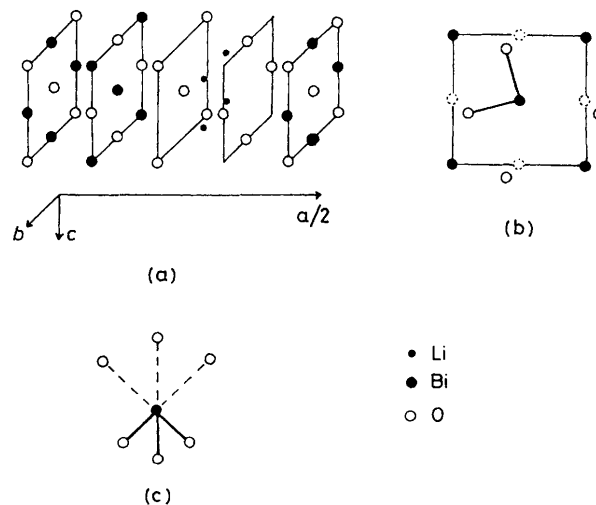


Figure 1. (a) Idealized structure of LiBiO₂ [the co-ordinates of Table 1 have been translated by (0, - $\frac{1}{4}$, 0) for clarity]; (b) oxygen displacements in BiO layer to give 2 short bonds; (c) resultant stereochemistry of Bi³⁺.

Table 1. Refined structural parameters for LiBiO₂.

Atom	x	y	z	B/A ² ^a	Site occupancy
Bi	0.0892(1)	0.2439(3)	0.0	0.84(4)	1.0
Li	0.2490(7)	0.0	0.25	1.6(1)	1.0
O(1)	0.2024(1)	0.2520(7)	0.0	1.05(5)	1.0
O(2)	0.0828(2)	0.8421(5)	0.0885(5)	1.27(9)	0.5

$R_p = 7.08\%$, $R_{wp} = 9.60\%$, $R_1 = 2.55\%$, $R_{exp} = 5.22\%$

^a All thermal parameters have been corrected for the absorption effects of lithium.

data ($\lambda = 1.958 \text{ \AA}$, D1A diffractometer, Institut Laue-Langevin, Grenoble) implied slight contamination with Li₂CO₃, which was not apparent in X.R.D. traces. Two-phase Rietveld refinement techniques were therefore used and these confirmed the basic structural properties, which are shown in idealised form in Figure 1a. However, significant displacements of O, and to a lesser extent Bi, within the BiO layers were implied, which were in strong contrast to the minor distortions suggested by the earlier X.R.D. study. However, the refinement was considered unsatisfactory due to high *R*-factors ($R_{wp} = 16.4\%$; $R_{exp} = 5.2\%$), a low bond strength sum for Bi³⁺ (2.50), and a high thermal parameter (8.2 Å²) for O ions in these layers. According to the space group *Ibam*, these ions are confined to the mirror planes at $z = 0$ and $z = \frac{1}{2}$. Satisfactory agreement between observed and calculated data was achieved by relaxing this constraint to allow an essentially random displacement of these ions off the mirror planes by about 0.44 Å along *z*. The space group *Ibam* was maintained such that split O sites were introduced, with half being displaced along $+z$ and half along $-z$. Refinement therefore related to an average unit cell in which the split O positions cannot both be occupied at a given site due to their unacceptably small separation (0.88 Å). This model resulted in significant reductions in *R*-factors and realistic temperature factors for all atoms, Table 1. Although local order probably exists, the adoption of space groups consistent with long-range order (e.g. *Iba2*, which allows parallel shifts for all O ions along $+z$) produced inferior fits to the data and confirmed that

any order that exists extends over relatively short distances. Bi³⁺ ions have three short Bi–O bonds, two within the BiO layer [2.096(4) and 2.130(4) Å] and one to an O atom in the adjacent BiO layer [2.038(3) Å]. These bonds form a pyramid [O–Bi–O angles 89.5(2), 93.4(2), and 94.3(2)°] opposite to three much longer bonds [around 3.1 Å]. The bond angles are similar to those in BiCl₃, and are consistent with a high degree of *s*-character in the lone pair orbital. The O shifts within a layer and resulting Bi co-ordination are shown in Figure 1(b) and 1(c).

Similar co-ordination for Bi³⁺ has recently been proposed in Bi₂Sr₂CaCu₂O₈,³ although the Bi–O distances are somewhat longer (average 2.18 Å) leading to a bond strength sum of only 2.5. Bearing in mind the complications associated with this phase, especially the fact that excess oxygen may reside within the BiO layers, the present study strongly supports the presence of pyramidally co-ordinated Bi in this family of high temperature superconductors. However, since LiBiO₂ shows no superstructure reflections, it can be concluded that such BiO layers are not necessarily responsible for the incommensurate properties of Bi₂Sr₂CaCu₂O₈, although excess oxygen in these, or other, layers could provide a suitable mechanism.

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