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Dielectric Properties of Lead Zirconate

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In order to distinguish whether it is really a ferroelectric or not, the dielectric response of $PbZrO_3$ ceramic to biasing dc field has been examined. In contrast to ordinary ferroelectrics, an effect is scarcely detected below the Curie point of 233°C even up to a field strength of 20 kv/cm, except for a slight increase of permittivity at the vicinity of the transition point. In addition, the Curie temperature decreases with increasing biasing field attaining the value $\Delta T_c = -1.7$°C for 20 kv/cm.

The hysteresis loops of this ceramic have been studied. So long as the amplitude of the applied ac field is less than a critical field of about 23 kv/cm, the *D-E* curves are almost always linear, except that a slight upward curvature becomes perceptible just at the temperature range wherein permittivity increases, and never show any hysteresis characteristics even just below the Curie point. But if the amplitude of the applied field is greater than this threshold value, anomalous hysteresis loops of very impressive form are observed in a narrow temperature range just below the Curie point.

These experimental facts all seem to suggest that $PbZrO_3$ may be, not a ferroelectric, but an antiferroelectric. A preliminary pyroelectric test also seems to show that no net polarization grows spontaneously when the sample is cooled through its Curie point.

I. INTRODUCTION

BARIUM titanate[1] has attracted much interest because of its peculiar ferroelectric properties. Lead titanate,[2] as well as several colombates and tantalates[3] of perovskite structure, were also reported to be ferroelectrics of the same type. Recently, Roberts[4] has reported that the variation of the dielectric constant of lead zirconate is also very similar to that of barium titanate, having its Curie point at 236°C. But our recent investigation[5] on $PbZrO_3$ has revealed several intrinsic differences between this material and $BaTiO_3$, not only in dielectric properties but also in dilatometric and calorimetric ones.

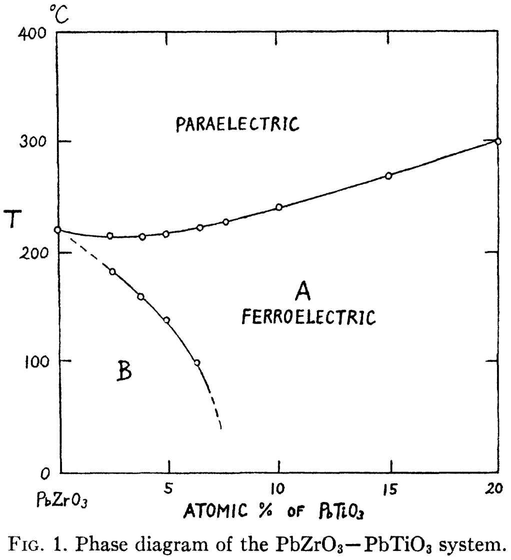

FIG. 1. Phase diagram of the $PbZrO_3-PbTiO_3$ system.

Moreover, our investigation[6] on the solid solutions of the $Pb(Zr-Ti)O_3$ system has shown the existence of another transition, for example at 140°C in $Pb(Zr95-Ti5)O_3$, besides the ordinary ferroelectric-paraelectric Curie point (Fig. 1). The phase denoted by *A* is surely ferroelectric, for hysteresis loops of typical form have been observed there. On the other hand, the intrinsic nature of the phase denoted by *B*, including pure $PbZrO_3$ itself, has remained open to question, because in this region neither hysteresis loop nor piezoelectric effect has been observed yet. Since this phase is merely a continuation of pure $PbZrO_3$, its nature will become clear if we investigate the pure material itself.

Two possibilities are conceivable: (1) although $PbZrO_3$ is indeed a ferroelectric, yet it is accompanied by an enormously large coercive field; or (2) it is in fact an antiferroelectric, in which spontaneous polarizations of component sublattices are antiparallel to each other producing no net polarization as a whole. Of course, a direct and decisive method of discriminating between these two hypotheses may be provided by x-ray analysis of precise atomic displacements. In addition, however, among purely phenomenological methods, a pyroelectric test and an examination of its dielectric response to the dc field may be the most helpful. The results of such investigations on pure $PbZrO_3$ will be reported here.

II. SPECIMEN

Specimens were prepared from reagent-grade PbO and ZrO_2 of high purity containing as impurities only very small amounts of Ti (0.21 percent), Fe (0.05 percent) and Si (0.03 percent). These ingredients were mixed in equimolar proportion and sintered at about 1250°C after a preliminary calcination. It is difficult to

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[1] See for instance, A. von Hippel, Revs. Modern Phys. **22**, 221 (1950).

[2] Shirane, Hoshino, and Suzuki, Phys. Rev. **80**, 1105 (1950).

[3] B. Matthias, Phys. Rev. **75**, 1771 (1949).

[4] S. Roberts, J. Am. Ceram. Soc. **33**, 63 (1950).

[5] Shirane, Sawaguchi, and Takeda, Phys. Rev. **80**, 485 (1950). Sawaguchi, Shirane, and Takagi, J. Phys. Soc. Japan **6** (to be published).

[6] G. Shirane and A. Takeda, J. Phys. Soc. Japan (to be published).

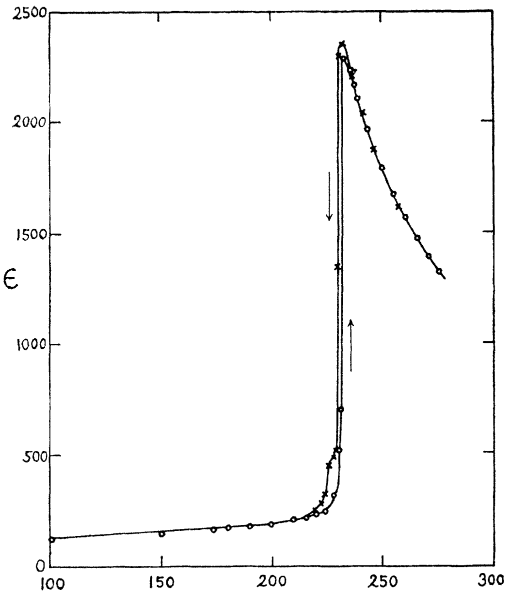

FIG. 2. Dielectric constant of lead zirconate at varying temperatures.

obtain a very tight specimen but the sintered ceramics were good enough for dielectric measurements, being free from porosity.

Dielectric test samples, 1 mm in thickness, were coated on both sides with evaporated gold film. Permittivity was measured with a heterodyne method at 1 Mc/sec and 10 v/cm. Curves for both rising and falling temperatures are shown in Fig. 2. Above the Curie point of 233°C, it was found that the Curie-Weiss law $\epsilon = C/(T-T_p)$ is valid to a good approximation with $C = 1.2 \times 10^5$ °C and $T_p = 185$°C. These results are in good agreement with those obtained by Roberts.[4] It should be pointed out here that the paraelectric Curie point T_p is somewhat lower than the transition point, in contrast to the case of $BaTiO_3$.

The small anomaly at 225°C observed in the permittivity curve on cooling is similar in its shape, though less distinct, to that previously found at 203°C on the cooling curve of our former $PbZrO_3$ of lower purity,[5] and hence it seems to be due to the same sort of origin.

III. EFFECT OF DC BIAS ON THE CURIE POINT

We have measured the permittivity of $PbZrO_3$ ceramic under a biasing dc field of 10 kv/cm as a function of temperature (Fig. 3). Measurements were carried out in a bath of liquid paraffin which was stirred vigorously, and the temperature of the specimen was measured by a potentiometer using a copper-constantan thermocouple directly attached to one of the electrodes.

As shown in Fig. 3, the permittivity below the Curie point is scarcely influenced by the dc field except that it does increase slightly just below the Curie point. On the other hand, a decrease of permittivity is observed above the Curie point. At room temperature, the permittivity is strictly invariant even up to a biasing field of 20 kv/cm. In addition, the Curie point is shifted towards lower temperature by 1.5(±0.2)°C under this biasing field, and at the same time the peak value of the permittivity increases slightly. These results are just opposite to the case of barium titanate,[7] in which a rise of the Curie temperature and a considerable decrease of permittivity even below the Curie point were observed under a biasing field.

Figure 4 shows the transition temperature of $PbZrO_3$ as a function of biasing dc field for both rising and falling temperatures. It decreases with increasing dc field and begins to show a tendency of saturation at about 20 kv/cm. Such an effect should be rather difficult to understand if this crystal belongs to a ferroelectric, because the dc field must surely compel every dipole moment to be in one direction, so that a certain amount of rise in the Curie temperature may be expected, as is actually observed in $BaTiO_3$.

IV. HYSTERESIS LOOPS

A. Hysteresis Loops at an ac Amplitude of 20 kv/cm

A circuit essentially similar to that of Sawyer and Tower[8] was used to display the polarization-electric

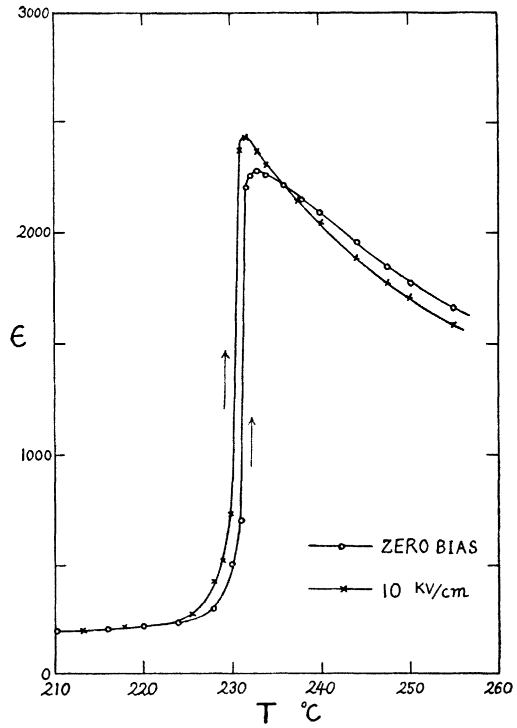

FIG. 3. Effect of a biasing dc field of 10 kv/cm on the permittivity (at 1 Mc/sec) of $PbZrO_3$ at rising temperatures.

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[7] S. Roberts, Phys. Rev. **71**, 890 (1947). Cross, Dennison, Nicolson, and Widdington, Nature **163**, 635 (1949).

[8] C. Sawyer and C. Tower, Phys. Rev. **35**, 269 (1930).

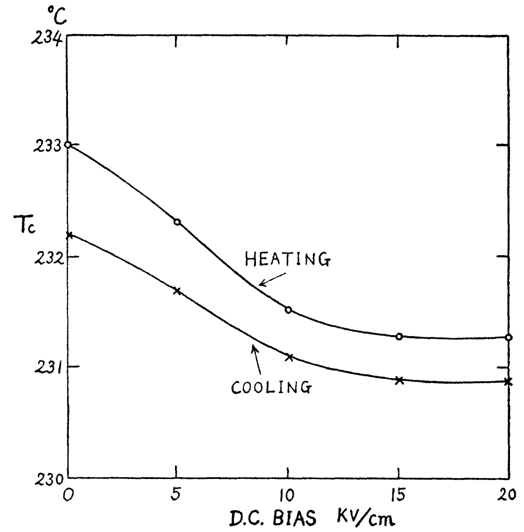
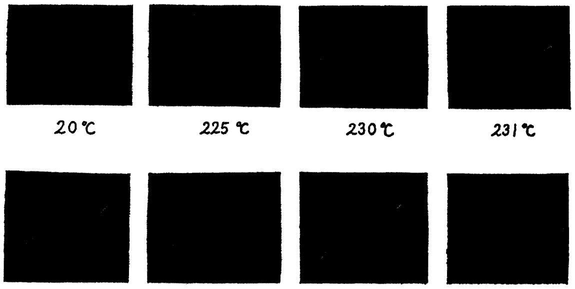


FIG. 4. Curie temperature of $PbZrO_3$ at rising and falling temperatures as a function of biasing dc field.

field curve on a cathode-ray tube. Figure 5 shows a series of results obtained by the ac field of 20 kv/cm and 50 cycles sec at various increasing temperatures. Ordinary hysteresis loops have not been observed; the curves are always almost linear, except that a slight upward curvature is noticeable just below the Curie point. The situation is also quite similar in the case of falling temperature. These characteristics of the D–E relation are of course consistent with the results of the preceding section.

The maximum polarization at this field strength can be estimated on oscillographs as a function of temperature (Fig. 6); in marked contrast with the case of barium titanate,[9] a sudden increase of polarization was observed at the Curie point. The resemblance of Fig. 6 to Fig. 2 is very impressive. In fact, if $P_{\max}$ is reduced to $4\pi P_{\max}/E$ (Fig. 7), that is, to the average dielectric constant for field strength E, the reduced value turns out over the whole temperature range to be approximately equal to the true dielectric constant. Corresponding to a small anomaly at 225°C on the cooling curve of permittivity, a small anomaly of the same nature was also observed in this figure, but no essential change of hysteresis characteristics was found around this point.


20°C 225°C 230°C 231°C

231.5°C 232°C 233°C 245°C

FIG. 5. Hysteresis loops of $PbZrO_3$ at rising temperatures. $E_{\max}=20$ kv/cm.

This sudden change of polarization at the Curie point seems to suggest the absence of spontaneous polarization below the Curie point. If this crystal had any spontaneous polarization at all, such a phenomenon could possibly be interpreted only if the coercive field of this crystal would remain extraordinary large even until just below the Curie point. It seems unlikely that this would happen. Now, if we assume that this substance is an antiferroelectric, then this increase of polarization at the Curie point may at once be interpreted; it is a mere consequence of an abrupt increase of permittivity at this point. In fact the jump of $4\pi P_{\max}/E$ is about 2500, being of the same order of magnitude as the jump of permittivity which is estimated to be 2000.

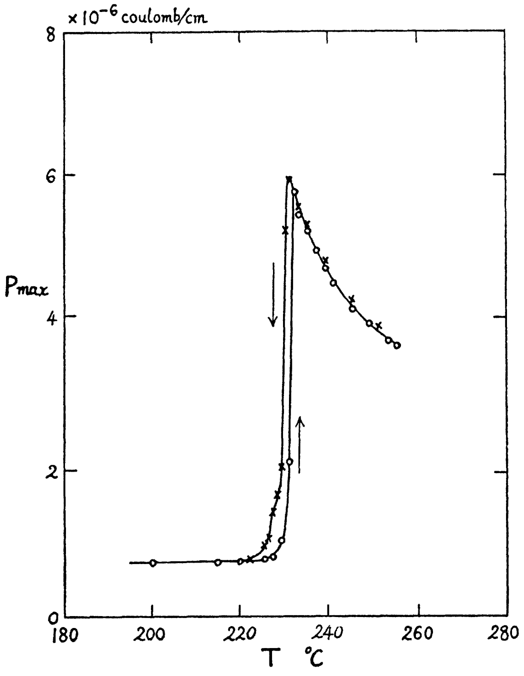


FIG. 6. Maximum polarization as a function of varying temperature at $E_{\max}=20$ kv/cm.

Considering the dielectric, dilatometric, and calorimetric data, it seems certain that the transition in $PbZrO_3$ is of the first order; hence we can apply the Clausius-Clapeyron equation. It can be written, in the general case,

$$\frac{dT_c}{dE}=-\frac{T_c}{L}\left(\Delta P_s+\frac{\Delta\epsilon\cdot E}{4\pi}\right),$$

where E denotes the applied dc field, L the latent heat, ΔP_s the jump of spontaneous polarization if it exists, and $\Delta\epsilon$ the jump of permittivity. In the absence of ΔP_s,

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[9] J. K. Hulm, Nature **160**, 127 (1947).

this equation can be written in the integrated form:

$$\Delta T_c = -(T_c/L)(\Delta\epsilon \cdot E^2/8\pi).$$

Upon inserting the observed values of $\Delta\epsilon = 2000$, $T_c = 506°\text{K}$ and $L = 300$ cal/mole, we get $\Delta T_c = -0.16°\text{C}$ for $E = 10$ kv/cm and $\Delta T_c = -0.62°\text{C}$ for $E = 20$ kv/cm. Although these values are smaller than the observed ones, at least the direction of the change is right.

B. Hysteresis Loops at an ac Amplitude of 30 kv/cm

Figure 8 shows the results of $E_{\max} = 30$ kv/cm as a function of rising temperature. As seen in this figure, anomalous hysteresis loops were observed near the Curie point, namely, at temperatures from 227° to 233°C. The temperature range becomes narrower with decreasing ac amplitude and completely disappears at a field strength of 23 kv/cm. Outside this anomalous range, D-E characteristics are almost strictly linear.

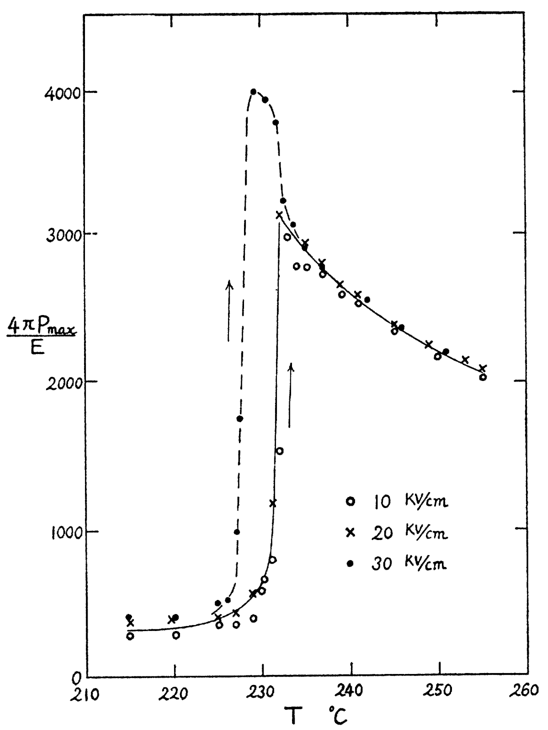

FIG. 7. $4\pi P_{\max}/E$ of $PbZrO_3$ for 10 kv/cm, 20 kv/cm, and 30 kv/cm as a function of rising temperature.

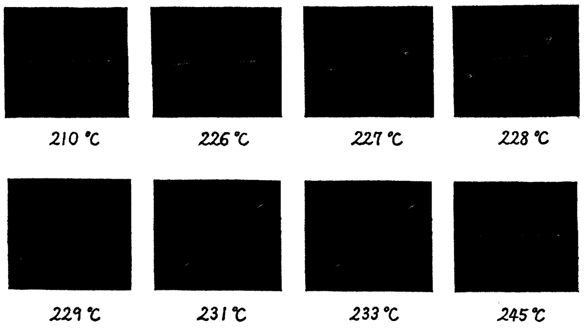

FIG. 8. Hysteresis loops of $PbZrO_3$ at rising temperatures. $E_{\max} = 30$ kv/cm.

We have estimated the maximum polarization at 30 kv/cm and plotted the reduced values of $4\pi P_{\max}/E$ in Fig. 7, in which for comparison the results for 20 kv/cm and 10 kv/cm are also plotted. The broken line in the figure corresponds to the region in which strange hysteresis loops, and accordingly an anomalous increase of polarization, are observed. The good agreement of these three curves with each other may be considered to be proof of the good linearity of the D-E characteristics over a sufficiently large amplitude of the ac field.

A careful study of Fig. 8 reveals that the anomalous hysteresis loops show a tendency toward saturation, as in the case of the normal hysteresis loops of barium titanate, suggesting that this substance shows ferroelectric characteristics if it is subject to this high field strength. Taking account of our assumption that $PbZrO_3$ may be antiferroelectric below its Curie point, we can at once arrive at a reasonable interpretation as schematically shown in Fig. 9. When the external field increases beyond a critical field E_c, the ferroelectric state may become more stable than the antiferroelectric one; hence typical hysteresis loops may be seen only above E_c. Such a situation should be realized if the free energy curves for this substance have characteristics as shown in Fig. 10. By the application of the external field it is certain that the free energy of the ferroelectric state, if compared with those of the antiferroelectric and paraelectric ones, must be lowered considerably.

This critical field E_c depends sensitively on the temperature and also on the amounts and species of the impurities contained in the specimen, though the reason is yet unknown. This field seems to be higher when the specimen is of higher purity. With increasing amounts of impurity or of Ti concentration in the $Pb(Zr-Ti)O_3$ series, E_c decreases until at last it becomes negative and a stable ferroelectric region appears between the para-

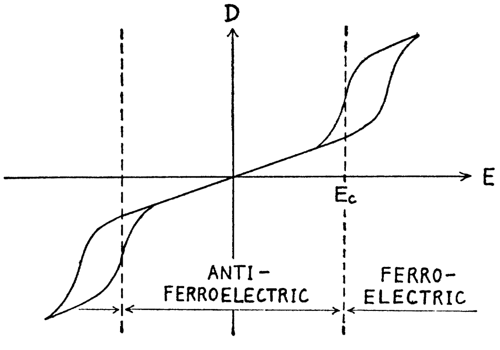

FIG. 9. Tentative explanation of the anomalous hysteresis loops of $PbZrO_3$ at 30 kv/cm.

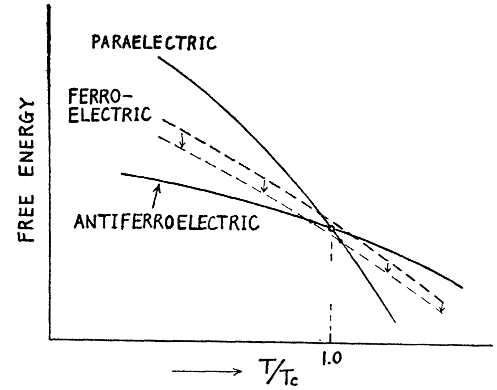

FIG. 10. Schematic curves for the free energies of the three phases of $PbZrO_3$. The free energy of the ferroelectric phase should be lowered by an electric field, as shown in this figure.

electric and antiferroelectric ones (Fig. 1). For the present specimen, E_c starts from about 23 kv/cm at 233°C and reaches about 30 kv/cm at 226°C. As already shown in Fig. 4 the Curie temperature *versus* the biasing dc field curve shows a saturation tendency at about 20 kv/cm. This effect will be understood if we take into account the fact that a ferroelectric state is forced to be realized under the very high field.

In the course of our observations we found an interesting phenomenon. If a specimen is heated or cooled several times through the Curie point, being always subject to a high ac field beyond E_c, it gradually shows large hysteresis loops of elliptic form at the vicinity of the Curie point; the loops may presumably be due to some increase in conductivity. At the same time, the specimen becomes more and more fragile, and is eventually reduced to a powder. Nevertheless, a Debye photograph of this specimen shows completely the same reflection patterns as those of the initial one.

This effect is probably due to the fact that the stresses produced in polycrystalline ceramics by the high field strength, which enforces alignment of the dipoles in one direction, are large enough to cause internal cracks. Such an effect has never been observed so long as the specimen is kept under a field not stronger than 23 kv/cm.

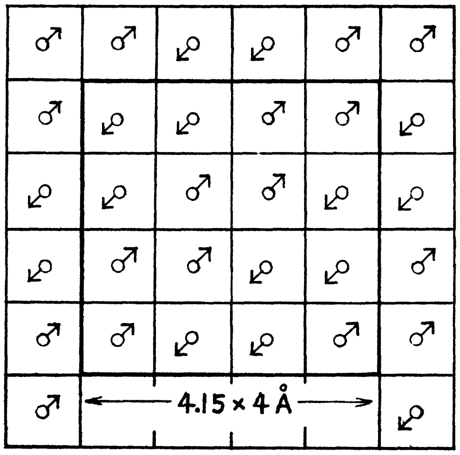

FIG. 11. A model of the atomic arrangement of $PbZrO_3$, (001) plane. Although the true symmetry may be orthorhombic, we choose here tetragonal axes. An arrow shows the displacement of a heavy ion (probably a Pb ion).

V. DISCUSSION

The close resemblance of the dielectric constant curves of $PbZrO_3$ and $BaTiO_3$ is insufficient by itself to secure the ferroelectricity of $PbZrO_3$. Rather, all the experimental facts described above seem to support unanimously our present assumption of the antiferroelectricity of $PbZrO_3$.

Further, the following pyroelectric test has been carried out. At first, under the application of a dc field of 10 kv/cm, the specimen was slowly cooled from 250° to 200°C, passing through the Curie point at 233°C. Then the electrodes were connected to a galvanometer circuit. After an initial discharging current had disappeared, we raised the temperature up to 250°C, but no more discharging current was observed around the Curie point.

On the contrary, whenever we gave a similar field treatment to a ceramic plate of $BaTiO_3$, a great deal of discharging current was observed around its Curie point.[10] Moreover, it was observed that, if we heated a barium titanate ceramic without any field treatment, a current (although very weak) flows at its Curie point. This may perhaps be due to some imperfection in the isotropic distribution of the polarized domains. Hence the above discrepancies between the two materials may be regarded as further evidence for the absence of net polarization in $PbZrO_3$.

According to Megaw,[11] the crystal structure of $PbZrO_3$ is a tetragonal modification of perovskite type with $a=4.150$A and $c/a=0.988$. This tetragonality is just opposite in sign to that of $BaTiO_3$. In addition, the Debye photograph of $PbZrO_3$ shows some extra lines[11, 12] besides the ordinary tetragonal ones, and these extra lines completely disappear in the cubic region above the Curie point.[13] Attention must be paid to these extra lines, because an existence of superstructure is at least a necessary condition for antiferroelectricity.

We have synthesized minute single crystals and have examined several specimens of flake-like form under a polarization microscope. It turned out that single domain crystals show symmetry extinction and are biaxial crystals; that is to say, they do not have tetragonal symmetry but have an orthorhombic one, although the deviation from the tetragonal structure is very small. X-ray patterns[14] of this single crystal clearly show

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[10] E. Sawaguchi and T. Akioka, J. Phys. Soc. Japan **4**, 117 (1949).

[11] H. D. Megaw, Proc. Phys. Soc. (London) **58**, 113 (1946).

[12] A. Hoffmann, Z. physik. Chem. **B28**, 65 (1935).

[13] R. Ueda and G. Shirane, J. Phys. Soc. Japan **6** 209 (1951).

[14] Sawaguchi, Maniwa, and Hoshino, presented at the meeting of the Phys. Soc. Japan on April 1, 1951, held at T.I.T. Tokyo, Japan.

the existence of a superstructure having a unit cell of $4a \times 4a \times c$. Our analysis, which is near completion, seems at present to give the atomic arrangement shown schematically in Fig. 11, in which an antiparallel set of dipolar orientations due to opposite shifts of heavy ions (probably Pb ions) may be noted. Details of the x-ray analysis will be published in the near future.

In conclusion, we wish to express our sincere thanks to Dr. S. Roberts for his many helpful comments on our work.

Note added in proof.—Recently, C. Kittel [Phys. Rev. **82**, 729 (1951)] discussed the possibility of realization of antiferroelectricity, showed that antiferroelectric crystals may be expected to occur in nature, and gave some criteria for identifying them. Very recently, S. Roberts [Phys. Rev. **83**, 1078 (1951)] has observed a very small but definite piezoelectric effect in polarized $PbZrO_3$ ceramic, in contrast to the negative result of our pyroelectric test. But the observed effect is very small, being approximately one-thousandth that of $BaTiO_3$, and this suggests that the spontaneous polarization of this crystal may also be so small that its detection by a pyroelectric test is beyond the limit of our apparatus. Our experiments have shown that the spontaneous polarization of $PbZrO_3$ may be, if it exists, far less than one-hundredth that of $BaTiO_3$. So it must be concluded, in reference to the recent result of x-ray analysis of $PbZrO_3$ single crystal by Sawaguchi, Maniwa, and Hoshino [Phys. Rev. **83**, 1078 (1951)], that $PbZrO_3$ is strongly antiferroelectric in the direction perpendicular to the *c*-axis and very weakly ferroelectric in the *c*-direction.

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Bombardment of Copper with Tritons

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Tritons have been accelerated to 6.5 Mev in a cyclotron and made to bombard stacks of copper foils. Among the triton induced reactions, the following have been identified: $Cu^{63}(t,d)Cu^{64}$ (12.9 hours), $Cu^{63}(t,n)$-Zn^{65} (250 days), $Cu^{65}(t,He^3)Ni^{65}$ (2.6 hours), and $Cu^{65}(t,p)Cu^{67}$ (2.44 days) with relative cross sections for the various reactions as 11:64:6:10, respectively. The Oppenheimer-Phillips process appears to be operative in case of tritons of this order of energy.

I. INTRODUCTION

TRITONS have already been used as bombarding particles for effecting nuclear reactions. In the earlier experiments,[1] the tritons had been produced by some suitable primary reaction, like $Be+d$, and the tritons thus obtained were then made to bombard various target nuclei. The maximum energy of the tritons was about 10.5 Mev. Later workers[2–5] used low-energy tritons and obtained reactions on tritium and lithium.

In the present investigations, tritium gas obtained in small amounts through the courtesy of the Isotopes Division of the Oak Ridge National Laboratory have been accelerated to 6.5 Mev in the cyclotron.[6] Various triton reactions with copper have been made. Relative cross sections and certain other reaction characteristics have been studied.

II. EXPERIMENTAL

A few cubic centimeters of tritium gas were sealed in glass capsules which were contained in a special housing connected to the cyclotron vacuum chamber through suitable capillary tubes and stop cocks. Arrangements were made so that from the outside the seal of a capsule could be crushed open and the gas fed between the dees in controlled amounts. The ion source was a single tungsten filament at the center of the vacuum chamber with the accelerating plates placed above and below the dee surfaces. The frequency of the oscillator was reduced from its normal 10.4 to 6.7 megacycles by the use of a bank of vacuum condensers placed in parallel both with the dee and the grid lines. The maximum current rating of the magnet could then be utilized. The natural leakage of the vacuum system was reduced to a practical minimum of 2 to 3 cc per hour. The gas from the exhaust of the backing pump was reinjected in controlled amounts through a closed recirculation system. The gaseous impurities introduced into the vacuum system through natural leakage consisted of nitrogen and oxygen. A stage of purification was incorporated in the circulation system so that the tritium could be freed from these gases, if and when necessary, with the use of a liquid hydrogen trap.

A stack of copper foils each 0.001 inch thick was mounted in a special target holder. The stack was thus shielded on all sides except for a small slot through which the triton beam bombarded the foils. The bombardment was continued, through the recirculation system, for two hours. The activities produced in

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[1] D. N. Kundu and M. L. Pool, Phys. Rev. **72**, 101 (1947); **73**, 22 (1948).

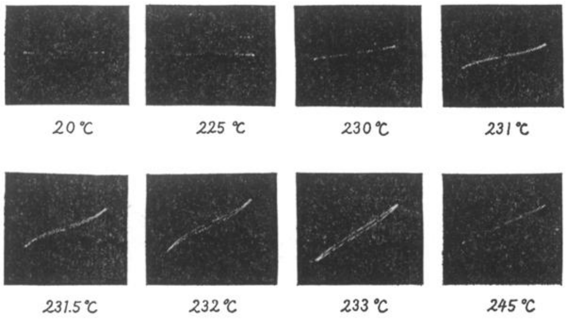
[2] Sanders, Allen, Almquist, Dewan, and Pepper, Phys. Rev. **79**, 238 (1950).

[3] Los Alamos Group, Phys. Rev. **79**, 238 (1950).

[4] Allen, Almquist, Dewan, and Pepper, Phys. Rev. **81**, 315 (1951).

[5] E. Almquist, Can. J. Research **28A**, 433 (1950).

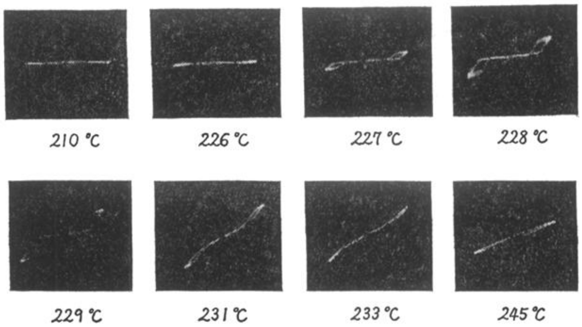
[6] Pool, Kundu, Weiler, and Donaven, **82**, 305 (1951).



20 °C 225 °C 230 °C 231 °C

231.5 °C 232 °C 233 °C 245 °C

FIG. 5. Hysteresis loops of $PbZrO_3$ at rising temperatures. $E_{\text{max}} = 20$ kv/cm.



210 °C 226 °C 227 °C 228 °C

229 °C 231 °C 233 °C 245 °C

FIG. 8. Hysteresis loops of $PbZrO_3$ at rising temperatures. $E_{max}=30$ kv/cm.