Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A ferroelectric barium titanate, $BaTi_2O_5$

Teiichi Kimura,[a]* Takashi Goto,[a] Hisanori Yamane,[b] Hiroaki Iwata,[a] Takashi Kajiwara[c] and Takaya Akashi[a]

[a]Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan, [b]Center for Interdisciplinary Research, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan, and [c]Graduate School of Science, Department of Chemistry, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8578, Japan
Correspondence e-mail: tei@imr.edu

Received 23 June 2003
Accepted 29 September 2003
Online 8 November 2003

The crystal structure of monobarium dititanium pentaoxide, $BaTi_2O_5$, synthesized by a floating-zone method, was studied by X-ray diffraction. Previous reports describe the structure as being in the monoclinic centrosymmetric space group *C*2/*m*. We have recently found that this material exhibits ferroelectricity, and therefore $BaTi_2O_5$ should have lower symmetry. The crystal structure of $BaTi_2O_5$ was refined in space group *C*2, revealing a displacement of the Ti atoms along the *b* axis. This result is consistent with the fact that the ferroelectricity of $BaTi_2O_5$ was only observed along the *b* axis.

Comment

Since $BaTi_2O_5$ decomposes into $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$ at temperatures higher than 1400 K (Ritter *et al.*, 1986), this compound has been regarded as a metastable phase or a low-temperature phase. Harrison (1956) reported the crystal structure of $BaTi_2O_5$, based on Weissenberg camera data, and showed the crystal structure to be monoclinic [space group *C*2/*m*, with $a = 16.892$ (13) Å, $b = 3.930$ (1) Å, $c = 9.410$ (4) Å and $\beta = 103.03$ (5)°; the original description was in the *A*2/*m* setting]. The *R* value of that analysis was ~20%. The reported density measured by a flotation method was 4.4 Mg m^{-3}, which differs significantly from the value calculated from the lattice parameters and *Z* value (5.1 Mg m^{-3}).

The crystal structure of $BaTi_2O_5$ was also refined using data collected with a four-circle X-ray diffractometer (Tillmanns, 1974). The single crystal used for that analysis was prepared by rapid solidification of a melt composed of BaO/TiO_2 in a 30:70 molar ratio. The crystal structure was refined using the *C*2/*m* model of Harrison (1956), giving *R*2 and *R*1 values of 0.031 and 0.026, respectively [with intensity data of $I > 2\sigma(I)$].

Recently, we have synthesized $BaTi_2O_5$ single crystals of more than 1 cm in size by a floating-zone method (Akashi *et al.*, 2003*a*) and characterized the dielectric properties. The electric-field–polarization (P–E) curves along the *b* axis showed the existence of ferroelectricity (Akashi *et al.*, 2003*b*). However, this result is not consistent with the centrosymmetric structure of space group *C*2/*m*.

The X-ray diffraction data collected for the present study were indexed with a monoclinic lattice. The refined lattice parameters agree with the previously reported values within the standard uncertainties, and the space group could be *C*2, *Cm* or *C*2/*m* according to the experimental systematic extinctions. The measured density agrees well with the calculated density.

Refinement using the structural model in *C*2/*m* reported by Harrison (1956) converged to an *R*1 value of 0.051 ($wR2 = 0.143$). The U_{22} anisotropic displacement parameter for the Ti1 site was refined to 0.020 (1) Å^2, which is 3–4 times greater than the values of U_{11} [0.005 (1) Å^2] and U_{33} [0.006 (1) Å^2] for the same site, and of U_{22} [0.004 (1)–0.006 (1) Å^2] for other Ti sites. The B_{22} anisotropic displacement parameter of the Ti1 site reported by Tillmanns (1974) was also over 10 times greater than the other parameters.

Since the displacement parameter of the Ti1 site along the *b* axis was so large, we refined the structure in space group *C*2, in which the mirror plane of *C*2/*m* perpendicular to the *b* axis is removed. The *R*1 and *wR*2 values using all data were 0.046 and 0.112, respectively, and the U_{22} value of the Ti1 site refined to 0.0054 (6) Å^2. The crystal structure refined with the *C*2 model is illustrated in Fig. 1. As can be seen, the elongation of the displacement ellipsoids was insignificant.

The arrangement of the Ba and O atoms is close to the cubic closest packing, and the most closely packed layers are aligned parallel to the $(3\bar{1}\bar{3})$, $(\bar{3}\bar{1}3)$, $(5\bar{1}1)$ and $(\bar{5}\bar{1}1)$ planes. Fig. 2 shows the crystal structure of $BaTi_2O_5$ using Ti-atom-centered O-atom octahedra. All atoms in the structure are arranged approximately along the (104), $(40\bar{1})$ and (010) planes.

There are three kinds of Ti sites in the crystal structure of $BaTi_2O_5$. The vertex O atoms link octahedra of the same kind of Ti site along the *b* axis. In the *ac* plane, the Ti1-centered O-atom octahedra ($Ti1O_6$) connect to the $Ti1O_6$ and $Ti3O_6$ octahedra *via* shared apices, and to the $Ti2O_6$ octahedra *via* shared edges. The $Ti2O_6$ and $Ti3O_6$ octahedra share edges continuing along the *b* axis.

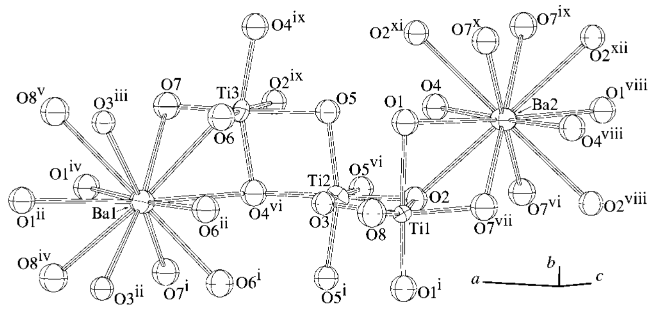

Figure 1
The arrangement of atomic positions in the structure of $BaTi_2O_5$; displacement ellipsoids are shown at the 99% probability level for Ba and Ti atoms, and O atoms are shown as spheres. For symmetry codes, see Table 1.

DOI: 10.1107/S0108270103021395

The Ba1 atoms are surrounded by 12 O atoms and in the large tunnels of TiO_6 octahedra along the *b* axis. The Ba2 atoms are situated in the 12-fold coordination sites of the O atoms belonging to the $Ti1O_6$ and $Ti3O_6$ octahedra. The arrangement of the Ba2 atoms and the $Ti1O_6$ and $Ti3O_6$ octahedra along the *b* axis is similar to that in the perovskite-type structure.

Selected interatomic distances and bond angles are listed in Table 1. The Ba1—O distances [2.673 (9)–3.279 (7) Å] are close to the Ba—O distances (2.653–3.278 Å) reported for $Ba_5Ti_{17}O_{40}$, in which the Ba atoms are coordinated by 12 O atoms (Hofmeister *et al.*, 1984). The Ba2—O distances [2.766 (8)–2.998 (5) Å] have a smaller deviation than the Ba1—O distances. The bond-valence sums calculated from the parameters presented by Brese & Keeffe (1991) are 2.49 and 2.45 for atoms Ba1 and Ba2, respectively. These values are smaller than that calculated for the Ba atom in tetragonal $BaTiO_3$ (2.78; Buttner & Maslen, 1992) and are close to the values for the Ba atoms in $Ba_6Ti_{17}O_{40}$ (2.13–2.64).

The Ti3—O bond lengths are in the range 1.710 (5)–2.474 (5) Å and are greater than the Ti1—O [1.765 (10)–2.171 (10) Å] and Ti2—O [1.796 (5)–2.150 (5) Å] distances. The bond-valence sums for atoms Ti1, Ti2 and Ti3 are 3.99, 3.95 and 4.09, respectively, implying that the valence of the Ti atoms is 4. The bond-valence sums for the O atoms (1.93–2.19) are close to 2, except for sites O3 (2.31) and O6 (2.32). Atom O6 is surrounded by one Ti3 and three Ba1 atoms, and the O6—Ti3 distance [1.710 (5) Å] is the shortest of the Ti—O bond lengths in $BaTi_2O_5$. The O6—Ba distances [2.673 (9), 2.703 (5), 2.727 (9) Å] are also shorter than the average O—Ba distance in $BaTi_2O_5$ (2.908 Å). Atoms Ti1 and Ti2 and two Ba1 atoms coordinate with atom O3, and the O3—Ba1 distances [2.673 (7) and 2.742 (8) Å] are shorter than the average O—Ba distance. These short O—Ba distances are related to the large bond-valence sums of atoms O3 and O6.

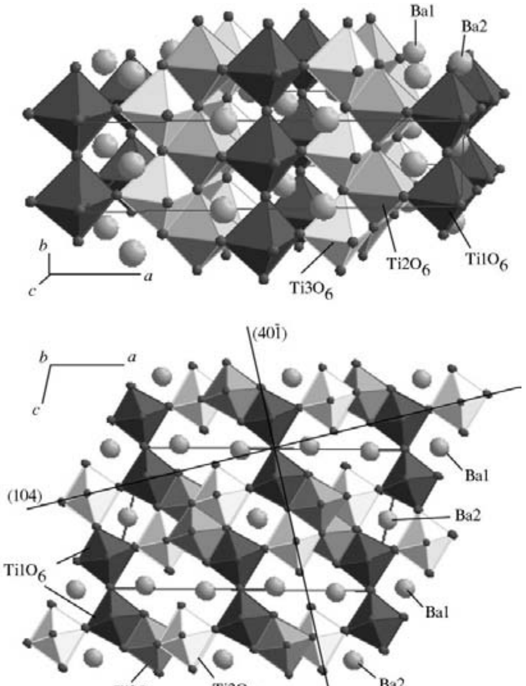

Figure 2
The structure of $BaTi_2O_5$, with Ti-centered O-atom octahedra.

The O1—Ti1—O1 and Ti1—O1—Ti1 bond angles are both 176.5 (3)°, meaning that atoms O1 and Ti1 are aligned almost linearly along the *b* axis. The Ti1—O1 bond lengths are alternately 1.765 (10) and 2.171 (10) Å; atom Ti1 shifts from the center of the $Ti1O_6$ octahedron along the *b* axis. On the other hand, atoms Ti2 and Ti3 lie almost in the *ac* plane and apart from the (104) and (40$\bar{1}$) planes in the $Ti2O_6$ and $Ti3O_6$ octahedra. The O5—Ti2—O5 and Ti2—O5—Ti2 bond angles are 152.3 (3)°, and the O4—Ti3—O4 and Ti3—O4—Ti3 angles are 159.3 (3)°. The Ti2—O5 bond lengths [2.025 (10) and 2.028 (10) Å] are close to the Ti3—O4 bond lengths [1.983 (11) and 2.018 (11) Å].

The atomic coordination of (x, y, z) is equivalent to that of $(-x, y, -z)$ because of the twofold symmetry along the *b* axis in space group *C*2, and therefore ferroelectricity is expected only in the direction of the *b* axis. This fact is in accordance with the observed dielectric properties of a $BaTi_2O_5$ single crystal (Akashi *et al.*, 2003*a*,*b*). By selecting the Ba1 site as a reference ($y = 0.000$), the *y* positions are +0.002 for atom Ba2, +0.012 for atom Ti2, +0.009 for atom Ti3 and +0.009–0.021 for atoms O1–O8. On the other hand, the Ti1 site is at −0.031, and the displacement is ~0.18 Å from the average *y* position of the O-atom sites. The spontaneous polarization ($0.10\ \mathrm{C\ m^{-2}}$) can be calculated by assuming nominal charges of Ba^{2+}, Ti^{4+} and O^{2-}. This value is about two-thirds of that calculated for tetragonal $BaTiO_3$ ($0.16\ \mathrm{C\ m^{-2}}$). The value of $0.10\ \mathrm{C\ m^{-2}}$ was measured at 523 K, applying an electric field of $10^6\ \mathrm{V\ m^{-1}}$ (Akashi *et al.*, 2003*b*). Generally, the Ti^{4+} ion has a d_0 electron configuration and tends to stay in a distorted O-atom octahedron because of the second-order Jahn–Teller effect (Wheeler *et al.*, 1986), and hence the Ti^{4+} ions of $BaTi_2O_5$ are situated in the distorted O-atom octahedra. The displacement of Ti atoms in the Ti1 sites is mainly responsible for the ferroelectricity.

Experimental

$BaCO_3$ (99.9%) and TiO_2 (99.9%) powders in a Ba/Ti molar ratio of 2:1 were weighed and mixed in an agate motor. The mixed powder was pressed isostatically into a rod at 10 MPa and heated at 1503 K for 43 ks. The sintered rod, about 6 mm in diameter, was melted and solidified directionally by the floating-zone method at a rate of $5.6 \times 10^{-6}\ \mathrm{m\ s^{-1}}$ in flowing 79% Ar–21% O_2 gas. Colorless and transparent single crystals of $BaTi_2O_5$ (3 mm in diameter and 2 mm in length) were synthesized. The crystals were cleaved into smaller pieces for use in the X-ray diffraction experiment.

Crystal data

$BaTi_2O_5$
$M_r = 313.14$
Monoclinic, *C*2
$a = 16.899\ (3)$ Å
$b = 3.9350\ (6)$ Å
$c = 9.4105\ (15)$ Å
$\beta = 103.103\ (3)^\circ$
$V = 609.48\ (17)$ Å^3
$Z = 6$
$D_x = 5.119\ \mathrm{Mg\ m^{-3}}$
$D_m = 5.09\ \mathrm{Mg\ m^{-3}}$
D_m measured by the Archimedean method
Mo $K\alpha$ radiation
Cell parameters from 818 reflections
$\theta = 2.2$–30.0°
$\mu = 13.32\ \mathrm{mm^{-1}}$
$T = 293\ (2)$ K
Prism, colorless
$0.20 \times 0.14 \times 0.12$ mm

Table 1
Selected geometric parameters (Å, °).

Ba1—O6^{i}	2.673 (9)	Ti1—O1^{i}	1.765 (10)
Ba1—O3^{ii}	2.673 (7)	Ti1—O7^{vii}	1.947 (5)
Ba1—O6^{ii}	2.703 (5)	Ti1—O8	1.9502 (19)
Ba1—O6	2.727 (9)	Ti1—O3	1.996 (5)
Ba1—O3^{iii}	2.742 (8)	Ti1—O2	2.123 (5)
Ba1—O8^{iv}	2.954 (9)	Ti1—O1	2.171 (10)
Ba1—O1^{ii}	2.960 (5)	Ti1—Ti2	2.9069 (19)
Ba1—O1^{iv}	2.980 (5)	Ti2—O3	1.796 (5)
Ba1—O8^{v}	3.035 (10)	Ti2—O2	1.849 (5)
Ba1—O7^{i}	3.186 (7)	Ti2—O5^{i}	2.025 (10)
Ba1—O4^{vi}	3.258 (5)	Ti2—O5	2.028 (10)
Ba1—O7	3.279 (7)	Ti2—O4^{vi}	2.099 (5)
Ba2—O7^{vii}	2.766 (8)	Ti2—O5^{vi}	2.150 (5)
Ba2—O7^{vi}	2.766 (8)	Ti2—Ti3	3.067 (3)
Ba2—O2^{viii}	2.858 (9)	Ti2—Ti3^{i}	3.083 (3)
Ba2—O2	2.858 (9)	Ti2—Ti2^{ix}	3.1853 (19)
Ba2—O7^{ix}	2.862 (8)	Ti2—Ti2^{vi}	3.1853 (19)
Ba2—O7^{x}	2.862 (8)	Ti2—Ti3^{vi}	3.2536 (17)
Ba2—O2^{xi}	2.899 (9)	Ti3—O6	1.710 (5)
Ba2—O2^{xii}	2.899 (8)	Ti3—O7	1.879 (5)
Ba2—O1	2.928 (5)	Ti3—O4^{vi}	1.983 (11)
Ba2—O1^{viii}	2.928 (5)	Ti3—O4^{ix}	2.018 (11)
Ba2—O4	2.998 (5)	Ti3—O5	2.047 (5)
Ba2—O4^{viii}	2.998 (5)	Ti3—O2^{ix}	2.474 (5)
O1^{i}—Ti1—O7^{vii}	94.1 (4)	O5^{i}—Ti2—O4^{vi}	79.3 (3)
O1^{i}—Ti1—O8	94.9 (4)	O5—Ti2—O4^{vi}	79.0 (3)
O7^{vii}—Ti1—O8	104.55 (18)	O3—Ti2—O5^{vi}	176.2 (2)
O1^{i}—Ti1—O3	96.7 (3)	O2—Ti2—O5^{vi}	87.1 (2)
O7^{vii}—Ti1—O3	161.8 (3)	O5^{i}—Ti2—O5^{vi}	80.7 (3)
O8—Ti1—O3	89.03 (15)	O5—Ti2—O5^{vi}	80.6 (3)
O1^{i}—Ti1—O2	95.2 (4)	O4^{vi}—Ti2—O5^{vi}	85.73 (19)
O7^{vii}—Ti1—O2	87.8 (2)	O6—Ti3—O7	97.3 (2)
O8—Ti1—O2	163.4 (4)	O6—Ti3—O4^{vi}	97.1 (4)
O3—Ti1—O2	76.7 (2)	O7—Ti3—O4^{vi}	98.0 (4)
O1^{i}—Ti1—O1	176.5 (3)	O6—Ti3—O4^{ix}	96.8 (4)
O7^{vii}—Ti1—O1	82.8 (3)	O7—Ti3—O4^{ix}	95.4 (4)
O8—Ti1—O1	84.3 (5)	O4^{vi}—Ti3—O4^{ix}	159.3 (3)
O3—Ti1—O1	86.7 (3)	O6—Ti3—O5	102.3 (2)
O2—Ti1—O1	86.4 (3)	O7—Ti3—O5	160.2 (2)
O3—Ti2—O2	89.1 (2)	O4^{vi}—Ti3—O5	81.3 (3)
O3—Ti2—O5^{i}	100.0 (3)	O4^{ix}—Ti3—O5	80.7 (3)
O2—Ti2—O5^{i}	99.3 (4)	O6—Ti3—O2^{ix}	177.0 (2)
O3—Ti2—O5	100.0 (3)	O7—Ti3—O2^{ix}	85.61 (19)
O2—Ti2—O5	99.9 (4)	O4^{vi}—Ti3—O2^{ix}	82.6 (3)
O5^{i}—Ti2—O5	152.3 (3)	O4^{ix}—Ti3—O2^{ix}	82.7 (3)
O3—Ti2—O4^{vi}	98.0 (2)	O5—Ti3—O2^{ix}	74.69 (18)
O2—Ti2—O4^{vi}	172.8 (2)		

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iv) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (v) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, 1-z$; (vii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (viii) $-x, y, 1-z$; (ix) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (x) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (xi) $x, 1+y, z$; (xii) $-x, 1+y, 1-z$.

Data collection

Bruker SMART area-detector diffractometer
ω scans
Absorption correction: analytical face-indexed (*XPREP*; Bruker, 1997)
$T_{\rm min} = 0.189$, $T_{\rm max} = 0.347$
2619 measured reflections
1636 independent reflections
1557 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$
$\theta_{\rm max} = 30.0°$
$h = -17 \rightarrow 23$
$k = -5 \rightarrow 5$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.112$
$S = 1.08$
1636 reflections
74 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 2.76$ e Å^{-3}
$\Delta\rho_{\rm min} = -3.05$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0254 (11)
Absolute structure: Flack (1983), 636 Friedel pairs
Flack parameter = 0.30 (8)

The largest densities in the difference map were close to atoms Ba1 and Ba2. The refinement of the Flack (1983) parameter was obtained by way of the TWIN/BASF instructions (Flack & Bernardinelli, 2000). The Flack parameter indicates a 70:30 ratio of two possible polarities of the structure. Since one of the three principal mean-square atomic displacements for the O5 site tended to a small negative value when the refinement included anisotropic displacement parameters, all O-atom sites were refined with isotropic displacement parameters.

Data collection: *SMART* (Bruker, 1999) and *SAINT* (Bruker, 1999); cell refinement: *SMART* and *SAINT*; data reduction: *XPREP* in *SHELXTL* (Bruker, 1997); program used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999) and *CrystalMaker* (Palmer, 2002); software used to prepare material for publication: *SHELXL*97.

The authors would like to thank Professor T. Ito for his encouragement and support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1654). Services for accessing these data are described at the back of the journal.

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