Subsolidus Phase Relations in the BaTiO$_3$–TiO$_2$ System

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Ba$_6$Ti$_{17}$O$_{40}$, Ba$_4$Ti$_{13}$O$_{30}$, BaTi$_4$O$_9$, and Ba$_2$Ti$_9$O$_{20}$ are the only compounds which were found to have a stability range in the subsolidus of the BaTiO$_3$–TiO$_2$ system. BaTi$_2$O$_5$ and BaTi$_5$O$_{11}$, reported in other studies, apparently are not stable. The compound reported as Ba$_2$Ti$_5$O$_{12}$ appears to have been mistaken for Ba$_6$Ti$_{17}$O$_{40}$. X-Ray diffraction powder data are given for this phase which is monoclinic with $a = 9.890$, $b = 17.117$, $c = 18.933$ Å and $\beta = 98°42.6'$. The phase formulated previously as BaTi$_3$O$_7$ is shown to be Ba$_4$Ti$_{13}$O$_{30}$ based on structural and density considerations, phase equilibria, and single crystal and powder X-ray diffraction data. This compound is orthorhombic with $a = 17.072$, $b = 9.862$, and $c = 14.059$ Å, probable space group, *Cmca*. An idealized structure for this phase is proposed. Ba$_2$Ti$_9$O$_{20}$ decomposes above 1300°C in the solid state to BaTi$_4$O$_9$ plus rutile. Single crystals were grown using BaF$_2$ as a mineralizer.

Introduction

Rase and Roy (*1*) published the first comprehensive phase equilibria study of the BaO–TiO$_2$ system. They reported the following compounds: Ba$_2$TiO$_4$, BaTiO$_3$ (hexagonal and cubic-tetragonal modifications), BaTi$_2$O$_5$, BaTi$_3$O$_7$, and BaTi$_4$O$_9$. Crystal structures have been determined for Ba$_2$TiO$_4$ (*2*), cubic BaTiO$_3$ (*3*), hexagonal BaTiO$_3$ (*4*), BaTi$_2$O$_5$ (*5*), and BaTi$_4$O$_9$ (*6*). Crystallographic data for BaTi$_3$O$_7$, however, are not available except for the unindexed *d*-spacings provided by Rase and Roy (*1*).

Recent studies have suggested that additional compounds can be prepared but their stability fields in the binary remain uncertain. Jonker and Kwestroo (*7*) reported the unindexed X-ray diffraction powder patterns for two phases which they formulated as Ba$_2$Ti$_5$O$_{12}$ and Ba$_2$Ti$_9$O$_{20}$. They also suggested that BaTi$_2$O$_5$ is a metastable phase which forms only from a cooled liquid. Tillmanns and Baur (*8*) and Tillmanns (*9*) determined the crystal structures of Ba$_6$Ti$_{17}$O$_{40}$ and BaTi$_5$O$_{11}$, respectively. Single crystals of these phases were prepared from melted specimens.

In view of the importance of the BaO–TiO$_2$ system to materials science and technology, we reinvestigated the BaTiO$_3$–TiO$_2$ subsystem. It was found necessary to utilize a crystallographic approach combined with phase equilibria data to characterize the system and to reconcile the existing published data.

Experimental Procedure

The following starting materials were used for the preparation of specimens:

BaTiO$_3$. Prepared from BaTiO(C$_2$O$_4$)$_2 \cdot$4H$_2$O by the method described by Clabaugh, Swiggard and Gilchrist (*10*) to achieve a Ba to Ti ratio of unity. The product was calcined at 900°C for 1 day. Spectrographic analysis indicated <0.0001% Ca, Mg and 0.001–0.01% Si, Sr.

TiO$_2$ (rutile)—high purity. Spectrographic analysis indicated <0.02% SiO$_2$, <0.003% Al$_2$O$_3$, <0.002% SnO$_2$ and Fe$_2$O$_3$, <0.003% Sb$_2$O$_3$, and <0.0005% Mg, Cu, Pb, Mn, V, and Cr.

Weighed amounts of the starting materials were mixed in a mechanical shaker (metal–specimen contact was avoided by using plastic elements), packed in Au or Pt trays, and calcined for 3 days at 1000°C in air, with periodic remixing. Portions of the calcined specimens were equilibrated in sealed Pt capsules within a vertical tube, resistance-type, quench furnace. After sufficient heating periods the capsules were quenched in water. The furnace used and the methods of temperature control and measurement are described elsewhere (*11*).

Table 1. Summary of Experimental Data for the $BaTiO_3$-TiO_2 System.

Composition	Heat Treatment		X-ray Diffraction Analysis and Comments*
Ba:Ti Ratio	Temp (°C)	Time (hr)	
1:2	1235	192	1:1 + 6:17
	1300	74	1:1 + 6:17
	1330	1	melted; quenched liquid yields the diffraction pattern characteristic of the 1:2 phase.
	1290	3	reheat of specimen initially melted at 1330°; 1:2 + 1:1 + 6:17.
2:5	1235	192	6:17 + 1:1
	1300	74	6:17 + 1:1
	1330	1	partly melted; 6:17 + 1:1 + 1:2
	1290	3	reheat of specimen initially melted at 1330°; 6:17 + 1:1 + tr. 1:2.
6:17	1300	120	6:17
	800		6:17; specimen heated 72 hr, 1300°, then slow-cooled to 800° before quenching.
1:3	1300	120	6:17 + 4:13
	800		6:17 + 4:13; specimen heated 72 hr, 1300°, then slow-cooled to 800° before quenching.
4:13	1300	120	4:13
	800		4:13; specimen heated 72 hr, 1300°, slow-cooled to 800° before quenching.
	1225	120	4:13; reheat of slow-cooled, 800°, specimen.
1:4	1300	120	1:4
	1400	74	1:4
2:9	1235	192	2:9
	1300	74	2:9 + tr. 1:4
	1400	74	1:4 + rutile
	1235	192	2:9, reheat of 1300° specimen
	1445	1	melted; 1:4 + rutile + tr. 1:2
1:5	1235(a)	192	2:9 + rutile
	1300	74	2:9 + 1:4 + rutile
	1400	74	1:4 + rutile
	1421	96	2:9 + 1:4 + rutile; reheat of 1235° specimen (a).
	1235(b)	192	2:9 + rutile; reheat of 1400° specimen.
	800		2:9 + rutile; specimen heated 72 hr, 1300°, slow-cooled to 800° before quenching.
	1565	1	melted; 1:4 + rutile.

*tr. = trace; 1:1, tetragonal $BaTiO_3$; 1:2, $BaTi_2O_5$; 6:17, $Ba_6Ti_{17}O_{40}$; 4:13, $Ba_4Ti_{13}O_{30}$; 1:4, $BaTi_4O_9$.

X-Ray diffraction powder patterns of specimens were made at room temperature using a high-angle, Geiger counter diffractometer and Ni-filtered Cu radiation. Interplanar d-spacings from these patterns were used to compute unit cell dimensions by a least squares refinement computer program. Cell dimensions are estimated to be accurate to within three standard deviations. Single crystals were investigated with an X-ray diffraction precession camera using Mo$K\alpha$ radiation. X-Ray diffraction powder pattern intensities were calculated using the program of Smith (12).

Experimental Results and Discussion

The $BaTiO_3$–TiO_2 Subsystem

Based on the experimental data, summarized in Table I, modifications to the previously published phase diagram (1) for a portion of the BaO–TiO_2 system are presented in Fig. 1. Liquidus temperatures are from Ref. (1). Solidus phase relations, where modified, are not in-

consistent with the temperature-composition data also reported in Ref. (1). Each revision, together with additional supporting data, is discussed separately.

The $BaTi_5O_{11}$ (1:5) and $Ba_6Ti_{17}O_{40}$ (6:17) Phases

Tillmanns (9) obtained a small number of single crystals of a phase determined to be $BaTi_5O_{11}$ by melting a BaO:4TiO_2 composition between 1400–1500°C. These grew intimately with rutile crystals. The phase was found to be monoclinic, $P2_1/n$, with $a = 7.67$, $b = 14.02$, $c = 7.52$ Å and $\beta = 98.33°$. We calculated a theoretical X-ray diffraction powder pattern using the above cell dimensions and the atomic parameters derived by Tillmanns from his determination of the structure. Initially, we considered the possibility that the compound formulated tentatively as $Ba_2Ti_9O_{20}$ (7) might be the (1:5) phase. A comparison of our theoretical pattern with the reported, but not indexed, powder data for the (2:9) and later with our own
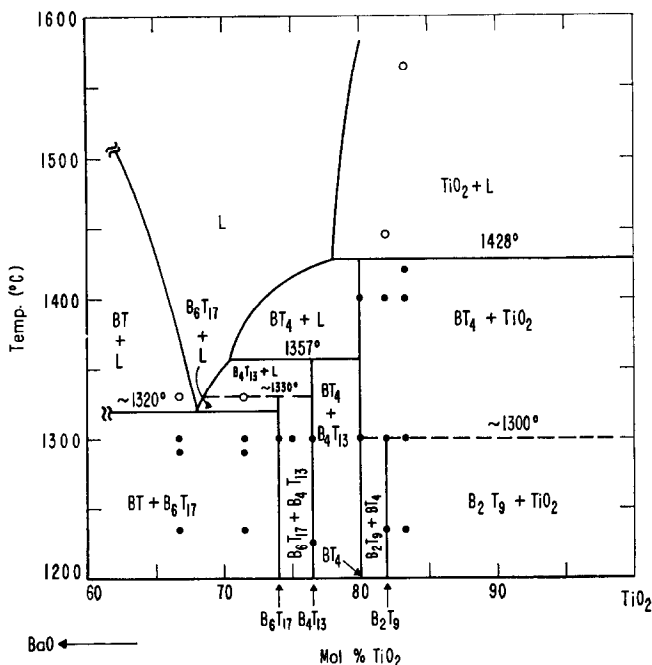
FIG. 1. Phase relations in the BaO–TiO$_2$ system for compositions with > 60 mole % TiO$_2$. Subsolidus relations are from this work, liquidus curves are from Ref. (1). Solidus temperatures from (1) are modified where necessary. Abbreviations and symbols used include: BT (BaTiO$_3$); B$_6$T$_{17}$ (Ba$_6$Ti$_{17}$O$_{40}$); B$_4$T$_{13}$ (Ba$_4$Ti$_{13}$O$_{30}$); BT$_4$ (BaTi$_4$O$_9$); B$_2$T$_9$ (Ba$_2$Ti$_9$O$_{20}$); L (liquid); (●) solid phase(s), quenched; (○) melted, quenched. The formulation Ba$_2$Ti$_9$O$_{20}$ is accepted, tentatively, as a structure determination has not been performed; see Table I for additional data.

data for this compound (to be discussed) proved conclusively that the two phases are distinct. Attempts to prepare BaTi$_5$O$_{11}$ in the subsolidus were not successful. Pertinent compositions which were melted above 1425° (see Table I) and quenched did not yield quantities of BaTi$_5$O$_{11}$ detectable by X-ray powder diffraction. We conclude, from the experimental conditions imposed, that BaTi$_5$O$_{11}$ does not have a stability field in the subsolidus at ambient pressure.

Tillmanns and Baur (8) also reported the crystal structure of Ba$_6$Ti$_{17}$O$_{40}$. They grew a few single crystals of this phase by melting a BaO:3TiO$_2$ composition at 1400°C. The phase was reported as monoclinic, C2/c, with a = 9.883, b = 17.08, c = 18.92 Å and β = 98°42′. Using these dimensions together with the published atomic positional parameters, a theoretical X-ray diffraction powder pattern was calculated. The possibility that the reported, but not indexed, powder data for the phase formulated as Ba$_2$Ti$_5$O$_{12}$ (7) are consistent with the (6:17) data was examined. Although some similarity is evident, a simple comparison of the two sets of

data proved insufficient to equate the two phases. This point is discussed below. From a 6BaO· 17TiO$_2$ composition, we prepared a single-phase material which is stable to at least 1300°C in the subsolidus. The calculated powder pattern of Ba$_6$Ti$_{17}$O$_{40}$ is in excellent agreement with the diffraction pattern observed for the phase prepared in the subsolidus. A comparison of a portion of the data is shown in Fig. 2. The powder pattern for our Ba$_6$Ti$_{17}$O$_{40}$, given in Table II, was indexed on the basis of a monoclinic cell with a = 9.890, b = 17.117, c = 18.933 Å, and β = 98°42.6′. Without prior knowledge of the relative intensities of the diffraction lines of Ba$_6$Ti$_{17}$O$_{40}$, the complex powder pattern obtained from the 6BaO:17TiO$_2$ composition easily could be mistaken as being a mixture of the phase reported as BaTi$_3$O$_7$ (1) plus a phase containing less TiO$_2$. This is due to the near coincidence of several of the strongest lines of each phase (compare, for example the d-spacing data in Tables II and III). Rase and Roy (1) report only combinations of BaTiO$_3$, BaTi$_2$O$_5$, and BaTi$_3$O$_7$ as equilibrium assemblages within

Table 2. X-ray Diffraction Powder Data for $Ba_6Ti_{17}O_{40}$

d_{obs}	d_{calc}	hkl[1]	I_{calc}[2]	I_{obs}
7.762	7.783	021	28	18
6.316	6.315	022	17	11
4.679	4.678	131	39	16
4.170	4.172	041	66	48
(s)	3.746	223	{60	{33 (vb)
3.731	3.731	133		
3.606	3.604	115	7	9
3.270	3.271	134	{26	{29 (b)
	3.270	115		
3.229	3.231	150	23	29
3.202	3.201	310	31	31
3.176	3.177	312	58	51
3.149	3.150	204	73	60
3.118	3.119	006	15	20
3.095	3.102	152	{85	{83
	3.097	135		
(m)	3.080	311	46	(m)
3.061	3.061	116	91	92
(s)	3.038	313	5	9
2.985	2.985	243	77	60
2.954	2.955	242	6	7
2.853	2.854	331	{100	{100
	2.853	060		
2.812	2.812	153	32	38
2.753	2.751	243	9	8
2.731	2.731	136	6	9
2.641	2.640	225	15	21
2.634	2.634	315	5	9
2.599	2.599	154	19	22
2.552	2.552	027	6	9
2.463	2.465	206	{16	{11 (vb)
	2.464	260		
	2.459	117		
2.429	2.429	137	{14	{11 (b)
	2.429	262		
2.340	2.339	262	4	8
2.330	2.329	245	12	16
2.281	2.282	402	{23	{36
	2.280	172		
2.252	2.252	264	6	35
2.232	2.234	263	{9	{11 (b)
	2.231	352		
2.148	2.148	174	13	23
2.114	2.114	264	19	67
2.083	2.083	406	19	44
2.079	2.078	441	27	46
2.040	2.043	404	{5	{8 (vb)
	2.039	318		
	2.036	444		
2.020	2.024	083	{5	{8 (vb)
	2.020	354		
2.009	2.010	266	6	13
1.9890	1.9895	265	{7	{13 (b)
	1.9872	424		
1.9560	1.9601	445	{17	{18 (b)
	1.9559	370		
1.9502	1.9504	372	21	22
1.9225	1.9222	176	18	18
1.8707	1.8714	425	{7	{10
	1.8703	049		
1.8653	1.8655	139	{21	{35
	1.8654	266		
1.8454	1.8483	284		
	1.8475	512	{10	{13 (vb)
	1.8469	533		
	1.8434	2,0,10		
1.8347	1.8344	408	13	18
1.7801	1.7814	285		
	1.7801	447	{19	{11 (vb)
	1.7790	1,1,10		
1.7647	1.7651	268	{7	{11
	1.7644	086		
1.7618	1.7615	535	9	11
1.7078	1.7079	533	15	15

plus additional weak lines, which can be indexed, at $2\theta > 54°$, CuKα.

abbreviations used: (s), shoulder; (b), broad; (vb), very broad; (m), masked by adjacent strong line(s).

[1] Indexed on the basis of a monoclinic cell with $a=9.890\pm0.001Å$, $b=17.117\pm0.002Å$, $c=18.933\pm0.002Å$, and $\beta=98°$ $42.6\pm0.6'$.

[2] Calculated on the basis of atomic parameters given in reference (8). Atomic thermal parameters were not used. Space group is C2/c.

the 50–75 mole % TiO_2 interval. Their failure to recognize the (6:17) compound may be the result of: (a) insufficient heating times, especially at temperatures $>1230°C$ or, (b) incorrect assignment of observed diffraction lines to the (1:3)

phase. Their tabulated equilibria data, however, indirectly suggest the existence of the (6:17). A composition with 73 mole % TiO_2 (nearest 6:17), denoted as "melting (?)" or "melting" from 1314 to 1325°C, yielded a diffraction pattern characteristic of $BaTi_2O_5$ plus a phase denoted as "phase (?)." Although not discussed, it is possible that the unidentified phase might be the (6:17).

The $BaTi_2O_5$ (1:2) and $Ba_2Ti_5O_{12}$ (2:5) Phases

The equilibrium subsolidus phase assemblage observed for all compositions with less TiO_2 than the (6:17) is $BaTiO_3$ plus $Ba_6Ti_{17}O_{40}$. $BaTi_2O_5$ could not be prepared, even in small quantities, in the solid state. Jonker and Kwestroo (7) suggested that the (1:2) is a metastable phase formed only in the presence of liquid. Our data support this conclusion. The compositions containing 1:2, 2:5 and 2:9 (Ba:Ti) were melted and quenched. Small amounts of $BaTi_2O_5$ were produced from the 2:5 and 2:9 compositions while the 1:2 was nearly single-phase $BaTi_2O_5$ and even yielded numerous single crystals. The X-ray diffraction powder data for $BaTi_2O_5$ are in relatively good agreement with the previous data (1). When reheated in the subsolidus, $BaTi_2O_5$ converts slowly to $BaTiO_3$ plus $Ba_6Ti_{17}O_{40}$.

Jonker and Kwestroo (7) melted at 1320°C and quenched a composition containing 72 mole % TiO_2 (near 2:5). Their resulting products, $BaTi_2O_5$ + $BaTiO_3$ + "$BaTi_3O_7$" + "$Ba_2Ti_5O_{12}$" were reheated in the subsolidus at 1300°C for several hours and quenched. The X-ray lines for $BaTi_2O_5$ were found to disappear and the intensities of the lines assigned to the other phases increased. They, therefore, concluded that a "fairly unstable" compound, $Ba_2Ti_5O_{12}$, exists although it cannot be prepared in single-phase form. We suggest, after repeating the above experiments and comparing our X-ray data with the reported, unindexed, data for $Ba_2Ti_5O_{12}$, that Jonker and Kwestroo observed the $Ba_6Ti_{17}O_{40}$ compound. Their inability to prepare a single-phase material is the result of attempting to equilibrate a 2:5 composition which is located within the (6:17) plus $BaTiO_3$ two-phase field. Because of the near superposition of X-ray lines of "$BaTi_3O_7$", as well as $BaTiO_3$, with some of the lines for $Ba_6Ti_{17}O_{40}$, the interpretation of the X-ray pattern of a multiphase specimen, as prepared, is most difficult. The reported pattern appears to be

Table 3. Summary of X-ray Diffraction Powder and
Crystallographic Data for $Ba_4Ti_{13}O_{30}$.

	This Study				Previous Work[1/]			This Study				Previous Work[1/]	
d_{obs}	d_{calc}	hk$l$[2/]	I_{obs}	I_{calc}[3/]	d_{obs}	I_{obs}	d_{obs}	d_{calc}	hk$l$[2/]	I_{obs}	I_{calc}[3/]	d_{obs}	I_{obs}
5.427	{5.427 / 5.426	112 / 202	{16 (vb)	{49			2.115	{2.116 / 2.114 / 2.113	026 / 243 / 713	{24	{23	{2.108	20
4.655	{4.653 / 4.651	021 / 311	{26 (vb)	{75			2.054	2.054	406	11	5	2.049	20
4.265	{4.270 / 4.268	220 / 400	{62	{70	{4.250	40	2.018	{2.018 / 2.018	044 / 624	{55	{72	{2.014	70
4.035	4.038	312	42	80	4.022	40	2.002	2.000	335	11	14	1.994	10
3.515	3.515	004	12	16	3.507	10	1.9604	{1.9636 / 1.9551	714 / 117	{16 (vb)	13	{1.957	20
3.396	3.397	023	30	49	3.389	20		1.9428	443				
3.250	3.250	114	59	68	3.243	60	1.9410	{1.9406 / 1.9399 / 1.9397	151 / 731 / 821	{25 (vb)	{28	{1.937	30
3.147	{3.156 / 3.146 / 3.145	223 / 131 / 421	{100	{100	{3.143	100	1.8956	{1.8961 / 1.8633	426 / 640	5	3	1.892	10
2.932	{2.934 / 2.932	132 / 422	{30	{11	{2.912	40	- (s)	{1.8601 / 1.8600	027 / 317	- (s),(b)	{13		
2.861	{2.862 / 2.862	024 / 314	{84	{79	{2.858	100	1.8535	{1.8538 / 1.8533	045 / 625	{38 (b)	{77	{1.848	40
- (s)	2.845	600	- (s)	43			1.8084	{1.8088 / 1.8077	606 / 153	{9 (b)	{12		
2.791	2.790	331	58	96	2.788	80	1.8010	{1.8014 / 1.8006	352 / 912	{16	{15	{1.804	30
2.714	{2.714 / 2.713	224 / 404	{12 (b)	{9			1.7311	1.7314	643	5	7		
- (s)	2.671	115	- (s)	15			1.7212	1.7213	118	11	10		
	{2.658	133					1.6993	{1.7003 / 1.6985	445 / 046	{7	{5		
2.658	{2.658	423	{75	{64	{2.667	100	1.6590	1.6589	10,0,2	10	3		
	{2.658	513					1.6554	{1.6554 / 1.6553	028 / 318	{15	{13	{1.650	35
2.638	2.637	602	10	19				{1.6465	354				
2.465	{2.465 / 2.464	040 / 620	{10	{16	{2.455	15	1.6461	{1.6462 / 1.6459	644 / 914	{19 (vb)	{29	{1.642	35
2.443	{2.443 / 2.442	025 / 315	{16	{25			- (s)	1.6436	060	- (s)	10		
	{2.343	006					1.6143	1.6140	260	5	4		
	{2.336	241					1.6073	{1.6076 / 1.6072 / 1.6070	155 / 735 / 825	{14	{6	{1.603	20
2.336	{2.335 / 2.335	531 / 711	{14 (eb)	{32	{2.338	30	1.5781	1.5781	446	6	2	1.568	15
	{2.326 / 2.326	042 / 622					1.5571	{1.5572 / 1.5569	047 / 627	{26	{17	{1.554	35
2.243	{2.244 / 2.244	532 / 712	{14	{8	{2.238	30							
2.181	{2.182 / 2.181	043 / 623	{80	{98	{2.176	60							

plus additional weak lines, which can be indexed, at
$2\theta > 60°$, $CuK\alpha$.

abbreviations used: (s), shoulder; (b), broad; (vb),
very broad; (eb), extremely broad.

[1/] Unindexed data for $BaTi_3O_7$, reference (1).

[2/] Indexed on the basis of an orthorhombic cell with
$a=17.072\pm0.002Å$, $b=9.862\pm0.001Å$, and $c=14.059\pm0.001Å$.
$V=2367.002[Å]^3$

[3/] Peak height intensities calculated using space group $Cmca$
and the following:

	Position	x	y	z	B
Ba(1)	16(g)	1/6	1/6	1/12	0.81
Ti(1)	16(g)	1/12	7/12	1/6	0.34
Ti(2)	16(g)	1/6	5/6	1/6	0.34
Ti(3)	8(f)	0	5/6	1/6	0.34
Ti(4)	8(d)	1/3	0	0	0.34
Ti(5)	4(b)	1/2	0	0	0.34
O(1)	16(g)	1/12	3/4	1/4	0.60
O(2)	16(g)	1/6	1/2	1/4	0.60
O(3)	16(g)	1/12	5/12	1/12	0.60
O(4)	16(g)	1/6	2/3	1/12	0.60
O(5)	16(g)	1/12	11/12	1/12	0.60
O(6)	16(g)	1/4	11/12	1/12	0.60
O(7)	8(f)	0	0	1/4	0.60
O(8)	8(f)	0	2/3	1/12	0.60
O(9)	8(e)	1/4	1/4	1/4	0.60

Positional parameters are ideal and were derived from
close packing considerations. The isotropic thermal
parameters (B) used were obtained by averaging for
each atom type the B values reported for $Ba_6Ti_{17}O_{40}$
(reference 8). I_{calc} varies insignificantly when B
values are excluded from the calculation.

composed of an incomplete set of data for $Ba_6Ti_{17}O_{40}$ (strongest lines only), plus additional, weak, lines which can be assigned to the reported "$BaTi_3O_7$" and, perhaps, $BaTiO_3$ phases.

The $BaTi_4O_9$ (1:4) and $Ba_2Ti_9O_{20}$ (2:9) Phases

The stability of $BaTi_4O_9$ is not questioned. Our X-ray data for this phase are in good agreement with the previously published pattern (1). ASTM X-ray powder diffraction file, Card 8-367, lists these data together with indices deduced

by the compilers from the available cell parameters and orthorhombic symmetry determined by Harrison (5) from single crystals. Two lines at $d = 3.363$ Å $(I/I_1 = 40)$ and $d = 2.858$ Å $(I/I_1 = 5)$, however, could not be indexed. The weaker line appears to correspond with the strongest line for the compound reported as $BaTi_3O_7$. The other line is too intense to be an impurity phase. Our pattern also contains an unreported line, but at $d = 3.252$ Å rather than $d = 3.363$ Å and with a relative intensity of about
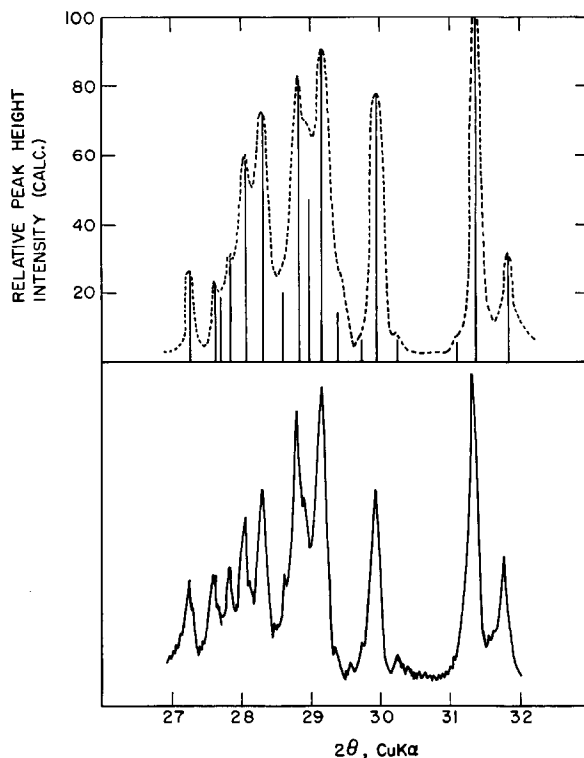
FIG. 2. A tracing of a portion of the X-ray diffraction powder pattern (lower) of $Ba_6Ti_{17}O_{40}$ compared with the pattern calculated (upper) using the program of Smith (12). A complete set of indexed d-spacing and intensity data is provided in Table II.

40. It is not the strongest (110) line for rutile ($d = 3.247$ Å) as other strong rutile lines are absent. Furthermore, the line can be indexed as (101) which, according to the structure determination and listing of structure factor calculations by Lukaszewicz (6), is of sufficient intensity to appear in the powder pattern. With Cu$K\alpha$ radiation, the reported d-spacing is displaced almost exactly ($-1°$) 2θ from our observed line.

Jonker and Kwestroo (7) reported the preparation of a new compound, mixed with traces of (1:4) and rutile by heating above 1400°C. Further preparation details are not given. They assigned the formula $Ba_2Ti_9O_{20}$ to this phase. Our experiments indicate that not only does $Ba_2Ti_9O_{20}$ exist but can be prepared as a single phase in the binary from $BaTiO_3$ plus TiO_2 or from $BaCO_3$ plus TiO_2. When the calcined starting materials are heated below 1300°C, $Ba_2Ti_9O_{20}$ can be prepared from the 2:9 composition. Below 1300°C, the 1:5 composition yields $Ba_2Ti_9O_{20}$ plus TiO_2. When heated above 1300°C, the compound decomposes sluggishly

to $BaTi_4O_9$ plus TiO_2. If the calcined starting materials are heated directly above 1300°C only the decomposition products, $BaTi_4O_9$ plus TiO_2, are formed. This evidence suggests that the (2:9) phase has a temperature stability maximum, probably near 1300°C. The reaction is reversible, as the assemblage (1:4) plus TiO_2 converts to $Ba_2Ti_9O_{20}$ when reheated below 1300°C. In their phase diagram, Rase and Roy (1) show only $BaTi_4O_9$ plus TiO_2 for compositions > 80 mole % TiO_2. Apparently, they failed to observe the (2:9) compound because they calcined their $BaCO_3:TiO_2$ starting materials at about 100°C below the solidus temperature which they report as 1428°C in the TiO_2-rich portion of the system. Compositions with > 80 mole % TiO_2 were equilibrated only at temperatures > 1400°C, well above the decomposition temperature of the (2:9) phase.

The relatively low decomposition temperature of the (2:9) phase precludes growth of single crystals from a melt in the binary system as well as grain growth by prolonged sintering. Experi-

ments using MoO_3, Li_2MoO_4:1.25MoO_3, Li_2-TiO_3, KF, or $BaCl_2$ as fluxes failed to produce single crystals or to promote large grain growth of the desired phase. Clear, almost spherically shaped, crystals (maximum diameter ~0.1 mm) were grown from a $3BaTiO_3$:16TiO_2:BaF_2 composition which was heated (64 hr) at 1250°C in a sealed Pt capsule and quenched. The sintered but not melted specimen was washed in warm, dilute HCl to remove excess BaF_2, then washed in water and in acetone. The X-ray diffraction powder pattern of a portion of the specimen revealed only the (2:9) phase plus a trace of rutile. The powder pattern is identical with that of the pure (2:9) phase, although the crystals have a blue coloration which suggests the incorporation of fluorine. Preliminary single crystal precession data suggest a large unit cell with either monoclinic or triclinic symmetry. We hope to report at a later time the unit cell, symmetry and the detailed indexing of the complex powder pattern of the (2:9) after cell reduction computations are completed. Until a structure determination is performed, other Ba:Ti contents near 2:9 are not precluded and, therefore, we accept the formulation $Ba_2Ti_9O_{20}$ tentatively.

The $Ba_4Ti_{13}O_{30}$ (4:13) Phase, Formerly $BaTi_3O_7$ (1:3)[1]

During the initial stage of this investigation, we prepared small (1/4–3/4 mm), clear, irregularly shaped crystals of "$BaTi_3O_7$," suitable for single crystal X-ray diffraction analysis using Li_2TiO_3 as a flux. Compositions corresponding to (a), 21.43, 7.14, and 71.43, and (b), 23.75, 2.50, and 73.75 mol % BaO, Li_2O, and TiO_2, respectively, were formulated from the starting materials, $BaTiO_3$, Li_2TiO_3, and TiO_2. These were mixed, then calcined at 1000°C for 36 hr in air. Portions of each batch were sealed in small Pt tubes, equilibrated at several temperatures and quenched in water. Single crystals obtained from composition (a), partially melted at 1250°C

(1 hr) and from composition (b), partially melted at 1325°C (16 hr), proved to be of the desired phase.[2]

Zero and upper level X-ray precession photographs around [100], [010], and [001] indicated orthorhombic symmetry; systematically absent reflections are consistent with space groups *Cmca* (No. 64) and *C2cb* (No. 41). Preliminary cell dimensions were obtained from the photographs and later refined using *d*-spacings from powder data. Crushed single crystals yielded a powder pattern with *d*-spacings and line intensities similar to the data reported for $BaTi_3O_7$ (1). We later prepared the single-phase material in powder form directly from $BaTiO_3$ and TiO_2. The X-ray diffraction powder patterns could be indexed only with the aid of the precession data. Even with space group absences, many lines have numerous possible indices. Indices, therefore, were assigned by eliminating those which are extremely weak or not present in the precession data. Intensity calculations based on a proposed structural model (to be discussed) later proved to be consistent with the assignments. The powder pattern of the pure material, given in Table III, was indexed on the basis of $a = 17.072$, $b = 9.862$, and $c = 14.059$ Å. A comparison with the original, unindexed, powder data for $BaTi_3O_7$ (1) is also shown. The powder pattern of the crushed crystals, prepared with Li_2TiO_3, was indexed on the basis of $a = 17.152 \pm 0.002$, $b = 9.893 \pm 0.001$, and $c = 14.059 \pm 0.002$ Å. The *a* and *b* parameters are significantly larger than the pure end-member suggesting that the phase can accept some lithium in solid–solution.

Assuming a density value between 4–5 g cm^{-3} and considering the number of equivalent positions in the space groups noted above, the number of $BaTi_3O_7$ units per cell would appear

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[1] During the process of publication, we communicated with Dr. E. Tillmanns (Ruhr-Universitat Bochum) who brought to our attention and provided us two of his recent publications (14, 15). The structure and composition of $Ba_4Ti_{13}O_{30}$, herein reported, was determined independently (14) and the structure of a new phase, $BaTi_6O_{13}$ was solved (15). $BaTi_6O_{13}$ was found together with the (4:13), (1:5) and rutile phases when the composition BaO:4TiO_2 was, at least, partly melted at 1460°C and quenched. We did not obtain this phase at subsolidus temperatures.

[2] Other compositions investigated in the $BaTiO_3$–TiO_2–Li_2TiO_3 system, yielded crystals of two new phases of unknown stoichiometry. Crystals of phase (I) were prepared from a $3BaTiO_3$:Li_2TiO_3:6TiO_2 composition which was partially melted at 1230°C. The phase is monoclinic with $a = 15.25$, $b = 3.91$, $c = 9.14$ Å and $\beta = 99°$. Possible space groups are *C2*, *Cm*, *C2/m*. Crystals of phase (II) were obtained from the composition $BaTiO_3$:Li_2TiO_3:2TiO_2, partly melted at 1202°C. This phase is orthorhombic with $a = 5.81$, $b = 9.94$, and $c = 14.02$ Å. Probable space group is *Pmcn* (No. 62). A structural similarity between orthorhombic phase (II) and hexagonal $BaTiO_3$ probably exists in view of the following cell dimension relations: $a_{ortho.} \approx a_{hex.} \approx 5.8$ Å, $b_{ortho.} \approx a_{hex.} \cdot \sqrt{3} \approx 9.9$ Å, $c_{ortho.} \approx c_{hex.} \approx 14$ Å.

to be 16. The density calculated with $Z = 16$ and our cell volume is 4.4 g cm^{-3}. Rase and Roy (*1*) report a measured density of 4.7 g cm^{-3} for their BaTi$_3$O$_7$. This measured value should be nearly correct as the compounds from BaTiO$_3$ through TiO$_2$ in the binary show a progressive, almost linear, decrease in density. The decrease is illustrated by the following measured or calculated values: BaTiO$_3$, 5.9 (*1*); BaTi$_2$O$_5$, 5.1 (*5*); Ba$_6$Ti$_{17}$O$_{40}$, 4.8 [(*8*), this study]; BaTi$_4$O$_9$, 4.6 (*1, 6*); BaTi$_5$O$_{11}$, 4.58 (*9*); rutile, 4.25 (*16*). This phenomenon results from a structural similarity among these phases. They consist of a basic, close-packed, oxygen plus barium, framework in which space is provided for octahedral coordination of Ti atoms. This point is discussed further by Tillmanns and Baur (*8*). Although the measured density of 4.7 falls appropriately between the densities of the (6:17) and (1:4) compounds, the calculated density appears far too low. Density values of 4.69 and 4.96 can be derived by assuming $Z = 17$ and $Z = 18$, respectively. These, however, are not in accord with space group requirements unless partial occupancy of positions is assumed. Moreover, the 4.96 value appears too high. At this point we proceeded on the assumption that the stoichiometry, "BaTi$_3$O$_7$," is incorrect. Prior to this, we were unable to derive a structural model based on BaTi$_3$O$_7$ stoichiometry while conforming to requirements imposed by space group symmetry. Our only satisfactory model had the stoichiometry Ba$_4$Ti$_{13}$O$_{30}$; 4:13 rather than 1:3. This model not only accounted for the line intensities of the powder data (Table III) but reconciled the measured versus calculated densities. Using $4(Ba_4Ti_{13}O_{30})$ as the stoichiometry, the calculated density is 4.64 which is in better agreement with the 4.7 value. To confirm the stoichiometry deduced by density and structural considerations, we carefully prepared two sets of three compositions having Ba:Ti ratios of 6:17, 1:3, and 4:13. Set (1) was formulated from BaTiO$_3$ plus TiO$_2$ and set (2) from spectrographic grade BaCO$_3$ plus TiO$_2$. After a 3 day calcine at 1000°C, specimens of set (1) were equilibrated at 1300°C, 120 hr, and quenched while specimens of set (2) were treated at 1240°C, 35 hr, and quenched. The X-ray powder patterns for the 6:17 and 4:13 compositions consisted of single-phase Ba$_6$Ti$_{17}$-O$_{40}$ and Ba$_4$Ti$_{13}$O$_{30}$ ("BaTi$_3$O$_7$"), respectively. The 1:3 composition unequivocally yielded a two-phase mixture, Ba$_6$Ti$_{17}$O$_{40}$ plus Ba$_4$Ti$_{13}$O$_{30}$.

The structures of BaTiO$_3$ (cubic), Ba$_6$Ti$_{17}$O$_{40}$,

and BaTi$_5$O$_{11}$ are similar to the structure of hexagonal, 6-layer BaTiO$_3$. Each contains a close-packing of [Ba, O] layers stacked perpendicular to a *pseudohexagonal* c-axis corresponding to 3, 24 and 6 layers, respectively. The composition of each layer depends on the bulk stoichiometry. The average layer thickness in c is ~2.34 Å while the average pseudohexagonal a-dimension is a multiple of ~5.7 Å. Hexagonal BaTiO$_3$ has $a = 5.73$ and $c = 14.05$ Å. The geometry of the orthorhombic unit cell of Ba$_4$Ti$_{13}$O$_{30}$ also appears to be related to hexagonal BaTiO$_3$ and, therefore, can be classified within the above group of phases. The relationship can be expressed according to:

$$a_{ortho.} \approx 3a_{hex.} \approx 17 \text{ Å},$$
$$b_{ortho.} \approx \sqrt{3}a_{hex.} \approx 9.9 \text{ Å},$$
$$c_{ortho.} \approx c_{hex.} \approx 14 \text{ Å}.$$

Thus, it appears that the structure of Ba$_4$Ti$_{13}$O$_{30}$ consists of a stacking of *six* [(2.34) (6) = 14.04 Å $\approx c$] close-packed [Ba, O] layers. Furthermore, it also became apparent that the geometry of the monoclinic cell of Ba$_6$Ti$_{17}$O$_{40}$ can be directly correlated with that of Ba$_4$Ti$_{13}$O$_{30}$. The following relationship exists:

$$a_{6:17(mon.)} \approx b_{4:13(ortho.)} \approx 9.9 \text{ Å},$$
$$b_{6:17(mon.)} \approx a_{4:13(ortho.)} \approx 17 \text{ Å},$$
$$c_{6:17(mon.)} \approx c_{4:13} + 4.8 \approx 18.9 \text{ Å}.$$

The c-axis correlation indicates that the (6:17) phase contains *two* additional [Ba, O] layers, each ~2.4 Å in thickness. Ba$_6$Ti$_{17}$O$_{40}$, therefore, contains a stacking of eight [Ba, O] layers rather than six. The dimensions of the ab planes of both compounds are practically identical, suggesting a close structural similarity.

As the structure of the (4:13) phase can be derived from that of the (6:17), a more detailed discussion of the latter is appropriate. The contents of the eight layers of Ba$_6$Ti$_{17}$O$_{40}$ were constructed from the data in Ref. (*8*) and are shown, somewhat idealized, in Fig. 3. Each layer is linked to adjacent layers along the c direction by sharing elements of octahedra. Ti atoms, located, but not shown, within the octahedra, occur at intervals of $1/8c$ from $z \approx 0$ (level 1) to $z \approx 7/8$ (level 8). Oxygen and barium atoms are packed in planes approximately $(\pm 1/16)c$ above and below each level of Ti atoms. For a given Ti level, the oxygens at $(+1/16)$ are located at each apex of a shaded, triangular, face of an octahedron. The octahedra are completed by
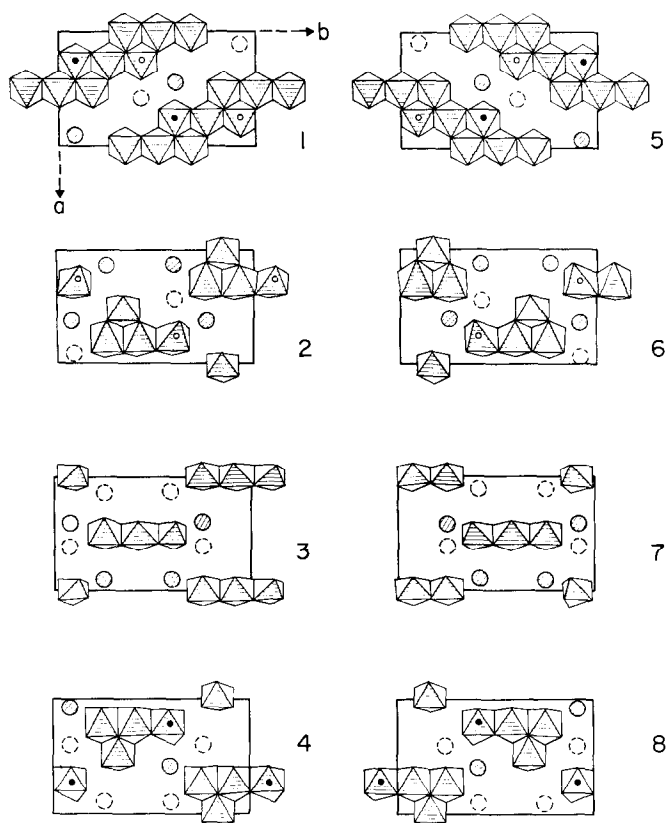
FIG. 3. An *ab* plane view illustrating the eight layers of the structure of $Ba_6Ti_{17}O_{40}$ determined by Tillmanns and Baur (*8*). The dimensions of *a* and *b* are approximately 9.9 and 17 Å, respectively. Layers are stacked along *c* (18.9 Å) by sharing common faces, edges, and corners of oxygen octahedra. Starting with level 1, Ti atoms are located, within every octahedron, at intervals of $1/8c$ from $z \approx 0$ (level 1) to $z \approx 7/8$ (level 8). Oxygen and barium atoms occur at approximately $(\pm 1/16)c$ from each Ti level. Oxygens defining the shaded, triangular faces of the octahedra are at $(+1/16)c$ from every Ti level. The remaining oxygens of each octahedron are at $(-1/16)c$. These also constitute the plane of atoms $(+1/16)c$ above the Ti atoms located immediately below a given Ti level. Large shaded and unshaded circles are Ba atoms above and below, respectively, a given Ti level. Small solid and open circles define octahedra which share a face above and below, respectively, a given Ti level.

oxygens located at $(-1/16)$ below the given Ti level. Thus, it is apparent that the oxygens at $(-1/16)$ must be the same as those which exist at $(+1/16)$ of the Ti level immediately *below* a given level. *All* oxygens (even when not shown) about a given Ti level, may be found at $(-1/16)$ of the next level *above* and $(+1/16)$ of the adjacent level *below*. Barium atoms essentially disrupt the framework of octahedra generated by the anion packing as they occupy potential oxygen sites within the layers. Shaded and unshaded circles are Ba atoms above and below, respectively, a Ti level. In the *ab* plane, octahedra are linked by sharing edges. Octahedra in layers 2, 3, 4 and in 6, 7, 8 are linked via common edges and corners

along the *c* direction. Linkage between layers 8, 1, 2 and layers 4, 5, 6 also includes the sharing of octahedral faces as in hexagonal $BaTiO_3$. Octahedra which share a triangular face immediately *above* a given Ti level are denoted by a small solid circle. Faces, shared *below* a given Ti level are indicated by small open circles. This elegant structure determined by Tillmanns and Baur (*8*) has a cell content of $4[Ba_6Ti_{17}O_{40}]$. Barium atoms at $z \approx 15/16$, $1/16$, $7/16$, and $9/16$ (total of eight) are coordinated by 12 oxygens while the remainder are 11-fold coordinated.

Given the various ways of arranging Ba and O atoms to yield sheets having the dimensions 17×9.9 Å, it was apparent that two of the levels

in Fig. 3 could be eliminated to generate a six-layer (14 Å) structure from the eight-layer phase. Our space group determination from single crystals provided the necessary information for this choice. Assuming the centrosymmetric space group, $Cmca$, a mirror plane must be present perpendicular to the a-axis [b-axis of the (6:17) phase in Fig. 3]. Layers which do not conform or which cannot be slightly modified to conform with this symmetry element can be eliminated. If the distortion of the octahedra is eliminated and the origin is shifted, a potential mirror plane exists perpendicular to b (Fig. 3) for layers 3 and 7. Layers 2, 4, 6, and 8 can be made to conform with this mirror symmetry when a slight adjustment in stoichiometry is imposed. Layers 1 and 5 are the only units which show little potential for mirror plane symmetry unless their atom contents are drastically altered. If layers 1 and 5 are eliminated, the following are evident:

a. *All* face-sharing of octahedra is eliminated thereby obviating the distortion of octahedra in the remaining layers,

b. Only the eight, 12-fold coordinated, Ba atoms, in the 8(f) position of $C2/c$, are eliminated,

c. The positions previously occupied by the eliminated Ba atoms can now be "filled" with additional oxygens which generate new octahedral voids in adjacent layers, and

d. The resulting Ba:Ti content is 16:44, which now must be adjusted appropriately toward greater TiO_2 content.

By "filling" all vacant Ba sites in layers 2, 4, 6, and 8 according to (c) above, the new octahedra which are generated can be "filled" with a maximum of 8 Ti atoms. This adjustment now permits every layer to conform to mirror plane symmetry perpendicular to b and yields a Ba:Ti content of 16:52. Without interrupting the general progression in the stacking of the remaining six levels and without disrupting the sharing of octahedral elements inherent between and within these layers, the units can be easily described with the symmetry of $Cmca$. The six layers of the proposed, idealized, structure are shown in Fig. 4. Interpretation of the diagram is
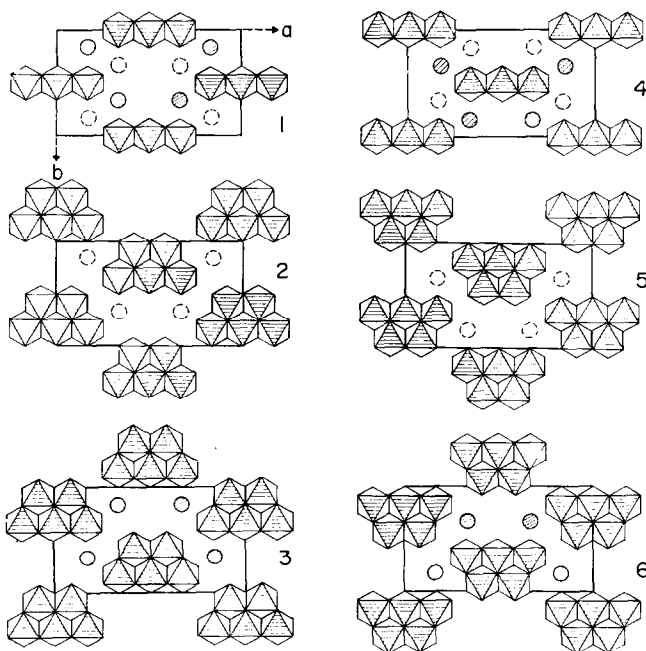

FIG. 4. An ab plane view illustrating the six layers of the proposed, idealized, structure of $Ba_4Ti_{13}O_{30}$. The a and b dimensions are approximately 17 and 9.9 Å, respectively. Layers are stacked along c (14 Å) by sharing edges and corners of oxygen octahedra. Ti atoms are located within every octahedron at intervals of $1/6c$ from $z \approx 0$ (level 1) to $z \approx 5/6$ (level 6). Oxygen and barium atoms occur at approximately $(\pm 1/12)c$ from each Ti level. See Table III for coordinates of atoms in space group $Cmca$. Compare with the structure of $Ba_6Ti_{17}O_{40}$ in Fig. 3.

as described for Fig. 3. Ti atoms occur at intervals of $1/6c$ from $z \approx 0$ (level 1) to $z \approx 5/6$ (level 6). Oxygen and barium atoms are packed in planes approximately $(\pm 1/12)c$ above and below each Ti level. The cell content is $4[Ba_4Ti_{13}O_{30}]$. Linkage between adjacent levels is entirely via corner- and edge-sharing. All Ba atoms are 11-fold coordinated.

We believe that the proposed structure in Fig. 4 is essentially correct and is supported by the following:
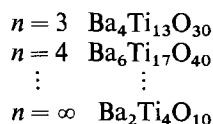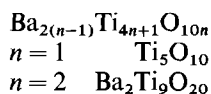
a. Structural and geometric features of the phase nearest in stoichiometry, $Ba_6Ti_{17}O_{40}$, are not only retained but correspond with the observed space group,

b. X-Ray powder pattern intensity calculations based on ideal atomic parameters, given in Table III, are in particularly good agreement with the observed data,

c. The cell content, $4[Ba_4Ti_{13}O_{30}]$, deduced from geometry and symmetry considerations, provides for a calculated density which is in better agreement with the value measured for $BaTi_3O_7$ and,

d. The material was prepared as a single phase at the 4:13 rather than the 1:3 composition using $BaTiO_3$ plus TiO_2 and $BaCO_3$ plus TiO_2 as starting materials.

It may appear unusual that this system contains compounds of such complex ratios as 6:17 and 4:13 rather than the simpler ratios of 2:5 and 1:3 previously reported. However, at least some of the compounds in this system belong to a chemical homologous series:

$$Ba_{2(n-1)}Ti_{4n+1}O_{10n}$$
$$n = 1 \qquad Ti_5O_{10}$$
$$n = 2 \qquad Ba_2Ti_9O_{20}$$

$$n = 3 \qquad Ba_4Ti_{13}O_{30}$$
$$n = 4 \qquad Ba_6Ti_{17}O_{40}$$
$$\vdots \qquad \vdots$$
$$n = \infty \qquad Ba_2Ti_4O_{10}$$

Undoubtedly, a more complex structural homologous series could be derived to account for all of the compounds in this system plus an infinite number of unobserved phases, but it is questionable whether such a formulation would have any predictive value.

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