way. The δ_{max} was higher than normal, about 1.6, presumably because of surface contamination, since there was no detectable change in $V_{p\max}$. There was still no step at the junction. Evaporation of a constituent could not have been a factor in this test.

If indeed, then, the space-charge layer exists as calculated and there is no change in material constituents to within very close to the surface, hypothesis *c* remains. It does not seem plausible if the internal secondaries lose energy in steps at each collision that are nearly independent of their energy. If, on the other hand, the energy lost at a collision is proportional to the energy of the colliding electron, then these results would probably ensue.

CONCLUSIONS

1. The yield from Ge is independent of normal donor or acceptor additives and is, therefore, determined by the intrinsic properties of the Ge lattice.

2. The yield from Ge has a small but appreciable temperature coefficient. This is taken as evidence for a small interaction between the internal secondaries and the lattice.

3. The interaction is negligible between internal secondaries and free electrons or positive holes up to concentrations of about $10^{19}/cm^3$.

4. No evidence has been found that strong subsurface fields affect the yield from Ge. It is believed that this is a result of the detailed mechanism of energy loss of the internal secondaries and that it does not rule out the possibility of field effects in other materials such as insulators.

ACKNOWLEDGMENTS

We wish to acknowledge stimulating discussions with Conyers Herring and W. H. Brattain. The specimens were prepared by H. C. Meier.

PHYSICAL REVIEW VOLUME 93, NUMBER 4 FEBRUARY 15, 1954

Phase Transitions in Ferroelectric $KNbO_3$†

G. SHIRANE, H. DANNER, A. PAVLOVIC,* AND R. PEPINSKY
X-Ray and Crystal Structure Laboratory, Pennsylvania State University, State College, Pennsylvania

(Received October 30, 1953)

It is shown that ferroelectric $KNbO_3$ undergoes another phase transition at −10°C in addition to two phase transitions previously reported at 225° and 435°C. At this lowest phase transition $KNbO_3$, on cooling, changes its orthorhombic structure to a rhombohedral one, and this change is accompanied by a sharp change of the dielectric constant. The specific heat anomalies at three transitions were measured, and the results are compared with the case of $BaTiO_3$.

DIELECTRIC measurements of $KNbO_3$ by Matthias and Remeika[1] revealed a ferroelectric Curie point at 435°C and a further transition at 225°C. An x-ray and optical study by Wood[2] revealed a cubic perovskite structure above the Curie point at 435°C, which transforms on cooling first to a tetragonal structure and then to an orthorhombic structure at the aforementioned two transition points. These transitions are related to the phase transitions in $BaTiO_3$ at 120°C and 0°C.[3] A further transition occurs in $BaTiO_3$ at −80°C, in which the structure changes from orthorhombic to rhombohedral. The above investigators found no significant change in the dielectric constant of $KNbO_3$ between room temperature and −190°C,[1] and no optical change was observed between 25° and −50°C.[2]

A preliminary dielectric study[4] carried out in our laboratory on $KNbO_3$ single crystals, prepared without flux, did show a sharp peak in the dielectric constant at −50°C on cooling and −35°C on heating, indicating the existence of a phase transition at this point. A further study has now been carried out on the dielectric, structural, and thermal properties of this lowest phase.

$KNbO_3$ single crystals were prepared as described by Wood,[2] using KCO_3 as a flux and cooling down from 1000°C. The crystals were generally rectangular, transparent, light yellow plates. Optical observation showed them to be multidomain crystals. Dielectric tests were made on crystals 2–3 mm on edge and about 0.3 mm in thickness.

Figure 1 shows the dielectric constant *vs* temperature curve measured at 10 kc/sec and a field strength of about 5 v/cm. The heating and cooling rate was about 1°C/min. In agreement with previous data, this curve shows a very sharp change in dielectric constant at

† Research supported by Contract No. N6onr-26919 with the U. S. Office of Naval Research, and Contract No. AF33(039)-12645 with the Aeronautical Research Laboratory, Wright Air Development Center.

* Owens-Illinois Research Fellow.

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

[2] E. A. Wood, Acta Cryst. **4**, 353 (1951).

[3] See, for instance, A. Von Hippel, Revs. Modern Phys. **22**, 221 (1950).

[4] Pepinsky, Thakur, and McCarty, Phys. Rev. **86**, 650 (1952).

220° and 420°C on heating. In addition to these, there is an abrupt change in the dielectric constant at −10°C on heating. On cooling, these three transitions occur at 410°, 200°, and −55°C. A very large temperature hysteresis of about 45°C at the lowest phase change appears in the several crystals examined.

Powder photographs of $KNbO_3$ were taken with CuK_α radiation in a Norelco powder camera of 11.4-cm diameter. Orthorhombic cell dimensions $a=5.721$A, $b=3.973$A, $c=5.695$A were obtained at room temperature, in good agreement with the previous data.[2,5] The lowest-temperature phase was examined in our low-temperature camera, 10-cm diameter, using CuK_α radiation. Diffraction patterns at −140°C showed pseudo-cubic lines of perovskite type, but small although definite line splittings were observed in a few high angle lines such as (422), (332), and (420). The line splittings could be explained by assuming a rhombohedral lattice and considering both line spacings and intensities. Special attention was paid to the (400) reflections, which show no multiplet except that due to the α_1,α_2 doublet; and this excluded the possibilities of tetragonal or orthorhombic lattices. The lattice parameters calculated from (422) and (332) line groups are $a=4.016\pm0.002$A and $\alpha=89°50'\pm1'$.

Since $\alpha<90°$, this rhombohedral lattice is derived from an ideal cubic lattice by an elongation along [111]. This corresponds to the same lattice as that of the lowest phase in $BaTiO_3$. Polarizing microscope observations also showed the three phase transitions at temperatures of the dielectric anomalies; and extinction positions are in accordance with the x-ray determined symmetry of each phase. If we reduce the three transition temperatures by dividing by the Curie temperature, they are 1, 0.69, 0.49 and 1, 0.71, 0.38 for $BaTiO_3$ and $KNbO_3$, respectively. $KNbO_3$ is the only one perovskite-type ferroelectric which has been found to show three transitions similar to those of $BaTiO_3$.

To further compare the transitions in these two crystals, a study was made of the specific heat anomaly at the three transitions in $KNbO_3$. Ceramic $KNbO_3$ was prepared by firing a mixture of K_2CO_3 and Nb_2O_5 at 1050°C. An adiabatic calorimeter of the Nernst type,[6] holding about 50 g of $KNbO_3$ powder, was used for the lower-temperature measurements. Another adiabatic calorimeter of Nagasaki-Takagi[7] type, containing about 15 g of $KNbO_3$ powder, was used at high temperatures. The measurements were carried out by heating the specimens continuously at a rate of 0.5 to 1°C/min. Sharp peaks in the specific heats appeared at the three transition temperatures.

TABLE I. Transition energy ΔE (cal/mole) and entropy change ΔS (cal/mole degree) at the three transitions in $BaTiO_3$ and $KNbO_3$.

		Cubic —	Tetragonal —	Orthorhombic —	Rhombohedral
$BaTiO_3$	ΔE	47∼50[a,b,c]	16∼26[a,b,c,d]		8∼14[b,c,d]
	ΔS	0.12∼0.13	0.06∼0.09		0.04∼0.07
$KNbO_3$	ΔE	190±15	85±10		32±5
	ΔS	0.28	0.17		0.12

[a] Blattner, Kaenzig, and Merz, Helv. Phys. Acta **22**, 35 (1949).
[b] G. Shirane and A. Takeda, J. Phys. Soc. Japan **7**, 1 (1952).
[c] J. Volger, Philips Research Repts. **7**, 21 (1952).
[d] S. S. Todd and R. E. Lorenson, J. Am. Chem. Soc. **74**, 2043 (1952).

[5] P. Vousden, Acta Cryst. **4**, 373 (1951).

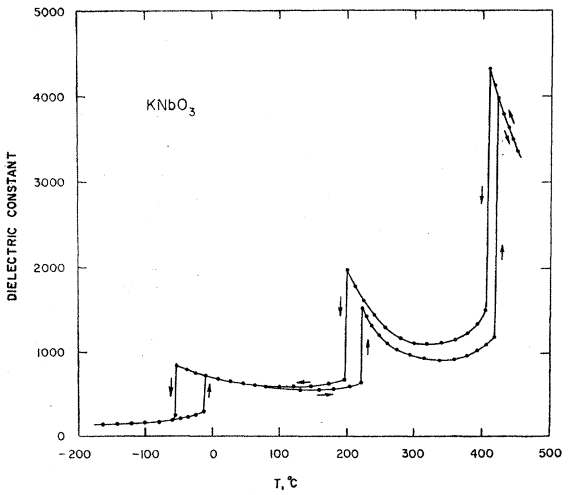

FIG. 1. Dielectric constant of $KNbO_3$.

The values of the transition energies integrated from the curves are shown in Table I, together with data on $BaTiO_3$. The larger transition energies in $KNbO_3$ could be explained in terms of the larger lattice distortions in $KNbO_3$ as compared with the corresponding transitions in $BaTiO_3$. It may be interesting to point out that the relative ratio of the three entropy changes are nearly the same in these two crystals; and, moreover, the entropy changes at the Curie points of these two crystals are approximately proportional to their $[(c/a)-1]$ values in the tetragonal phase.

To permit a more detailed comparison of these two crystals, and especially to apply Devonshire's theory[8] of $BaTiO_3$ to $KNbO_3$, we must know the values of the Curie constant and the spontaneous polarization at the Curie point. Unfortunately, reliable values of these quantities in $KNbO_3$ are difficult to obtain, because of the relatively high conductivity near the Curie point at 430°C.

The authors express their gratitude to Mr. R. E. Newnham for preparation of the single crystals.

[6] See for example, J. C. Southard and F. G. Brickwedde, J. Am. Chem. Soc. **55**, 4378 (1933).
[7] S. Nagasaki and Y. Takagi, J. Appl. Phys. Japan **17**, 104 (1948).
[8] A. F. Devonshire, Phil. Mag. (7) **40**, 1040 (1949).