

Dielectric Properties and Phase Transitions of NaNbO_3 and $(\text{Na,K})\text{NbO}_3$ [†]

G. SHIRANE,* R. NEWNHAM, AND R. PEPINSKY

X-Ray and Crystal Analysis Laboratory, The Pennsylvania State University, State College, Pennsylvania

(Received May 12, 1954)

An optical, dielectric, and structural study has been carried out on NaNbO_3 and the solid solution $(\text{Na, K})\text{NbO}_3$, 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 Matthias¹ 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 Vousden² 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 properties³ 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 Remeika⁴ have studied the dielectric properties of these crystals, and Wood⁵ has reported on both the optical and structural properties. The crystals show the following transitions, according to these workers:

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

NaNbO_3 : Orthorhombic $\xleftrightarrow{370^\circ\text{C}}$ tetragonal $\xleftrightarrow{480^\circ\text{C}}$ 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. Vousden⁸ 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, Vousden¹⁰ 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 observations⁵ 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 Remeika⁴ and at 0°C by Wainer and Wentworth.¹¹ Vousden, however, failed to

[†] Investigation supported by contracts with the U. S. Office of Naval Research, and with the Wright Air Development Center.

* On leave from Tokyo Institute of Technology, Tokyo, Japan.

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

² P. Vousden, *Acta Cryst.* **4**, 373 (1951).

³ Hulm, Matthias, and Long, *Phys. Rev.* **79**, 885 (1950).

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

⁵ E. A. Wood, *Acta Cryst.* **4**, 353 (1951).

⁶ A. von Hippel, *Revs. Modern Phys.* **22**, 221 (1950).

⁷ Shirane, Danner, Pavlovic, and Pepinsky, *Phys. Rev.* **93**, 672 (1954).

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 $-175^{\circ}\text{C}.$ 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 $\text{NaNbO}_3\text{-KNbO}_3$ 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 $3\times 3\times 1$ 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: < 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 $\text{CuK}\alpha$ 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

$$a' = c' = 3.915 \text{ \AA}, \quad b = 3.881 \text{ \AA}, \quad \text{and} \quad \beta = 90^{\circ} 40'.$$

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 domains¹³ and very sharp extinction positions. These crystals were used in an optical study of the phase

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 $\text{CuK}\alpha_1$ radiation was taken as 1.5405 \AA in all calculations.

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

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 $700^{\circ}\text{C}.$

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 $480^{\circ}\text{C}.$ The crystals continued to show parallel extinction even above these transitions. A third transition took place at $640^{\circ}\text{C}.$ 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 $640^{\circ}\text{C}.$ Furthermore, it was relatively easy to recognize an optical transition at $640^{\circ}\text{C}.$ 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 $640^{\circ}\text{C}.$ 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 $640^{\circ}\text{C}.$ 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.

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 $\text{CuK}\alpha$ 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 $\text{CuK}\alpha_1$, α_2 doublet at an angle $\theta=40^\circ$. 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

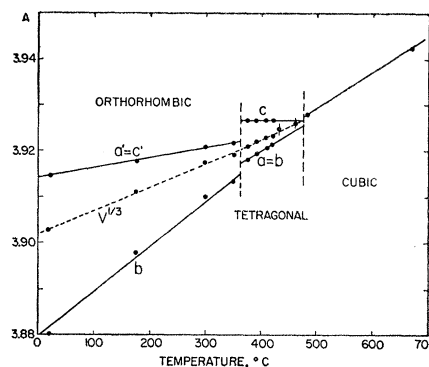


FIG. 1. Lattice parameters of NaNbO_3 .

reported by Wood⁵), but no definite conclusions could be drawn as to their character.

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

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

$T(^{\circ}\text{C})$	$a' = c' (\text{\AA})$	$b (\text{\AA})$	a'/b	β	$\nu (\text{\AA}^3)$
20	3.915	3.880	1.009	$90^\circ 41'$	59.45
175	3.918	3.898	1.005	$90^\circ 32'$	59.82
300	3.921	3.910	1.003	$90^\circ 25'$	60.11
350	3.922	3.913	1.002	$90^\circ 23'$	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

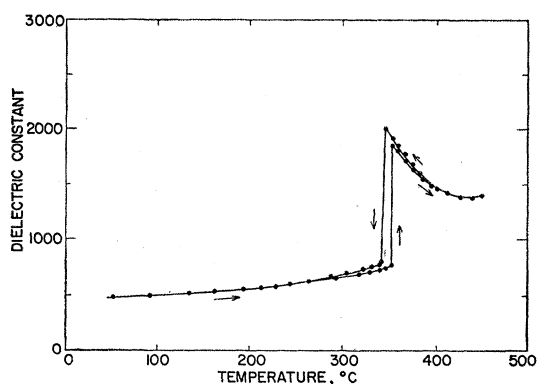


FIG. 2. Dielectric constant of NaNbO_3 single crystal.

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 observations² 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 Cross¹⁷ 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

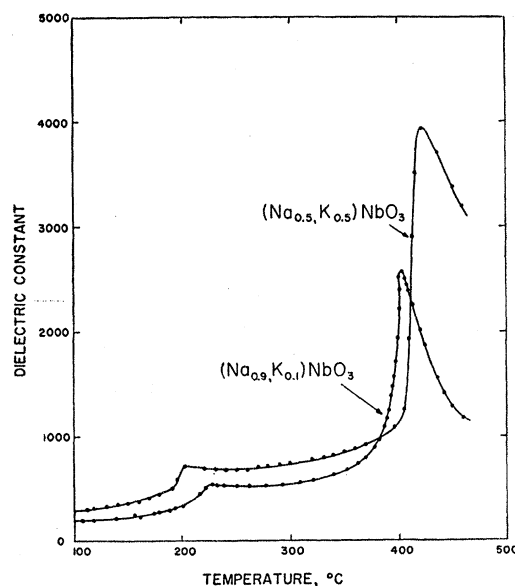
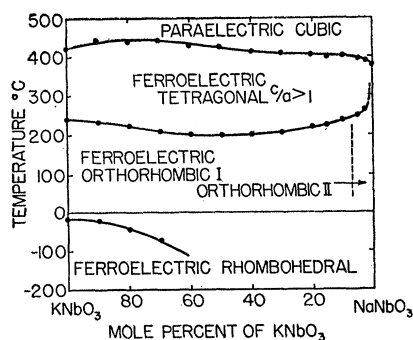


FIG. 3. Dielectric constant of $(\text{Na}, \text{K})\text{NbO}_3$ solid solution.

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 .

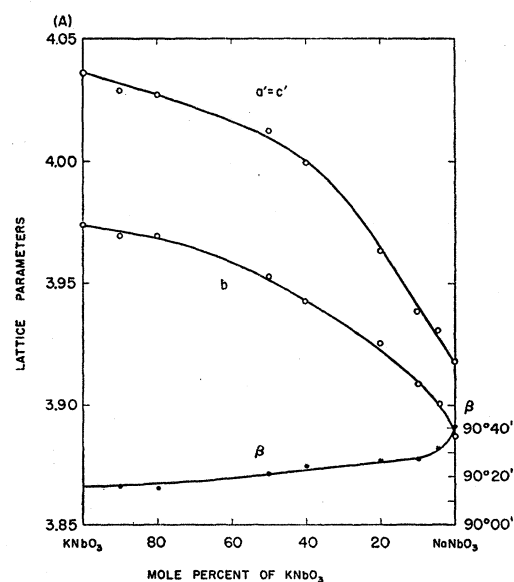
One particularly important result came out of the dielectric study of the KNbO_3 - NaNbO_3 solid solutions. When a small amount of KNbO_3 is added to pure NaNbO_3 , a second small anomaly appears in the dielectric constant near 200°C , in addition to the usual dielectric transition observed around 400°C . The result for $(\text{Na}_{0.9}\text{K}_{0.1})\text{NbO}_3$ 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 diagram¹⁸ 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 $(\text{Na}_{0.9}\text{K}_{0.1})\text{NbO}_3$. By comparing the hysteresis loops of a single specimen in both the orthorhombic and

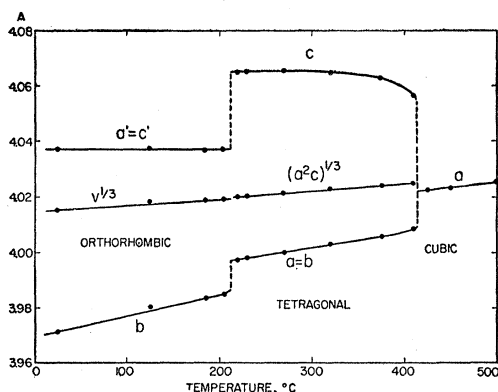
tetragonal phases, we found that the coercive field was much larger and the polarization much further from saturation in the orthorhombic phase.

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 $(\text{Na}_{0.90}\text{K}_{0.10})\text{NbO}_3$ and $(\text{Na}_{0.95}\text{K}_{0.05})\text{NbO}_3$, 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 $(\text{Na}_{0.95}\text{K}_{0.05})\text{NbO}_3$, 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 $(\text{Na}_{0.9}\text{K}_{0.1})\text{NbO}_3$, θ is about 300°C and C is the order of 1 to 2×10^5 . In pure NaNbO_3 ,

FIG. 5. Lattice parameters of $(\text{Na}, \text{K})\text{NbO}_3$ system.

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 $4 \times 10^5^\circ\text{C}$. θ , on the other hand, changes little in comparison, generally having values between 60° and 80° .

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 $(\text{Na}_{0.98}\text{K}_{0.02})\text{NbO}_3$ 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 $\text{CuK}\alpha$ 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, $(\text{Na}_{0.9}\text{K}_{0.1})\text{NbO}_3$ 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 $(\text{Na}_{0.9}\text{K}_{0.1})\text{NbO}_3$ were measured as a function of temperature with a

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

Temp ($^\circ\text{C}$)	$a' = c'$ (Å)	b (Å)	b/a	β	$v(\text{\AA}^3)$
25	4.0375	3.9711	1.0167	$90^\circ 15'$	64.73
125	4.0374	3.9797	1.0145	$90^\circ 15'$	64.87
185	4.0363	3.9830	1.0134	$90^\circ 13'$	64.89
205	4.0369	3.9839	1.0133	$90^\circ 14'$	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

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 SiO₂ as a standard substance.

The specific heat anomalies observed in NaNbO₃ and (Na_{0.9}K_{0.1})NbO₃ are small in comparison with those observed in KNbO₃.⁷ This result was to be expected, since the structural anomaly is much more pronounced in KNbO₃. The integrated transition energies are listed in Table III.

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

The optical study of NaNbO₃ crystals showed three phase transitions at 360°, 480°, and 640°C, while dielectric measurements carried out on NaNbO₃ ceramics up to temperatures as high as 500°C showed only the lowest transition. To complete the phase diagram of the (K-Na)NbO₃ system, mixed crystals were prepared from the appropriate mixtures of NaNbO₃ and KNbO₃, NaF being used as a flux. The compositions of the mixed crystals are not exactly in proportion to the percentages of KNbO₃ and NaNbO₃ because additional Na is introduced by the flux.

Crystals were prepared of several compositions between (K_{0.5}Na_{0.5})NbO₃ and pure NaNbO₃. 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})NbO₃ could be obtained by melting a mixture of equal parts of NaNbO₃ and KNbO₃ 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

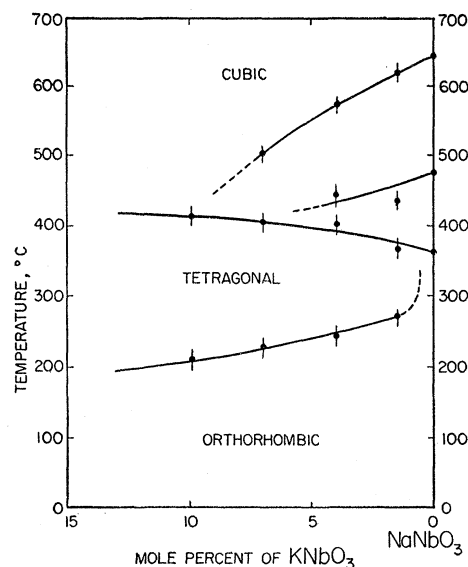


FIG. 7. Phase diagram of NaNbO₃-KNbO₃ system determined from mixed crystals, showing behavior near pure NaNbO₃. The vertical lines show the range of fluctuation of the transition temperatures of the same melt.

amount of KNbO₃ to NaNbO₃ greatly altered its physical characteristics. The optical properties of the tetragonal phase in (Na_{0.9}K_{0.1})NbO₃ are much more similar to those in KNbO₃ than to those in NaNbO₃. In mixed crystals such as this we observed both domains of parallel extinction and plates oriented in the *c* direction.

The two tetragonal phases observed optically in pure NaNbO₃ were also observed for mixed crystals containing less than 10 percent KNbO₃. The temperatures of these optical transitions decreased rapidly with increasing concentration of KNbO₃. As in the case of pure NaNbO₃, 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})NbO₃. 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 NaNbO₃ 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

TABLE III. Transition energy of KNbO₃, NaNbO₃, and (K_{0.1}Na_{0.9})NbO₃.

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

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 Vousden⁸ 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 $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ²³ and $(\text{Ba}, \text{Pb})\text{ZrO}_3$ 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 $\Delta W = 4 \times 10^{-3}$ cal/cm³. 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/cm² 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.

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).