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POLARIZED OCTAHEDRA IN BARIUM TETRATITANATE

David H. Templeton and Carol H. Dauben

October 1959

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ABSTRACT

Single-crystal x-ray diffraction studies show that $BaTi_4O_9$ is orthorhombic, space group Pmmn, with $\underline{a}$ = 14.53 ± 0.02, $\underline{b}$ = 3.79 ± 0.01, and c = 6.29 ± 0.01 Å, 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 Å, 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 Å, with standard deviations of 0.03 Å or less. Titanium atoms occur at points 0.30 and 0.21 Å 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 $BaO \cdot 4TiO_2$, is one of several compounds which occur in the $BaO-TiO_2$ system.[1-5] Its crystal structure has attracted

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

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

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

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

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

attention in several laboratories. The orthorhombic unit cell was reported by Lukazewicz and Trzebiatowski[6] and by Harrison.[7] The atomic positions were

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

[7] F. W. Harrison, Acta Cryst. 9, 198 (1956).

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

[8] K. 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

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

of the orthorhombic unit cell are listed in Table I. We determined a and c from a quartz-calibrated[10] zero-layer Weissenberg pattern, and b from a

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

rotation pattern using the other axes as a secondary calibration. The radiation used was CuKα, with $\lambda = 1.5405$ Å for the $K\alpha_1$ component. Our results are in excellent agreement with the published values, with one exception.[11]

[11] The b axis is given as 3.75 Å 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 Å appears elsewhere in reference 8, as well as in reference 6.

Table I. Unit cell dimensions of $BaTi_4O_9$

Authors	a, Å	b, Å	c, Å
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

[a] Lukaszewicz and Trzebiatowski, references 6 and 8.
[b] See reference 11.
[c] Harrison, 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 Roy[5] to be 4.6 g cm^{-3}.

The systematic absences and diffraction symmetry correspond to space groups Pmmn, $P2_1mn$, and $Pm2_1n$. Weissenberg photographs taken with MoKα radiation showed that the intensities for a given hl 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): ±(1/4,3/4,z).

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

2(a): ±(1/4,1/4,z).

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

4(f): ±(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 CuKα 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 calculation, atomic form factors from International Tables[13] were used for Ti^{+4} and

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

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

O^{-2}. Form factors for Ba^{+2} were estimated from the values[13] for Ba, with 2.1 electrons subtracted for the real dispersion effect.[14] Because no y parameters

[14] C. 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

[15] M. 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 Lukaszewicz[8] 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,

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

Atom	x	y	z	σ(x)	σ(z)	B, Å^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

[a]Values 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	81X	146-	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	98X	165	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	71X	130	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	119X	179-	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, $BaTi_4O_9$.

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.

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 Å ± 0.02 Å, four (O_4) are at 3.09 ± 0.02 Å, and two (O_5) are at 2.96 ± 0.03 Å. 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 Å, with standard deviations of about 0.05 Å.

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

[16] G. Shirane, H. Danner, and R. Pepinsky, Phys. Rev. 105, 856 (1957).
[17] B. C. Frazer, H. R. Danner, and R. Pepinsky, Phys. Rev. 100, 745 (1955).
[18] G. 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

[19] S. 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.

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
-O_1[a]	1.94 ± 0.01	-O_2[a]	1.93 ± 0.01
-O_2	2.09 ± 0.03	-O_3	1.89 ± 0.03
-O_3	1.95 ± 0.03	-O_4	2.03 ± 0.03
-O_4	1.77 ± 0.03	-O_5	1.85 ± 0.02

[a]Two 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

[a]Lukaszewicz, reference 8.
[b]Åsbrink and Magneli, reference 19.
[c]Shirane, Danner and Pepinsky, reference 16.
[d]Frazer, Danner and Pepinsky, reference 17.
[e]Shirane, Pepinsky and Frazer, reference 18.

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]

[20] H. 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.

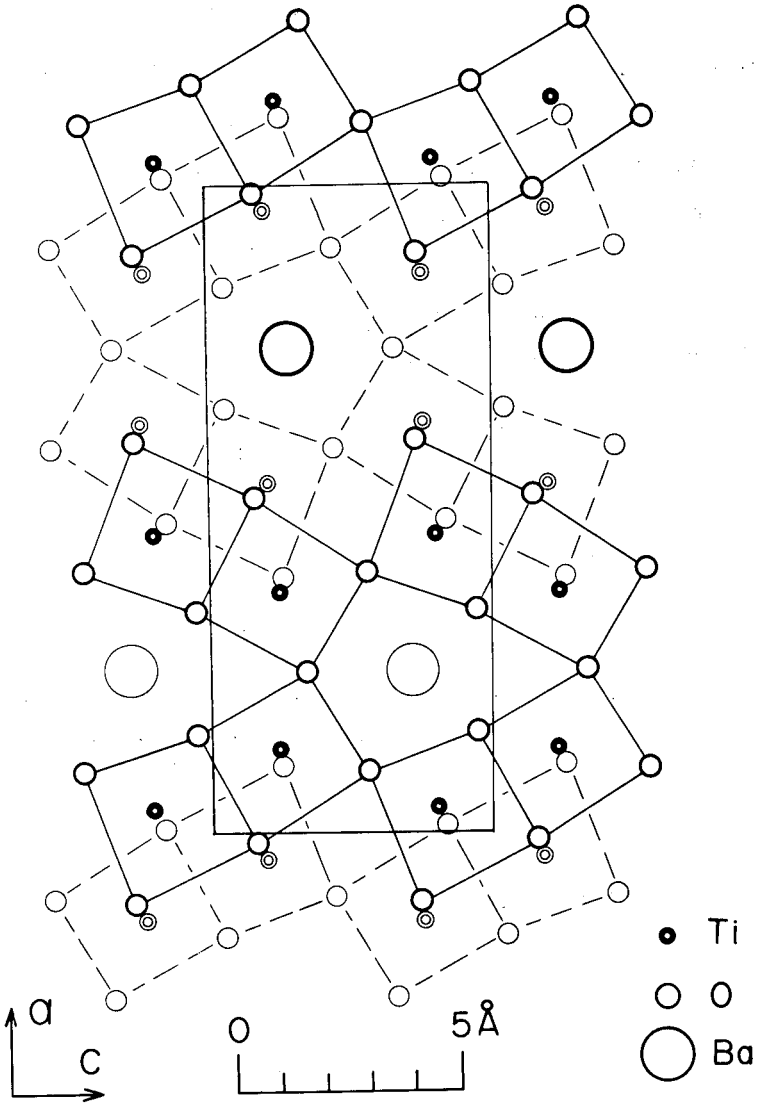

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Fig. 1. Crystal structure of $BaTi_4O_9$. The rectangle outlines one unit cell. The atoms at y = 1/4 are drawn more heavily than those at y = 3/4. Lines join oxygen atoms to show the linking of the octahedra in each layer. Each octahedron also shares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

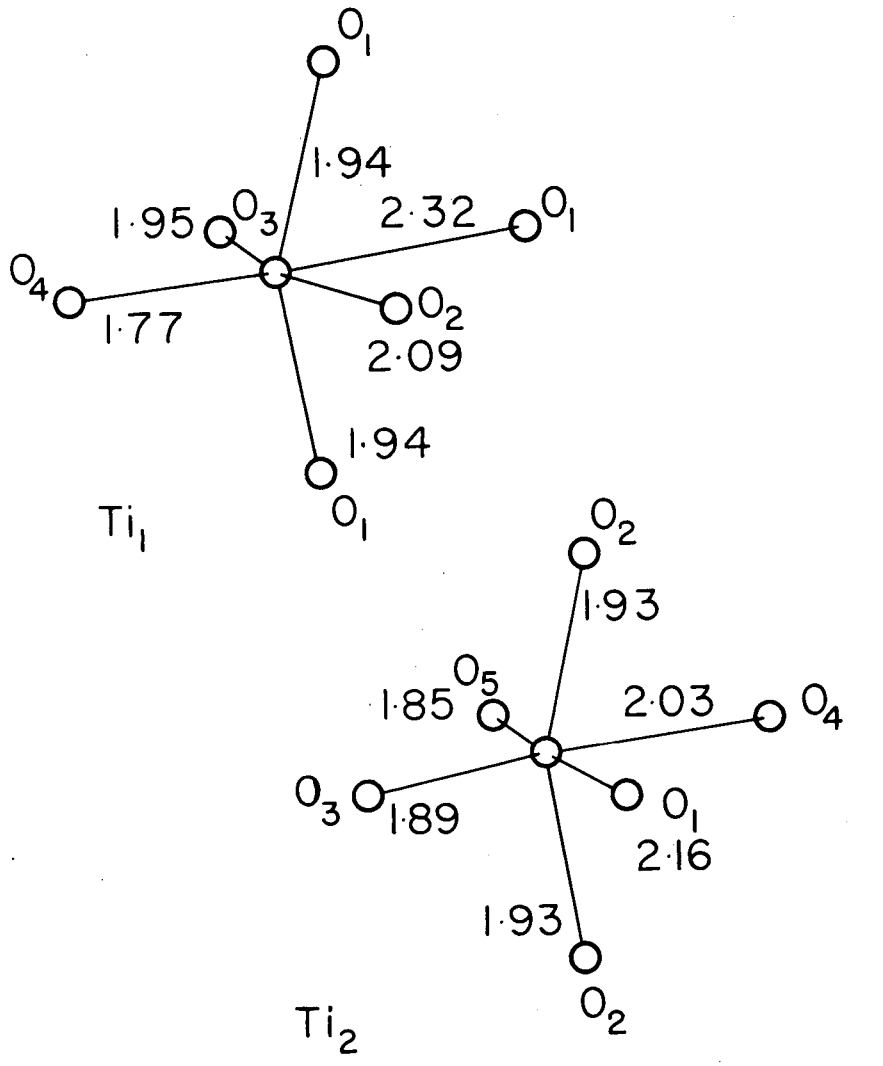

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Fig. 2. Ti-O distances (in Ångstrom units) in the two kinds of octahedra in $BaTi_4O_9$.

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