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Refinement of Hexagonal $BaTiO_3$

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Abstract

Pure single crystals of barium titanate have been synthesized and the structure refined using the atomic coordinates of Burbank & Evans [*Acta Cryst.* (1948), **1**, 330–336]. The short Ti—Ti distance in the face-sharing Ti_2O_9 group was determined to be 2.690 (4) Å, which is significantly shorter than in other barium titanate compounds.

Comment

The crystal structure of hexagonal $BaTiO_3$ was originally determined by Burbank & Evans (1948), using crystals synthesized by Matthias (1948) that had a light amber colour, attributed to dissolved platinum from the reaction vessel (Dickson, Katz & Ward, 1961; Tillmanns, Hofmeister & Baur, 1985). The hexagonal $BaTiO_3$ structure can be obtained by the addition of small amounts of other octahedral cations (Dickson, Katz & Ward, 1961). The substitution of Ti by transition elements in the double group of face-sharing octahedra has been shown to give significantly short metal-metal distances, *e.g.* 2.655 (1) Å in $Ba(Ti_{0.88}Pt_{0.12})O_3$ (Fischer & Tillmanns, 1981). Pure single crystals of hexagonal $BaTiO_3$ have been obtained recently by partial melt growth at 1853 K, below the melting temperature, using a molybdenum crucible (Akimoto, Gotoh, Sohma, Kawaguchi & Oosawa, 1994). The chemical composition was determined using an energy-dispersive X-ray analyser. No contamination, such as by molybdenum from the crucible, was observed. The cell parameters are consistent with the powder data (JCPDS File No. 34-129). The length of the *c* axis is slightly shorter than those of 14.05 (Burbank & Evans, 1948) and 14.023 (1) Å (Fischer & Tillmanns, 1981) found in $Ba(Ti,Pt)O_3$ compounds.

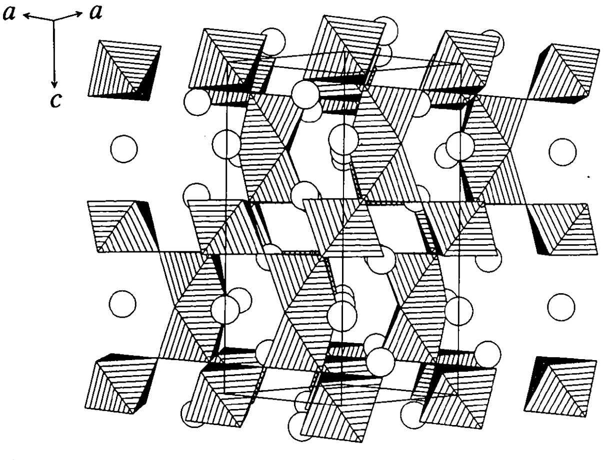

Fig. 1. *STRUPLO90* (Fischer, le Lirzin, Kassner & Rüdinger, 1991) drawing of $BaTiO_3$ viewed along [110].

Experimental

Crystal data

$BaTiO_3$
M_r = 233.2
Hexagonal
$P6_3/mmc$
a = 5.7238 (7) Å
c = 13.9649 (7) Å
V = 396.22 (9) Å^3
Z = 6
D_x = 5.865 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 25–35°
μ = 17.57 mm^{-1}
T = 296 K
Plate
0.100 × 0.088 × 0.051 mm
Colourless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans [ω-scan width $(1.0 + 0.5\tan\theta)°$ and rate 2.0° min^{-1}]
Absorption correction: by integration from crystal shape (*ACACA*; Wuensch & Prewitt, 1965)
T_{min} = 0.257, T_{max} = 0.428

1280 measured reflections
676 independent reflections
591 observed reflections [$F > 3\sigma(F)$]
θ_{max} = 45°
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 27$
3 standard reflections monitored every 50 reflections intensity variation: 0.98%

Refinement

Refinement on F
R = 0.037
wR = 0.036
591 reflections
22 parameters
Weighting scheme based on measured e.s.d.'s, $w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = <0.01

$\Delta\rho_{max}$ = 3.7 e Å^{-3}
$\Delta\rho_{min}$ = −6.8 e Å^{-3}
Extinction correction: Coppens & Hamilton (1970)
Extinction coefficient: $g = 0.96\,(3) \times 10^{-4}$
Atomic scattering factors from Cromer & Mann (1968)

Data collection: Rigaku AFC software. Cell refinement: Rigaku AFC software. Program(s) used to refine structure: *RFINE2* (Finger, 1969). Molecular graphics: *STRUPLO90* (Fischer, le Lirzin, Kassner & Rüdinger, 1991).

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
Ba(1)	0	0	1/4	0.43
Ba(2)	1/3	2/3	0.09671 (5)	0.52
Ti(1)	0	0	0	0.67
Ti(2)	1/3	2/3	0.84633 (14)	0.62
O(1)	0.5185 (6)	0.0370	1/4	0.65
O(2)	0.8349 (6)	0.6698	0.0802 (2)	0.66

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

Ti(1)O$_6$ octahedron					
O(2)—O(2)	3.965 (4)	× 3	O(2)—Ti(1)—O(2)	180.00 (1)	
O(2)—O(2)	2.8334 (3)	× 6	O(2)—Ti(1)—O(2)	91.2 (1)	
O(2)—O(2)	2.774 (7)	× 6	O(2)—Ti(1)—O(2)	88.8 (2)	
Ti(1)—O(2)	1.983 (2)	× 6			
Ti(1)—Ti(2)	3.940 (1)				
Ti(2)O$_6$ octahedron					
O(1)—O(2)	3.932 (2)	× 3	O(1)—Ti(2)—O(2)	169.1 (1)	
O(1)—O(1)	2.5434 (3)	× 3	O(1)—Ti(2)—O(1)	79.37 (6)	
O(2)—O(2)	2.8904 (3)	× 3	O(2)—Ti(2)—O(2)	95.1 (1)	
O(1)—O(2)	2.848 (4)	× 6	O(1)—Ti(2)—O(2)	92.3 (1)	
Ti(2)—O(1)	1.991 (1)	× 3			
Ti(2)—O(2)	1.959 (2)	× 3			
Ti(2)—Ti(2)	2.690 (4)				
Ba—O cuboctahedra					
Ba(1)—O(1)	2.868 (4)	× 6	Ba(2)—O(1)	2.820 (6)	× 3
Ba(1)—O(2)	2.881 (3)	× 6	Ba(2)—O(2)	2.871 (4)	× 6
			Ba(2)—O(2)	2.981 (3)	× 3

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71575 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1053]

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Structural Reinvestigation of $Ba_3Zr_2S_7$ by Single-Crystal X-ray Diffraction

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Abstract

Single crystals of barium zirconium sulfide, $Ba_3Zr_2S_7$, were prepared from BaS, Zr and S at 1323 K by using a $BaCl_2$ flux. The compound belongs to the Ruddlesden-Popper ($A_{n+1}B_nX_{3n+1}$) family with A = Ba, B = Zr, X = S and n = 2. It is isostructural to $Sr_3Ti_2O_7$ and crystallizes in alternately stacked double perovskite $BaZrS_3$ layers and rocksalt BaS layers.

Comment

A number of new Ruddlesden-Popper $A_{n+1}B_nX_{3n+1}$ compounds (Ruddlesden & Popper, 1957, 1958) have been discovered recently where A = Ba, B = Zr, Hf and X = S. The previous studies have shown that the Ba_2MS_4 phases (n = 1) are body-centered tetragonal, *I*4/*mmm* (No. 139) (Chen & Eichhorn, 1991; Saeki, Yajima & Onoda, 1991), the $Ba_3Zr_2S_7$ compound (n = 2) is *C*-centered orthorhombic, *Cccm* (No. 66) (Saeki, Yajima & Onoda, 1991), the n = 3, 4, 5 members are face-centered orthorhombic, *Fmmm* (No. 69) (Chen, Eichhorn & Fanwick, 1992; Chen, Wong-Ng & Eichhorn, 1993), and the $BaMS_3$ ($n = \infty$) compounds are orthorhombic, *Pnma* (No. 62) (Clearfield, 1963; Lelieveld & IJdo, 1980).

A review of these structures reveals that the lower n members of the Ruddlesden-Popper sulfides have high crystal symmetry (*I*4/*mmm*) whereas the higher n members ($\infty > n > 2$) display lower *Fmmm* crystal symmetry. The exception is the n = 2 member, $Ba_3Zr_2S_7$ (Saeki, Yajima & Onoda, 1991), which was shown by electron diffraction and Rietveld profile refinement to have *Cccm* symmetry. This phase was prepared by a different synthetic method and displayed trends in bond lengths at odds with those of the other members of the $Ba_{n+1}M_nS_{3n+1}$ series (Chen, Wong-Ng & Eichhorn, 1993). Therefore, a reinvestigation of the synthesis and structure (single-crystal X-ray diffraction) of $Ba_3Zr_2S_7$ was undertaken to address this structural discrepancy.

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