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Dielectric Properties and Phase Transitions of $NaNbO_3$ and $(Na,K)NbO_3$†

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An optical, dielectric, and structural study has been carried out on $NaNbO_3$ and the solid solution $(Na, K)NbO_3$, both single crystals and ceramics being used. No evidence for ferroelectricity in $NaNbO_3$ was found, and the crystal seems to be antiferroelectric in accordance with the nonpolar structure reported by Vousden. It is shown that a small addition of $KNbO_3$ to pure $NaNbO_3$ produces a new ferroelectric phase, the existence of which suggests a possible explanation of the conflicting dielectric and structural properties previously reported.

The phase diagram of $NaNbO_3$-$KNbO_3$ is given. This, together with the optical and x-ray studies of pure $NaNbO_3$, shows that the three phase transitions in $NaNbO_3$ are quite different in nature from the $BaTiO_3$-type transitions in $KNbO_3$.

I. INTRODUCTION

In 1949 Matthias[1] reported the perovskite-type niobates and tantalates of sodium and potassium to be ferroelectric. The lattice parameters of $NaTaO_3$ and $KTaO_3$ were reported by Vousden[2] at room temperature, and the Curie temperatures were reported as 13°K for $KTaO_3$[3] and 475°C for $NaTaO_3$.[1] However, no detailed investigation has been published on the ferroelectric transitions of the tantalates except the dielectric properties[3] of $KTaO_3$ near the Curie point at 13°K.

On the other hand, the ferroelectric transitions in the niobates, $KNbO_3$ and $NaNbO_3$, have been studied in some detail. Matthias and Remeika[4] have studied the dielectric properties of these crystals, and Wood[5] has reported on both the optical and structural properties. The crystals show the following transitions, according to these workers:

$$KNbO_3\text{: Orthorhombic} \xleftrightarrow{225°C} \text{tetragonal} \xleftrightarrow{435°C} \text{cubic;}$$

$$NaNbO_3\text{: Orthorhombic} \xleftrightarrow{370°C} \text{tetragonal} \xleftrightarrow{480°C} \text{cubic.}$$

The ferroelectricity of $KNbO_3$ below 435°C has been well demonstrated. The structural changes at the two transitions are quite similar to those of $BaTiO_3$ at 0°C and 125°C.[6] Moreover, a recent study at our laboratory has revealed the existence of an additional phase change at −10°C, below which the crystal symmetry is rhombohedral.[7] Hence the transitions in $KNbO_3$ are analogous to those of $BaTiO_3$.

In contrast to this, the situation with $NaNbO_3$ is rather confusing. Consider first the x-ray powder photographs obtained with $NaNbO_3$ and $KNbO_3$. In both the orthorhombic and tetragonal phases, superlattice lines were observed on the powder photographs of $NaNbO_3$.[5] $KNbO_3$, on the other hand, shows a simple unit cell, so that the phases in $KNbO_3$ do not correspond crystallographically to those in $NaNbO_3$. A second point of confusion arises from the structural study of $NaNbO_3$ at room temperature. Vousden[8] reported the structure to be nonpolar, which necessarily rejects the existence of ferroelectricity in the crystal.[9] However, he also observed domain movement under a large dc field, which is usually indicative of ferroelectric behavior, as were the hysteresis loops reported by Matthias and Remeika.[4] In defense of his space group assignment, Vousden[10] indicated a possible explanation of this conflicting data by proposing the existence of a less stable, closely related polar structure which may be produced under a strong electric field yielding the observed ferroelectric phenomena. Since no new experimental results either confirming or disproving this hypothesis have been reported, the whole question still remains open to conjecture.

Thirdly, there are discrepancies between the x-ray and optical observations. Optical observations[5] indicate that $NaNbO_3$ crystals are still birefringent above 480°C, and do not become isotropic until 640°C. To add to the confusion, Wood reports that at 300°C $NaNbO_3$ is orthorhombic by optical measurement, while it should be tetragonal according to x-ray evidence. Observations carried out at 425° and 490°C show the crystal to be optically tetragonal, while x-ray evidence indicates a cubic lattice. As the result of his optical observations, Vousden reports that $NaNbO_3$ changes from orthorhombic to tetragonal at about 300°C, and to cubic at 600°C.[2] It should be mentioned here that small anomalies in the dielectric constant were observed at −80°C by Matthias and Remeika[4] and at 0°C by Wainer and Wentworth.[11] Vousden, however, failed to

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[1] B. T. Matthias, Phys. Rev. **75**, 1771 (1949).

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[4] B. T. Matthias and J. Remeika, Phys. Rev. **82**, 727 (1951).

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[8] P. Vousden, Acta Cryst. 4, 545 (1951).

[9] R. Pepinsky, Acta Cryst. **5**, 228 (1952).

[10] P. Vousden, Acta Cryst. 5, 690 (1952).

[11] E. Wainer and C. Wentworth, J. Am. Ceram. Soc. **35**, 207 (1952).

observe any structure changes optically down to $-175°C$.[2]

In order to resolve these questions concerning the phase transitions and possible existence of ferroelectricity in pure $NaNbO_3$, detailed optical, x-ray, and dielectric measurements on single crystals and ceramic specimens have been undertaken in this laboratory. A study has also been made of the $NaNbO_3$-$KNbO_3$ system in order to show the relationship between the various phases in the two crystals.

II. OPTICAL STUDY OF THE PHASE TRANSITIONS IN $NaNbO_3$

$NaNbO_3$ single crystals were prepared by the method suggested by Wood.[5] A mixture of 5.3 g of Na_2CO_3, 13.3 g of Nb_2O_5, and 8.9 g of NaF was heated to 1500°C in a platinum crucible, and then cooled to 900°C in 7 hours. This method generally gave rectangular plates which were yellow in color. Well-shaped, thin plates up to $3\times3\times1$ mm in size were often produced. A spectroscopic analysis, kindly carried out by Dr. Lovell of the Mineral Science Department of The Pennsylvania State University, showed the following impurities: K: ≈ 0.005 percent, Li: <0.001 percent, Rb: $\ll 0.001$ percent, Ta: no trace.

Powder photographs were taken of these crystals by means of a Norelco powder camera (11.4-cm diam) with $CuK\alpha$ radiation filtered through a nickel foil. The photographs taken at room temperature showed well-resolved line splitting due to an orthorhombic distortion of the ordinarily cubic perovskite structure. Monoclinic axes were taken,[12] and the lattice parameters were calculated from the (422) and (332) groups, with the results

$$a'=c'=3.915 \text{ A}, \quad b=3.881 \text{ A}, \quad \text{and} \quad \beta=90°40'.$$

These values are in good agreement with earlier measurements, particularly those of Vousden.[2]

Extra lines were observed in $NaNbO_3$ powder photographs by Wood,[5] who gave the multimolecular unit cell dimensions. A multiple cell structure was also reported by Vousden in his analysis.[8] A comparison of the extra lines observed by Wood (see Fig. 5 of reference 5) with our own showed the two sets of lines to be identical.

When the larger $NaNbO_3$ crystals were viewed under a polarizing microscope, multidomains in complicated patterns were observed. However, several thin plates, approximately 1 mm^2 in area, showed only a few domains[13] and very sharp extinction positions. These crystals were used in an optical study of the phase transitions in $NaNbO_3$. Measurements were carried out with a high-temperature optical stage of simple design, which permitted observation under a polarizing microscope at temperatures as high as 700°C.

At room temperature the crystals showed two types of domains. In some domains extinction occurred at positions making an angle of 45° with the crystal edges, while the remaining domains showed parallel extinction. This behavior is quite characteristic of orthorhombic crystals with pseudocubic habit. At 360°C a sudden change was noted in the optical properties of the crystals; above 360°C only parallel extinction was observed. A less pronounced domain-boundary movement was observed to occur at 480°C. The crystals continued to show parallel extinction even above these transitions. A third transition took place at 640°C, above which no extinction was observed; thus it may be safely assumed that the crystal becomes isotropic there.

Although these results are in good agreement with the three optical transitions observed by Wood,[5] the following points of interest should be noted. The optical change at 360°C is much more violent in nature than the phase transitions at 480° and 640°C. Furthermore, it was relatively easy to recognize an optical transition at 640°C, since a change from anisotropy to isotropy is involved; but the transition at 480°C was observed only in exceptionally clear, well-shaped specimens.

In the two phases of $NaNbO_3$ between 360° and 640°C, each crystal showed parallel extinction. In tetragonal crystals, parallel extinction is observed when the *c* axis lies in the plane of the plate, and optical isotropy is found when the *c* axis is perpendicular to the plate. The latter case was not observed in the ten or more $NaNbO_3$ crystals we examined. Since the crystals were all primarily thin plates, this optical peculiarity is probably due to some special orientation of the crystal habit.

Color changes were observed between 360° and 480°C as the crystals were heated. Constantly shifting spectra were observed with white light; and when the crystals were illuminated with sodium light, a series of black strips transversed the crystals, one by one. Although there is a possibility that the phenomenon is due to a thickness change, the exact origin of the effect is not known.

Thus optical study clearly shows three phase transitions in $NaNbO_3$. Moreover, the symmetry is definitely orthorhombic below 360°C and cubic above 640°C; but the supposedly tetragonal phases between the two leave some doubt as to their true nature. The three phase transitions in $NaNbO_3$ were recently observed in a differential thermal analysis performed by Dr. Rustum Roy *et al.* of the School of Mineral Industries, The Pennsylvania State University.[14] The transition temperatures are in good agreement with those given above.

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[12] Throughout the paper, the monoclinic parameters $a'=c'$, b, and β have been substituted for the orthorhombic unit cell distances a, b, and c so that the lattice parameters can be more conveniently compared with those of the cubic and tetragonal phases. The monoclinic and orthorhombic lattice parameters are related as follows: $a=2a'\sin\frac{1}{2}\beta$, $b=b'$, $c=2a'\cos\frac{1}{2}\beta$. The wavelength of $CuK\alpha_1$ radiation was taken as 1.5405 A in all calculations.

[13] "Domain" is to be understood as "twin" if these crystals are not ferroelectric.

[14] Roy, deVries, Rase, Shafer, and Osborn, Second Annual Report to the U. S. Army Signal Corps, July 15, 1953 (unpublished).

III. X-RAY STUDY OF THE PHASE TRANSITIONS IN $NaNbO_3$

A series of powder photographs were taken of $NaNbO_3$ over a wide temperature range by means of a Unicam 19-cm high-temperature camera with $CuK\alpha$ radiation filtered through nickel. A sample consisting of powdered $NaNbO_3$ crystals was sealed in a glass capillary having an outside diameter of 0.3 mm and a wall thickness of 0.01 mm. The diffraction patterns showed very sharp line splitting, permitting resolution of the $CuK\alpha_1$, α_2 doublet at an angle $\theta=40°$. The lattice parameters were calculated from the line groups $N=h^2+k^2+l^2=25$, 24, and 22. The results are tabulated as a function of temperature in Table I and plotted in Fig. 1.

Below 360°C the symmetry is obviously orthorhombic, in agreement with optical observation. Although the parameters listed are those corresponding to a simple unit cell, the extra lines present in the photographs may well indicate a multiple cell. The intensity of these extra lines rapidly decreases as the temperature is raised above room temperature.

At the transition temperature near 360°C the diffraction patterns change quite abruptly, so that the line splitting is greatly reduced. For example, at 375°C only the (510), (431), and (422) line groups are well resolved. The line splitting above 360°C appears to be typical tetragonal splitting, in agreement with the optical measurements. It is difficult, however, positively to exclude other possible lattice forms, since the distortion is so slight.

If the crystal is assumed to be tetragonal, the calculated c/a ratio shows a very small deviation from unity, c/a being 1.0023 at 375°C. Moreover, this distortion continues to decrease with increasing temperature, and at temperatures above 430°C no definite line splitting can be observed. Thus if a tetragonal distortion from the cubic perovskite lattice exists above this temperature, the axial deviation is certainly less than 0.1 percent. No structure changes were observed with x-rays at the transition temperatures of 480° and 640°C. Extra lines were again observed above 360° (as first reported by Wood[5]), but no definite conclusions could be drawn as to their character.

TABLE I. Lattice parameters of $NaNbO_3$ as a function of temperature.

T(°C)	$a'=c'$(A)	b(A)	a'/b	β	v(A³)
20	3.915	3.880	1.009	90° 41′	59.45
175	3.918	3.898	1.005	90° 32′	59.82
300	3.921	3.910	1.003	90° 25′	60.11
350	3.922	3.913	1.002	90° 23′	60.18
	$a=b$	c	c/a		
375	3.918	3.927	1.0023		60.28
390	3.919	3.927	1.0020		60.33
410	3.921	3.926	1.0014		60.35
420	3.921	3.927	1.0014		60.38
430	3.925				60.44
460	3.926				60.52
480	3.928				60.61
670	3.942				61.27

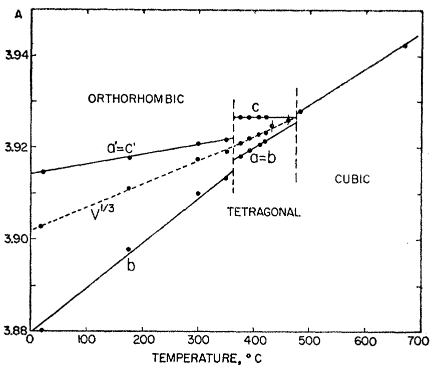

FIG. 1. Lattice parameters of $NaNbO_3$.

Some of the discrepancies observed by Wood between the optical and x-ray measurements on $NaNbO_3$ have been removed by our measurements. Our x-ray powder photographs taken at 300°C indicate an orthorhombic, not a tetragonal lattice, so there is no disagreement between x-ray and optical observation. Wood also reported cubic diffraction lines above 370°C, whereas optical measurements indicated tetragonal symmetry. We were able to observe tetragonal line splitting at temperatures well above 370°C although this distortion became negligible at about 430°C.

Wood hypothesized that the x-ray photographs gave the symmetry of the niobium array, whereas the optical properties were determined principally by the combined oxygen-sodium array. In this way she was able to account for obvious differences between the x-ray and optical observations. However, since the principal differences between these results have been removed by our measurements, it seems more natural to conclude that the optical measurements are simply more sensitive to slight lattice distortions than the x-ray technique.

IV. DIELECTRIC PROPERTIES OF $NaNbO_3$

Dielectric measurements were made on $NaNbO_3$ single crystals using rectangular plates 2–3 mm on edge and having a thickness of approximately 0.5 mm. The dielectric constant ϵ is plotted as a function of temperature in Fig. 2. The measurements were made at a frequency of 10 kc/sec with an alternating electric field of 5 v/cm. The sharp change in the dielectric constant was observed at 355°C, as reported by Matthias and Remeika.[5] This anomaly undoubtedly corresponds to the orthorhombic-tetragonal phase transformation observed in our optical and x-ray measurements at 360°C.

An effort was made to measure the dielectric constant in the vicinity of the second optical transition at 480°C. No dielectric anomaly could be detected in this region. However, since the loss becomes quite appreciable above

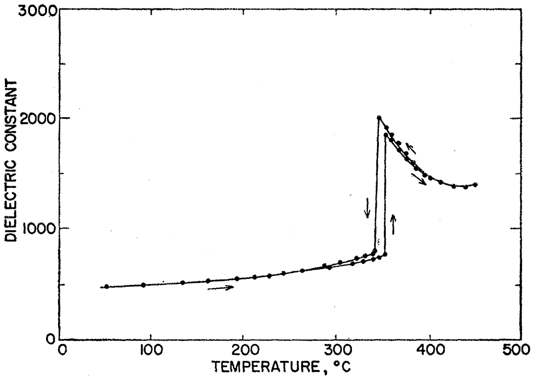

FIG. 2. Dielectric constant of $NaNbO_3$ single crystal.

400°C, a small anomaly could have easily been obscured by the inaccuracy of our measurements.

No dielectric anomalies were detected between room temperature and -185°C, in agreement with Vousden's optical observations[2] but in contradiction with previous dielectric measurements.[4,11]

Several measurements employing various techniques were made in an effort to detect ferroelectricity in $NaNbO_3$. First of all, the relation between polarization and electric field was investigated using a modified Sawyer-Tower's circuit. The $P-E$ relation proved to be quite linear even in fields as high as 15 kv/cm. No hysteresis loops were observed. The relationship was studied over a temperature range extending from 20°C to 420°C and at a frequency of 60 cycles/sec.

Pyroelectric tests were also carried out to detect any spontaneous polarization. First, a dc field of 10 kv/cm was applied across the specimen for five minutes at 300°C, to enable the domains at least partially to align themselves in one direction. The electrodes were then connected across a sensitive galvanometer and the specimen heated to a temperature above the transition at 355°C. A change in the spontaneous polarization should give a current through the galvanometer on passing through the transition, but no discharge current could be detected with $NaNbO_3$. When a similar test is performed on $KNbO_3$, large discharge currents are observed at both the 225° and 435°C transitions.

The effect of a dc biasing field on the dielectric constant has also been studied. In all known ferroelectrics (including Rochelle salt, KH_2PO_4,[15] and $BaTiO_3$)[16] the application of such a field drastically reduces the dielectric constant. With $NaNbO_3$ crystals, however, the application of a dc field of 8 kv/cm does not affect the value of the dielectric constant at room temperature. The application of a similar field at a temperature slightly below the transition at 355°C even resulted in a slight increase in the dielectric constant.

The experiments described above gave no evidence for ferroelectricity in $NaNbO_3$. Recently Cross[17] studied the dielectric properties of pure $NaNbO_3$ and found no evidence for ferroelectricity. Only by assuming the crystal to possess an extremely high coercive field, even in the vicinity of the transition at 355°C, can we justify the existence of ferroelectricity in $NaNbO_3$. A more likely hypothesis is that $NaNbO_3$ is not ferroelectric but is actually antiferroelectric, in accordance with the antiparallel niobium displacement reported by Vousden.[8]

V. PHASE DIAGRAM OF $NaNbO_3$-$KNbO_3$

In contrast with the peculiar properties of $NaNbO_3$ just described, $KNbO_3$ shows typical ferroelectric behavior closely similar to that of $BaTiO_3$. To account for the differences in $NaNbO_3$ and $KNbO_3$, the phase diagram of their solid solution has been studied in some detail. Both ceramics and mixed crystals were used in the investigation.

(a) Dielectric Measurements on Ceramics

Ceramic specimens were prepared in the desired percentages from appropriate mixtures of K_2CO_3, Na_2CO_3, and Nb_2O_5. The firing temperatures ranged from 1050°C for pure $KNbO_3$ to 1200°C for pure $NaNbO_3$. Only by adjusting the firing temperature of pure $KNbO_3$ to just below its melting point could a suitable ceramic be obtained. Silver paste electrodes were applied to the ceramics for dielectric measurements.

The temperature dependence of the dielectric constant was investigated for an ac field of 5 v/cm at a frequency of 10 kc/sec. Some of the results are shown in Fig. 3. The dielectric behavior of pure $NaNbO_3$ and pure $KNbO_3$ ceramics proved to be quite similar to

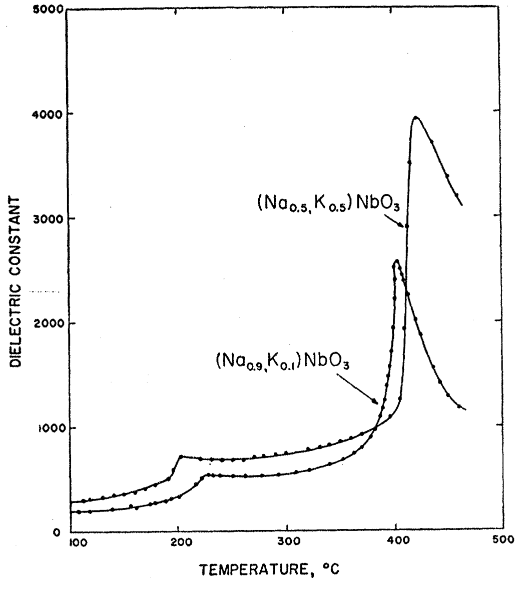

FIG. 3. Dielectric constant of $(Na, K)NbO_3$ solid solution.

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[15] H. Baumgartner, Helv. Phys. Acta **23**, 651 (1950).

[16] S. Roberts, Phys. Rev. **71**, 890 (1947).

[17] L. E. Cross, Paper read before British Physical Society Spring Meeting, Leeds. Abstract in Nature **171**, 1057 (1953).

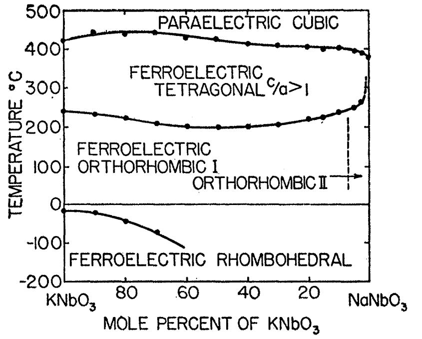

FIG. 4. Phase diagram of $NaNbO_3$-$KNbO_3$ system.

that obtained with single crystals, except that the changes in the dielectric constant accompanying the structural transitions were much sharper for single crystals. No anomaly was observed in the pure $NaNbO_3$ ceramic near the temperature of the second optical transition at 480°C.

One particularly important result came out of the dielectric study of the $KNbO_3$-$NaNbO_3$ solid solutions. When a small amount of $KNbO_3$ is added to pure $NaNbO_3$, a second small anomaly appears in the dielectric constant near 200°C, in addition to the usual dielectric transition observed around 400°C. The result for $(Na_{0.9}K_{0.1})NbO_3$ is shown in Fig. 3. With increasing $KNbO_3$ concentration the two dielectric anomalies continue to appear near 200° and 400°C, so that the lines joining these transition temperatures for various compositions extend continuously to the transitions observed in pure $KNbO_3$. The third and lowest phase transition in pure $KNbO_3$, below which the crystal symmetry is rhombohedral, occurs at -10°C for pure $KNbO_3$, but decreases in temperature with increasing $NaNbO_3$ concentration.

The phase diagram[18] shown in Fig. 4 was drawn from the data gathered with the dielectric measurements on the mixed $KNbO_3$-$NaNbO_3$ ceramics. A standard procedure was used to check each phase in the diagram for ferroelectricity. The hysteresis loops of a number of different compositions were examined at various temperatures by using an ac field of 10–20 kv/cm at a frequency of 60 cycles/sec. As expected, the $P-E$ relationship is always linear above the upper phase line near 400°C. Well defined hysteresis loops were observed in the intermediate phase for all compositions. Hysteresis loops were also found in the orthorhombic phase for all compositions from $KNbO_3$ to $(Na_{0.9}K_{0.1})NbO_3$. By comparing the hysteresis loops of a single specimen in both the orthorhombic and tetragonal phases, we found that the coercive field was much larger and the polarization much further from saturation in the orthorhombic phase.

The $P-E$ relation is almost linear in the orthorhombic phase for compositions containing less than 10 percent $KNbO_3$, even for fields as high as 15 kv/cm. The absence of hysteresis loops might be explained by a sudden increase in the coercive field; but no reasonable explanation for such an increase is immediately obvious. The extra lines observed in the x-ray powder photographs of $NaNbO_3$ indicated structural differences in the orthorhombic phases of this crystal and $KNbO_3$; hence there must be a separating phase line somewhere in the $KNbO_3$-$NaNbO_3$ solid solution. Such a phase line could well be the dividing line between ferroelectric and nonferroelectric phases, explaining the absence of hysteresis loops on the $NaNbO_3$ side. According to our dielectric measurements, the phase line lies somewhere between $(Na_{0.90}K_{0.10})NbO_3$ and $(Na_{0.95}K_{0.05})NbO_3$, as tentatively indicated in Fig. 4.

When measured as a function of increasing temperature, the dielectric constant for the various solid solutions shows a high peak at the upper transition temperature. This peak is followed by a sharp decrease, thereby obeying the Curie-Weiss law $\epsilon = C/(T-\theta)$ which is typical of ferroelectrics above their Curie point. It should be pointed out that even ceramics made up almost entirely of $NaNbO_3$, such as $(Na_{0.95}K_{0.05})NbO_3$, obey the Curie-Weiss law quite closely. In pure $NaNbO_3$ the peak dielectric constant is low even for single crystals, but the behavior of the dielectric constant above the Curie point closely approximates a Curie-Weiss relation until well above 400°C, where the dielectric loss becomes troublesome. For the compositions from $KNbO_3$ to $(Na_{0.9}K_{0.1})NbO_3$, θ is about 300°C and C is the order of 1 to 2×10^5°C. In pure $NaNbO_3$,

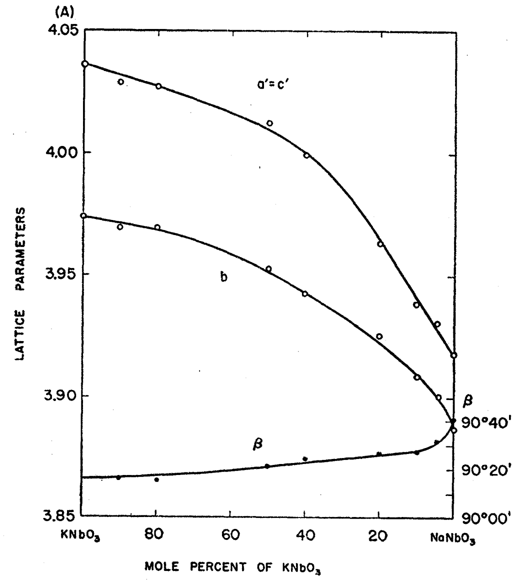

FIG. 5. Lattice parameters of (Na, K)NbO_3 system.

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[18] Strictly speaking, each phase line shown in Fig. 4 should be drawn as two slightly separated lines between which both the phases above and below the phase line coexist as a mixture. However these double lines are never observed experimentally, principally because the neighboring phases in this type of compound are so closely related that the line separation is very small and a long time interval is required for the mixed phase to appear. The authors wish to thank Dr. Rustum Roy and Professor A. J. C. Wilson for illuminating discussions concerning this point.

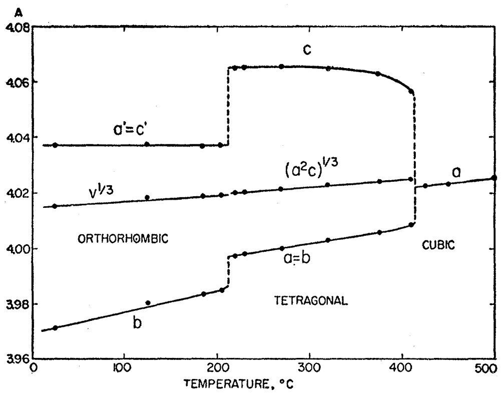

FIG. 6. Lattice parameters of $KNbO_3$.

C varies quite appreciably from specimen to specimen, being of the order of 2 to 4×10^5°C. θ, on the other hand, changes little in comparison, generally having values between 60° and 80°C.

The optical and x-ray measurements previously described showed $NaNbO_3$ to be tetragonal above 360°C, not cubic. Moreover, it will be subsequently demonstrated that the mixed crystal $(Na_{0.95}K_{0.05})NbO_3$ also is tetragonal above the transition. It is therefore possible that the validity of the Curie-Weiss law for these particular compounds is only accidental; but it may also mean that the tetragonal phases of $NaNbO_3$ above 360°C are actually paraelectric.

(b) X-Ray Study of the Phase Diagram

The lattice parameters of the $NaNbO_3$-$KNbO_3$ system were determined from powder photographs taken with a Unicam 9-cm powder camera and CuKα radiation. It was difficult to obtain clearly resolved lines, particularly with ceramics consisting principally of $NaNbO_3$. However, after firing several ceramics under slightly different conditions we obtained powder photographs showing sufficient resolution in the (422) and (400) groups to permit calculation of the lattice parameters. The results are shown in Fig. 5. Note that the lattice parameters decrease continuously from $KNbO_3$ to $NaNbO_3$, so that a solid solution is formed over the entire range of concentrations.

We were not able to define clearly the phase line separating the orthorhombic phases of $NaNbO_3$ and $KNbO_3$ by x-ray measurements. Such a phase line should be accompanied by discontinuities in the lattice parameters and a sudden appearance of extra lines with increasing $NaNbO_3$ content. For the $NaNbO_3$-$KNbO_3$ system the lattice parameters, particularly β, show sharp changes near pure $NaNbO_3$. Moreover, the intensities of the extra lines observed in pure $NaNbO_3$ decrease rapidly with the addition of small amounts of $KNbO_3$. It is not possible, however, to point to any particular composition as a point of discontinuity for the lattice parameters, because of the great similarity between the orthorhombic cells of $KNbO_3$ and $NaNbO_3$. Similarly the low intensity of the extra lines also makes it difficult to tell at what composition they first appear.

The crystal structure of the three upper phases of $KNbO_3$ have been clearly identified by Wood as being cubic, tetragonal, and orthorhombic with decreasing temperature. A more detailed investigation of the lattice changes in the vicinity of each transition has been undertaken in our laboratory for comparison with the $NaNbO_3$ data. The unit cell dimensions of $KNbO_3$ were calculated from the (510), (431), (422), and (332) line groups observed on photographs taken with a 19-cm Unicam high-temperature camera. The results are given in Fig. 6 and in Table II. It is obvious from these graphs that the temperature variation of the $KNbO_3$ cell dimensions is quite similar to that observed with $BaTiO_3$.[19]

A comparison of Fig. 6 with Fig. 1 reveals the following important differences between $KNbO_3$ and $NaNbO_3$. The axial ratio observed in the tetragonal phase is much larger for $KNbO_3$ ($c/a=1.016$) than for $NaNbO_3$ ($c/a=1.002$). Moreover, the axial ratio of $KNbO_3$ shows very little temperature dependence in the tetragonal region, and an abrupt discontinuity at the cubic-tetragonal transition. $NaNbO_3$, on the other hand, shows a marked temperature dependence and an extremely small discontinuity at the transition. Similar differences occur in the pseudomonoclinic parameters a'/b and β, used to describe the crystal in the orthorhombic phase.

By way of comparison, $(Na_{0.9}K_{0.1})NbO_3$ shows orthorhombic symmetry at room temperature, which changes to tetragonal ($c/a=1.010$) at 240°C. The tetragonal-cubic transition takes place at 400°C. In general, the behavior of this mixed crystal is much more similar to $KNbO_3$ than to $NaNbO_3$.

(c) Specific Heat Measurements

The specific heats of $NaNbO_3$ and $(Na_{0.9}K_{0.1})NbO_3$ were measured as a function of temperature with a

TABLE II. Lattice parameters of $KNbO_3$ as a function of temperature.

Temp (°C)	$a'=c'$(A)	b(A)	b/a	β	v(A³)
25	4.0375	3.9711	1.0167	90° 15′	64.73
125	4.0374	3.9797	1.0145	90° 15′	64.87
185	4.0363	3.9830	1.0134	90° 13′	64.89
205	4.0369	3.9839	1.0133	90° 14′	64.93
	$a=b$	c	c/a		
220	3.9972	4.0636	1.0166		64.92
230	3.9978	4.0640	1.0166		64.95
270	3.9992	4.0647	1.0164		65.01
320	4.0023	4.0639	1.0154		65.10
375	4.0048	4.0620	1.0143		65.15
410	4.0080	4.0567	1.0122		65.18
425	4.0214				65.03
450	4.0225				65.09
510	4.0252				65.22

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[19] H. F. Kay and P. Vousden, Phil. Mag. (7) **40**, 1019 (1949).

Nagasaki-Takagi adiabatic calorimeter,[20] which is a modification of Sykes' calorimeter.[21] The specific heat specimens were prepared by powdering ceramics of the same type used in the dielectric and x-ray studies. About 15 grams of the powdered ceramic was placed in a platinum vessel and heated at a rate of approximately 1°C/min. The heat content of the empty calorimeter was calibrated using SiO_2 as a standard substance.

The specific heat anomalies observed in $NaNbO_3$ and $(Na_{0.9}K_{0.1})NbO_3$ are small in comparison with those observed in $KNbO_3$.[7] This result was to be expected, since the structural anomaly is much more pronounced in $KNbO_3$. The integrated transition energies are listed in Table III.

(d) Further Study of the Phase Diagram of Mixed Crystals

The optical study of $NaNbO_3$ crystals showed three phase transitions at 360°, 480°, and 640°C, while dielectric measurements carried out on $NaNbO_3$ ceramics up to temperatures as high as 500°C showed only the lowest transition. To complete the phase diagram of the $(K\text{-}Na)NbO_3$ system, mixed crystals were prepared from the appropriate mixtures of $NaNbO_3$ and $KNbO_3$, NaF being used as a flux. The compositions of the mixed crystals are not exactly in proportion to the percentages of $KNbO_3$ and $NaNbO_3$ because additional Na is introduced by the flux.

Crystals were prepared of several compositions between $(K_{0.5}Na_{0.5})NbO_3$ and pure $NaNbO_3$. Small rectangular plates, yellow or brown in color, were obtained from the melt. The crystals gave excellent powder diffraction photographs, showing lines which clearly indicated an orthorhombic lattice of the perovskite type at room temperature. Approximate composition values were assigned to the crystals by comparing the unit cell dimensions of the mixed crystals with those obtained with ceramics of various compositions (see Fig. 5). In this manner it was found that crystals of $(Na_{0.9}K_{0.1})NbO_3$ could be obtained by melting a mixture of equal parts of $NaNbO_3$ and $KNbO_3$ along with a NaF flux. It should be emphasized, however, that the estimated compositions shown in Fig. 7 are only approximate, so that the results are only semiquantitative.

Optical observations of the mixed crystals under a polarizing microscope led to the phase diagram shown in Fig. 7. Again we found that the addition of a small amount of $KNbO_3$ to $NaNbO_3$ greatly altered its physical characteristics. The optical properties of the tetragonal phase in $(Na_{0.9}K_{0.1})NbO_3$ are much more similar to those in $KNbO_3$ than to those in $NaNbO_3$. In mixed crystals such as this we observed both domains of parallel extinction and plates oriented in the *c* direction.

TABLE III. Transition energy of $KNbO_3$, $NaNbO_3$, and $(K_{0.1}, Na_{0.9})NbO_3$.

Composition	Lower phase change	Upper phase change
$KNbO_3$	85 cal/mole	190 cal/mole
$(Na_{0.9}, K_{0.1})NbO_3$	20 cal/mole	60 cal/mole
$NaNbO_3$	···	50 cal/mole

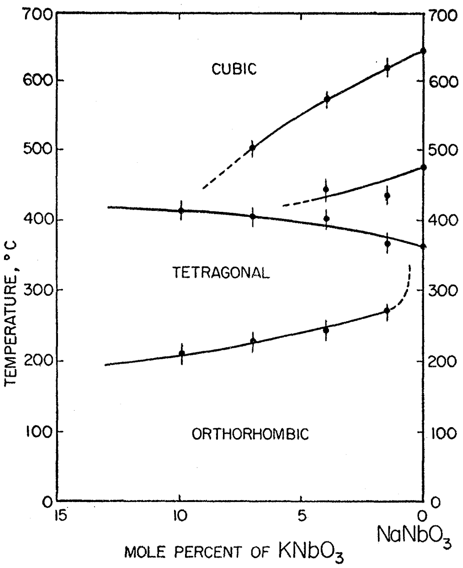

FIG. 7. Phase diagram of $NaNbO_3$-$KNbO_3$ system determined from mixed crystals, showing behavior near pure $NaNbO_3$. The vertical lines show the range of fluctuation of the transition temperatures of the same melt.

The two tetragonal phases observed optically in pure $NaNbO_3$ were also observed for mixed crystals containing less than 10 percent $KNbO_3$. The temperatures of these optical transitions decreased rapidly with increasing concentration of $KNbO_3$. As in the case of pure $NaNbO_3$, only parallel extinction was observed in the tetragonal phases above 360°C. No examples of complete extinction (i.e., *c*-axis plates) were found in the twenty or more crystals examined in this range of compositions.

Single crystals large enough for dielectric tests were obtained from the mixed crystal growth of $(Na_{0.9}K_{0.1})NbO_3$. The dielectric constant, measured at a field of 10 v/cm and a frequency of 10 kc/sec, showed two anomalies, corresponding to those obtained in optical observations on the crystal. Hysteresis loops were observed in both the tetragonal and orthorhombic phases, for an ac field of 10 kv/cm.

VI. DISCUSSION

The optical observations just described point to the existence of three phase transitions in $NaNbO_3$ at 360°, 480°, and 640°C, although the latter two could not be verified by either dielectric or x-ray measurement since the structural perturbation is undoubtedly very small. These two phases are certainly different from the

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[20] S. Nagasaki and Y. Takagi, J. Appl. Phys. Japan **17**, 104 (1948).

[21] C. Sykes, Proc. Roy. Soc. (London) **A143**, 422 (1935).

tetragonal phase in $KNbO_3$; in fact, there seems to be no known similar phases in any of the perovskite-type ferroelectrics. The dielectric properties of these phases and their relation to the crystal structure are still very much open to question.

Our experiments on $NaNbO_3$ ceramics and crystals failed to give any evidence for ferroelectricity, although the possibility of antiferroelectricity arising from an antiparallel displacement of the niobium atoms still remains. Other observers, however, have reported positive evidence for ferroelectricity. Hysteresis loops were obtained by Matthias and Remeika,[4] while Vousden[8] observed twin boundary movement under a strong dc field of 20 kv/cm.

We attempted to repeat the latter's experiment by observing the behavior of $NaNbO_3$ crystals in an electric field with a polarizing microscope. Most of the crystals showed no domain boundary movement for fields of 15–20 kv/cm. A few, however, displayed a slight pattern change in the domains just before an electrical breakdown occurred. No positive conclusion could be drawn from the experiments.

It is obvious that the conflicting results could be clarified by assuming Vousden's space group assignment to be in error and by assuming $NaNbO_3$ to have an extremely high coercive field, preventing the observation of hysteresis loops in our dielectric tests. At the same time, however, there is another possible explanation for the disagreement.

The phase diagram shown in Fig. 4 indicates that the ferroelectric tetragonal phase observed in $KNbO_3$ extends to compositions consisting almost entirely of $NaNbO_3$. The ferroelectric orthorhombic phase also extends to within several percent of pure $NaNbO_3$. It is also possible that the addition of other impurities to these mixed crystals would move the ferroelectric phase even closer to pure $NaNbO_3$. Thus a strong electric field might induce the ferroelectric phase in $NaNbO_3$ crystals. This induced ferroelectric phase would be characterized by all the usual phenomena accompanying ferroelectricity, including hysteresis loops and domain boundary movement. In such a case this hypothesis almost exactly fits that proposed by Vousden,[10] who assumed the existence of a ferroelectric state which, under normal conditions, is slightly less stable than a closely related nonferroelectric state. According to Vousden, the ferroelectric structure becomes stable under an applied external field, giving rise to the observed ferroelectric phenomena. This situation is surprisingly similar to the "forced transition by electric field" observed in $PbZrO_3$ [22] and in $Pb(Zr, Ti)O_3$ [23] and $(Ba, Pb)ZrO_3$ [24] solid solutions, for which ample dielectric and structural evidence has been given.

In conjunction with this assumption of a metastable ferroelectric state, it is interesting to note that Roy *et al.*[14] obtained a $NaNbO_3$ compound which showed no extra lines in the powder photograph, by quenching the compound near its melting point. The powder photographs are exactly the same as those usually obtained with $NaNbO_3$, except that the extra lines are missing. After annealing the quenched $NaNbO_3$ overnight at 350°C, the extra lines reappear. This quenched phase could be identical with the induced ferroelectric phase described above; but until the dielectric properties of the quenched phase have been examined, any conclusion would be premature.

It is also interesting to note that the domain movement observed by Vousden can be explained without resorting to an "induced ferroelectricity" hypothesis. If the dielectric constants of a nonpolar crystal differ greatly for different crystallographic directions, a strong electric field can create large energy differences in domains of different orientation. This energy difference may be sufficiently large to cause a domain boundary movement, in such a way that each domain is aligned with the direction of the larger dielectric constant parallel to the external field. The energy difference ΔW may be calculated from $\Delta\epsilon \cdot E^2/8\pi$, where $\Delta\epsilon$ is the difference of the dielectric constant. To obtain an approximate order of magnitude for ΔW, we take $\Delta\epsilon = 1000$, and $E = 20$ kv/cm, which yields $\Delta W = 4\times10^{-3}$ cal/cm^3. Such an energy difference is equivalent to the energy, $P_s \cdot E$, of a crystal having a spontaneous polarization P_s of 1×10^{-6} coulomb/cm^2 at a field of 20 kv/cm. This condition could give rise to the domain boundary movement observed in $NaNbO_3$. The difference of the dielectric constants for different axes of $NaNbO_3$ could be of the same order as those used in the calculation; and since the orthorhombic distortion is extremely small, it is conceivable that the domains are reoriented in a large field. Such a reorientation due to the induced polarization could also lead to an anomalous P *vs* E relationship observed on the oscilloscope.

We are grateful to Dr. R. Roy and Dr. F. Jona for helpful discussions, and to Mr. J. McLaughlin for assistance in specimen preparation and dielectric measurements.

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[22] Shirane, Sawaguchi, and Takagi, Phys. Rev. **84**, 476 (1951).
[23] E. Sawaguchi, J. Phys. Soc. Japan **8**, 615 (1953).
[24] G. Shirane, Phys. Rev. **86**, 219 (1952).