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Ferroelectricity, Domain Structure, and Phase Transitions of Barium Titanate*†

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A summarizing account is given of the research on barium titanate in progress at the Laboratory for Insulation Research at M. I. T. since 1943. The investigations have led to an understanding of the mechanism of ferroelectricity in the titanates and to discoveries such as the piezoelectric effect in the ceramics and the domain structure of the single crystals of $BaTiO_3$. The high dielectric constant, field strength and temperature sensitivity, and piezo-response of the barium titanate dielectrics make them useful for numerous technical applications.

INTRODUCTION

FERROMAGNETISM, the spontaneous alignment of permanent magnetic dipoles in parallel orientation, was observed even in ancient times and is one of the foundations of today's electric age. Ferroelectricity, the spontaneous alignment of electric dipoles by mutual interaction, was not observed until recently and its role in technical devices for the concentration of electric energy, its use in electromechanical transducers and control mechanisms of all kinds is just beginning.

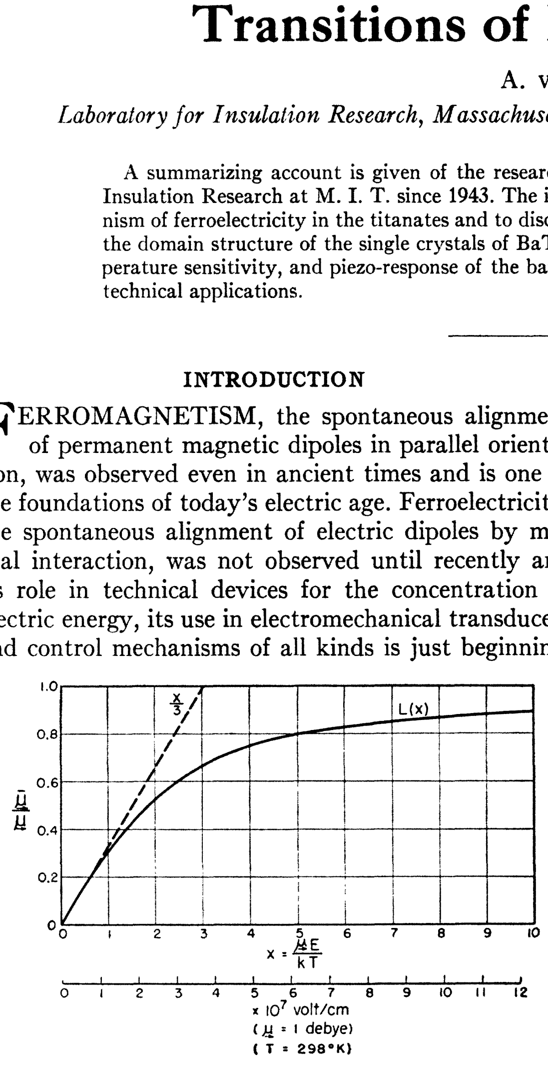
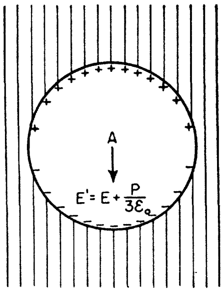


FIG. 1. Langevin function of dipole orientation.

The occurrence of ferroelectric materials could have been suspected after Debye[1] in 1912 postulated the existence of permanent electric dipoles. Such dipoles are bound to arise when atoms of different types form molecules, since the partners differ in electron affinity and their electron clouds are displaced eccentrically towards the stronger binding atoms.

In an external field these permanent dipoles experience a torque which tends to align them in the field direction. However, as Langevin[2] first showed in the case of magnetic dipoles, nearly unattainable fields are required before an appreciable amount of order can be enforced at normal temperatures against the randomizing action of the Brownian movement. Figure 1 shows the Langevin characteristic for the electric case,[3] with

FIG. 2. Locally acting field (after Mosotti).



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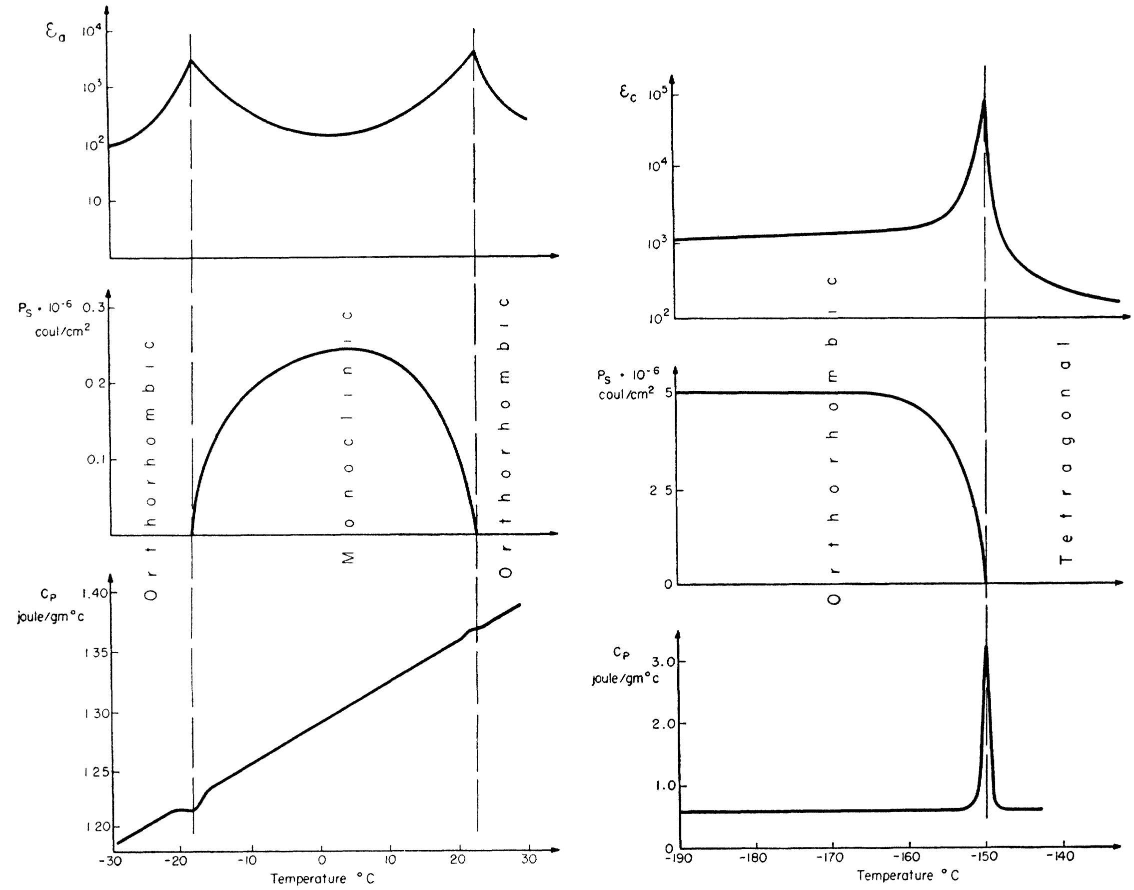
† An abbreviated version of this paper was presented by invitation of the American Association for the Advancement of Science at the annual meeting in New York on December 30, 1949, and by invitation of the American Physical Society at the meeting of the Solid State Division in Oak Ridge on March 17, 1950.

[1] P. Debye, Physik. Zeits. **13**, 97 (1912).

[2] P. Langevin, J. de Phys. **4**, 678 (1905).

[3] P. Debye, *Polare Molekeln* (S. Hirzel, Leipzig, 1929); *Polar Molecules* (The Chemical Catalog Company, Inc., New York, 1929).



Rochelle Salt
KNa $C_4H_4O_6 \cdot 4H_2O$

KH_2PO_4

FIGS. 3 and 4. Dielectric constant, spontaneous polarization, and specific heat.

the ratio of field energy to thermal energy

$$x = \boldsymbol{\mu}E'/kT$$

plotted as the abscissa, and the ratio of average dipole moment to true dipole moment, $\bar{\boldsymbol{\mu}}/\boldsymbol{\mu}$, as the ordinate. The field scale refers to the orientation of a dipole molecule of unit moment,‡ against the thermal agitation at room temperature (298°K).

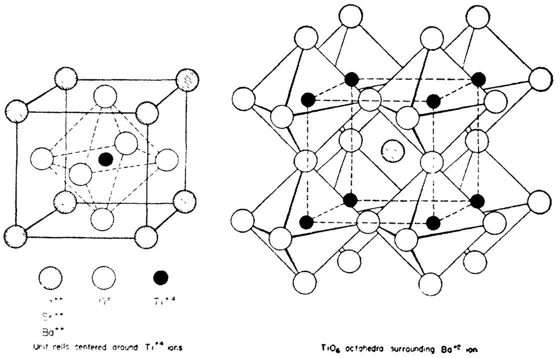


FIG. 5. Ideal perovskite structure.

The Langevin function corresponds mathematically to the expression

$$\bar{\boldsymbol{\mu}}/\boldsymbol{\mu} = L(x) = \coth(x) - (1/x).$$

For sufficiently small fields this curve can be approximated by its tangent $\frac{1}{3}x$; that is, the average moment in this limiting case,

$$\bar{\boldsymbol{\mu}} = \boldsymbol{\mu}\tfrac{1}{3}x = \frac{\boldsymbol{\mu}^2}{3kT}E',$$

increases proportionately to the orienting field strength E'.

If one identifies this acting field E' with the externally applied field E, the case for a parallel alignment of the dipoles at reasonable temperatures appears to be hopeless. In the condensed phases of solids and liquids, however, the field acting on a molecule is decisively modified by the polarization of the surroundings. We may consider this effect by drawing an imaginary sphere

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‡ The separation of the nuclei in molecules is of the order of 10^{-8} cm, the magnitude of the displaced charge comparable to that of an electron ($e = 4.8 \times 10^{-10}$ e.s.u.). The dipole moment, the product of dipole charge and dipole length, is therefore conveniently expressed in units of 1×10^{-18} e.s.u., called 1 debye.

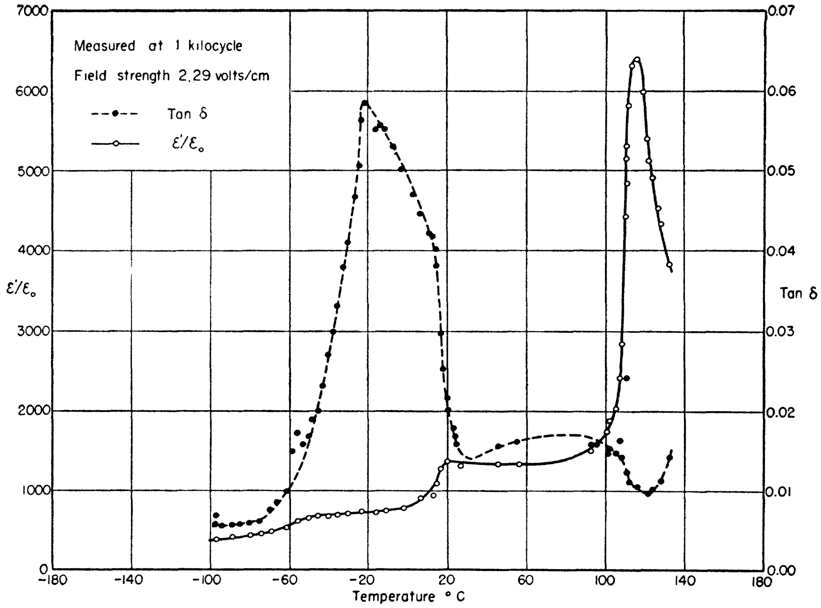

Fig. 6. Dielectric constant and loss of barium titanate ceramic.

around our reference molecule A of such an extent that beyond it the material can be treated as a polarized continuum (Fig. 2). The free dipole ends of this outer material lining the wall of the cavity would contribute a term $P/3\epsilon_0$ to the orienting field at its center, if the cavity were empty; the vector P in this expression, called polarization, represents the dipole moment per unit volume and ϵ_0 the dielectric constant (or permittivity) of vacuum. By neglecting any further contribution of the molecules inside the sphere, we arrive at the Mosotti expression for the locally acting field[4]

$$E' = E + \frac{P}{3\epsilon_0}.$$

The same field expression can be shown to be valid for dipoles in cubic array.[5]

A local field of this sort leads to the situation ex-

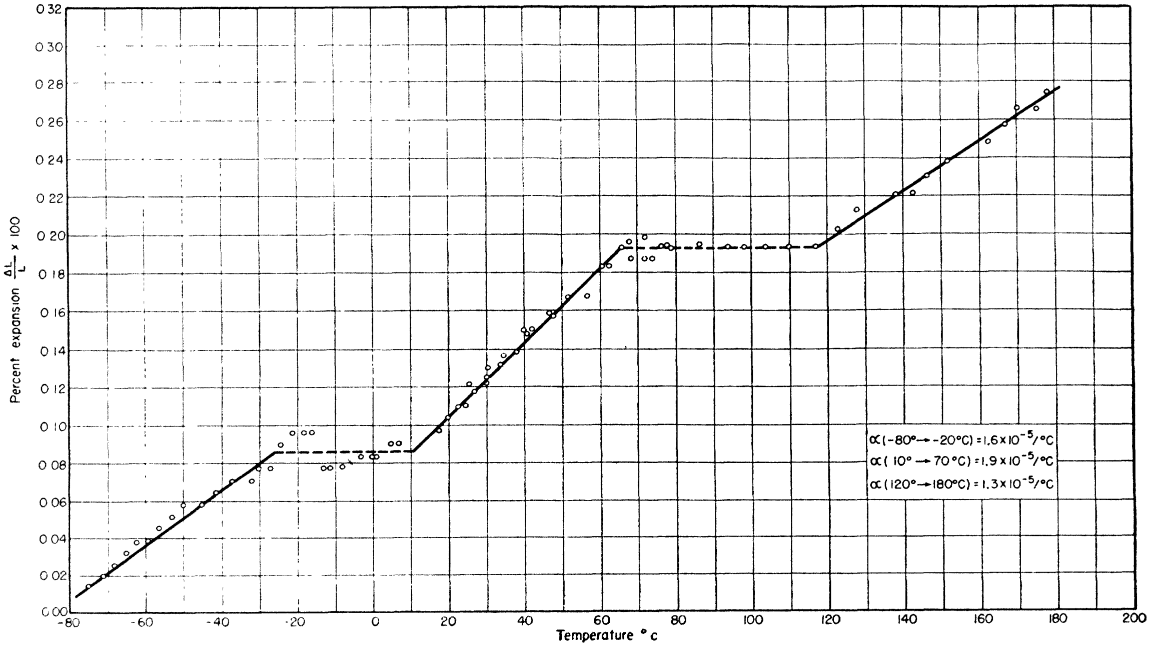

Fig. 7. Linear thermal expansion of $BaTiO_3$ ceramic.

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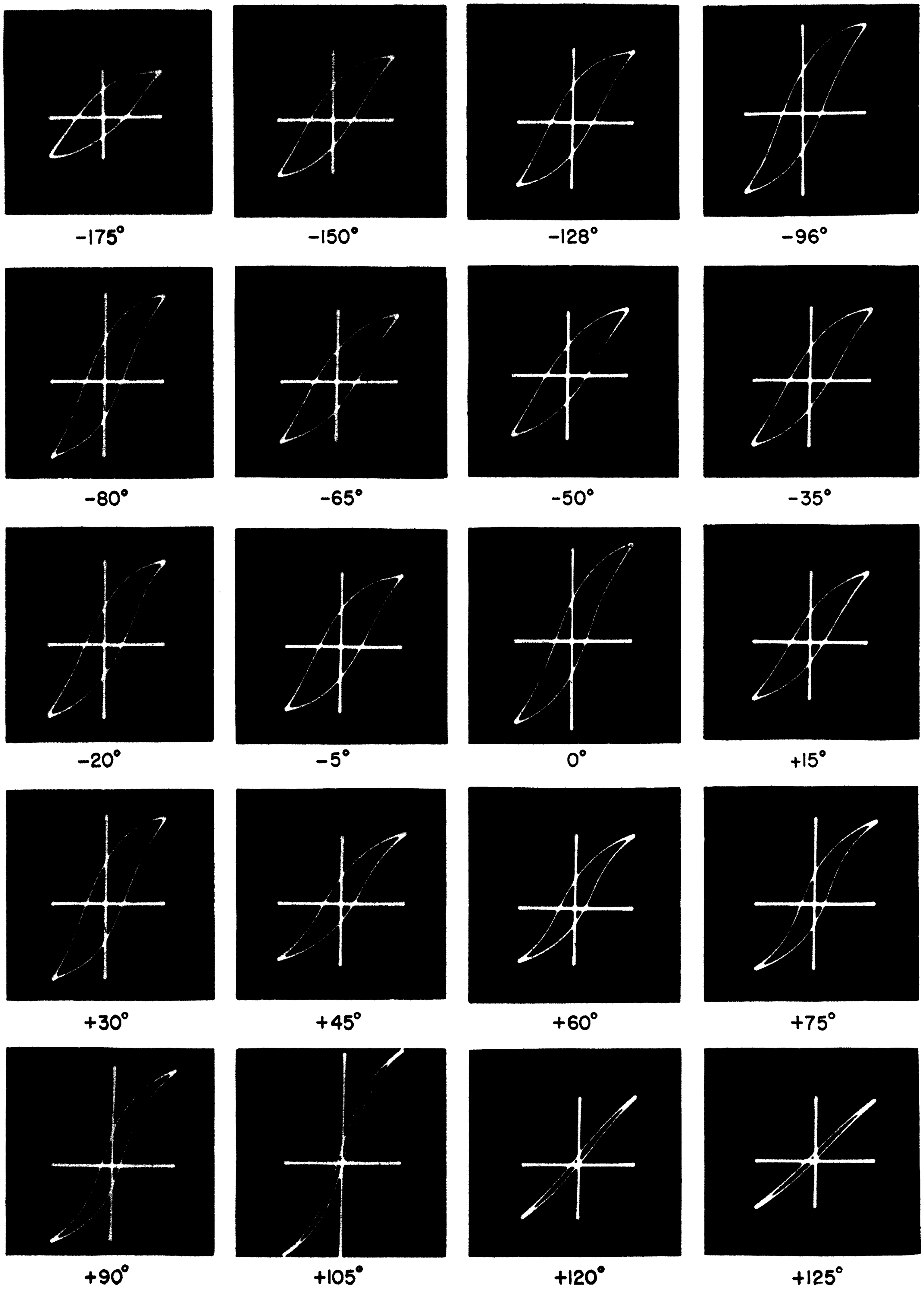
[4] O. F. Mosotti, Mem. Soc. Ital. **14**, 49 (1850).

[5] See H. Mueller, Phys. Rev. **47**, 947 (1935).



-175° -150° -128° -96°

-80° -65° -50° -35°

-20° -5° 0° +15°

+30° +45° +60° +75°

+90° +105° +120° +125°

FIG. 8. Hysteresis loops of barium titanate ceramic.

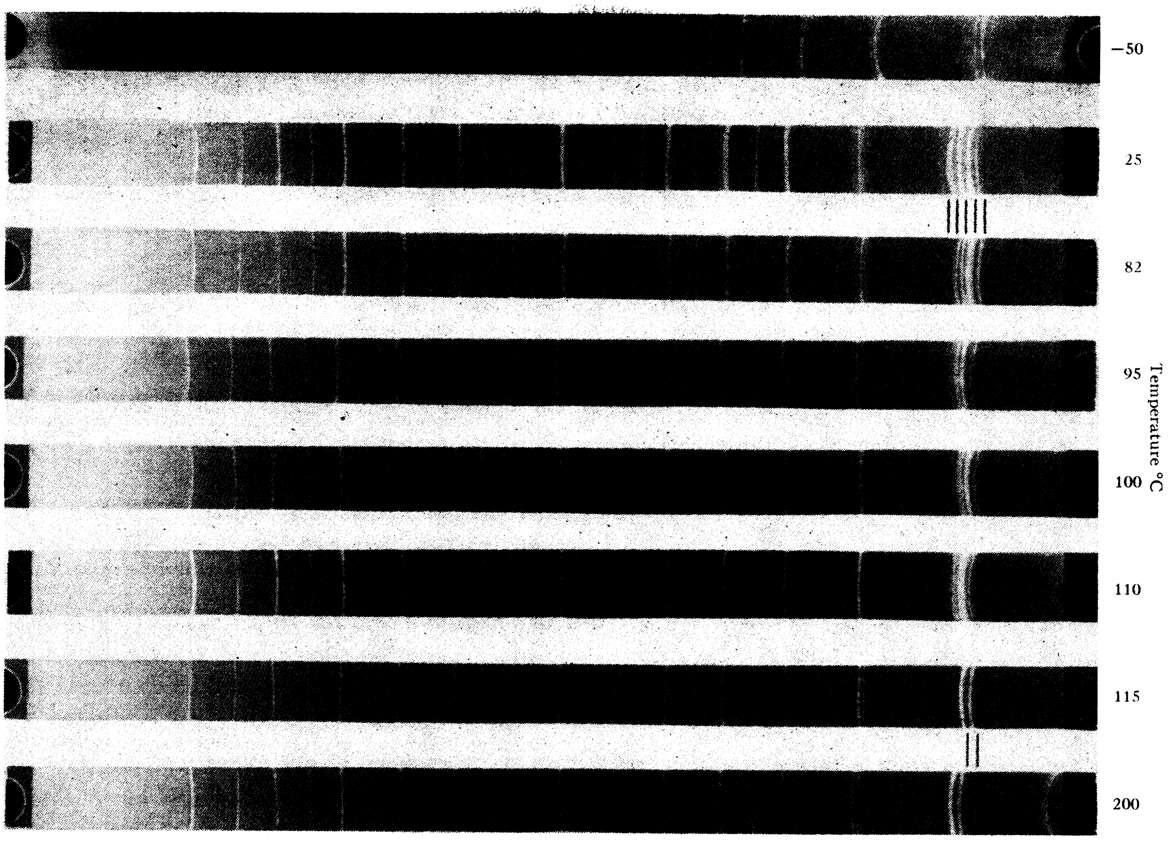


FIG. 9. X-ray patterns of barium titanate ceramics.

perienced by Munchausen's soldier who lifted himself out of the swamp by his own boot straps. The acting field increases the polarization and the polarization, in turn, the acting field, until some counteraction stabilizes the situation or a catastrophe occurs. Mathematically expressed, the polarization P corresponds to the number N of dipoles per unit volume multiplied with their average moment $\bar{\mu}$, hence

$$P = N\bar{\boldsymbol{\mu}} = N\frac{\boldsymbol{\mu}^2}{3kT}\left(E+\frac{P}{3\epsilon_0}\right).$$

Solving for P we obtain

$$P = \frac{3T_c}{T-T_c}\epsilon_0 E$$

with

$$T_c = N\boldsymbol{\mu}^2/9k\epsilon_0.$$

In other words, thermal agitation keeps the polarization within bounds, until the temperature has been lowered to a "critical" or "Curie" temperature T_c. At this point the randomizing action of the temperature is overcome, spontaneous polarization sets in, and the electric susceptibility

$$\chi = \kappa' - 1 = \frac{P}{\epsilon_0 E} = \frac{3T_c}{T-T_c}$$

approaches infinity. ($\kappa' = \epsilon'/\epsilon_0$ designates the relative permittivity or dielectric constant of the medium as compared to vacuum.) The linear dependence of $1/\chi$ on $(T-T_c)$, first derived in the theory of ferromagnetics, is known as the Curie-Weiss law.[6]

Fortunately the "Mosotti catastrophe"[7] thus predicted normally does not take place; for water it should

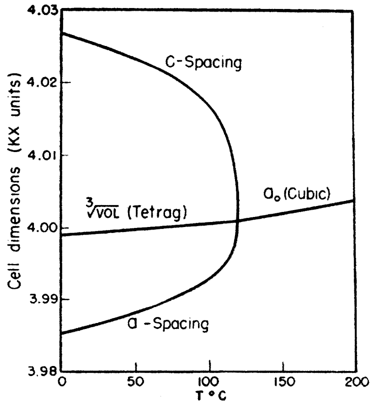


FIG. 10. Variation of cell dimensions of barium titanate with temperature (after Megaw).

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[6] P. Weiss, J. de Phys. **6**, 661 (1907).

[7] J. H. Van Vleck, Ann. N. Y. Acad. Sci. **40**, 293 (1940).

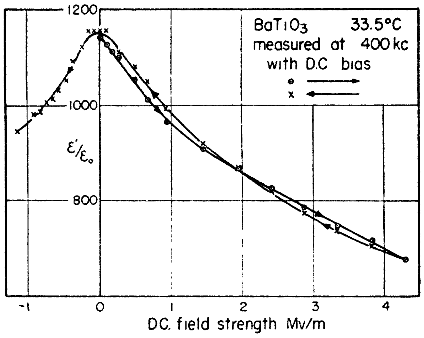

FIG. 11. Field strength dependence of the dielectric constant of $BaTiO_3$ ceramic.

occur near 1000°K, solidifying it at this high temperature and making life impossible on this earth. We are spared because the local field E' is normally not as simple as assumed[8] and because permanent dipoles tend to lose their freedom of orientation in condensed phases through association and steric hindrance.[9]

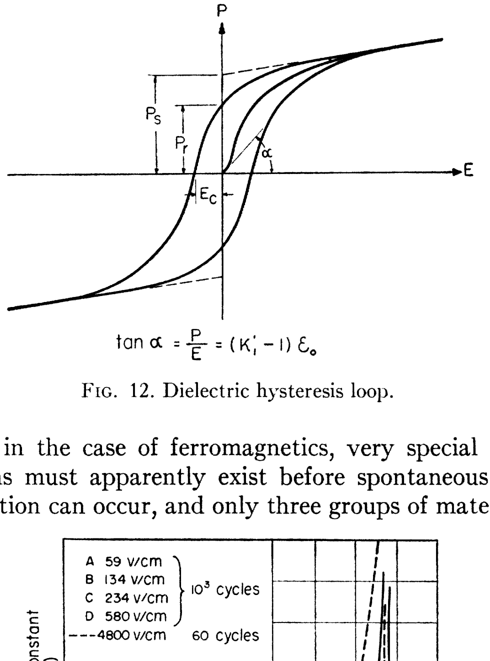

FIG. 12. Dielectric hysteresis loop.

As in the case of ferromagnetics, very special conditions must apparently exist before spontaneous polarization can occur, and only three groups of materials are, as yet, known as true ferroelectrics. Their representatives are rochelle salt, the tetrahydrate of potassium-sodium tartrate, recognized as a ferroelectric by Valasek in 1921;[10] dihydrogen potassium phosphate and arsenate by Busch and Scherrer in 1935;[11] and finally barium titanate, noticed for its unusual dielectric properties by Wainer and Salomon in 1942–43[12] and established as a new ferroelectric material in our laboratory at M. I. T. in 1943–44.[13] The crystals of the first and second group are of relatively complicated structure; the ferroelectric range of rochelle salt is very narrow (Fig. 3) and that of the phosphates and arsenates limited to low temperatures (Fig. 4). Barium titanate, in contrast, crystallizes in the simple perovskite

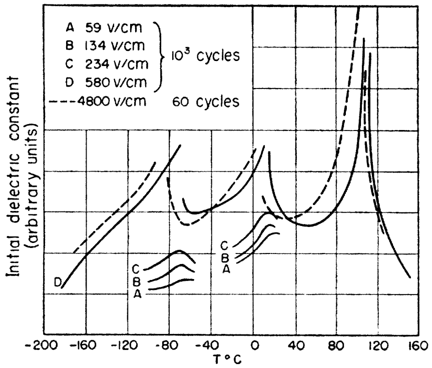

FIG. 13. Initial dielectric constant of barium titanate ceramic from hysteresis loops.

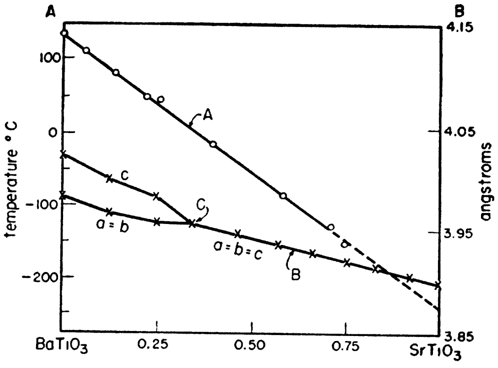

FIG. 14. Curve A: decrease of Curie temperature with increasing strontium content. Curve B: decrease of cell parameters at room temperature with increasing strontium content. Up to composition *C* the material is ferroelectric at room temperature (see reference 17).

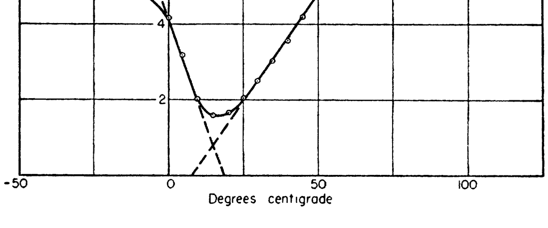

FIG. 15. Confirmation of Curie-Weiss laws in $(Ba\text{-}Sr)TiO_3$ (400 kc).

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[8] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936); J. G. Kirkwood, J. Chem. Phys. **7**, 911 (1939).

[9] R. H. Fowler, Proc. Roy. Soc. **149A**, 1 (1935); P. Debye, Physik. Zeits. **36**, 100, 193 (1935).

[10] J. Valasek, Phys. Rev. **17**, 475 (1921).

[11] G. Busch and P. Scherrer, Naturwiss. **23**, 737 (1935).

[12] E. Wainer and A. N. Salomon, Titanium Alloy Manufacturing Company Elect. Rep. **8** (1942), **9** and **10** (1943).

[13] A. von Hippel and co-workers, N.D.R.C. Rep. No. 300 (August, 1944). See von Hippel, Breckenridge, Chesley, and Tisza, Ind. Eng. Chem. **38**, 1097 (1946).

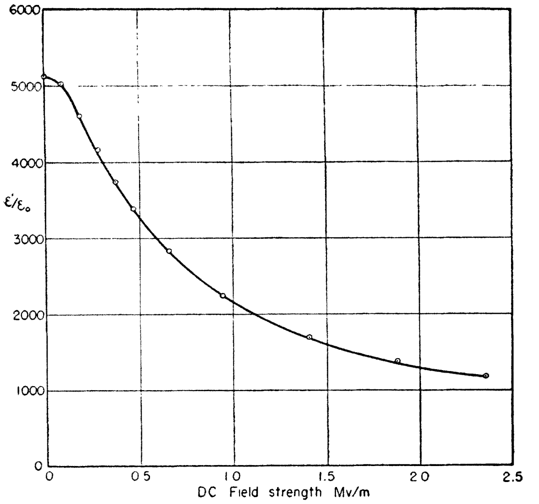

FIG. 16. Field strength dependence at 25°C of dielectric constant of (Ba-Sr)TiO_3 (above Curie point).

structure (Fig. 5), is ferroelectric below 120°C (Fig. 6) and may be employed as a single crystal or as a rugged ceramic material which can be formed into any shape desired. Thus this substance lends itself better than the earlier-discovered groups to fundamental investigations and applications.

It is the purpose of this paper to review what we have learned about $BaTiO_3$, and thus about ferroelectricity, in our researches at M. I. T.

BARIUM TITANATE CERAMICS

When a multicrystalline sample of $BaTiO_3$ cools down through the Curie region, a number of properties undergo rapid changes. The dielectric constant and loss tangent traverse a sharp maximum and minimum respectively (see Fig. 6),[13] the slope of the thermal expansion characteristic alters (Fig. 7),[13] and ferroelectric hysteresis loops appear (Fig. 8).[14] The x-ray diagram of the cubic structure simultaneously becomes transformed progressively into that of a pseudocubic arrangement, expressed clearly in the multiplicity of the CuK_α-doublet of the back-reflection lines (Fig. 9).[13] Accurate measurements of Megaw[15] in England have established this new phase as tetragonal (Fig. 10).

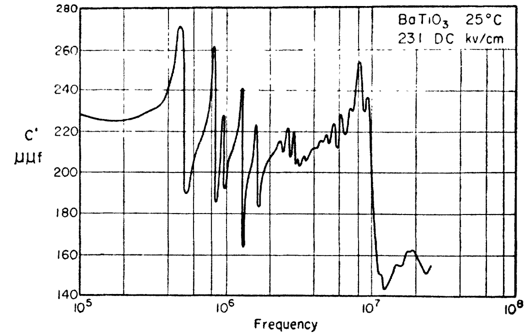

FIG. 18. Resonance frequency of $BaTiO_3$ disk.

Since the polarization of a ferroelectric, like the magnetization of a ferromagnetic, is a function of the applied field (Fig. 11), several parameters are required for its characterization. We will refer to the initial permittivity $\kappa_i' = \epsilon_i'/\epsilon_0$, the spontaneous polarization P_s, the coercitive field E_c and the remanent polarization P_r (Fig. 12).

The loss curve in Fig. 6 and the expansion char-

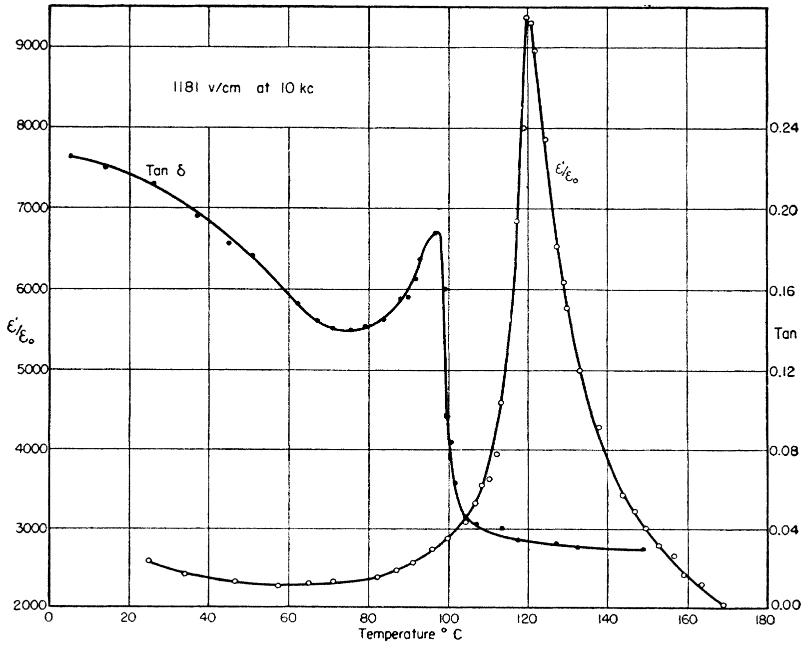

FIG. 17. Temperature dependence of dielectric constant and loss tangent of barium titanate ceramic under high field strengths.

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[14] A. von Hippel and co-workers, N.D.R.C. Rep. No. 540 (October, 1945). See von Hippel, Breckenridge, Chesley, and Tisza, Ind. Eng. Chem. **38**, 1097 (1946).

[15] H. D. Megaw, Trans. Faraday Soc. **42A**, 224 (1946); Proc. Roy. Soc. **189A**, 261 (1947).

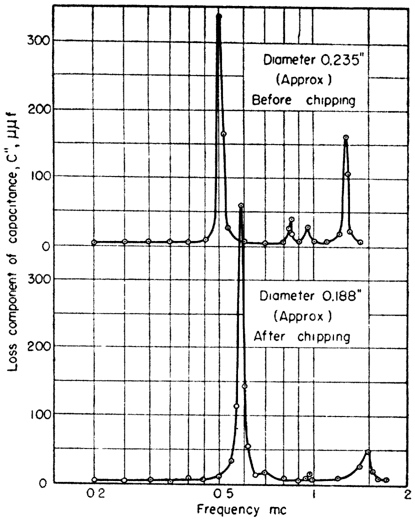

FIG. 19. Dependence of absorption on disk diameter. $BaTiO_3$ thickness 0.0080 in. Silver paste electrodes. Electrode thickness 0.0033 in. total (approx.). D.c. field strength 1.48 mv/m (300 v). C' at 300 kc $\mu\mu f$. Before chipping 315. After chipping 306.

acteristic of Fig. 7 make it apparent that some additional phase transition occurs near 0°C. When the initial permittivity derived from the hysteresis loops of Fig. 8 is plotted as $f(T)$, two lower transition points, located near 0°C and −70°C become clearly visible (Fig. 13).[14] They become more pronounced as the voltage increases, but the material remains ferroelectric throughout as the existence of the hysteresis loops indicates.

A successive replacement of barium by strontium ions lowers the Curie point systematically as Wainer and Salomon[11] have already observed. Jackson and Reddish[16] followed this shifting down to −190°C, and Rushman and Strivens[17] established a linear dependence of the Curie temperature on the lattice constant of the barium-strontium titanate mixed crystals (Fig. 14).

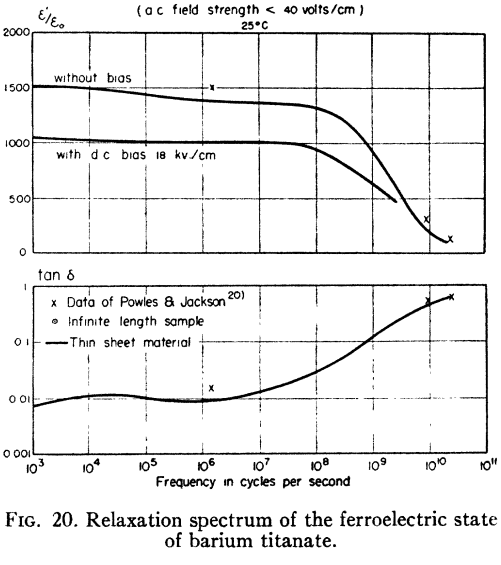

FIG. 20. Relaxation spectrum of the ferroelectric state of barium titanate.

If one observes the temperature dependence of the electric susceptibility above the Curie point, one finds at low field strength the Curie-Weiss law fulfilled (Fig. 15),[18] but at higher fields a strong dependence of χ on the applied field (Fig. 16).[18] The useful range of this non-linearity of the polarization extends to about 40°C above the Curie point and promises to be especially important since the accompanying losses are much smaller than below the Curie point (Fig. 17). The constant in the Curie-Weiss law is not $3T_c$ as the simple theory predicts but much larger; for the (Ba-Sr)TiO_3 sample of Fig. 15 with $T_c = 281°K$, a value of 88,000 is obtained.

Since the field strength dependence of the dielectric constant makes the ceramics useful as nonlinear dielectrics for a number of applications like amplifiers, modulators, and for the tuning of circuits, their behavior under the action of a biasing field was investigated in more detail. To our surprise, extremely strong resonance effects occurred as the measuring frequency approached the megacycle range (Fig. 18).[18] These resonances persisted after the biasing d.c. voltage was disconnected, but could be wiped out by a bias of the opposite sign. When this resonance absorption of a disk was measured and then a piece of the sample broken off, the spectrum shifted to higher frequencies (Fig. 19).[18] The biasing field transformed the ceramic disk into a piezoelectric resonator, and its piezoelectric response persisted also without this field because of the remanence of the polarization.

This observation opened the way for the use of barium titanate ceramics as electromechanical transducers. The development of ultrasonic generators, pick-ups, microphones, and numerous other devices has since been carried forward by a number of industrial laboratories.

From the standpoint of experimental research two principal problems remained in the ceramics field. The frequency response of the ferroelectric state had to be studied over a wide range of temperatures, and a detailed investigation of the hysteresis loops was in order, paralleling the well-known ferromagnetic research on metals. Just as the size and shape of magnetic hysteresis loops can today be controlled within wide limits by alloying agents and the proper pretreatment, the electric remanence and coercive force should be amenable to control.

Systematic frequency response measurements have been in progress in our laboratory for some time;[19] the high dielectric constant and absorption makes it very

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[16] W. Jackson and W. Reddish, Nature **156**, 717 (1945).

[17] D. F. Rushman and M. A. Strivens, Trans. Faraday Soc. **42A**, 231 (1946).

[18] S. Roberts, Phys. Rev. **71**, 890 (1947).

[19] A. von Hippel and W. B. Westphal, National Research Council Conference on Electrical Insulation (October, 1948).

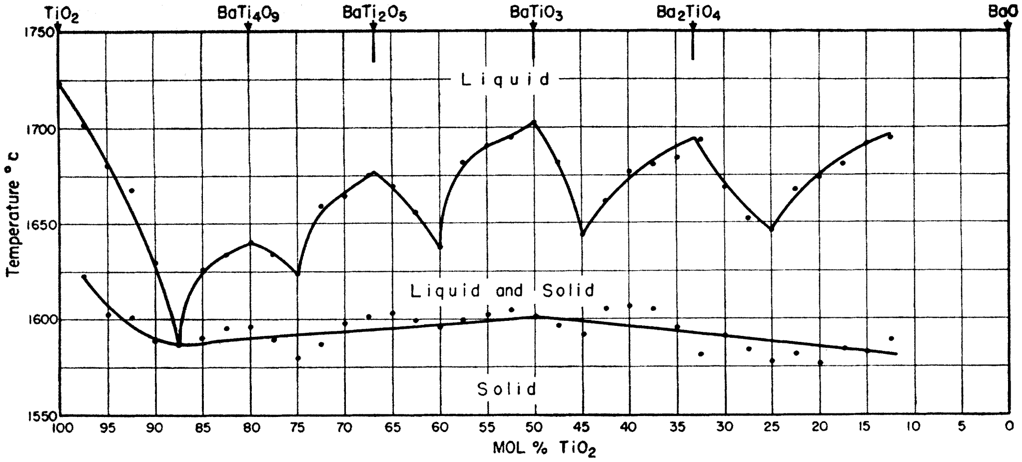


FIG. 21. Phase diagram of the BaO-TiO_2 system.

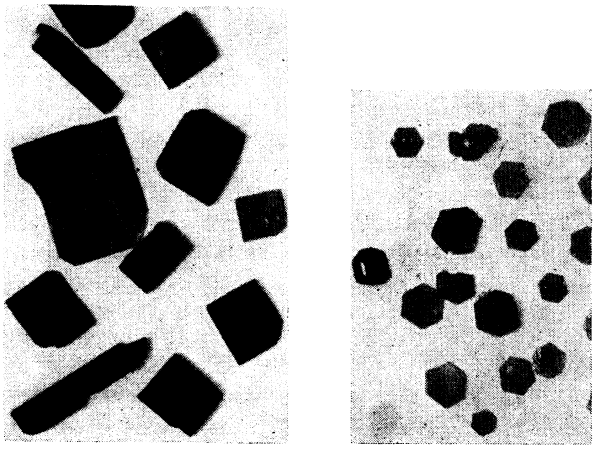
difficult to obtain accurate temperature characteristics in the microwave range. The essential phenomenon is a relaxation spectrum, as also Powles and Jackson[20] found, commencing at about 10^8 cycles and reducing the dielectric constant at about 3×10^{10} cycles to a value of *ca.* 150 (Fig. 20). Conforming with this tapering off of the ferroelectric response, the effect of a biasing voltage declines and seems to disappear in the 1-cm region.

A prerequisite for systematic hysteresis studies is to know the phase diagram BaO-TiO_2 and the influence which various addition agents exercise upon it. Extensive studies of ternary diagrams are being undertaken in the National Bureau of Standards by Bunting and his co-workers[21] with well-established ceramic methods. We have tried a somewhat unorthodox microanalytical approach, and Fig. 21 shows the BaO-TiO_2 diagram according to this nearly completed study.[22] It is obvious from the numerous compounds which can be formed that a careful structure analysis of the ceramics has to parallel the electric investigations.

BARIUM TITANATE SINGLE CRYSTALS

We could not expect to arrive at a real understanding of the ferroelectricity of $BaTiO_3$ without a study of its single crystals. Consequently, already during the war, the Linde Air Products Company tried the growing of single crystals on our behalf by its boule method, but, at that time, without success. Later, crystals of hexagonal and of cubic symmetry were obtained in Switzerland by Blattner, Matthias, Merz, and Scherrer[23] from ternary melts, and this method was taken up in our laboratory and further improved by Matthias. Since then we have investigated the production of both crystal forms in detail; Fig. 22 shows samples of these crystals, generally obtained as flat plates up to several millimeters in length.

A microscopic inspection of the pseudocubic type revealed that the crystals, cooled to room temperature, contained a variety of shaded areas (Fig. 23).[24] In an electric field these areas were seen to grow or contract, sections of new shading appeared suddenly, and disconnecting of the voltage left a remanent state which required a counter voltage for its removal. Observed in an alternating field with stroboscopic illumination the whole crystal appeared to be in violent agitation, and viewed in polarized light the flickering of the transmitted colors resembled Broadway at night. The domain structure of the material, only indirectly deducible in the case of the opaque ferromagnetics, lay in the case of the transparent ferroelectrics in all its details before our eyes.[24]



(a) (b)

FIG. 22. Small crystals of the cubic and hexagonal modifications of $BaTiO_3$. 27×.

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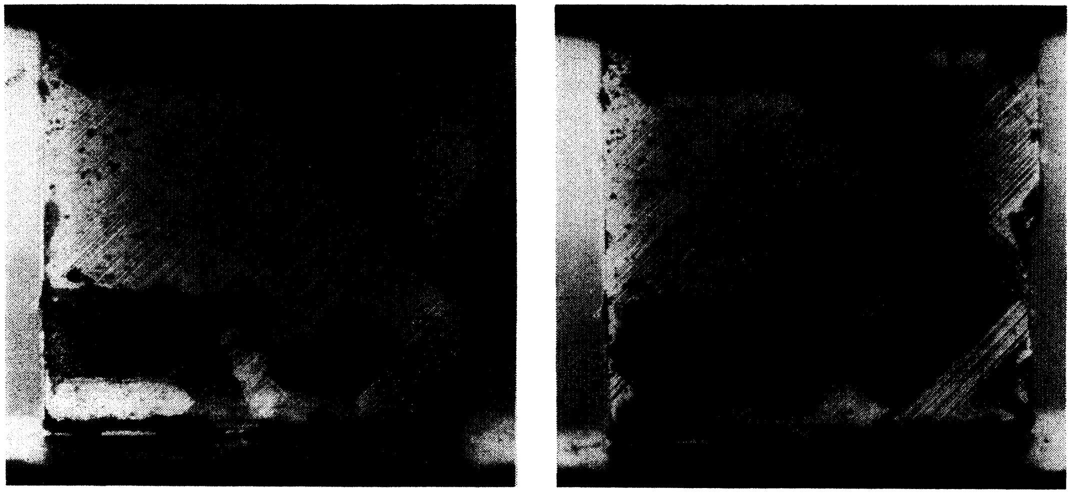
[20] J. G. Powles and W. Jackson, Proc. Inst. Elec. Eng. **96**, III, 383 (1949).

[21] Bunting, Shelton, and Creamer, J. Research. Nat. Bur. Stand. **38**, 337 (1947); **41**, 17 (1948).

[22] W. O. Stratton, ONR Contract N5ori-07801, Tech. Rep. No. 31, Lab. Ins. Res., M. I. T. (March, 1950).

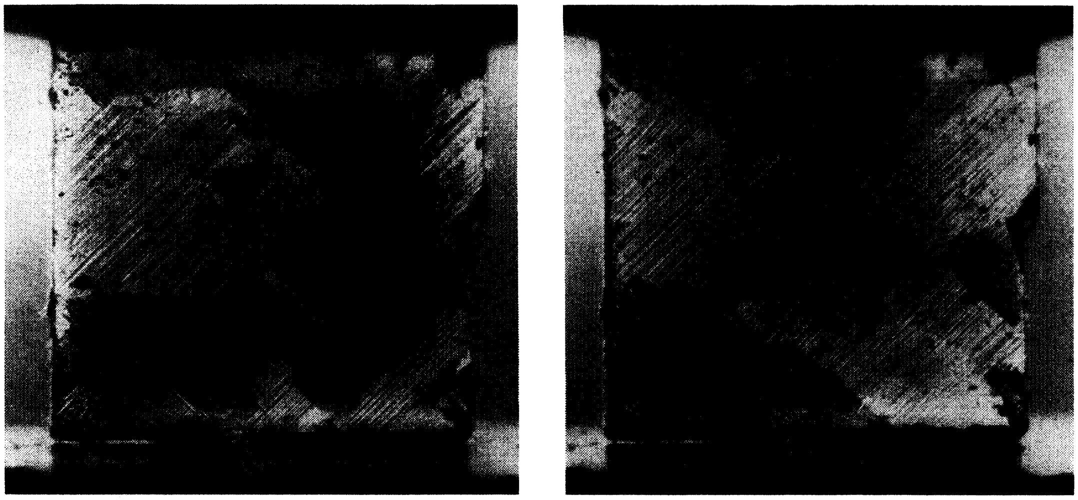
[23] Blattner, Matthias, Merz, and Scherrer, Experientia **3**, 4 (1947).

[24] B. Matthias and A. von Hippel, Phys. Rev. **73**, 1378 (1948).



No field applied

+2000 volts/cm



Field removed

−2000 volts/cm

FIG. 23. Effect of electric field on domain structure of $BaTiO_3$ crystal.

A careful analysis of the patterns revealed their laws of formation in all ramifications.[24,25] As the cubic crystal cools through the Curie temperature, a polar axis develops and forces the crystal into tetragonal symmetry, with the axis forming the *c*-direction (Fig. 24). Since any one of the cube edges may develop into the polar axis, a twinning in the (110) planes tends to take place and laminae form with the *c*-axis alternating its direction by 90°. Seen from the front these laminae produce a diagonal striation while in the top and side views striae parallel to the cube edges result. Since the optical index of refraction is smaller parallel to the polar axis than perpendicular to it ($n_c - n_a = -0.055$ for sodium light at room temperature), the orientation of the axis and the thickness of the lamellae can be measured by the birefringence colors in polarized light. A strong electric field may wipe out the domain pattern more or less completely; when viewed parallel to this field direction in polarized light the well-known cross of a uniaxial crystal appears (Fig. 25). The crystallographer has thus to accept the unusual situation that the *c*-axis of the $BaTiO_3$ crystal can be turned around at will by the application of an electric field.

The build-up of the domains begins with the formation of wedge-shaped laminae (Fig. 26). Mechanical pressure or electric fields can drive these wedges through the crystal or squeeze them out again. The final domain structure is therefore dependent on the strains originally contained in the material and on their modification by the domains of the ferroelectric state. If the first set of wedges is crossed by a second one at right angles (Fig. 27), a system of intersecting laminae can be developed which leads finally to the beautiful square-net pattern

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[25] P. W. Forsbergh, Jr., Phys. Rev. **76**, 1187 (1949).

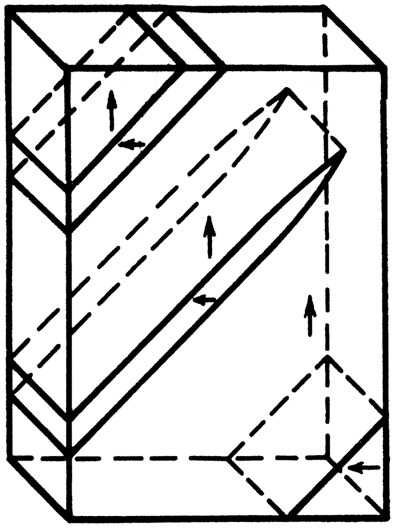

FIG. 24. Twinning in $BaTiO_3$ as determined by polar axes.

of Fig. 28. Its building blocks have been identified in successive stages by birefringence measurements[25] (Fig. 29), and similarly the various other patterns, which rival in beauty Persian carpet designs, have been analyzed in detail.

Above the Curie point the cubic crystal appears dark between crossed nicols; as it cools through the Curie region, the domain patterns develop as just described. Further cooling through the transition regions near 0°C and −70°C, produces sudden changes in the domain structure. Optical analysis[25] established the fact that the polar axis, originally formed in the cube edge direction, jumps abruptly, first in the face diagonal, and near −70°C into the space diagonal position (Fig. 30). The cubic $BaTiO_3$, changing at the Curie point by a second-order transition into a tetragonal crystal, transforms by these two subsequent first-order transitions into an orthorhombic and finally a trigonal modification. Electrical analysis[26] and a careful x-ray study carried through in England by Kay and Vousden[27] have led to the same conclusion.

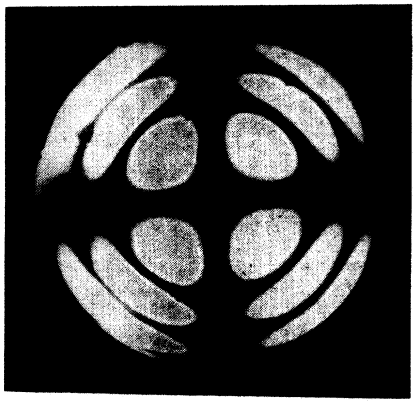

FIG. 25. $BaTiO_3$ crystal viewed in polarized light parallel to strong field.

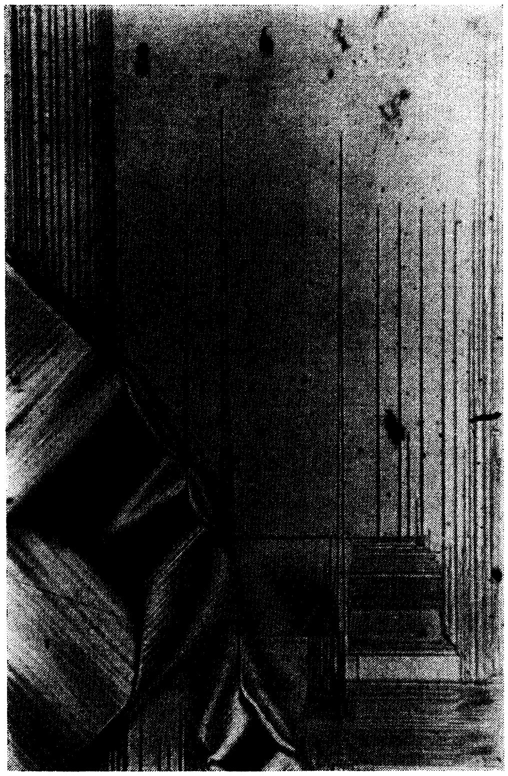

FIG. 26. Wedge-shaped laminar domains in $BaTiO_3$ single crystal.

A decisive factor in the formation of ferromagnetic domains is the demagnetizing field which originates from the free ends of dipole chains at the boundaries of the material. By breaking up a single macroscopic block of parallel dipoles into a compensating array of micro-blocks, this field can be practically eliminated (Fig. 31). In the case of ferroelectrics the free surface charge of terminating dipoles may be compensated for by the attraction of counter-charges through conduction. We were therefore not completely surprised to find crystals which gave the optical appearance of a single domain. Such crystals, as Matthias found, were preferentially obtained from ternary melts with boron oxide added as a mineralizer. Since, for the theory of ferroelectricity, the properties of a single domain are decisive these crystals were investigated in detail.

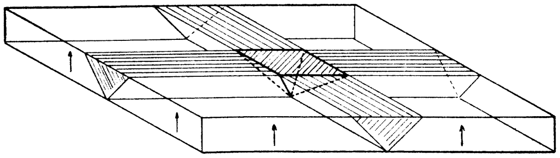

FIG. 27. Intersection of two perpendicular laminar groups.

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[26] W. J. Merz, Phys. Rev. **76**, 1221 (1949).

[27] H. F. Kay and P. Vousden, Phil. Mag. (7) **40**, 1019 (1949).

FIG. 28. Square net domain pattern of $BaTiO_3$ single crystal.

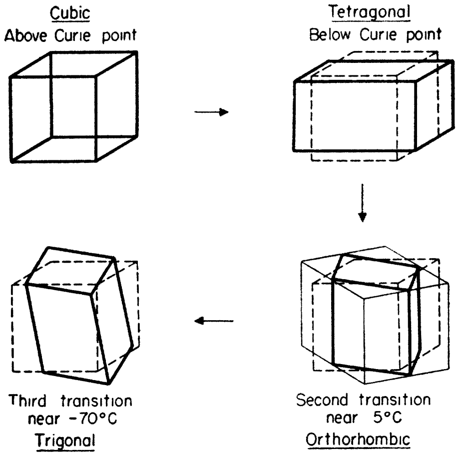

FIG. 30. Phase transitions of barium titanate.

Application of an alternating field produces initially distorted hysteresis loops, but the disturbances disappear after the crystal has been taken through several heating cycles with systematically increased field strength[26] (Fig. 32). It seems, therefore, that these "single domain crystals" consist initially of antiparallel domains; their final loops are nearly rectangular like those observed for ferromagnetic single crystals. The electric pulses which accompany the successive switching of the domains, an analogy to the Barkhausen noise of ferromagnetics, have then disappeared and the spontaneous polarization P_s of Fig. 33 is observed. Noise and a temperature hysteresis accompany the two lower transitions, where the reorientation of the polar axis creates new domain patterns. Figure 34 shows the same situation for the initial permittivity κ_i.

A discussion has arisen whether the electromechanical response of $BaTiO_3$ should be characterized as electrostrictive or piezoelectric.[28] This argument can be settled and the piezoelectric behavior of the material understood by reference to Fig. 35. The formation of the polar axis stretches the crystal in the c-direction by placing permanent dipole moments end-wise in this direction. An external field may vary these permanent moments and with them the stretch, as in any piezoelectric material. The essential difference is that a normal material, when the electric field parallel to the polar axis is reduced to zero and then increased in the opposite direction, will contract along a line B-C-D and beyond D. In a "single-domain" ferroelectric crystal the permanent dipole moments can reverse their direction at D, thus a sudden expansion takes place to C' followed by a continuous expansion along the line C'-B' as the reverse field increases. On the return path the switch takes place at D' to C; that is, because of remanence the deformation characteristic traverses a hysteresis loop instead of the simple fork B-A-B'. But the material is, in the main, piezoelectric, since this term implies that the distortion results from the action of the field in changing the magnitude of pre-existing permanent moments ($0 \rightarrow A$). The name "electrostrictive" has so far been reserved for electromechanical distortions caused by induced moments

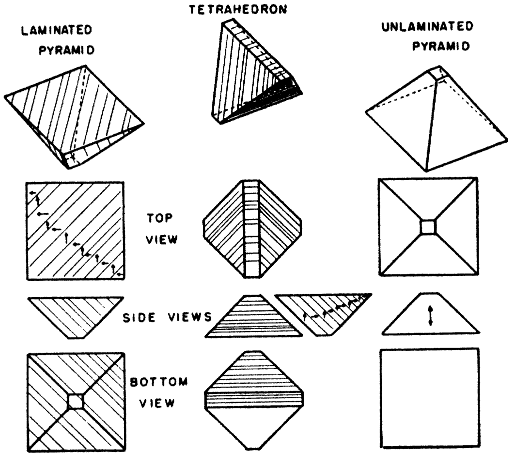

FIG. 29. Three types of building blocks composing square net pattern.

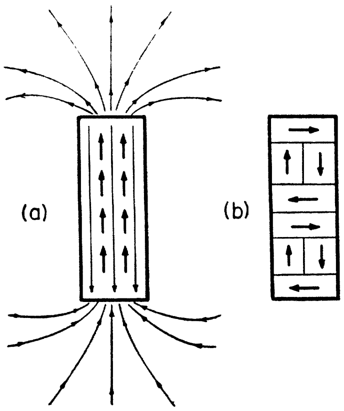

FIG. 31. (a) Single-domain crystal producing demagnetizing field. (b) Domain structure eliminating demagnetizing field.

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[28] W. P. Mason, Phys. Rev. **72**, 869 (1947); B. Matthias and A. von Hippel, Phys. Rev. **73**, 268 (1948); W. P. Mason, Phys. Rev. **73**, 1398 (1948).

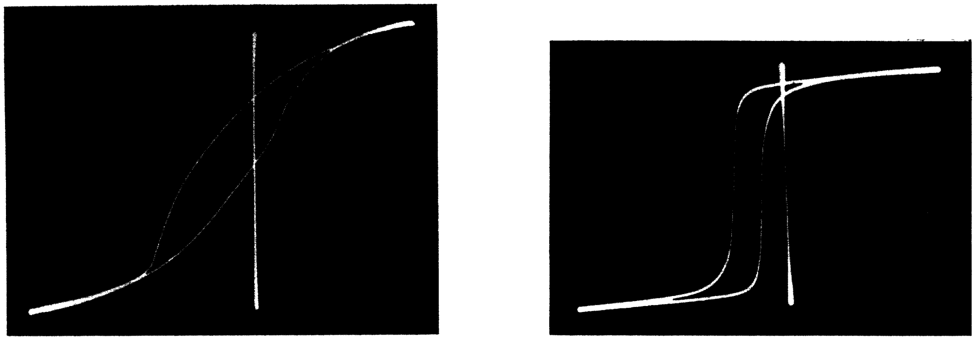
(a) (b)

FIG. 32. Hysteresis loops before and after the forming treatment.

which are created by the external field and disappear with it. At the Curie point $BaTiO_3$ reacts therefore initially only electrostrictive, but becomes immediately also piezoelectric, because the concerted action of the induced moments creates again permanent moments by displacing the titanium ions off-center. Unfortunately the issue becomes still more beclouded by the fact that the term "magnetostriction" applies to the mechanical distortion caused by the orientation of permanent magnetic moments. This is the analog to the electromechanical distortion produced in ferroelectrics by the orientation of domains and the turning of the polar axis from its preferred direction into the field direction. Such domain effects make the deformation characteristics (Fig. 36) much more complex than Fig. 35 indicates, and high prepolarizing fields were required before the actual piezoelectric coefficients of $BaTiO_3$ could be determined (Fig. 37).[29]

High hydrostatic pressure moves the Curie point of $BaTiO_3$ toward lower temperature as shown in Fig. 38.[30]

ORIGIN OF THE FERROELECTRIC STATE

It is obvious that the perovskite structure of the cubic $BaTiO_3$ (Fig. 5) does not contain permanent dipole moments. Such dipoles might anyhow be of little use, as pointed out in the beginning because they would be frozen into the structure and probably unable to align themselves freely in field direction. Spectroscopically speaking, the rotation spectra of molecules are, in general, destroyed in the solid phase due to space limitations and replaced by relaxation spectra, but the vibration spectra persist. And in the proper use of dipole moments induced by vibrations lies apparently the principle employed by nature for the production of these ferroelectrics.

That the vibrational modes of the titanium against

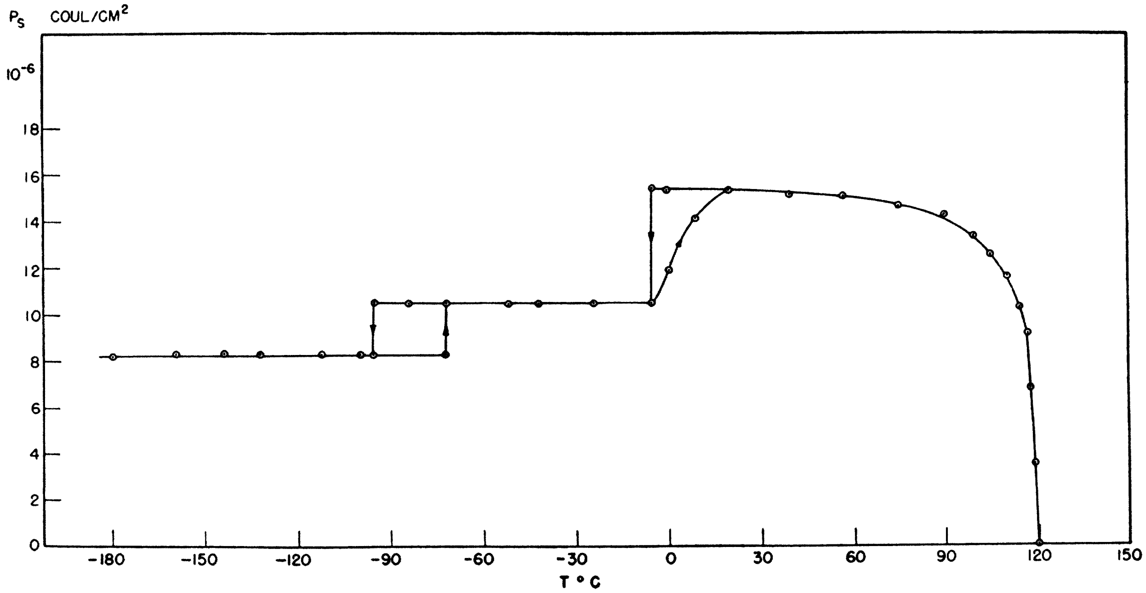

FIG. 33. Spontaneous polarization P_s as function of temperature.

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[29] M. E. Caspari, Proc. Am. Phys. Soc. **25**, No. 1, 36 (1950).

[30] W. J. Merz, Proc. Am. Phys. Soc. **25**, No. 1, 36 (1950).

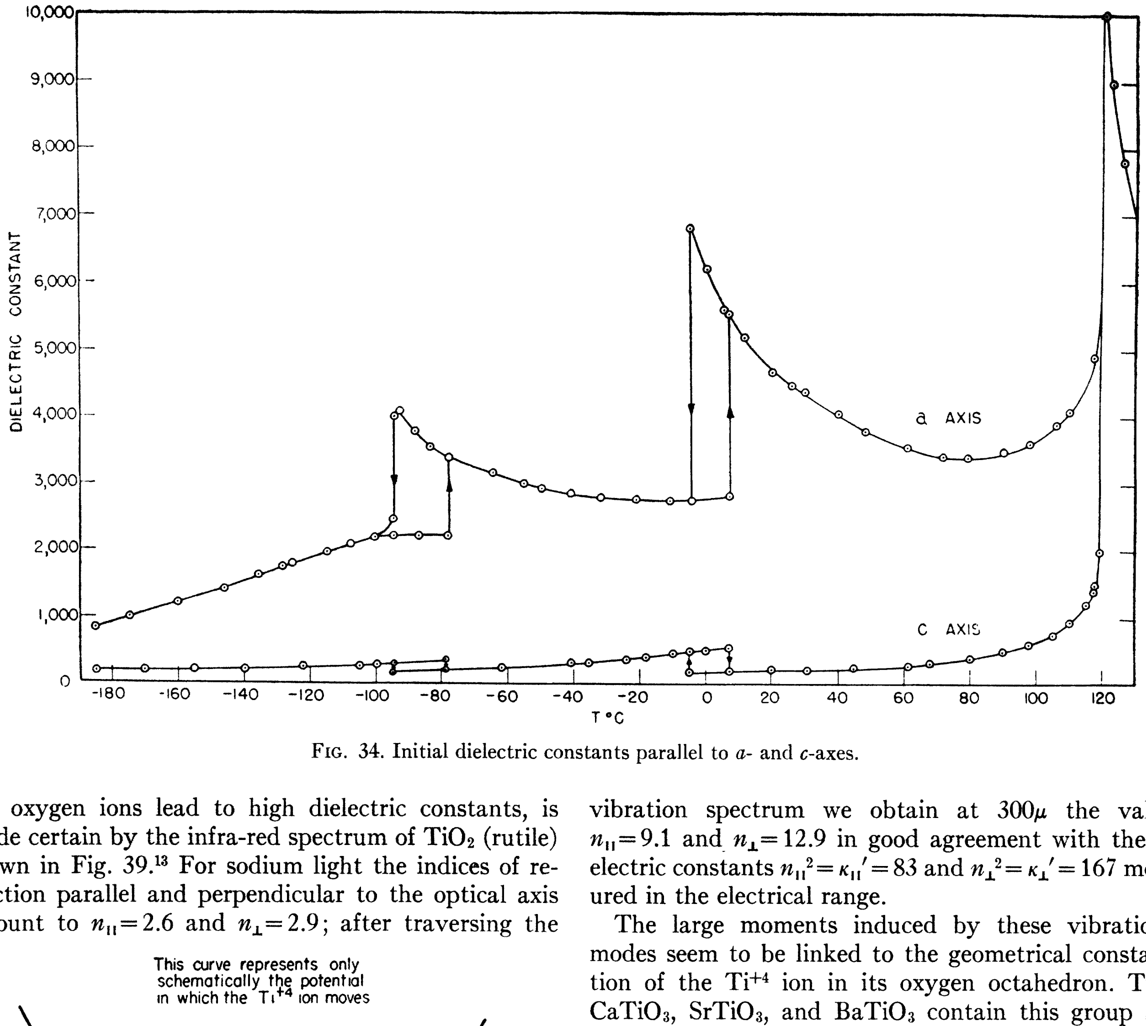

FIG. 34. Initial dielectric constants parallel to a- and c-axes.

the oxygen ions lead to high dielectric constants, is made certain by the infra-red spectrum of TiO_2 (rutile) shown in Fig. 39.[13] For sodium light the indices of refraction parallel and perpendicular to the optical axis amount to $n_{\parallel}=2.6$ and $n_{\perp}=2.9$; after traversing the vibration spectrum we obtain at 300μ the values $n_{\parallel}=9.1$ and $n_{\perp}=12.9$ in good agreement with the dielectric constants $n_{\parallel}^2=\kappa_{\parallel}'=83$ and $n_{\perp}^2=\kappa_{\perp}'=167$ measured in the electrical range.

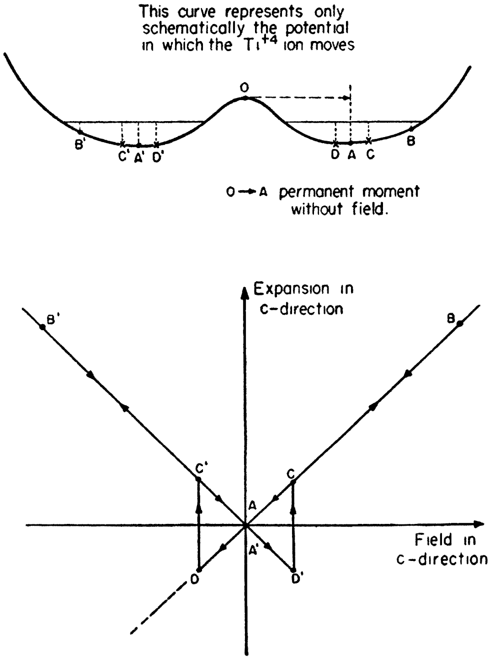

FIG. 35. Piezoelectric response of ideal $BaTiO_3$ "single-domain" crystal.

The large moments induced by these vibrational modes seem to be linked to the geometrical constallation of the Ti^{+4} ion in its oxygen octahedron. TiO_2, $CaTiO_3$, $SrTiO_3$, and $BaTiO_3$ contain this group and show increasingly high dielectric constants, while $MgTiO_3$, with the titanium ion sharing only three oxygen ions in corundum structure, falls back into the range of normal ionic crystals.[13]

The location of the Ti^{+4} ions in the well-shielding and symmetrical oxygen octahedra appears to be one prerequisite for the ferroelectric state in the titanates; the proper size and space arrangement of these octahedra are two additional requirements. The size sensitivity is illustrated in Figs. 14 and 38; a reduction of the lattice parameter of $BaTiO_3$ by the addition of strontium or by hydrostatic pressure lowers the Curie point linearly and by about equal amounts.[30] The effect of the arrangement becomes convincingly clear when we compare the structures of the cubic and hexagonal barium titanate modifications (Fig. 40).[31] In the cubic phase the octahedra share corners only, while in the hexagonal form two-thirds of them occur in groups of two which share one face. Consequently in these groups the Ti^{+4} ions face each other relatively closely and unshielded, and their mutual repulsion is not conducive to the

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[31] R. D. Burbank and H. T. Evans, Jr., Acta Crys. **1**, 330 (1948).

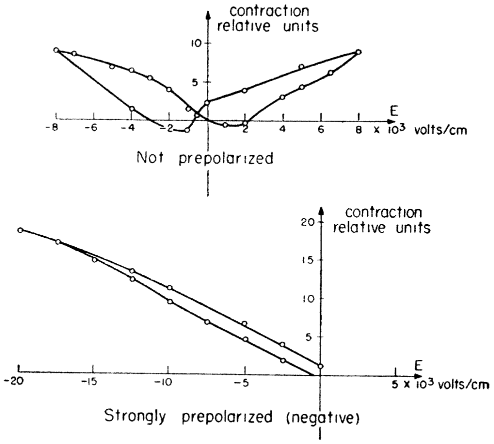

FIG. 36. Piezoelectric contraction of actual $BaTiO_3$ crystal.

promotion of a concerted action as required in ferroelectrics. The hexagonal modification is therefore not ferroelectric and its permittivity reaches only the value of *ca.* 100 at room temperature.

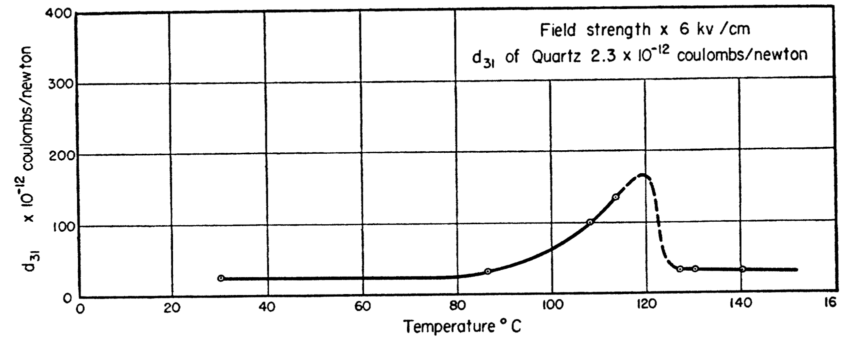

FIG. 37. Piezoelectric d_{31} coefficient of $BaTiO_3$ single crystal as function of temperature.

A theory of the ferroelectric state of $BaTiO_3$ has therefore to be based on the polarization induced when the Ti^{+4} ions move in valence vibrations against their oxygen surroundings. Above the Curie point the material is cubic and not piezoelectric; hence the equilibrium position of the titanium seems to be still in the center of the octahedra. The binding to this center position, as the analysis of TiO_2 shows,[13] is not that of a simple linear oscillator; the dipole moment rises faster than linearly with the displacement of the ions. This, one would expect, as Eucken and Büchner[32] first pointed out, if the Ti—O bond represents a transition case between ionic and covalent binding.

As the temperature falls through the Curie region, a λ-point transition with a very small change Δc_p of the specific heat is observed; Wul[33] found 3×10^{-3}, Harwood, Popper, and Rushman[34] 2.5×10^{-3} cal. per g and degree, while our original measurements with a less sensitive apparatus gave no effect. We classified therefore the transformation at the Curie point as a second-order "displacive" transformation[13] in which the crystal is reduced from higher to lower symmetry by a minute change of a lattice parameter.[35] This change consists in a systematic displacement of the equilibrium position of the titanium ion from the center of the octahedron towards the oxygen ions. Preliminary x-ray measurements[36] indicate that this reaches an amount <0.1A at room temperature.

Thus we have to assume that the titanium ion near the Curie point moves in a shallow potential well and that any displacement from the center of this well results in large dipole moments. As soon as a number of adjacent moments are pointed in the same direction, whether by an external field or a thermal fluctuation, a local field of the Mosotti type increases the polarization and displaces the potential minimum toward one of the oxygens. Thus a permanent moment results, the structure becomes tetragonal, and, since it loses its center of symmetry, piezoelectric. That the potehtial well is very shallow in the Curie region follows directly from the fact that the dielectric constant is still high above the Curie point and strongly affected by the application of an external field (see Fig. 16). Also the domain structure and the piezoelectric response re-

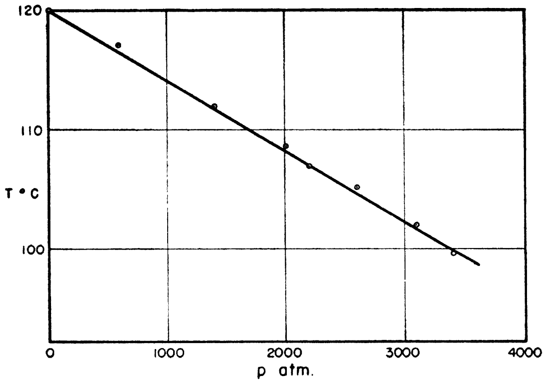

FIG. 38. Dependence of Curie temperature on hydrostatic pressure for $BaTiO_3$ single crystal.

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[32] A. Eucken and A. Büchner, Zeits. f. physik Chemie **B27**, 321 (1934).

[33] B. M. Wul, J. Phys. USSR **10**, 95 (1946).

[34] Harwood, Popper, and Rushman, Nature **160**, 58 (1947).

[35] L. Tisza, "On the general theory of phase transitions," N.R.C. Symposium, Cornell University (August, 1948).

[36] H. T. Evans, Jr. (unpublished).

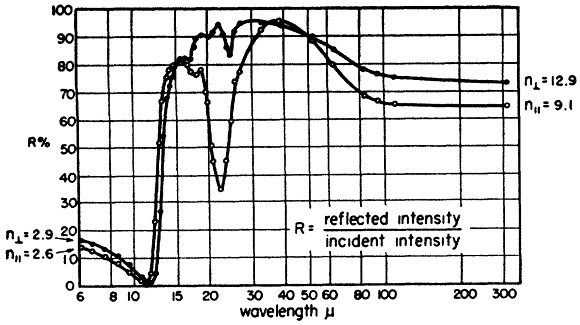


FIG. 39. Infra-red reflection of rutile crystal (after Liebisch and Rubens).

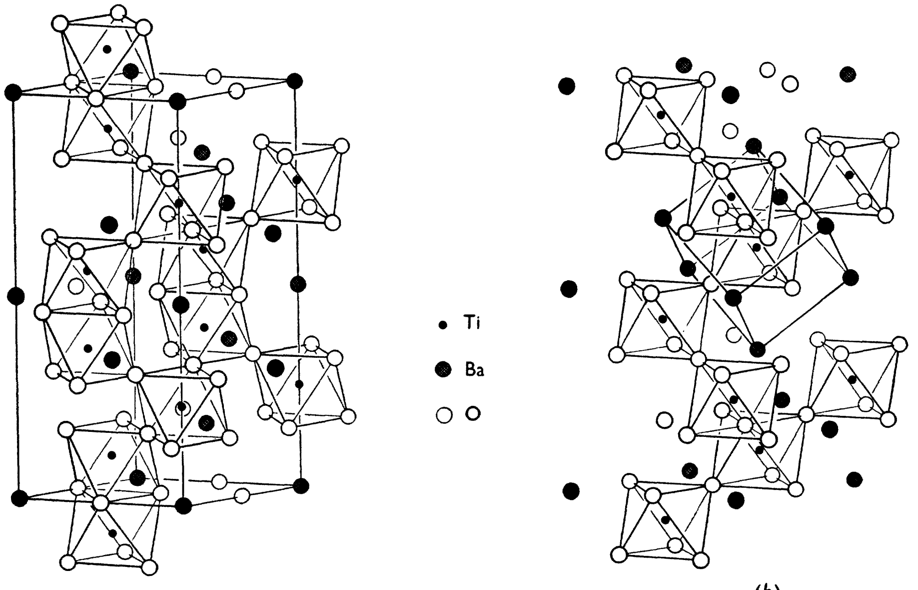
appear above the Curie point under the influence of an external voltage.[37]

A quantitative theory of the ferroelectric state of $BaTiO_3$ has to derive the Curie-Weiss law without resort to the permanent moments of the Langevin function, and with its proper constant. Attempts to base this law only on the electronic polarizability[38] or only on the thermal expansion of the lattice[39] are unsatisfactory: the optical index of refraction of TiO_2 is higher than that of $BaTiO_3$ (2.9 as compared to 2.4) but rutile does not become ferroelectric, and the dependence of the Curie point on the applied field shows that the thermal expansion does not play the decisive role. In the case of ferromagnetism, the exchange forces are responsible for the alignment of the magnetic moments. In barium titanate it seems plausible that the cubic array makes a Mosotti field possible and that the electromechanical coupling between the octahedra plays the role of the magnetic exchange forces. This coupling may bring the interaction between the vibrating dipoles to the proper magnitude and enforce the displacement of their centers towards the same direction, thus leading to an array of permanent dipole moments in parallel alignment. A promising beginning has been made in several laboratories[40] towards the development of such a theory.

ACKNOWLEDGMENT

In presenting this report the author has acted as the spokesman for a group of co-workers who have investigated the ferroelectric behavior of barium titanate as physicists, chemists, electrical engineers, and ceramicists. Two extensive reports rendered during the war were unfortunately not declassified before 1946, thus a number of our results were rediscovered in independent research in Russia, England, Holland, and Switzerland. This account does not purport to give a complete survey of the literature but refers only to those papers that have influenced our studies.

F. C. Chesley and later R. D. Burbank and H. T. Evans, Jr. were responsible for the structure research; S. Roberts for the detailed electric study of the ceramics, which led to the discovery of the piezoeffect; B. Matthias for the growing of single crystals from ternary melts and the initial investigation of the domain struc-



(a) Hexagonal modification

(b) Cubic modification

FIG. 40. Crystal structures of barium titanate.

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[37] M. E. Caspari and W. J. Merz, Tech. Rep. No. 30, ONR Contract N5ori-07801, Lab. Ins. Res., M.I.T. (July, 1950).

[38] S. Roberts, Phys. Rev. **76**, 1215 (1949).

[39] G. H. Jonker and J. H. van Santen, Science **109**, 632 (1949).

[40] A. F. Devonshire, Phil. Mag. [7] **40**, 1040 (1949); P. W. Anderson, Phys. Rev. **78**, 341 (1950); J. C. Slater, Phys. Rev. **78**, 748 (1950).

ture; P. W. Forsbergh, Jr. for its complete evaluation; W. J. Merz for the studies on single domain crystals; M. Caspari for measurements of the piezoelectric coefficients; and W. O. Statton for phase diagram studies. During the war, R. G. Breckenridge was in charge of the preparation of the ceramics and in general connected with the research; and L. Tisza was advising on theoretical problems. In addition to these co-workers whose names appear as authors or co-authors in the references of this report, the contributions of A. P. deBretteville, Jr., who established the lowest transition point by the hysteresis measurements of Fig. 8; of J. M. Brownlow, who prepared the ceramic samples and measured their expansion; and of W. B. Westphal, who determined the dielectric characteristics of many samples, should be gratefully acknowledged.

Erratum: Nuclear Isomerism

[Rev. Mod. Phys. **21**, 271 (1949)]

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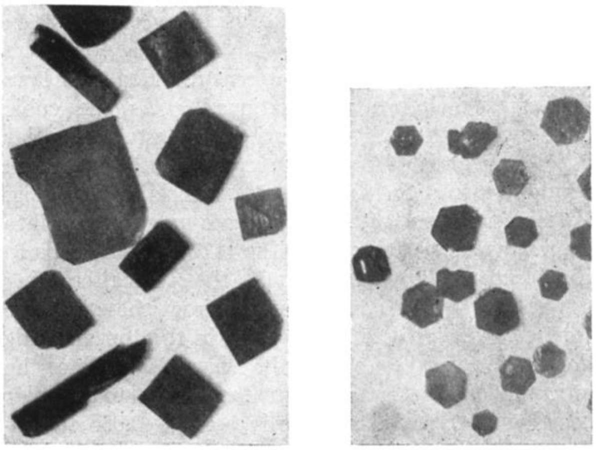
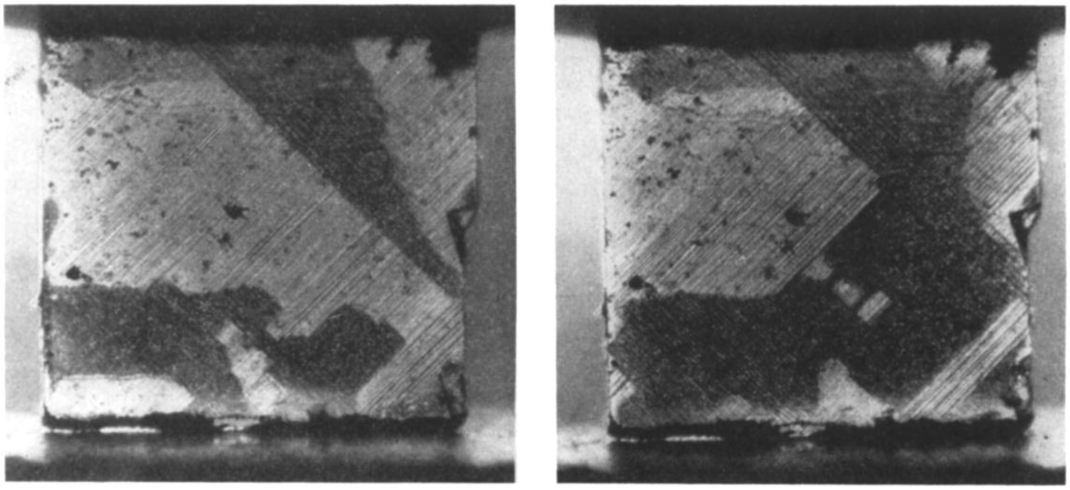
EQUATION (44), page 282, should read

$$\alpha_K{}^l = Z^3 \alpha^4 \frac{l}{l+1} \left(\frac{2}{\nu} \right)^{l+\frac{5}{2}} . \tag{44}$$



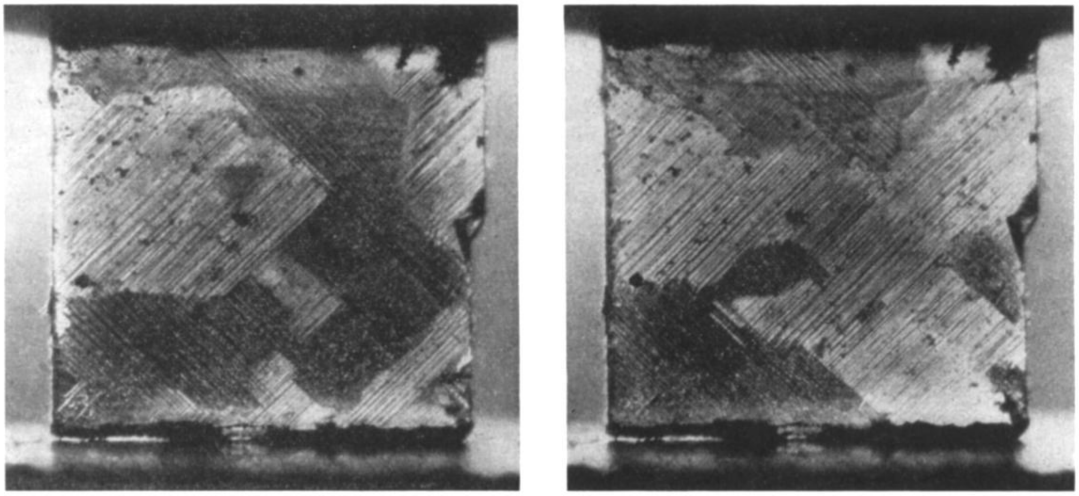
(a) (b)

FIG. 22. Small crystals of the cubic and hexagonal modifications of $BaTiO_3$. 27×.



No field applied

+2000 volts/cm



Field removed

−2000 volts/cm

FIG. 23. Effect of electric field on domain structure of $BaTiO_3$ crystal.

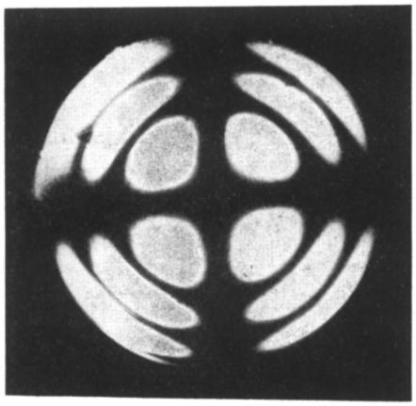


FIG. 25. $BaTiO_3$ crystal viewed in polarized light parallel to strong field.

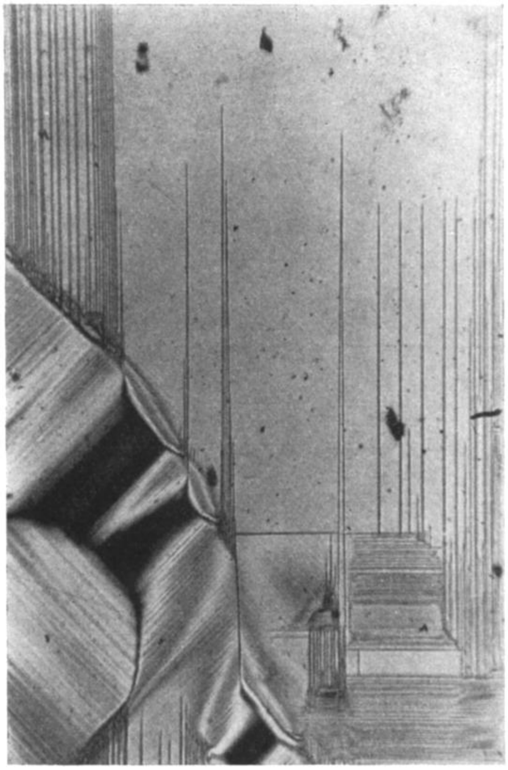


FIG. 26. Wedge-shaped laminar domains in $BaTiO_3$ single crystal.

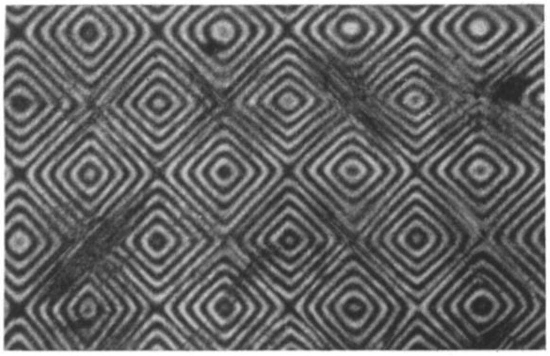
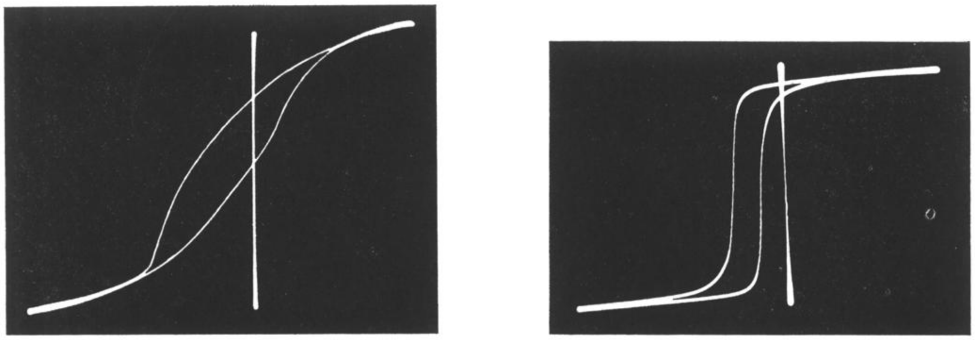
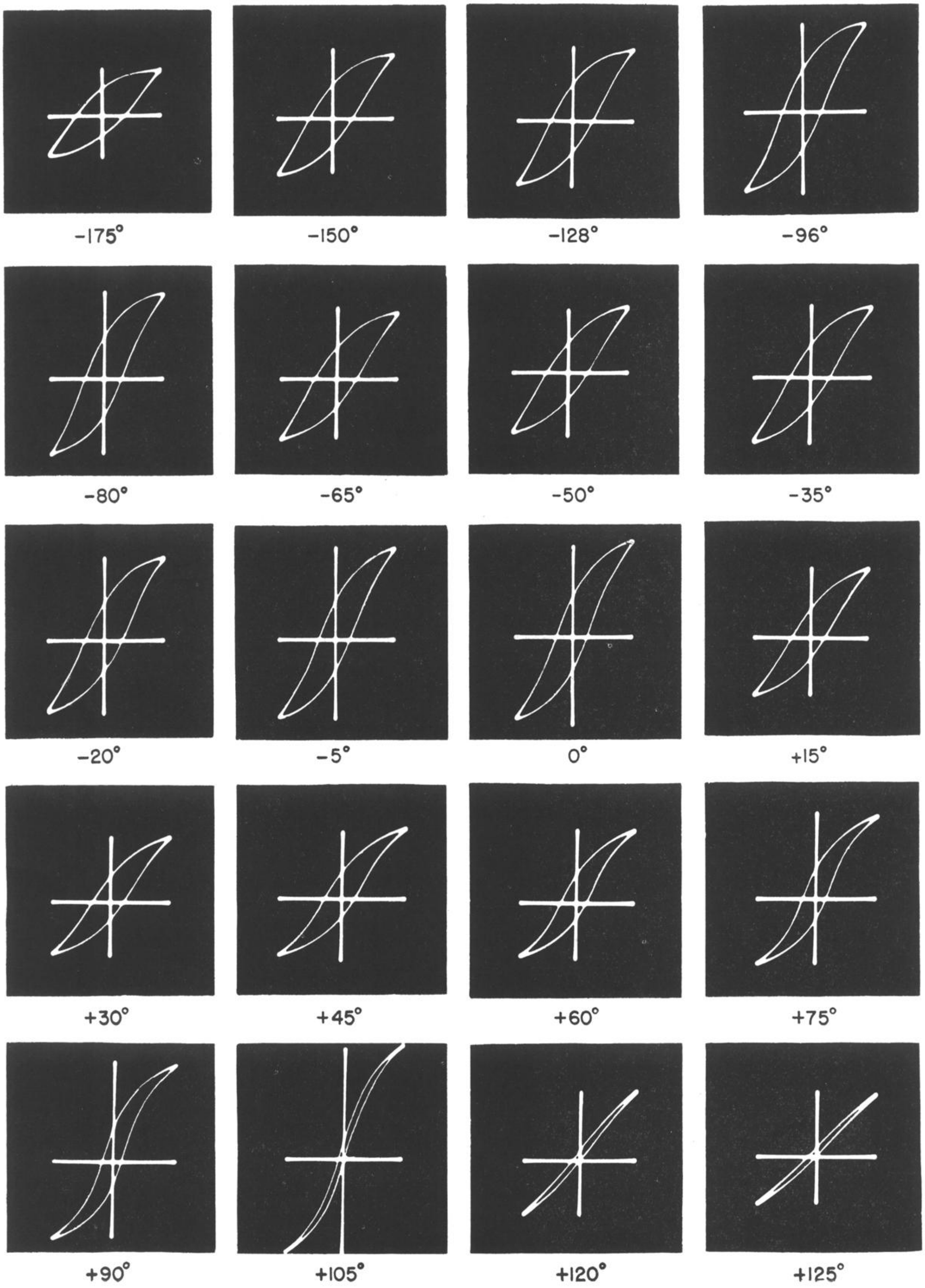


FIG. 28. Square net domain pattern of $BaTiO_3$ single crystal.



(a) (b)

FIG. 32. Hysteresis loops before and after the forming treatment.



-175° -150° -128° -96°

-80° -65° -50° -35°

-20° -5° 0° +15°

+30° +45° +60° +75°

+90° +105° +120° +125°

FIG. 8. Hysteresis loops of barium titanate ceramic.

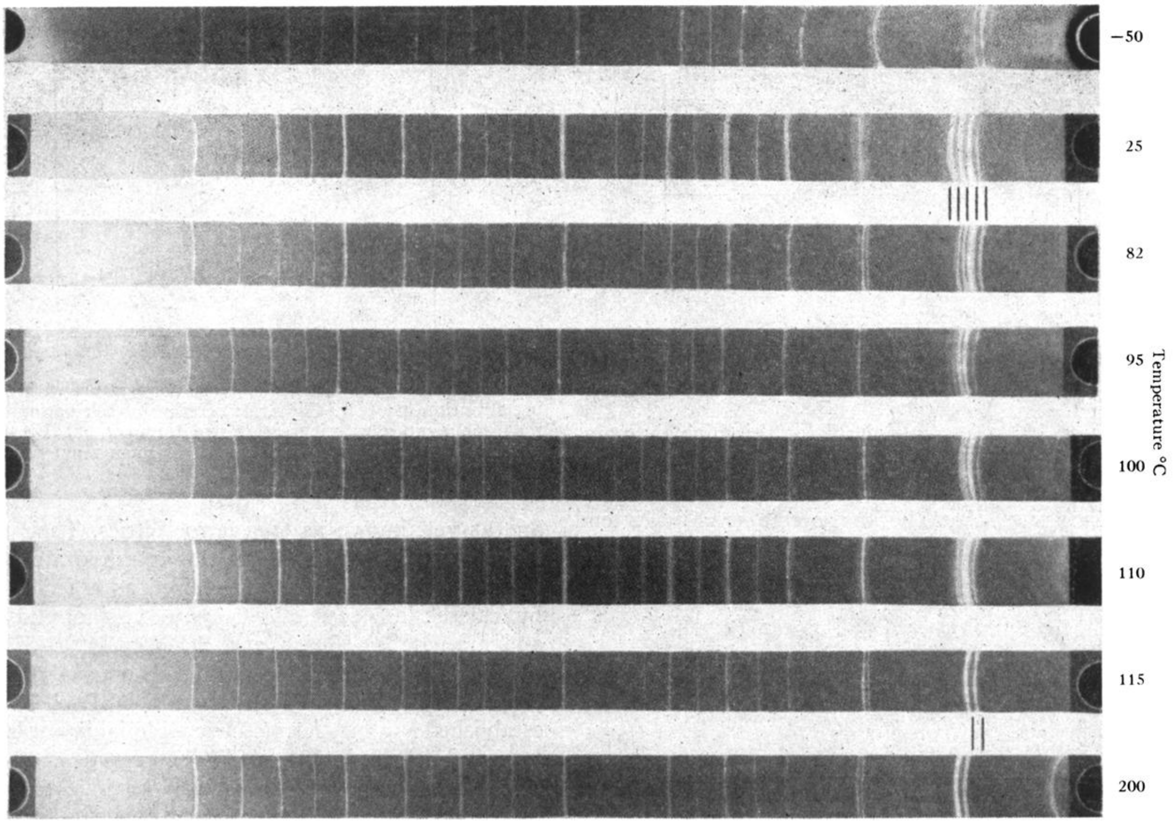


FIG. 9. X-ray patterns of barium titanate ceramics.