A Neutron Diffraction Determination of the Structures of $Ba_2Sb^{V}Bi^{III}O_6$ and $Ba_2Bi^{V}Bi^{III}O_6$

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The structures of $Ba_2Sb^{V}Bi^{III}O_6$ and $Ba_2Bi^{V}Bi^{III}O_6$ have been determined by profile analysis of powder neutron diffraction data. Both compounds have structures which may be described by a monoclinic distortion of an ordered double perovskite cell with space group $I2/m$ [$a = 6.0675$ (3), $b = 6.0156$ (3), $c = 8.5041$ (5) Å, $\beta = 90.23$ (1)° and $a = 6.1736$ (5), $b = 6.1237$ (4), $c = 8.6507$ (6) Å, $\beta = 90.29$ (1)° respectively at 4.2 K, and $a = 6.1895$ (4), $b = 6.1418$ (3), $c = 8.6741$ (5) Å, $\beta = 90.18$ (1)° for $BaBiO_3$ at 293 K].

Introduction

The perovskite system $BaPb_{1-x}Bi_xO_3$ has recently been shown to be superconducting in the composition range $0.05 < x < 0.31$ (Sleight, Gillson & Bierstedt, 1975). Consequently, there has been interest in establishing the structures of the end members $BaPbO_3$ and $BaBiO_3$ and of their solid solutions. The structure of metallic $BaPbO_3$ has been determined by neutron diffraction (Thornton & Jacobson, 1976; Cox & Sleight, 1976a) and shown to be body-centered orthorhombic, space group *Imma*, and not primitive as previously reported (Shannon & Bierstedt, 1970; Shuvaeva & Fesenko, 1970). The structure of the semiconductor $BaBiO_3$ has variously been described as an orthorhombic (Sleight, Gillson & Bierstedt, 1975), rhombohedral (Venevtsev, 1971), monoclinic (Shuvaeva & Fesenko, 1970) and triclinic (Nakamura, Kose & Sata, 1971) distortion of a simple cubic perovskite cell. However, Cox & Sleight (1976b) have determined the structure by neutron diffraction and shown that the true cell is monoclinic, space group $I2/m$, and contains four formula units per unit cell. The Bi^{III} and Bi^{V} atoms are ordered so that the compound is correctly formulated as $Ba_2Bi^{III}Bi^{V}O_6$ and not $BaBi^{IV}O_3$ as suggested by de Hair & Blasse (1973). We note that a recent study of the X-ray photoelectron spectrum of $BaBiO_3$ also shows the presence of two nonequivalent Bi atoms (Orchard & Thornton, 1977).

In the present work, we describe a neutron diffraction investigation of the structure and cation ordering in the related system Ba_2SbBiO_6 and present our independent results for the structure of $BaBiO_3$ at 4.2 and 293 K.

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Experimental

Preparation of samples

The starting materials used were $BaCO_3$, Bi_2O_3, and Sb_2O_3 ('Specpure', Johnson Matthey Chemicals). Ba_2BiSbO_6 and $BaBiO_3$ were prepared by firing stoichiometric mixtures in air for 240 h at 1000 and 800°C respectively, with four intermediate regrinds. The reaction mixtures were contained in alumina crucibles. After reaction, weight changes corresponded to the formation of stoichiometric products and no reflections due to starting materials or other phases were observed in X-ray powder patterns. The X-ray diffractometer patterns could be roughly indexed on the basis of a doubled cubic perovskite cell with lattice parameters 8.55 and 8.71 Å for Ba_2SbBiO_6 and $BaBiO_3$ respectively. However, high-angle line splittings indicated that the true symmetry is lower and an examination of the 444 double cubic reflection indicated that a monoclinic distortion was present in both compounds. The doubled cubic 111 reflection is observed for Ba_2SbBiO_6 but not for $BaBiO_3$ as a consequence of the cation ordering and the difference in the X-ray scattering factors of Bi and Sb.

Analysis

$BaBiO_3$

Analysis of Ba as sulfate and Bi as oxyiodide gave 34.9 and 52.9% respectively, as compared with the corresponding values of 34.8 and 52.9% calculated for $BaBiO_{3.00}$.

Table 1. *Experimental conditions*

Sample	Temperature (K)	Wavelength (Å)	Angular range (°)
$BaBiO_3$	4·2	1·327	$10 < 2\theta < 94$
$BaBiO_3$	293	1·525	$10 < 2\theta < 109$
Ba_2SbBiO_6	4·2	1·321	$10 < 2\theta < 100$

Ba_2SbBiO_6

An estimate of Ba as sulfate, and Bi and Sb by atomic absorption gave 39·8, 17·2 and 30·8% respectively, the corresponding values for perfect stoichiometry being 39·2, 17·4 and 29·8%.

Neutron diffraction

Neutron diffraction measurements were made at 4·2 and 293 K on a powder diffractometer at the reactor PLUTO, AERE Harwell. The samples were contained in 10 mm diameter thin-walled vanadium cans and the neutron beam was monochromated by reflection from the (511) planes of a Ge crystal. The sample weight in each case was 12 g. The experimental conditions are summarized in Table 1.

The neutron diffraction patterns of both compounds contain extra reflections not observed in the X-ray patterns arising from oxygen displacements from ideal sites. The reflections are observed to be asymmetric or split at high angles but all derive from doubled cubic reflections with hkl all odd or all even. Glazer (1972, 1975) has discussed distortions of perovskite structures in terms of rotations of rigid BO_6 octahedra about the simple cubic axes. The extra reflections which appear in the neutron diffraction pattern and which are sensitive to the oxygen displacements together with the symmetry of the distortion may be used to determine the direction of the octahedra rotations and the likely space group. In Ba_2SbBiO_6 and $BaBiO_3$ only extra reflections with hkl all odd are observed, indicating only negative tilts. The extra reflections in $BaPbO_3$ obey the same conditions suggesting that the tilt systems are similar. However, all the Pb atoms in *Imma* are equivalent and, consequently, in order to accommodate the cation ordering of different size atoms, Bi^{III} and Sb^V or Bi^{III} and Bi^V, the symmetry is reduced further to monoclinic $I2/m$. With this trial model the structure parameters were refined from the three sets of data by least-squares analysis of the powder diffraction profiles (Rietveld, 1967). The starting parameters corresponded to the positions for an ideal cubic perovskite structure and individual isotropic temperature factors were included in the refinement. The scattering lengths used were b_{Ba} = 0·52, b_{Bi} = 0·864, and b_O = 0·58 ($\times 10^{-12}$ cm) (Neutron Diffraction Commission, 1972) and b_{Sb} = 0·56 × 10^{-12} cm from a recent compilation by Shull (see Willis, 1973). The data were refined until all parameter shifts were less than 0·3σ. The counter zero-

Table 2. *Positional and isotropic thermal parameters*

	Position	x	y	z	$B(Å^2)$
Ba_2SbBiO_6 ($I2/m$) (4·2 K)					
Ba	4(i)	0·5006 (11)	0	0·2475 (11)	0·49 (5)
Bi	2(a)	0	0	0	0·46 (8)
Sb	2(c)	0	0	$\frac{1}{2}$	0·04 (11)
O(1)	4(i)	0·0505 (8)	0	0·2482 (7)	0·58 (10)
O(2)	8(j)	0·2702 (6)	0·2670 (9)	−0·0270 (4)	0·78 (7)

R (profile) = 7·3% R (expected) = 4·4%

	Position	x	y	z	$B(Å^2)$
$BaBiO_3$ ($I2/m$) (4·2 K)					
Ba	4(i)	0·5085 (14)	0	0·2506 (15)	0·32 (6)
Bi(1)	2(a)	0	0	0	0·08 (18)
Bi(2)	2(c)	0	0	$\frac{1}{2}$	0·14 (19)
O(1)	4(i)	0·0698 (9)	0	0·2602 (10)	0·40 (13)
O(2)	8(j)	0·2604 (10)	0·2541 (17)	−0·0376 (4)	0·94 (9)

R (profile) = 8·5% R (expected) = 6·0%

	Position	x	y	z	$B(Å^2)$
$BaBiO_3$ ($I2/m$) (293 K)					
Ba	4(i)	0·5057 (3)	0	0·2507 (18)	0·89 (7)
Bi(1)	2(a)	0	0	0	0·62 (21)
Bi(2)	2(c)	0	0	$\frac{1}{2}$	0·12 (19)
O(1)	4(i)	0·0622 (10)	0	0·2559 (15)	1·62 (15)
O(2)	8(j)	0·2639 (11)	0·2513 (22)	−0·0344 (4)	1·61 (9)

R (profile) = 9·2% R (expected) = 4·6%

point, reflection half-width parameters and the lattice parameters were included in the refinement. For Ba_2SbBiO_6, refinement of the Sb and Bi occupation numbers indicated complete cation ordering on the B cation sublattice within statistical errors. The atom positions are given in Table 2, the lattice parameters in the abstract and interatomic distances and angles in Table 3. The experimental and calculated profiles for Ba_2SbBiO_6 and $BaBiO_3$ at 4·2 K are shown in Figs. 1 and 2. The R factors in Table 2 are those defined by Rietveld (1967).

Table 3. *Interatomic distances* (Å) *and angles* (°)

	Ba_2SbBiO_6 (4·2 K)	$BaBiO_3$ (4·2 K)	$BaBiO_3$ (293 K)
Ba—O(1)	2·734 (2)	2·707 (2)	2·741 (3)
Ba—O(1)	3·026 (2)	3·101 (2)	3·099 (3)
Ba—O(1)	3·344 (2)	3·469 (2)	3·449 (3)
Ba—O(2)	2·839 (2)	2·808 (3)	2·818 (4)
Ba—O(2)	2·881 (2)	2·833 (3)	2·894 (4)
Ba—O(2)	3·154 (2)	3·307 (3)	3·267 (4)
Ba—O(2)	3·215 (2)	3·349 (3)	3·349 (4)
Bi(1)—O(1)	2·300 (1)	2·290 (1)	2·251 (1)
Bi(1)—O(2)	2·307 (2)	2·262 (2)	2·268 (2)
Sb[Bi(2)]—O(1)	1·996 (1)	2·120 (1)	2·154 (1)
Sb[Bi(2)]—O(2)	1·990 (2)	2·134 (2)	2·134 (2)
O(1)—Bi(1)—O(2)	90·40	90·62	90·51
O(2)—Bi(1)—O(2)	91·75	93·08	94·21
O(1)—Sb[Bi(2)]—O(2)	90·22	90·28	90·76
O(2)—Sb[Bi(2)]—O(2)	90·45	90·26	91·39
Bi(1)—O(2)—Sb[Bi(2)]	167·63	162·91	164·11

Discussion

Ba_2SbBiO_6 has a monoclinic distorted perovskite structure, space group $I2/m$, with Sb^V and Bi^{III} ordered on the B sites. The Sb—O bond lengths are 2·00 and 1·99 Å, in good agreement with the value of 2·00 Å calculated from radii ($r_{O^2} = 1·40$, $r_{Sb^{5+}} = 0·60$ Å, Shannon, 1976) confirming the Sb^V, Bi^{III} distribution of oxidation states. In the $Bi^{III}O_6$ octahedron the bond distances, 2·30 and 2·31 Å, give a radius for Bi^{3+} of 0·90 Å, somewhat shorter than Shannon's value of 0·98 Å. However, Shannon has pointed out that the effective radius of Bi^{3+} is sensitive to the degree of $6s^2$ lone-pair character. When Bi^{3+} is constrained in a site of high symmetry, its radius is typically less than in systems where the site is distorted and dominated by the lone-pair character.

$BaBiO_3$ has essentially the same structure at 293 and 4·2 K, with slightly larger atom displacements from ideal positions at the lower temperature. The similarity to Ba_2SbBiO_6 confirms that we have an ordered perovskite which contains two oxidation states of the same element. The Bi^V atoms occupy the 2(c) positions occupied by Sb^V in Ba_2SbBiO_6, as evidenced by the Bi—O distances of 2·13 and 2·15 Å at 293 K. The Bi^V radius is 0·74 Å (*cf.* $r_{Bi^{5+}} = 0·76$ Å, Shannon, 1976). The Bi^{III} distances average 2·26 Å (giving $r_{Bi^{3+}} = 0·86$ Å), shorter than that found in Ba_2SbBiO_6.

Cation ordering in $A_2BB'O_6$ perovskites is usually only observed for B/B' charge differences of <3 when there is a large difference in B/B' radii. However, when the enthalpy difference between the ordered and
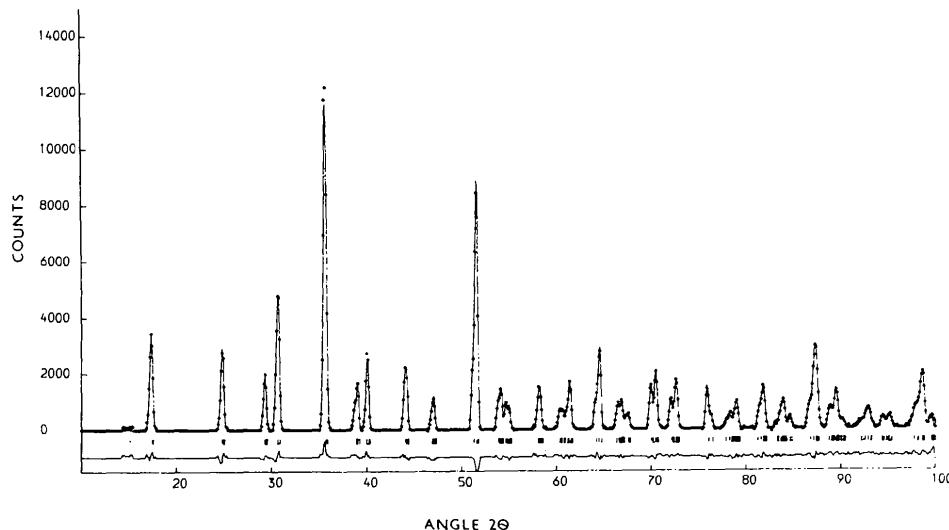

Fig. 1. Powder neutron diffraction profile for Ba_2SbBiO_6 at 4·2 K. Small circles are the experimental points, and the full curve passes through the calculated points. The small vertical lines mark the positions of the Bragg reflections and the bottom trace is the difference profile.
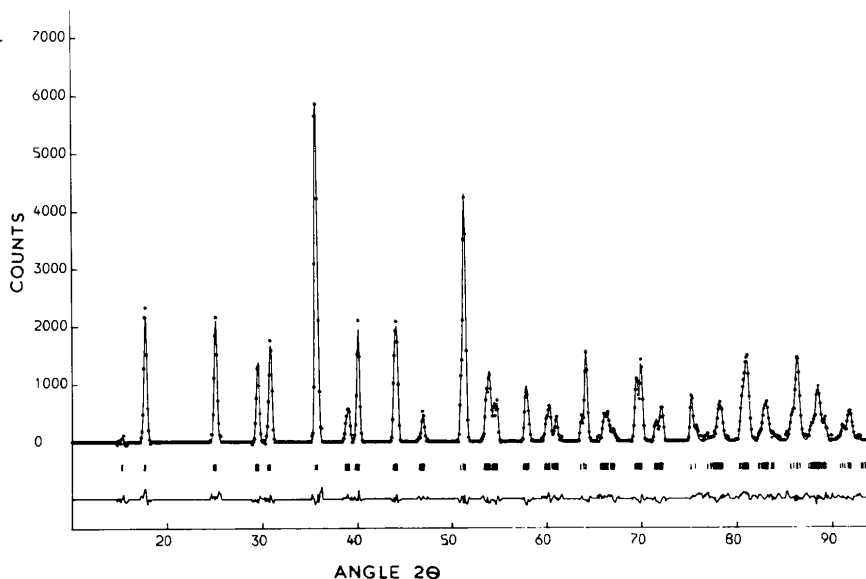
Fig. 2. Powder neutron diffraction profile for $BaBiO_3$ at 4·2 K. Small circles are the experimental points, and the full curve passes through the calculated points. The small vertical lines mark the positions of the Bragg reflections and the bottom trace is the difference profile.

disordered form is small, the disordered form may be favored at temperatures high enough to obtain significant cation diffusion. The difference in size between Bi^{III} and Bi^V is smaller than that for Bi^{III} and Sb^V, but in the former case ordering involves only electron rearrangement and not cation diffusion and hence is not subject to the same kinetic limitations.

Finally, we have compared our results for $BaBiO_3$ at room temperature with those of Cox & Sleight (1976a,b). The results are in very good agreement; all positional parameters agree within the statistical precision of the data. We conclude that the structure determination of $BaBiO_3$ is a striking example of the ability of the profile technique to handle powder data with many overlapping reflections in a situation where the distortion to low symmetry is small.

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