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## Refinement of Barium Tetratitanate, BaTi<sub>4</sub>O<sub>9</sub>, and Hexabarium 17-Titanate, Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub>

BY WOLFGANG HOFMEISTER AND EKKEHART TILLMANN

*Institut für Geowissenschaften, Postfach 3980, Universität Mainz, D-6500 Mainz, Federal Republic of Germany*

AND WERNER H. BAUR

*Department of Geological Sciences, Box 4348, University of Illinois at Chicago, Chicago, Illinois 60680, USA*

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**Abstract.** BaTi<sub>4</sub>O<sub>9</sub>:  $M_r = 472.9$ , orthorhombic, *Pmmn*,  $a = 14.527(2)$ ,  $b = 3.794(1)$ ,  $c = 6.293(1)$  Å,  $V = 346.8$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 4.53$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 10.00$  mm<sup>-1</sup>,  $F(000) = 431.9$ ,  $T = 293$  K, final  $R = 0.033$  for 1614 unique reflexions. Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub>:  $M_r = 2278.3$ , monoclinic, *C2/c*,  $a = 9.887(1)$ ,  $b = 17.097(2)$ ,  $c = 18.918(2)$  Å,  $\beta = 98.72(2)^\circ$ ,  $V = 3160.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 4.79$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 11.47$  mm<sup>-1</sup>,  $F(000) = 3958.9$ ,  $T = 293$  K, final  $R = 0.051$  for 6945 unique reflexions. Single crystals from both compounds were grown from the melt. The BaTi<sub>4</sub>O<sub>9</sub> compound is best described as a '4.0 Å' structure similar to many alkali titanates, in which the long axes of the octahedra are lined up parallel to the short cell constant. The Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> compound can be described as a hexagonal closest packing of Ba and O atoms, with Ti in octahedral interstices.

**Introduction.** With the determination of the crystal structure of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> (Tillmanns, Hofmeister & Baur, 1983) all the structures of the compounds in the system BaO–TiO<sub>2</sub> are known. Structure determinations have been reported for BaTi<sub>4</sub>O<sub>9</sub> by Lukaszewicz (1957) and Templeton & Dauben (1960) and for Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> by Tillmanns & Baur (1970). In the course of an investigation of the crystal chemistry of the barium titanate system a refinement of these structures proved necessary in order to obtain more precise coordinates and distances. With bond distances from these newly refined structures a statistically significant dependence of mean bond lengths on octahedral distortions can be established for the titanates (Tillmanns, Hofmeister & Baur, 1984).

**Experimental.** Single crystals of Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> and BaTi<sub>4</sub>O<sub>9</sub> were taken from a sample of composition BaO:TiO<sub>2</sub> = 1:3 partly melted on a platinum plate at about 1673 K and quenched. Three-dimensional X-ray diffraction intensities were collected with a Nonius CAD-4 computer-controlled diffractometer. For Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub>: crystal irregularly shaped, approximate diameter 0.2 mm; 25 reflexions with  $20 < \theta < 30^\circ$  used for determination of lattice parameters; a total of 7464 reflexions collected in range  $0.03 < \sin\theta/\lambda < 0.81$  Å<sup>-1</sup> with  $0 \leq h \leq 15$ ,  $0 \leq k \leq 27$  and  $-30 \leq l \leq 30$  giving 6945 unique reflexions ( $R_{\text{int}} = 0.038$ ) of which 699 considered unobserved ( $I < 2\sigma_I$ ); intensities of three standard reflexions monitored after every 6 h, their orientation after every 400 reflexions, measurement instability 0.008; min. and max. transmission factors for absorption correction 0.09 and 0.27; function minimized  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  for each reflexion is set to  $1/\sigma^2(F)$ ; ratio of max. least-squares shift to error in final cycle 0.2; after a secondary extinction correction ( $g = 0.0005$ ) final  $R = 0.051$ ,  $R_w = 0.053$ ; final difference synthesis had max.  $\Delta\rho$  excursions of  $-1.9$  e Å<sup>-3</sup> at the Ba positions and  $1.1$  e Å<sup>-3</sup> at distances of 0.6–0.7 Å. Atomic scattering factors and real and imaginary anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974).

Most experimental conditions were the same for BaTi<sub>4</sub>O<sub>9</sub>: orthorhombic prism with dimensions  $0.15 \times 0.1 \times 0.325$  mm; min. and max. transmission factors 0.23 and 0.40; a total of 1614 unique reflexions collected between  $0.02 < \sin\theta/\lambda < 0.90$  Å<sup>-1</sup> (measurement instability 0.008,  $0 \leq h \leq 28$ ,  $0 \leq k \leq 7$ ,  $0 \leq l \leq 12$ ) of which 75 considered unobserved; ratio of

Table 1. Fractional atomic coordinates with the significant figures of the e.s.d.'s in parentheses and vibrational parameters (in Å<sup>2</sup>)

$B_{eq} = \frac{2}{3}\pi^2 \text{ trace } U.$				
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
<b>(a) Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub></b>				
Ba(1)	0.07008 (3)	0.09000 (2)	0.44271 (1)	0.49
Ba(2)	0.86241 (3)	0.42567 (2)	0.82139 (1)	0.52
Ba(3)	0.85354 (2)	0.28328 (2)	0.31481 (1)	0.53
Ti(1)	0.0	0.10418 (7)	0.25	0.36
Ti(2)	0.0	0.93798 (7)	0.25	0.45
Ti(3)	0.72171 (7)	0.90091 (4)	0.86124 (4)	0.27
Ti(4)	0.0	0.74701 (6)	0.25	0.29
Ti(5)	0.70366 (9)	0.92594 (4)	0.36886 (5)	0.48
Ti(6)	0.70950 (8)	0.75308 (4)	0.37315 (4)	0.33
Ti(7)	0.97748 (7)	0.16022 (5)	0.88116 (4)	0.42
Ti(8)	0.25	0.25	0.0	0.42
Ti(9)	0.96749 (7)	0.32412 (4)	-0.00125 (4)	0.34
Ti(10)	0.25621 (7)	0.41971 (4)	0.01330 (4)	0.24
Ti(11)	0.0	0.5	0.0	0.48
O(1)	0.9327 (3)	0.0807 (2)	0.5582 (2)	0.48
O(2)	0.9384 (3)	0.2439 (2)	0.5525 (2)	0.37
O(3)	0.9403 (3)	0.4134 (2)	0.5537 (2)	0.40
O(4)	0.2024 (3)	0.0155 (2)	0.0666 (2)	0.37
O(5)	0.1859 (3)	0.1580 (2)	0.5735 (2)	0.29
O(6)	0.1886 (3)	0.3261 (2)	0.5668 (2)	0.39
O(7)	0.1789 (3)	0.4962 (2)	0.0602 (2)	0.35
O(8)	0.9295 (3)	0.4170 (2)	0.0579 (2)	0.41
O(9)	0.9308 (3)	0.2546 (2)	0.0688 (2)	0.48
O(10)	0.1756 (3)	0.3299 (2)	0.0546 (2)	0.41
O(11)	0.2051 (3)	0.1655 (2)	0.0596 (2)	0.27
O(12)	0.9014 (3)	0.0178 (2)	0.1991 (2)	0.35
O(13)	0.9099 (3)	0.1615 (2)	0.6917 (2)	0.26
O(14)	0.8910 (3)	0.3293 (2)	0.6955 (2)	0.52
O(15)	0.8750 (3)	0.4885 (2)	0.6848 (2)	0.45
O(16)	0.1269 (3)	0.0796 (2)	0.6800 (2)	0.38
O(17)	0.1300 (3)	0.2431 (2)	0.6824 (2)	0.36
O(18)	0.8783 (3)	0.3423 (2)	0.1829 (2)	0.41
O(19)	0.8848 (3)	0.1801 (2)	0.1908 (2)	0.60
O(20)	0.1307 (3)	0.1110 (2)	0.1823 (2)	0.56
<b>(b) BaTi<sub>4</sub>O<sub>9</sub></b>				
Ba	0.25	0.75	0.70824 (4)	0.96
Ti(1)	0.03677 (2)	0.25	0.80405 (5)	0.24
Ti(2)	0.12901 (2)	0.25	0.24858 (5)	0.32
O(1)	0.5098 (1)	0.25	0.1504 (2)	0.36
O(2)	0.6012 (1)	0.25	0.7400 (3)	0.43
O(3)	0.1520 (1)	0.25	0.9547 (2)	0.46
O(4)	0.0934 (1)	0.25	0.5610 (2)	0.68
O(5)	0.25	0.25	0.3430 (4)	0.62

max. least-squares shift to error 0.08; after correction for secondary extinction ( $g = 0.018$ ) final  $R = 0.033$ ,  $R_w = 0.036$ ; max.  $\Delta\rho$  excursions  $-1.2 \text{ e } \text{Å}^{-3}$  at the Ba position and  $0.3 \text{ e } \text{Å}^{-3}$  at a distance of  $1.0 \text{ Å}$  from this site. A list of computer programs is given by Tillmanns *et al.* (1983).

**Discussion.** Final atomic parameters are given in Table 1.\*

The new refinements of both structures are, as far as the positional parameters are concerned, within two standard deviations of the older and much less precise structure determinations. Consequently, the previous descriptions of both structures still do apply. This is true not only for their general features, such as the description of Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> as a hexagonal closest

Table 2. Interatomic distances (Å) and angles (°)

Standard deviations of O—O distances are less than 0.005 Å.

<b>(a) Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub></b>				
Ba(1)—O(1)	2.747 (3)	Ti(4)—O(14)	2 × 1.894 (3)	
Ba(1)—O(6)	2.813 (3)	Ti(4)—O(17)	2 × 1.954 (3)	
Ba(1)—O(5)	2.815 (3)	Ti(4)—O(13)	2 × 2.040 (3)	
Ba(1)—O(9)	2.822 (3)			
Ba(1)—O(20)	2.870 (3)	Ti(5)—O(18)	1.850 (3)	
Ba(1)—O(1)	2.918 (3)	Ti(5)—O(15)	1.880 (3)	
Ba(1)—O(4)	2.960 (3)	Ti(5)—O(5)	2.020 (3)	
Ba(1)—O(7)	2.963 (3)	Ti(5)—O(16)	2.034 (3)	
Ba(1)—O(12)	3.005 (3)	Ti(5)—O(8)	2.056 (3)	
Ba(1)—O(11)	3.006 (3)	Ti(5)—O(4)	2.088 (3)	
Ba(1)—O(19)	3.048 (3)			
Ba(1)—O(4)	3.086 (3)	Ti(6)—O(19)	1.883 (3)	
		Ti(6)—O(9)	1.895 (3)	
Ba(2)—O(7)	2.692 (3)	Ti(6)—O(6)	1.947 (3)	
Ba(2)—O(12)	2.753 (3)	Ti(6)—O(18)	1.981 (3)	
Ba(2)—O(15)	2.819 (3)	Ti(6)—O(5)	2.021 (3)	
Ba(2)—O(6)	2.819 (3)	Ti(6)—O(17)	2.032 (3)	
Ba(2)—O(15)	2.829 (3)			
Ba(2)—O(3)	2.835 (3)	Ti(7)—O(13)	1.899 (3)	
Ba(2)—O(14)	2.945 (3)	Ti(7)—O(1)	1.909 (3)	
Ba(2)—O(14)	3.000 (3)	Ti(7)—O(5)	1.941 (3)	
Ba(2)—O(19)	3.022 (3)	Ti(7)—O(16)	1.985 (3)	
Ba(2)—O(17)	3.124 (3)	Ti(7)—O(2)	2.000 (3)	
Ba(2)—O(20)	3.278 (3)	Ti(7)—O(17)	2.048 (3)	
Ba(3)—O(10)	2.653 (3)	Ti(8)—O(11)	2 × 1.925 (3)	
Ba(3)—O(18)	2.737 (3)	Ti(8)—O(10)	2 × 1.925 (3)	
Ba(3)—O(13)	2.756 (3)	Ti(8)—O(2)	2 × 1.976 (3)	
Ba(3)—O(18)	2.831 (3)			
Ba(3)—O(9)	2.866 (3)	Ti(9)—O(6)	1.828 (3)	
Ba(3)—O(20)	2.949 (3)	Ti(9)—O(9)	1.857 (3)	
Ba(3)—O(19)	2.988 (3)	Ti(9)—O(2)	1.990 (3)	
Ba(3)—O(14)	3.073 (3)	Ti(9)—O(8)	2.011 (3)	
Ba(3)—O(17)	3.112 (3)	Ti(9)—O(3)	2.102 (3)	
Ba(3)—O(19)	3.146 (3)	Ti(9)—O(10)	2.168 (3)	
Ba(3)—O(11)	3.233 (3)			
		Ti(10)—O(7)	1.813 (3)	
Ti(1)—O(12)	2 × 1.943 (3)	Ti(10)—O(11)	1.821 (3)	
Ti(1)—O(20)	2 × 1.956 (3)	Ti(10)—O(10)	1.947 (3)	
Ti(1)—O(19)	2 × 1.963 (3)	Ti(10)—O(4)	1.966 (3)	
		Ti(10)—O(11)	2.081 (3)	
Ti(2)—O(12)	2 × 1.859 (3)	Ti(10)—O(3)	2.155 (3)	
Ti(2)—O(16)	2 × 1.981 (3)			
Ti(2)—O(13)	2 × 2.145 (3)	Ti(11)—O(3)	2 × 1.938 (3)	
		Ti(11)—O(7)	2 × 1.954 (3)	
Ti(3)—O(20)	1.793 (3)	Ti(11)—O(8)	2 × 1.983 (3)	
Ti(3)—O(14)	1.880 (3)			
Ti(3)—O(15)	1.914 (3)			
Ti(3)—O(11)	1.931 (3)			
Ti(3)—O(4)	2.040 (3)			
Ti(3)—O(3)	2.446 (3)			
<b>(b) BaTi<sub>4</sub>O<sub>9</sub></b>				
Ba—O(3)	4 × 2.834 (1)	Ti(2)—O(5)	1.855 (1)	
Ba—O(5)	2 × 2.980 (2)	Ti(2)—O(3)	1.879 (1)	
Ba—O(4)	4 × 3.103 (1)	Ti(2)—O(2)	2 × 1.941 (1)	
		Ti(2)—O(4)	2.032 (2)	
Ti(1)—O(4)	1.737 (2)	Ti(2)—O(1)	2.109 (1)	
Ti(1)—O(3)	1.923 (2)	O(5)—O(3)	2.828	
Ti(1)—O(1)	2 × 1.958 (1)	O(5)—O(2)	2 × 2.924	
Ti(1)—O(2)	2.044 (2)	O(5)—O(4)	2.657	
Ti(1)—O(1)	2.282 (1)	O(5)—O(1)	3.963	
O(4)—O(3)	2.619	O(3)—O(2)	2 × 2.799	
O(4)—O(1)	2 × 2.894	O(3)—O(4)	3.909	
O(4)—O(2)	3.043	O(3)—O(1)	2.653	
O(4)—O(1)	4.000	O(2)—O(2)	3.794	
O(3)—O(1)	2 × 2.882	O(2)—O(4)	2 × 2.683	
O(3)—O(2)	3.917	O(2)—O(1)	2 × 2.583	
O(3)—O(1)	2.653	O(4)—O(1)	2.987	
O(1)—O(1)	3.794			
O(1)—O(2)	2 × 2.583			
O(1)—O(1)	2 × 2.695			
O(2)—O(1)	2.904			

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39375 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

packing of Ba and O atoms and the characterization of BaTi<sub>4</sub>O<sub>9</sub> as a '4.0 Å' structure similar to the alkali titanates described among others by Andersson & Wadsley (1961), but also for the detailed distortions of individual titanium oxygen octahedra. However, these

distortions are now more precisely described, are quite clearly real and cannot be suspected to be artifacts of refinement.

In both the Ti(1) and the Ti(2) coordination octahedra in  $\text{BaTi}_4\text{O}_9$ , the Ti atoms are displaced away from the centers of the octahedra as already observed by Templeton & Dauben (1960). Such distortions have been described and compared with similar observations in other compounds by Shirane, Pepinsky & Frazer (1956) in  $\text{PbTiO}_3$ , by Baur (1961) in brookite and by Tillmanns (1974) in  $\text{BaTi}_2\text{O}_5$ . In  $\text{BaTi}_4\text{O}_9$ , in  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$  and in  $\text{BaTi}_2\text{O}_5$  these octahedral distortions can be correlated with the bond-strength deviations at the O atoms (Baur, 1970).

The  $b$  cell edge of about 4.0 Å in the Wadsley/Andersson type phases corresponds to the corner-to-corner distance of the coordination octahedra or to twice the Ti—O distance in a titanate. In the barium titanates which adopt this structural type this means that the  $b$  edges are about 3.9 Å long. However, the  $b$  constant of  $\text{BaTi}_4\text{O}_9$  measures only 3.794 Å and is thus the shortest on record for any barium titanate. This shortness is connected to the above-mentioned off-centering of the Ti atoms and results in angles O—Ti—O

parallel to [010] of 151 and 156° instead of the expected 180° (see Table 2).

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## Structures of Phase IV Rubidium Nitrate, $\text{RbNO}_3$ , and Phase II Caesium Nitrate, $\text{CsNO}_3$

BY CHRISTOPHER DEAN, TREVOR W. HAMBLEY\* AND MICHAEL R. SNOW

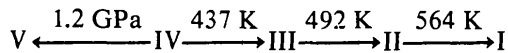
Department of Physical and Inorganic Chemistry, University of Adelaide, GPO Box 498, Adelaide, South Australia 5001, Australia

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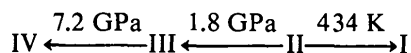
**Abstract.**  $\text{RbNO}_3$ :  $M_r = 147.47$ , trigonal,  $P3_2$ ,  $a = 10.502$  (1),  $c = 7.473$  (1) Å,  $V = 713.8$  (1) Å<sup>3</sup>,  $Z = 9$ ,  $D_x = 3.106$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 152.5$  cm<sup>-1</sup>,  $F(000) = 612$ ,  $T = 299.5$  K, final  $R = 3.3\%$  for 797 unique observed reflections.  $\text{CsNO}_3$ :  $M_r = 194.91$ , trigonal,  $P3_1$ ,  $a = 10.931$  (2),  $c = 7.763$  (3) Å,  $V = 803.1$  (4) Å<sup>3</sup>,  $Z = 9$ ,  $D_x = 3.626$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 100.96$  cm<sup>-1</sup>,  $F(000) = 774$ ,  $T = 299.5$  K, final  $R = 4.7\%$  for 760 unique observed reflections. The structures were found to be isomorphous and similar to that of  $\text{TlNO}_3(\text{III})$ . The three unique nitrates have site symmetries of  $C_1$  but the symmetry of two of them is close to  $C_s$  or  $C_2$ . Large nitrate-ion reorientations are

proposed for transformation to the high-pressure phases.

**Introduction.** The known polymorphs of  $\text{RbNO}_3$  are related as follows:



and  $\text{CsNO}_3$  undergoes the polymorphic transformations:



(Kalliomäki & Meisalo, 1979; Adams & Tan, 1981). A comprehensive review of the above thermal-phase transformations is given by Pistorius (1976). It has been suggested (Brooker, 1973; DeLacy & Kennard, 1971) that the room-temperature phases  $\text{RbNO}_3(\text{IV})$

\* Present address: CSIRO Division of Energy Chemistry, Lucas Heights Research Laboratories, Private Mail Bag 7, Sutherland, New South Wales 2232, Australia.