



# Synthesis and crystal structure analysis of titanium bismuthide oxide, $\text{Ti}_8\text{BiO}_7$



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## ABSTRACT

Silver metallic luster columnar single crystals of a novel compound,  $\text{Ti}_8\text{BiO}_7$ , were synthesized using a bismuth flux.  $\text{Ti}_8\text{BiO}_7$  having a new structure type crystallizes in an orthorhombic cell,  $a = 7.8473(4)$  Å,  $b = 16.8295(10)$  Å,  $c = 3.0256(2)$  Å, space group:  $Cmmm$ . The Ti atoms enter the sites of isosceles-triangle 3-fold and rectangular 4-fold coordination of O atoms and the site of octahedral 6-fold coordination of O and Bi atoms. O atoms are in the rectangles, tetrahedra, and orthogonal pyramids of Ti atoms. The electrical resistivity measured for a  $\text{Ti}_8\text{BiO}_7$  single crystal in the  $c$ -axis direction was  $6.2 \times 10^{-7}$  Ωm at 300 K and  $1.3 \times 10^{-7}$  Ωm at 10 K.

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## 1. Introduction

Besides a ferroelectric compound,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , which has been studied intensively for many years, as referred to in the paper by Shrinagar et al. [1],  $\text{Bi}_2\text{Ti}_2\text{O}_7$  [2],  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$  [3],  $\text{Bi}_{12}\text{TiO}_{20}$  [4], and  $\text{Bi}_{20}\text{TiO}_{32}$  [5] have been synthesized in the bismuth, titanium, and oxygen ternary system. Bi in the structure of  $\text{Bi}_2\text{O}_3$  was partially replaced with Ti in  $\text{Bi}_{7.68}\text{Ti}_{0.32}\text{O}_{12.16}$  [6]. In these Bi–Ti–O ternary compounds, Bi and Ti atoms have the oxidation state of +3 and +4, respectively. Richter and Jeitschko described the presence of  $\text{Ti}_{3.0(1)}\text{Bi}_2\text{O}$  and  $\text{Ti}_{3.10(4)}\text{Bi}_2\text{O}$  [7], but no report on the synthesis and crystal structures of these compounds was published.

$\text{Ti}_{11.3}\text{Sn}_3\text{O}_{10}$ , in which Ti atoms bind to O and Sn atoms, combines the structural features of oxides and intermetallics [8].  $\text{Ti}_3\text{PO}_2$  has a distorted structure in which O atoms of  $\gamma$ -TiO (NaCl-type structure) are replaced in part by P atoms [9]. In these oxygen poor compounds, O atoms bind to only Ti atoms. Since the report of  $\text{Ce}_2\text{BiO}_2$  containing  $\text{Bi}^{2-}$  has been reported by Benz [10], isomorphous compounds,  $\text{R}_2\text{BiO}_2$  ( $R$  = rare-earth elements or Y), have been synthesized [11–13]. In addition,  $\text{AE}_4\text{Bi}_2\text{O}$  ( $\text{AE}$  = Ca, Sr, Ba) [14,15] and  $\text{RE}_4\text{Bi}_2\text{O}$  ( $\text{RE}$  = Sm, Eu) [16,17] containing  $\text{Bi}^{3-}$  have also been reported. These compounds contain bismuthide ions ( $\text{Bi}^{2-}$  or  $\text{Bi}^{3-}$ ) and oxide ions ( $\text{O}^{2-}$ ) and are termed complex anion compounds or bismuthide oxides.

Rotundu et al. synthesized a novel Ba–Ti–O ternary compound,

$\text{Ba}_{1+\delta}\text{Ti}_{13-\delta}\text{O}_{12}$  ( $\delta = 0.11$ , cubic  $a = 6.8334(6)$  Å, space group  $Pm\bar{3}m$ ) using a flux method [18]. The oxidation state of Ti determined by XAS was 2+. In the crystal structure of  $\text{Ba}_{1+\delta}\text{Ti}_{13-\delta}\text{O}_{12}$ , Ba and Ti atoms are in the channels of a three-dimensional  $\text{TiO}_4$  network. Recently, we have synthesized single crystals of a new polymorph of titanium monoxide,  $\epsilon$ -TiO, using a bismuth flux [19]. Theoretical calculation revealed that  $\epsilon$ -TiO is the most stable phase among the titanium monoxide phases. In the course of this research, we found some single crystals of a novel compound,  $\text{Ti}_8\text{BiO}_7$ . The present paper reports the preparation of  $\text{Ti}_8\text{BiO}_7$  single crystals and its crystal structure determined by single crystal X-ray diffraction (XRD). The electrical resistivity of  $\text{Ti}_8\text{BiO}_7$  was measured for a single crystal.

## 2. Experiment

Ti powder (Mitsuwa Chemicals, 99.99%) and  $\text{Bi}_2\text{O}_3$  powder (Mitsuwa Chemicals, 99.999%) were used as starting powders. Ti (1 mmol) and  $\text{Bi}_2\text{O}_3$  (0.333 mmol) were weighed, mixed in an agate mortar with a pestle, and pressed into pellets at 100 MPa in air. The pellets were placed in Ta boats (Nilaco, 99.95%) and sealed in SUS316 tubes in a glove box filled with Ar gas (Taiyo Nippon Sanso, 99.9999%). The pellets were heated to 900 °C at a rate of 7.5 °C/min and this temperature was maintained for 12 h, followed by cooling to room temperature in the furnace, the power to the furnace having been shut off. The SUS316 tubes were opened in air. The samples were washed with nitric acid aqueous solution ( $\text{HNO}_3$ , 4 mol/L) to dissolve away Bi, and then washed with water. The

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residual substances was observed with an optical microscope and a scanning electron microscope (SEM, KEYENCE, VE-8800SP1614).

Parts of the residual samples were pulverized with an agate mortar and a pestle to identify the crystalline phases by powder XRD using CuK $\alpha$  radiation (Bruker, D2 phaser). Quantitative analysis of Ti, O and Bi was performed on the flat surface of the single crystals formed in the sample by using an electron probe micro-analyzer (EPMA, JEOL, JXA-8200) with wavelength dispersive X-ray (WDX) detectors. The crystals were fixed on an indium metal plate. Bi and TiO<sub>2</sub> were used as standard samples for quantitative WDX analysis. A single crystal was fixed to the tip of a glass fiber with epoxy resin, and the X-ray data were collected with a Bruker D8 QUEST diffractometer with monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega$ - $\phi$ -scan technique. Data collection and unit-cell refinement were performed with the APEX2 software package [20]. Absorption correction was applied using the numerical procedure SADABS [21]. The structure parameters of the crystal were refined by the full-matrix least-squares on  $F^2$  using the SHELXL-97 program [22]. The crystal structure was illustrated with the VESTA program [23]. The electrical resistivity from 10 K to 300 K was measured by the direct current four-terminal method using silver paste as electrodes.

### 3. Results and discussion

The powder XRD pattern of the obtained sample is shown in Fig. 1. The main diffraction peaks could be indexed with the lattice parameters of  $\epsilon$ -TiO and  $\gamma$ -TiO. Other small XRD peaks could be explained by residual Bi metal and the new compound of Ti<sub>8</sub>BiO<sub>7</sub>. The obtained sample consisted mainly of silver needle-like single crystals of  $\epsilon$ -TiO with lengths of under 30  $\mu\text{m}$  and brown grains of  $\gamma$ -TiO. The sample also contained a small number of silver metallic luster columnar-like single crystals of Ti<sub>8</sub>BiO<sub>7</sub> with lengths of 200  $\mu\text{m}$ –1.0 mm. Fig. 2 shows an SEM photograph of a single crystal of Ti<sub>8</sub>BiO<sub>7</sub>. The composition of the single crystal analyzed by WDX was Ti: 53.0(6), Bi: 30.0(2), and O: 15.7(3) mass% (total 98.7(2) mass %). The Ti:Bi:O atomic ratio calculated from the composition was 7.9(1):1:7.0(1), which agreed with the ratio from the formula of Ti<sub>8</sub>BiO<sub>7</sub>.

A single crystal of Ti<sub>8</sub>BiO<sub>7</sub> was cut to a size of about 50  $\mu\text{m}$  to collect the XRD data. The X-ray reflections could be indexed with orthorhombic cell parameters  $a = 7.8473(4) \text{ \AA}$ ,  $b = 16.8295(10) \text{ \AA}$ ,

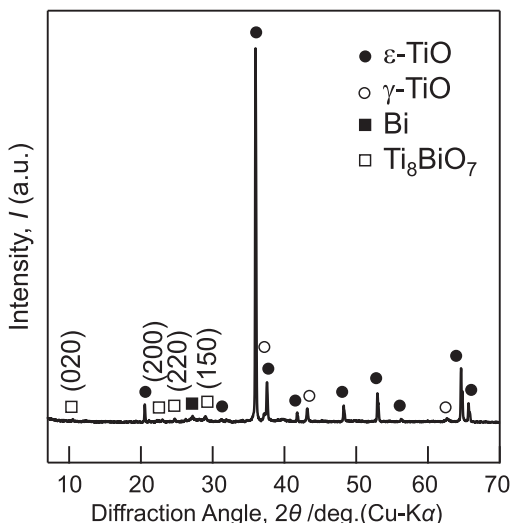


Fig. 1. Powder XRD patterns of the sample.

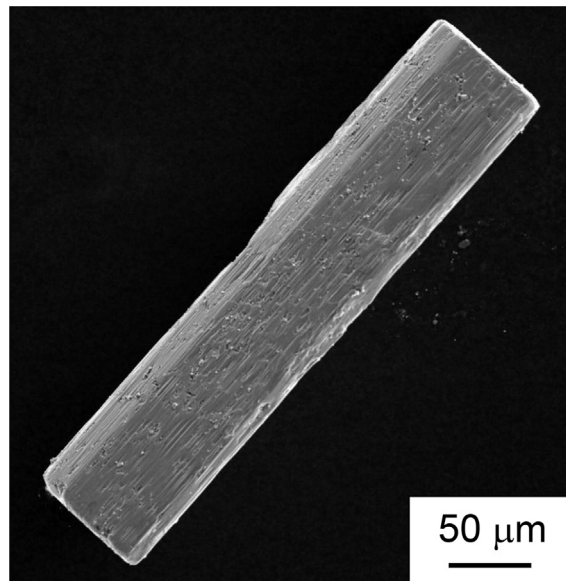


Fig. 2. SEM image of a Ti<sub>8</sub>BiO<sub>7</sub> single crystal.

and  $c = 3.0256(2) \text{ \AA}$ . Possible space groups of  $C222$ ,  $Cmm2$ ,  $Cm2m$ ,  $C2mm$ , and  $Cmmm$  were selected by systematic extinction. The crystal structure model was obtained by Intrinsic Phasing in the APEX2 software package [20] with the composition of Ti<sub>8</sub>BiO<sub>7</sub>,  $Z = 2$  and the most symmetrical space group,  $Cmmm$ . The crystal structure parameters of Ti<sub>8</sub>BiO<sub>7</sub> were refined well with an  $R1$ -value ( $2\sigma$ ) of 1.49%. The results of the structure analysis, refined atomic coordinates, anisotropic atomic displacement parameters, interatomic distances, and bond angles are shown in Tables 1–4.

As listed in Table 2, there are three sites (8 $q$ , 4 $g$ , 4 $i$ ) for Ti, one site (2 $c$ ) for Bi, and three sites (8 $p$ , 4 $i$ , 2 $d$ ) for O. The crystal structure of Ti<sub>8</sub>BiO<sub>7</sub>, illustrated with Ti atom centered O and O–Bi polyhedra, is shown in Fig. 3(a). The atomic arrangements around the Ti atoms are shown in Fig. 3(b–d). The Ti1 site is surrounded by two O1 atoms and two O2 atoms. Ti1–O1 and Ti1–O2 bond lengths are 2.0480(12)  $\text{\AA}$  ( $\times 2$ ) and 2.0919(4)  $\text{\AA}$  ( $\times 2$ ), respectively. The Ti1 atom is shifted toward the neighboring Ti1 site from the rectangle plane of the O atoms. The Ti1–Ti1 interatomic distance of 2.8839(8)  $\text{\AA}$  (Fig. 3(b)) is close to the Ti–Ti distances in  $\alpha$ -Ti (2.897–2.951  $\text{\AA}$ ) and in Ba<sub>1+ $\delta$</sub> Ti<sub>13- $\delta$</sub> O<sub>12</sub> ( $\delta = 0.11$ , 2.895  $\text{\AA}$ ). A similar location of Ti atoms away from the rectangular planes of O atoms has been reported in the structure of Ti<sub>11.3</sub>Sn<sub>3</sub>O<sub>10</sub> (O–Ti lengths: 1.953(1) ( $\times 2$ ), 2.043(2)  $\text{\AA}$  ( $\times 2$ ) [8]) and Ba<sub>1+ $\delta$</sub> Ti<sub>13- $\delta$</sub> O<sub>12</sub> (O–Ti lengths: 2.051(5)  $\text{\AA}$  ( $\times 4$ ) [18]). The Ti1–Bi interatomic distance of 3.2048(6)  $\text{\AA}$  is close to the longest Ti–Bi distances reported for Ti<sub>8</sub>Bi<sub>9</sub> (2.818(4)–3.122(6)  $\text{\AA}$ ) [7] and BiTi<sub>2</sub> (2.86–3.19  $\text{\AA}$ ) [24].

The Ti2 site is octahedrally surrounded by O1 ( $\times 2$ ), O3 ( $\times 2$ ), and Bi ( $\times 2$ ) sites. The bond lengths of Ti2–O1, Ti2–O3, and Ti2–Bi are 2.0088(17)  $\text{\AA}$ , 2.0429(5)  $\text{\AA}$ , and 2.9656(6)  $\text{\AA}$ , respectively. The Ti2–Bi bond length is in the range of the Ti–Bi lengths observed in Ti<sub>8</sub>Bi<sub>9</sub> and BiTi<sub>2</sub>. A Ti3 atom is at the isosceles triangular planar coordination site of O1 ( $\times 2$ ) and O2 ( $\times 1$ ). The Ti3–O1 and Ti3–O2 bond lengths are 1.9883(17)  $\text{\AA}$  and 2.002(3)  $\text{\AA}$ , respectively, and the O1–Ti3–O2 bond angle is 135.21(6) $^\circ$ . The bond valence sum of Ti3 calculated with the bond lengths and the Ti (II) bond valence parameter ( $R_{0,\text{Ti(II)}} = 1.734 \text{ \AA}$ ) obtained from the observed Ti–O bond lengths of  $\epsilon$ -TiO [19] with  $b = 0.37$  was 1.491. This is smaller than the bond valence sum of Ti (1.566) in a regular triangular planar coordination of O in  $\epsilon$ -TiO (Ti–O bond lengths: 1.9746(9)  $\text{\AA}$  ( $\times 3$ )). The Ti–O bond lengths of Ti<sub>8</sub>BiO<sub>7</sub> are from 1.9883(17)  $\text{\AA}$

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