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The Crystal Structure of β-Barium Orthotitanate, β-Ba_2TiO_4, and the Bond Strength–Bond Length Curve of Ti–O

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The crystal structure of β-barium orthotitanate, β-Ba_2TiO_4, has been refined using 1693 non-equivalent reflexions measured from a twinned synthetic crystal with an automatic X-ray single-crystal diffractometer. It is monoclinic with cell dimensions $a=6{\cdot}096$ (4), $b=7{\cdot}681$ (6), $c=10{\cdot}545$ (9) Å, $\beta=92{\cdot}99$ (6)°, $Z=4$, space group $P2_1/n$. The final weighted agreement index is 0·051. The asymmetric unit contains one almost regular TiO_4 tetrahedron (mean Ti–O = 1·808 Å) and two crystallographically distinct barium atoms. A revised bond strength (s)–bond length (R) relationship of the form $s=0{\cdot}666\,(R/1{\cdot}953)^{-5{\cdot}25}$ is proposed for Ti–O bonds.

Introduction

The crystal structure of β-barium orthotitanate, β-Ba_2TiO_4, was first determined by Bland (1961). Because this compound is one of the few examples of Ti coordinated by four oxygen atoms, it is of particular importance in determining the bond strength (s)–bond length (R) curve for Ti–O (Brown & Shannon, 1973). Unfortunately, because of the twinning, Bland was only able to measure the Ti–O bond length to an accuracy of 0·2 Å. We have therefore redetermined the crystal structure in order to obtain a more accurate Ti–O distance.

Structure determination

Crystals of β-Ba_2TiO_4 were prepared by the method described by Bland (1961). The white crystals (Ba_2iT_4O) were separated from the dark crystals ($BaTiO_3$) by hand. Weissenberg and precession photographs showed that most crystals contained not only twinned β-Ba_2TiO_4 but also at least one related orthorhombic phase with a tripled b axis. Such polymorphism is expected from Todd & Lorenson's (1952) observation that the heat capacity and entropy of Ba_2TiO_4 are anomalously large at room temperature. Ca_2SiO_4 has a similar series of polymorphs including a monoclinic phase, β-Ca_2SiO_4, similar in structure to β-Ba_2TiO_4 and an orthorhombic phase, α'-Ca_2SiO_4, with a tripled b axis (Saalfeld, 1972). A crystal containing only β-Ba_2TiO_4 [twinned on (001)] was ground into an approximate cylinder (0·4 mm long by 0·2 mm diameter). A Syntex automatic X-ray diffractometer ($p\bar{1}$) with crystal monochromated Mo $K\alpha$ radiation was used to measure the cell dimensions and intensities. Most reflexions were measured with the stationary crystal–stationary counter technique but some were also measured with a $\theta/2\theta$ scan as a check. The crystal data are given in Table 1.

Table 1. *Crystal data for* β-Ba_2TiO_4

Monoclinic

a = 6·096 (4)*
b = 7·681 (6)
c = 10·545 (9) Å
β = 92·99 (6)°
U = 493·1 Å^3
D_m = 5·07 (15) (Bland, 1961)
D_x = 5·21
Z = 4
Space group $P2_1/n$ (C_{2h}^5)
Systematic absences: $h0l$, $h+l=2n+1$
$0k0$, $k=2n+1$
λ(Mo $K\alpha$) = 0·7107 Å
μ(Mo $K\alpha$) = 30·9 mm^{-1}
Scattering factors: Ba^{2+}, Ti^{4+}, O given by Cromer & Waber (1965),
Anomalous dispersion correction: Ba^{2+}, Ti^{4+} given by Cromer (1965).

* Figures in parentheses are standard deviations in the last digit quoted.

The intensities of a total of 2044 reflexions with $2\theta \le 65°$ were measured from the major twin. Unfortunately 381 of these (those with $|l| < 3$) were overlapped by reflexions from the minor twin. In order to determine the true intensities of these reflexions, it was necessary to determine the relative volumes of the two twins present. By comparing the intensities of 50 equivalent resolved reflexions of the two twins this ratio was found to be 13:1. The true intensities (I) of the reflexions hkl and $\bar{h}kl$ could then be found using the relations

$$I_{\text{obs}}(hkl) = I(hkl) + I(\bar{h}kl)/13$$

and

$$I_{\text{obs}}(\bar{h}kl) = I(\bar{h}kl) + I(hkl)/13$$

where I_{obs} is the intensity measured for the overlapped reflexions indexed according to the major twin. Equivalent reflexions were then averaged to give 1693 non-equivalent reflexions of which 667 reflexions were treated as unobserved.

Lorentz and polarization corrections were applied. An absorption correction was applied with the program *ABSCOR* (de Meulenaer & Tompa, 1965; Alcock 1970) by assuming that the crystal was a 12-sided cylinder with the cylindrical axis (a^*) mounted along the goniometer axis. The structure was solved from three-dimensional Patterson and difference Fourier syntheses with the structure of Bland (1961) as a guide. It was refined by full-matrix least-sqaures calculations, a secondary extinction correction (Zachariasen, 1963; Larson, 1967) being applied in the final cycle. Reflexions were weighted by $\omega = (6{\cdot}12 - 0{\cdot}048F + 0{\cdot}0028F^2)^{-1}$. The final agreement indices were $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}037$ and $R_2 = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2} = 0{\cdot}051$. The average shift/error for the last cycle was 0·060. The coordinates and thermal parameters are given in Table 2.*

Description of the structure

The general features of the structure proposed by Bland (1961) have been confirmed. Each unit cell contains four isolated TiO_4 tetrahedra linked by barium atoms (Fig. 1). The bond lengths and angles are given in Table 3 and the bond lengths around Ba are also shown in Fig. 1. In contrast to Bland's observations, we

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* The structure-factor table has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30120. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters of* Ba_2TiO_4

Figures in parentheses are standard deviations in the last digit quoted. Fractional coordinates are × 10^4.

Anisotropic thermal parameters (in Å^2) appear in the expression

$$\exp\,[-2\pi^2(u_{11}h^2a^{*2} + u_{22}k^2b^{*2} + u_{33}l^2c^{*2} + 2u_{12}hka^*b^* + 2u_{13}hla^*c^* + 2u_{23}klb^*c^*) \times 10^{-4}]\,.$$

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ba(1)	7654 (1)	8412 (1)	754 (1)	234 (2)	194 (2)	253 (2)	−5 (2)	−6 (2)	−8 (2)
Ba(2)	2279 (1)	4998 (1)	1994 (1)	231 (2)	189 (2)	198 (2)	−2 (2)	−11 (2)	−3 (2)
Ti	7411 (2)	2798 (2)	824 (1)	204 (6)	179 (6)	185 (6)	2 (5)	−12 (5)	2 (5)
O(1)	7818 (13)	5066 (9)	690 (7)	433 (41)	171 (28)	345 (35)	26 (27)	29 (30)	27 (25)
O(2)	5190 (11)	2366 (10)	1857 (7)	273 (30)	325 (35)	346 (34)	38 (29)	66 (26)	78 (29)
O(3)	9951 (10)	1757 (10)	1396 (7)	234 (28)	301 (32)	300 (30)	73 (26)	−48 (23)	5 (27)
O(4)	6762 (11)	1801 (9)	−733 (6)	266 (28)	270 (31)	255 (29)	33 (26)	−27 (22)	−26 (25)

Table 3. *Interatomic distances* (Å) *and angles* (°) *in* β-Ba_2TiO_4

Figures in parentheses are standard deviations in the last digit quoted

TiO_4 tetrahedron

Ti——O(1)	1·766 (7)	O(1)—Ti–O(2)	110·0 (4)
Ti——O(2)	1·812 (7)	O(1)—Ti–O(3)	109·8 (3)
Ti——O(3)	1·818 (7)	O(1)—Ti–O(4)	111·4 (3)
Ti——O(4)	1·836 (7)	O(2)—Ti–O(3)	111·8 (3)
		O(2)—Ti–O(4)	109·2 (3)
		O(3)—Ti–O(4)	104·7 (3)

Ba(1)–O(1^{i})	2·573 (7)	Ba(2)–O(2^{vii})	2·689 (7)
Ba(1)–O(4^{iii})	2·696 (7)	Ba(2)–O(3^{iv})	2·695 (7)
Ba(1)–O(3^{vi})	2·763 (7)	Ba(2)–O(2^{i})	2·699 (7)
Ba(1)–O(2^{iv})	2·894 (7)	Ba(2)–O(4^{ii})	2·799 (7)
Ba(1)–O(3^{v})	2·987 (7)	Ba(2)–O(1^{iii})	2·828 (8)
Ba(1)–O(4^{v})	3·073 (7)	Ba(2)–O(4^{iii})	2·870 (7)
Ba(1)–O(2^{iii})	3·232 (7)	Ba(2)–O(3^{i})	2·918 (7)
		Ba(2)–O(1^{viii})	2·983 (8)

The superscripts refer to the following symmetry transformations:

i	x	y	z	v	x	$1+y$	z
ii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	vi	$2-x$	$1-y$	$-z$
iii	$1-x$	$1-y$	$-z$	vii	$\frac{3}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
iv	$\frac{3}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	viii	$-1+x$	y	z

find that the tetrahedron is almost regular, the Ti–O distances range only from 1·766 to 1·836 Å and the O–Ti–O angles from 104·7 to 111·8°. However, the Ti–O(1) bond (1·766 Å) is significantly shorter than the other three Ti–O bonds (mean 1·822 Å), an effect which is the result of O(1) being bonded to only three Ba atoms while each of the other O atoms are bonded to four Ba atoms.

Ti–O bond strength–bond length curve

Brown & Shannon (1973) have recently proposed empirical bond strength–bond length curves for oxides of elements in the first half of the periodic table. In order to calculate the curve for Ti–O, they were forced to use data from $TiCl_4$ and $TiBr_4$ to obtain an effective Ti–O distance of 1·77 Å for four-coordinated Ti and to constrain their curve to pass through this point. The resultant expression for the bond strength (s) as a function of bond length (R) was $s=0{\cdot}666(R/1{\cdot}952)^{-0{\cdot}4}$. The average four-coordinate Ti–O distance of 1·808 Å obtained in this work is significantly different from that assumed by Brown & Shannon, but agrees very well with the pre-

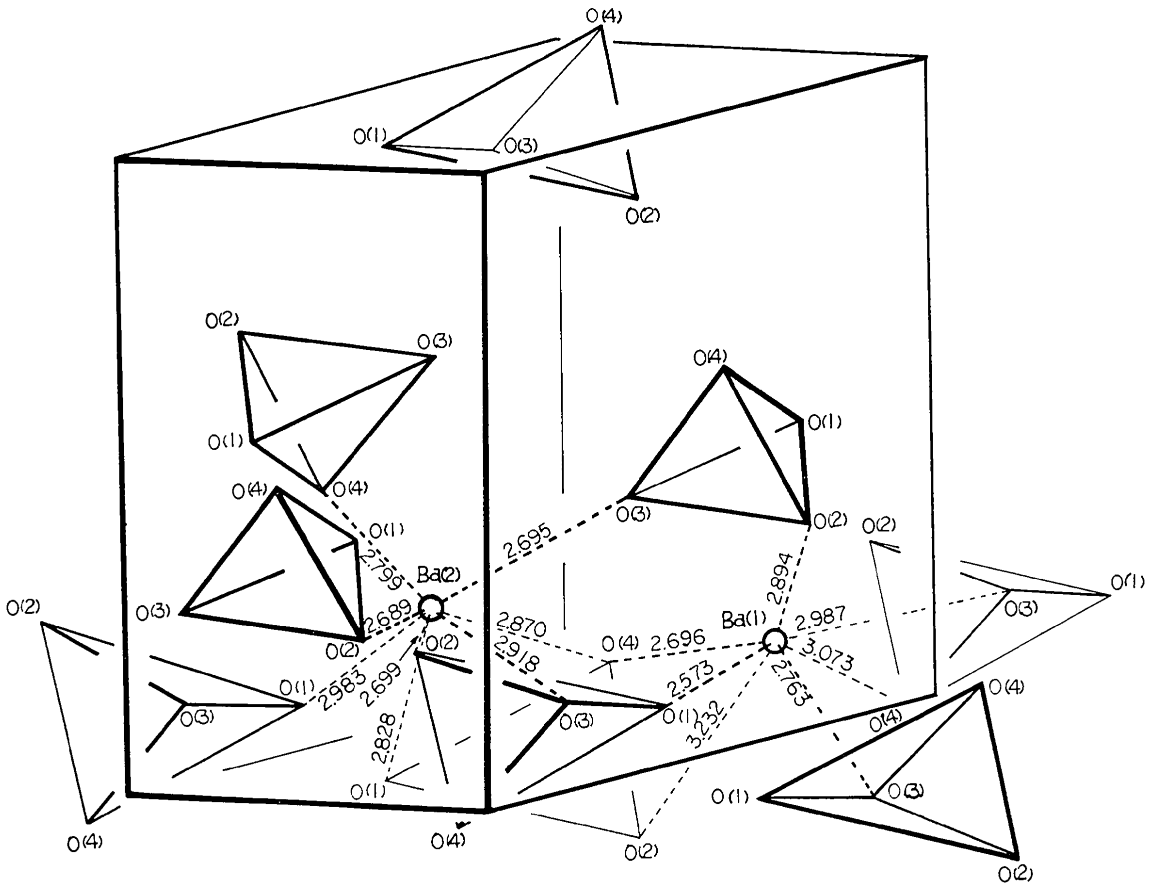

Fig. 1. The structure of β-Ba_2TiO_4 showing the environment of Ba(1) and Ba(2). Ti atoms (not shown) are at the centres of the tetrahedra.

diction of 1·81 Å from their universal curve for the isoelectronic series of 18 electron ions. In the light of present work, we propose the revised bond strength–bond length expression $s=0{\cdot}666(R/1{\cdot}953)^{-5{\cdot}25}$ for Ti–O. This curve together with that for Ba–O (Wu & Brown) has been used to calculate the bond strengths given in Table 4. The r.m.s. deviation of the bond strength sums from the valence is 0·12 valence units or 5·9% indicating a satisfactory refinement.

Table 4. *Bond strengths* (in valence units) in* β-Ba_2TiO_4

	Ba(1)	Ba(2)	Ti	Anion sums
O(1)	0·45	0·18 0·25	1·13	2·01
O(2)	0·22 0·11	0·34 0·33	0·99	1·99
O(3)	0·18 0·29	0·34 0·21	0·97	1·99
O(4)	0·34 0·15	0·27 0·23	0·92	1·91
Cation sums	1·74	2·15	4·01	

* The expression used in this calculation is

$$s=s_0(R/R_o)^{-N},$$

where

	S_o	R_o	N
Ti–O	0·666	1·953	5·25
Ba–O	0·286	2·766	6·15

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