Dielectric Properties of Sodium and Potassium Niobates

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The following paper deals with evidence of ferroelectricity in $KNbO_3$ and $NaNbO_3$. Temperatures at which both materials undergo crystallographic changes and corresponding changes in dielectric constant and loss tangent are reported. Photographs of dielectric hysteresis loops and values of saturation polarization taken at various points over a temperature range are given for $KNbO_3$.

INTRODUCTION

WE have recently reported[1] finding evidence of ferroelectric behavior in a number of substances not previously known to be ferroelectric. The evidence for ferroelectricity has included one or more of the following: (1) unusually high dielectric constant, (2) crystal structure changes accompanied by optical and dielectric constant changes, (3) spontaneously polarized domains visible with the polarizing microscope and showing dielectric hysteresis loops and saturation of the polarization, and (4) a Curie temperature above which spontaneous polarization disappears and the crystal becomes cubic. Many crystals have been observed to show either or both of the first two phenomena without showing evidence of spontaneous polarization. In some cases this has appeared to be due to impurities and a resulting increase in conductivity sufficient to obscure the dielectric hysteresis.

The substances for which some of the above-listed evidences of ferroelectricity have been obtained are $KNbO_3$, $NaNbO_3$, $LiNbO_3$, $KTaO_3$, $NaTaO_3$, $LiTaO_3$, and WO_3. This paper presents more complete dielectric information on $KNbO_3$ and $NaNbO_3$ crystals and shows that they meet the above criteria for ferroelectricity. A paper by Dr. E. A. Wood[2] presents the results of optical and x-ray examination of these materials.
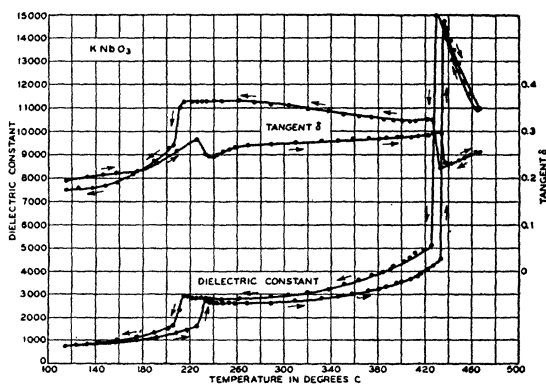
The difficulty of growing large single crystals of these materials with sufficiently low conductivity has been an impediment to further dielectric measurements. There is a strong tendency for some of these materials to be reduced at the high temperatures necessary for their preparation. This usually results in discolored and semiconducting crystals. The preparation of polarizable ceramics of these materials has been a separate and frequently more difficult task. Such materials will not be considered here.

PREPARATION OF CRYSTALS

Growth of $NaNbO_3$ crystals has been reported by Holmquist,[3] who obtained them from a flux of NaF which contained Na_2CO_3 and Nb_2O_5 in the stoichiometric proportions. With minor variations in temperature and composition, we found it possible to obtain crystals of several mm edge length which permitted x-ray identification and were large enough for reliable optical and dielectric measurements.

The growth of $KNbO_3$ crystals had been reported by Joly,[4] who used CaF_2 as a flux at rather high temperatures. Repeating this method several times as described and with variations, we were not able to obtain crystals. Using a low melting K-salt as flux, such as KF or KCl, large and clear crystals were obtained up to 1-cm edge length. They were, unfortunately, of a dark blue color, probably caused by the formation of a small amount of
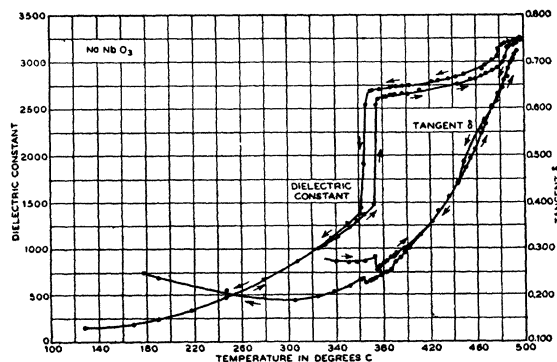

Fig. 1. Dielectric constant and loss tangent curves for single crystals of $KNbO_3$ at 10 kc.

Fig. 2. Dielectric constant and loss tangent curves for single crystal of $NaNbO_3$ at 10 kc.

[1] B. T. Matthias, Phys. Rev. 75, 117 (1949); 76, 430 (1949); B. T. Matthias and J. P. Remeika, Phys. Rev. 76, 1886 (1949).
[2] E. A. Wood, Acta Cryst. (to be published).
[3] Holmquist, Z. Krist. 31, 306 (1896).
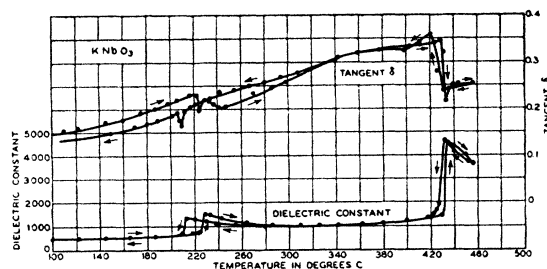[4] Joly, Ann Sci. de l'ecole Norm. Sup. Paris 6, 164 (1877).

FIG. 3. Dielectric constant and loss tangent curves at 150 kc for same single crystal if $KNbO_3$ as in Fig. 1.

Nb_2O_4. These colored crystals were useful for optical and x-ray investigation, but because of their high conductivity were not suitable for dielectric tests. The final crystals were clear cubes from 1 to 3 mm edge length. Somewhat less perfect crystals have been obtained as large as 1 cm on a side. It has not been possible to obtain single domain crystals of either sodium or potassium niobate. X-ray analyses by Mrs. Wood have checked the identification of both substances and confirmed that they have the pseudocubic perovskite structure.

DIELECTRIC MEASUREMENTS

Figures 1 and 2 show the curves of dielectric constant and $\tan\delta$ for $KNbO_3$ and $NaNbO_3$ over a range of temperatures and at a frequency of 10 kc. These measurements are for small signal voltages and on crystals not subjected to polarizing voltage. Large changes in dielectric constant and loss tangent are
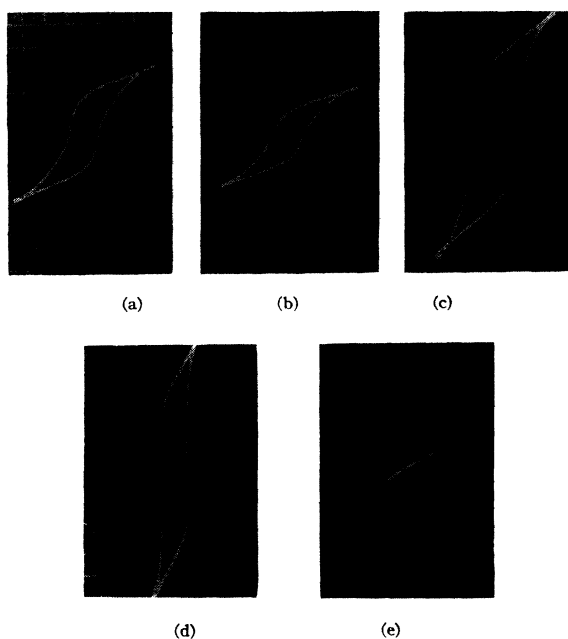

(a)   (b)   (c)

(d)   (e)

FIG. 4. Dielectric hysteresis loops for $KNbO_3$ crystals. (a) 220°C $P_s=1.33\times10^{-6}$ coulombs/cm²; (b) 237°C $P_s=0.92\times10^{-6}$ coulombs/cm²; (c) 329°C $P_s=3.03\times10^{-6}$ coulombs/cm²; (d) 410°C $P_s=3.78\times10^{-6}$ coulombs/cm²; (e) 472°C crystal is cubic.

observed at about 224° and 434° for $KNbO_3$ and at about −80°, 370°, and 480° for $NaNbO_3$. These measurements were made on small single crystals of a few mm² electrode area and about 0.5 mm thick. They were repeated on several samples, all of which showed the same discontinuities and approximately the same value of dielectric constant. The dielectric loss varied somewhat from sample to sample being highest in crystals which were discolored. The values given are for the clearest crystals. The dielectric constant for $KNbO_3$ remained at essentially the same value as shown for 100° even down to −190°, where the conductivity was much lower. Figure 3 for $KNbO_3$ at 150 kc shows the same discontinuities as observed at 10 kc. Here, however, the level of dielectric constant is lower, although the loss tangent has about the same value. Measurement at the high temperatures made necessary the use of gold electrodes evaporated on the crystals and a crystal holder which when empty showed little change of dielectric properties with temperature.

The Curie temperature for $KNbO_3$ is found to be at 434°C. Above this temperature, optical and x-ray studies show that the crystals become cubic. Here, also, the hysteresis and saturation of polarization disappear. Below 434° the $KNbO_3$ crystals are tetragonal. The change in dielectric constant at 220° corresponds to a change in crystal structure from tetragonal to orthorhombic. No further changes of structure have been observed in $KNbO_3$, unlike $BaTiO_3$, which shows an additional low temperature change to rhombohedral symmetry. All of these changes in crystal structure and dielectric properties show a temperature hysteresis which is, however, smaller at high than at low temperatures.

In $NaNbO_3$ two breaks are shown in the dielectric constant curve, the lower at about 370° and the upper at 480°C. In contrast to $KNbO_3$, the larger dielectric constant change occurs at the lower temperature discontinuity. A third and smaller change in dielectric constant, which is not shown, occurs at −80°C. Changes in optical properties also occur at 370° and 480°, but the crystals are still birefringent above 480°. The birefringence gradually decreases up to 640°C, at which temperature they become suddenly isotropic. The x-ray data, however, indicate that $NaNbO_3$ crystals are cubic above 480°. The spontaneous polarization which is observed at lower temperatures is not present above 480°. However, the conductivity has become so large at that temperature that the dielectric hysteresis may be obscured by high conductivity. Although the optical measurements cast some doubt, all of the other evidence points to 480° as the Curie temperature for $NaNbO_3$.

Field polarization hysteresis loops have been obtained for $KNbO_3$ crystals which tend to saturate and resemble those obtained for $BaTiO_3$ crystals. The photographs, Fig. 4, show these hysteresis curves at several temperatures. Figure 4(a) was obtained just below the 224°

transition and Fig. 4(b) just above it. A decrease in the value of the polarization is observed with little change in coercive force. Midway between the two transitions, the polarization has increased and the coercive force decreased, as shown in Fig. 4(c). Just below the Curie temperature, Fig. 4(d), the polarization is nearly double its low temperature value. At 472°, Fig. 4(e), the trace is an ellipse and when compensated

for dielectric loss becomes a single line. Values of the saturation polarization have been estimated from these photographs and the calibrating data to be 0.9×10^{-6} coulombs/cm^2 at room temperature and 3.8 just below the curie temperature.

It is clear from the work reported here that sodium and potassium niobates are ferroelectric and are comparable with the more thoroughly investigated BaTiO$_3$.

Theory of Antiferroelectric Crystals

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An antiferroelectric state is defined as one in which lines of ions in the crystal are spontaneously polarized, but with neighboring lines polarized in antiparallel directions. In simple cubic lattices the antiferroelectric state is likely to be more stable than the ferroelectric state. The dielectric constant above and below the antiferroelectric curie point is investigated for both first- and second-order transitions. In either case the dielectric constant need not be very high; but if the transition is second order, ϵ is continuous across the Curie point. The antiferroelectric state will not be piezoelectric. The thermal anomaly near the Curie point will be of the same nature and magnitude as in ferroelectrics. A susceptibility variation of the form $C/(T+\theta)$ as found in strontium titanate is not indicative of antiferroelectricity, unlike the corresponding situation in antiferromagnetism.

I. INTRODUCTION

IN the ferroelectric state a crystal exhibits a spontaneous electric polarization. We define the antiferroelectric state as one in which lines of ions in the crystal are spontaneously polarized, but with neighboring lines polarized in antiparallel directions, so that the spontaneous macroscopic polarization of the crystal as a whole is zero. We exclude molecular crystals from the present discussion, and we do not explicitly consider antiferroelectric arrays in which more than two sublattices are involved. It is not yet certain that realizations of antiferroelectrics have been observed,[1] as it has not previously been known how to recognize them correctly.

In ferroelectrics the occurrence of spontaneous polarization is believed at present to be the result of a Lorentz catastrophe in which the constant of proportionality connecting the applied electric field with the polarization exhibits a singularity. Illuminating contributions to the theory of the effect have been made, in particular by Wul,[2] Devonshire,[3] and Slater.[4] It would

appear to be quite possible for an antiferroelectric arrangement of dipole moments to be produced by a somewhat generalized form of the Lorentz catastrophe. We shall speak throughout of crystals (such as perovskites) in which specifically quantum-mechanical effects are not of major importance.

We need only consider an arrangement of highly polarizable ions located at the lattice points of a simple tetragonal lattice with an axial ratio[5] $c/a \ll 1$, so that the structure may be thought of as constructed of lines of atoms parallel to the c-axis. Because of the geometry of dipolar fields, ions in the same line will tend to be polarized parallel to each other, but the sense of adjacent lines will be opposite.[6]

In looking for realizations of antiferroelectricity in

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[1] Private communication from Professor B. T. Matthias; I am also indebted to Professor P. Scherrer for a discussion of possible realizations. *Note in proof:* Kehl, Hay, and Wahl have recently observed by x-ray methods the occurrence of an antiferroelectric arrangement in tungsten trioxide crystals above 750°C (private communication from G. Jeffrey).

[2] B. Wul, J. Phys. U.S.S.R. **10**, 95 (1946), V. Ginsburg, J. Phys. U.S.S.R. **10**, 107 (1946).

[3] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949).
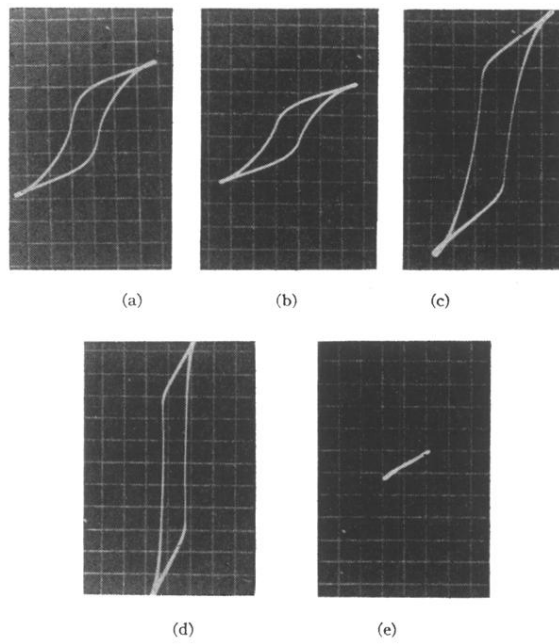
[4] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[5] Actually, as we know from the work of J. A. Sauer and A. N. V. Temperley [Proc. Roy. Soc. (London) **A176**, 203 (1940)] and J. M. Luttinger and L. Tisza [Phys. Rev. **70**, 954 (1946)], even in a simple cubic crystal ($c = a$) the alternating polarized line arrangement of dipoles is the lowest state. This is just our antiferroelectric arrangement. Calculations for barium titanate currently being made by Mr. M. H. Cohen suggest that almost exactly the same polarizabilities as lead to a ferroelectric catastrophe in BaTiO$_3$ would also lead to an antiferroelectric catastrophe. The observed ferroelectricity may be the consequence of short-range interactions.

[6] We may of course discuss by methods similar to those employed in the present paper the case of "quasi-ferroelectricity," in which different types of ions are spontaneously polarized in different directions, but still give a net macroscopic polarization. The ferromagnetic analog of this condition actually occurs in the ferrites and perhaps in other compounds, as suggested by Guillaud and Néel. Jonkers and van Santen [Science **109**, 632 (1949)] have suggested that this situation may obtain in barium titanate.

FIG. 4. Dielectric hysteresis loops for $KNbO_3$ crystals. (a) 220°C $P_s=1.33\times10^{-6}$ coulombs/cm²; (b) 237°C $P_s=0.92\times10^{-6}$ coulombs/cm²; (c) 329°C $P_s=3.03\times10^{-6}$ coulombs/cm²; (d) 410°C $P_s=3.78\times10^{-6}$ coulombs/cm²; (e) 472°C crystal is cubic.