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Reactions of the Group VB Pentoxides. VIII. Thermal, Density and X-Ray Studies of the Systems $KNbO_3$–$NaNbO_3$ and $KTaO_3$–$KNbO_3$

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RECEIVED OCTOBER 2, 1957

The heterogeneous equilibria in the system $KNbO_3$–$NaNbO_3$ have been investigated using differential thermal analysis, density and X-ray techniques. The system was found to exhibit continuous solid solution in all phases, and an explanation is offered to account for absence of expected miscibility gap behavior. Certain ambiguities in previous work have been clarified and, on the basis of the results a discontinuous transition from antiferroelectric to ferroelectric states is postulated, consistent with a theory of "interaction isomorphism." Previously determined unit cell volume variations in the mixed phases have been verified using refined powder density measuring techniques. In order to compare two solid solutions, one of which would be expected to be more nearly ideal than the other, a density phase diagram of the $KTaO_3$–$KNbO_3$ system has been constructed. In addition, the phase transformations of this system have been traced with DTA until they approach second order.

Introduction

In 1954 Shirane, *et al.*,[3] investigated the solid state equilibria in the system $KNbO_3$–$NaNbO_3$ using X-ray, dielectric and optical techniques. The phase diagram obtained is reproduced in Fig. 1 and 2a. One of the interesting aspects of this system is that $NaNbO_3$ exhibits three, and $KNbO_3$ two, phase transformations above room temperature. Although the previous investigators were aware of the three $NaNbO_3$ transformations, the constructed diagram, Fig. 1, accounts for only two of them. Figure 2a is based on light optical measurements of mixed single crystals of uncertain composition and also fails to clarify the $NaNbO_3$ four phase interaction.

In a recent study of the polymorphism of $NaNbO_3$ using differential thermal analysis,[4] an attempt was made to resolve some of the ambiguities concerning its phase changes. Above room temperature, the material was found to exhibit first-order phase transformations at 354, 562 and 640°, the latter two being extremely sensitive to mechanical treatment. In view of the thermal data, a reinterpretation of Francombe's X-ray results[5] indicates that the structure of $NaNbO_3$ is orthorhombic from r.t. to 354°, "pseudotetragonal" from 354 to 562°, tetragonal from 562–640° and cubic above 640°. As the sodium salt is antiferroelectric at r.t., its unit cell is a multiple of the distorted perovskite structure.[6] This multiplicity continues up to the 640° transition, as evidenced by the persistence of the misnamed superlattice or extra lines observed by Francombe and previous workers.[3,6,7] Since $KNbO_3$ and $NaNbO_3$ are not, therefore, crystallographically or electrically isomorphic, regions of heterogeneity might be expected in the mixed phases. However, Shirane and co-workers were unable to detect any miscibility gap behavior, an apparent inconsistency with their observations that small additions of $KNbO_3$ to the $NaNbO_3$ caused the resulting solid solution to become ferroelectric.

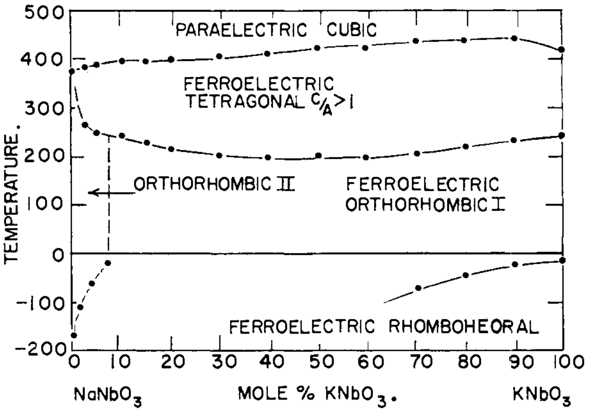

Fig. 1.—Phase diagram of system $KNbO_3$–$NaNbO_3$ after data of Shirane, *et al.*[3]

The previous efforts have been concerned only with the solid state characteristics of the mixed system. In this the eighth paper dealing with the chemistry of the Group VB pentoxides and their interesting alkali metal salts an attempt has been made to resolve the solid–liquid equilibria, as well as to add to the extant information concerning the solid–solid equilibria. It is believed that this study is of interest because it involves the effect on over-all solid solution caused by different types of distortions of a basic unit cell in the two interacting materials. In order to show comparison between two solid solution systems, one of which would be expected to be more nearly ideal than the other, a density phase diagram of the system $KTaO_3$–$KNbO_3$ also has been determined.

Experimental Procedure

1. **Reagents.**—Nb_2O_5 and Ta_2O_5 were obtained from the Fansteel Metallurgical Company. The Nb_2O_5 was reported to contain 0.2% Ta, and the Ta_2O_5 0.001% TiO_2 as the major contaminant. Both oxides were ignited at 1100° for 24 hr. and stored in a desiccator prior to use. Reagent grade Mallinkrodt Na_2CO_3 and K_2CO_3 dried at 400° for 4 hr. served as the basic components in the reactions.

2. **Sample Preparation.** (a) **DTA Cooling Curves.**—Samples were weighed so as to provide 8 grams of charge after completion of reaction. The components were weighed in a glass vial, rolled for 15 minutes, loaded into 10-cc. platinum crucibles, placed in position in the DTA furnace at room temperature and finally heated at 100°/hr. until molten. The relatively slow rate of temperature rise enabled the reactions to proceed smoothly with a minimum of

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[1] This paper represents a second part of a thesis submitted by A. Reisman to the graduate school of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] G. Shirane, R. Newnham and R. Pepinsky, *Phys. Rev.*, **96**, 581 (1954).

[4] A. Reisman, F. Holtzberg and E. Banks, THIS JOURNAL, **80**, 37 (1958).

[5] M. H. Francombe, *Acta Cryst.*, **9**, 256 (1956).

[6] P. Vousden, *ibid.*, **4**, 545 (1951).

[7] E. A. Wood, *ibid.*, **4**, 353 (1951).

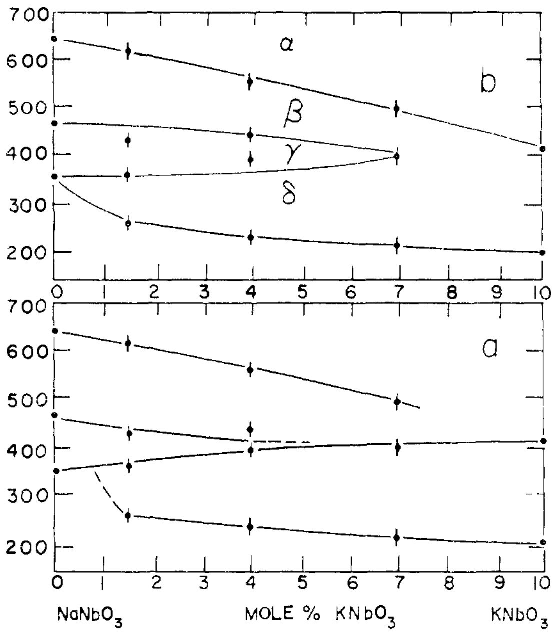

Fig. 2.—Phase diagram of system $KNbO_3$–$NaNbO_3$, 0–10 mole % $NaNbO_3$: a, construction of Shirane, *et al.*;[3] b, proposed construction using data of ref. 3.

spattering, since the observed excess weight loss on duplicate samples never exceeded 4 mg. When the samples had become molten, the temperature was raised an additional 20–30° and the thermocouples and bubbling apparatus were inserted.

(b) **High Temperature D.T.A. Heating Curves, Density Measurements.**—Samples suitable for solidus studies and density measurements must be completely reacted and homogeneous. The charges, weighed and mixed as described, were fired three times at temperatures 25–50° below the melting region as determined from preruns. The cycling was performed at 100°/hr. rates with 24 hr. soakings at the maximum temperatures. Prior to each reheating, the reaction mixtures were ground for 15 minutes in mullite.

(c) **Sub-solidus DTA Heating Curves, X-Ray Analysis.**—As previously reported,[4] the phase changes in $NaNbO_3$ result in appreciable strain of the crystallites. A preliminary survey of the $KNbO_3$–$NaNbO_3$ system indicated similar behavior, and rather special treatment of the samples was required. After an initial preparation as described in section 2b, the charges were soaked at the maximum firing temperature for three days and then cooled at 25°/hr. to r.t. They were then pulverized slightly, loaded into 1-cc. platinum crucibles which were set into the DTA furnace with the thermocouples in position. The samples were recycled until the transitions became sharp and reproducible. This procedure required anywhere from 7–20 cycles at 1°/minute, each cycle consuming at least one day. After the DTA data had been obtained, the materials were used for X-ray examination after a minimum of pulverization.

3. **Differential Thermal Analysis.**—The apparatus used for studying the liquidus, solidus and transformation temperatures have been described previously[4,8–11] and were used with only one modification. Because of the small latent heats involved in the phase transformations, the differential signals were amplified up to 50×, which meant that these signals were recorded on a 10 inch chart with a 50 μv. full scale range. The noise at this gain was approximately 0.1 μv. Since the problems of noise, pickup and methods for achieving high level amplifications of DTA signals are of general interest, these topics will be discussed in a separate publication.

4. **Density Measurements.**—The powder density measuring apparatus and basic technique have been previously described.[4,10] Great care was exercised in the drying of samples prior to weighing, which resulted in precisions of ±0.005 g./cm.^{3} at 25° as compared to the previous limit of ±0.01 g./cm.^{3} at the same temperature.

5. **X-Ray Analysis.**—All X-ray measurements were made with N. A. Philips powder and diffractometer equipment using both filtered and unfiltered Cu radiation. The unfiltered examinations were conducted in order to readily distinguish between Kβ radiation and the multiple unit cell lines of $NaNbO_3$.

Discussion of Experimental Results

The thermal and density data obtained in this investigation are given in Tables I–II. The proposed equilibrium diagrams based on these results are depicted in Figs. 3–7.

A. **The System $KNbO_3$–$NaNbO_3$.**—The high temperature phase diagram of the system $KNbO_3$–$NaNbO_3$, Fig. 3, shows continuous solid solution over the entire composition range. Although the liquidus is quite regular, the solidus shows a marked humping on the high $NaNbO_3$ side. The freezing point of $NaNbO_3$ was found to be 1422° and of $KNbO_3$ 1060°. As mentioned, a pertinent feature of this system is that it involves the interaction of ferro- and antiferroelectric end members. If one considers an isolated perovskite unit cell of each material, and then examines the structural modifications accompanying passage through the different transitions, each successive distortion can be related to the original cell. In the case of the ferroelectric, $KNbO_3$, in addition to slight elongations of crystal axes and minor deviations from orthogonality, the characterizing feature is that there is an undirectional shift of the heavy atom relative to certain other atoms. Thus, with the onset of polarization each original cell undergoes an identical distortion. The antiferroelectric situation is, however more complicated, because in addition to the axial and angular variations it has been deduced in the case of $NaNbO_3$[6] that alternate pairs of niobium atoms are displaced an equal amount in opposite directions. Such behavior requires the choice of a multiple unit cell with one of the axes approximately four times the length of the unperturbed perovskite cell. This multiplicity would be expected to cause miscibility gap behavior in the solid interaction, since crystallographically and electrically the reactants are not isomorphic. Shirane, *et al.*,[3] were aware of this possibility and mention in their paper that "The extra lines observed in the X-ray powder photographs of $NaNbO_3$ indicated structural differences in the orthorhombic phases of this crystal ($NaNbO_3$) and $KNbO_3$, hence there must be a separating phase line somewhere in the $KNbO_3$–$NaNbO_3$ solid solution." Extending this further it is to be remembered that Francombe observed that the "extra lines" in $NaNbO_3$ persisted up to the tetragonal-cubic transition, and thus if the previous reasoning is employed it would not be unreasonable to expect miscibility gaps throughout all the mixed system solid phases.

The entire matter can, however, be considered from a different viewpoint. Returning to the discussion of the distortions accompanying the phase changes of $NaNbO_3$ and $KNbO_3$, it has been ade-

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(8) A. Reisman and F. Holtzberg, THIS JOURNAL, **77**, 2115 (1955).

(9) A. Reisman, S. Triebwasser and F. Holtzberg, *ibid.*, **77**, 4228 (1955).

(10) A. Reisman, F. Holtzberg, M. Berkenblit and M. Berry, *ibid.*, **78**, 4514 (1956).

(11) F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, *ibid.*, **79**, 2039 (1957).

TABLE I

THERMAL DATA FOR THE SYSTEMS $KNbO_3$–$NaNbO_3$ AND $KTaO_3$–$KNbO_3$

System $KNbO_3$–$NaNbO_3$

$KNbO_3$, mole %	Transitions	Solidus	Liquidus
0	354		1422
	562		
	640		
1	344		
	523		
	622		
1.5	340		
	515		
	618		
2.5	321		
	342		
4	293		
	408		
	567		
5	270		
	372		
	523		
7	243		
	427		
7.5	230		
	392		
10	199	1308	1400
	390		
20	191	1232	1370
	380		
25	177	1206	
	381		
30			1341
40	174	1162	1302
	393		
50		1139	1267
60	180	1114	1228
	399		
70			1187
80		1084	1146
85	196		
	405		
90			1098
95	198		
	399		
100	214		1060
	416		

System $KTaO_3$–$KNbO_3$

$KTaO_3$, mole %	Transitions
0	214
	416
3	197
	397
6	184
	374
9	174
	353
12	157
	329
15	143
	311
20	120
	277
30	210

TABLE II

DENSITY AND DERIVED DATA FOR THE SYSTEMS $KNbO_3$–$NaNbO_3$ AND $KTaO_3$–$KNbO_3$

System $KNbO_3$–$NaNbO_3$

$KNbO_3$, mole %	Av. exptl. density, g./cm.^{3} at 25°	Av. dev. g./cm.^{3}	Smoothed curve density	Calcd. v./unit cell in Å^3	v./unit Cell from X-ray data of ref. 3
0	4.573	±0.003	4.576	59.474	59.699
2	4.570	.000			
6	4.554	.004			
10	4.542	.001	4.542	60.507	60.666
15	4.527	.001			
20	4.515	.004	4.515	61.462	61.581
25	4.507	.005			
30	4.506	.006	4.502	62.233	62.441
35	4.496	.007			
40			4.501	62.841	63.088
45	4.504	.005			
50	4.514		4.508	63.337	63.485
55	4.514	.005			
60			4.521	63.746	63.851
65	4.523	.003	4.529	63.928	
70	4.540	.003	4.537	64.110	64.107
75	4.543	.002	4.546	64.277	
80	4.563	.002	4.555	64.443	64.348
85	4.568	.006	4.565	64.596	
90	4.572	.004	4.576	64.732	64.540
92.5	4.579				
95	4.592	.005	4.591	64.812	
97.5	4.595				
100	4.640	.000	4.640	64.416	64.749

System $KTaO_3$–$KNbO_3$

$KTaO_3$, mole %	Av. exptl. density, g./cm.^{3} at 25°	Smoothed curve density	Calcd. v./unit cell in Å.^{3}
0	4.64	4.64	64.401
10		4.86	
18	5.03		
20		5.10	63.994
30		5.33	
33	5.39		
40		5.57	64.135
45	5.68		
50		5.81	64.066
60		6.04	
69	6.26		
70		6.28	
80		6.51	63.943
87	6.69		
90		6.74	
100	6.96	6.97	63.915

quately demonstrated[3,5] that the volume changes involved, even in the most drastic case, are less than 1%. Furthermore, calculations of the unit cell volume variation in the system $KNbO_3$–$NaNbO_3$ from the data of Shirane, *et al.*, Table II, Fig. 4b, which have been verified in the present study with both X-ray and density studies, show a maximum change of approximately 7.5%. The lattice parameters themselves, referred to the original cells, show correspondingly small variations, and the total displacement of the heavy atoms is between 2 and 3%.[6] Since the actual dimensions of the "boxes" are only slightly altered by the perturbations involved, the question arises as to whether the crystallographic multiplicity exhibited by $NaNbO_3$ will affect the continuous substitution of Na for K. Upon reappraisal it would appear that in terms of

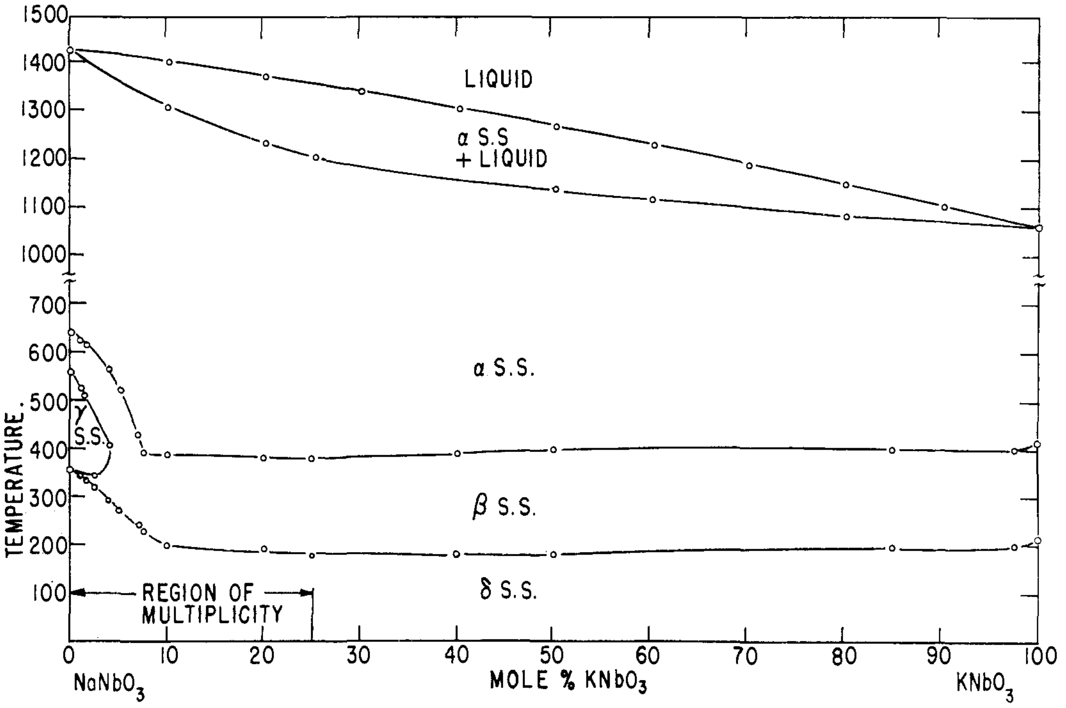

Fig. 3.—Proposed phase diagram of system $KNbO_3$-$NaNbO_3$.

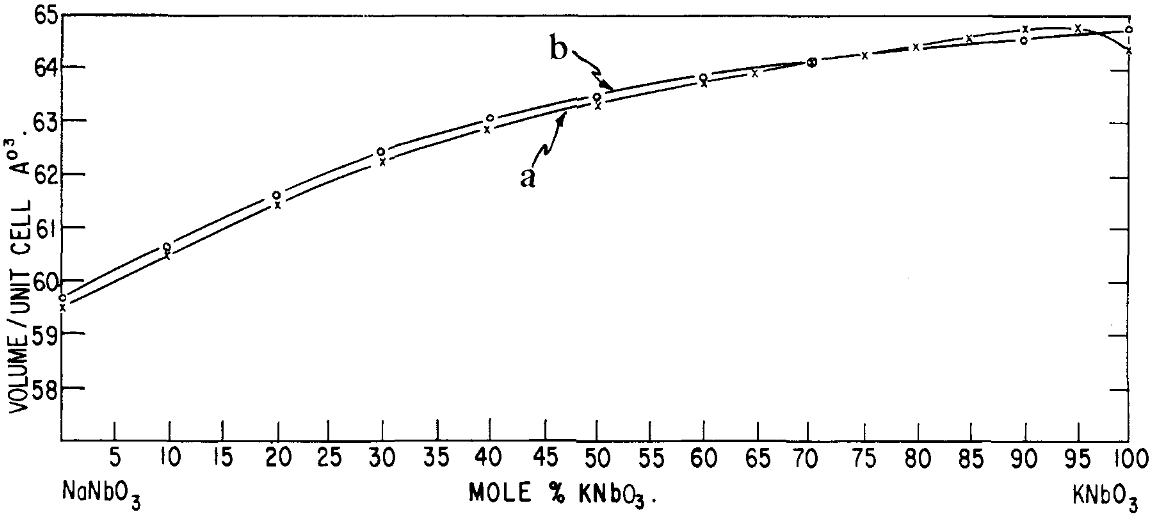

Fig. 4.—Volume/unit cell variation in system $KNbO_3$-$NaNbO_3$: a, present study; b, Shirane, *et al.*[3]

solid solution interaction the reacting structures would be "isomorphic," and probably more so than most materials which are crystallographically identical, and which give undisturbed series of solid solutions notwithstanding rather large volume differences. In the present case it is believed that a sharp distinction has to be made between a crystallographic non-isomorphism, occasioned by minor displacement of the heavy atom, and "interaction isomorphism" which may well be insensitive to such displacement, and completely dependent on the oxygen octahedral arrangement.

In conformity with the X-ray volume phase diagram calculated from the data of Shirane and from the thermal and density data of this study, Fig. 3–5 show that the δ, orthorhombic, mixed phases are continuous over the entire composition range with the δ-β transformation curve exhibiting a broad minimum. The γ, "pseudo tetragonal phase," is seen to be of the minimum, closed or γ-loop variety characteristic of iron systems. Referring to the data of Fig. 2a and constructing phase lines in a thermodynamically more acceptable fashion, as shown in Fig. 2b, the optical data obtained by Shirane can be correlated readily with the thermal data of the present study. It is believed that the lower transformation temperatures of the γ-phase can be attributed to the strain sensitivity previously discussed. The tetragonal phases of Na and K niobates are also seen to form a continuous series with a broad minimum. It might be argued that the shape of the β–α transformation curve strongly resembles that of a eutectic type gap, but since the continuous variation of lattice constant and density in the room temperature diagram prohibits such a description of the δ-phase, the presence of a gap in the next higher temperature phase is simultaneously prohibited.

The broad transition minima extend from approximately 90–95 mole % $NaNbO_3$ and occur at approximately 200 and 400°. Within the limits of the experimental error the actual minima appear to lie at approximately 75 mole % $NaNbO_3$ in the α–β curve and 60 mole % $NaNbO_3$ in the β–δ curve. In the region below room temperature Shirane traced the γ–δ transition of $KNbO_3$ with increasing Na concentration. Recently Johns[12] found an ε, rhombohedral[13] phase of $NaNbO_3$ and Shirane traced the mixed phase transition,[14] dashed portion of Fig. 1.

The DTA traces from which the present data were obtained exhibit certain features of interest. Even in solid–liquid interaction, in which diffusion rates are at a maximum, it is impossible to maintain equilibrium through a freezing cycle, and consequently solidus data must be obtained from heating curves on solid state reacted samples. Nevertheless, during the phase transformations studied, during which time diffusion rates must be very low, very sharp transitions were observable in most cases. The fact that these transformations were observable at all indicates that the upper and lower boundaries of each mixed system phase change must be extremely close to one another[15] in order that any semblance of equilibrium is achieved during the dynamic DTA experiments.

Another feature of the thermal data is significant. In $NaNbO_3$, the α–β transition shows the smallest latent heat change and the γ–δ the largest. These appear to be in accord with the relative magnitude of the volume changes, referred to the non-multiple unit cell. In $KNbO_3$ the situation is different, since its β–γ transition involves the smaller latent heat. Examination of the traces starting at pure $NaNbO_3$ showed that the latent heat of the α–β transformation continually increased, while that of the β–δ transformation decreased until at approximately 90 mole % $NaNbO_3$ the mixed phase traces were characteristic of pure $KNbO_3$. Shirane claimed that from approximately 90 mole % on, the mixed phases are ferroelectric, which appears consistent with the DTA data. However, a critical X-ray examination of the mixed system unequivocally shows the persistence of the "extra lines" down to at least 75 mole % $NaNbO_3$. Since the "extra lines" could arise only from the alternate displacement of pairs of Nb atoms which is characteristic of the antiferroelectric state, it is inconceivable that the mixed phases are ferroelectric in concentrations greater than 75 mole % $NaNbO_3$. Using polarization *vs.* electric field measurement techniques, especially with the poor hysteresis loops given by ceramics, it is not a simple matter to distinguish between a ferroelectric with a high coercive field and an antiferroelectric requiring a relatively low field to convert it to a pseudo ferroelectric. The fact that Cross and Nicholson[16] were able to observe double loops with $NaNbO_3$ indi-

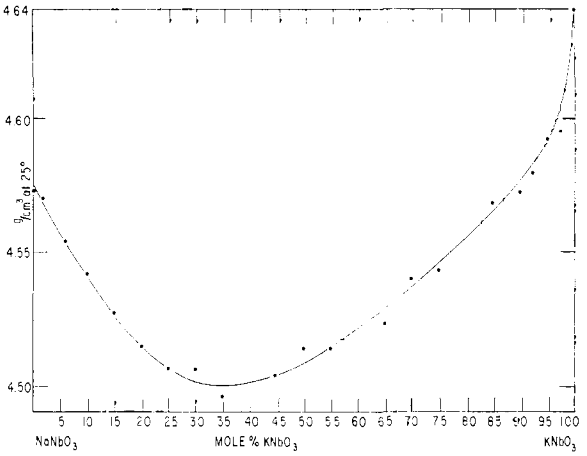

Fig. 5.—Density phase diagram of system $KNbO_3$–$NaNbO_3$.

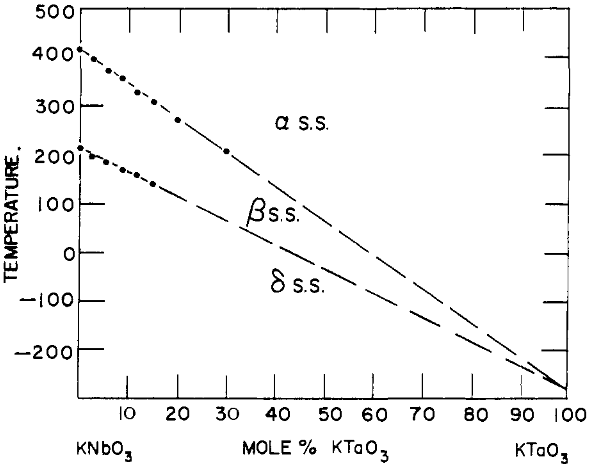

Fig. 6.—Thermal phase diagram of the system $KTaO_3$–$KNbO_3$.

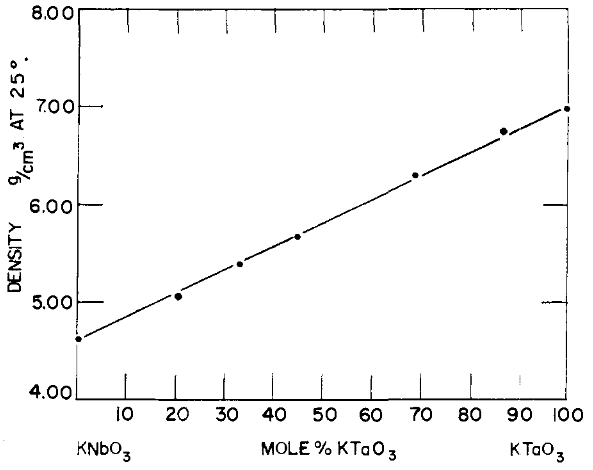

Fig. 7.—Density phase diagram of system $KTaO_3$–$KNbO_3$.

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[12] J. F. Johns, Master's thesis at the Pennsylvania State University, Graduate School of Physics, May 13, 1957.

[13] Referred to the non-multiple cell.

[14] Work completed after publication of ref. 3. See ref. 12.

[15] Generally, mixed phase boundaries will consist of upper and lower curves as a consequence of the laws of solutions, *viz.*, this is the basis for fractional distillation and crystallization. In special cases where ideal interaction occurs, and parameters such as atomic size, vapor pressure, melting point, polarizability, etc., are practically identical, the composition of both components in both phases of the two phase equilibrium may be the same.

[16] L. E. Cross and B. J. Nicholson, *Phil. Mag.*, **46**, 453 (1955).

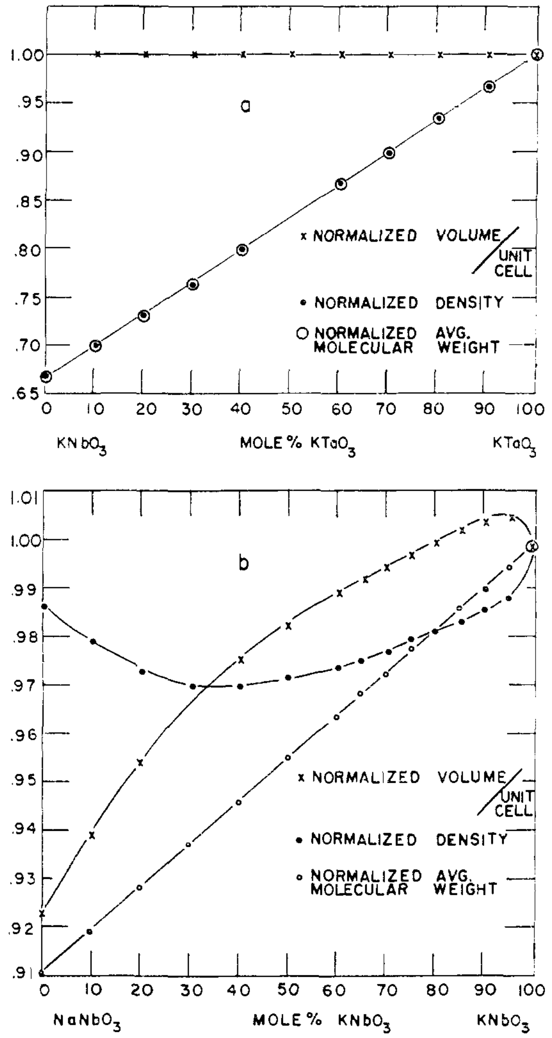

Fig. 8.—Normalized data: a, system $KTaO_3$-$KNbO_3$; b, system $KNbO_3$-$NaNbO_3$.

cates that the free energy curves for anti- and ferroelectric $NaNbO_3$ must lie close to one another. Coupled with this Shirane observed that the "coercive" fields for the δ-mixed phases were large[17] compared to those of the β-phases. As Francombe found that the intensity of the "extra lines" decreases with each higher temperature phase, the indications are that the antiferroelectric nature of $NaNbO_3$ decreases with increasing temperature. It is therefore postulated that in the δ-mixed phase the solution becomes decreasingly antiferroelectric down to 75 mole % $NaNbO_3$.[18] In this region, the free energy curves for the ferro- and antiferroelectric mixed phases probably intersect, and while the antiferroelectric displacement is very small but finite, the material transforms to the ferroelectric state. The ferroelectric nature of the solid solution would then continue to increase.[19] This theory is believed to be consistent with the proposed "interaction isomorphism" hypothesis, X-ray observations and dielectric data. Further verification awaits detailed measurement of the variation of coercive field with composition on reliable mixed single crystals.

B. **The System $KTaO_3$-$KNbO_3$.**—The system $KTaO_3$-$KNbO_3$ has been studied previously with reference to its solid–liquid equilibra,[9] variation of cubic lattice parameter with composition[10] and variation of transformation temperatures with composition using dielectric techniques.[20] This system is of interest because it involves the interaction of two perovskite ferroelectrics. $KNbO_3$ exhibits phase changes at 416, 214 and −10 to −30°, the sequence being cubic-tetragonal–orthorhombic–rhombohedral, respectively. $KTaO_3$ on the other hand shows only one phase transformation, at −260°, involving a change from cubic to an uncharacterized structural form. As the differences between the room temperature structures of both materials is extremely small, even though their structures are not crystallographically isomorphic, and as the descending cubic-tetragonal transformation appears to become second order in the 50 mole % room temperature region,[20] it was felt that the interactions would be ideal. Figures 6 and 7 show the thermal phase and density diagrams of the system $KTaO_3$-$KNbO_3$ determined in the manner described. Within the limits of experimental error the density variation is linear over the entire composition range indicating that the interaction is ideal and that the volume/unit cell remains constant. In agreement with the results obtained by Triebwasser[20] the latent heats of the α–β and β–γ transformations continually decrease with increasing $KTaO_3$ concentrations. As the volume changes involved in passing isothermally through two transitions are therefore continuous, the linearity of the density diagram is not unexpected. In order more clearly to relate the mass, volume and density relationships of the $KTaO_3$–$KNbO_3$ and $KNbO_3$–$NaNbO_3$ systems, normalized density data, volume/unit cell and average mol. wt. were calculated and graphed in Fig. 8a and 8b, respectively. The significant features are that in the ideal $KTaO_3$-$KNbO_3$ system the normalized mol. wt. and density curves coincide, resulting in a constant value for the normalized volume. In the $KNbO_3$–$NaNbO_3$ system the rate of change of the normalized density is different from that of the normalized mol. wt., which results in a non-constant, non-linear, normalized volume curve.

Acknowledgment.—The author wishes to thank Dr. F. Holtzberg for performing the X-ray studies and for his many helpful discussions.

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[17] In the region 100–90 mole % $NaNbO_3$ Shirane was unable to observe loops.

[18] The latent heats in this region are smaller than for pure $KNbO_3$ as would be expected for smaller antiferroelectric displacement, and X-ray examination indicates super lattice separation is decreasing.

[19] In order for the anti- to ferroelectric transition to be continuous that is, in order for the alternate displacement to become zero, succeeded by a undirectional displacement, one would expect to observe a non-multiple, cubic symmetry in the 75–60 mole % $NaNbO_3$ range of the δ-phase. Such behavior was not indicated by X-ray analysis.

[20] S. Triebwasser, Proc. Spec. Tech. Conf. Solid State Dielectric and Magnetic Devices, Paper 2, April 22, 1957, Washington, D. C.