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Phase Equilibria and Crystal Chemistry in the Ternary System $BaO-TiO_2-Nb_2O_5$

II. New Barium Polytitanates with <5 mole% Nb_2O_5

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Four new compounds were found in the $BaO-TiO_2-Nb_2O_5$ system, each containing <5 mole% Nb_2O_5. $Ba_6Ti_{14}Nb_2O_{39}$ is an 8-layer orthorhombic phase, $Cmc2_1$[1], with $a = 17.138(.011)$, $b = 9.868(.011)$, $c = 18.759(.010)$ Å. The other three phases have similar a and b parameters ($a_{mon} \approx b_{orth} \approx 9.9$ Å, $b_{mon} \approx a_{orth} \approx 17$ Å). $Ba_{14}Ti_{40}Nb_2O_{99}$ is a 20-layer orthorhombic phase, Cmc^*, with $c \approx 46.86$ Å. $Ba_{10}Ti_{28}Nb_2O_{72}$ is a 7-layer monoclinic phase, $C2/m$, $c \approx 16.72$ Å, $\beta \approx 101.2°$. $Ba_{18}Ti_{54}Nb_2O_{132}$ is a 13-layer monoclinic phase, $C2/m$, $c \approx 30.65$ Å, $\beta \approx 96°$. The compositions were derived by analogy to the layers in $Ba_4Ti_{13}O_{30}$ and $Ba_6Ti_{17}O_{40}$ and are consistent with limited phase equilibria data. © 1987 Academic Press, Inc.

Introduction

The barium polytitanates are of great interest and technological importance because of their high dielectric constant, low temperature coefficient of the dielectric constant, and low dielectric loss (*1*). Previous phase equilibria studies (*2, 3*) have established the existence of compounds with the $BaO:TiO_2$ ratios of 6:17, 4:13, 1:4, and 2:9 as stable high-temperature phases; the 1:4 and 2:9 phases are currently being used in microwave-filter devices. The structures were refined (*4–9*) mostly by Baur and Tillmanns. Two other compounds with ratios of 1:2 and 1:5 were shown to be stable only at low temperatures (*10*) and the stability of the 2:5 phase reported by Jonker and Kwestroo (*11*) has been reinvestigated and this study was reported recently (*12*). The equilibrium relations between all the Ba-polytitanates and other oxide compounds are of great technological interest in connection with modification of the existing stability and resultant properties of these phases. For these reasons, previous studies were reported earlier of equilibria in systems involving BaO and TiO_2 with CaO and SrO (*13*), with SnO_2 and ZrO_2 (*2*), and with P_2O_5 (*14*). Recent studies with B_2O_3, V_2O_5, and MoO_3 (*15*) and new studies with P_2O_5 (*16*) by the authors and collaborators are being published. A detailed study of a large part of the system $BaO-TiO_2-Nb_2O_5$ was published as Part I of this series (*17*). In this system eight new ternary phases were reported and two previously reported (*18, 19*) ternary phases confirmed. In that paper (*17*) it was pointed out that "The addition of a small amount of Nb_2O_5 to the Ba-polytitanates causes abrupt shifts in many of the X-ray diffrac-

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[1] Preliminary crystal structure analyses by R. J. Cava has identified the true space group as uniquely noncentrosymtetric $Cmc2_1$.

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tion lines associated with these phases." The ternary phase diagram was left blank in this portion of the system. Further work has now established the existence of at least four new phases, with 1 to 5 mole% Nb_2O_5, occurring in this previously undefined region. The synthesis and crystal chemistry of these phases are reported here.

Experimental Techniques

Most of the experimental techniques were reported in Part I (*17*) and techniques involving alkoxide precursor synthesis was previously reported by Ritter *et al.* (*10*). Due to the difficulty of obtaining equilibrium by solid state techniques with such small amounts of a third component (0.1–5.0 mole%) it was necessary in many cases to prepare some compositions using hydrolysis of mixed ethoxide solutions in order to obtain homogeneity. Single crystals were obtained from partially melted specimens and used to determine unit cell dimensions and symmetry. The compositions studied and the results of the synthesis and X-ray diffraction analyses are summarized in Fig. 1 in the high-TiO_2 quarter of the ternary system and in Tables I and II. The proposed phase equilibria are shown more

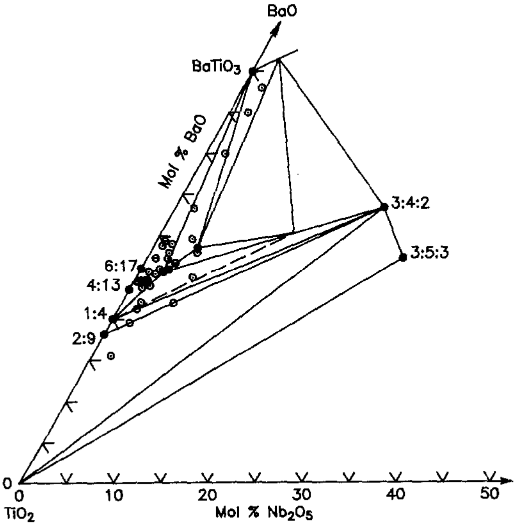

FIG. 1. Subsolidus section of the phase equilibria relations in the high-TiO_2 portion of the system $BaO-TiO_2-Nb_2O_5$ (temperature ~1275–1300°C). ●, solid state specimens; ○, ethoxide hydrolyzed specimens.

TABLE I

COMPOSITIONS STUDIED AND PHASES PRESENT AT JUST BELOW THE SOLIDUS ~1260–1300°C

Composition (mole%)			Phases identified by X-ray powder diffraction analyses[a]
BaO	TiO_2	Nb_2O_5	
(a) Specimens prepared by conventional solid state techniques			
48	50	2	BTss + 6:14:1
45	53	2	BTss + 6:14:1
40	58	2	BTss + 6:14:1
33.33	64.67	2	BTss + 10:28:1
29.63	66.67	3.70	6:14:1 + BTss
29.09	69.09	1.82	14:40:1 + 10:28:1 + BTss
28.83	70.27	0.90	6:17 + 14:40:1
28.57	66.67	4.76	6:14:1
28	67	5	6:14:1 + 3:4:2ss + 10:28:
28	70	2	14:40:1 + BTss
27.27	70.45	2.27	10:28:1 + BTss
26	71	3	10:28:1
26	72	2	14:40:1
25.74	73.27	0.99	6:17 + 18:54:1 + 14:40:1
25.64	71.79	2.56	10:28:1
25.45	72.73	1.82	14:40:1
25	69	6	1:4 + 3:4:2ss
24.72	74.16	1.12	4:13 + 1:4
24.44	74.44	1.11	18:54:1
24	74	2	1:4 + 10:28:1
23.75	75	1.25	1:4 + 18:54:1
22	76	2	1:4 + 3:4:2ss
21.92	72.60	5.48	2:9 + 3:4:2
21.20	76.80	2	1:4 + 3:4:2
19.54	78.45	2	2:9 + 3:4:2
15.50	82.50	2	2:9 + 3:4:2 + TiO_2
(b) Specimens prepared by hydrolysis of mixed ethoxide solutions			
29.40	69.67	0.93	6:17 + BT + 6:14:1
27.37	71.70	0.93	6:17 + 6:14:1 + 14:40:1
26.78	69.91	3.31	6:14:1 + 10:28:1
24.69	73.95	1.36	18:54:1
24.48	75.15	0.37	4:13 + 1:4

[a] 6:14:1 = 8L-orth, 10:28:1 = 7L-mon, 14:40:1 = 20L-orth, 18:54:1 = 13L-mon.

TABLE II

SPECIMENS FROM WHICH SINGLE CRYSTALS WERE EXAMINED

Composition (mole ratio $BaO : TiO_2 : Nb_2O_5$)	Heat treatment	Crystals identified	Probable composition of crystal
28 : 67 : 5	1350°C/10 min → 1325°C/64 hr	8-layer orthorhombic	$Ba_6Ti_{14}Nb_2O_{39}$
14 : 35 : 1	1320°C → 1314°C/24 hr	20-layer orthorhombic	$Ba_{14}Ti_{40}Nb_2O_{99}$
28 : 67 : 5	1350°C/10 min → 1325°C/64 hr	7-layer monoclinic	$Ba_{10}Ti_{28}Nb_2O_{72}$
6 : 14 : 1	1325°C/44 hr	7-layer monoclinic	$Ba_{10}Ti_{28}Nb_2O_{72}$
27.37 : 71.7 : 0.93	1310°C/165 hr	13-layer monoclinic	$Ba_{18}Ti_{54}Nb_2O_{132}$

clearly in Fig. 2 in the enlarged low-Nb_2O_5 portion of the ternary diagram near the Ba-polytitanates.

Results and Discussion

A series of compositions containing 2 mole% Nb_2O_5 were prepared by conventional solid state techniques and heat treated for long periods at about 1300°C, very near the solidus temperature. None of the specimens between 20 and 50 mole% BaO showed, in their X-ray diffraction powder patterns, any sign of the peaks belonging to either the 6 : 17 or 4 : 13 phases. Other compositions containing between about 3 and 15 mole% Nb_2O_5 showed the presence of one or more phases which had not been identified in other portions of the ternary system.

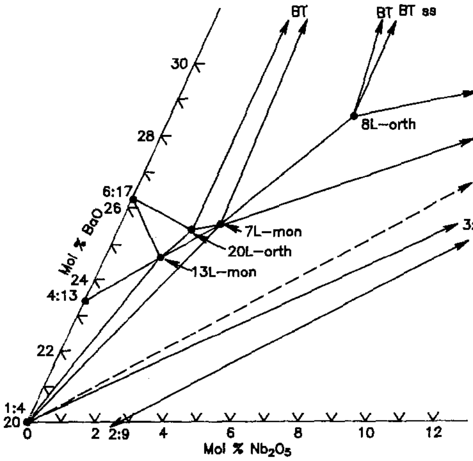

FIG. 2. Enlarged portion of Fig. 1 illustrating most likely phase relations in the low-Nb_2O_5 portion of the system $BaO–TiO_2–Nb_2O_5$.

$Ba_6Ti_{14}Nb_2O_{39}$

In order to identify the unknown(s) a specimen was chosen (28 : 67 : 5) the diffraction pattern of which contained many unidentifiable peaks plus a trace of the hexagonal solid solution $Ba_3Ti_{4+5x}Nb_{4-4x}O_{21}$ ($x \approx 0.3$) (see Ref. (*18*)). A specimen of this composition was melted in an unsealed Pt tube at 1350°C for a few minutes. The temperature of the furnace was then lowered to 1325°C and held for ~64 hr. The specimen was then removed from the furnace, allowed to cool in air, gently crushed, and examined under a polarizing microscope for small single crystals. Most of the crystals examined by single crystal X-ray precession patterns belonged to the same phase (Fig. 3, upper level data not shown) and looked very much like crystals of the 4 : 13 phase. However, the unit cell dimensions and the patterns showed that this phase has a structure with an orthorhombic close-packed lattice with *a* and *b* parameters essentially the same as those of the 4 : 13 phase but with a *c* parameter similar to that of the monoclinic 6 : 17 phase rather than the *c* of the 4 : 13 phase. (Note that

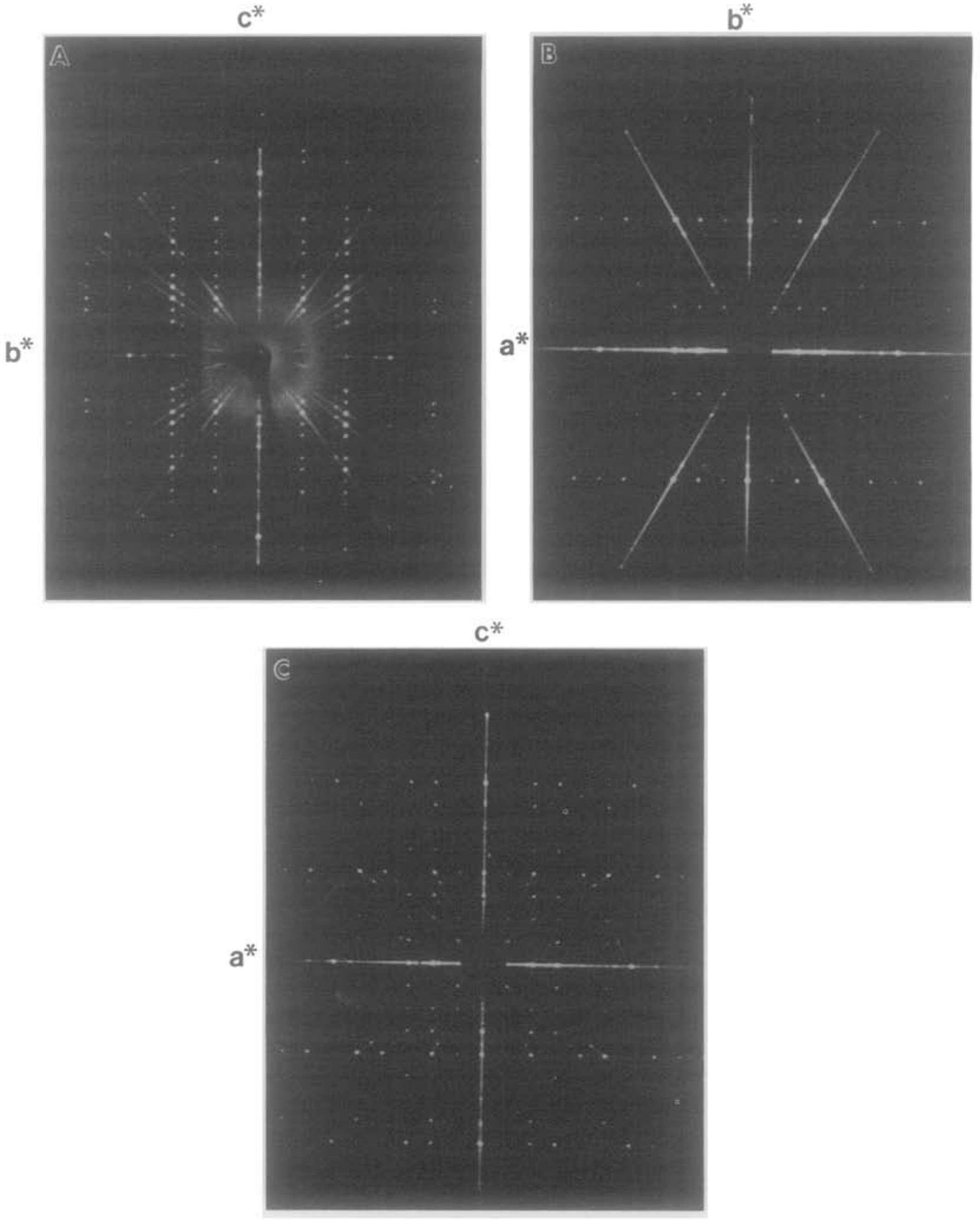

FIG. 3. Single crystal X-ray precession patterns (Mo radiation) of the 8-layer orthorhombic phase $Ba_6Ti_{14}Nb_2O_{39}$, space group *Cmcm*. A—(0*kl*), B—(*hk*0), C—(*h*0*l*), upper level data not shown.

$a_{\text{mon}} \approx b_{\text{orth}} \approx 9.9$ Å and $b_{\text{mon}} \approx a_{\text{orth}} \approx$ 17 Å.)

The structures of the 6:17 and 4:13 phases are known to be very similar (*4*, *5*). Indeed, Negas *et al.* (*2*) were able to derive the existence and structure of the 4:13

phase from the published (*4*) single crystal structure analyses of the 6 : 17 and only realized after the fact that such a phase had already been described in (*5*). Both of these compounds can be described as containing layers of oxygen close-packed ions with one Ba^{+2} cation occasionally substituting for two missing oxygens and with Ti^{+4} ions occurring in octahedral coordination between the layers in patterns obeying the space group symmetry. The 6 : 17 phase is monoclinic, space group *C*2/*c*, and the repeat distance perpendicular to the Ba–oxygen close packing is 18.76 Å, ≈ 8 × 2.31 Å, close to the normal 0–0 distance for close-packed layers. For a description of this 8-layer monoclinic structure, the reader is referred to the paper by Negas *et al.* (*2*). The 4 : 13 phase, on the other hand, although still made up of close-packed layers, has a much more symmetrical distribution of the Ti^{+4} ions. It is orthorhombic, space group *Cmca*, with the repeat distance perpendicular to the close-packed layers being 14.06 Å, ≈ 6 × 2.32 Å. This 6-layer orthorhombic structure is also described in (*2*).

It can now be seen from Fig. 3 that the new compound is an 8-layer phase with an orthorhombic distribution of the cations. The actual space group is $Cmc2_1$ rather than *Cmca*, as reported for the 4 : 13 phase, due to the presence of (*hk*0) peaks with *h* odd, for instance (330) (see Fig. 3). The composition of the 8 layers can be hypothesized to be formed by a redistribution of the known layers of the 4 : 13 phase. The first half of the unit cell of $Ba_4Ti_{13}O_{30}$ is made up of 3 layers, each with a different composition. Layer 1 is $[Ba_4Ti_6O_{18}V_2]^{-4}$ (V = vacancy); layer 2 is $[Ti_{10}O_{24}]^{-8}$; and layer 3 is $[Ba_4Ti_{10}O_{18}V_2]^{+12}$. The other half of the unit cell is made up of three layers related by symmetry, each with the same composition as the first half. The formula $Ba_4Ti_{13}O_{30}$ can thus be arrived at by considering only half the unit cell. By adding another layer of $[Ba_4Ti_6O_{18}V_2]^{-4}$ to each half unit cell the composition $[Ba_{12}Ti_{32}O_{78}]^{-4}$ would be realized:

$$\begin{array}{l} 4:13\left\{\begin{array}{l}[Ba_4Ti_6O_{18}V_2]^{-4}\\ [Ti_{10}O_{24}]^{-8}\\ [Ba_4Ti_{10}O_{18}V_2]^{+12}\end{array}\right. \\ \qquad\quad \underline{[Ba_4Ti_6O_{18}V_2]^{-4}} \\ \qquad\quad [Ba_{12}Ti_{32}O_{78}V_6]^{-4}\end{array}$$

In deriving the formulas it is important to always consider the number of vacancies as, for this size unit cell, the total number of Ba + O + V should always equal 24 for each layer. By substituting four Nb^{+5} atoms for four of the Ti^{+4} atoms in the above formula $[Ba_{12}Ti_{32}O_{78}V_6]^{-4}$ it can be made electrically neutral with no change in the cation/anion ratio. The new formula is $Ba_{12}Ti_{28}Nb_4O_{78}$ or $Ba_6Ti_{14}Nb_2O_{39}$ equal to $6BaO \cdot 14TiO_2 \cdot Nb_2O_5$ (6 : 14 : 1). This composition is so close to the original specimen from which the crystals were derived that a great deal of confidence can be placed in the crystallographic derivation of this formula. A new specimen was prepared of the composition 6 : 14 : 1 and found to be single phase after heat treatment at 1230°C for 23 hr, then 1300°C for 122 hr. The resultant X-ray diffraction powder pattern was analyzed by a least-squares technique using the unit cell derived from the photographs shown in Fig. 3. The results of the analysis are given in Table III and show that $Ba_6Ti_{14}Nb_2O_{39}$ is orthorhombic, space group *Cmcm* (or its noncentrosymmetric equivalents $Cmc2_1$, *C*2*cm*), with parameters a = 17.138(.011), b = 9.868(.011), c = 18.759(.010) Å.

$Ba_{14}Ti_{40}Nb_2O_{99}$

After the identification of the 8-layer orthorhombic phase at a composition of 6 : 14 : 1 and the clarification of its X-ray diffraction powder pattern, it was found that many of the specimens prepared with 2 mole% Nb_2O_5 still contained an unknown phase or phases. The unexplained diffraction peaks occurred most often in the compositions between 25 and 30 mole% BaO. Consequently, a specimen of the composition 14 : 35 : 1 was heated at 1320°C and allowed to cool only about 5–6°C, over 24 hr, then removed from the furnace, gently crushed, and examined for small single crystals. Again most of the crystals examined belonged to the same phase with essentially the same a and b parameters as the 4 : 13, 6 : 17, and the 8-layer orthorhombic 6 : 14 : 1. However, the c parameter was very large ~46.86 Å or 20 × 2.343 Å (Fig. 4, upper level data not shown). This phase is also orthorhombic, but the space group could not be determined exactly as the c axis is so large that upper level diffraction spots could not be screened out in ($hk0$) precession patterns. It was therefore not possible to decide between *Cmcm* or *Cmca* and the notation must be left as *Cmc** until the structure is refined. The most likely composition of this phase was arrived at partly by examination of the X-ray powder diffraction data of the many prepared specimens and partly by analogy to the 4 : 13 and 6 : 14 : 1 phases. As this is a 20-layer orthorhombic phase, it can be thought of as an ordered arrangement containing one 8-layer 6 : 14 : 1 composition and two 6-layer 4 : 13 compositions. The following would be for one-half a unit cell.

$$\begin{array}{lcl} 6:14:1 & = & \text{4 layers—}Ba_{12}Ti_{28}Nb_4O_{78}V_6 \\ 4:13 & = & \text{3 layers—}Ba_8Ti_{26}\quad O_{60}V_4 \\ \underline{4:13} & = & \underline{\text{3 layers—}Ba_8Ti_{26}\quad O_{60}V_4} \\ & & \text{10 layers—}Ba_{28}Ti_{80}Nb_4O_{198}V_{14} \\ 14:40:1 & & \qquad Ba_{14}Ti_{40}Nb_2O_{99} \end{array}$$

There is, as yet, no obvious reason why a 20-layer orthorhombic 2 : 1 arrangement of the 4 : 13 and 6 : 14 : 1 compounds should be more stable than a 14-layer orthorhombic 1 : 1 or 22-layer orthorhombic 1 : 2 arrangement. This may be related to the symmetry requirements of the arrangement of the individual layers within the space group versus geometric packing and the stability of possible face-sharing octahedra. At any rate, the composition derived above, 14 : 40 : 1, is very close to the composition needed to best explain the X-ray powder diffraction data. The composition 14 : 40 : 1 is therefore tentatively accepted as the

TABLE III

X-RAY DIFFRACTION POWDER PATTERN TO 45°2θ OF THE 8-LAYER ORTHORHOMBIC PHASE, $Ba_6Ti_{14}Nb_2O_{39}$

d obs	I/I_0	2θ obs	2θ calc[a]	*h k l*
8.598	5	10.28	10.31	2 0 0
6.329	10	13.98	13.99	2 0 2
4.7793	10	18.55	18.54	3 1 1
4.3775	40	20.27	20.29	3 1 2
4.2855	30	20.71	20.72	4 0 0
4.1681	5	21.30	21.30	2 2 1
3.8804	28	22.90	22.91	3 1 3
3.4399	40	25.88	25.91	1 1 5
3.4024	25	26.17	26.17	3 1 4
3.1817	100	28.02	28.00	1 3 1
3.1293	18	28.50	28.53	0 0 6
3.0569	25	29.19	29.18	4 2 2
2.9889	67	29.87	29.87	3 1 5
2.9397	37	30.38	30.41	2 0 6
2.8752	65	31.08	31.08	5 1 3
2.8555	25	31.30	31.29	6 0 0
2.8186	54	31.72	31.72	3 3 1
2.7323	10	32.75	32.75	6 0 2
2.6651	50	33.60	33.60	5 1 4
2.6436	26	33.88	33.90	3 1 6
2.5940	13	34.55	34.55	3 3 3
2.5253	7	35.52	35.52	4 0 6
2.4695	5	36.35	36.39	0 4 0
2.4500	17	36.65	36.65	4 2 5
2.3571	10	38.15	38.14	7 1 1
2.3511	12	38.25	28.23	2 4 1
2.2980	27	39.17	39.16	2 4 2
2.2631	17	39.80	39.82	2 0 8
2.2212	12	40.58	40.58	7 1 3
2.1853	33	41.28	41.25	6 2 4
			41.31	0 4 4
2.1187	15	42.64	42.64	3 1 8
2.1154	13	42.71	42.70	2 4 4
2.0594	56	43.93	43.88	0 4 5
			43.98	4 0 8
2.0250	7	44.72	44.72	1 1 9

[a] Calculated on the basis of an orthorhombic unit cell, space group $Cmc2_1$, with $a = 17.138$, $b = 9.868$, $c = 18.759$ Å.

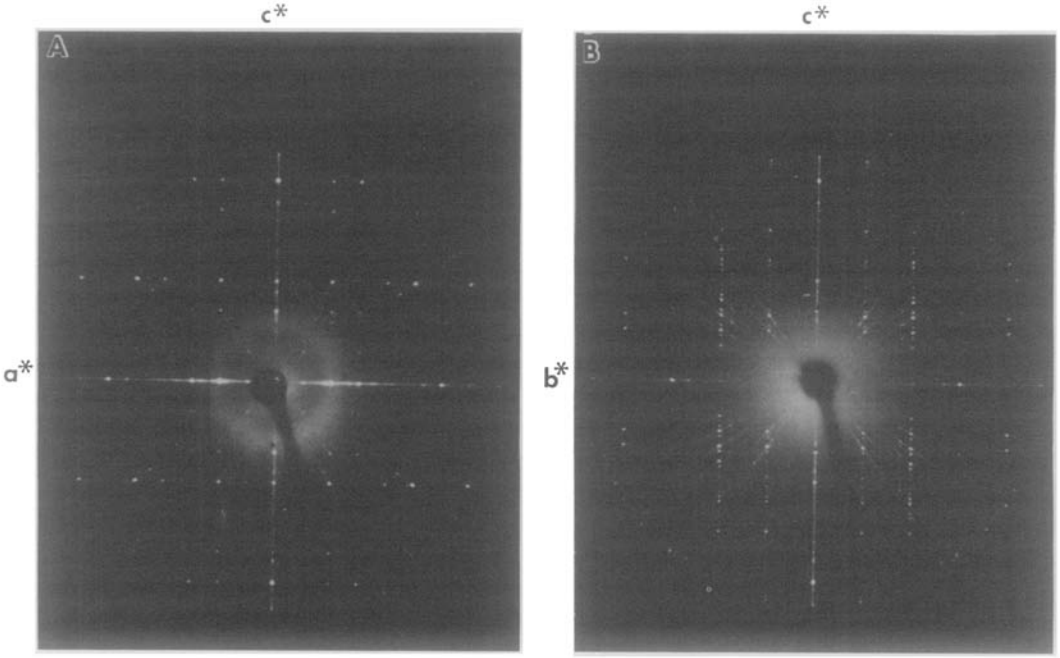

FIG. 4. Single crystal X-ray precession patterns (Mo radiation) of the 20-layer orthorhombic phase, space group *Cmc**, most likely composition $Ba_{14}Ti_{40}Nb_2O_{99}$. A—($h0l$), B—($0kl$), upper level data not shown.

most likely composition of the 20-layer orthorhombic phase until the structure is refined from the single crystal X-ray diffraction data.

$Ba_{10}Ti_{28}Nb_2O_{72}$

Several of the X-ray diffraction powder patterns from specimens containing 20–30 mole% BaO, especially those around 24–26 mole%, still contained diffraction peaks that could not be explained by the calculated X-ray diffraction powder patterns for the 8- and 20-layer orthorhombic phases. However, one of the crystals examined from the batch of the 28 : 67 : 5 composition turned out to be a different phase than all the other 8-layer orthorhombic crystals. Indeed, a specimen of the 6 : 14 : 1 composition, which had been single phase 8-layer orthorhombic, was held above its incongruent melting point at 1325°C for 44 hr. After removal from the furnace, the specimen was gently crushed and single crystals were examined. Many more crystals of the new phase were now found (Fig. 5, upper level data not shown). This phase looked much more like the 6 : 17 compound than like the 4 : 13 or 6 : 14 : 1 phase. It proved to be monoclinic, $\beta \approx 101.2°$, with a and b parameters similar to the other phases but with $c = 16.72$ Å (7×2.39 Å). This phase, therefore, has a 7-layer monoclinic structure, space group $C2/m$ (or equivalent), as the c-glide present in the 6 : 17 structure appears to be absent in this phase. The most likely composition for this 7-layer monoclinic structure is an ordered arrangement of layers similar to the 4 : 13 and 6 : 17 phases with some Nb^{+5} substituted for Ti^{+4}. Again, as for the 6 : 17, 4 : 13, 6 : 14 : 1, and 14 : 40 : 1 phases a compound with these a and b parameters must have a composition with the Ba + O + V = 24 per layer. The most probable compositions can be arrived

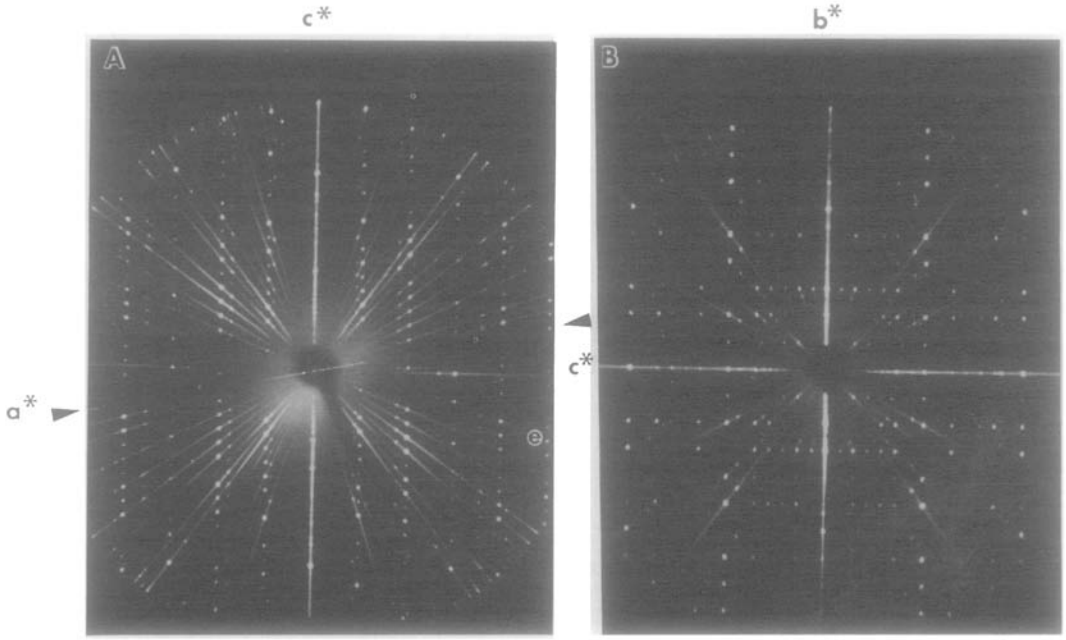

FIG. 5. Single crystal X-ray precession patterns (Mo radiation) of the 7-layer monoclinic phase, space group $C2/m$, most likely composition $Ba_{10}T_{28}Nb_2O_{72}$. A—($h0l$), B—($0kl$), upper level data not shown.

at by adding the 3 layers of one-half the unit cell of the 4 : 13 phase to the 4 layers of one-half the unit cell of the 6 : 17 phase and allowing substitution of Nb^{+5} for Ti^{+4}:

$$\begin{array}{rl} 4:13 \left\{ \begin{array}{l} (1)\ Ba_4Ti_6O_{18}V_2 \\ (2)\ \quad Ti_{10}O_{24} \\ (3)\ Ba_4Ti_{10}O_{18}V_2 \end{array} \right. \\ 6:17 \left\{ \begin{array}{l} (4)\ Ba_2Ti_{12}O_{22} \\ (5)\ Ba_4Ti_8O_{18}V_2 \\ (6)\ Ba_4Ti_6O_{18}V_2 \\ (7)\ \underline{Ba_2Ti_8O_{22}} \end{array} \right. \end{array}$$

$0\text{-}Nb_2O_5$	$Ba_{20}Ti_{60}O_{140}$	(1 : 3 does not exist)
$1\text{-}Nb_2O_5$	$Ba_{20}Ti_{58}Nb_2O_{142}$	(20 : 58 : 1)
	or	
$2\text{-}Nb_2O_5$ 7-layer	$Ba_{20}Ti_{56}Nb_4O_{144}$	
monoclinic	$Ba_{10}Ti_{28}Nb_2O_{72}$	(10 : 28 : 1)

This later composition (10 : 28 : 1) corresponds most closely with the possible interpretation of the X-ray diffraction powder data of the various specimens and is taken as the most likely composition of the 7-layer monoclinic phase.

$Ba_{18}Ti_{54}Nb_2O_{132}$

The X-ray powder diffraction data of most of the compositions containing 2–15 mole% Nb_2O_5 could be completely accounted for by known phases plus the calculated d-spacings of the 8-layer orthorhombic (6 : 14 : 1), 20-layer orthorhombic (14 : 40 : 1), and 7-layer monoclinic (10 : 28 : 1) phases. However, several of the specimens containing ~1 mole% Nb_2O_5 still contained unknown diffraction peaks. Therefore, one of the specimens prepared via the ethoxide precursor route with a composition of $27.37BaO : 71.70TiO_2 : 0.93Nb_2O_5$ was held just above its solidus temperature at 1310°C for ~165 hr. After removal from the furnace, the specimen was gently crushed and small single crystals were examined in the precession camera. Some of the crystals were the 8-layer monoclinic 6 : 17 type structure. However, many belonged to a new phase (Fig. 6, upper level data not shown), again with *a* and *b* parameters about the same as the previously described compounds but with monoclinic symmetry, $\beta \sim 96^\circ$ and $c \approx 30.65$ Å (13×2.36 Å). This phase therefore has a 13-layer monoclinic structure, space group again *C*2/*m* (or equivalent), with no *c*-glide. As this phase seems to occur with only about 1.0 to 1.5 mole% Nb_2O_5, its most likely composition is that of a 1 : 1 ordered phase of the 7-layer monoclinic and the 6-layer 4 : 13 compound:

$$\begin{array}{l} 7 \text{ layers—}Ba_{20}Ti_{56}Nb_4O_{144} \\ \underline{6 \text{ layers—}Ba_{16}Ti_{52}O_{120}} \\ 13 \text{ layers—}Ba_{36}Ti_{108}Nb_4O_{264} \end{array}$$

or $Ba_{18}Ti_{54}Nb_2O_{132}$, $z = 2$ (18 : 54 : 1) with only 1.37 mole% Nb_2O_5.

Most of the X-ray diffraction powder patterns of specimens so far prepared in this part of the system can be accounted for on the basis of these four new phases and the previously reported compounds. However, there are still some possible discrepancies and it is by no means certain that all of the complex chemistry has been elucidated.

Conclusion

A small amount of Nb_2O_5 (1–5 mole%) is enough to change the stability for the close-packed layers of the Ba-polytitanate phases $Ba_6Ti_{17}O_{40}$ and $Ba_4Ti_{13}O_{30}$ so that new phases form instead. The new phases are apparently structurally related to the previous two, containing layers of similar Ba–Ti–O configurations except with some Nb^{+5} substituting for Ti^{+4}, changing the electronic configuration of each layer while maintaining the cation/anion ratio. Four new phases have been found and their symmetries, unit cell dimensions, number of layers per unit cell, and space groups were

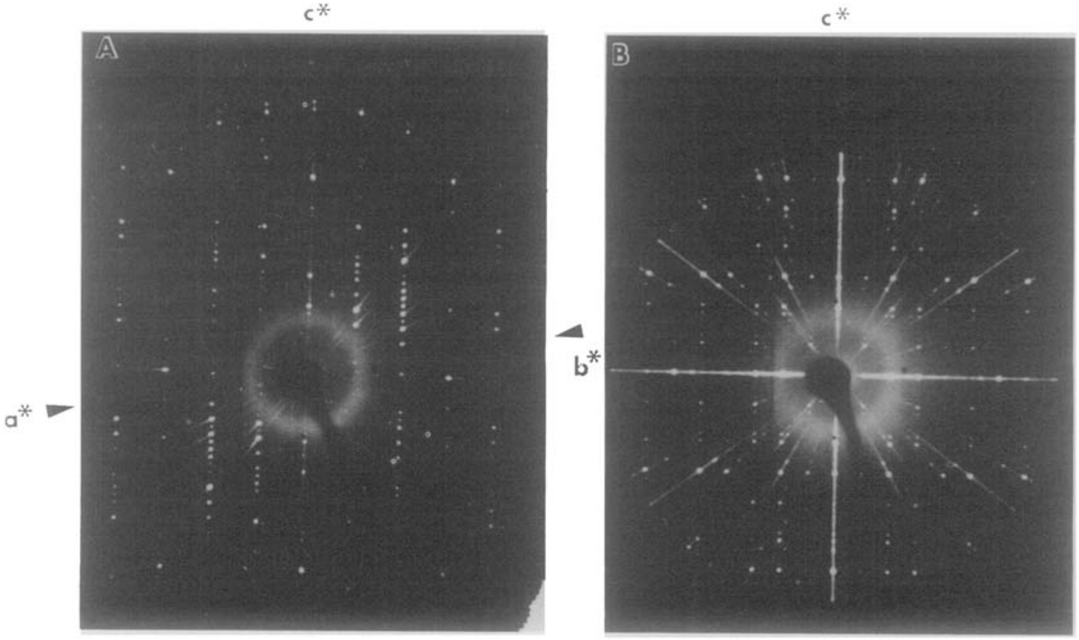

FIG. 6. Single crystal X-ray precession patterns (Mo radiation) of the 13-layer monoclinic phase, space group *C*2/*m*, most likely composition $Ba_{18}Ti_{54}Nb_2O_{132}$. A—(*h*0*l*), B—(0*kl*), upper level data not shown.

determined from single crystal X-ray precession patterns. Their compositions were derived by analogy to the compositions of the layers of the 4 : 13 and 6 : 17 phases. The compositions so determined are consistent with the data obtained from preparation, heat treatment, and X-ray powder diffraction patterns of a limited number of specimens. The four new phases were found to have 8-layer orthorhombic, 20-layer orthorhombic, 7-layer monoclinic, and 13-layer monoclinic lattices. Only the first $Ba_6Ti_{14}Nb_2O_{39}$ was obtained as an entirely single phase specimen. The exact compositions of the other three phases must await refinement of the crystal structure. The structure of all four of the new compounds will be examined by single crystal X-ray diffraction and reported in the near future.

Acknowledgments

The nature of the uninterpretable X-ray diffraction patterns of the specimens between 3 and 5 mole% Nb_2O_5 was first noted by J. M. Millet and this paper is a direct result of his original research findings. The five specimens listed in Table Ib were prepared by J. J. Ritter by hydrolyses of mixed ethoxide precursor solutions. The phase diagrams were prepared at NBS by American Ceramic Society Research Associates of the "Phase Diagram for Ceramists Data Center" using computer graphics in the style which will be used for future editions of the compliation series "Phase Diagrams for Ceramists."

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