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Authors

Templeton, David H.

Dauben, Carol H.

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October 1959

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POLARIZED OCTAHEDRA IN BARIUM TETRATITANATE

David H. Templeton and Carol H. Dauben

University of California
Department of Chemistry and
Lawrence Radiation Laboratory
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ABSTRACT

Single-crystal x-ray diffraction studies show that BaTi_4O_9 is orthorhombic, space group Pmmn , with $a = 14.53 \pm 0.02$, $b = 3.79 \pm 0.01$, and $c = 6.29 \pm 0.01 \text{ \AA}$, with two formula units per unit cell and calculated density 4.54 g cm^{-3} . Each barium atom has four oxygen neighbors at $2.81 \text{ \AA}$, two at 2.96 , and four at 3.09 , at the corners of a pentagonal prism. Titanium atoms are in distorted octahedra of oxygen atoms. The Ti-O distances range from 1.77 to $2.32 \text{ \AA}$, with standard deviations of $0.03 \text{ \AA}$ or less. Titanium atoms occur at points 0.30 and $0.21 \text{ \AA}$ from the centers of gravity of the oxygen atoms of the two kinds of octahedra. This polarization of the two octahedra is similar to or greater in magnitude than that observed in the ferroelectric phases of BaTiO_3 and PbTiO_3 .

INTRODUCTION

Barium tetratitanate, BaTi_4O_9 or $\text{BaO} \cdot 4\text{TiO}_2$, is one of several compounds which occur in the BaO-TiO_2 system.¹⁻⁵ Its crystal structure has attracted

¹E. N. Bunting, G. R. Shelton, and A. S. Creamer, J. Am. Ceram. Soc. 30, 114 (1947).

²G. I. Skanavi, Doklady Akad. Nauk S. S. S. R. 59, 41 (1948).

³W. O. Statton, J. Chem. Phys. 19, 33 (1951).

⁴W. Trzebiatowski, M. Drys, and J. Berak, Roczniki Chem. 28, 21 (1954).

⁵D. E. Rase and R. Roy, J. Am. Ceram. Soc. 38, 102 (1955).

attention in several laboratories. The orthorhombic unit cell was reported by Lukaszewicz and Trzebiatowski⁶ and by Harrison.⁷ The atomic positions were

⁶K. Lukaszewicz and W. Trzebiatowski, Roczniki Chem. 29, 943 (1955).

⁷F. W. Harrison, Acta Cryst. 2, 198 (1956).

determined by Lukaszewicz.⁸ We were also investigating its structure prior to

⁸K. Lukaszewicz, Roczniki Chem. 31, 1111 (1957).

these reports. In this paper we describe our results, which agree with those mentioned above except for minor details. An interesting feature of this structure is that it contains polarized octahedra, somewhat like those found in the ferroelectric phases of BaTiO_3 , but in a centric symmetry.

UNIT CELL AND SPACE GROUP

Single crystals were prepared by Dr. L. K. Templeton by heating stoichiometric proportions of BaCO_3 and TiO_2 (rutile) to about 1450°C .⁹ The dimensions

⁹L. K. Templeton and J. A. Pask, J. Am. Ceram. Soc. 42, 212 (1959).

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of the orthorhombic unit cell are listed in Table I. We determined a and c from a quartz-calibrated¹⁰ zero-layer Weissenberg pattern, and b from a

¹⁰A. Pabst, Am. Mineral 42, 664 (1957).

rotation pattern using the other axes as a secondary calibration. The radiation used was $\text{CuK}\alpha$, with $\lambda = 1.5405 \text{ \AA}$ for the $\text{K}\alpha_1$ component. Our results are in excellent agreement with the published values, with one exception.¹¹

¹¹The b axis is given as $3.75 \text{ \AA}$ in the English summary of the article by Lukaszewicz,⁸ and this value is repeated in Acta Cryst. 10, 792 (1957). This value seems to be a misprint, since $3.79 \text{ \AA}$ appears elsewhere in reference 8, as well as in reference 6.

Table I. Unit cell dimensions of $\text{BaTi}_{49}\text{O}_{90}$

Authors	<u>a</u> , $\text{\AA}$	<u>b</u> , $\text{\AA}$	<u>c</u> , $\text{\AA}$
This work	14.53 ± 0.02	3.79 ± 0.01	6.29 ± 0.01
L. and T. ^a	14.53 ± 0.02	3.79 ± 0.01 ^b	6.30 ± 0.01
H. ^c	14.51 ± 0.04	3.79 ± 0.01	6.30 ± 0.02

^aLukaszewicz and Trzebiatowski, references 6 and 8.

^bSee reference 11.

^cHarrison, reference 7.

The density calculated from our cell dimensions, with two formula units per cell, is 4.54 g cm^{-3} . The measured density is reported by Rase and Roy⁵ to be 4.6 g cm^{-3} .

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The systematic absences and diffraction symmetry correspond to space groups $Pmmn$, $P2_1mn$, and $Pm2_1n$. Weissenberg photographs taken with $MoK\alpha$ radiation showed that the intensities for a given h_l depend only on whether k is even or odd, up to $k = 4$; thus the atoms lie in (or at least very near to) planes half a cell apart and perpendicular to b . If the atoms are exactly in these planes, the symmetry includes mirror planes in this orientation. A structure was easily found which ultimately gave good agreement with the data when the higher symmetry $Pmmn$ was assumed. This agreement gives good support for the assumption of mirror planes perpendicular to a . The present x-ray data are not sensitive to small deviations from the mirror plane perpendicular to b . Probably the best evidence against such deviations is the normal dielectric behavior observed by Skanavi.² A polar structure which deviated slightly in that way from the structure reported here would be expected to be ferroelectric.

ATOMIC COORDINATES

Barium atoms are located in twofold special positions on the intersections of the mirror planes; they may be designated

$$2(b): \pm(1/4, 3/4, z).$$

Oxygen atoms, designated O_5 , are in the other twofold set,

$$2(a): \pm(1/4, 1/4, z).$$

Two fourfold sets of titanium atoms and four fourfold sets of oxygen atoms are distributed in positions

$$4(f): \pm(x, 1/4, z; 1/2 - x, 1/4, z).$$

Fourier methods were used to derive an approximate structure. At an early stage of our work, before any correction was made for absorption, we obtained atomic parameters that were not greatly different from our final values, but the unreliability index

$$R_1 = \sum \|F_o\| - \|F_c\| / \sum |F_o|$$

could not be reduced below 0.35. The intensity data came from a crystal in the form of an asymmetric but approximately circular prism, of diameter large enough to be quite opaque to the $CuK\alpha$ radiation. The zero-layer data ($k = 0$) were corrected laboriously by a method which took account of this irregular

shape, as measured with the graduated objective of a microscope. The first-layer data were corrected for absorption with the assumption that the crystal was a circular cylinder, with results not substantially worse than for the zero layer.

Our final atomic parameters were derived by least-squares refinement with the IBM-650 computer and the program known as LSII.¹² Throughout these calculations, atomic form factors from International Tables¹³ were used for Ti^{+4} and

¹²M. E. Senko, Acta Cryst. 10, 385 (1957).

¹³Internationale Tabellen zur Bestimmung von Kristallstrukturen, Vol. II (Borntraeger, Berlin, 1935).

O^{-2} . Form factors for Ba^{+2} were estimated from the values¹³ for Ba, with 2.1 electrons subtracted for the real dispersion effect.¹⁴ Because no y parameters

¹⁴C. H. Dauben and D. H. Templeton, Acta Cryst. 8, 841 (1955).

were refined, we used only the data for $k = 0$ and 1, corrected for absorption as described above. In the last cycles, the weighting of strong, weak, and undetected reflections was as described for the last cycles of choline chloride.¹⁵ The final atomic coordinates, their standard deviations, and

¹⁵M. E. Senko and D. H. Templeton, Acta Crystl. (to be published).

individual isotropic temperature factors are listed in Table II. For comparison, the values obtained by Lukaszewicz⁸ by Fourier methods are given in parentheses. It is apparent that the structures are substantially the same, but the parameters differ by more than the accuracy claimed for this work. The largest discrepancies of atomic position are 0.18 Å for O_2 , 0.12 Å for O_1 , and 0.10 Å for O_4 .

Observed structure factors and those calculated for the parameters listed in Table II are compared in Table III. For these data, R_1 is 0.154 and R_3 ,

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Table II. Atomic coordinates, standard deviations,
and temperature factors for BaTi_4O_9

Atom	x	y	z	$\sigma(x)$	$\sigma(z)$	B, $\text{\AA}^2$
Ba	1/4	3/4	0.7076 (0.709) ^a		0.0005	2.6
Ti ₁	0.0363 (0.035) ^a	1/4	0.807 (0.807)	0.0005	0.001	1.7
Ti ₂	0.1298 (0.126)	1/4	0.248 (0.250)	0.0005	0.001	1.7
O ₁	0.514 (0.510)	1/4	0.158 (0.140)	0.002	0.004	2.8
O ₂	0.604 (0.592)	1/4	0.740 (0.733)	0.002	0.003	2.3
O ₃	0.155 (0.154)	1/4	0.952 (0.958)	0.002	0.004	2.9
O ₄	0.095 (0.100)	1/4	0.560 (0.550)	0.002	0.004	3.1
O ₅	1/4	1/4	0.346 (0.340)		0.006	2.8

^aValues in parentheses are those of Lukaszewicz.⁸

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
2 0 0	11	15-	11 0 3	41	32	7 0 7	5	2-	6 1 3	24	26-
4 0 0	33	43	12 0 3	48	43	8 0 7	26	19	7 1 3	10	13-
6 0 0	55	62-	13 0 3	43	33-	9 0 7	33	29	8 1 3	43	59
8 0 0	103	122	14 0 3	4*	3-	0 0 8	12	10-	9 1 3	28	38
10 0 0	70	72-	15 0 3	25	15	1 0 8	19	16	10 1 3	24	31-
12 0 0	6*	1	16 0 3	32	26	2 0 8	5	5-	11 1 3	8	7-
14 0 0	67	51-	0 0 4	67	75				12 1 3	11	13
16 0 0	30	17	1 0 4	38	36	3 1 0	81x146-		13 1 3	15	18
18 0 0	49	35-	2 0 4	25	25-	5 1 0	99	80	14 1 3	3*	5
0 0 1	12	7	3 0 4	69	76-	7 1 0	94	77-	15 1 3	24	22-
1 0 1	37	43	4 0 4	36	31-	9 1 0	25	14-	16 1 3	25	31
2 0 1	44	50	5 0 4	11	7-	11 1 0	48	50-	0 1 4	72	71-
3 0 1	62	88-	6 0 4	23	21-	13 1 0	46	52	1 1 4	5*	3
4 0 1	4*	5-	7 0 4	53	56-	15 1 0	15	14-	2 1 4	16	15
5 0 1	98x165		8 0 4	44	43	17 1 0	16	16	3 1 4	44	45-
6 0 1	60	69	9 0 4	16	12	0 1 1	88	77-	4 1 4	51	60-
7 0 1	36	33	10 0 4	28	21-	1 1 1	42	28-	5 1 4	39	45
8 0 1	14	17-	11 0 4	49	46-	2 1 1	71x130		6 1 4	39	49
9 0 1	52	61	12 0 4	16	11-	3 1 1	24	19	7 1 4	18	21-
10 0 1	8	7-	13 0 4	14	9	4 1 1	43	41-	8 1 4	14	21-
11 0 1	44	38-	14 0 4	18	8-	5 1 1	6*	5-	9 1 4	12	13-
12 0 1	23	20-	15 0 4	16	12-	6 1 1	42	47	10 1 4	28	37
13 0 1	62	60	16 0 4	18	16	7 1 1	16	15-	11 1 4	19	23-
14 0 1	11	7	0 0 5	6*	7-	8 1 1	97	106-	12 1 4	3*	4-
15 0 1	20	15-	1 0 5	6*	5-	9 1 1	34	31-	13 1 4	30	30
16 0 1	17	13-	2 0 5	65	68	10 1 1	39	41	14 1 4	37	39
17 0 1	6	5-	3 0 5	38	36-	11 1 1	14	13	15 1 4	8	7-
18 0 1	7	3	4 0 5	25	21-	12 1 1	37	35-	0 1 5	12	13-
0 0 2	119x179-		5 0 5	27	21	13 1 1	5*	1-	1 1 5	48	47-
1 0 2	17	19-	6 0 5	41	41	14 1 1	4*	7-	2 1 5	15	10
2 0 2	21	24	7 0 5	5*	1-	15 1 1	7	8	3 1 5	13	14
3 0 2	41	48	8 0 5	41	34-	16 1 1	51	58-	4 1 5	13	9
4 0 2	50	52-	9 0 5	16	16-	17 1 1	2*	2	5 1 5	46	53-
5 0 2	5*	2-	10 0 5	15	12	18 1 1	14	18	6 1 5	2*	0
6 0 2	50	51	11 0 5	33	27-	0 1 2	78	58	7 1 5	10	11
7 0 2	57	69	12 0 5	42	38-	1 1 2	50	48-	8 1 5	16	18-
8 0 2	72	88-	13 0 5	26	19	2 1 2	43	41-	9 1 5	38	43-
9 0 2	17	15	14 0 5	5	3	3 1 2	82	79	10 1 5	18	19
10 0 2	53	53	0 0 6	19	12-	4 1 2	51	51	11 1 5	12	10
11 0 2	31	29	1 0 6	28	26-	5 1 2	46	48-	12 1 5	23	22
12 0 2	22	16	2 0 6	13	13	6 1 2	25	25-	13 1 5	21	20-
13 0 2	14	8-	3 0 6	46	41	7 1 2	51	65	0 1 6	47	46
14 0 2	49	37	4 0 6	49	44	8 1 2	14	15	1 1 6	11	12
15 0 2	15	11	5 0 6	20	16-	9 1 2	17	15	2 1 6	10	13-
16 0 2	12	26-	6 0 6	7	4	10 1 2	44	51-	3 1 6	10	7
17 0 2	19	14-	7 0 6	51	46	11 1 2	44	51	4 1 6	44	41
18 0 2	32	27	8 0 6	34	19-	12 1 2	5*	2	5 1 6	28	27-
0 0 3	5*	3	9 0 6	10	8-	13 1 2	43	52-	6 1 6	13	13-
1 0 3	14	10	10 0 6	9	5-	14 1 2	29	28-	7 1 6	17	16-
2 0 3	90	115-	11 0 6	30	24	15 1 2	7	6	8 1 6	19	16
3 0 3	81	94	12 0 6	14	8	16 1 2	3*	1	9 1 6	9	8
4 0 3	7	12	0 0 7	18	13	17 1 2	5	3-	10 1 6	26	32-
5 0 3	94	103-	1 0 7	33	29	0 1 3	76	72	0 1 7	28	25
6 0 3	56	53-	2 0 7	30	25-	1 1 3	47	44	1 1 7	28	27
7 0 3	24	14-	3 0 7	28	22	2 1 3	63	67-	2 1 7	17	16
8 0 3	39	38	4 0 7	18	15	3 1 3	5*	9-	3 1 7	17	14-
9 0 3	27	20-	5 0 7	4	2	4 1 3	25	19-	4 1 7	20	17-
10 0 3	32	24-	6 0 7	27	22-	5 1 3	52	65	5 1 7	28	27

Table III. Observed and calculated structure factors, BaTi₄O₉.

Values marked with asterisk (*) are the estimated limit of detection for undetected reflections; the letter "x" marks four strong reflections which seem to be affected by extinction and which were omitted from the final refinement cycles of refinement.

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defined as $(\sum_w (|F_o| - |F_c|)^2 / \sum_w F_o^2)^{1/2}$, is 0.179. It is believed that errors in the absorption correction are the limiting factor in the agreement.

DISCUSSION OF THE STRUCTURE

The structure is shown in Fig. 1. Barium atoms are packed among the oxygen atoms, with ten oxygen neighbors at the corners of a pentagonal prism. Four oxygen atoms (O_3) are at $2.81 \text{ \AA} \pm 0.02 \text{ \AA}$, four (O_4) are at $3.09 \pm 0.02 \text{ \AA}$, and two (O_5) are at $2.96 \pm 0.03 \text{ \AA}$. Titanium atoms are in oxygen octahedra which share edges and corners in a three-dimensional array. These octahedra are considerably distorted, as can be seen in Fig. 1, and the lengths of their edges (oxygen-oxygen distances) range from 2.62 to 3.11 $\text{\AA}$, with standard deviations of about 0.05 $\text{\AA}$.

Titanium-oxygen distances are listed in Table IV, and their configurations in the two kind of octahedra are shown in Fig. 2. The titanium atoms are significantly displaced from the centers of these octahedra in much the same way as in the ferroelectric perovskite phases, BaTiO_3 ^{16,17} and PbTiO_3 .¹⁸ Similar

¹⁶G. Shirane, H. Danner, and R. Pepinsky, Phys. Rev. 105, 856 (1957).

¹⁷B. C. Frazer, H. R. Danner, and R. Pepinsky, Phys. Rev. 100, 745 (1955).

¹⁸G. Shirane, R. Pepinsky, and B. C. Frazer, Phys. Rev. 97, 1179 (1955).

displacements occur in the structure of low Ti_3O_5 ,¹⁹ which like that of BaTi_4O_9 is centric rather than polar. We have calculated, as a parameter for comparison

¹⁹S. Åsbrink and A. Magneli, Acta Cryst. 12, 575 (1959).

of the extents of polarization of these octahedra, the displacement of the titanium atom from the center of gravity of the six oxygen atoms of each octahedron. Values of this parameter are listed in Table V. It may be noted that for BaTi_4O_9 our values for this polarization parameter are in excellent agreement with those calculated from the coordinates of Lukaszewicz,⁸ even though the agreement is not this good for coordinates of certain oxygen atoms.

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Table IV. Titanium-oxygen distances in BaTi_4O_9

Atoms	Distance, Å	Atoms	Distance, Å
Ti_1-O_1	2.32 ± 0.03	Ti_2-O_1	2.16 ± 0.03
$-\text{O}_1^a$	1.94 ± 0.01	$-\text{O}_2^a$	1.93 ± 0.01
$-\text{O}_2$	2.09 ± 0.03	$-\text{O}_3$	1.89 ± 0.03
$-\text{O}_3$	1.95 ± 0.03	$-\text{O}_4$	2.03 ± 0.03
$-\text{O}_4$	1.77 ± 0.03	$-\text{O}_5$	1.85 ± 0.02

^aTwo neighbors at this distance.

Table V. Displacement of titanium atom from center of gravity of six oxygen atoms in various structures

Structure	Displacement, Å
BaTi_4O_9 , Ti_1	$0.30 (0.28)^a$
Ti_2	$0.21 (0.19)^a$
Ti_3O_5 (low), ^b Ti_1	0.25
Ti_2	0.24
Ti_3	0.18
BaTiO_3 (orthorhombic) ^c	0.13
BaTiO_3 (tetragonal) ^d	0.13
PbTiO_3 (tetragonal) ^e	0.29

^aLukaszewicz, reference 8.^bAsbrink and Magneli, reference 19.^cShirane, Danner and Pepinsky, reference 16.^dFrazer, Danner and Pepinsky, reference 17.^eShirane, Pepinsky and Frazer, reference 18.

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The polarization in the centric phases exceeds that observed in both TaBiO_3 phases, and in one case is as great as that in PbTiO_3 .

These results show that the phenomenon of ferroelectricity is not a necessary companion of the polarization of titanium-oxygen octahedra, though the interactions responsible for this polarization must be essentially the same in the centric phases as in the polar ones. These centric structures are not examples of antiferroelectricity as that term is defined by Megaw,²⁰

²⁰H. D. Megaw, Ferroelectricity in Crystals (Methuen and Co., London, 1957).

since small shifts of atoms cannot lead to higher symmetry by a "pseudosymmetric transition".

We thank Dr. Lieselotte Templeton for providing the crystals used in this study. This research was performed under the auspices of the U. S. Atomic Energy Commission.

MU-18441

Fig. 1. Crystal structure of BaTi_4O_9 . The rectangle outlines one unit cell. The atoms at $y = 1/4$ are drawn more heavily than those at $y = 3/4$. Lines join oxygen atoms to show the linking of the octahedra in each layer. Each octahedron also shares edges with octahedra in adjacent layers.

MU-18442

Fig. 2. Ti-O distances (in Angstrom units) in the two kinds of octahedra in $BaTi_4O_9$.

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