Some Experiments on the Motion of 180° Domain Walls in BaTiO₃

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Single-crystal BaTiO₃ samples with aqueous LiCl electrodes in place of the customary noble metal electrodes are observed to undergo polarization reversal with electric fields of several hundreds of volts per cm in a manner very much analogous to certain ferromagnetic materials. It is shown for the first time that polarization reversal in BaTiO₃ can take place by the expansion of a few domains through extensive sideways 180° domain wall motion. The observed domain configurations show that the smallest switched domains are probably circular in cross section and do not appear to go through the thickness direction of the crystal. The small domains grow through sideways 180° domain wall motion into large ones which have approximately square cross sections with the straight sides at 45° to the *a* axes. It is also noted that few, and sometimes no, ferroelectric Barkhausen pulses are observed during polarization reversal, and that Barkhausen pulses can occur when two switched domains come together.

THE question of the motion of 180° domain walls in single-crystal BaTiO₃ has been the subject of a number of experimental and theoretical investigations. Electrical measurements of the switching transients (dP/dt as a function of time and field) and optical studies described by Merz[1] indicate that polarization reversal in BaTiO₃ with fields of several thousands of volts per cm is brought about by many nucleations of domains which appear to grow only in the forward direction. Merz quotes some theoretical considerations by P. W. Anderson which give a 180° domain wall energy of about 7 ergs cm⁻² and a thickness of the order of one to a very few lattice constants. Anderson estimates that the energy required to move a thin 180° domain boundary will be of the order of the wall energy itself, i.e., 10 ergs cm⁻². In addition, Anderson concludes that since the energy gained in moving a 180° domain wall sideways by one lattice constant is much smaller than the wall energy, sideways 180° domain wall motion is unlikely. This situation is very different from the ferromagnetic case where magnetization reversal takes place largely by the sideways motion of domain boundaries which are several hundred lattice constants thick.[2]

Little[3] has observed optically the motion of 180° domain boundaries in the presence of an electric field which is at about 45° to the polarization direction and concludes that the 180° walls do not move sideways in reasonable laboratory times with a field less than 2.4 kv cm⁻¹. What appears as sideways 180° domain wall motion is attributed to unit-cell dipole reversal propagated in the forward direction rather than by motion of the entire domain wall parallel to itself which is ruled out by energy considerations like those given by Anderson.

Cameron[4] studied domain patterns on acid-etched partially switched BaTiO₃ single crystals. The observed domain configurations agree with a growth mechanism in which cone-shaped domains go through the thickness direction of the crystal and then grow sideways as a truncated cone. Kinase and Takahasi[5] presented theoretical arguments which indicate that the 180° domain walls are about one lattice constant thick and have an energy of 1.4 ergs cm⁻². Electric fields of the order of 10⁶ volts cm⁻¹, predicted solely on theoretical grounds, should be required for polarization reversal and for sideways 180° domain wall motion. The authors described some mechanisms which may allow polarization reversal to take place at much lower fields, as is observed.

From an electrical study of ferroelectric Barkhausen pulses in BaTiO₃, Chynoweth[6] concludes that a Barkhausen pulse could arise from the nucleation and growth through the thickness direction of a domain which is cylindrically shaped by the end of the Barkhausen event. Since the total charge represented by the Barkhausen pulses accounts for only 0.1% to 1% of the charge required for complete polarization reversal, Chynoweth pictures a further growth of the Barkhausen domains through a sideways expansion of 100 to 1000 times, thus accounting for the required charge.

The conclusions reached by the above-mentioned investigators are quite varied, but the trend in both the experimental and theoretical work does seem to be in the direction of increasing the amount of polarization reversal brought about by sideways 180° wall motion. It should be added that the techniques used by these
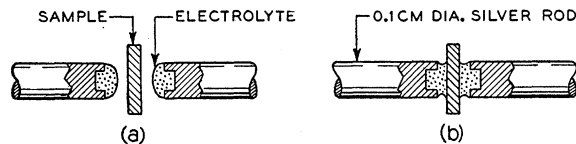

FIG. 1. Schematic drawing of part of the liquid-electrode crystal holder; (a) and (b) are before and after contact with the sample, respectively.

[1] W. J. Merz, Phys. Rev. **95**, 690 (1954).
[2] C. Kittel and J. K. Galt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3.
[3] E. A. Little, Phys. Rev. **98**, 978 (1955).
[4] D. P. Cameron, I.B.M. J. Research and Development **1**, 2 (1957).
[5] W. Kinase and H. Takahasi, J. Phys. Soc. Japan **12**, 464 (1957).
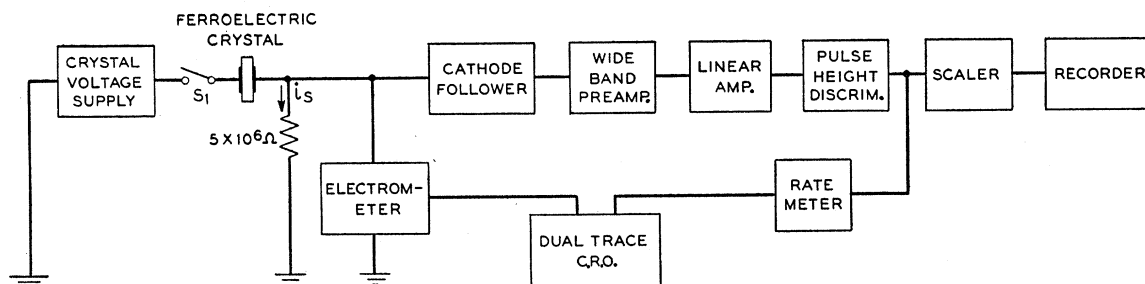[6] A. G. Chynoweth, Phys. Rev. **110**, 1316 (1958).

FIG. 2. Block diagram of the circuit used to observe simultaneously the occurrence of Barkhausen pulses and the switching current i_s, (dP/dt). The circuit is also used to obtain a pulse-height analysis of the Barkhausen pulses.

researchers were quite varied which might account for the lack of uniformity in their conclusions. A still different technique has been used in the present work to study the motion of 180° domain boundaries and once again, somewhat different conclusions are reached. The present experiments grew out of a study of polarization reversal in BaTiO₃ single crystals in which aqueous lithium chloride electrodes were substituted for the more usual metal electrodes. It has been found that the electrical stability of BaTiO₃ crystals with certain liquid electrodes[7-9] is greatly improved over the stability observed with metal-electroded crystals. All the experimental investigations described above were with metal-electroded crystals.

METHOD

It appears that the experimental procedures may be important insofar as sideways domain wall motion is concerned, so the techniques used in this work will be described in some detail. The single-crystal butterfly wings were grown from undoped material by the Remeika method[10] in an oxygen atmosphere. Clear crystal plates with good clean surfaces were selected and etched in concentrated H₃PO₄ at 155°C long enough to reduce the sample thickness by about 5×10^{-3} cm. Then they were rinsed in water, alcohol, and dc-poled in water with platinum electrodes. The specimens were then examined with a polarizing microscope, and only those with c-domain areas considerably larger than the electrode size employed were used for the experiments. A cross-sectional schematic diagram of part of the liquid electrode holder is shown in Fig. 1. In most of this work, the electrolyte used was a room temperature saturated solution of lithium chloride in water. After the solution is applied to the silver electrodes, they are brought up to the sample as shown in Fig. 1(b).

A block diagram of the circuit employed is shown in Fig. 2. The crystal voltage supply is battery operated and automatically cycled plus and minus. The signal

across the 5×10^6-ohm resistor is fed into two channels; an electrometer which measures the switching current i_s, i.e., dP/dt, and a circuit described in detail by Chynoweth[6] which permits one to observe ferroelectric Barkhausen pulses. The electrometer and rate-meter outputs are fed into a dual trace CRO so that both the occurrence of Barkhausen pulses and the switching current can be observed simultaneously as a function of time.

The crystals are cycled several times, during which the switching current is observed as well as the occurrence of Barkhausen pulses as a function of time. These measurements are made for only one sign of the applied voltage and this voltage, which is positive with respect to ground, is adjusted such that the time to achieve complete polarization reversal is about one minute. With these long switching times, the voltage drop across the load resistor is negligible compared to the applied voltage. The voltage to polarize the crystal in the other direction is made sufficiently large to insure that the crystal is completely switched prior to applying the positive voltage. The switching can be interrupted at any time during the cycle by opening a manually operated switch, S_1. When it is decided during the measuring portion of the cycle that the domain pattern might be of interest, switch S_1 may be opened and the sample immediately removed from the holder and etched in acid to bring out the c-domain configuration.[4,11-13] The c-domain pattern on the etched specimen is readily observed with a microscope by reflected light.

RESULTS AND DISCUSSION

One of the most striking observations with liquid-electroded specimens is the small number and large size of the domains observed on many of the samples, an example of which is shown in Fig. 3. In numerous cases, a single switched domain larger than half the electrode area $(8 \times 10^{-3}$ cm²) was observed. Another interesting result is that the time rate of change of polarization, i_s, is usually quite irregular. A typical example of this is shown in Fig. 4.

[7] E. A. Wood (private communication).
[8] C. F. Pulvari, Proc. Spec. Tech. Conference, Solid State Dielectric and Magnetic Devices, April, 1957, Catholic University of America, Washington, D. C. (unpublished), Paper 4.
[9] A. W. Ziegler (private communication).
[10] J. P. Remeika, J. Am. Chem. Soc. 76, 940 (1954).

[11] J. A. Hooton and W. J. Merz, Phys. Rev. 98, 409 (1955).
[12] D. Kontoleon and J. Tomlinson, Metal Progr. 69, 98 (1956).
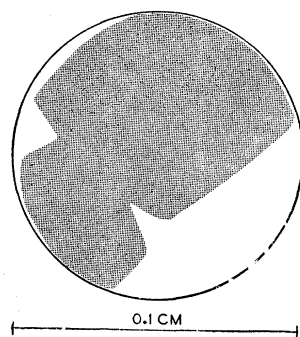[13] R. C. DeVries and J. E. Burke, J. Am. Ceram. Soc. 40, No. 6, 200 (1957).

FIG. 3. An accurate reproduction of the domain pattern observed on a BaTiO₃ sample partially switched with a field of 350 v cm⁻¹. The electroded area was circular as shown and 10^{-1} cm in diameter. The dark area has been switched and shows that two large domains had just come together.

|—————— 0.1 CM ——————|

The Barkhausen spectrum is also most unusual in that the number of pulses observed during a complete polarization reversal is smaller than one observes with evaporated metal electrodes. When the crystals have metal electrodes, of the order of 10^6 Barkhausen pulses per cm² are usually observed,[6,14,15] whereas samples with liquid electrodes as described above, may give from zero to about 10^5 per cm². The number varies widely from one sample to another. The total number of pulses is arrived at through normal pulse-height counting techniques; however, the measurement is somewhat uncertain when only a few pulses are counted at a level just above noise. It was noticed that discontinuous decreases in the switching current were usually coincident with one or more Barkhausen pulses. The Barkhausen pulses observed under these conditions, and their origin, will be described in detail in a future paper. Most of the emphasis here will be on other aspects of the observed polarization-reversal characteristics.

The sample whose domain configuration is shown in Fig. 3 illustrates the phenomena just described. It was 8×10^{-3} cm thick and was cycled with fields of -1000 v cm⁻¹ and $+350$ v cm⁻¹. During complete polarization reversal, nine Barkhausen pulses were observed with the pulse-height discriminator set just above the noise level. It was noticed that at a certain point there was a sharp decrease in i_s coincident with a Barkhausen pulse. After this phenomenon was shown to be reproducible, the voltage was removed immediately after the decrease in i_s and the sample etched to bring out the domain pattern which is reproduced in Fig. 3. A reproduction of the switching current and time of occurrence of Barkhausen pulses up to the time of the partial switch is shown in Fig. 5. Each vertical line on the pulse-height discriminator output shown in Fig. 5 represents one pulse. The linear rise with time of i_s which starts at about 12 sec is
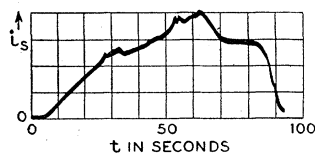

FIG. 4. The switching current i_s as a function of time for a sample switched with a field of 350 v cm⁻¹.

[14] A. G. Chynoweth (private communication).
[15] A. Savage and R. C. Miller (unpublished data).

consistent with a switched domain, or domains, expanding in two directions with uniform velocities in each direction such that the switched area on the electroded surface increases as t^2. The increase in the slope at 42 sec can be interpreted as the result of the introduction of another domain, or domains, which also expand such that the switched area increases as t^2. The sudden decrease in i_s at 74 sec would be expected if two growing domains had just come together. Figure 3 shows that two growing domains had indeed just come together and that only two observable domains, both large, were taking part in the switching at the time the voltage was removed. It is interesting to note that the increases in the slope of i_s shown in Fig. 5 do not occur at the same time or soon after a Barkhausen pulse. Thus there is no evidence in these data that Barkhausen pulses are associated with the nucleation of domains as suggested by Chynoweth[6] on the basis of less direct experimentation. These same type of phenomena have been seen many times; however, every sample does not behave in this
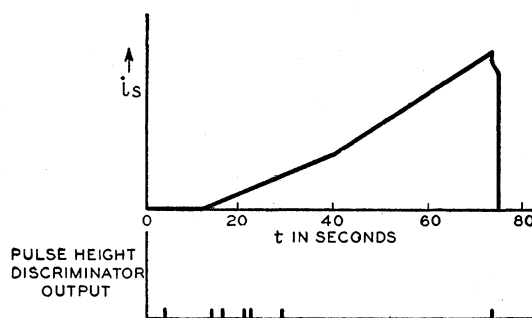

FIG. 5. Reproduction of i_s and the occurrence of Barkhausen pulses as a function of the time a field of 350 v cm⁻¹ has been on the sample. Each vertical line on the discriminator output represents one Barkhausen pulse. The field was removed about 1 sec after the pulse shown at $t=74$ sec. The resultant domain configuration is shown in Fig. 3.

manner. In fact, it is very seldom that the switching transient and the etch pattern can be interpreted as completely as the case described above. In several samples the voltage was removed just prior to a decrease in i_s which had been shown to occur in a reproducible fashion. Figure 6 shows a photomicrograph of such a sample. The two dark areas are growing domains which are about ready to come together.

These experiments have also shed some light on the manner in which c domains grow. Some partially switched crystals have a distribution in size of c domains. The smallest ones observed are circular in cross section on one side of the crystal and cannot be seen on the opposite side. If it is assumed that they are conical in shape and just go through the crystal in the thickness direction, the apex angle is something like $1°$. The diameter of the base of the cone is 4μ which is well within the resolution of the microscope. There is a very strong preference for the base to appear on the side of

the sample facing the negative electrode. Then expansion takes place such that the original volume goes over into a truncated cone of smaller apex angle and larger base. By the time the base is about $10\,\mu$ in diameter, the truncated cone is nearly a cylinder and further expansion gives rise to a domain with a strong preference for a square cross section. Chynoweth[6] would expect this general type of growth up to the cylinder stage, but with smaller radial dimensions. These observations are not in agreement with those of Cameron[4] which indicate that the domains continue to retain a truncated cone shape as they grow. The shapes of the larger domains can be seen in Figs. 3 and 6. The straight sides are at 45° to the crystalline a axes. Thus it appears that the 180° domain walls can move more easily in a direction parallel to the crystalline a axes than in any other direction. A strong preference among the larger domains to have square cross sections with sides at 45° to the a axes has also been observed by the author on partially switched metal-electroded crystals.

CONCLUSIONS

Several important conclusions can be drawn from these observations. It is clear that polarization reversal in BaTiO₃ requiring many nucleations followed by domain growth in the forward direction, as originally pictured by Merz[1] to apply at fields of several thousands of volts per cm, does not describe polarization reversal under the conditions described here. It has been shown that polarization reversal in BaTiO₃ can take place by expansion of a few domains at low fields through extensive sideways 180° domain wall motion. In this respect, this behavior is then analogous to magnetization reversal in some ferromagnetic materials.[16] The sideways 180° domain wall motion observed with aqueous-like electrodes is much more extensive than other investigations indicate. The fields at which the domain wall motion takes place are much less than reported by Little[3] and many orders of magnitude less than theoretical considerations alone would predict.[1,5] It has also

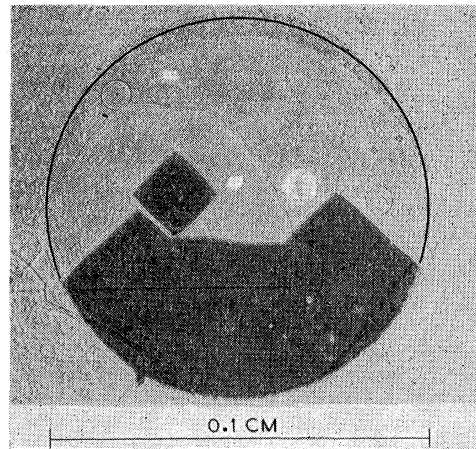[16] H. J. Williams and W. Shockley, Phys. Rev. **75**, 178 (1949).

FIG. 6. A photomicrograph of the domain pattern on a BaTiO₃ sample which had been observed to exhibit a sharp decrease in the switching current a few seconds later than the time at which the field of 300 v cm⁻¹ was removed. The dark areas have been switched. The electrode periphery has been drawn in.

been shown that polarization reversal can be accomplished with very few, or maybe even no Barkhausen pulses, and that Barkhausen pulses occur when two growing domains come together. A number of important experiments which should be done in view of the results presented here are now in progress or contemplated. Most of these experiments were not possible up to this time because of the large number of domains usually encountered during polarization reversal where the customary noble metal electrodes are used. It is clear that the electrode plays a most important role in determining the characteristics of polarization reversal in BaTiO₃, a role which is not yet understood.

ACKNOWLEDGMENTS

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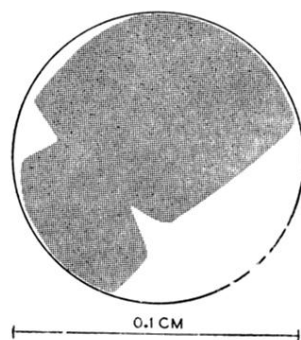
FIG. 3. An accurate reproduction of the domain pattern observed on a BaTiO$_3$ sample partially switched with a field of 350 v cm^{-1}. The electroded area was circular as shown and 10^{-1} cm in diameter. The dark area has been switched and shows that two large domains had just come together.
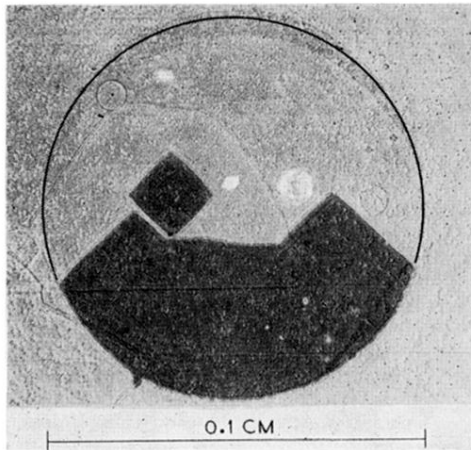
FIG. 6. A photomicrograph of the domain pattern on a BaTiO₃ sample which had been observed to exhibit a sharp decrease in the switching current a few seconds later than the time at which the field of 300 v cm⁻¹ was removed. The dark areas have been switched. The electrode periphery has been drawn in.