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The Dielectric Properties of Barium Titanate at Low Temperatures

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The complex dielectric constant of ceramic barium titanate has been measured as a function of temperature from 300°K down to 2.8°K. The large value of the slope of the real part of the dielectric constant, K', *versus* temperature curve in the 4°K region previously reported by Wul was observed in the measurements described here, and a large hump in the $\tan\delta$ *versus* temperature curve was observed at low temperatures. Measurements were also made on barium titanate diluted with 15 percent and 30 percent strontium titanate. The dilution in both cases gave large slopes in the K' *versus* temperature curve at low temperatures. The measurements were made largely at 500 kilocycles per second.

INTRODUCTION

RECENTLY a great deal of interest has arisen in the dielectric properties of barium titanate and other compounds of titanium because they show such an enormous dielectric constant,[1,2] exhibit domain properties,[3] and may behave like transducers with modes of mechanical resonance to alternating electric fields.[3] Wul[1] reported studies of the dielectric constant as a function of temperature on barium titanate and found, at temperatures available with liquid helium, a remarkably large dependence of the dielectric constant on temperature. Considering the negligible expansion at these low temperatures and the inference from the third law of thermodynamics that such properties of matter as the dielectric constant should have zero temperature slope at 0°K, it was deemed important to repeat Wul's experiment on $BaTiO_3$ and measure both the real and imaginary parts of the dielectric constant. We have found complete agreement with Wul at 4°K on the temperature dependence of the real part, K'. Our studies show an interesting dependence of the imaginary part of the dielectric constant, K'', on temperature and on frequency.

It is generally believed that the high values of K' existing in the titanium compounds are due to the loose binding of the Ti ion in the unit crystalline cell. X-ray powder diffraction studies made by Megaw[4] reveal that the unit cell is tetragonal with the Ti ion shifted from its normal central position toward one of the oxygen atoms on the face of the cube. The unit cell is elongated about 1 percent in the direction of motion of the Ti ion, while the other dimensions are shortened by half this amount so as to keep the volume constant. Above 393°K, where the peak value of K' occurs, the tetragonal form goes into the cubic. The permanent dipole moment of the unit cell below the transition point suggests the possibility of a resultant macroscopic polarization and a domain structure analogous to ferromagnetic materials. Indeed, changes in the dielectric property, which are analogous to the Barkhausen jumps in ferromagnetic materials, have been observed by Matthias[5] and others. Thus it is inadequate to describe the motion of the Ti ion as a simple damped oscillator driven by an alternating electric field. Yet, as we shall show, such a theory may be useful in describing the experimental results on K', but cannot be used to explain the behavior of K''.

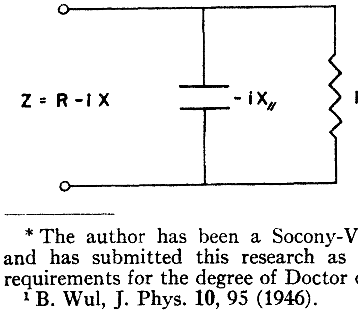

FIG. 1. Equivalent circuit of impedance of $BaTiO_3$ specimens.

EXPERIMENTAL

The experimental work was done in the Collins cryostat, which is capable of producing any temperature from room temperature down to 2°K. The ceramic specimens of barium titanate and barium titanate diluted with 15 percent and 30 percent strontium titanate were kindly supplied by the Bell Telephone Laboratories. They were in the form of parallel plate condensers consisting of ceramic disks about 25 mm in diameter and 1.6 mm thick on the average. The electrodes were silver and were applied by baking on silver paste. The leads were soldered directly onto the electrodes. Four pure specimens of barium titanate were labeled respectively: *A*, *B*, *C*, *D* and gave identical results. The disk which was diluted 15 percent with strontium titanate is specimen *E*, and the 30 percent diluted specimen *F*. Edge effects were neglected in all measurements for two reasons; first, the large value of K' reduces edge effects, and second, the electrodes were quite irregular in shape, making the measurement of electrode area difficult.

The electronic equipment used to measure the complex dielectric constant was of two types. During

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the preliminary measurements a Boonton Type 160-A Q-meter was used. This is a calibrated radiofrequency oscillator which applies a regulated 0.02 volt r.m.s. signal across a 0.04 ohm non-inductive resistance which excites a series resonant circuit composed of a calibrated tuning condenser, standard inductance, and the unknown impedance of the test specimen. Frequencies of 50 kilocycles were used. Values of K' were obtained from the capacity value which the Q-meter indicated for the specimen. "Q" readings obtained indicated only roughly a high energy loss or a low energy loss in the test condenser. For this reason, a second piece of electronic equipment was introduced for measuring directly the real and imaginary parts of the dielectric constant. A radiofrequency signal generator, General Radio Type 805-C, was used to send signals at 500, 750, 1000, and 2000 kilocycles per second to an impedance bridge. General Radio Type 916-A. This impedance bridge measures directly the series resistance and reactance of the unknown impedance, which in these experiments, consists of the barium titanate condenser and the coaxial cable connecting it with the impedance bridge.

Small corrections for the impedance of the coaxial cable yielded the impedance of the specimen condenser. The calculation of the complex dielectric constant is made from the measured impedance as follows: Fig. 1 shows the specimen condenser considered as an equivalent circuit composed of a parallel capacitance and resistance. The parallel capacitive reactance, $X_{||}$ gives K', while the parallel resistance, $R_{||}$, gives K''.

TABLE I. Values of K', K'' and $\tan\delta$ for pure barium titanate, specimen C.

Temperature °K	Frequency kc	K'	$\tan\delta\times10^3$	K''
298	1000	1164	3.78	4.4
297	500	1162	3.47	4.0
291	500	1227	4.91	6.0
287	500	1274	7.01	8.9
284	500	1320	8.30	11.0
281	500	1350	9.44	12.7
276	500	1351	10.4	14.1
270	500	1210	13.9	16.8
267	500	1121	13.1	14.8
264	500	1068	10.9	11.7
262	500	1050	8.38	8.8
248	500	956	15.5	14.8
227	1000	858	21.4	18.4
201	750	658	28.1	18.5
180	500	515	29.5	15.2
159	1000	431	32.6	14.1
145	500	390	35.1	13.7
125	1000	332	41.4	13.8
100	750	282	45.0	12.7
85	1000	240	48.6	11.7
64	750	193	47.5	9.2
39	500	150	43.3	6.2
25	500	129.3	37.7	4.9
17	500	111.6	30.4	3.4
8.0	2000	98.4	19.2	1.9
4.3	500	96.8	14.1	1.4
2.8	500	94.6	10.8	1.0

It follows from elementary a.c. circuit theory that

$$X_{||}=(R^2+X^2)/X \quad \text{and} \quad R_{||}=(R^2+X^2)/R.$$

Further, from the capacitive reactance $X_{||}=1/\omega C$ and the familiar parallel plate condenser formula $C=(\epsilon_0 K'A)/d$, where d is the distance between the electrodes, and A the area of each of the plates, we have

$$K'=(d/\epsilon_0 A)[X/\omega(R^2+X^2)].$$

Similarly, from $K''=(\sigma/\omega\epsilon_0)$ and $R_{||}=d/\sigma A$, where σ is the specific a.c. conductivity, we have

$$K''=(d/\epsilon_0 A)[R/\omega(R^2+X^2)].$$

Finally, we define the much used "loss factor,"

$$\tan\delta=K''/K'.$$

We have followed convention in plotting $\tan\delta$ in the figures representing our experimental results rather than K''.

Temperatures were measured by a series of overlapping thermometers consisting of thermocouples, constant volume thermometers, vapor pressure thermometers, and carbon resistance thermometers. By keeping the temperature drifts slow, temperatures are accurate to about $\frac{1}{10}$ of a degree at the extreme low temperatures, and to about $\frac{1}{2}$ degree at temperatures above 20°K.

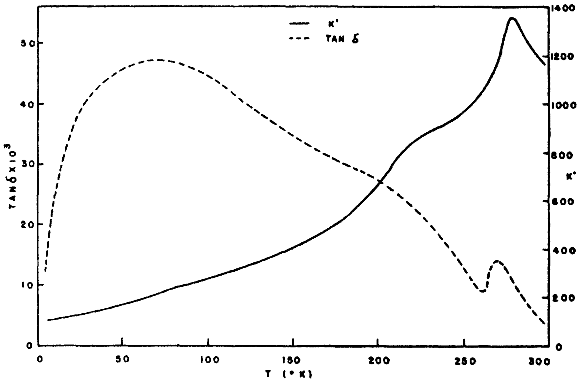

FIG. 2. K' and $\tan\delta$ of $BaTiO_3$ *versus* temperature.

RESULTS

Figure 2 shows the plot against temperature of K' and $\tan\delta$, for the four pure barium titanate specimens, A, B, C, D. Table I gives the values for specimen C at several temperatures and frequencies. Figure 3 shows the extreme low temperature portion of the curve so that some idea of the large slope may be obtained; the experimental points on all four pure specimens are plotted on this curve. In Fig. 4 the results of the studies on barium titanate diluted with a solid solution of 15 percent and 30 percent strontium titanate are shown as a function of temperature.

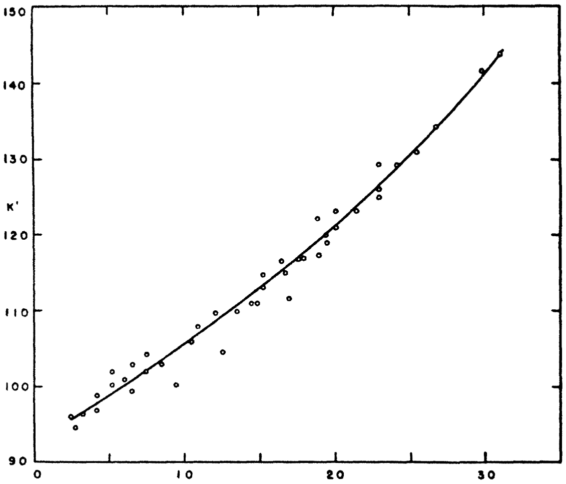

FIG. 3. K' of $BaTiO_3$ *versus* temperature below 30°K.

DISCUSSION

For the pure barium titanate the real part of the dielectric constant agrees in magnitude and in its temperature dependence with the work of Wul[1] and of von Hipple.[2] The peak at 280°K is not to be confused with the much larger peak found by many investigators at 393°K where there is a structure chance; possibly the peak at 280°K is to be identified with changes in domain size. Below 280°K, K' falls off with decreasing temperature to a value of about 100 in the 4°K region. The large slope gave a value of $1/K' \cdot dK'/dT$ of 0.01 per °K in the 4°K region for both the pure barium titanate and the diluted specimens. There appeared to be no frequency dependence of K' within experimental error over the entire temperature region studied. The temperature dependence of K' at low temperature could be explained on the basis of an increase in the binding of the titanium ion as the temperature decreases. Such a theoretical model of the damped oscillator driven by the periodic electric field gives an equation of motion:

$$m\ddot{x}+r\dot{x}+fx=eE_0e^{i\omega t}.$$

The well-known solution for the displacement, x, may be used to calculate the polarization $p=Nex$ for N oscillators per unit volume. From the relation $\epsilon_0KE=\epsilon_0E+P$, we obtain the complex dielectric constant

$$K=K'-iK''=1+\frac{Ne^2/m\epsilon_0}{(\omega_0{}^2-\omega^2)+ir\omega/m}.$$

For very low frequencies where $\omega \ll \omega_0$, the real part, K', is independent of the frequency of the electric field and depends on the force constant, f, in a way to satisfy the qualitative aspects of the experiments. Such a model predicts a dependence of K'' on the frequency and this has not been observed in our experiments.

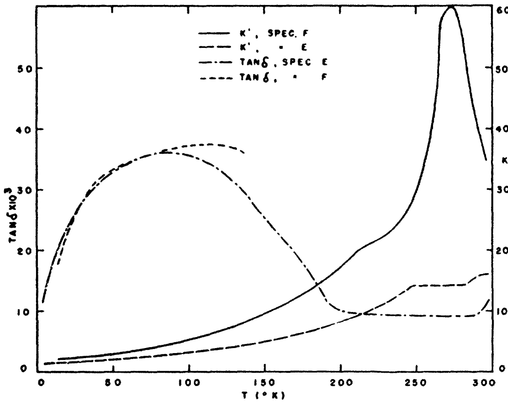

FIG. 4. K' and tanδ of diluted specimens *versus* temperature.

The large hump in tanδ at low temperatures observed on all specimens, pure and dilute, has not been observed previously. The values near room temperature are in agreement with those given by von Hipple[2] and by Roberts,[6] but disagree with their work at lower temperatures.

The effect of the dilution of barium titanate with 15 percent and 30 percent strontium titanate seems to have been a shifting of the normal barium titanate K' curve to lower temperatures. Thus the 30 percent dilution (specimen F) has its transition point peak of 6000 at 280°K and a value of 200 at 14°K. This shift in the transition point peak in K' is in agreement with the measurements reported by Jackson and Reddish.[7] The dilution with strontium ions in place of barium ions does very little to the temperature dependence of K''.

The theoretical interpretation presents a challenging problem both with respect to the surprisingly large dependence of K' on temperature at 4°K and with respect to the behavior of K'' with temperature and frequency. We suggest that the concept of domain growth must be introduced into the theory of K''.

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