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The Structure of β-Bi_2O_3 from Powder Neutron Diffraction Data

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Abstract. Bismuth oxide, $M_r = 465{\cdot}96$, tetragonal, $P\bar{4}2_1c$, $a = 7{\cdot}741$ (3), $c = 5{\cdot}634$ (2) Å, $V = 337{\cdot}6$ (3) Å^3, $Z = 4$, $D_x = 9{\cdot}17$ g cm^{-3}. Rietveld refinement using powder neutron diffraction data [$\lambda = 1{\cdot}9587$ Å, $T = 298$ K, $F(000) = 137{\cdot}96$ fm, 116 contributing reflections] resulted in $R_p = 0{\cdot}047$, $R_{wp} = 0{\cdot}060$ ($R_{exp} = 0{\cdot}034$), $R_B = 0{\cdot}071$. No absorption corrections were necessary. Previous structure determinations are shown to be invalid owing to convergence at a false minimum in the R factors. Bi has pseudo-trigonal-bipyramidal coordination with its lone-pair electrons occupying an equatorial position. Bond distances and angles are consistent with related materials containing stereochemically active lone pairs.

Introduction. The tetragonal form of bismuth oxide, β-Bi_2O_3, is metastable at low temperatures (von Gattow & Schütze, 1964) and forms at about 920 K (Harwig & Gerards, 1979) on cooling the high-temperature cubic phase, δ-Bi_2O_3. At lower temperatures, transformation to monoclinic α-Bi_2O_3 occurs. β-Bi_2O_3 can, however, be synthesized at low temperatures, for example by pouring bismuth salts into alkaline solutions (Aurivillius & Malmros, 1972) or from the thermal decomposition of certain bismuth compounds at approximately 670 K (Levin & Roth, 1964). β-Bi_2O_3 has also been observed to form in preference to α-Bi_2O_3 during the low-temperature oxidation of pre-reduced Bi_2MoO_6 catalysts (Buker & Greaves, 1987). In order to consider the reasons for the formation of this thermodynamically unstable phase under these conditions, reliable structural data are required. Detailed structural parameters are also essential to explain the wide variation in oxide ion conductivity in the various modifications of Bi_2O_3 (Laarif & Theobald, 1986). β-Bi_2O_3 is known to be structurally related to fluorite, but has 25% of the anions missing in an ordered fashion. The vacancy arrangement proposed by Sillen (1937) was subsequently shown to be incorrect by a more complete study using single-crystal X-ray diffraction and powder neutron diffraction (Aurivillius & Malmros, 1972). In this later investigation, both data sets implied the same basic structure (tetragonal, $P\bar{4}2_1c$) in which strings of O atoms along $\langle 001 \rangle$ are missing from the fluorite structure. However, certain aspects of these refinements appeared unsatisfactory: (1) the X-ray and neutron refinements unexpectedly disagreed with respect to the Bi position ($\Delta z = 0{\cdot}0134$, e.s.d. $= 0{\cdot}0011$), not the O atoms; (2) additional peaks were observed in the neutron diffraction profile, which was analysed using Rietveld techniques; (3) deconvolution of the neutron diffraction profile revealed some unusually large discrepancies between observed and calculated integrated intensities, *e.g.* $102_{obs} = 449$, $102_{calc} = 1080$; and (4) although the suggested trigonal-bipyramidal stereochemistry with equatorial lone pair is rational for Bi^{3+}, the equatorial O—Bi—O angle (115°) is considerably larger than that observed for other Bi^{3+} and Sb^{3+} compounds considered by Aurivillius & Malmros (1972). In an effort to clarify these anomalies, the structure has been re-examined using powder neutron diffraction data for a sample obtained from a different synthetic route.

Table 1. *Neutron diffraction data collection and structure refinement*

Diffractometer	*D1A*, Institut Laue–Langevin; 10 counters, angular separation 6·0° 2θ
Wavelength	1·9587 Å; 122° take-off angle from (511) planes of Ge monochromator
Angular range	6–156° 2θ, step 0·05°
Container	16 mm diameter vanadium can
Scattering lengths	Bi 8·53 fm; O 5·81 fm
Refinement	Rietveld technique; program *DBW*3.2, Wiles & Young (1981)
Background	Refined (6 parameters)
Function minimized	$\sum w_i(y_{obs,i} - y_{calc,i})^2$; $w_i = 1/y_{obs,i}$
Peak shape	Pseudo-Voigt

Experimental. $Bi_2O_2CO_3$ was prepared by slowly adding an acidic solution of $Bi(NO_3)_3.5H_2O$ to excess Na_2CO_3 solution, with vigorous stirring. The $Bi_2O_2CO_3$ precipitate was filtered, washed, dried, and decomposed to give β-Bi_2O_3 by heating in air in an alumina boat at 650 K (approximately 1·5 h). Characterization by powder X-ray diffraction implied a single tetragonal phase with unit-cell parameters $a = 7{\cdot}741$ (3), $c = 5{\cdot}634$ (2) Å, in good agreement with those previously reported (Aurivillius & Malmros, 1972). Essential details of neutron diffraction data collection and structure refinement are given in Table 1.

Discussion. Initial structure refinement was based on the structural parameters of Aurivillius & Malmros

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(1972), space group $P\bar{4}2_1c$. As shown in Table 2, the results of this refinement are essentially the same as those from the earlier study. However, the R factors were not entirely satisfactory [$R_p = 0{\cdot}070$, $R_{wp} = 0{\cdot}094$ ($R_{exp} = 0{\cdot}034$), $R_B = 0{\cdot}126$], and discrepancies between the observed and calculated profiles were attributable to differences in observed and calculated integrated peak intensities. Significantly, these differences were similar to those noted in the Aurivillius & Malmros (1972) investigation, *e.g.* $102_{obs} = 21$, $102_{calc} = 55$, and this consistency supported the view that the structural model was deficient in some respect. Lower-symmetry tetragonal and orthorhombic space groups were examined but gave no significant improvements. The monoclinic space group $P2_1$, however, produced lower R factors, which were accompanied by a large displacement of the O2 oxygen atoms. Close inspection of this structural model suggested that it was, to a close approximation, compatible with the original tetragonal space group $P\bar{4}2_1c$, with z(O2) approximately 0·4 rather than the refined value of 0·1. With this revised coordinate as starting value, refinement in $P\bar{4}2_1c$ was again tried and produced substantially improved R factors [$R_p = 0{\cdot}047$, $R_{wp} = 0{\cdot}060$ ($R_{exp} = 0{\cdot}034$), $R_B = 0{\cdot}071$] and satisfactory agreement between observed and calculated profiles (Fig. 1)* and integrated peak intensities. Refined parameters are given in Table 3. It was inferred that the initial Aurivillius & Malmros (1972) structural model had converged to a false minimum, and this was confirmed by monitoring R_{wp} as a function of z(O2), whilst allowing all other parameters to vary (Fig. 2).

It is interesting to compare the refined data, Table 3, with those of earlier refinements, Table 2. Concomitant with the change in z(O2), z(Bi) has reduced to a value consistent with that derived from the X-ray diffraction study. At the true minimum of R_{wp}, these parameters have a correlation coefficient of only 16%, but clearly a high correlation exists between them when comparing the two minima in R_{wp} (Fig. 2). In the X-ray diffraction study, scattering-amplitude considerations render z(Bi) insensitive to z(O2) such that the correct value for z(Bi) was indicated despite the incorrect value for z(O2).

The structure, shown in projection in Fig. 3, displays most of the important characteristics previously described (Aurivillius & Malmros, 1972). BiO_4e trigonal bipyramids (e = equatorial lone pair) are linked *via* oxygens at corners to give a network with empty channels at (00z) and ($\frac{1}{2}\frac{1}{2}z$); the lone-pair electrons are directed towards these channels. Bond distances and angles are given in Table 4. The axial bonds to oxygens

* A list of observed and calculated values for each point of the profile has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44603 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Comparison of refined structural parameters, Aurivillius & Malmros* (1972) *model*

	Position	x	y	z	B_{iso}(Å^2)	Note
Bi	8(e)	0·0208 (4)	0·2559 (5)	0·2363 (7)	0·56 (10)*	(a)
		0·0170 (8)	0·2555 (9)	0·2497 (8)	0·05 (14)	(b)
		0·0178 (8)	0·2539 (7)	0·2532 (10)	1·18 (11)	(c)
O1	8(e)	0·290 (7)	0·320 (9)	0·027 (11)	0·3 (9)	(a)
		0·292 (1)	0·312 (1)	0·034 (2)	0·53 (18)	(b)
		0·295 (1)	0·3074 (7)	0·027 (2)	1·7 (2)	(c)
O2	4(d)	0	0·5	0·146 (16)	0·4 (14)	(a)
		0	0·5	0·103 (2)	1·20 (27)	(b)
		0	0·5	0·101 (2)	1·6 (2)	(c)

Notes: (a) Single crystal X-ray diffraction (Aurivillius & Malmros, 1972). (b) Powder neutron diffraction (Aurivillius & Malmros, 1972). (c) Powder neutron diffraction, this work, using values from (b) as initial values.

* Based on mean displacement of anisotropic thermal motion.

Table 3. *Refined parameters, $P\bar{4}2_1c$, using revised z(O2) starting parameter*

	Position	x	y	z	B_{iso}(Å^2)
Bi	8(e)	0·0174 (5)	0·2545 (4)	0·2385 (6)	1·11 (7)
O1	8(e)	0·2905 (7)	0·3125 (7)	0·0286 (10)	1·71 (11)
O2	4(d)	0	0·5	0·3939 (11)	1·27 (13)

$a = 7{\cdot}739$ (1), $c = 5{\cdot}636$ (1) Å.
Pseudo-Voigt parameter – 29% Lorentzian.
Additional refined parameters – scale (1), asymmetry correction (1), background (6), FWHM (3), zero correction (1).
Structural parameters with correlation coefficients > 40% – none.

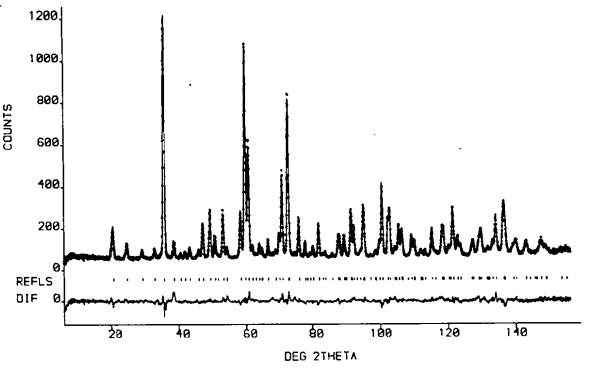

Fig. 1. Observed (dots), calculated and difference profiles with reflection positions.

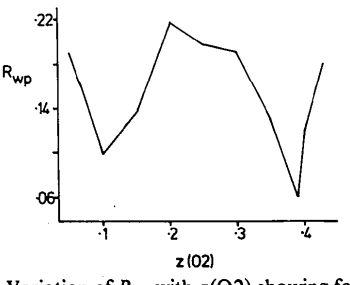

Fig. 2. Variation of R_{wp} with z(O2) showing false minimum.

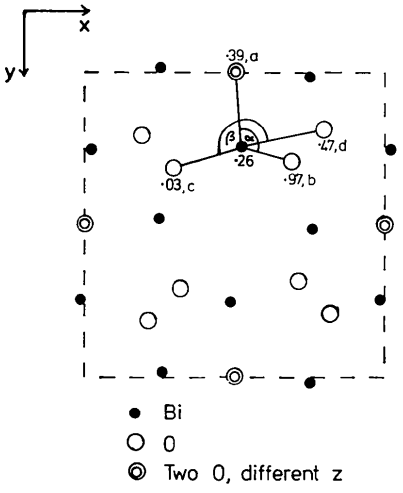

Fig. 3. Unit cell projected along ⟨001⟩; approximate z coordinates and the angles α and β are indicated for one BiO_4 polyhedron.

c and d (indicated in Fig. 3) are somewhat longer than the equatorial bonds to a and b. Whereas β, angle c—Bi—d = 172·1 (3)°, is identical to that indicated by the single-crystal X-ray diffraction measurements, 172 (2)°, the equatorial angle, $\alpha = a$—Bi—b = 82·4 (2)°, is very much lower than that previously reported, 115 (2)°. Aurivillius & Malmros (1972) compared a range of Sb^{3+} and Bi^{3+} compounds for which $78 < \alpha < 96°$ and $143 < \beta < 172°$. Whereas the X-ray structure is incompatible with these observations, the present results are consistent, and comply with the general observation that long equatorial bonds and high values for β tend to be associated with low α values, due to changes in electron pair repulsions.

Table 4. *Selected bond distances* (Å) *and angles* (°)

Bi—O1, d	2·463 (7)	O2—Bi—O1, α	82·4 (2)
O2, a	2·096 (4)	O1—Bi—O1, β	172·1 (3)
O1, c	2·253 (7)	O1—Bi—O2	95·2 (2)
O1, b	2·128 (7)	O1—Bi—O1	82·4 (2)
		O2—Bi—O1	85·1 (2)
		O1—Bi—O1	89·8 (2)
O1—Bi	2·463 (7)	Bi—O1—Bi	110·3 (2)
Bi	2·253 (7)	Bi—O1—Bi	109·9 (2)
Bi	2·128 (7)	Bi—O1—Bi	135·9 (3)
O2—Bi	2·096 (4)	Bi—O2—Bi	130·6 (3)
Bi	2·096 (4)		

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Chlorosilicate with the $12CaO.7Al_2O_3$ Structure and its Relationship to Garnet

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Abstract. $Ca_{12}Al_{10.6}Si_{3.4}O_{32}Cl_{5.4}$, M_r = 1565·88, cubic, $I\bar{4}3d$ (No. 220), a = 11·981 (6) Å, Z = 2, D_x = 3·023 Mg m^{-3}, V = 1719·8 Å^3, Mo$K\alpha$, λ = 0·71069 Å, μ = 2·706 mm^{-1}, $F(000)$ = 1546·4. Single crystals have been prepared and characterized by electron microprobe and X-ray crystal structure analysis; R = 0·056 for 225 unique reflections. The structure is closely related to that of $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$ in oxide notation) but with Cl substituted for some of the oxide of the type structure and Si replacing some Al to provide charge balance for Cl present in excess of the stoichiometric requirement. The structure exhibits many similarities to that of garnet.

Introduction. Several compounds of the type $Ca_{12}Al_{14}O_{32}X$ have been reported; $X = O^{2-}$: Bartle (1969*b*), Bussem & Eitel (1936), Jeevaratnam, Dent Glasser & Glasser (1962) and Hentschel (1964); $X = 2(OH^-)$: Bartl (1969*a*); $X = 2(F^-)$: Williams (1973); $X = 2(O_2^-)$ (superoxide): Hosono & Abe (1987). The substitution of OH^-, F^-, Cl^- for O^{2-} has hitherto been believed to be limited to a maximum of four monovalent anions per

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