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Phase Equilibria and Crystal Chemistry in the Ternary System BaO–TiO_2–Nb_2O_5, I

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A partial subsolidus phase diagram is presented of the BaO–TiO_2–Nb_2O_5 ternary system. Ten compounds or solid solutions in the ternary system are described. $BaTi_3Nb_4O_{17}$, $BaTi_5Nb_4O_{21}$, $BaTi_7Nb_4O_{25}$, and $BaTi_9Nb_4O_{29}$ belong to a chemically and structurally homologous series $AB_{2n+1}O_{4n+5}$ with $3 \leqq n \leqq 6$, the first member of which is isomorphous with $KTi_2Ta_5O_{17}$. They all crystallize in the orthorhombic system, space group *Cmcm* with essentially constant **a** and **b** parameters (**a** = 6.6, **b** = 8.9 Å). The **c** parameter varies approximately linearly with composition from 21.148 Å for $BaTi_3Nb_4O_{17}$ to 34.321 Å for $BaTi_9Nb_4O_{29}$. $BaTiNb_4O_{13}$, isomorphous with KTa_5O_{13}, could be considered as a member of the chemical series described above but it crystallizes in the orthorhombic system, space group *Pbcm* with unit cell parameters **a** = 5.640, **b** = 10.738, **c** = 16.488 Å. A nonstoichiometric phase with a composition close to $3BaO : 5TiO_2 : 3Nb_2O_5$ crystallizes in the monoclinic system, space group $P2_1/c$ with parameters **a** = 9.991, **b** = 9.970, **c** = 7.311 Å, β = 111°25′. Two other new phases are solid solutions extended on the quasi-binary join $BaTiO_3$–$Ba_5Nb_4O_{15}$. $Ba_8Ti_3Nb_4O_{24}$ ($Ba_8Ti_{3+5x/4}Nb_{4-x}O_{24}$ with $0 \leqq x \leqq 0.7$) crystallizes with a primitive hexagonal cell with parameters **a** = 5.794 and **c** = 18.868 Å. The other phase is an incommensurate solid solution which extends from $Ba_5Nb_4O_{15}$ to the end member compound $Ba_6TiNb_4O_{18}$ ($Ba_{5+x}Ti_xNb_4O_{15+3x}$ with parameters $0 \leqq x \leqq 1$) crystallizing in the rhombohedral system, space group *R*3*m*, parameters **a** = 5.765, **c** = 42.348 Å. The three solid solutions previously described, $Ba_3Ti_4Nb_4O_{21}$ ($Ba_3Ti_{4+5x}Nb_{4-4x}O_{21}$ with $0 \leqq x \leqq 0.3$), $Ba_6Ti_2Nb_8O_{30}$ ($Ba_{6-x}Ti_{2-2x}Nb_{8+2x}O_{30}$), and $BaTiO_3$ ($BaTi_{1-5x}Nb_{4x}O_3$ with $0 \leqq x \leqq 0.02$) were confirmed and further studied.

I. Introduction

Dielectric ceramics based on the $BaTiO_3$–TiO_2 system are characterized by high permittivity, high-temperature stability, and low dielectric losses. Other dielectric ceramics based on ternary systems with BaO and TiO_2, like BaO–TiO_2–Nd_2O_3 (*1*), have been shown to have similar properties. The BaO–TiO_2–Nb_2O_5 system which may contain ternary phases with interesting and useful properties has never been studied in detail. However, as Nb^{5+} is used as a donor dopant in ceramics based on $BaTiO_3$, a study was reported of the $BaTiO_3$ solid solution in terms of phase equilibria in the ternary system (*2*). The study of additions of Nb_2O_5 to the barium polytitanates is also of interest and is part of a general study undertaken on the influence of the addition

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of a third oxide to the polytitanates of barium (*3, 4*).

The phase equilibria diagrams of the three binary systems TiO_2–Nb_2O_5, BaO–Nb_2O_5, and BaO–TiO_2 have been reported previously (*5–7*). The only alteration needed for these binary systems is to the composition of the phase previously reported as 6BaO : $7Nb_2O_5$ (*6*). In the present work single crystals of this phase were grown and the unit cell was found to be similar to the high-temperature form of Ba Ta_2O_6, hexagonal **a** = 21.09, **c** = 3.98 Å. For reasons not yet known, this phase is nonstoichiometric in the BaO–Nb_2O_5 system and occurs not at 6:7 (53.85 mol% Nb_2O_5) but at approximately 53.5 mol% Nb_2O_5 or $Ba_{0.89}Nb_{2.04}O_6$.

In this work the ternary system BaO–TiO_2–Nb_2O_5 was investigated. The presence of two previously reported solid solutions (*8, 9*) was confirmed and the existence of many other compounds and solid solutions was noted. They have been identified and characterized and their stability relations in the system have been determined. It is known that BaO reacts with Pt (*10, 11*) and the high BaO portion of the system, therefore, could not be studied by the present methods. Although this portion of the phase diagram is not given, preliminary experiments on this portion of the system show complex phase equilibrium relations, not yet understood, and further studies in this area are continuing.

The addition of a small amount of Nb_2O_5 to the Ba-polytitanates causes abrupt shifts in many of the X-ray diffraction lines associated with these phases. Either the solid solutions associated with Nb^{5+} additions cause large deviations in the unit cell dimensions of the known phases with very complex shifts in the diffraction lines or one or more new phases replace those which occur in the binary system. Due to the complexity of this problem it is necessary to restudy this portion of the ternary system with specimens prepared by hydrolysis of mixed Ba–, Ti–, and Nb–alkoxide solutions as was previously done for the polytitanates (*12*), in order to obtain homogeneous distribution of very small amounts of Nb^{5+} ions. This study will be the subject of a future publication (*13*).

II. Experimental

The experimental equipment and the methods used have been discussed in previous works (*3–7*). The starting materials were titanium dioxide, barium titanate, barium carbonate, and niobium pentoxide, all of at least 99.9% purity. Appropriate proportions of the powdered materials were mixed and calcined above 1200°C for prolonged periods in platinum crucibles.

Attainment of equilibrium was tested by X-ray diffraction at room temperature after intermittent coolings and grindings. Equilibrium was judged to be obtained when no change was observed in the X-ray pattern of the composition between two heat treatments. The equilibration of the samples has been a problem in this study as some of the ternary compounds could be equilibrated only 10 or 20°C below their melting temperature. For this reason, a few compositions were prepared by hydrolysis of mixed metal–organic precursors, and, in general, equilibrium was obtained more easily than for solid state preparations. X-ray powder patterns of specimens were made using a high-angle goniometer and monochromatized Cu radiation. The scanning rate was $1/4°2\theta$/min. Unit cell dimensions were refined by a least-squares computer program based on parameters and symmetry elements obtained from single crystals. Single crystals of the ternary compounds were grown principally from solid plus liquid regions of the phase diagram for different compositions and have been investigated with an X-ray diffraction precession camera using Mo radiation.

III. Results and Discussion

The phase diagram $BaO-TiO_2-Nb_2O_5$ constructed on the basis of our X-ray diffraction analysis is shown in Fig. 1a. The complexity of the phase diagram makes it expedient to present separately several portions of it. Each of these regions, noted on the complete phase diagram (Fib. 1b) are shown on enlarged scale diagrams and discussed later in the paper. The region close to the polytitanates of barium, noted with an asterisk (*) in the phase diagram (Fig. 1b) is not presented here. Phase equilibria in this region are too complex, as at least four new phases were found containing 1–4 mol% Nb_2O_5. This part of the study will be published separately (*13*). The phase equilibria in the subsystem $BaO-BaTiO_3-Ba_5Nb_4O_{15}$ will be the subject of future study.

The compounds in the system are presented separately or together when they can be chemically or structurally related to each other. Samples of the compounds have been given to the Joint Committee for Powder Diffraction Standards at NBS and the indexed X-ray diffraction powder patterns will be published in the new journal, *Powder Diffraction* (*14*).

1. $Ba_3Ti_4Nb_4O_{21}$ Solid Solution

The existence of this solid solution, previously reported (*8*), was confirmed. $Ba_3Ti_4Nb_4O_{21}$ is characterized by a hexagonal $A_3M_8O_{21}$-like structure. The composition of the solid solution is $Ba_3Ti_{4+5x}Nb_{4-4x}O_{21}$ with x varying from 0 to 0.3. The solid solution, therefore, contains interstitial Nb^{5+} in a tricapped trigonal prism coordination. Parameters of the unit cell vary from 9.040 to 9.010 Å (precision: ±0.004 Å) for **a** and from 11.767 to 11.830 Å (precision ± 0.008 Å) for **c**. This phase is in equilibrium with the $Ba(Ti_{1-5x}Nb_{4x})O_3$ solid solution as well as with at least seven other phases in the system as shown in Fig. 1. However, the addition of Nb_2O_5 to $BaTiO_3$ in commercial ceramics will cause the appearance of this solid solution as a second phase if the solubility limit is exceeded and no compensation is made for nonstoichiometry.

2. $Ba_6Ti_2Nb_8O_{30}$ Solid Solution

This solid solution crystallizes in the tetragonal tungsten bronze structure (*9*). The limits of its composition, $Ba_{6-x}Ti_{2-2x}Nb_{8+2x}O_{30}$ with $0 \leqq x \leqq 0.5$, have been confirmed experimentally. Unit cell parameters do not vary significantly, **a** = 12.52 to 12.55 ± 0.01 Å and **c** = 4.005 to 3.995 ± 0.001 Å (*9*).

3. The Composition $3BaO:5TiO_2:3Nb_2O_5$

This composition is very close to a single phase although the exact composition of the phase has not been determined exactly. The X-ray powder pattern of the $3BaO:5TiO_2:3Nb_2O_5$ composition shows the presence of a very small amount of TiO_2 with this phase.

A single crystal of this phase, obtained from the melt at 1340°C of a sample with the bulk composition $7BaO:5TiO_2:8Nb_2O_5$, was used to determine the unit cell parameters and symmetry. It crystallizes in the monoclinic system, space group $P2_1/c$ with parameters **a** = 9.999; **b** = 9.970; **c** = 7.311 Å; β = 111°25′. The compound is pseudo-orthorhombic and the X-ray diffraction powder pattern can be completely indexed on the basis of a *Bmcm* space group **a** = 18.64, **b** = 9.97, **c** = 7.31 Å, although the true symmetry is monoclinic. From the study of the $3BaO:5TiO_2:3Nb_2O_5$ composition, the melting point of this phase should be close to 1400°C. This is apparently the same phase reported by Gasperin (*15*) as $Ba_2Ti_3Nb_4O_{18}$. Although the composition reported by Gasperin is derived from

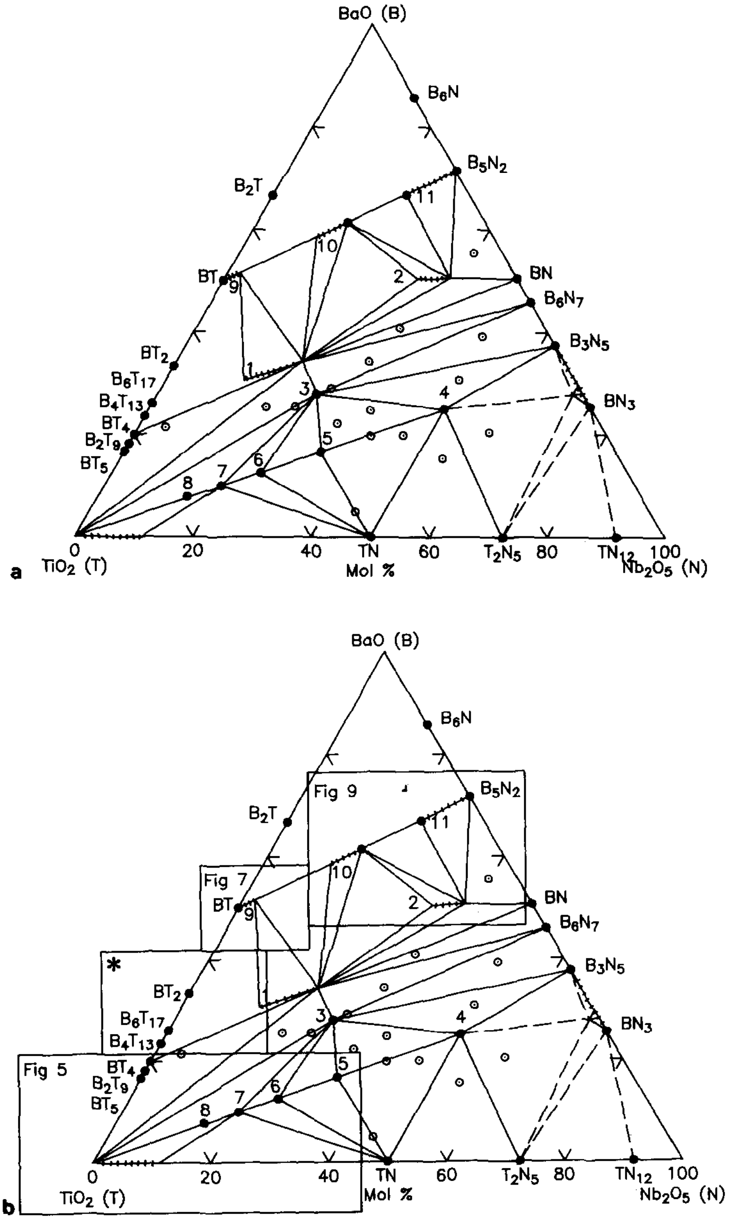

FIG. 1. (a) Phase diagram of a portion of the system $BaO-TiO_2-Nb_2O_5$. $BT_9N_2 = BaTi_9Nb_4O_{29}$, BN = $BaNb_2O_6$, etc. Crosshatched lines, solid solutions; light lines, tie lines between compounds; dashed lines, nonconfirmed equilibria. 1, $B_3T_4N_2$ ss; 2, $B_6T_2N_4$ ss; 3, "$B_3T_5N_3$"; 4, BTN_2; 5, BT_3N_2; 6, BT_5N_2; 7, BT_7N_2; 8, BT_9N_2; 9, BT ss; 10, $B_8T_3N_2$ ss; 11, (B_6TN_2–B_5N_2) ss. (b) The enlarged scale figures that are presented in Figs. 5, 7, and 9 are represented as well as the part of the diagram (noted *) which will be given in Part II (*13*). ●, ⊙, Compounds and compositions studied in the system.

TABLE I

PARAMETERS OF UNIT CELLS OF FOUR COMPOUNDS

Compounds	**a** (Å)	**b** (Å)	**c** (Å)	L	ρ/cal (g/cm^3)	Preparation of single crystals	Temperature of melting
$BaTi_3Nb_4O_{17}$	6.636 ± 0.001	8.972 ± 0.001	21.148 ± 0.003	10	4.87	Partial melt of $3BaO : 10TiO_2 : 7Nb_2O_5$ at 1350°C	1377 ± 3°C
$BaTi_5Nb_4O_{21}$	6.631 ± 0.003	8.947 ± 0.002	25.532 ± 0.012	12	4.75	$BaO : 5TiO_2 : 2Nb_2O_5$ composition fired at 1330°C with 5 wt% BaF_2 as flux resulted in crystals of $BaTi_9Nb_4O_{29}$	1352 ± 3°C
$BaTi_7Nb_4O_{25}$	6.601 ± 0.002	8.908 ± 0.002	29.96 ± 0.01	14	4.69	Partial melt of $BaO : 5TiO_2 : 2Nb_2O_5$ at 1355°C	1357 ± 3°C
$BaTi_9Nb_4O_{29}$	6.626 ± 0.001	8.965 ± 0.001	34.32 ± 0.01	16	4.57	Partial melt of $BaO : 6TiO_2 : 2Nb_2O_5$ at 1360°C	1362 ± 3°C

a structural formula a specimen with the 2 : 3 : 2 ratio always shows a small amount of both $Ba_3Ti_4Nb_4O_{21}$ and the "6 : 7" BN phase. Apparently this compound is always slightly nonstoichiometric, resulting in a phase which is always Ba-poor and (Ti + Nb)-rich (3 : 5 : 3 = $Ba_{1.928}Ti_{3.214}Nb_{3.857}O_{18}$).

4. *The Compound $BaTiNb_4O_{13}$*

The compound $BaTiNb_4O_{13}$ melts at 1275 ± 5°C and crystallizes in the orthorhombic system, space group *Pbcm* with parameters $\mathbf{a} = 5.640 \pm 0.002$; $\mathbf{b} = 10.738 \pm 0.004$; $\mathbf{c} = 16.488 \pm 0.005$ Å. Calculated density is 5.08 g/cm^3 ($Z = 4$). This unit cell and space group are similar to those of KTa_5O_{13} (*16*). Neutron powder diffraction Rietveld analysis has confirmed that $BaTiNb_4O_{13}$ is isomorphous with KTa_5O_{13} (*17*). $BaTiNb_4O_{13}$ could be considered as a member of the "chemical" homologous series $AB_{2n+1}O_{4n+5}$ ($n = 2$) although it is not a member of the "structural" homologous series of the same formula. It is interesting to note that the **c** parameter of $BaTiNb_4O_{13}$ can be related to the **c** parameters of the compounds in the structural series (see below).

5. *The Chemical and Structural Homologous Series $AB_{2n+1}O_{4n+5}$ ($3 \leqq n \leqq 6$)*

Four compounds which are members of this series have been found: $BaTi_3Nb_4O_{17}$ (1 : 3 : 2), $BaTi_5Nb_4O_{21}$ (1 : 5 : 2), $BaTi_7Nb_4O_{25}$ (1 : 7 : 2), and $BaTi_9Nb_4O_{29}$ (1 : 9 : 2). All crystallize in the orthorhombic system, space group *Cmcm*. Parameters of the unit cells of these compounds are shown in Table I. They have been determined by an X-ray study of single crystals and were refined from powder X-ray diffraction data by a least-squares computer technique. Compositions and temperatures used to grow single crystals of each phase are also given in Table I. The different compositions studied and the suggested equilibria are presented in a large-scale representation of a portion of the ternary phase diagram (Fig. 2). A phase equilibrium diagram is proposed in Fig. 3 for the portion of the quasi-binary system $TiO_2-BaTi_3Nb_4O_{17}$ in which all the compounds occur. In this figure, a thermal cut (1340–1390°C) is given of the region of the ternary phase diagram considered. It

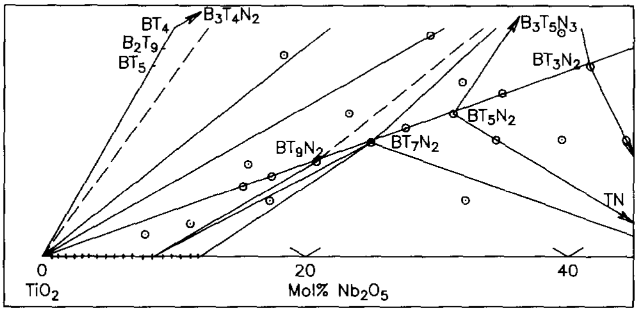

FIG. 2. Enlarged scale portion of the $BaO-TiO_2-Nb_2O_5$ system showing phase equilibria between the compounds of the homologous series $AB_{2n+1}O_{4n+5}$ ($3 \leq n \leq 6$) and the other ternary compounds at ~1350°C. The crosshatched line represents the TiO_2 solid solution in the binary system $TiO_2-Nb_2O_5$. Light lines represent tie lines between compounds and dashed lines, nonconfirmed tie lines. The different compositions studied are reported as ⊙, TiO_2 = T, Nb_2O_5 = N, BaO = B, BT_9N = $BaTi_9Nb_4O_{29}$, etc.

shows the phase relations between the compounds and the other phases, as well as the compositions studied. The **c** parameters of these compounds increase approximately linearly by 4.25 Å when the molar amount of TiO_2 increases by an addition of 2. This increase corresponds, for the close-packed layer structure of these compounds, to two layers of oxygens. However, the **a** and **b** axes as well as the space group of $BaTi_3Nb_4O_{17}$, $BaTi_5Nb_4O_{21}$, $BaTi_7Nb_4O_{25}$, and $BaTi_9Nb_4O_{29}$ are different from those of

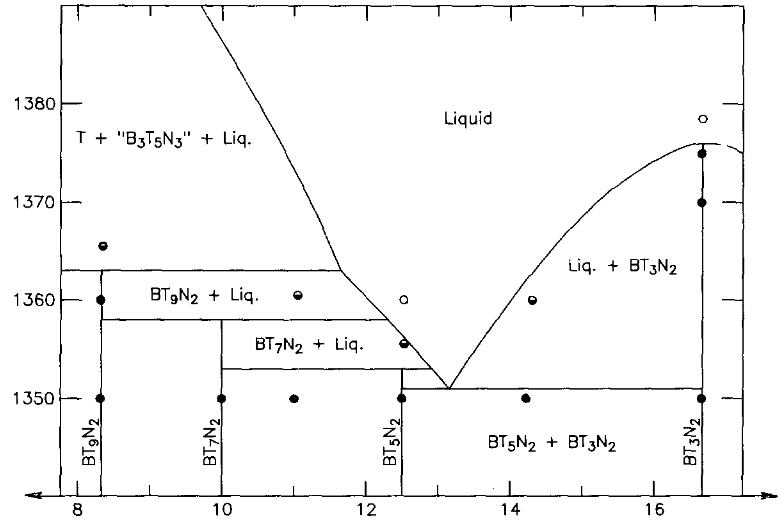

FIG. 3. Portion of the postulated phase diagram for the quasi-binary system $TiO_2-BaTi_3Nb_4O_{17}$ in which all the compounds of the $AB_{2n+1}O_{4n+5}$ structural homologous series are present. The phase diagram has been constructed with a very limited number of experimental data points indicated in the figure: ●, not melted; ◒, partially melted; ○, completely melted. TiO_2 = T; $BaTi_9Nb_4O_{29}$ = BT_9N_2; $BaTi_7Nb_4O_{25}$ = BT_7N_2; etc.

$BaTiNb_4O_{13}$ and the phase KTa_5O_{13} (*16*), which have structures based on a "chemical twinning" of the α-PbO_2-type structure. These four new compounds must be compared instead to the structure of $KTi_2Ta_5O_{17}$ (*18*) with which $BaTi_3Nb_4O_{17}$ is isomorphous and $KTi_6Nb_5O_{25}$ (*19*) isomorphous with $BaTi_7Nb_4O_{25}$. If the structure of $BaTiNb_4O_{13}$ can be thought of as an eight-layer "chemically twinned" α-PbO_2 structure, as shown in (*16*), and $BaTi_3Nb_4O_{17}$ as a 10-layer "chemically twinned" rutile structure then the other three related phases are 12-, 14-, and 16-layer TiO_2-type phases (see Table I for unit cell dimensions). Neutron powder diffraction Rietveld analysis has confirmed this structure for $BaTi_3Nb_4O_{17}$ (*17*). The other compounds have structures which can be generated by the addition of two TiO_2 layers per compound to the previous member of the series. As yet, no similar series of phases has been synthesized with structures related to the KTa_5O_{13} structure. Gatehouse (*16, 18*) has pointed out that KTa_5O_{13} ($BaTiNb_4O_{13}$) is related to the α-PbO_2 type structure and ($KTi_2Ta_5O_{17}$) ($BaTi_3Nb_4O_{17}$) is related to the rutile structure. It may be possible to synthesize a series of phases related to the $BaTiNb_4O_{13}$ structure by substituting ZrO_2 for one-half of the TiO_2 in the 10-, 12-, 14-, and 16-layer compositions, as $ZrTiO_4$ has the α-PbO_2-type structure. The system $BaO-TiO_2-ZrO_2-Nb_2O_5$ is currently being studied and results will be reported in the near future. These compounds rich in titanium and niobium could present interesting properties similar to those of the polytitanates of barium (*12, 20*) and be useful as dielectric materials.

6. The Quasi-binary System $BaTiO_3-Ba_5Nb_4O_{15}$

6.1. The $BaTiO_3$ solid solution. Jonker and Havinga have previously studied the $BaTiO_3$ solid solution in the system $BaO-TiO_2-Nb_2O_5$ (*2*). They noted that at low temperature (1200°C) the solid solution is extended on the join to $Ba_5Nb_4O_{15}$ as the addition of niobium is completely compensated by the occurrence of Ti vacancies. At higher temperature (1350°C) they observed the maximum of extension of the solid solution in the direction of the composition $2BaO:Nb_2O_5$ (not a compound) and explained it as a mixed compensation by Ti and Ba vacancies.

This result has not been confirmed by our experiments. We observed at 1350°C a solid solution in the direction of the compound $Ba_5Nb_4O_{15}$ considerably greater than the amount toward $2BaO:Nb_2O_5$. The end-point of the solid solution on the join was found to correspond at 1350°C approximately to an atomic ratio of $Nb/Nb + Ti = 0.0844$. The compensation mechanism involving the substitution of Nb^{5+} for Ti^{4+} is apparently the formation of Ti vacancies at all temperatures of stability of the solid solution. This was confirmed by refinement of the neutron powder diffraction pattern of a specimen with 2.25 mol% Nb_2O_5, corresponding to $BaTi_{0.891}Nb_{0.087}O_3$ (Ti vacancies $= 0.022$). The different compositions studied and the suggested phase equilibria are presented in a large-scale representation of a portion of the phase diagram (Fig. 4). In Fig. 5 the variation of the cubic cell parameter of the solid solution is shown. X-ray diffraction powder patterns of the two compositions with the higher content of Ti on the join after firing at 1500°C show only the cubic form. This polymorph is stabilized in the ternary system even at higher temperature. No sign of the six-layer hexagonal polymorph of $BaTiO_3$ was found in the ternary solid solutions.

6.2. The $Ba_8Ti_3Nb_4O_{24}$ solid solution. The compound $Ba_8Ti_3Nb_4O_{24}$ has not been reported previously. This new compound can be observed easily by X-ray diffraction studies of compositions between the end member of the $BaTiO_3$ solid solution and

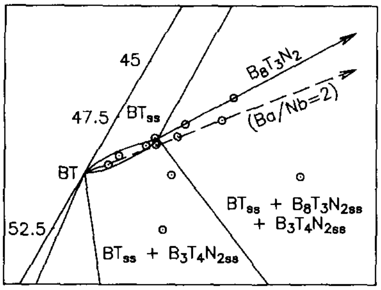

FIG. 4. Enlarged scale region of an isothermal cut at 1350°C of the phase diagram of the system $BaO-TiO_2-Nb_2O_5$ containing the $BaTiO_3$ solid solution (BT_{ss}) BT = $BaTiO_3$, $B_8T_3N_2$ = $Ba_8Ti_3Nb_4O_{24}$, etc. Compositions on the binary $BaO-TiO_2$ are given in mol%. ⊙, Compositions studied.

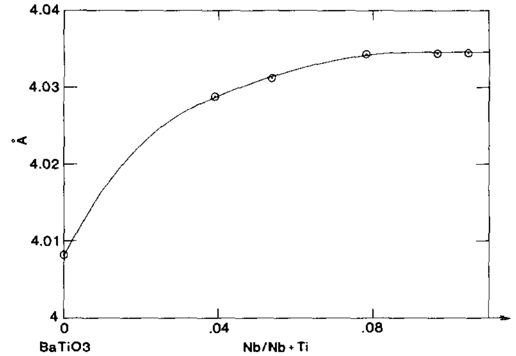

FIG. 5. Variation of the cubic cell parameter of $BaTiO_3$ solid solution, on the join toward $Ba_5Nb_4O_{15}$.

the compound $Ba_6TiNb_4O_{18}$ fired at 1400°C (Fig. 6). It forms a solid solution on the quasi-binary join extended in the direction of the $BaTiO_3$ solid solution: $Ba_8Ti_{3+5x/4}Nb_{4-x}O_{24}$ with $0 \leqq x \leqq 0.7$. Only twinned crystals were obtained from melted or partially melted specimens from compositions near this phase. From these twinned crystals and the X-ray powder diffraction data it was found that the phase crystallizes in the hexagonal system with a primitive cell of **a** = 5.7944 ± 0.0005 Å and **c** = 18.868 ± 0.003 Å. Rietveld analysis of neutron powder diffraction patterns was used to solve the structure of the compound $Ba_8Ti_3Nb_4O_{24}$ (*21*).

6.3. The $Ba_5Nb_4O_{15}$–$Ba_6TiNb_4O_{18}$ solid solution. It has been shown that the binary compound $Ba_5Nb_4O_{15}$ crystallizes in the trigonal system, space group *P*3*m*1 with parameters **a** = 5.776 Å and **b** = 11.82 Å (*6*).

In the ternary system, substitution of Ti^{4+} for Nb^{5+} changes this structure and gives rise to an incommensurate rhombohedral solid solution which extends in the direction toward $BaTiO_3$ from $Ba_5Nb_4O_{15}$ to the end-member compound $Ba_6TiNb_4O_{18}$ ($Ba_{5+x}Ti_xNb_4O_{15+3x}$ with $0 \leqq x \leqq 1$). This phase crystallizes in the rhombohedral system, space group *R*3*m* parameters **a** = 5.7645, **c** = 42.348 Å (Fig. 7). The incommensurate vector of the rhombohedral solid solution varies continuously between its two end members. This variation can be seen by the variation of angular position of the two diffraction peaks labeled (018) and (107) in the X-ray diffraction powder patterns of different compositions prepared at 1400°C (Fig. 8) and in the single-crystal pat-

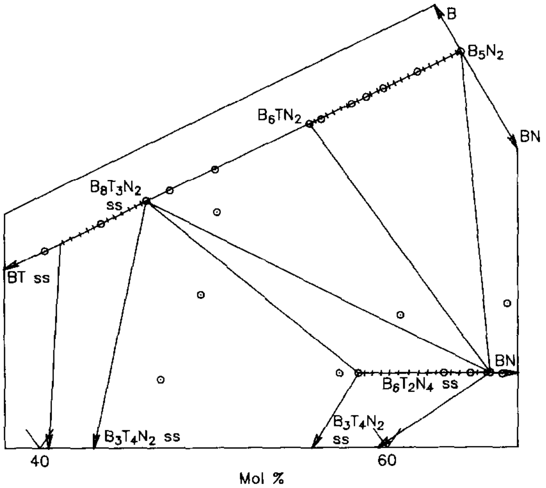

FIG. 6. Enlarged scale portion of the phase diagram containing the $B_8T_3N_2$ solid solution, the $B_6T_2N_4$ solid solution, and the (B_6TN_2–B_5N_2) incommensurate solid solution; B = BaO; T = TiO_2; N = Nb_2O_5.

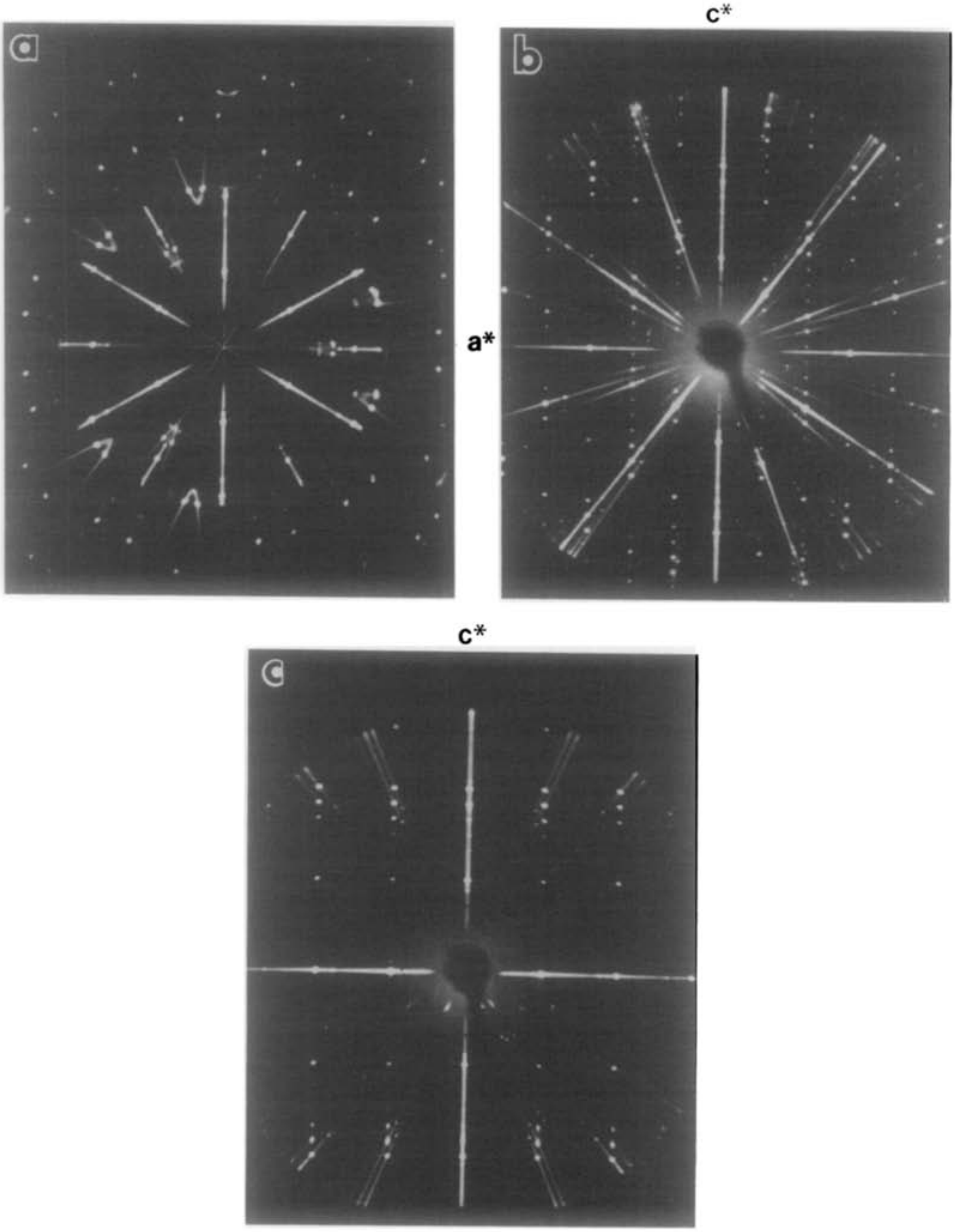

FIG. 7. X-ray diffraction single-crystal precession photographs (unfiltered Mo radiation) of the compound $6BaO \cdot TiO_2 \cdot 2Nb_2O_5$ ($Ba_6TiNb_4O_{18}$) rhombohedral space group *R*3*m*. (a) Unscreened [*hh*0] showing threefold axes of symmetry. (b) [*h*0*l*]. (c) [*hhl*].

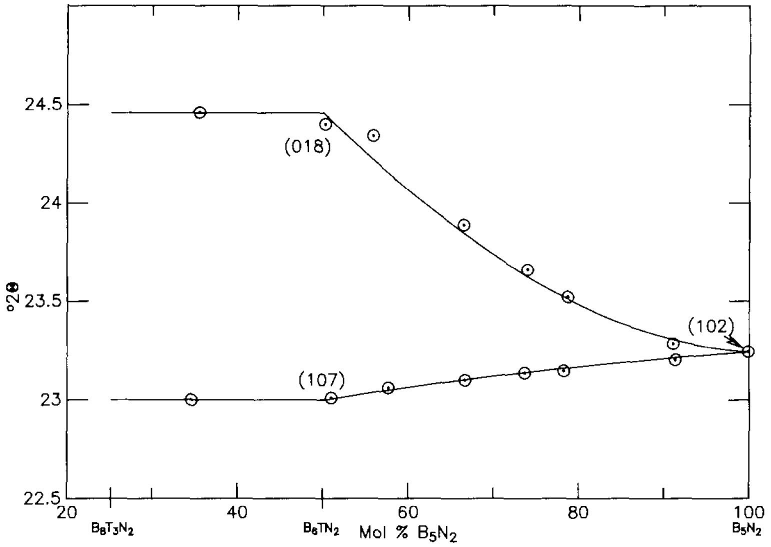

FIG. 8. Variation of the angular position (°2Θ) of two peaks corresponding to the planes (107) and (018) for $Ba_6TiNb_4O_{18}$ of the X-ray powder patterns of the compositions of the incommensurate solid solution (B_6TN_2–B_5N_2). B = BaO; T = TiO_2; N = Nb_2O_5.

terns from the incommensurate solid solution (Fig. 9). The structure of $Ba_6TiNb_4O_{18}$ was postulated by its relation to the structure of $Ba_5Nb_4O_{15}$ and was refined by neutron powder diffraction Rietveld analysis (*21*). High-resolution electron microscope lattice images show a disordered array of the two structures in the region of the incommensurate solid solution.

Conclusion

In the ternary system BaO–TiO_2–Nb_2O_5, ten ternary compounds or solid solutions have been identified. Data are reported on their synthesis, fields of stability, crystal chemistry and structure. Based upon compositions containing high (Ti + Nb)/Ba ratios, four of them are expected to have dielectric properties comparable to those of the polytitanates of barium. These are members of a chemically and structurally homologous series, $AB_{2n+1}O_{4n+5}$ with $3 \leqq n \leqq 6$. They have respectively the compositions $BaTi_3Nb_4O_{17}$ (T_f = 1377 ± 3°C), $BaTi_5Nb_4O_{21}$ (T_f = 1352 ± 2°C), $BaTi_7Nb_4O_{25}$ (T_f = 1357 ± 3°C), $BaTi_9Nb_4O_{25}$ (T_f = 1362 ± 3°C). $BaTiNb_4O_{13}$ (T_f = 1275 ± 5°C), which could be considered a member of the chemical series, has a different type of structure, isomorphous to KTa_5O_{13}.

Another compound with a composition close to 3BaO : $5TiO_2$: $3Nb_2O_5$ was also characterized as a nonstoichiometric phase with the structural formula $Ba_2Ti_3Nb_4O_{18}$. The existence of the $Ba_3Ti_4Nb_4O_{21}$ (*8*) and $Ba_6Ti_2Nb_8O_{30}$ (*9*) solid solutions has been confirmed, as well as the $BaTiO_3$ ternary solid solution reported by Jonker and Havinga (*2*). However, in contrast to these authors, it was found that the maximum of extension of the solid solution in the ternary system is on the join to $Ba_5Nb_4O_{15}$ rather than on the join to 2BaO : Nb_2O_5. In $BaTiO_3$ the solid solution addition of niobium is apparently completely compensated by the occurrence of Ti vacancies.

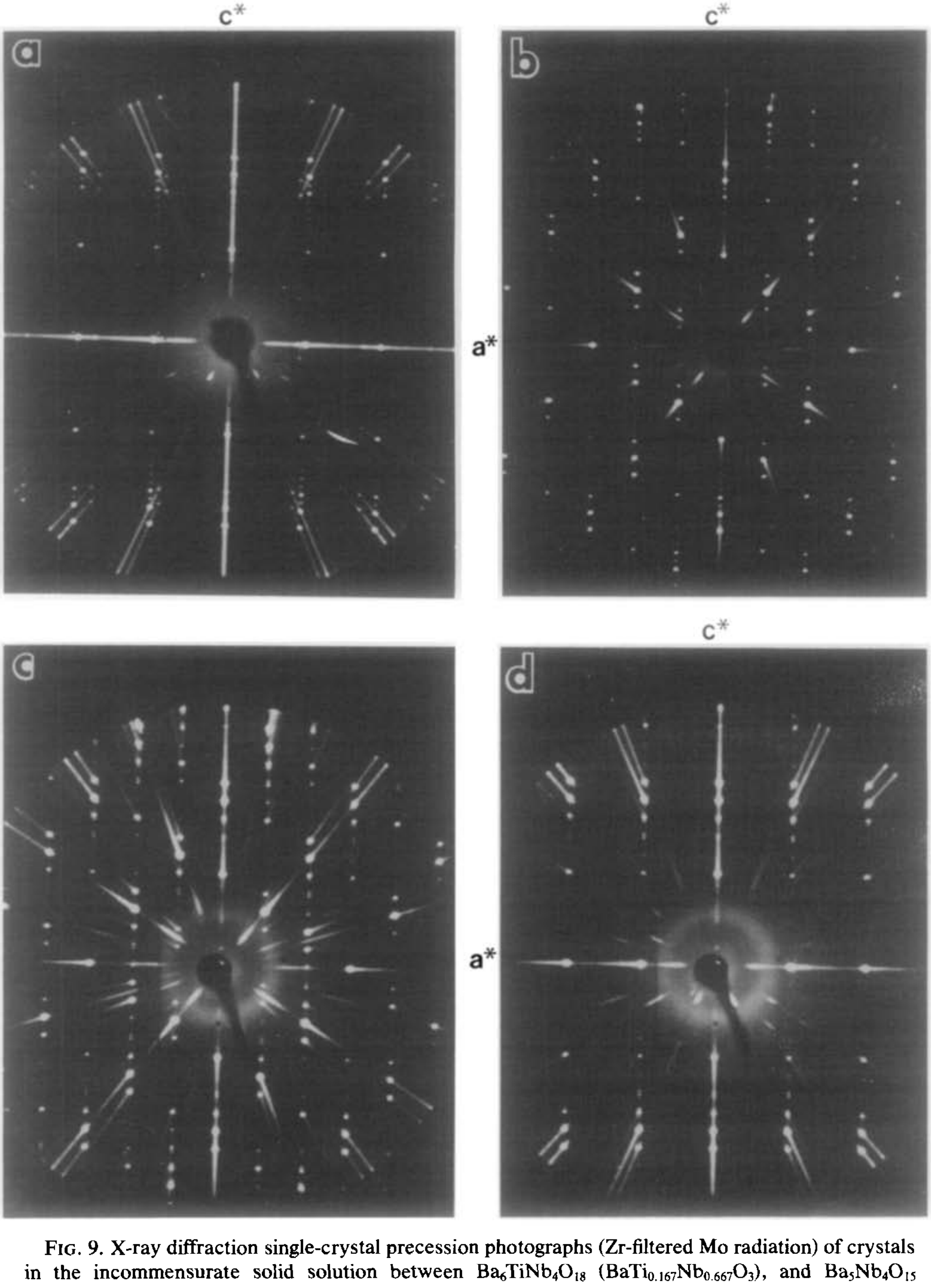

FIG. 9. X-ray diffraction single-crystal precession photographs (Zr-filtered Mo radiation) of crystals in the incommensurate solid solution between $Ba_6TiNb_4O_{18}$ ($BaTi_{0.167}Nb_{0.667}O_3$), and $Ba_5Nb_4O_{15}$ ($BaNb_{0.8}O_3$). (a) $39BaO : 4TiO_2 : 14Nb_2O_5$ ($BaTi_{0.103}Nb_{0.718}O_3$) [*hhl*]; (b) 39 : 4 : 14 [*h*0*l*]; (c) $69BaO : 4TiO_2 : 26Nb_2O_5$ ($BaTi_{0.058}Nb_{0.754}O_3$) [*hhl*]; (d) 69 : 4 : 26 [*h*0*l*].

On the quasi-binary join from $BaTiO_3$ solid solution to $Ba_5Nb_4O_{15}$ two new distinct solid solutions have also been found. The $Ba_8Ti_3Nb_4O_{24}$ solid solution is extended in the direction of $BaTiO_3$: $Ba_8Ti_{3+5x/4}Nb_{4-x}O_{24}$ with $0 \leqq x \leqq 0.7$. The $Ba_5Nb_4O_{15}$–$Ba_6TiNb_4O_{18}$ solid solution is an incommensurate solid solution with the two compounds $Ba_5Nb_4O_{15}$ and $Ba_6TiNb_4O_{18}$ as end members. The high BaO portion of the system is not presented in this work and further studies on the subsystem BaO–$BaTiO_3$–$Ba_5Nb_4O_{15}$ are continuing. The complexity of the phase equilibria in the portion of the ternary system near the polytitanates of barium has required further study, and the results obtained have made it necessary to present these data in a future publication (Part II) (*13*).

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