

Domain Clamping Effect in Barium Titanate Single Crystals

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We have found that the dielectric constant of good single crystals of barium titanate decreases as the average polarization is decreased by means of an electric field. This has been interpreted as being due to a domain clamping effect arising from the multidomain situation in the crystal that accompanies the reduction in polarization. These measurements give a value for the coefficient of coupling of 0.50 which is in agreement with Caspari and Merz's value of d_{33} and our measurement of S_{33} . The coupling coefficient has been studied as a function of temperature using this clamping effect.

I. INTRODUCTION

IN view of the possible applications of BaTiO_3 for memory devices, it is desirable to know more about the phenomena which take place as the polarization is reversed from one direction to the other. Dielectric constant measurements can be used as one means of giving useful information about the nature of this process.

The effect on the dielectric constant that is to be described depends on the magnitude of the average polarization and can only be observed in a simple form if crystal plates are used in which the polarization is always normal to the surface of the plate. In addition, the polarization must be reversed at a slow rate, otherwise additional effects enter that are to be described in a subsequent publication.

The plots shown were obtained using crystals grown by J. Remeika of Bell Telephone Laboratories. We have observed similar effects using crystals grown in our laboratory. They are characterized as having a low dielectric constant ($k=185$) in the c direction normal to the surface of the plate and a low 60 cycle per second coercive field strength (675 v/cm).

II. DIELECTRIC CONSTANT MEASUREMENTS

A. Equipment

As illustrated by Fig. 1, the crystal under study is subjected at the same time to a slowly varying biasing field and to an audio-frequency (20 kc) sine wave of

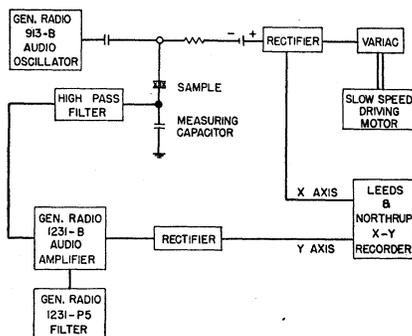


FIG. 1. Arrangement for recording the dielectric constant as a function of applied field.

constant low amplitude (1/500 of the coercive field). The biasing field is obtained from a rectifier which is fed from a Variac transformer. This Variac is driven by means of a motor and a set of gears at extremely slow speed, so that the voltage coming out of the rectifier can be considered as a dc voltage (the corresponding field across the crystal varies at the rate of 30 v/cm per minute). A complete cycle usually requires three hours. Under such conditions it is known from previous measurements that the imaginary part of the dielectric constant remains negligible even during the switching time, so that the fraction of the high-frequency voltage appearing across the series measuring condenser is a measure of the real part of this dielectric constant. This voltage is amplified, rectified, and fed into the y axis of an x - y recorder, the x axis of which is used for the low-frequency field. A battery is interposed between the rectifier and the crystal, so that the zero field point can be brought to mid-scale of the recorder x axis.

B. Results

The plots obtained have the aspect shown by Fig. 2. The sample had been "depolarized" by "walking" it down its hysteresis loop using 60-cycle ac and was plugged in at A , in the absence of any dc field. The low-frequency field was then increased to about twice the value of the coercive field, which is shown by the solid line ABC . The dotted line CDE corresponds to the reversal of this field to the opposite value. In the

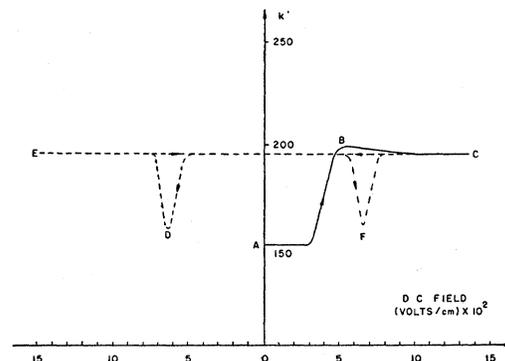


FIG. 2. Dielectric constant as a function of dc field.

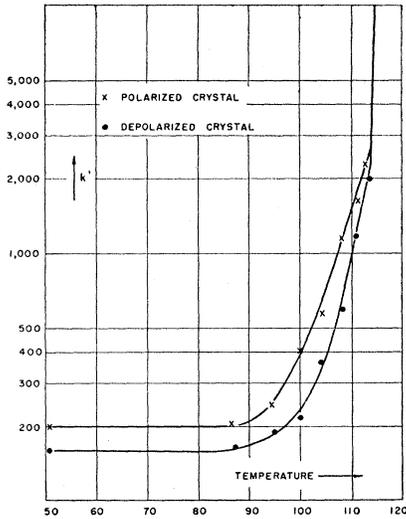


FIG. 3. Dielectric constant as a function of temperature for depolarized and saturated crystals.

region D , the polarization of the crystal reverses itself, and the dielectric constant goes to a minimum, then comes back to its initial value. The low-frequency field is then reversed, and the plot obtained is the dotted line EFC .

It is apparent from the figure that the effect is completed for a smaller value of the field for the case of the initially "depolarized" crystal than it is when we start from a saturated crystal. The minimum values of the dielectric constant are also somewhat different. The slight overshoot which appears at B in the case of an initially "depolarized" crystal has not been explained.

The experimental arrangement described in section A has been used to record the variation of the dielectric constant of the same sample with temperature. (This was done by feeding into the x axis of an x - y recorder the output of a thermocouple and slowly increasing the temperature by means of the same automatically controlled Variac.) The two plots shown in Fig. 3 have been obtained, respectively, from a depolarized crystal and from the same sample polarized to saturation. It can be seen that the curve corresponding to the first case stays constantly below the curve obtained for the polarized crystal until the temperature of the ferroelectric to nonferroelectric transition is reached.

III. DISCUSSION

This behavior of the dielectric constant can easily be understood if we picture the crystal as breaking up into a large number of elementary domains of opposite polarization as the average polarization decreases during switching. This situation is illustrated by Fig. 4, from which it is seen that domains having opposite orientations tend to be given opposite strains for a given half-cycle of the high-frequency field. The elementary

domains, therefore, mutually clamp each other, and we measure the "thickness-clamped" dielectric constant.

For a tetragonal crystal such as barium titanate, the equations relating the electric displacement D , the stress T , the strain X , and the field E using non-rationalized units are:

$$D_3 = 4\pi d_{33}T_3 + \epsilon_{33}E_3, \quad (1)$$

$$X_3 = S_{33}T_3 + d_{33}E_3, \quad (2)$$

where d_{33} , S_{33} , and ϵ_{33} are, respectively, the corresponding piezoelectric and elastic compliance coefficient and the permittivity of the material (or dielectric constant in cgs units).

For two domains having opposite polarity, the coefficient d_{33} takes opposite values. If we have the same number of such domains, addition of the corresponding Eq. (2) shows that

$$\sum X_3 = S_{33} \sum T_3.$$

Since there is no external applied stress, $\sum T_3 = 0$ which shows that the strain must be zero. Then, for either kind of region,

$$T_3 = -(d_{33}/S_{33})E_3$$

and from (1)

$$\frac{D_3}{E_3} = \epsilon_{33} - 4\pi \frac{d_{33}^2}{S_{33}} = \epsilon_{33} \left(1 - \frac{4\pi d_{33}^2}{\epsilon_{33} S_{33}} \right), \quad (3)$$

while, if all domains had the same orientations, the electrical displacement would be given by:

$$D_3 = \epsilon_{33}E_3.$$

For a crystal having zero average polarization, we then measure a dielectric constant

$$K_c' = \frac{D_3'}{\epsilon_0 E_3} = \frac{\epsilon_{33}}{\epsilon_0} \left(1 - \frac{4\pi d_{33}^2}{\epsilon_{33} S_{33}} \right) = K_f' (1 - C^2), \quad (4)$$

where K_f' is the "free" dielectric constant and C is the electromechanical coupling coefficient for thickness vibrations. It appears then that in the case of a crystal having zero average polarization we are measuring the so-called "thickness-clamped" dielectric constant.

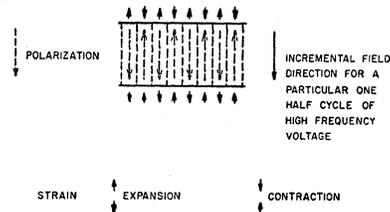


FIG. 4. Tendency of oppositely oriented domains to develop opposite strains in response to the same increment of field.

Bond, Mason, and McSkimmin,¹ working on BaTiO₃ single crystals, have found for C a value of 0.67. If we use this value in Eq. (4), we find:

$$K_c' = 0.55K_f',$$

obviously not in good agreement with the results shown in Fig. 2. However, the crystals available to those authors were certainly different from ours (they had a very high low-frequency dielectric constant¹ of 2890).

Measurements have been taken, however, in this laboratory on the thickness piezoelectric resonance mode; these measurements, described in Sec. IV of this paper, have given for S_{33} the approximate value

$$S_{33} = 4.5 \times 10^{-12} \text{ cm}^2/\text{dyne}.$$

In an earlier study, Caspari and Merz² found

$$d_{33} = 396 \times 10^{-8} \text{ cgs units}.$$

If we put these values into Eq. (3), the corrective term $4\pi(d_{33}^2/S_{33})$ becomes equal to 45, while the largest difference we observed is 40, indicating almost complete clamping. The coefficient of coupling is about 0.50.

From the plots shown on Fig. 3 it is possible to study the variation of the electromechanical coupling coefficient C with temperature. C can be determined from Eq. (4), which gives

$$C^2 = 1 - (K_c'/K_f').$$

The results are illustrated by the solid line on Fig. 5. No data were available to us on the temperature dependence of the thickness electromechanical coupling coefficient, but we can compare our results to Caspari and Merz's earlier studies of piezoelectric longitudinal modes.² The electromechanical coupling coefficient for

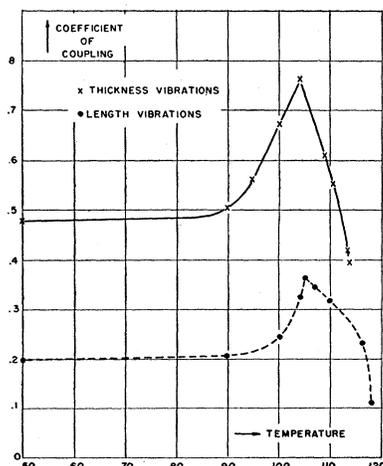


FIG. 5. Electromechanical coupling coefficient for thickness vibrations (from our measurements) and for longitudinal vibrations [from Merz's (see reference 2) measurements] as a function of temperature.

¹ Bond, Mason, and McSkimmin, Phys. Rev. **82**, 443 (1951).

² M. E. Caspari and W. J. Merz, Phys. Rev. **80**, 1084 (1950).

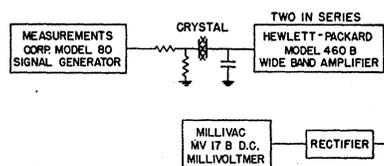


FIG. 6. Experimental arrangement for investigation of thickness piezoelectric modes.

the samples used by these authors can be approximately determined from the data shown in Fig. 10 of their article by using the relation:

$$K = \frac{1}{2}\pi(\Delta\nu/\nu_R)^{\frac{1}{2}}.$$

The curve obtained has been drawn in dotted lines on Fig. 5, and it can be seen that its aspect is quite similar to that of our thickness coupling coefficient curve.

IV. ELASTIC-CONSTANT MEASUREMENTS

The experimental arrangement shown by Fig. 6 is the classical arrangement for investigations of the piezoelectric resonances of a crystal. The high-frequency voltage applied to the crystal is of the order of one thousandth of the coercive voltage.

Few crystals have been found to be uniform enough in thickness to give a very sharp and well-defined thickness resonance. For the same reason, the accuracy in the measurement of the frequency constant for such modes is at present no better than 10 percent. It is about 10^5 cps-cmp, yielding for S_{33} the value

$$S_{33} = \frac{1}{4(tF_r)^2\rho} = 4.5 \times 10^{-12} \text{ cgs units}.$$

(t is the thickness, F_r is the resonant frequency, and ρ is the density.)

V. SUMMARY

We have found that if a BaTiO₃ single crystal goes slowly from one state of polarization to the opposite state, the dielectric constant decreases noticeably with a minimum at zero average polarization. This low value is also observed if the crystal is initially at zero polarization and it can be interpreted as being the "initial" dielectric constant for a crystal plate in which the polarization is normal to the surface of the plate. We have interpreted this behavior as being a "clamping" effect due to the multidomain situation that arises. The clamped case corresponds to the initial dielectric constant, the unclamped case is for the dielectric constant at saturation. There is a satisfactory agreement between our measurements and the value expected on this basis by using Merz and Caspari's² values of the piezoelectric coefficient d_{33} and our value for the elastic coefficient S_{33} .

A field strength of 350 volts/cm was required to

polarize the crystal from an unpolarized state, whereas a field of 675 volts/cm was required to reverse the direction of polarization. The clamping was more complete for the case where the crystal was forced to zero polarization by walking down the hysteresis loop than for the case where the crystal goes to zero polarization while traversing the hysteresis loop. This indicates that the elementary domains are smaller in the former case than in the latter case. It is interesting to note that the configuration with the smaller domains is less stable than for the larger domains as is evidenced by the observation that a smaller field is required to change the configuration.

Our measurements show no indication of the ele-

mentary domain walls moving to any appreciable extent in response to the high-frequency field. Otherwise, the dielectric constant would be expected to increase in the multidomain region.

The temperature dependance of the coefficient of coupling is similar to that computed from earlier measurements.

VI. ACKNOWLEDGMENT

We are indebted to Dr. S. O. Morgan and J. Remeika of the Bell Telephone Laboratories for the crystals used in this study. Our crystals were grown by C. Karan and B. Skinner and the samples were prepared by H. Dunn and E. Davin of our laboratory.

Photomagnetolectric Effect in Germanium and Silicon

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The transient part of the photomagnetolectric (p.m.e.) voltage in germanium has been studied. It has been observed that the p.m.e. voltage reached its steady-state value by passing through a maximum instead of reaching it by progressive increase. The p.m.e. effect in silicon has been observed and a few experimental results are given.

I. INTRODUCTION

THE photomagnetolectric effect first reported by Kikoin and Noskov,¹ and by Groetzinger² in cuprous oxide has been observed recently by Aigrain and Bulliard³ and independently by Moss, Pincherle, and Woodward⁴ in germanium. A communication on the effect has been given by Oberly⁵ at the 1953 Thanksgiving Meeting at Chicago. It has been observed also in lead sulfide by Moss,⁶ and, as will be reported here, in silicon. The effect is the following:

If a slab of semiconductor is illuminated on one face and introduced in a magnetic field parallel to the plane of the slab, then an emf arises in a direction perpendicular to both the light and the magnetic field (Fig. 1). If the light is oriented parallel to the x axis and the field parallel to the y axis, the emf appears along the z axis.

The action of the light is to produce hole-electron pairs near the surface of the semiconductor sample,

provided that the wavelength is shorter than 1.8μ , thus producing a very high concentration of carriers next to the surface. These added carriers tend to diffuse towards the interior of the slab. If a magnetic field is introduced in the direction previously described, the carriers will be deflected, the electrons upward and the holes downward, thus giving rise to an emf between the ends of the slab.

A theoretical derivation of this effect in germanium has been given independently in the papers of Aigrain and Bulliard³ (more extensively published in Bulliard's thesis⁷) and of Moss, Pincherle, and Woodward.⁴ In this paper we describe observations of transient effects in the photomagnetolectric effect on germanium and some observations of the effect on silicon.

II. TRANSIENTS IN THE PHOTOMAGNETOELECTRIC EFFECT ON GERMANIUM

(a) Experimental Study

The apparatus consisted of a 500-watt lamp, a chopper, and lenses (Fig. 2). The source was focused with the first lens on the chopper in order that the rise time of the light pulse be as short as possible compared to the pulse duration. With the second lens, the source was focused again on the germanium sample. The signal developed across the sample was amplified with a

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² G. Groetzinger, *Physik. Z.* (5), **36**, 169-179 (1935).

³ P. Aigrain and H. Bulliard, *Compt. rend.* **236**, 595 and 672 (1953).

⁴ Moss, Pincherle, and Woodward, *Proc. Phys. Soc. (London)* **B66**, 743 (1953).

⁵ John J. Oberly, *Phys. Rev.* **93**, 911 (1954).

⁶ T. S. Moss, *Proc. Phys. Soc. (London)* **B66**, 993 (1953).

⁷ Hubert Bulliard, *Ann. phys.* **9**, 52 (1954).