Transitions in Ferroelectric KNbO₃

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Dielectric measurements of KNbO$_3$ by Matthias and Remelka revealed a ferroelectric Curie point at 435°C and a further transition at 225°C. An X-ray and optical study by Wood 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 above two transition points. These transitions are related to the phase transitions in BaTiO$_3$ at 120°C and 0°C. 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, and no optical change was observed between 25°C and -50°C.

A preliminary dielectric study 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.

KNbO₃ single crystals were prepared as described by Wood(2), using KCO₃ as a flux and cooling down from 1000°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°C/min. In agreement with previous data, this curve shows a very sharp change in dielectric constant at 220°C 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°C, 290°C 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 KNbO₃ were taken with CuKa radiation in a Norelco powder camera of 11.4 cm diameter. Orthorhombic cell dimensions a = 5.721Å, b = 3.973Å, c = 5.695Å 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 CuKa 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 a₁,a₂ doublet;
and this excluded the possibilities of tetragonal or orthorhombic lattices. The lattice parameters calculated from (422) and (332) line groups are $a = 4.016 \pm 0.002$ Å and $\alpha = 89^\circ 50' \pm 1'$.

Since $\alpha < 90^\circ$, 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, holding about 50 grams of KNbO$_3$ powder, was used for the lower temperature measurements. Another adiabatic calorimeter of Nagasaki-Takagi 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 \(\frac{a}{2} - 1\) values in the tetragonal phase.

To permit a more detailed comparison of these two crystals, and especially to apply the 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 \(430^\circ\text{C}\).

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**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).


\(^{(5)}\) P. Vousden, Acta Cryst. 4, 373 (1951).

\(^{(6)}\) See for example, J. C. Southard and F. C. Dickhues, J. Am. Chem. Soc. 55, 4378 (1933).


\(^{(8)}\) 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 $\text{BaTiO}_3$ and $\text{KNbO}_3$

<table>
<thead>
<tr>
<th></th>
<th>Cubic</th>
<th>Tetragonal</th>
<th>Orthorhombic</th>
<th>Rhombohedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$ $\text{BaTiO}_3$</td>
<td>$\Delta S$</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>$\Delta S$</td>
<td>0.12 $\sim$ 0.13</td>
<td>0.06 $\sim$ 0.09</td>
<td>0.04 $\sim$ 0.07</td>
<td></td>
</tr>
<tr>
<td>$\Delta E$ $\text{KNbO}_3$</td>
<td>$\Delta S$</td>
<td>190 $\pm$ 15</td>
<td>85 $\pm$ 10</td>
<td>32 $\pm$ 5</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>0.28</td>
<td>0.17</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1

Dielectric Constant of KNbO$_3$