

Refinement of Barium Dtitanate

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Abstract. BaTi₂O₅, monoclinic, $A2/m$, $a=9.409$ (3), $b=3.932$ (1), $c=16.907$ (5) Å, $\beta=103^\circ 5$ (2)', $Z=6$, $D_x=5.12$ g cm⁻³. Crystals were prepared by rapidly cooling a melt of composition BaO:TiO₂=30:70 mol.%. Edge-sharing titanium coordination octahedra form infinite zigzag chains parallel to **b**. The structure can also be described as an almost close-packed array of barium and oxygen atoms with titanium atoms in octahedral voids. The direction of packing is approximately $[\bar{1}3\bar{1}]$ and the stacking sequence is *ABCABCABC*. TiO₆ octahedra show appreciable distortions similar to those observed in PbTiO₃.

Introduction. A crystal with dimensions approximately 0.07 × 0.04 × 0.2 mm was used to measure the cell parameters and intensities. The cell constants were refined by a least-squares fit to the angular settings of 12 reflexions with $25^\circ \leq \theta \leq 30^\circ$ (Mo $K\alpha_1$, $\lambda=0.70926$ Å). The systematic absences are *hkl* for $k+l$ odd. The intensities of 6691 reflexions with $\theta \leq 38^\circ$ were collected on an automatic four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation, θ - 2θ step-scan mode with 60 steps of 0.01° and 2 s counting time per step. The background was measured for 10 s at each end of the scanning interval. After correction for absorption [$\mu(\text{Mo } K\alpha)=136.9$ cm⁻¹, transmission factors between 0.33 and 0.62] reduction and averaging of the intensities resulted in 1843 unique structure factors, 431 of which were considered to be of zero intensity ($I < 2\sigma_I$). The structure was refined by full-matrix least-squares calculations starting from the atomic coordinates given

by Harrison (1956). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962); the observed structure factors were weighted according to $w=1/\sigma^2(F)$. Other experimental procedures and the computer programs used are the same as given by Tillmanns & Gebert (1973).

The final weighted residual $R_2=(\sum w(\Delta F)^2/\sum wF_o^2)^{1/2}$ was 0.031, the corresponding unweighted R_1 was 0.026 for observed reflexions only and 0.072 including the 431 unobserved reflexions with $F_o=0$. The resulting positional and thermal parameters are given in Table 1.*

Discussion. The structural principle of barium dtitanate has already been determined by Harrison (1956) from two-dimensional photographic data. The proposed structure was essentially correct although the spread in Ti-O distances was large and there was some uncertainty about the position of O(4) because of diffraction ripples around the Ba atoms. Fig. 1 shows a projection of the structure along **b**. Edge-sharing TiO₆ octahedra form planar groups of three octahedra each, which are linked by common corners to other groups in the plane (010). In the direction of **b**, infinite zigzag chains are formed *via* common octahedral edges.

The two independent Ba atoms in the asymmetric unit have a cuboctahedral 12-coordination with mean Ba-O distances of 2.929 and 2.884 Å respectively (*cf.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30616 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional atomic coordinates and vibrational parameters (Å²) with the significant figures of the estimated standard deviations in parentheses

All atoms are situated on the mirror plane at $y=0$. The definition of the Debye-Waller temperature factor is $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hla^*c^*B_{13})]$.

	x/a	z/c	B_{11}	B_{22}	B_{33}	B_{13}
Ba(1)	0.48223 (3)	0.13107 (2)	0.70 (1)	0.49 (1)	0.62 (1)	0.18 (1)
Ba(2)	0.0	0.0	0.54 (1)	0.43 (1)	0.67 (1)	0.09 (1)
Ti(1)	0.19441 (10)	0.66610 (6)	0.32 (3)	0.17 (3)	0.14 (3)	0.13 (3)
Ti(2)	0.12731 (10)	0.29292 (6)	0.22 (3)	0.20 (3)	0.11 (3)	-0.01 (3)
Ti(3)	0.28946 (11)	0.46098 (7)	0.34 (3)	2.07 (6)	0.10 (3)	0.11 (2)
O(1)	0.1625 (4)	0.1749 (3)	0.8 (2)	0.8 (2)	0.5 (1)	0.3 (2)
O(2)	0.1015 (4)	0.7651 (3)	0.1 (1)	0.6 (1)	0.2 (1)	0.0 (1)
O(3)	0.2902 (4)	0.9646 (3)	0.8 (1)	0.4 (1)	0.7 (1)	0.2 (1)
O(4)	0.3154 (4)	0.3472 (3)	0.5 (1)	0.4 (1)	0.3 (1)	0.2 (1)
O(5)	0.5	0.5	0.0 (2)	0.9 (2)	0.6 (2)	-0.2 (2)
O(6)	0.2107 (4)	0.5576 (2)	0.8 (1)	0.9 (2)	0.3 (1)	0.3 (1)
O(7)	0.0710 (4)	0.3911 (3)	0.5 (1)	0.7 (2)	0.2 (1)	0.1 (1)
O(8)	0.3780 (4)	0.7113 (3)	0.5 (1)	0.7 (2)	0.6 (1)	0.0 (1)

Table 2). All O atoms are also cuboctahedrally surrounded by 12 other O or Ba atoms and like most other barium titanates the structure of BaTi_2O_5 is based on a nearly close-packed array of Ba and O atoms with 9 layers stacked along $[\bar{1}3\bar{1}]$ in the sequence *ABCABCABC*.

One interesting feature of the crystal structure is that O(8) is coordinated by only one Ti and three Ba atoms, thus receiving a bond strength sum (Pauling, 1960) of only 1.17 valence units. This extreme undersaturation of O(8) seems to be compensated by a pronounced distortion of the coordination octahedron around Ti(1). Ti(1) is displaced from the centre of the octahedron towards O(8); the resulting Ti(1)–O(8) distance is 1.724 Å. Four Ti–O distances are in the range 1.875–2.056 Å, the sixth [Ti(1)–O(7)] is considerably longer, 2.466 Å. While the short Ti(1)–O(8) distance could be interpreted with the extended electrostatic valence rule (Pauling, 1960; Baur, 1970), there is only poor agreement between other observed Ti–O distances and the distances calculated according to Baur's (1970) rule 3. O(7) for example is coordinated by three Ti and two Ba atoms and receives a bond-strength sum $\rho(\text{O}) = 2.33$ v.u., which would correspond to calculated Ti–O distances of 2.01, 1.96 and 2.05 Å

for O(7)–Ti(1), O(7)–Ti(2) and O(7)–Ti(3) respectively (Baur, 1970, rule 3). The observed distances, however, are 2.466, 1.853 and 2.126 Å respectively. The bond-strength sums calculated from the interatomic distances with Brown & Shannon's (1973) empirical bond-strength–bond-length curves deviate appreciably from the atomic valences; both Ba atoms for example are overbonded by 25%.

A computer simulation of the crystal structure with the distance least-squares method (Meier & Villiger, 1969) where the prescribed interatomic distances were calculated with Baur's (1970) rule 3 and their weights were based on the electrostatic strengths of these bonds (Baur, 1972), showed that such an electrostatic model

Table 2. *Interatomic distances and angles*

Standard deviations are approximately 0.004 Å for Ba–O and Ti–O distances, 0.002 for Ti–Ti and 0.006 for O–O distances. Bond angles have a standard deviation of 0.2°.

Central Atom: Ba(1)		O(1)–O(7)	85.6°	2.889 Å
Ba(1)–O(8)	2.692 Å	Central Atom: Ti(3)		
–O(8)	2.695 (2x)	Ti(3)–O(6)		1.940 Å
–O(4)	2.704 (2x)	–O(5)		1.941
–O(3)	2.962	–O(3)		1.967 (2x)
–O(3)	2.980	–O(4)		1.993
–O(5)	2.995 (2x)	–O(7)		2.126
–O(6)	3.240 (2x)	O(6)–O(5)	105.6°	3.091
–O(1)	3.257	O(6)–O(3)	88.4	2.725 (2x)
Central Atom: Ba(2)		O(6)–O(4)	165.0	3.900
Ba(2)–O(6)	2.805 (4x)	O(6)–O(7)	87.9	2.824
–O(7)	2.874 (4x)	O(5)–O(3)	89.6	2.754 (2x)
–O(3)	2.924 (2x)	O(5)–O(4)	89.4	2.768
–O(1)	3.006 (2x)	O(5)–O(7)	166.6	4.040
Central Atom: Ti(1)		O(3)–O(3)	176.5	3.932
Ti(1)–O(8)	1.724	O(3)–O(4)	91.7	2.842 (2x)
–O(6)	1.875	O(3)–O(7)	90.8	2.916 (2x)
–O(1)	1.999 (2x)	O(4)–O(7)	77.2	2.571
–O(2)	2.056	Central Atom: O(1)		
–O(7)	2.466	Ti(1)–Ti(1)	159.0	3.932
O(8)–O(6)	37.9°	Ti(1)–Ti(2)	97.4	3.078 (2x)
O(8)–O(1)	96.8	Central Atom: O(2)		
O(8)–O(2)	102.0	Ti(2)–Ti(2)	152.7	3.932
O(3)–O(7)	176.9	Ti(2)–Ti(1)	93.0	3.073 (2x)
O(6)–O(1)	36.3	Ti(2)–Ti(2)	99.3	3.184 (2x)
O(6)–O(2)	160.1	Ti(1)–Ti(2)	101.2	3.255
O(6)–O(7)	85.2	Central Atom: O(3)		
O(1)–O(1)	159.0	Ti(3)–Ti(3)	176.5	3.932
O(1)–O(2)	80.8	Central Atom: O(4)		
O(1)–O(7)	82.7	Ti(2)–Ti(3)	99.9	2.905
O(2)–O(7)	74.9	Central Atom: O(5)		
Central Atom: Ti(2)		Ti(3)–Ti(3)	180.0	3.882
Ti(2)–O(4)	1.799	Central Atom: O(6)		
–O(7)	1.853	Ti(1)–Ti(3)	162.7	3.712
–O(2)	2.023 (2x)	Central Atom: O(7)		
–O(1)	2.096	Ti(2)–Ti(3)	93.5	2.905
–O(2)	2.154	Ti(2)–Ti(1)	96.8	3.255
O(4)–O(7)	89.5	Ti(3)–Ti(1)	169.7	4.574
O(4)–O(2)	99.8			
O(4)–O(1)	97.8			
O(4)–O(2)	176.5			
O(7)–O(2)	99.5			
O(7)–O(1)	172.7			
O(7)–O(2)	87.1			
O(2)–O(2)	152.7			
O(2)–O(1)	79.3			
O(2)–O(2)	80.7			

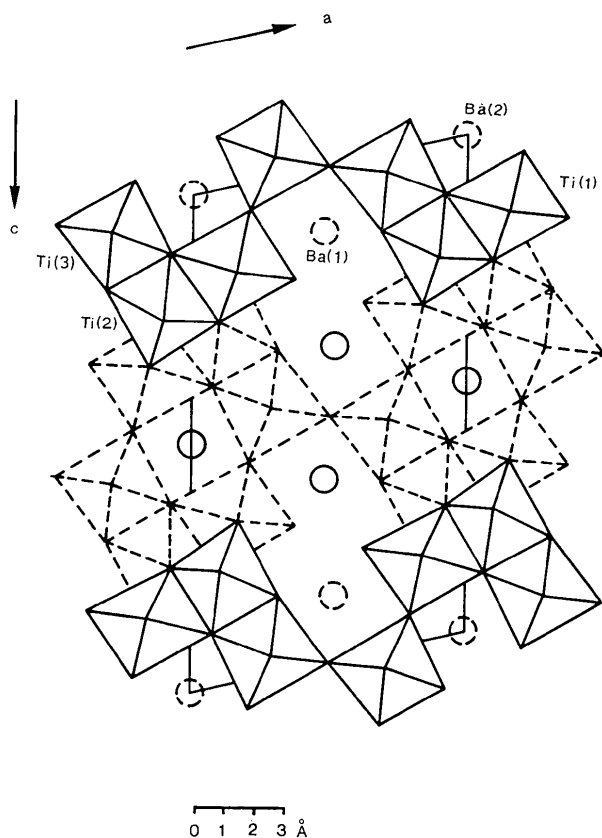


Fig. 1. Projection of the structure along $[010]$. All atoms are located in the mirror planes at $y = 0.5$ (solid lines) and $y = 0$ (broken lines).

could easily be constructed without a change of the unit-cell parameters.

It therefore seems that the distortions of the TiO_6 octahedra in BaTi_2O_5 are not caused by the bond-strength distribution and cannot be interpreted on electrostatic grounds only. Baur (1961) pointed out that the Ti coordination in PbTiO_3 (Shirane, Pepinsky & Frazer, 1956) with Ti–O distances of 1.78, 4×1.98 and 2.38 Å should be described as a 5 + 1 coordination and a similar distortion of a TiO_6 octahedron in $\text{Na}_2\text{Ti}_3\text{O}_7$ has been interpreted by Andersson & Wadsley (1961) as a tendency of Ti towards 5 coordination. Table 3 gives distances between Ti atoms and their six nearest O neighbours for a number of compounds

Table 3. Distances between titanium atoms and their six nearest oxygen neighbours for a number of compounds with different Ti coordinations

Compound	Bond lengths (Å)
Y_2TiO_5^a	Ti–O: 1.78, 1.87, 1.91, 2×1.94 , 3.89
Fresnoite $\text{Ba}_2\text{TiOSi}_2\text{O}_7^b$	Ti–O: 1.63, 4×2.00 , 3.58
Innelite	Ti(1)–O: 1.62, 1.99, 2.00, 2.05, 2.06, 3.67
$\text{Na}_2\text{Ba}_3(\text{Ca}, \text{Na}) (\text{Ba}, \text{K}, \text{Mn})$	Ti(2)–O: 1.90, 1.92, 2.00, 2.04, 2.09, 2.16
$\text{Ti}_3\text{O}_4(\text{SO}_4)_2(\text{Si}_2\text{O}_7)_2^c$	Ti(3)–O: 1.71, 1.93, 1.96, 1.98, 2.01, 3.17
$\text{BaTi}_2\text{O}_5^d$	Ti(1)–O: 1.71, 1.87, 2×2.00 , 2.06, 2.47
PbTiO_3^e	Ti–O: 1.78, 4×1.98 , 2.38
$\text{Na}_2\text{Ti}_3\text{O}_7^f$	Ti(2)–O: 1.71, 1.87, 1.91, 2×1.94 , 2.34

References: (a) Mumme & Wadsley (1968); (b) Moore & Louisnathan (1969); (c) Chernov *et al.* (1971); (d) This work; (e) Shirane *et al.* (1956); (f) Andersson & Wadsley (1961).

with Ti in different coordinations. It can be seen that there is no sharp limit between 5 and 6-coordinated Ti. While Ti is clearly 5-coordinated in Y_2TiO_5 , fresnoite, and partly in innelite, other Ti atoms in innelite, in BaTi_2O_5 , PbTiO_3 and $\text{Na}_2\text{Ti}_3\text{O}_7$ have a 5 + 1 coordination.

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1,6:8,13-Cyclopropanediylidene[14]annulene

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Abstract. $\text{C}_{17}\text{H}_{12}$, monoclinic, $C2/c$, $Z=8$, $a=19.485(3)$, $b=6.812(2)$, $c=17.881(5)$ Å, $\beta=108.52(2)^\circ$, $D_m=1.273$, $D_x=1.277$ g cm $^{-3}$, m.p. 169–170°C. Mo $K\alpha$ diffractometer data. Final $R=0.054$ on all observed amplitudes. The strain imposed by the bridges of the annulene perimeter and by the cyclopropane ring seem to have a balancing rather than a synergic effect; as a result the annulene ring is nearly planar with bond lengths close to the aromatic value.

Introduction. X-ray diffraction data were measured with Mo $K\alpha$ radiation on a Syntex $P\bar{1}$ four-circle diffractom-

eter equipped with graphite monochromator. Cell dimensions were obtained from 26 reflexions (plus their equivalents) for $\lambda=0.71069$ Å. Systematic absences were hkl for $h+k$ odd, $h0l$ for l odd. A crystal of dimensions $0.30 \times 0.35 \times 0.40$ mm was used. Intensities were collected to a maximum 2θ value of 55° (θ – 2θ scan mode, scan width $2.1^\circ + \alpha_1\alpha_2$ separation, variable scan speed between 1 and 12° min $^{-1}$, dead time for coincidence correction 2.1×10^{-6} s). The background was counted for half the total scanning time on each side of the reflexion. Three check reflexions were monitored periodically to test crystal