The Structural Chemistry of Li_5BiO_5

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The structure of Li_5BiO_5, determined by *X*-ray and neutron diffraction, is of the rocksalt type, but exhibits ordering of cations and anion vacancies related to that found in the ordered, low temperature TiO phase.

The existence of a phase of stoicheiometry Li_5BiO_5 has previously been suggested[1,2] but no structural or chemical characteristics have been described. In view of the high Li^+ ionic conductivity associated with Li_7BiO_6,[3] the synthesis, electrical properties, and structure of Li_5BiO_5 have been studied. Powder *X*-ray and neutron diffraction data have shown the structure to be of a novel oxygen-deficient rocksalt type, which is closely related to the ordered defect structure of the binary oxide TiO.[4] Oxygen displacements towards vacancies result in a particularly interesting unique polar structure; ionic conductivity data are consistent with a structural transition at approximately 120 °C, which might be associated with a ferroelectric–paraelectric transition.

Li_5BiO_5 was prepared from an intimate mixture of Li_2O and α-Bi_2O_3 by heating at 650 °C for 24 h in dry oxygen. An indexing computer program[5] revealed the *X*-ray powder diffraction pattern to be consistent with a C-centred monoclinic unit cell: $a = 9.978(4)$, $b = 4.155(1)$, $c = 5.947(3)$ Å, and $\beta = 109.24(2)°$. Since the structure of Li_3BiO_4 may be related to a rocksalt lattice, $a_c \approx 4.2$ Å, with cation ordering producing a tetragonal superstructure,[6] the implied cell appeared plausible since a similar, but more complicated, relationship was apparent: $a \approx \sqrt{5}\,a_c$, $b \approx a_c$, $c \approx \sqrt{2}\,a_c$; for an undistorted rocksalt cell, the equivalent angle for β is 108.4°. The proposed cell is thus related to the subcell in exactly the same way as observed for the fully ordered structure of TiO,[4] space group *C2/m*. The metallic nature of TiO is largely responsible for its unique defect and structural chemistry and, to our knowledge, a similar structure has not been reported for any other binary or ternary oxide. In view of this, and the obvious difference in stoicheiometry between TiO and Li_5BiO_5, the apparent structural similarity may appear surprising. However, the relationship can be rationalised by consideration of the defect structure of TiO, which consists of incomplete cation and anion sublattices. The unit cell contents may be represented $[Ti_{10}V_2][O_{10}V'_2]$, where V and V′ represent cation and anion vacancies, and may be compatible with $[Li_{10}Bi_2][O_{10}V'_2]$ for Li_5BiO_5.

Rietveld refinement of powder neutron diffraction data [$\lambda = 1.958$ Å, D1A powder diffractometer, Institut Laue Langevin (I.L.L.)] confirmed the basic structure type, which is shown in idealised form in Figure 1, but indicated the lower

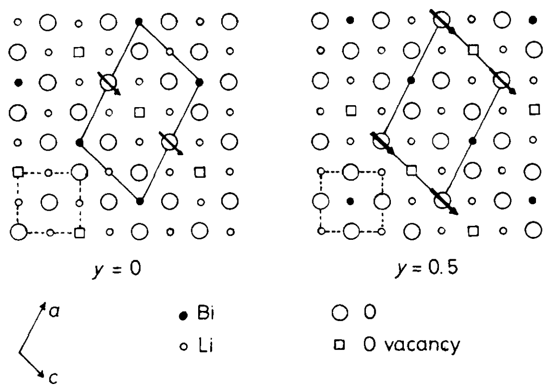

Figure 1. The idealized monoclinic structure of Li_5BiO_5, showing its relationship to the rocksalt subcell. The arrows represent oxygen displacements.

symmetry, non-centrosymmetric space group *Cm* to allow displacements of one fifth of the oxygen atoms (located on the C_2 axis in *C2/m*) by approximately 0.36 Å towards adjacent oxygen vacancies. The shifts, along <001>, are indicated by arrows in Figure 1 and are seen to result in a polar structure. The oxygen vacancy arrangement and resulting anion adjustments maintain octahedral stereochemistry for Bi, but Li occupies sites with reduced co-ordination number: one approximately square planar, and four nominally square pyramidal. The acentric structure was supported by Madelung energy computations in which polarisation effects for O^{2-} ions were included, the total attractive electrostatic energies being 2.791×10^4 kJ mol^{-1} (*C2/m*) and 2.803×10^4 kJ mol^{-1} (*Cm*).

The ionic conductivity, σ, of Li_5BiO_5 was determined at various temperatures using A.C. impedance techniques. At 300 °C, the conductivity was 4.9×10^{-4} ohm^{-1} cm^{-1}. Although the oxygen ion displacements towards vacant anion positions might appear to favour oxygen conduction, this particular oxygen is unique in being bonded to two Bi^{5+} and four Li^+ (other oxygens are bonded to one Bi^{5+} and five Li^+) and is probably quite firmly bound. Nevertheless, the possibility of anion conduction was assessed by comparing the voltage across the oxygen concentrations cells $O_2|Ca_{0.21}BiO_{1.71}|$Air and $O_2|Li_5BiO_5|$Air. The rhombohedral phase $Ca_{0.21}BiO_{1.71}$ is a known oxygen ion conductor with similar conductivity to that of Li_5BiO_5. Whereas at 300 °C the calcium bismuth oxide rapidly developed the theoretical voltage for the concentration cell, no measurable signal was found for the Li_5BiO_5 electrolyte, supporting the view that Li^+ is the dominant charge carrier.

An interesting feature of log σ_T *vs.* $1/T$ plots is a change in slope at approximately 120 °C, consistent with activation energies for conduction of 0.90 and 0.75 eV at lower and higher temperatures, respectively. This characteristic could be associated with a structural transition from acentric to centric symmetries, *i.e.* a ferroelectric–paraelectric transition. Further structural investigations at elevated temperatures are planned to examine this possibility. Li_5SbO_5, which appears to be isostructural with Li_5BiO_5, is also being studied.

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