Transitions in Ferroelectric KNbO₃

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This report concerns developments supported at The Pennsylvania State College in part by Contract No. N6onr-26919 with the Acoustics Branch of the Office of Naval Research, and in part by Contract No. AF33(616)-2133 with the Aeronautical Research Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base.

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15 October 1953
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Dielectric measurements of KNbO$_3$ by Matthias and Remelka$^1$ revealed a ferroelectric Curie point at $435\,^\circ\mathrm{C}$ and a further transition at $225\,^\circ\mathrm{C}$. An X-ray and optical study by Wood$^2$ revealed a cubic perovskite structure above the Curie point at $435\,^\circ\mathrm{C}$, which transforms on cooling first to a tetragonal structure and then to an orthorhombic structure at the above two transition points. These transitions are related to the phase transitions in BaTiO$_3$ at $120\,^\circ\mathrm{C}$ and $0\,^\circ\mathrm{C}$$^3$. A further transition occurs in BaTiO$_3$ at $-80\,^\circ\mathrm{C}$, 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\,^\circ\mathrm{C}$$^1$, and no optical change was observed between $25\,^\circ\mathrm{C}$ and $-50\,^\circ\mathrm{C}$$^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 $-50\,^\circ\mathrm{C}$ on cooling and $-35\,^\circ\mathrm{C}$ 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.

$\text{KNbO}_3$ single crystals were prepared as described by Wood\(^{(2)}\), using $\text{KCO}_3$ as a flux and cooling down from $1000^\circ\text{C}$. The crystals were generally rectangular, transparent, light-yellow plates. Optical observation showed them to be multi-domain 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 5v/cm. The heating and cooling rate was about $1^\circ\text{C}$/min. In agreement with previous data, this curve shows a very sharp change in dielectric constant at $220^\circ\text{C}$ and $420^\circ\text{C}$ on heating. In addition to these, there is an abrupt change in the dielectric constant at $-10^\circ\text{C}$ on heating. On cooling, these three transitions occur at $410^\circ\text{C}$, $230^\circ\text{C}$, and $-55^\circ\text{C}$. A very large temperature hysteresis of about $45^\circ\text{C}$ at the lowest phase change appears in the several crystals examined.

Powder photographs of $\text{KNbO}_3$ were taken with CuKα radiation in a Norelco powder camera of 11.4 cm diameter. Orthorhombic cell dimensions $a = 5.721\AA$, $b = 3.973\AA$, $c = 5.695\AA$ 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 diam., using CuKα radiation. Diffraction patterns at $-140^\circ\text{C}$ 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 $a_{1}, a_{2}$ doublet;
and this excluded the possibilities of tetragonal or orthorhombic lattices.
The lattice parameters calculated from (422) and (332) line groups are
\(a = 4.016 \pm 0.002 \text{Å} \) and \(a = 89° 50' \pm 1'.\)

Since \(a < 90°\), 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\(_2\)CO\(_3\) and Nb\(_2\)O\(_5\) at 1050°C. An adiabatic
calorimeter of the Nernst type\(^6\), holding about 50 grams of KNbO\(_3\) powder, was
used for the lower temperature measurements. Another adiabatic calorimeter of
Nagasaki-Takagi\(^7\) type, containing about 15 grams 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.

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 $\left(\frac{2}{3}-1\right)$ values in the tetragonal phase.

To permit a more detailed comparison of these two crystals, and especially to apply the Devonshire's theory 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 $\Delta 30^\circ$C.

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

*Research supported by Contract No. N6onr-26919 with Office of Naval Research, and Contract No. AF33(039)-12645 with Air Research and Development Command.

**Owens-Illinois Research Fellow.

(1) B. T. Matthias and J. P. Remeika, Phys. Rev. 82, 727 (1951).
(3) See for instance, A. Von Hippel, Rev. of Modern Physics 22, 221 (1950).
(8) A. F. Devonshire, Phil. Mag. (7) 40, 1040 (1949).
Table I. Transition Energy $\Delta E$ (cal/mole) and Entropy Change $\Delta S$ (cal/mole degree) at the Three Transitions in BaTiO$_3$ and KNbO$_3$

<table>
<thead>
<tr>
<th></th>
<th>Cubic</th>
<th>Tetragonal</th>
<th>Orthorhombic</th>
<th>Rhombohedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$</td>
<td>$\Delta E$</td>
<td>47 $\sim$ 50$^{a,b,c}$</td>
<td>16 $\sim$ 26$^{a,b,c,d}$</td>
<td>8 $\sim$ 14$^{b,c,d}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta S$</td>
<td>0.12 $\sim$ 0.13</td>
<td>0.06 $\sim$ 0.09</td>
<td>0.04 $\sim$ 0.07</td>
</tr>
<tr>
<td>KNbO$_3$</td>
<td>$\Delta E$</td>
<td>190 $\pm$ 15</td>
<td>85 $\pm$ 10</td>
<td>32 $\pm$ 5</td>
</tr>
<tr>
<td></td>
<td>$\Delta S$</td>
<td>0.28</td>
<td>0.17</td>
<td>0.12</td>
</tr>
</tbody>
</table>

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Figure 1

Dielectric Constant of KNbO₃