

It may be seen from Eqs. (30) and (31) that the customary addition of reciprocal time constants is justified only when $\mu_i \ll 1$ and $\mu_i \nu_i < 1$. Both conditions are met when the recombination-center density is sufficiently small. For recombination centers near the middle of the gap, this requires that

$$\alpha_{pi} N_i^- / \alpha_{ni} n_0 < 1,$$

which suggests that deviations may be found when one or both of the centers are negatively charged, so that $\alpha_p > \alpha_n$.

APPENDIX I

Following injection of a short pulse of carriers in equal number $\delta n(0) = \delta p(0) = \Delta$ we have

$$\begin{aligned} A_n &= 0, & A_p &= 0, \\ B_n &= \frac{\alpha - \beta - \omega_+}{\omega_- - \omega_+} \Delta, & B_p &= \frac{\eta - \gamma - \omega_+}{\omega_- - \omega_+} \Delta, \\ C_n &= \Delta - B_n, & C_p &= \Delta - B_p, \end{aligned}$$

where $\omega = \tau^{-1}$.

If injection is suddenly begun at a rate g , then

$$\begin{aligned} A_n &= \left(\frac{\beta + \eta}{\alpha \eta - \beta \gamma} \right) g, & A_p &= \left(\frac{\gamma + \alpha}{\alpha \eta - \beta \gamma} \right) g, \\ B_n &= \frac{(\alpha - \omega_+) A_n - \beta A_p}{\omega_+ - \omega_-}, & B_p &= \frac{(\eta - \omega_+) A_p - \gamma A_n}{\omega_+ - \omega_-}, \\ C_n &= -(A_n + B_n), & C_p &= -(A_p + B_p). \end{aligned}$$

The same time constants are obtained in both cases.

Dielectric Properties of Single Domain Crystals of BaTiO₃ at Microwave Frequencies

T. S. BENEDICT AND J. L. DURAND

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received October 3, 1957)

Small-signal dielectric constant measurements were made on single domain crystals of BaTiO₃ from 25°C to 170°C at 24 kMc/sec. A typical Curie behavior was observed with a dielectric constant ϵ_{11} of about half the dc value below the upper Curie point. Measurements of ϵ_{11} were also made with a dc field (E_3) applied along the c axis in order to obtain information concerning the distortion of the potential well perpendicular to the c axis when the ion is displaced along the c axis. The change $\Delta \epsilon_{11}$ observed was about 50 for an applied field of 10⁴ volts/cm.

INTRODUCTION

THE dielectric properties of ceramic and polycrystalline samples of BaTiO₃ have been studied by other authors¹ at microwave frequencies. These results show a relaxation effect in the neighborhood of 10¹⁰ cps which has been attributed to inertia of the domain boundaries² and the piezoelectric resonance of the crystallites.³ These experiments also show a variation of the dielectric constant with an applied dc field. The sections which follow describe experiments done on single domain crystals. The experiments were of two different kinds: (a) measurement of the small-signal dielectric constant at 24 kMc/sec as a function of temperature, and (b) measurement of the effect of a dc field on the dielectric constant at that frequency.

DIELECTRIC CONSTANT VS TEMPERATURE

Single crystals of area ~ 1 cm² and thickness ~ 0.040 cm were grown by the method described by Remeika.⁴ The crystals were inspected under a polarizing microscope and those in which the c axis was aligned predominantly perpendicular to the plane of the crystal plate were chosen for investigation. These crystals were then poled at 60 cps until microscopic observation showed them to be polarized in the c direction (c domain) over an area large enough to fill the cross section of a standard K -band wave guide (0.420 in. \times 0.170 in.). The crystals were shaped to fit the guide by sandblasting away the unwanted portion. It was found that sandblasting was preferred to shaping with a diamond saw because fewer strains were produced near the edges of the crystals during the cutting operation. The crystals were then mounted in brass slugs with silver paste providing the contact between the crystal and the brass. The plate was mounted perpendicular to the

¹ A. von Hippel, *Revs. Modern Phys.* **22**, 221 (1950); J. G. Powles and W. Jackson, *Proc. Inst. Elec. Engrs. (London)* **96**, 383 (1949).

² C. Kittel, *Phys. Rev.* **83**, 458 (1951).

³ A. F. Devonshire, *Phil. Mag.* **42**, 1065 (1951).

⁴ J. P. Remeika, *J. Am. Chem. Soc.* **76**, 940 (1954).

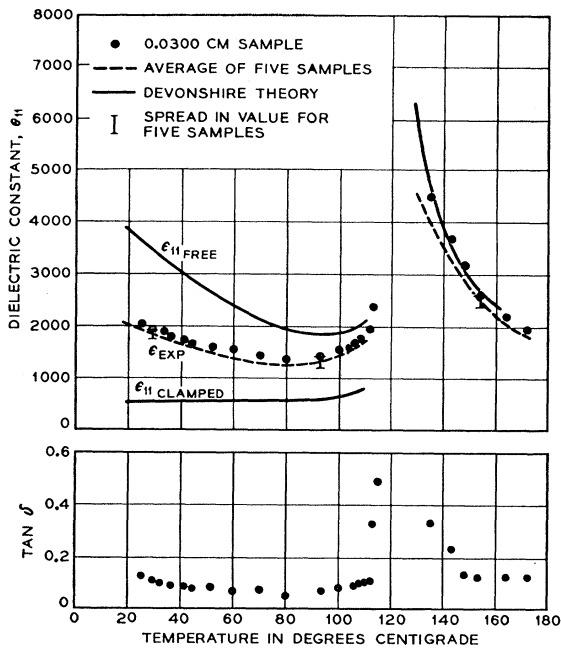


FIG. 1. Dielectric constant (ϵ_{11}) vs temperature for BaTiO_3 single crystal. The solid lines give the theoretical values from reference 3. The dashed line gives the average value for the five crystals used and the points are those obtained for the "best" of the crystals used. $\text{Tan } \delta$ vs temperature for the "best" crystal.

direction of propagation of the microwaves. Best results were obtained for those crystals which were measured at approximately the grown thickness. Some of the crystals were lapped to the desired thickness but in those cases it was difficult to obtain complete polarization of a large enough area. All of the crystals were given a light etch in H_3PO_4 .

In order to be sure that the samples preserved their single-domain character as the temperature was increased, it was necessary to mount the crystals in the crystal holder and observe them between polaroids with light passing down the guide as the temperature was increased. It was found that those crystals which were easily poled at 60 cps preserved their single domain character up to about 115°C ; however, when the temperature was allowed to exceed the Curie temperature (T_c) and then return to a value below T_c , both a and c domains were observed. Preliminary measurements were taken on a number of crystals as the temperature was increased to 115°C in order to show that no appreciable temperature lag existed. The final measurements were made while increasing the temperature slowly to 170°C , a point well above the Curie point.

The microwave bridge⁵ used in these experiments incorporated a phase shifter and an attenuator which

were of the rotating vane type. These elements had the advantage that they were essentially pure elements. The attenuator would attenuate over a range of 0 to 50 db with less than 1° of phase shift and the phase shifter could shift phase from 0° to 360° with an attenuation variation of less than 0.8 db. The detector used was the usual double detection set with a beat frequency of 60 Mc/sec. From measurements of the phase shift and attenuation, it was possible to obtain unambiguously the dielectric constant and loss tangent of the sample⁶ by using more than one sample thickness. In order to make sure that higher microwave modes were not present in the sample it was thought advisable to use at least 5 crystals of varying thickness and to make a number of runs on each sample, remounting the sample after each run. The thicknesses chosen were 0.0144, 0.0185, 0.0167, 0.0300, 0.0333 cm. The best crystal was the 0.0300-cm sample from the standpoint of low coercive field.

The results of the temperature variation of the dielectric constant and loss tangent at 24 kMc/sec are shown in Fig. 1. It is seen that a typical Curie curve is obtained with a sharp rise in ϵ_{11} at the Curie point. The value of $\text{tan } \delta$ observed is somewhat lower than those observed in ceramics. The small variation of ϵ_{11} from sample to sample is probably due to very small domains which would cause a decrease in ϵ_{11} and therefore the most reliable data is that which shows the highest value of ϵ_{11} . The 0.0300-cm crystal gave the highest values as expected. The dielectric constant is about one-half that observed at low frequency below the Curie point but is in essential agreement with the low-frequency value above the Curie point.

Because of the great improvement which has taken place in the art of growing BaTiO_3 in recent years and because of the difficulty in making low-frequency measurements of ϵ_{11} , it was felt that a repetition of this measurement⁶ at room temperature was necessary in order to verify the observed decrease at microwave frequencies. One crystal was selected which was predominantly polarized in the plane of the crystal. This crystal was poled with a field in the plane of the plate and the faces were gold-plated. The value obtained was $\epsilon_{11} = 4100$, in agreement with results of reference 6.

If the results shown in Fig. 1 are compared with the Devonshire theory,³ we find that above the Curie point the agreement is as expected if the resonance frequency for the potential well is much greater than 24 kMc/sec and no relaxation is observed. Below the Curie point it is reasonable to expect that at this frequency the clamped dielectric constant would be measured. This value is predicted in reference 3 at about 600 at room temperature; however, the value shown in Fig. 1 is about 2000. At this time no explanation is given for this high value. It should be pointed out, however, that previous dielectric constant measurements made above

⁵ See, for example, *Technique of Microwave Measurements*, edited by C. G. Montgomery, Radiation Laboratory Series No. 11, Chap. 10 (McGraw-Hill Book Company, Inc., New York, 1947).

⁶ W. J. Merz, *Phys. Rev.* **76**, 1221 (1949).

and below the piezoelectric resonance⁷ show a decrease in the value of ϵ_{33} by a factor of two. The values given were 2740 below the resonance and 1500 above the resonance. From these high values we must conclude that the crystals used there were multidomain crystals and that the values of ϵ are more closely connected with the a direction than the c direction. We therefore conclude that this factor of two decrease in ϵ_{11} sets in at low frequencies and is essentially constant to 24 kMc/sec.⁸

MEASUREMENTS ON DC BIASED CRYSTALS

If a dc field is applied to a ceramic sample it is found that the dielectric constant decreases. This is explained by a reorientation of the polarization in some of the crystallites. It was believed by the authors that it might be possible to gain information about the potential well in BaTiO₃ if a dc field were applied along the c axis of a single crystal while measuring the dielectric constant ϵ_{11} along the a axis. By this method one might hope to observe a distortion in the potential well or effectively a change in the "force constant" perpendicular to the c axis as the ion is displaced along the c axis.

Experiments of this type were done by passing microwaves through the edge of a single crystal which had been plated on both sides with gold. This structure serves as a wave guide whose width is equal to the thickness of the crystal. Because the high dielectric constant is perpendicular to the c axis (and in the plane of the crystal plate), it was possible to make such a structure with the available crystals without going beyond cutoff for the 24-kMc/sec waves. The crystal (about 1 cm long) was tapered at both ends to improve the matching and mounted in the center of the guide with the plane of the plate parallel to the short side of the wave guide. The insulation at the top and bottom of the guide was provided by the crystal itself by leaving a small gap between the gold plating and the top and bottom of the guide. The matching was improved further by tapering the guide into and out of the crystal. The gold plated sample was insulated from the sides of the guide with 0.002-inch mica sheets. With no sample the insertion loss of the structure was about 60 db, and with the sample about 44 db. Some leakage was present through the unplated part of the crystal; however, this does not effect the results appreciably since it is independent of the applied field. The field was reversed a number of times at each temperature before a reading was taken. For the crystals used, the bridge balance was the same for both positive and negative fields within the errors in reading the phase shifter.

Figure 2 shows the plot of phase shift *vs* temperature for zero applied field and 10⁴ volts/cm. The curve in

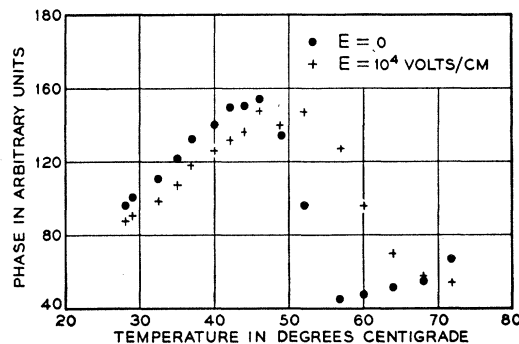


FIG. 2. Phase *vs* temperature for $E = \text{zero}$ and $E \approx 10^4$ volts/cm.

effect preserves its shape but shifts to higher temperature. Since the dielectric constant decreases with temperature in this region, this shift corresponds to an increase in the dielectric constant of about $\Delta\epsilon_{11} = 50$. The temperature shift in the curve becomes greater as the temperature approaches 80°C and we may therefore conclude the $\Delta\epsilon_{11}$ is approximately independent of temperature over this range. This field effect cannot be attributed to a piezoelectric dimensional change in the width of the crystal since the change in ϵ due to this effect would be much smaller (~ 1). One is almost restricted to this geometry or something equally as complicated for this experiment because of the shape and size of the presently available crystals. It is therefore very difficult to make accurate calculations for the structure because of the necessary insulators and contacts which must be placed in the guide. We believe, however, that the above method of analyzing Fig. 2 gives evidence for a dc field effect on the microwave properties of BaTiO₃.

It should be pointed out that a field effect at 5×10^8 volts/cm was not observed, which is an indication that the shift observed in Fig. 2 was not due to a reorientation of domains since the coercive field for the crystals was about 1.0×10^8 volts/cm.

CONCLUSION

We may conclude that ϵ_{11} is higher than that for the clamped dielectric constant given by the Devonshire theory below the upper Curie point, but from the values above the Curie point we must conclude that we are still far from any ionic resonance.

From the field measurements we find a change in ϵ_{11} with applied dc field which cannot be explained by the piezoelectric dimensional changes and which might be interpreted as a measure of the distortion of the potential well.

ACKNOWLEDGMENTS

The authors wish to thank P. W. Anderson and M. T. Weiss for helpful discussions during the course of this work.

⁷ Bond, Mason, and McSkimin, Phys. Rev. **82**, 422 (1951).

⁸ Recent measurements by R. F. Tromborullo at 50 kMc/sec give a value of 2000 at 25°C (private communication).