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Orthorhombic Barium Orthotitanate, α'-Ba_2TiO_4

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Abstract. $M_r = 386 \cdot 6$, orthorhombic, $P2_1nb$ (non-standard setting of $Pna2_1$), $a = 6 \cdot 1070\,(8)$, $b = 22 \cdot 952\,(4)$, $c = 10 \cdot 540\,(2)$ Å, $V = 1477$ Å^3, $Z = 12$, $D_x = 5 \cdot 212$ Mg m^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0 \cdot 7107$ Å, $\mu(\text{Mo}\,K\alpha) = 17 \cdot 29$ mm^{-1}, $F(000) = 1992$, $T = 295$ K. Final refinements on F^2 including $F^2 < 0$ (2486 data, $2\theta_{\max} = 60°$); $R(F^2) = 0 \cdot 063$, $R_w(F^2) = 0 \cdot 102$. The structure is related to that for monoclinic β-Ba_2TiO_4 but with pronounced superstructure derived from a tripling of the b axis. The TiO_4 tetrahedra are discrete; three Ba have irregular eightfold coordination (Ba—O 2·54–3·15 Å); the other three have irregular sixfold coordination (Ba—O 2·63–3·11 Å). The topotactic transformation from monoclinic β-Ba_2TiO_4 to α'-Ba_2TiO_4 is discussed.

Introduction. β-Barium orthotitanate, β-Ba_2TiO_4, is notable as the only example of Ti^{IV} tetrahedrally coordinated by oxygen (see, for example, Wells, 1975). Its preparation and crystal structure have been described by Bland (1961) and a crystal structure refinement by Wu & Brown (1973). β-Ba_2TiO_4 crystallizes in a monoclinic distorted β-K_2SO_4 type of structure; crystals are invariably twinned (Bland, 1961; Wu & Brown, 1973). The existence of an orthorhombic phase with superstructure was also noted by these authors, and more detailed observations have been made for the related Ca_2SiO_4 system (Saalfeld, 1972, 1975).

The compound is also of technical importance, since it is known that it occurs as an intermediate in the preparation of $BaTiO_3$ from TiO_2 and $BaCO_3$ (Yamaguchi, Cho, Nagai & Kuno, 1977). During preliminary experiments on the reaction of Ba_2TiO_4 with CO_2, we found the surprising result that the twinning seemed to disappear during annealing of the crystals at about 673 K. More careful investigation of the annealed crystals showed them to consist of a new, orthorhombic modification with a tripled b axis as compared to the monoclinic form. However, the phase transformation seems to be too sluggish to be detected by DTA and DSC.

Experimental. The orthorhombic modification of Ba_2TiO_4 can easily be prepared in single crystalline form in two ways. Twinned crystals, prepared according to Bland and annealed in air at 673 K for two to three days, transform in most cases into single crystals of the orthorhombic form. The same product may be obtained directly when similarly prepared crystals are cooled very slowly from 1613 K to room temperature (cooling rate of about 50 K h^{-1}).

Symmetry and systematic absences consistent with non-standard settings of the orthorhombic space groups $Pnma$ [$Pmnb$: x, y, z; $\frac{1}{2} - x, y, z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $x, \frac{1}{2} + y, \frac{1}{2} - z$; and four more by application of the inversion center at (000)] and $Pna2_1$ ($P2_1nb$: x, y, z; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} + x, -y, -z$; $x, \frac{1}{2} + y, \frac{1}{2} - z$) were observed by Weissenberg and precession photography. These non-standard settings are chosen to correlate the structure and unit cell of the orthorhombic Ba_2TiO_4 with monoclinic β-Ba_2TiO_4 [space group $P2_1/n$, $a = 6 \cdot 096\,(4)$, $b = 7 \cdot 681\,(6)$, $c = 10 \cdot 545\,(9)$ Å, $\beta = 92 \cdot 99\,(6)°$]. In addition, there was very pronounced superstructure with reflections hkl, $k \neq 3n$, $n = 0, 1, 2, \ldots$ being very weak. Further, reflections $0kl$, $k \neq 3n$, $n = 0, 1, 2 \ldots$ were almost systematically absent. Within the primary structure, $k = 3n$, pseudosymmetry was also apparent. The symmetry of the primary structure itself conforms to the same space group as the total structure.

Many crystals also showed weak reflections corresponding to the parent monoclinic phase. However, the crystal selected for data collection upon the automated Picker FACS-I diffractometer showed no such reflections with long-exposure photographs. Crystal mosaicities as determined by ω-scans with a tube take-off angle of 2·4° were ~0·14° – values typical in this laboratory for reasonable quality crystals. Orientation and cell parameters: determined using 17 automatically centered reflections in the range $40 \cdot 16° < 2\theta < 41 \cdot 81°$ with Mo $K\alpha_1$ radiation ($\lambda = 0 \cdot 70926$ Å); data measured: ~5000 reflections $\pm hkl$, to $2\theta = 60°$; scan range: 0·9° below $K\alpha_1$ to 0·9° above $K\alpha_2$, slight peak truncation on high-2θ side (<3%)

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chosen to avoid problems with overlapping reflections; scan speed: 2·0° $\min^{-1}$ in 2θ with weak reflections rescanned cumulatively up to three times or until criterion $I > 5\sigma_I$ satisfied (Lenhert, 1975); data processing: University of Zürich crystallographic program library (Jameson, Schneider, Dubler & Oswald, 1982); Lorentz, polarization and absorption corrections; crystal: flattened needle 0·33 × 0·15 × 0·10 mm, 2·29 × 10^{-3} mm^3, transmission factors 0·160–0·360; neutral-atom scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). To provide the necessary data so that the accuracy of this structure can be assessed a detailed description is supplied.

Initial refinements began in space group *Pmnb* – additional complications by removing a mirror plane were not sought at this stage. The data were appropriately averaged; the curved faces, rounded edges and non-symmetrical crystal shape and high absorption coefficient led to a less than ideal correction. The Patterson function was deconvoluted with reference to the structure of monoclinic β-Ba_2TiO_4 (Bland, 1961; Wu & Brown, 1973). For space group *Pmnb* the Ba and Ti atoms lay on mirror planes at $x = \frac{1}{4}, \frac{3}{4}$; in β-Ba_2TiO_4 these atoms lay near $x = \frac{1}{4}$ or $\frac{3}{4}$. From the tripling of the b axis (relative to β-Ba_2TiO_4) y coordinates, for at least the Ba and Ti atoms of the form $y, y + \frac{1}{3}$ and $y + \frac{2}{3}$ were deduced. Refinements on F (using the 1590 data with $I > 3\sigma$) of the y, z and B parameters of those nine independent atoms lowered R to ~0·39. However, further development of the structure proceeded poorly with refinement stalling at $R = 0{\cdot}22$ for the 1590 data with $I > 3\sigma_I$.

A test for piezoelectricity was made: a medium-strength signal was obtained. Refinements were begun, therefore, in space group $P2_1nb$. To our relief the values for R and R_w (on F) dropped to 0·107 and 0·139 for a model comprising six Ba atoms and three TiO_4 groups (Ti—O, 1·81 Å). Group constraints were released; leading to $R = 0{\cdot}054$ and $R_w = 0{\cdot}070$, but new problems arose when the temperature factor of an O atom became non-positive definite. Anisotropic refinement of the metal atoms led to values for R and R_w of 0·036 and 0·046 but the temperature factor of Ti(2) also became non-positive definite.

At this stage we carefully remeasured the crystal dimensions, made a new absorption correction, and henceforth only those data $+hkl$ were used, since in $P2_1nb$ reflections $+hkl$ and $-hkl$ should not be averaged in the presence of anomalous scattering. These modifications, alas, led to improvements in neither R values ($R = 0{\cdot}039$ and $R_w = 0{\cdot}050$ for the equivalent refinement) nor temperature factors. Ba atoms which were randomly reset to one or the other side of the pseudomirror plane always returned to their former positions upon refinement. Relative to the much more intense hkl, $k = 3n$ data, the data for which $k \neq 3n$ were underweighted. Granting these reflections greater weight produced no improvement in the thermal parameters. However, these reflections are not the only ones systematically weak. Thus we initiated refinements on F^2 using all 2486 unique data including $F_o^2 > 0$ but excluding systematic absences. The weighting scheme was $1/\sigma^2(F^2)$ where $\sigma(F^2)$ is derived from $\sigma_I^2 = \sigma_{\text{counting}}^2 + (0{\cdot}03I)^2$. Refinements eventually converged at values for R and R_w on F^2 of 0·063 and 0·102. In early cycles there were substantial changes in coordinates of Ba atoms with one Ba atom jumping through the pseudomirror plane. Since the incomplete data set (only $I > 3\sigma_I$) used previously had produced a false minimum this was expected. In the final cycles a parameter for secondary extinction was refined (giving a total of 130 parameters); at convergence its value was 0·50 (2) × 10^{-6}. For the portion of data having $I > 3\sigma_I$ the conventionally quoted values for R and R_w on F were 0·039 and 0·052. The minimized function appeared to be independent of the magnitudes of $|F_o|$ and $(\sin\theta)/\lambda$, and most importantly for most combinations of h,k,l including $k = 3n$ *versus* $k \neq 3n$. In the final difference Fourier map the biggest peaks (<2·16 e $Å^{-3}$) lay near Ba(22); ratio of maximum shift to error = 0·28. With the Ba atoms dominating the scattering, high correlation among the parameters describing the pseudo-symmetrically related Ba atoms was not unexpected and, of course, compromises seriously the precision of the structure. The absolute configuration was not determined.

Discussion. Final atomic coordinates are given in Table 1. Tables of distances and angles have been deposited. In addition, a table containing the transformed (to $Pna2_1$) unit-cell parameters and atomic coordinates is deposited.*

It is clear that refinements on F using the conventional cut-off criterion, $I > 3\sigma_I$, and conventional weighting scheme [$w = 1/\sigma^2(F)$] lead to false minima in this structure determination, in part because the cut-off criterion is not applied randomly to the data set and in part because the weights applied to the $|F_o - F_c|^2$ are invalid when $F_o^2 \sim \sigma(F_o^2)$. For refinement on F the formula customarily used to calculate $\sigma(F)$ from $\sigma(F_o^2)$, $\sigma(F) = \sigma(F_o^2)/(2F)$, where $\sigma(F^2)$ is derived from counting statistics, is valid only for $F_o^2 >> \sigma(F_o^2)$, a situation which does not apply when large amounts of data are systematically weak, and structurally very important. On the other hand for refinement on F^2 the $\sigma(F^2)$ are meaningful regardless of the magnitude of F^2.

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* Lists of structure factors [F_o^2, F_c^2 and $\sigma(F_o^2)$], anisotropic thermal parameters, the transformed coordinates, and the distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38867 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters for orthorhombic* Ba_2TiO_4

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

	x	y	z	B_{eq}(Å^2)
Ba(11)	0·740	0·28019 (5)	0·0757 (1)	0·93 (5)
Ba(12)	0·7612 (2)	0·61145 (6)	0·0775 (1)	1·09 (4)
Ba(13)	0·7850 (2)	0·94609 (7)	0·0745 (1)	1·09 (6)
Ba(21)	0·2546 (4)	0·16852 (6)	0·1995 (1)	0·90 (4)
Ba(22)	0·2860 (4)	0·50140 (6)	0·2008 (1)	0·76 (5)
Ba(23)	0·2375 (4)	0·83483 (6)	0·2010 (1)	0·85 (5)
Ti(1)	0·780 (1)	0·0948 (2)	0·0848 (4)	0·59 (13)
Ti(2)	0·757 (1)	0·4277 (2)	0·0843 (3)	0·63 (12)
Ti(3)	0·750 (1)	0·7598 (2)	0·0854 (4)	0·69 (12)
O(11)	0·524 (2)	0·0729 (7)	0·152 (1)	1·9 (2)
O(12)	0·998 (2)	0·0703 (7)	0·189 (2)	2·0 (3)
O(13)	0·809 (2)	0·1714 (6)	0·058 (1)	1·9 (2)
O(14)	0·801 (2)	0·0560 (6)	−0·065 (1)	1·8 (3)
O(21)	0·510 (2)	0·3927 (6)	0·144 (1)	1·2 (2)
O(22)	0·981 (2)	0·4159 (6)	0·195 (1)	0·9 (2)
O(23)	0·678 (2)	0·5021 (6)	0·056 (1)	0·9 (2)
O(24)	0·811 (2)	0·3899 (5)	−0·066 (1)	1·1 (2)
O(31)	0·533 (3)	0·7487 (7)	0·202 (2)	1·6 (2)
O(32)	1·004 (3)	0·7273 (7)	0·143 (2)	1·5 (3)
O(33)	0·808 (2)	0·8358 (6)	0·062 (1)	1·5 (2)
O(34)	0·684 (2)	0·7231 (5)	−0·064 (1)	1·1 (2)

The differences in the nature and orientation of the coordination polyhedra may be inspected in Fig. 1. The pseudomirror plane is perpendicular to the *a* axis which runs from left to right in the figure. The three crystallographically independent TiO_4 tetrahedra are only marginally more distorted than that for monoclinic β-Ba_2TiO_4 (Wu & Brown, 1973). For α′-Ba_2TiO_4, O—Ti—O angles lie in the range 103·9–116·7 (7)° and for β-Ba_2TiO_4 in the range 104·7–111·8 (4)°. The Ti(3) tetrahedron is oriented differently in space to the other two, but similar to that for β-Ba_2TiO_4.

The coordination polyhedra around Ba(11) and Ba(12) are roughly related in crystal space by a pseudoglide plane and their point symmetry is perhaps best described as a capped trigonal bipyramid with the trigonal axis coming approximately out of the page. Atom Ba(13) lies in a different environment. All three polyhedra involve one bridging TiO_4 tetrahedron; atoms O(24), O(34) and O(14)′, respectively, sit atop a face of the trigonal bipyramid. The general stereochemistry of Ba(12) is reminiscent of that of Ba(1) in β-Ba_2TiO_4.

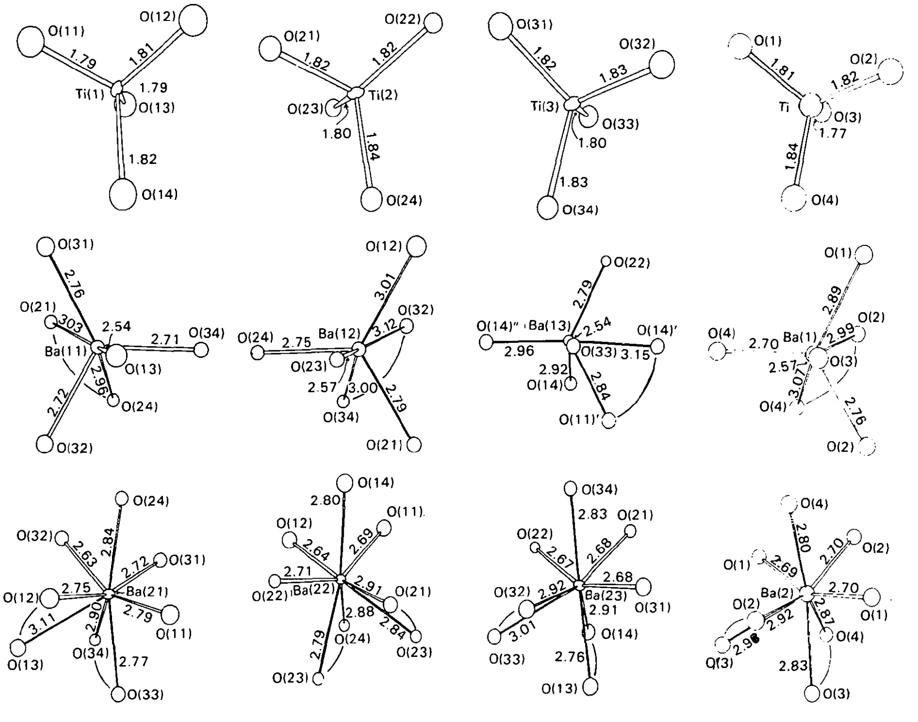

Fig. 1. The coordination polyhedra for orthorhombic α′-Ba_2TiO_4 (first three columns) and monoclinic β-Ba_2TiO_4 (last column). Boundary ellipses are shown at the 50% probability level, Ba—O separations less than 2·75 Å are drawn with broader sticks than the others for which 3·20 Å formed the upper limit. All diagrams are drawn with the *a* axis across the page and the *b* axis going into it. Atom labelling for O atoms corresponds to that for monoclinic β-Ba_2TiO_4 for which all atoms were given an isotropic thermal parameter, $B = 1{\cdot}5$ Å^2. For α′-Ba_2TiO_4 estimated standard deviations in Ti—O distances are in the range 0·014–0·017 Å and Ba—O bonds 0·012–0·017 Å.

The remaining three Ba polyhedra are generally similar to one another and to Ba(2) of β-Ba_2TiO_4; all involve two bridging TiO_4 tetrahedra. Polyhedra around Ba(21) and Ba(23) are rather similarly oriented in space; Ba(22) is related to the other two by a pseudoglide plane.

Fig. 2 illustrates the overall arrangement of TiO_4 tetrahedra and Ba atoms in the crystal. Among compounds which undergo topotactical transformations this compound is noteworthy. Crystals of monoclinic β-Ba_2TiO_4 which appear to be invariably twinned transform to give non-twinned crystals. Further, this reaction appears to have occurred in a concerted manner for an individual twinned crystal, since a centrosymmetric arrangement has been transformed to a non-centrosymmetric one, as a result of the *b* axis tripling in length. Symmetry elements which are conserved in the structural transformation are the *n* glide perpendicular to **b** and, for the heavy atoms located close to $x = \frac{1}{4}, \frac{3}{4}$, the inversion center and the 2_1 screw axis parallel to **b** are approximately conserved. With respect to Ba(1) in β-Ba_2TiO_4 and with reference to Fig. 1 the following detailed structural reorganization occurs to yield the coordination polyhedra around the corresponding atoms Ba(11), Ba(12) and Ba(13). Bonds Ba(1)—O(1) and the shorter Ba(1)—O(2) bond are replaced by Ba(12)—O(12) and Ba(12)—O(21). Considering Ba(11), the longer Ba(1)—O(2) bond is replaced by bond Ba(11)—O(21) – a change in the bridging TiO_4 tetrahedron. For Ba(13) more bond breaking and making relative to Ba(1) has occurred: bonds Ba(1)—O(1) and the shorter Ba(1)—O(2) are replaced, analogous to Ba(12), by Ba(13)—O(22) and Ba(13)—O(11)′. The longer Ba(1)—O(2) bond is replaced by Ba(13)—O(14)′ – a change in the bridging TiO_4 tetrahedron.

With respect to Ba(2) the following changes occur: The shorter Ba(2)—O(1) and Ba(2)—O(2) bonds are replaced by Ba(21)—O(32) and Ba(21)—O(31) bonds, and Ba(23)—O(22) and Ba(23)—O(21) bonds, respectively. A change in bridging TiO_4 tetrahedra occurs for Ba(22): bond Ba(2)—O(3) is replaced by Ba(22)—O(23), and bonds Ba(2)—O(1) and Ba(2)—O(2) are as above, transposed yielding Ba(22)—O(12) and Ba(22)—O(11), respectively.

Monoclinic β-Ba_2TiO_4 and β-Ca_2SiO_4 are similar in structure (Bland, 1961; Wu & Brown, 1973; Saalfeld, 1972, 1975). The unit cell and space group of orthorhombic α'-Ca_2SiO_4 have been characterized (Saalfeld, 1975): $a = 9{\cdot}41$, $b = 5{\cdot}53$, $c = 20{\cdot}43$ Å, *Pcmn*. Permutation of axes leads to a cell comparable to α'-Ba_2TiO_4 and space group *Pmnb*. However, the structure of α'-Ba_2TiO_4 indicates that space group $P2_1nb$ may well pertain also to α'-Ca_2SiO_4.

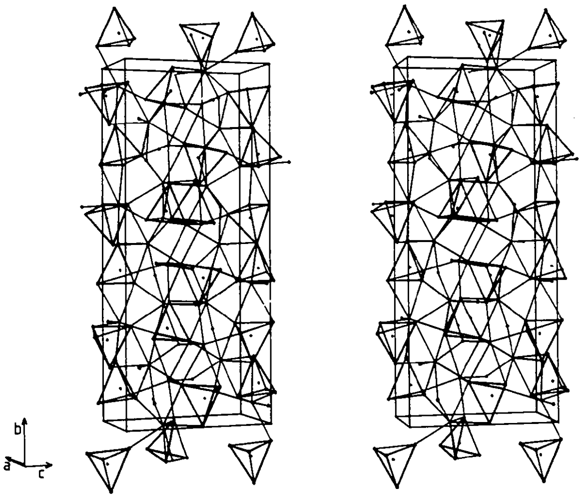

Fig. 2. Unit-cell diagram for orthorhombic α'-Ba_2TiO_4. TiO_4 tetrahedra are shown with thicker lines.

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