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Adiabatic Thermal Changes in Barium Titanate Ceramic at Low Temperatures*

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The adiabatic thermal changes at 4°K in barium titanate ceramic show a heating effect whether the the electric field is applied or removed. An interpretation of these results is that the polarization process is thermodynamically irreversible. The large temperature dependence of the dielectric constant at 4°K may be understood as a result of the thermodynamically irreversible polarization. Quantitative results are given as to the temperature rise as a function of electric field strength and as a function of temperature.

INTRODUCTION

BARIUM titanate in ceramic form has a dielectric constant of about one hundred at a temperature of 4°K and within the liquid helium temperature range the dielectric constant exhibits a large temperature dependence.[1,2] This temperature dependence suggests that one might be able to detect sizeable temperature changes in the material if its state of polarization were changed adiabatically, and in the experiment reported here such temperature changes are measured. By these measurements one can distinguish between thermodynamically reversible and irreversible polarization mechanisms. With reversible mechanisms, an increase in field strength will cause a temperature change opposite in sign to that caused by a decrease in field strength. With irreversible polarization mechanisms, however, any change in field strength causes an increase in entropy which manifests itself in adiabatic processes as an increase in temperature. The results presented in this paper point to irreversible processes as predominating in $BaTiO_3$ ceramic at low temperatures because all of the temperature changes represent heating. An interpretation of the large temperature dependence of the dielectric constant that is consistent with these results and also with those of Merz[3] is also given.

EXPERIMENTAL APPARATUS AND TECHNIQUE

To measure the adiabatic thermal changes in a dielectric at low temperatures one must be able to (1) cool the specimen to liquid helium temperatures, (2) thermally isolate it from the surroundings, (3) apply or remove high voltages, and (4) measure the resulting temperature changes. The cryostat used to accomplish these steps is shown in Fig. 1. Around the liquid helium Dewar, 0, is another Dewar flask, not shown, which contains liquid nitrogen. Temperatures below 4.2°K are attained by pumping on the liquid helium bath through the tube, M, and are measured by measuring the pressure above the bath with a mercury manometer (not shown). A constant bath temperature is maintained by the familiar technique of regulating the pumping speed and monitoring through use of a differential oil manometer.

The specimens are ceramic disks of $BaTiO_3$ 3.28 cm in diameter and 0.221 cm thick, kindly furnished by the Bell Telephone Laboratories. On one side of the specimen a circular disk of silver paste (No. 50, Hanovia Chemical Company) 2.54 cm in diameter is painted and fired. A flat silver strip to serve as a lead is attached to this condenser plate with additional silver paste. The opposite face of the specimen also has a condenser plate made with silver paste, but it has two areas separated by 2 mm. This side of the specimen is shown in Fig. 2. Each of the silver areas shown in the figure has a silver strip attached to it and to each silver strip is soldered a No. 40 copper wire lead. The carbon thermometer is made by painting a colloidal suspension of carbon in an alcoholic base (Dag Dispersion No. 154, Acheson Colloids Corporation) on the specimen to cover the 2-mm gap between the two silver patches. Upon drying, the colloidal suspension leaves a thin, hard layer of carbon that is in good thermal contact with the specimen and which, in addition to serving as the thermometer, serves

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[1] B. Wul, J. Phys. U.S.S.R. **10**, 64 (1946).
[2] R. F. Blunt and W. F. Love, Phys. Rev. **76**, 1202 (1949).
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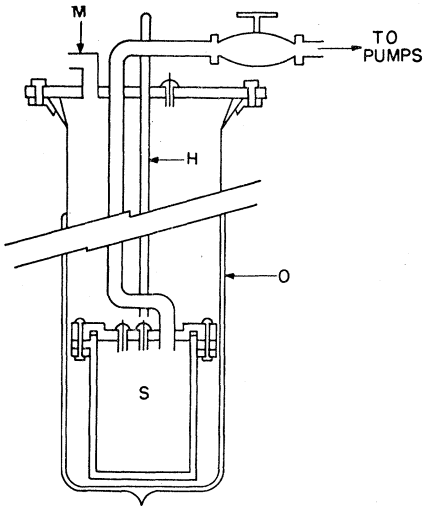

FIG. 1. The cryostat used for adiabatic application of electric field.

also to complete the condenser plate on the one face of the specimen.

The specimen is hung in the vacuum space, S of Fig. 1, into which exchange gas is introduced to establish good thermal contact between the specimen and the bath. The carbon thermometer is calibrated against the bath temperature with this exchange gas surrounding it. The specimen can then be partially isolated from the bath by pumping the gas out of S; however, the electrical leads still constitute a sizeable heat leak between the bath and specimen.

The value of the carbon resistance is measured with an ordinary Wheatstone bridge. A compensating resistance is placed in series with the unknown in order that all arms of the bridge always contain the same amount of resistance. In this way the current through the carbon thermometer is maintained approximately constant at 0.2 milliampere and gives only a small heat dissipation. A diagram of the bridge and high voltage circuits is shown in Fig. 3. The two circuits have one point in common and that is the point, A, (Figs. 2 and 3). From this point a No. 40 copper wire is taken to the

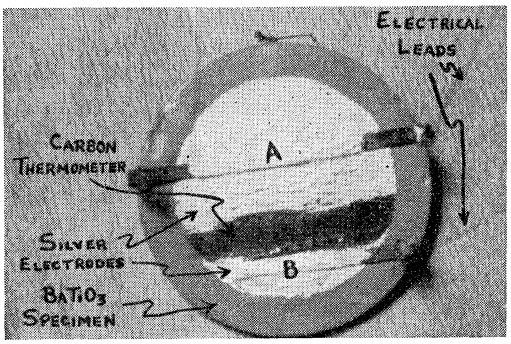

FIG. 2. The specimen of ceramic barium titanate showing electrodes and carbon thermometer.

wall of the vacuum jacket and soldered, thus allowing the pumping line and metallic frame of the apparatus to be used as the grounded lead of the high voltage circuit. Because of this, the two carbon thermometer leads emanating from A and B must everywhere be isolated electrically from the frame in order to prevent thermal emf's from being set up in the bridge circuit. These two leads are, therefore, taken out of the vacuum jacket through two Kovar seals, through the helium bath and then through two more Kovar seals in the top plate of the cryostat. The switch S_2 may be used to check that no thermal emf's are present and S_3 to obtain the zero position of the galvanometer.

The high voltage lead, C, is also taken out of the vacuum jacket through a Kovar seal and then into a glass tube, H of Fig. 1, which extends through the top plate of the cryostat. The glass tube is to prevent arcing in the helium gas above the liquid bath, particularly at pressures below atmospheric. The switch, S_1, is used to apply or remove voltage from the specimen. During either of these processes the charges that flow onto or off of the condenser plate, AB, can flow through both

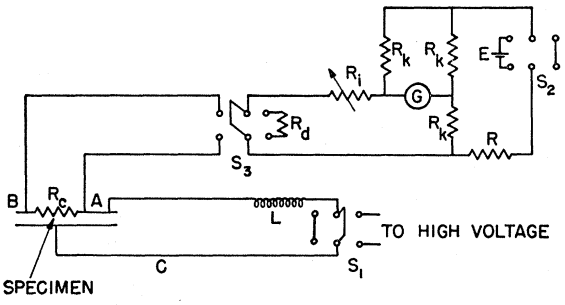

FIG. 3. The schematic of the electric circuit used in these experiments.

R_c and other parts of the bridge circuit, causing the galvanometer to suffer spurious deflections. The inductance, L, of ten henries is inserted in the charging circuit to minimize these. The spurious deflections can be measured by removing the battery from the bridge circuit with S_2 and noting the galvanometer deflections that occur when the specimen is charged or discharged. For the smallest temperature change observed these deflections were less than 10 percent of the deflections caused by thermometer changes.

After the exchange gas is pumped out of the vacuum jacket and equilibrium between the heat leaks and the power dissipated in the carbon resistor established, the bridge is set near balance and voltages applied to and removed from the specimen. During these processes the galvanometer deflection is followed as a function of time without changing the bridge settings. Thus the bridge is usually slightly off balance but the deviation from balance is never more than 0.1 percent.

The change in voltage across the specimen and hence the change in temperature of the specimen take place very rapidly compared to the rate at which heat leaks

out of the specimen into the bath. Furthermore, the time constant of response of the bridge galvanometer is made long compared to either of these processes. Therefore, to compute the initial temperature change, $(\Delta T)_0$, it is a sufficiently good approximation to assume that the temperature changes instantaneously upon application or removal of the voltage and then decays according to the law $\Delta T=(\Delta T)_0 e^{-wt}$. The deflection of the bridge galvanometer is governed by the equation

$$(dx/dt)+\beta x=\beta GA(\Delta T)_0 e^{-wt} \text{ for } t>0,$$

where $\gamma=1/\beta$ is the time constant of the bridge circuit, G is its sensitivity to changes of resistance in mm deflection per ohm change, A is the sensitivity of the carbon thermometer in ohms per millidegree temperature change, and x is the galvanometer deflection from its initial value. Since β, G, and A are measured directly,

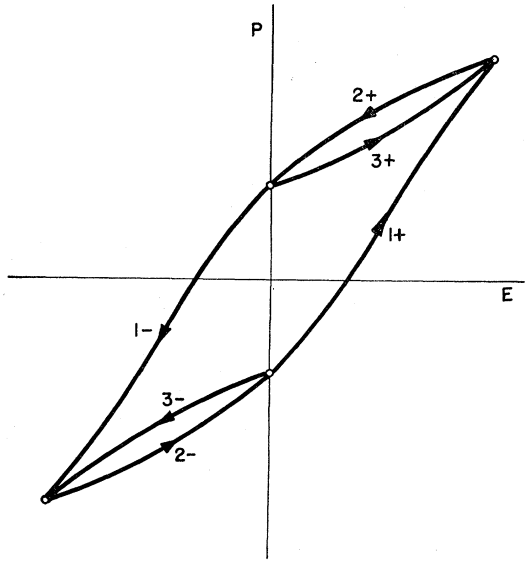

FIG. 4. Polarization processes for which the temperature rise is given in Table I.

it is necessary to measure only the peak value of the galvanometer deflection and the time at which it occurs in order to calculate w and $(\Delta T)_0$.

In the present experiment the major error in computing $(\Delta T)_0$ arises from the error in measuring the time at which the maximum deflection occurs. This error can be greatly reduced by a moderate reduction in the heat leaks. However, in view of the results obtained on barium titanate ceramic it is unlikely that more precise measurements would yield significant information not obtained from the present measurements. Hence no refinement of the measurements on this material is contemplated.

In view of the fact that barium titanate is ferroelectric the application and removal of voltages is always done in a definite sequence so as to be certain of the portion of the hysteresis loop over which the change is taking place. The various paths traversed in the measurements are shown in Fig. 4, where the small circles indicate the end states of a particular process and the arrows designate the direction in which the change takes place. The various processes are numbered for convenience in referring to them in Table I.

TABLE I. Adiabatic thermal changes in $BaTiO_3$.

ΔE volts/cm	ΔT in millidegrees 2.75°K	4.3°K	Process (see Fig. 4)
4520	+55±13	+22±6	1+
	51±13	19±6	1−
	44±12	19±6	2+
	46±14	23±6	2−
	41±13	15±5	3+
		14±5	3−
6790	+178±28	+67±13	1+
	187±35	66±13	1−
	123±28	45±10	2+
	121±27	49±12	2−
	88±20	35±12	3+
	94±20	35±12	3−
9040	+638±100	+266±58	1+
	235±45	110±25	2+
	207±37		3+

EXPERIMENTAL RESULTS

Measurements of the adiabatic thermal changes in barium titanate ceramic have been made at temperatures of 2.75°K and 4.3°K. The results are shown by Table I in which the first column gives the applied electric field, the second and third columns give the rise in temperature in millidegrees for the specimen at 2.75°K and 4.3°K respectively, and the fourth column gives the path designation for the state of polarization described by Fig. 4.

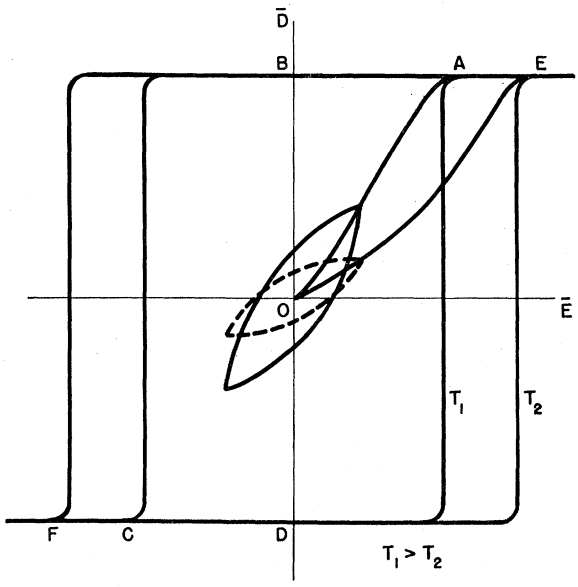

FIG. 5. The effect of temperature on the polarization of ceramic barium titanate.

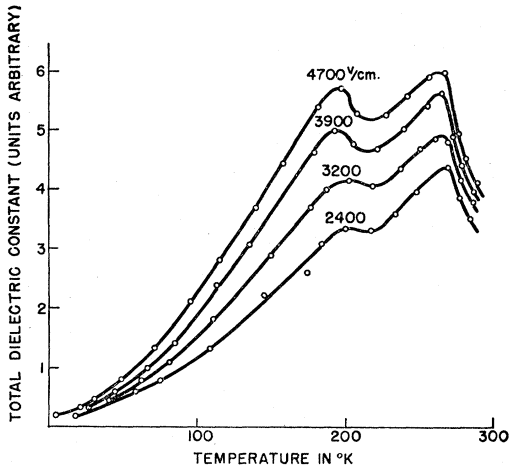

FIG. 6. Relative change of the total dielectric constant of ceramic barium titanate with temperature and with applied electric field.

The ratio of the ΔT at 2.75°K to that for the corresponding proces at 4.3°K is always close to $(4.3/2.75)^2$. If the heating per unit volume remained constant one would expect the ΔT-ratio to be close to the cube of the temperature ratio provided the specific heat decreases as T^3. The heating per unit volume, therefore, seems to decrease with decreasing temperature.

DISCUSSION

The results given in Table I suggest that the mechanisms which give rise to the macroscopic polarization when an electric field is applied to $BaTiO_3$ ceramic at low temperatures are almost entirely thermodynamically irreversible ones. The way that these can lead to a large temperature variation of dielectric constant is shown in Fig. 5, where the loops *ABCD* and *EBFD* represent hysteresis loops for an ideal single domain crystal at temperatures T_1 and T_2 respectively $(T_1 > T_2)$. This figure is a plot of the displacement vector, D, against the applied field, E. The virgin curves of a multidomain specimen will then be represented by the curves *OA* and *OE* in Fig. 5. If measurements are made at field strengths below saturation the hysteresis loops traced out will have their tips near points on the virgin curves. Hence for low field strengths the total dielectric constant, defined as the ratio D/E, will become smaller as the temperature decreases. This comes about not because of a change in the spontaneous polarization (thermodynamically reversible) but because an increase in coercivity makes it more difficult to change the domain structure (thermodynamically irreversible). This view is consistent with the results of Merz[3] who has shown that at low temperatures the coercivity of the material increases with decreasing temperature while the spontaneous polarization remains constant.

It should be noted that if the process described in the preceding paragraph and by Fig. 5 plays a significant part in determining the temperature variation of the dielectric constant, then one could expect this temperature variation of the total dielectric constant to increase with increasing field strengths as long as the measurements are made well below saturation. Such an effect is shown in Fig. 6, which is a plot of data taken from pictures of hysteresis loops, the pictures being obtained by a method similar to that of Mueller.[4] Below about 180°K the temperature variation of the dielectric constant is seen to be larger at higher fields.

The views described here are, of course, not contradictory to previous theoretical views[5,6] which attempt only to account for the occurrence of the ferroelectric state in $BaTiO_3$. The notion expressed here is simply that, given the ferroelectric state, the spontaneous polarization has attained essentially its saturation value at low temperatures and the temperature variation of the dielectric constant is most likely due entirely to thermodynamically irreversible domain effects. Thus, the third law of thermodynamics will not require the temperature variation of the dielectric constant to approach zero as the temperature approaches zero.

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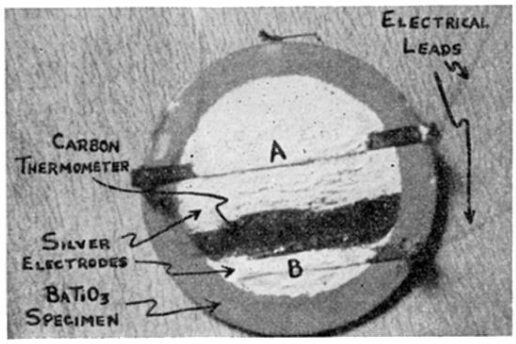

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