

Absolute Configuration and Optical Activity of Laevorotatory $\text{Bi}_{12}\text{TiO}_{20}$

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Abstract

Bismuth titanium oxide, $\text{Bi}_{12}\text{TiO}_{20}$, $M_r = 2875.64$, cubic, $I23 (T^3)$, $a = 10.188 (6) \text{ \AA}$, $V = 1057 (1) \text{ \AA}^3$, $Z = 2$, $D_x = 9.03 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$, $\mu = 99.60 \text{ mm}^{-1}$, $F(000) = 2356$, $T = 294 \text{ K}$, $R = 0.0205$ for 453 unique reflections. The atomic arrangement has the same chirality as that of other laevorotatory sillenites ($\text{Bi}_{12}\text{SiO}_{20}$ and $\text{Bi}_{12}\text{GeO}_{20}$). The optical rotatory power is calculated by the program of Devarajan & Glazer [*Acta Cryst.* (1986), A42, 560–569] and compared with experiment.

1. Introduction

A previously reported structure determination for bismuth titanium oxide, $\text{Bi}_{12}\text{TiO}_{20}$ (Efendiev, Kulieva, Lomonov, Chiragov, Grandolfo & Vecchia, 1982), henceforth to be called BTO, did not relate the structural chirality to any physical property; furthermore, only isotropic temperature factors were refined. This paper reports the absolute configuration of a laevorotatory crystal of BTO, and compares the structural results with those obtained previously, and with those for other sillenites $\text{Bi}_{12}\text{MO}_{20}$, $M = \text{Si, Ge}$ (Abrahams, Svensson & Tanguay, 1979) called BSO, BGO respectively.

Feldman, Brower & Horowitz (1970) reported the optical rotatory power as a function of wavelength (400–700 nm) at room temperature for five bismuth oxide compounds, which all showed a rotatory power of approximately the same size ($\sim 20^\circ \text{ mm}^{-1}$ at 6500 Å) except BTO, whose smaller rotatory power ($\sim 5.8^\circ \text{ mm}^{-1}$ at 6500 Å) was observed in samples from different boules. They concluded that the effect is intrinsic, although they mentioned the possibility that the samples were mixtures of enantiomorphic crystals.

Morrison (1971) measured the refractive index of BTO at 6328 Å by the total reflection technique, and gave a value of 2.55 ± 0.04 . Fox & Bruton (1975) quote a value of 2.25, but this would appear to be a misprint, since back-calculation from given values of $n_0^3 r_{41}$ and r_{41} (where n_0 is the refractive index and r_{41} the linear electro-optic coefficient) results in $n_0 = 2.55$, in agreement with Morrison's value.

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As well as giving possible structural reasons for the lower optical rotatory power of BTO, this paper reports the use of the computer program of Devarajan & Glazer (1986) to calculate the optical rotatory power and refractive index.

2. Experimental

A sphere of BTO of radius 0.075 mm was ground from a crystal slice supplied by GEC Hirst Research Centre. The slice had been taken from a boule grown by the Czochralski method from a melt of mixed oxides, and had been found to be uniformly laevorotatory (corresponding to a counter-clockwise rotation of the plane of polarization as detected by an observer facing the source) by investigating the amount of rotation for plates of different thickness and the completeness of extinction. Preliminary photographic work showed that the crystal was of good quality, and confirmed that the systematic absences were consistent with those for space group $I23 (T^3)$.

Data were collected using an Enraf–Nonius CAD-4 diffractometer, with graphite-monochromated Mo $K\alpha$ radiation. The lattice parameter was obtained from a least-squares refinement of $(\sin^2\theta)/\lambda^2$ values for 24 well-centred reflections (at $\theta \approx 20^\circ$). The directions of a , b and c were chosen so that certain structure factors are related to each other in the same way as in other sillenite structure determinations. In order to achieve this, a re-indexing procedure involving matrix multiplication for a 90° rotation about [001] was applied to the results of the automatic indexing routine. The reflections chosen for comparison were the non-equivalent pair (130) and (310), and the condition imposed was that $F(310) > F(130)$.

It is worth noting that the 'correctness' of the structure determination is in no way affected by the choice of directions of the cell edges, nor is the sense of optical rotation. The alternative ways of indexing the reflections arise merely because of the inequivalence of the two $\{hkl\}$ reflections ($h > k > l$) and ($h < k < l$) in Laue group $m\bar{3}$, and constraining $F(310) > F(130)$ simply makes it easier to compare the structure with those previously determined.

A total of 4378 reflections were measured in the range $1 \leq \theta \leq 30^\circ$; $-1 \leq h \leq 14$, $-1 \leq k \leq 14$, $-14 \leq l \leq 14$. The scans used were of the $\omega-2\theta$ type with

ω -scan width $(0.70 + 0.35 \tan \theta)^\circ$, and scan speed $1-5.5^\circ \text{ min}^{-1}$. Three standard reflections were measured every hour and were used to scale the data. No significant trend in the magnitudes of the intensities was seen, the variation being within $\pm 5\%$.

Structure analysis and refinement was carried out using the Oxford *CRYSTALS* system (Watkin, Carruthers & Betteridge, 1985) on a VAX11/750 computer in the Chemical Crystallography Laboratory, Oxford University. Data were corrected for Lorentz, polarization and absorption effects. Absorption correction factors for a spherical crystal were taken from *International Tables for X-ray Crystallography* (1959). Compensation for deviation from a perfect sphere was made by applying the correction method of North, Phillips & Mathews (1968). Minimum and maximum transmission factors were 0.00154 and 0.01247 respectively. The 4378 reflections measured included 1443 that were rejected as systematic absences. The remaining 2935 reflections were merged to give 517 unique reflections ($R_{\text{merge}} = 0.091$) of which 453 had $F^2 \geq 2\sigma(F^2)$ and were used in the subsequent refinement.

Initial atomic parameters were taken from Efendiev *et al.* (1982); by analogy with those of laevorotatory BSO (Abrahams, Bernstein & Svensson, 1979) and BGO (Svensson, Abrahams & Bernstein, 1979) it was anticipated that they would correspond to laevorotatory BTO.

Three cycles of full-matrix least-squares refinement (on F) with unit weights, isotropic temperature factors

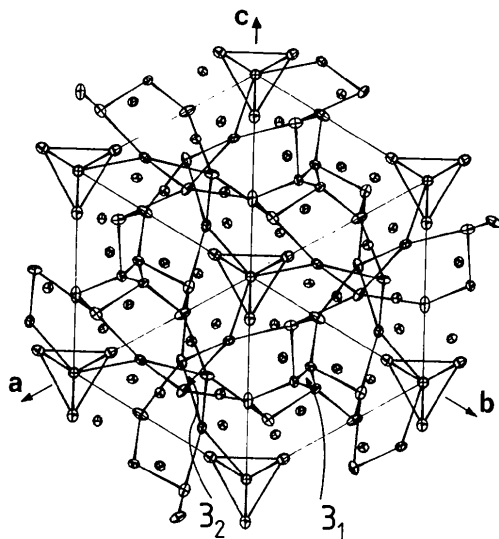


Fig. 1. (111) projection of the structure of $\text{Bi}_{12}\text{TiO}_{20}$. Thermal ellipsoids are drawn at the 90% probability level. Because only O—O connections $< 3.1 \text{ \AA}$ are drawn, the Bi atoms appear unbonded. In this projection the Ti atoms (at $0,0,0$ and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) are obscured by O atoms on the triad axes. This figure should be compared with Fig. 6 of Glazer & Stadnicka (1986), wherein the different O atoms and the different structural helices are depicted.

Table 1. Atomic coordinates and isotropic temperature factors (\AA^2)

$$U_{\text{eq}} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	$U_{\text{eq}}/U_{\text{iso}}$
Bi	0.17648 (4)	0.31862 (4)	0.01546 (4)	0.0099
Ti	0	0	0	0.007 (1)
O1	0.1341 (7)	0.2511 (7)	0.4881 (9)	0.0117
O2	0.1930 (8)	0.1930	0.1930	0.0132
O3	-0.1045 (8)	-0.1045	-0.1045	0.0142

Coordinates given without e.s.d.'s in parentheses are not independent values.

and scattering factors for neutral atoms [values taken from *International Tables for X-ray Crystallography* (1974)] gave $R = 0.062$, $wR = 0.072$. Corrections for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974) and isotropic extinction (Larson, 1970) were included in subsequent cycles. In the final stages of robust/resistant refinement (Prince, 1982), each reflection was given a weight computed from a Chebyshev series with three parameters 45.3, -50.7, 25.9 (Carruthers & Watkin, 1979). This weighting scheme resulted in the down-weighting of one reflection (888); in the final listing $10F_o(888) = 3470$, $10F_c(888) = 3877$.

Refinement converged to $R = 0.0205$, $wR = 0.0228$, with a maximum coordinate shift/e.s.d. = 2×10^{-5} . It is perhaps fortunate that the model fits the average data better than the multiple observations fit each other. The secondary-extinction parameter was 12.5 (6). The highest peak in the final difference Fourier map was 0.25 e \AA^{-3} located near Bi, and the deepest trough at atomic sites -0.07 e \AA^{-3} .

The structural chirality was confirmed by use of the enantiomorph-polarity estimation methods of Rogers (1981) and of Flack (1983). For the atomic arrangement reported below (Rogers η parameter set to 1 and atomic positional parameters as given), the amount of component related by a centre of symmetry to this arrangement was 4 (4)%.

Attempts to include Ti-site occupancy in the refinement were abandoned because of the high correlation between occupancy and thermal vibration factors.

3. Discussion

A projection of the structure is shown in Fig. 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The chirality is the same as that of the previous reported structure (Efendiev *et al.*, 1982); that crystal is therefore inferred to be laevo-

* Lists of structure factors, anisotropic thermal parameters, and additional bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44424 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

rotatory as well. No mention of absorption correction was made in that previous report, where the final R value was 0.095 and e.s.d.'s on O atoms were typically 3–4 times higher than those now reported.

Bond lengths are given in Table 2. The shift in atomic positions between this structure and that reported by Efendiev *et al.* causes differences of up to 0.16 Å in Bi–O bond lengths and of 0.035 Å in the Ti–O3 bond length.

Abrahams, Bernstein & Svensson (1979) compared the Bi–O distances in several isostructural sillenites, and showed that the Bi–O network in these sillenite compounds remains nearly unchanged. The increase in the M –O distance, however, through the series BSO, BGO, BTO, causes a corresponding decrease in the Bi–O3 distance (from 2.647 Å in BSO to 2.606 Å in BTO).

In view of the small amount of enantiomorphic component found when the Flack parameter was included in the structure refinement, it is necessary to look for reasons other than a mixture of enantiomorphs to explain the lower optical rotatory power. Glazer & Stadnicka (1986) have considered the origin of optical activity in crystal structures, and the sillenite structure is one of those studied. They were able to relate the optical activity to helical arrangements of O atoms, those around a 3_1 axis competing with others around a 3_2 axis. They comment that replacement of Si/Ge by other atoms would be expected to have only a minimal effect on the optical activity, which is dominated by the most polarizable ions, the oxygens.

As previously noted, however, the oxygen arrangement around Bi has been affected by replacement of Si/Ge with Ti. Table 3 lists the O–O distances along the relevant helices for the three structures. These structural helices are pointed out in Fig. 6(a) of Glazer & Stadnicka (1986), which also identifies the various O atoms and should be compared with Fig. 1 above. Bond distances for BGO are taken from the older structural data of Abrahams, Jamieson & Bernstein (1967) rather than the more recent data of Svensson, Abrahams & Bernstein (1979). Devarajan & Glazer (1986) comment that these earlier results give a better fit in their calculation of optical rotatory power (see below).

The simple model adopted by Glazer & Stadnicka can be applied to the family of sillenites BSO, BGO and BTO. In each case, the tighter helix is around the 3_1 axis; its effect must therefore dominate, and crystals with this chirality are all laevorotatory. Competition from the O atoms around the 3_2 axis, however, affects the overall optical rotatory power. Comparing BSO with BGO, the looser helix around the 3_1 axis in the latter is compensated by a looser helix around the 3_2 axis as well (Table 3) and the optical rotatory power is only slightly reduced (Abrahams, Svensson & Tanguay, 1979). In BTO the O–O distance around the 3_1 axis is the largest of the three considered and so its

Table 2. Bond lengths (Å)

		Relation to O1 in Table 1
Bi–O1 ^I	2.075 (7)	$\frac{1}{2}-x, \frac{1}{2}-y, -\frac{1}{2}+z$
Bi–O1 ^{II}	2.241 (8)	y, z, x
Bi–O1 ^{III}	2.603 (9)	$y, 1-z, -x$
Bi–O1 ^{IV}	3.094 (8)	$-\frac{1}{2}+z, \frac{1}{2}-x, \frac{1}{2}-y$
Bi–O1 ^V	3.209 (8)	$\frac{1}{2}-z, \frac{1}{2}-x, -\frac{1}{2}+y$
Bi–O2	2.222 (3)	
Bi–O3	2.606 (6)	
Ti–O3	1.844 (15)	

Table 3. O–O distances (Å) along structural helices

	3_1	3_2	Difference (3_2-3_1)
Bi ₁₂ SiO ₂₀	3.059 (13)	3.168 (13)	0.109 (18)
Bi ₁₂ GeO ₂₀	3.070 (43)	3.183 (43)	0.113 (61)
Bi ₁₂ TiO ₂₀	3.085 (13)	3.178 (13)	0.093 (18)

effect is the smallest. Further, the cancellation from the O atoms around the 3_2 axis is greater than that in BGO, again causing a smaller overall optical rotatory power.

Using the theory developed by Devarajan & Glazer (1986) a series of calculations of refractive index and rotatory power was performed using different values of Bi and O polarizability volumes ($\alpha' = \alpha/4\pi\epsilon_0$). This theory has shown itself to be a very effective method of calculating rotatory power from crystal structure data. The main contributors to the optical rotation are the highly polarizable O atoms [see Glazer & Stadnicka (1986) for comments on the dominant effect of oxygen in the sillenite family and other oxides, *e.g.* quartz]. The value of 0.272 Å³ for the polarizability volume for Ti was taken from Zhdanov (1965). The best fit to observed values of refractive index (2.55 ± 0.04 at 6328 Å; Morrison, 1971) and optical rotatory power ($\sim 5.8^\circ \text{ mm}^{-1}$ at 6500 Å; Feldman, Brower & Horowitz, 1970) was obtained for $\alpha'_{\text{Bi}} = 0.0625 \text{ Å}^3$ and $\alpha'_0 = 3.725 \text{ Å}^3$.

Table 4 gives the results of these calculations, and shows how it was possible to obtain the best-fit values of polarizability volumes by noticing the effects of adjustments to O and Bi independently. A crude contour map of calculated values of optical rotatory power and refractive index for these different polarizability volumes was useful in achieving the best fit.

The best-fit values obtained give closer agreement between observed and calculated values of rotatory power and refractive index than do those for BSO and BGO in Devarajan & Glazer (1986). Values of atomic polarizability volumes for O are comparable (3.725 Å³ for BTO and BGO, 3.54 Å³ for BSO), and this gives further supporting evidence for the validity of Glazer & Stadnicka's approach. Because of the extremely small contribution to overall rotatory power and refractive index by the Bi atoms, the difference between calculated values of the Bi polarizability volumes for the sillenites (0.15 Å³ for BSO, 0.025 Å³ for BGO and 0.0625 Å³ for BTO) is not thought to be significant; it is possible that if better agreement between observed and calculated values of optical rotatory power and

Table 4. Results of calculations of optical rotatory power and refractive index

Ti	Polarizability volumes, $\alpha' = \alpha/4\pi\epsilon_0(\text{\AA}^3)$		Refractive index	Optical rotatory power ($^\circ \text{mm}^{-1}$)
	O	Bi		
0.272	3.71	0.082	2.551	-8.33
0.272	3.70	0.080	2.540	-7.61
0.272	3.70	0.070	2.533	-6.10
0.272	3.72	0.075	2.557	-7.61
0.272	3.74	0.0575	2.565	-5.55
0.272	3.73	0.061	2.557	-5.75
0.272	3.72	0.064	2.549	-5.87
0.272	3.725	0.0625	2.553	-5.81

refractive index for BSO and BGO had been obtained by Devarajan & Glazer then the polarizability volumes for Bi would be closer.

The value of polarizability volume for Ti was kept constant throughout these calculations. Since Ti contributes so little (less than 0.5%) to the overall polarizability it was not considered a profitable exercise to adjust its polarizability volume. Also, no distinction was made between the three different oxygen sites, although there is no reason why each should have the same polarizability volume. To introduce such additional variable parameters into the system would be very expensive in terms of computing time required, and it was not considered relevant to the current discussion.

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