INORGANIC COMPOUNDS

Ba$_4$Ti$_{12}$O$_{27}$: Rietveld refinement using X-ray powder diffraction data

Antonio Currao†

Kyushu National Industrial Research Institute, Shuku-machi 807-1, Tosu-shi, Saga-ken 841-0052, Japan. E-mail: toni@solar.iac.unibe.ch
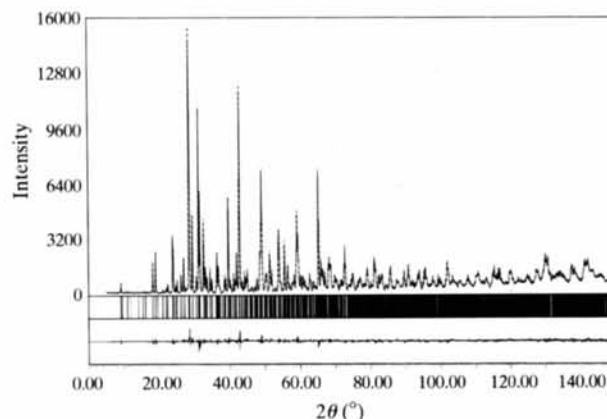
Fig. 1. The observed (dots) and calculated (solid) X-ray diffraction profiles from Rietveld analysis of Ba$_4$Ti$_{12}$O$_{27}$. Tick marks indicate the position of the allowed reflections for the Cu $K\alpha_1$ wavelength. The difference profile is located at the bottom of the figure.

Abstract

The title compound is a new mixed-valence barium titanate (Ba$_4^{II}$Ti$_2^{III}$Ti$_{10}^{IV}$O$_{27}$). A refinement using X-ray powder data was carried out using the Rietveld method, with the lattice parameters and atomic sites of the isostructural compound Ba$_4$Al$_2$Ti$_{10}$O$_{27}$ as a starting model.

Comment

During syntheses of known compounds in the ternary barium–titanium–oxygen system, a new ternary mixed-valence barium titanate, Ba$_4$Ti$_{12}$O$_{27}$, was synthesized and characterized by Rietveld refinement (Rietveld, 1969). The observed, calculated and difference profiles are shown in Fig. 1.

Roth *et al.* (1993) mentioned that the title compound was reported in the literature, citing a publication concerning the isostructural compound Ba$_4$Al$_2$Ti$_{10}$O$_{27}$ (Schmachtel & Müller-Buschbaum, 1981). However, on careful examination of that paper, no reference to Ba$_4$Ti$_{12}$O$_{27}$ could be found. The authors compared the overall composition of Ba$_4$Al$_2$Ti$_{10}$O$_{27}$ with Ba$_2$Ti$_6$O$_{13}$ (Schmachtel & Müller-Buschbaum, 1977). By doubling the composition of the mixed-valence compound Ba$_2$Ti$_6$O$_{13}$ (Ba$_4^{II}$Ti$_4^{III}$Ti$_8^{IV}$O$_{26}$), it is evident that the compounds differ by only one oxygen, but they have different structures.

A projection of the structure of Ba$_4$Ti$_{12}$O$_{27}$ along the *b* axis is shown in Fig. 2, emphasizing the main building units. The structure is rather compact, having narrow channels along this direction. Bond distances and angles are in good agreement with the isostructural compounds Ba$_4$Al$_2$Ti$_{10}$O$_{27}$ (Schmachtel & Müller-Buschbaum, 1981) and Ba$_4$ZnTi$_{11}$O$_{27}$ (Lindsay *et al.*,

1994). Comparing the distance ranges and coordination numbers of the barium and titanium sites in Ba$_4$Ti$_{12}$O$_{27}$ with other barium titanates [*e.g.* Ba$_2$Ti$_6$O$_{13}$ (Schmachtel & Müller-Buschbaum, 1977), BaTi$_8$O$_{16}$ (Schmachtel & Müller-Buschbaum, 1980), Ba$_2$Ti$_9$O$_{20}$ (Tillmanns & Hofmeister, 1983), BaTi$_4$O$_9$ (Hofmeister *et al.*, 1984) and Ba$_2$Ti$_{13}$O$_{22}$ (Möhr & Müller-Buschbaum, 1993)], one can see that they are all similar, except for the Ti4 site. With the exception of Ba$_2$TiO$_4$ (Wu & Brown, 1973; Günter & Jameson, 1984), where titanium has a distorted tetrahedral coordination of oxygen, in all other barium titanates, the Ti sites are surrounded by six O atoms, building an octahedron. In Ba$_4$Ti$_{12}$O$_{27}$ and the known isostructural compounds, the octahedral coordination around the Ti4 site is not only distorted but also
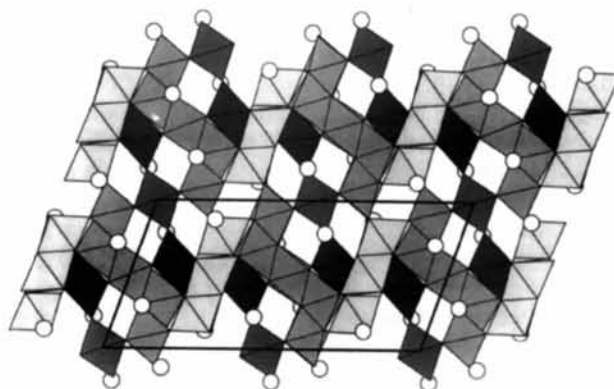

Fig. 2. Projection of the structure of Ba$_4$Ti$_{12}$O$_{27}$ along the *b* axis. The polyhedra represent the TiO$_6$ octahedra and the circles the Ba atoms. The gray scale emphasizes the different building units. The darkest octahedron represents the Ti4 site and the solid line the unit cell.

† Current address: University of Bern, Department of Chemistry and Biochemistry, Freiestrasse 3, 3000 Bern 9, Switzerland.

elongated (Table 2). The Ti4 site has five O atoms in the distance range 1.83 (2) to 1.95 (1) Å, and the sixth at a distance of 2.66 (1) Å. The Ti4 octahedron is connected by corner sharing with three neighboring titanium sites, and shares a face with the TiO_6 octahedron of the Ti5 site (see Fig. 3). While this face sharing affects one Ti—O distance for the Ti4 site, the Ti5 site exhibits only normal distances. A possible explanation for this could be found in the more rigid environment of the Ti5 octahedron, which shares edges with two Ti1 and two Ti8 octahedra, and one corner with two edge-sharing Ti2 octahedra.
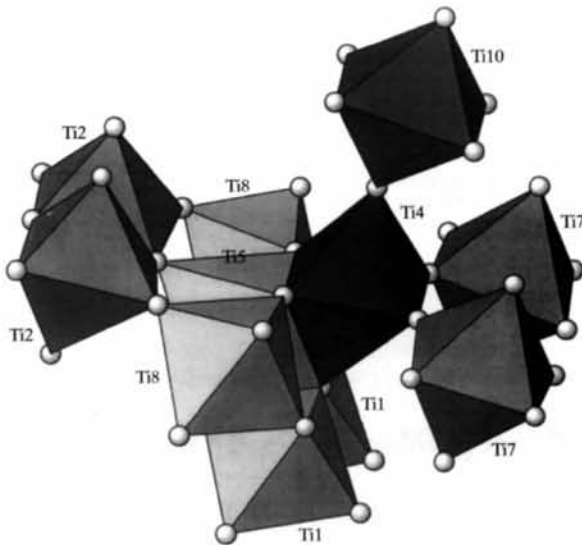

Fig. 3. Perspective view of the connectivity of the TiO_6 octahedra of the Ti4 and Ti5 sites in $Ba_4Ti_{12}O_{27}$. The Ti4 octahedron shares a face with the Ti5 and is connected through corners with one Ti10 and two Ti7 octahedra. On the other hand, the Ti5 octahedron shares edges with two Ti1 and two Ti8 octahedra, and one corner with two edge-sharing Ti2 octahedra. Spheres represent oxygen and the Ba atoms have been omitted for clarity.

Besides $Ba_4Ti_{12}O_{27}$, there is only one other barium titanate with a strongly distorted Ti site known, $i.e.$ $BaTi_2O_5$ (Tillmanns, 1974), with five O atoms in the distance range 1.72 (1) to 2.06 (1) Å, and the sixth at a distance of 2.47 (1) Å.

Due to the strong distortion of one TiO_6 octahedron in these compounds, the coordination should be described as a 5 + 1 coordination. This has already been pointed out by other authors in connection with other oxide compounds (Roth $et\ al.$, 1993; Tillmanns, 1974, and references therein).

Experimental

$Ba_4Ti_{12}O_{27}$ was prepared by heating a mixture of $BaCO_3$, TiO_2 and graphite in the molar ratio 1:3:1. The compound can also be synthesized when graphite as a reducing agent is substituted with Ti powder (molar ratio 2:5:1). The starting materials were mixed together using an agate mortar and pestle, and pressed into a pellet. The pellet was placed in a corundum crucible and heated in a corundum tube with a seal. The tube was evacuated and purged with argon several times. The synthesis was carried out under an argon atmosphere in a vertical tube furnace for 20 h at 1573 K. The starting Ar pressure on the gas cylinder was about 60 kPa. After heating, the pellet was still intact, exhibiting a dark-grey colour. For the powder diffraction measurement, the sample was ground using an agate mortar and pestle. The sample was then slurried in acetone and transferred onto a stainless-steel sample holder.

Crystal data

$Ba_4Ti_{12}O_{27}$	Cu $K\alpha$ radiation
$M_r = 1555.85$	$\lambda = 1.54056, 1.54439$ Å
Monoclinic	$T = 293$ K
$C2/m$	Specimen shape: flat
$a = 19.8165\,(2)$ Å	$15 \times 15 \times 2$ mm
$b = 11.4468\,(1)$ Å	Specimen cooling rate
$c = 9.9208\,(1)$ Å	8.5 K min^{-1}
$\beta = 109.1847\,(5)°$	Specimen prepared at
$V = 2125.41\,(4)$ Å^3	1573 K
$Z = 4$	Dark grey
$D_x = 4.862$ Mg m^{-3}	
D_m not measured	

Data collection

Philips X'Pert diffractometer	Specimen mounted in
$\theta/2\theta$ scans	reflection mode
Specimen mounting:	Absorption correction: none
stainless-steel sample	$2\theta_{min} = 5$, $2\theta_{max} = 150°$
holder	Increment in $2\theta = 0.02°$

Refinement

Refinement on I_{net}	90 parameters
$R_p = 0.038$	Weighting scheme based
$R_{wp} = 0.052$	on measured s.u.'s
$R_{exp} = 0.034$	$(\Delta/\sigma)_{max} = 0.01$
$R_B = 0.018$	Extinction correction: none
$S = 1.541$	Preferred orientation
Excluded region(s): none	correction: none
Profile function: pseudo-	Scattering factors from
Voigt (Young & Wiles,	*International Tables for*
1982)	*Crystallography* (Vol. IV)

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

$$U_{eq} = (1/3)\sum_i\sum_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba1	0.0649 (1)	0.2742 (1)	0.2154 (2)	0.0070 (3)
Ba2	0.0745 (1)	0	0.7123 (2)	0.0054 (5)
Ba3	0.2032 (1)	0	0.1265 (2)	0.0058 (5)
Ti1	0.2461 (2)	0.6328 (3)	0.2142 (4)	0.0049 (3)
Ti2	0.3680 (2)	0.8609 (4)	0.3397 (4)	0.0049 (3)
Ti3	0.3775 (2)	0.2582 (3)	0.0816 (4)	0.0049 (3)
Ti4	0.1118 (3)	0	0.3897 (5)	0.0049 (3)
Ti5	0.2636 (2)	0	0.5166 (6)	0.0049 (3)
Ti6	0.3879 (3)	0	0.0784 (6)	0.0049 (3)
Ti7	0	0.2319 (5)	1/2	0.0049 (3)
Ti8	1/4	1/4	1/2	0.0049 (3)
Ti9	0	1/2	1/2	0.0049 (3)
Ti10	0	0	0	0.0049 (3)
O1	0.0574 (7)	0.121 (1)	0.437 (1)	0.0024 (5)
O2	0.0607 (7)	0.631 (1)	0.465 (1)	0.0024 (5)

O3	0.1784 (7)	0.253 (1)	0.116 (2)	0.0024 (5)
O4	0.1851 (6)	0.115 (1)	0.392 (1)	0.0024 (5)
O5	0.1911 (6)	0.635 (1)	0.368 (1)	0.0024 (5)
O6	0.3037 (7)	0.749 (1)	0.357 (2)	0.0024 (5)
O7	0.3119 (6)	0.370 (1)	0.123 (1)	0.0024 (5)
O8	0.3274 (6)	0.126 (1)	0.135 (1)	0.0024 (5)
O9	0.4385 (7)	0.128 (1)	0.056 (1)	0.0024 (5)
O10	0.4326 (7)	0.250 (1)	0.306 (1)	0.0024 (5)
O11	0.4405 (7)	0.372 (1)	0.053 (1)	0.0024 (5)
O12	0.068 (1)	0	0.196 (2)	0.0024 (5)
O13	0.2030 (9)	0	0.655 (2)	0.0024 (5)
O14	0.3148 (9)	0	0.386 (2)	0.0024 (5)
O15	0.313 (1)	0	0.885 (2)	0.0024 (5)
O16	0.429 (1)	0	0.304 (2)	0.0024 (5)

Table 2. *Selected geometric parameters (Å, °)*

Ti4—O12	1.83 (2)	Ti5—O14	1.89 (2)
Ti4—O1	1.91 (1)	Ti5—O5^{iii}	1.96 (1)
Ti4—O1^i	1.91 (1)	Ti5—O5^{iii}	1.96 (1)
Ti4—O4	1.95 (1)	Ti5—O4	2.10 (1)
Ti4—O4^i	1.95 (1)	Ti5—O4^i	2.10 (1)
Ti4—O13	2.66 (1)	Ti5—O13	2.10 (1)
O12—Ti4—O1	98.4 (5)	O1^i—Ti4—O13	90.7 (4)
O12—Ti4—O1^i	98.4 (5)	O1—Ti4—O4^i	164.7 (5)
O12—Ti4—O4	96.2 (5)	O1—Ti4—O4	88.9 (5)
O12—Ti4—O4^i	96.2 (5)	O1—Ti4—O13	90.7 (4)
O12—Ti4—O13	166.7 (7)	O4^i—Ti4—O4	84.7 (5)
O1^i—Ti4—O1	93.8 (5)	O4—Ti4—O13	74.2 (4)
O1^i—Ti4—O4^i	88.9 (5)	O4—Ti4—O13	74.2 (4)
O1^i—Ti4—O4	164.7 (5)		

Symmetry codes: (i) $x, -y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$.

Data collection was performed using *PC-APD* software (Philips Electronics, 1997). The measurement was carried out using programmable optics for the primary and secondary paths. The sample was spun during the measurement, and the irradiated area had a width and a length of 10 mm. For data reduction, and cell and structure refinement, the program *PC-Rietveld Plus* (Philips Electronics, 1993) was used. Cell parameters and atomic sites were taken from the isostructural compound Ba$_4$Al$_2$Ti$_{10}$O$_{27}$ (Schmachtel & Müller-Buschbaum, 1981). The profile shape was corrected for peak asymmetry up to $2\theta = 30.1°$ (Rietveld, 1969). In addition, lattice and structure parameters, zero-point shift, six background parameters and the scale factor were refined. A refinement of the isotropic displacement parameters was possible for the barium sites. For the titanium sites, as well as for the oxygen sites, a common displacement parameter was refined. The structural graphics were created with *ATOMS* (Dowty, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1212). Services for accessing these data are described at the back of the journal.

References

Dowty, E. (1997). *ATOMS for Windows. A Computer Program for Displaying Atomic Structures.* Shape Software, Kingsport, Tennessee, USA.

Günter, J. R. & Jameson, G. B. (1984). *Acta Cryst.* C40, 207–210.
Hofmeister, W., Tillmanns, E. & Baur, W. H. (1984). *Acta Cryst.* C40, 1510–1512.
Lindsay, C. G., Rawn, C. J. & Roth, R. S. (1994). *Powder Diffr.* 9, 56–62.
Möhr, S. & Müller-Buschbaum, Hk. (1993). *J. Alloys Compd,* 199, 203–206.
Philips Electronics (1993). *PC-Rietveld Plus.* Version 1.1b. Philips Electronics NV, Almelo, The Netherlands.
Philips Electronics (1997). *PC-APD for Windows.* Version 4.0e. Philips Electronics NV, Almelo, The Netherlands.
Rietveld, H. M. (1969). *J. Appl. Cryst.* 2, 65–71.
Roth, R. S., Rawn, C. J., Lindsay, C. G. & Wong-Ng, W. (1993). *J. Solid State Chem.* 104, 99–118.
Schmachtel, J. & Müller-Buschbaum, Hk. (1977). *Z. Anorg. Allg. Chem.* 435, 243–246.
Schmachtel, J. & Müller-Buschbaum, Hk. (1980). *Z. Naturforsch.* 35, 332–334.
Schmachtel, J. & Müller-Buschbaum, Hk. (1981). *Z. Anorg. Allg. Chem.* 472, 89–94.
Tillmanns, E. (1974). *Acta Cryst.* B30, 2894–2896.
Tillmanns, E. & Hofmeister, W. (1983). *J. Am. Ceram. Soc.* 66, 268–271.
Wu, K. K. & Brown, I. D. (1973). *Acta Cryst.* B29, 2009–2012.
Young, R. A. & Wiles, D. B. (1982). *J. Appl. Cryst.* 15, 430–438.

Calcium pyroborate, Ca$_2$B$_2$O$_5$

QI-SHENG LIN, WEN-DAN CHENG, JIU-TONG CHEN AND JIN-SHUN HUANG

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China. E-mail: cwd@ms.fjirsm.ac.cn

Abstract

The title compound was synthesized by high-temperature solution reaction and its structure determined by X-ray diffraction techniques. The structure contains Ca$_4$O$_{19}$ tetramers which form double chains extending along the a direction. The double chains are linked to form layers and B$_2$O$_5$ groups bridge these adjacent chains and adjacent layers through O atoms to form a three-dimensional framework.

Comment

There are few papers on the CaO–B$_2$O$_3$ system in the literature. As examples, the detailed structures of Ca$_3$(BO$_3$)$_2$ (Schuckmann, 1969; Vegas *et al.*, 1975), Ca$_2$B$_6$O$_{11}$ (Zayakina & Brovkin, 1976) and CaB$_4$O$_7$ (Zayakina & Brovkin, 1977) have been reported.