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Yttrium and Titanium Bismuthates with Structures Related to β-Bi$_2$O$_3$

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Abstract

Y and Ti atoms in $Bi_{7.5}Y_{0.5}O_{12}$ and $Bi_{7.68}Ti_{0.32}O_{12.16}$ replace Bi atoms in the structure of β-Bi$_2$O$_3$ with additional O atoms completing their coordination polyhedra. Anti-glass disorder is indicated by neutron diffraction and EXAFS.

Comment

Metastable β-Bi$_2$O$_3$ (Sillén, 1937; Levin & Roth, 1964; Aurivillius & Malmros, 1972) is stabilized by various oxides. Such nonstoichiometric phases are known as β^*-Bi$_2$O$_3$ (Gattow & Schröder, 1962) or β^* bismuthates. Our aim was to locate the Y and Ti atoms and characterize their local environments in the structure of β-Bi$_2$O$_3$ by neutron powder diffraction. Many bismuthates show anti-glass disorder (Burckhardt & Trömel, 1983; Trömel, 1988), the characteristics of which are: (i) a nonstoichiometric composition, (ii) a high concentration of anion defects, (iii) large irregular atomic displacements, *i.e.* three-dimensional positional disorder and (iv) static disorder. In the case of β^* bismuthates, of which more than 50 are known (Ducke, 1993; Delicat, 1993), the presence of this kind of disorder cannot be proved by vibrational spectroscopy. For this reason, we studied the disorder by neutron diffraction and EXAFS, with which it is possible to investigate separately the environments of atoms which share the same crystallographic positions.

β-Bi$_2$O$_3$ has a fluorite-type superstructure, space group $P\bar{4}2_1c$, with $a = 7.739$, $c = 5.636$ Å, $Z = 4$, Bi in position ($8e$) and O in positions ($8e$) and ($4d$) according to X-ray single crystal and neutron powder diffraction (Aurivillius & Malmros, 1972; Blower & Greaves, 1988). BiO$_4E$ trigonal bipyramids (E = equatorial lone pair) form a network with empty channels along [00z] and $[\frac{1}{2}\frac{1}{2}z]$. Two more O atoms with Bi—O distances of about 2.7 Å are considered as neighbours of Bi (Fig. 1) according to the geometrical definition of coordination (Alig & Trömel, 1992), the definition of Frank & Kasper (1958) or the '*Wirkungsbereich*' (Niggli, 1927).

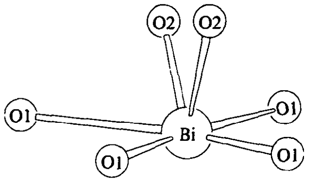

Fig. 1. Bi–O coordination in β-Bi$_2$O$_3$.

In the neutron powder patterns of $Bi_{7.5}Y_{0.5}O_{12}$, (I), and $Bi_{7.68}Ti_{0.32}O_{12.16}$, (II), the space groups $P\bar{4}2_1c$ and $P4_2/nmc$ cannot be distinguished by systematic absences. All calculations were performed assuming $P4_2/nmc$.† Satisfactory agreement was obtained assuming the Y and Ti atoms to be statistically distributed over the Bi positions. The agreement improved further when partial occupancy of additional O-atom positions was taken into account. In $Bi_{7.5}Y_{0.5}O_{12}$, O with an occupancy factor of 0.22 was found in ($2a$). The number of O3 atoms, 0.44 per cell, corresponds roughly to the number of Y atoms (0.5 per cell) and we assume that the additional O atoms are coordinated to Y. Thus, from the irregular sixfold coordination of Bi, an also irregular sevenfold coordination polyhedron results (Fig. 2). The presence of additional O atoms in ($2a$) is compensated for by 0.16 vacancies per cell in the O1 position ($8e$) and 0.28 vacancies per cell in the O2 position ($4d$), which implies that Bi, Y or both are not uniformly coordinated.

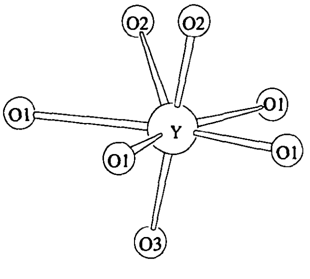

Fig. 2. Y–O coordination in $Bi_{7.5}Y_{0.5}O_{12}$.

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† Refinements in space group $P\bar{4}2_1c$ resulted in somewhat lower R values, presumably due to the greater number of free parameters. For these parameters see Ducke *et al.* (1996). The space group $P\bar{4}2_1c$ for β-Bi$_2$O$_3$ itself is not in doubt (Blower & Greaves, 1988).

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In $Bi_{7.68}Ti_{0.32}O_{12.16}$, additional O atoms were found in (2*a*) with an occupancy factor of 0.16 and in (2*b*) with an occupancy factor of 0.08. Again, the number of O atoms in (2*a*) corresponds to the number of Ti atoms (0.32 per cell). Occupation of position (2*b*), however, is incompatible with complete occupation of (8*e*) as this would result in short O···O distances of 2.2 Å. Therefore, the O1 atoms with distances of 2.20 Å to (Bi, Ti) must be missing if (2*a*) and (2*b*) are occupied, and a highly irregular sixfold coordination polyhedron for Ti will result (Fig. 3). In both cases, the additional O atoms are placed within the channels which are empty in the β-Bi_2O_3 structure.

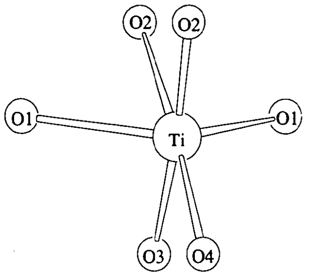

Fig. 3. Ti—O coordination in $Bi_{7.68}Ti_{0.32}O_{12.16}$.

Replacement of Bi by other atoms in connection with local modifications of the structure seems to be common in Bi_2O_3, and the β, γ and δ modifications are stabilized in this way. Local disorder in such phases has been investigated for sillenite-type γ^* bismuthates (Radaev *et al.*, 1988, 1989, 1994; Radaev, Muradyan & Simonov, 1991; Radaev, Simonov, Kargin & Skorikov, 1992). If Bi^{3+} in Bi_2O_3 is substituted by other than trivalent elements, the composition will vary and vacancies or atoms in additional positions will ensure electroneutrality. This type of replacement is observed here for the first time in β^* bismuthates and may be expected for many other phases that can be derived from β-Bi_2O_3.

In the case of δ^* bismuthates with the defect fluorite structure of δ-Bi_2O_3, the substitution of Bi by other atoms causes not only local disorder but all atoms are shifted irregularly and the coordination varies even for the same type of atom. This is a characteristic feature of anti-glass disorder, which is then recognized from the high displacement parameters of all atoms.

In $Bi_{7.5}Y_{0.5}O_{12}$ and $Bi_{7.68}Ti_{0.32}O_{12.16}$, all atoms in the positions of the β-Bi_2O_3 structure are irregularly shifted with displacement parameters *B* of 2 to 4 $Å^2$ (Tables 1 and 3) corresponding to mean displacements of 0.16 to 0.23 Å. This indication of anti-glass disorder is confirmed by the Fourier transforms of EXAFS data from the BiL_3 edges of both phases and from the Y*K* edge of $Bi_{7.5}Y_{0.5}O_{12}$. Beyond the first sphere of coordination, they show greatly reduced (almost missing) peaks due to the variable surroundings of Bi, which are connected with such irregular atomic shifts (Ducke *et al.*, 1992). The displacement parameters of the additional atoms could not be determined, probably due to their low occupancies.

Experimental

Powder samples were prepared by heating appropriate amounts of pre-heated high purity α-Bi_2O_3 (99.9%, Janssen) and TiO_2 (99.8%, Riedel-de-Haën) or Y_2O_3 (99.9%, Sigma) in gold vessels at 1123–1273 K and quenching in ice-water.

Compound (I)

Crystal data

$Bi_{7.5}Y_{0.5}O_{12}$
M_r = 1803.8
Tetragonal
$P4_2/nmc$
a = 7.7451 (7) Å
c = 5.6351 (6) Å
V = 338.03 $Å^3$
Z = 1
D_x = 8.860 Mg m^{-3}

Neutron radiation
λ = 1.2167 Å
Cell parameters from 23 reflections
θ = 3–45°
Room temperature
Powder
Orange

Data collection

Flat cone powder diffractometer with a multi-counter detector system
Absorption correction: none

36 groups of reflections with $I > 2\sigma(I)$ measured
θ_{max} = 35.23°
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 5$

Refinement

Refinement on I
R_I = 0.041 where $R_I = \Sigma|I_o - I_c|/\Sigma I_o$
36 groups of reflections

8 parameters
Scattering lengths from Sears (1992)

Table 1. *Fractional atomic coordinates and isotropic displacement parameters ($Å^2$) for (I)*

	Occupancy	Wyckoff position	x	y	z	B_{iso}
Bi,Y	1.0	8(*g*)	0	0.258 (2)	0.234 (2)	2.0 (2)
O1	0.98	8(*f*)	0.302 (3)	x	0	3.6 (4)
O2	0.93	4(*d*)	0	1/2	0.393 (6)	2.0 (5)
O3	0.22	2(*a*)	0	0	0	4 (5)

Table 2. *Selected geometric parameters (Å) for (I)*

Bi,Y—O1	2.19 (4)	Bi,Y—O2	2.68 (3)
Bi,Y—O1	2.71 (5)	Bi,Y—O3	2.39 (3)
Bi,Y—O2	2.08 (3)		

Compound (II)

Crystal data

$Bi_{7.68}Ti_{0.32}O_{12.16}$
M_r = 1814.8
Tetragonal
$P4_2/nmc$
a = 7.7069 (6) Å
c = 5.6735 (4) Å

Neutron radiation
λ = 1.2167 Å
Cell parameters from 24 reflections
θ = 3–45°
Room temperature

$V = 336.98$ Å^3
$Z = 1$
$D_x = 8.942$ Mg m^{-3}

Powder
Orange

Data collection

Flat cone powder diffractometer with a multicounter detector system
Absorption correction: none

32 groups of reflections with $I > 2\sigma(I)$ measured
$\theta_{\max} = 35.58°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 5$

Refinement

Refinement on I
$R_I = 0.043$ where $R_I = \Sigma|I_o - I_c|/\Sigma I_o$
32 groups of reflections

9 parameters
Scattering lengths from Sears (1992)

Table 3. *Fractional atomic coordinates and isotropic displacement parameters (Å^2) for (II)*

	Occupancy	Wyckoff position	x	y	z	$B_{\rm iso}$
Bi,Ti	1.0	8(*g*)	0	0.254 (3)	0.234 (3)	1.9 (2)
O1	0.96	8(*f*)	0.300 (4)	x	0	3.1 (3)
O2	1.0	4(*d*)	0	1/2	0.380 (7)	2.3 (5)
O3	0.16	2(*a*)	0	0	0	0 (4)
O4	0.08	2(*b*)	0	0	1/2	5 (21)

Table 4. *Selected geometric parameters (Å) for (II)*

Bi,Ti—O1	2.20 (3)	Bi,Ti—O2	2.76 (4)
Bi,Ti—O1	2.69 (3)	Bi,Ti—O3	2.37 (2)
Bi,Ti—O2	2.07 (3)	Bi,Ti—O4	2.47 (2)

Weight losses of slowly cooled samples were less than 0.2%. Determination of active oxygen (Cornwell, 1971) showed that no oxidation of bismuth had occurred. Therefore, any significant change of composition during the heating procedure can be excluded. All subsequent investigations were performed with homogeneous samples only. Neither their X-ray nor their neutron powder patterns showed reflections of other phases.

The crystal data were determined using a Siemens D5000 powder diffractometer with secondary monochromator, Cu $K\alpha_1$ radiation, $\lambda = 1.54056$ Å. The patterns were registered using a step scan (10 s per step) and corrected by least-squares calculations for zero-point shift using the program *XRAYPOWD* (Martin, 1991). The diffractometer was calibrated using silicon as external standard. The neutron diffraction data were collected at the BER II reactor at the Berlin Neutron Scattering Center (BENSC) of the Hahn-Meitner-Institut, Berlin, Germany.

Occupancy factors, connected appropriately by constraints according to the sample composition, were varied stepwise. The refinement of the structural and displacement parameters on groups of overlapping reflections was performed with our own trial-and-error program (*TRITM*; unpublished), which has been used successfully for evaluating powder data before (*e.g.* Trömel, Maetz & Müllner, 1977; von Beckh, Zegreanu & Trömel, 1981).

Lists of neutron diffraction intensities have been deposited with the IUCr (Reference: JZ1066). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$PdTe_2$

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Abstract

The structure of palladium(IV) telluride has been determined by single-crystal X-ray methods. The structure type is $Cd(OH)_2$-(C6). $PdTe_2$ has a layered structure with the layers stacking along the [001] direction. The Pd^{4+} cations are octahedrally coordinated. The layers are