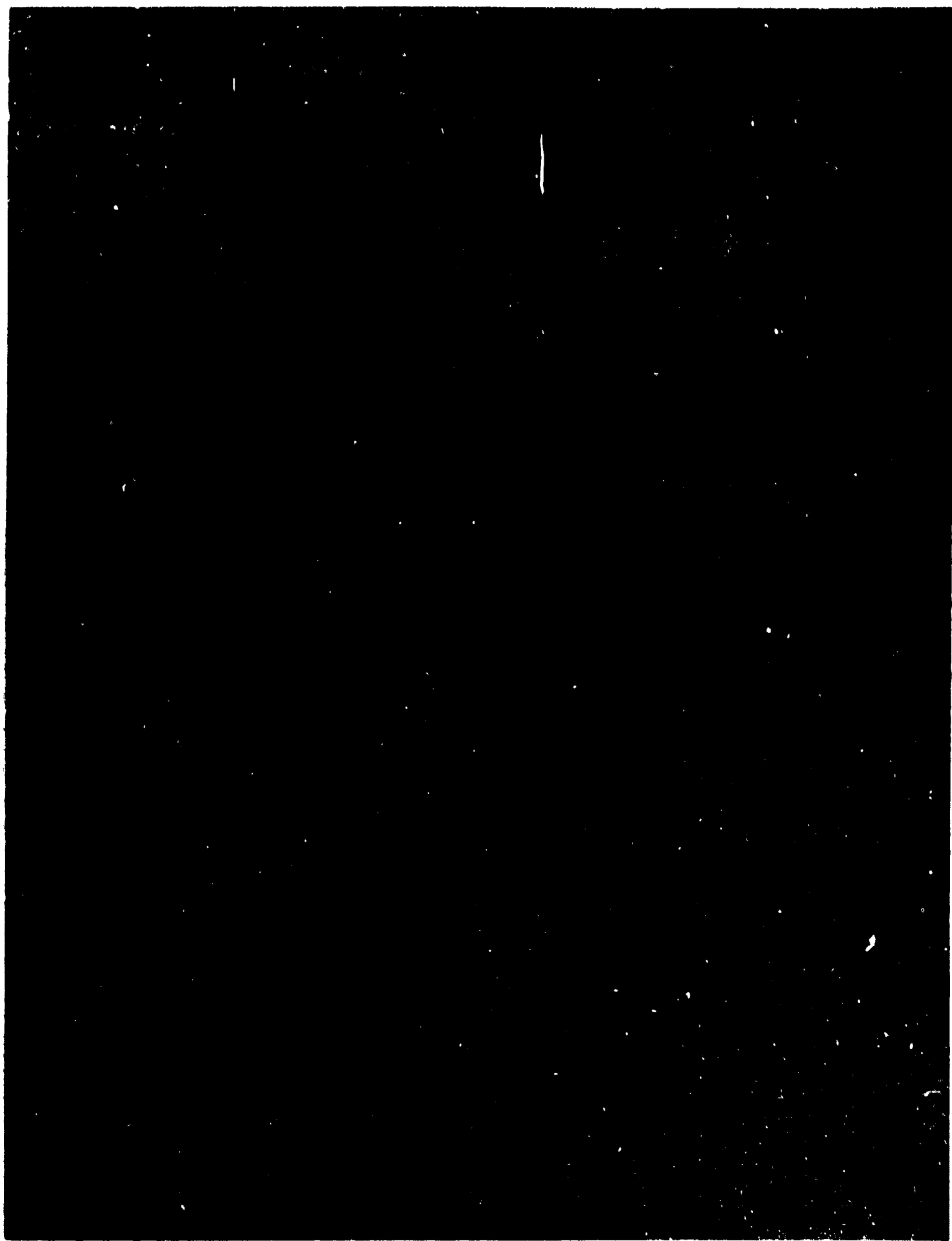


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SHOCK-INDUCED TRANSITION IN BARIUM TITANATE

by
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September 1970



U.S. ARMY MATERIEL COMMAND

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ABSTRACT

Measurements on BaTiO_3 ceramic were made of inverse dielectric constant versus uniaxial strain for values of strain ranging between -0.0043 and -0.013. The strain was produced in the region behind a shock front generated in a slab of the material by impacting it with a flying plate. The plate was accelerated in a gas gun. The slabs were disks with electrodes on the flat surfaces. The normal stress producing these strains ranged between 8.5 and 26 kbars. The dielectric constant was obtained from oscillograms of the shock-induced depolarization current through a circuit connecting the electrodes. A straight line was fitted to the curve of inverse dielectric constant versus strain. The slope of the line was -0.11 ± 0.04 . Thermodynamic theory was used to calculate this slope assuming the material was in the paraelectric phase for the range of experimental shock pressures. The calculated value was -0.13. The calculated value is in agreement with the experimental value and the assumption that the material is in the paraelectric phase for shock pressures between 8.5 and 26 kbars. The agreement implies that the transition at approximately room temperature is produced by a shock pressure less than or equal to about 8.5 kbars. This is markedly different from the experimental results for hydrostatic pressure where the transition occurs at 20 kbars at room temperature, and the material is in its paraelectric phase above 20 kbars. In both cases the temperature is approximately room temperature. The transition strain and shock pressure was calculated using thermodynamic theory and assuming that the transition could be approximated as a second order one. The result was a transition strain of -0.0044 and a transition shock pressure of 8.6 kbars. This is consistent with the preceding results and also supported by experimental findings by Doran who observed a discontinuity in sound velocity at that shock pressure.

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1. INTRODUCTION

Almost all solid materials undergo a yield under sufficiently high shock compression. This yield manifests itself as a change in slope of the shock pressure versus compression curve. The pressure at which yielding occurs is called the Hugoniot Elastic Limit (HEL), and is characteristic of the particular material. When the shock pressure is considerably above the HEL, the configuration of stress and strain can generally be assumed to approximate those produced by hydrostatic pressure (ref 1). A polymorphic solid-solid transition, which occurs at a shock pressure considerably above the HEL, can reasonably be expected also to be produced by a hydrostatic pressure equal in magnitude. This expectation has been verified in several instances (ref 2-4). Below the HEL, however, the strains behind the shock front can no longer be expected to approximate those due to hydrostatic loading. The strain now is uniaxial, involving no plastic flow and no molecular rearrangement (provided there is no transition). The stresses are now determined by the elastic stiffness coefficients and the requirement that the strain be uniaxial. In general, this means that it would be coincidental if below the HEL a phase transition produced by a certain hydrostatic pressure would also be produced by a shock pressure of the same magnitude, since the transition pressure depends on the relative free energy of the competing phases and the free energy depends on the stresses and strains.

The phase transition considered in this report is the ferroelectric-paraelectric transition in BaTiO_3 . The material is a ferroelectric with a tetragonal structure below approximately 120°C (at atmospheric pressure) and a paraelectric material with a cubic structure above 120°C . The material used in the experiments described is the polycrystalline ceramic, composed of relatively small crystals sintered together. The density is within a few percent of the crystal density. Increasing hydrostatic pressure reduces the transition temperature of both single crystal and ceramic at a rate of about 4°C per kbar. This was first observed by Merz (ref 5) and has been thoroughly investigated by Samara (ref 6). At room temperature, the ferroelectric-paraelectric transition occurs when a hydrostatic pressure of 20 kbars is applied to either the ceramic or the single crystal material (ref 6-10). The pressure at which this transition takes place and also the slope of the inverse dielectric constant versus hydrostatic pressure curve can be calculated from thermodynamic theory, and the results obtained are generally in agreement with the results of the hydrostatic measurements.

In this report, both experimental measurements and calculations are described which are analogous to those that have been made for hydrostatic pressure. This new work, however, deals with the dependence

of the ferroelectric paraelectric transition on uniaxial strain rather than hydrostatic pressure. The experimental work described consists of measurements of the inverse dielectric of the BaTiO_3 ceramic as a function of uniaxial strain. The uniaxial strains are produced by shock waves created in ceramic disks, using the impact of a flying plate to produce the shock. To produce uniaxial strain, the shock pressures are kept below the HEL of the material, which is approximately 25 kbars (ref 11,13). Temperatures behind these fronts are just slightly above room temperature (ref 12).

The inverse dielectric constant is obtained from oscillograms of shock-induced depolarization currents through an effective short circuit connecting electrodes on the ceramic disk. Thermodynamic calculations are made for the slope of the inverse dielectric constant versus strain and also of the transition pressure as a function of uniaxial strain. The experimental results are in approximate agreement with the theory. The experimental and calculated results for the shock pressure are, however, very different from those for hydrostatic pressure, and it is quite obvious that for the case of uniaxial strain, shock pressure and hydrostatic pressure, in general, are not equivalent as far as transitions are concerned.

There is a practical design reason for knowing at what shock pressure ferroelectric-paraelectric transition occurs. Barium titanate ceramics are used as piezoelectric power sources for contact fuzing. The power is developed as a depolarization current produced by an impact-created shock wave in ceramic. The ferroelectric-paraelectric transition produces complete depolarization in the ceramic. Knowledge of the shock pressure at which the transition occurs is an important asset when designing point-contact fuzes, since the shock pressure depends on the impact velocity and the impacting materials. Knowledge of this pressure, which produces full depolarization of the ceramic, is even more important than might first appear. There are experiments which indicate that for strong shocks there is marked increase in the conductivity of the ceramic element, shorting it, and thus reducing the charge released by depolarization into an external load (ref 14). The shock-transition pressure, therefore, is not only the minimum-pressure for maximum-charge release but also a pressure above which charge release may be expected to decrease. As a result maximum charge release is produced over a limited pressure range.

The next section describes and develops the thermodynamic theory relevant to this report.

2. THERMODYNAMIC THEORY

In a thermodynamic theory, the free energy is expressed as a function of independent thermodynamic variables. Devonshire (ref 15) has expressed the Helmholtz's free energy for the case of cubic symmetry in terms of strains x , polarization P , and temperature T as,

$$\begin{aligned} A(x, P, T) = & \frac{1}{2} c_{11}^P (x_x^2 + y_y^2 + z_z^2) + c_{12}^P (y_y z_z + z_z x_x + x_x y_y) \\ & + \frac{1}{2} c_{44}^P (x_x^2 + y_y^2 + z_z^2) + \frac{1}{2} \chi'' [P_x^2 + P_y^2 + P_z^2] + g_{11} [x_x P_x^2 + y_y P_y^2 + z_z P_z^2] \\ & + g_{12} [x_x (P_x^2 + P_z^2) + z_z (P_x^2 + P_y^2) + y_y (P_z^2 + P_x^2)] \\ & + g_{44} [y_z P_y P_z + z_x P_z P_x + x_y P_y P_x], \end{aligned} \quad (1)$$

plus terms of higher order in P . For a ferroelectric material, χ'' is a linear function of temperature T ; c_{11}^P , etc., are elastic stiffness constants at constant polarization; P_z , etc., are components of the polarization; z_z , etc., are strains; and g_{11} , etc., are electrostrictive constants. The BaTiO₃ ceramic considered here is macroscopically isotropic material strained by the shock pressure in the z -direction. The free energy is a special case of the free energy (eq 1). It is

$$A(x, P, T) = \frac{1}{2} \chi'' P_z^2 + \frac{1}{2} c_{11}^P z_z^2 + g_{11} z_z P_z^2. \quad (2)$$

We refer the free energy to the zero strain, zero polarization state.

The differential free energy is

$$dA = -SdT - Z_z dz_z + E_z dP_z, \quad (3)$$

S is the entropy, Z_z a stress component, and E_z an electric-field component.

Now the inverse susceptibility at constant strain is defined as

$$\chi^z \equiv \left(\frac{\partial E_z}{\partial P_z} \right)_{z_z}$$

Use of the Legendre transformation (eq 3) then gives for constant temperature stress

$$\left(\frac{\partial^2 A}{\partial P_z^2} \right)_{z_z} = \chi^z \quad (4)$$

and we see from (eq 2) that χ^z and χ'' are the same. In cgs units,

$$\chi^z = \frac{4\pi}{\epsilon - 1} \sim \frac{4\pi}{\epsilon}.$$

ϵ is the relative dielectric constant. $\epsilon - 1$ is approximately equal to ϵ , since for BaTiO_3 , $\epsilon \gg 1$. The slope of χ^z with respect to z_z is twice the ∂

$$\frac{d\chi^z}{dz_z} = \frac{d}{dz_z} \left(\frac{\partial^2 A}{\partial P_z^2} \right) = 2g_{11}. \quad (5)$$

A similar expression has been obtained for the slope of the inverse dielectric susceptibility with respect to hydrostatic pressure, p (ref 9, 16-19). In this case,

$$\frac{\partial \chi^p}{\partial p} = 2 \left(Q_{11} + 2Q_{12} \right), \quad (6)$$

where

$$\chi^p \equiv \left(\frac{\partial E_z}{\partial P_z} \right)_p$$

and Q_{11} and Q_{12} are again electrostrictive constants. This result is derived most easily from the Gibbs elastic function $G(X, P, T)$ X represents stress components.

The g -electrostrictive constants relate the stress and square of the polarization of a strain-free material. The Q -electrostrictive constants relate strain to the square of the polarization. This can be seen from equations (1) and (4). The stress component Z_z

at zero strain is,

$$z_z = -\frac{\partial A}{\partial z_z} = -[g_{11}P_z^2 + g_{12}P_y^2 + g_{12}P_x^2]. \quad (7)$$

At zero stress the strain component, z_z , is

$$z_z = \frac{\partial G}{\partial z_z} = Q_{11}P_z^2 + Q_{12}P_x^2 + Q_{12}P_y^2 \quad (8)$$

These are equations defining the electrostrictive constants. The Q-constants may be determined directly by measuring strains produced by an induced polarization. If,

$$P_y = P_x = 0,$$

then

$$Q_{11} = \frac{z_z}{P_z^2}, \quad (9)$$

$$\text{and, if } P_z = 0, P_x = P_y, \quad (10)$$

then

$$Q_{12} = \frac{z_z}{2P_x^2}.$$

The Q constants are also related to the inverse susceptibility versus pressure slope by expression (6). The Q and g constants are related by the elastic compliances. For a cubic crystal and also for isotropic material, the relations derived from the expression for the free energy are (ref 15,20)

$$Q_{11} - Q_{12} = -\left(s_{11}^P + 2s_{12}^P\right) \left(g_{11} + 2g_{12}\right)$$

and

(11)

$$Q_{11} + 2Q_{12} = -\left(s_{11}^P + 2s_{12}^P\right) \left(g_{11} + 2g_{12}\right).$$

The Q electrostrictive constants have been measured directly both for ceramic and single crystals (Ref 21, 22) using relations (9) and (10). The g_{11} constant can now be obtained from Q constants using expression (11). The g_{11} constant is related to the slope of inverse dielectric constant versus uniaxial strain by expression (5).

In summary: The slope of the inverse dielectric constant versus hydrostatic pressure and the slope of the same quantity versus uniaxial strain can be determined for a paraelectric isotropic material from the Q_{11} and Q_{12} electrostrictive constants and the s_{11} and the s_{12} elastic compliances.

It would also be useful if the actual transition strain and the actual transition shock pressure could also be predicted. For a first order transition the inverse dielectric constant reaches a minimum at the transition with the value itself discontinuous there. For a second order transition the inverse dielectric constant is again a minimum at the phase transition, vanishing completely at that point. There is, however, no discontinuity in the value as the transition pressure or strain is crossed. It is much easier to deal with the case of a second order transition. Devonshire and others have derived a relation predicting the transition pressure for the case of hydrostatic pressure, assuming that the ferroelectric-paraelectric transition could be approximated as a second order one although the transition in BaTiO_3 at atmosphere pressure is a first order one. There is fair agreement with experimental results (ref 16-18). The Devonshire relation is derived most easily from Gibbs elastic function. A similar relation for uniaxial strain can also be derived. In this case it is most convenient to use the Helmholtz free energy. At zero strain the Curie-Weiss law results from equation (2) if

$$\chi'' = \chi''_0 (T - T_C). \quad (12)$$

T_C is the Curie temperature. From equation (2), the inverse susceptibility at constant strain is

$$\chi^z = \left(\frac{\partial^2 A}{\partial P_z^2} \right)_{T, \epsilon_z} = \chi''_0 (T - T_C). \quad (13)$$

The Curie-Weiss law is usually written in terms of the dielectric constant ϵ and the Curie constant C as

$$\epsilon = \frac{C}{T - T_C}. \quad (14)$$

where

$$\epsilon = \frac{4\pi}{\chi}$$

Equation (13) is the Curie Weiss expression with χ'' defined equal to $4\pi/C$. It should be pointed out that equation (13) is valid only if terms of higher order than T^2 in equation (1) can be ignored.

From equation (2), we now obtain the expression

$$\left(\frac{1}{\epsilon''}\right)_{\omega} = \frac{1}{\epsilon'} - \chi'' = \frac{1}{C} (T - T_C) + 2\mu_{11}^2 \quad (15)$$

For a second-order transition, $\chi'' = 0$ at the transition. Therefore, at the transition,

$$T - T_C = -\frac{2\mu_{11}^2 C}{\epsilon''} \quad (16)$$

If we assume that the shift of Curie temperature with strain is linear over the range between the Curie temperature and room temperature, equation (16) becomes a relation, giving the shift of Curie temperature with strain.

3. THEORY OF MEASUREMENT

The dielectric constant of the shock-compressed region which is in a state of uniaxial strain was obtained from records of current versus time. The current is produced by the depolarizing effect of the shock wave as it propagates through the thickness of the BaTiO₃ disk. The current moves through an effective short circuit, connecting electrodes on the disk surfaces. The disk, showing electrode arrangement and current path, is shown in figure 1. The use of two concentric electrodes in a guard-ring arrangement eliminates rarefaction waves from the lateral surface. The shock front is plane and parallel to the electrode in the region between the front inner and the back electrode. The front is a discrete step, less than 0.2 mm thick in 5- and 10-mm samples. The pressure behind the shock front remains constant during the transit time of an elastic (below the HEL shock) front. This was verified, using a quartz shock gauge of the Graham type (ref 23). The initial polarization is axially directed. Figure 2 shows the cross section in detail. We assume that conditions behind the front are constant during the time the shock transits the thickness of the disk.

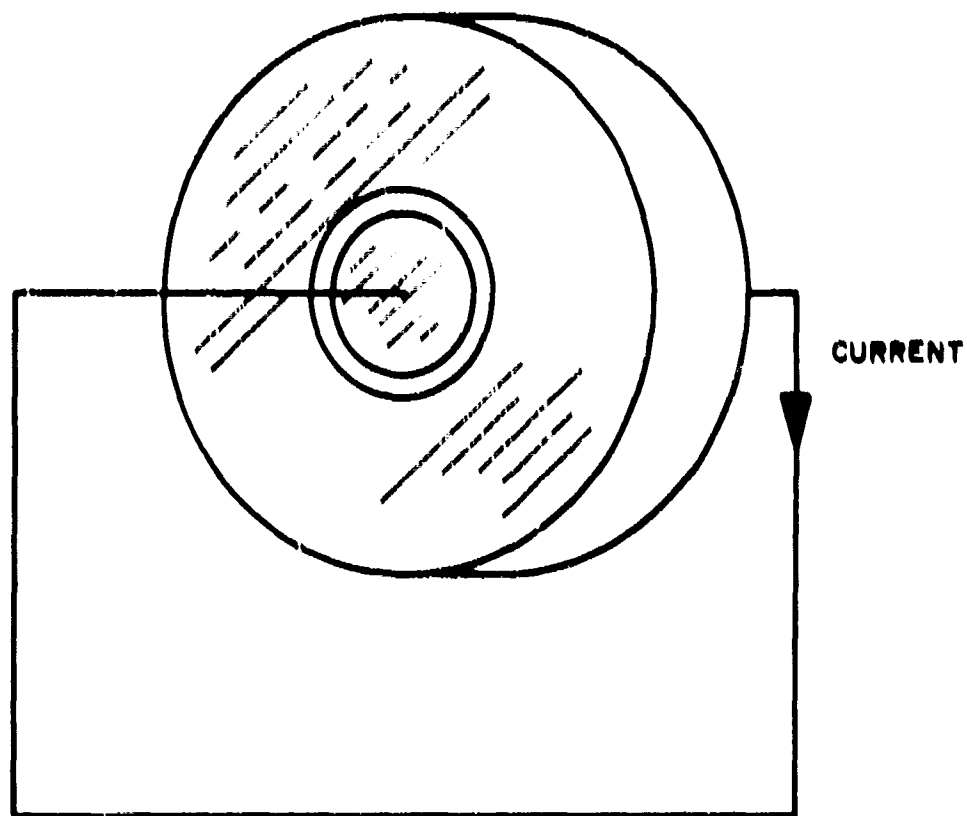


Figure 1. Barium titanate ceramic disk with electrodes. (The disks were 3.81 cm in diameter and either 0.5 or 1 cm thick).

Expressions have been derived and reported previously for the current through a short circuit or through a resistive load (ref 12, 24-26). For a single front and no dependence of the dielectric constant on the field, the current through a path shunting the electrodes is

$$i = A \frac{\delta P_s}{t_0} \frac{1 + S}{(1 + St)^2} , \quad (17)$$

where δP_s is the change in polarization produced by the shock, t_0 the transit time of the shock wave between electrodes, and t is the normalized time, which is the actual time divided by the transit time

of the shock front. A is the electrode area. $S + 1$ is the ratio of the final (shock-compressed material) to the initial (unshocked) dielectric constant. Because of the high dielectric constant of the material, susceptibility and dielectric constant are approximately equal except for a factor of 4π when cgs units are used. We now calculate the derivative, with respect to the current, of the natural logarithm of the current.

$$\frac{d}{dt} \ln I = \frac{d}{dt} [\ln A - \ln \delta P_0 - \ln t_0 + \ln(1 + S) - 2 \ln(1 + S)], \quad (18)$$

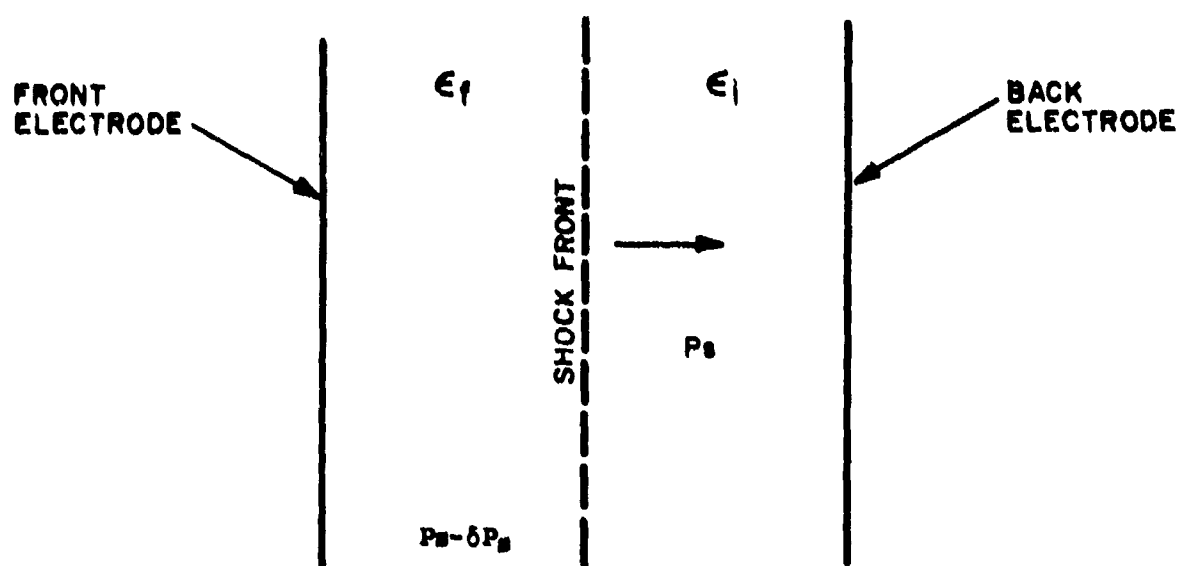


Figure 2. Cross section of disk in region of inner electrode where plane geometry is valid. ϵ_f is the dielectric constant of the shock-compressed region; ϵ_i is the initial dielectric constant of the material before it is compressed, that is the dielectric constant in front of the shock front; δP_s is the polarization removed by the shock compression.

Since all terms are independent of t except the last,

$$\frac{d}{dt} \ln i = -2 \frac{d}{dt} \ln(1 + St) = \frac{-2S}{1 + St} \quad (19)$$

The derivative just calculated can be obtained from the oscilloscope records of depolarization current versus time. Once it is known, S , and consequently the ratio of initial to final dielectric constant, is also known. The initial dielectric constant is a known value; therefore, the dielectric constant in the shock-compressed region is determined.

4. EXPERIMENTS AND RESULTS

The measurements of dielectric constant versus uniaxial strain were made on ceramic disks 95-wt percent BaTiO_3 , 5-wt percent CaTiO_3 . They were 3.81 cm in diameter and either 0.5 or 1 cm thick. The electrodes on the flat surfaces were of vapor-deposited gold. An elastic (pressure below the HEL) shock front was produced in the disk by impacting a stationary driving plate of either lead or aluminum, with a gas gun accelerated plate of plexiglas, aluminum, or a combination of plexiglas and aluminum. The disk was placed against the stationary plate. The electrodes were connected through a low resistance that was effectively a short circuit. The arrangement is shown in figure 3. Impact velocity was measured, using photocells and intercepted light beams. The disk was polarized to about 1 percent of the saturation polarization of the ceramic. This minimized the magnitude of the internal fields during the time the current pulse was produced. The internal fields that were estimated were low enough to avoid shifts in the dielectric constant due to field dependence. The results thus give essentially the zero-field dielectric constant. The current pulses were displayed on an oscilloscope and photographed; photographic records of these current pulses are shown in fig 4. The vertical direction is current. Time moves from left to right. Superimposed sine waves are calibration signals. The 5.2-kbar output shown in figure 4 was generated by the elastic precursor wave in a 1-inch-thick aluminum plate used in place of the lead plate shown in figure 3. The current pulse produced by the 5.2-kbar front is the first portion of the pulse in which the slope is positive; the remaining pulse was produced by a 60-kbar front.

The peculiar negative and positive leading spikes superimposed on the main current pulse, generally of swayback trapezoidal form, are due to the depolarization of surface regions in the ceramic (ref 14,27-29). They are thought to have a dielectric constant relatively

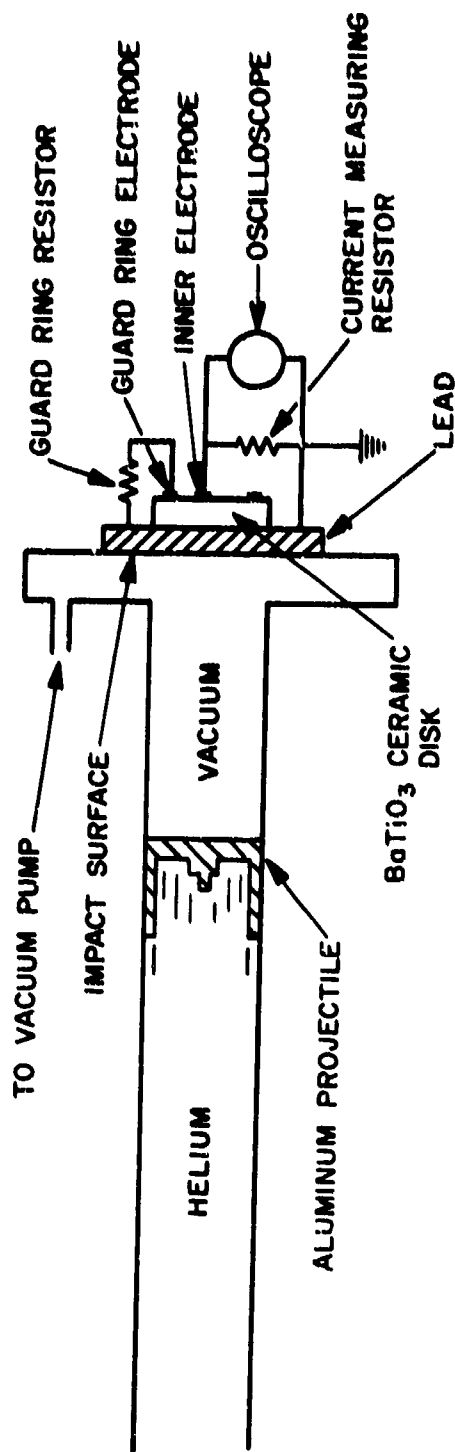


Figure 3. Experimental measurement arrangement. The tube has a 4-in. inner diameter. The projectile travels a distance of 84 ft before impacting the stationary plate. Both lead and aluminum plates were used.

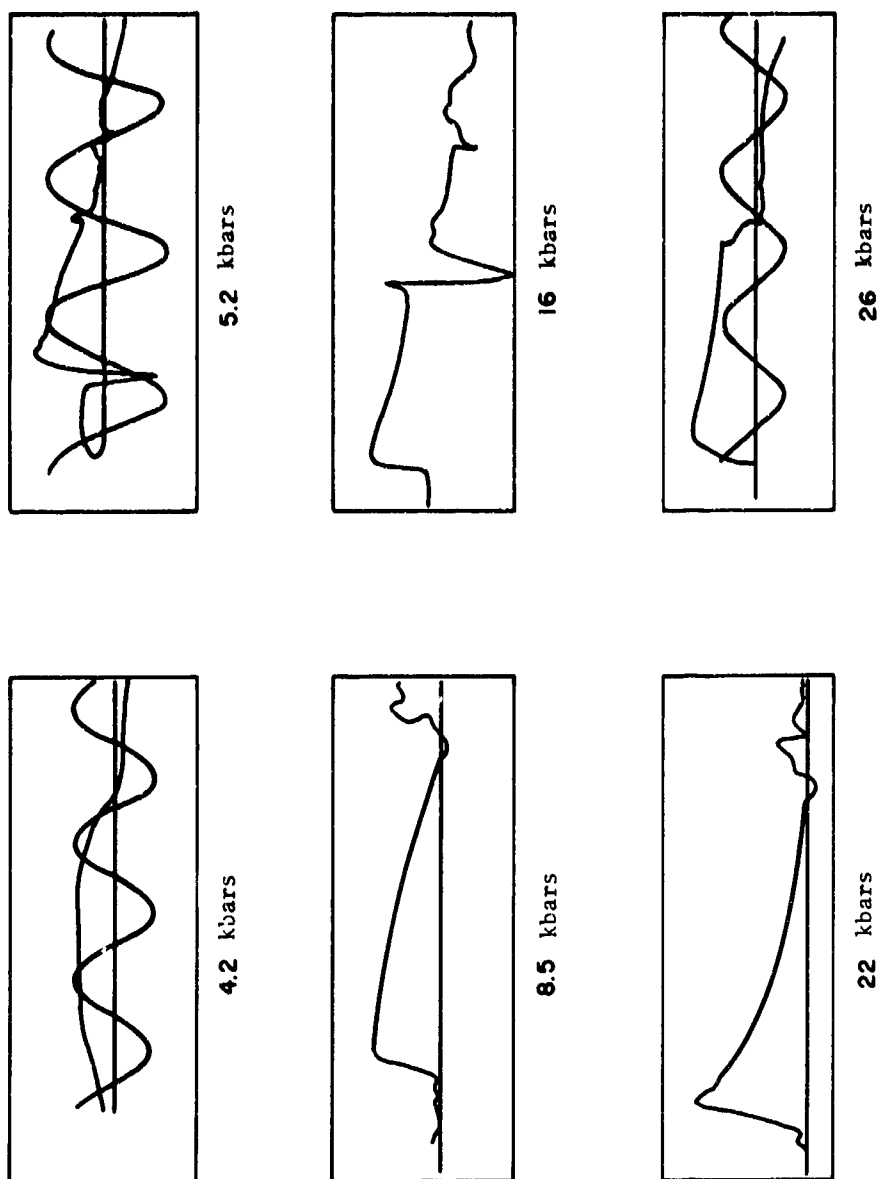


Figure 4. Current waveforms. The time scale is not the same for all records. It was 2- μ sec/cm when the samples were 1 cm thick. The negative portion of the waveforms following the main trapezoidal pulse is produced after the initial transit of the shock front. Only the initial portion of the waveform designated 5.2 kbars was produced by 5.2 kbars. The remaining portion following the negative dip was produced by a 60-kbar front following the 5.2 kbar front.

independent of the strain for the values of strain involved in the measurements and contribute little to the quantity $\frac{d}{d\tau} \ln i$, except in the immediate vicinity of the spikes themselves.

Values of uniaxial strain and shock pressure were obtained, using standard procedures (ref 1) from particle velocity versus shock velocity data found in the literature (ref 11, 13, 19, 25, 30). When guarded specimens were used, $\frac{d}{d\tau} \ln i$ was obtained from a digital reduction of waveforms for about 10 values of x between 0.2 and 0.8. These were then averaged and the standard deviation of the values averaged was calculated. There is always some slight angle (about 4' of arc) between the impacting plates. This results in a small tilt on the moving front. The effect of tilt on the output current waveform is to produce a distortion of the curve form. The analysis by Wittikindt (ref 24) shows that for intermediate values of τ , the difference in the slope of distorted and undistorted current waveforms was minimized. For unguarded arrangement, however, the results are additionally distorted for the larger values of τ by rarefaction waves originating at the lateral surfaces. All unguarded specimens were 0.5 cm thick; when $\tau = 0.2$, lateral rarefactions were disturbing about 7 percent of the area. For this reason, only qualitative results could be obtained from the unguarded specimens. An exception was the unguarded 26-kbar shot where a relatively high impact velocity produced a low apparent tilt, allowing a good value of $\frac{d}{d\tau} \ln i$ to be obtained from a small value of τ . The results and some experimental details are summarized in Table I.

5. COMPARISON OF THEORY AND EXPERIMENT

There are no direct measurements of g_{11} for BaTiO_3 ceramic. There is, however, a direct measurement of Q_{11} due to Schmidt (ref 21) who directly measured displacement versus polarization for a ceramic both below and above the Curie point. He obtained a value of $Q_{11} = 0.6 \times 10^{-12} \text{ cm}^2/\text{dyne}$ below the Curie point and $0.7 \times 10^{-12} \text{ cm}^2/\text{dyne}$ above the Curie point. He observed a decrease in value in the immediate vicinity of the Curie point. Estimates of the electrostrictive constants for the ceramic are also available, using single crystal constants and averaging formulas (ref 22). These are $Q_{11} = 0.7 \times 10^{-12} \text{ cm}^2/\text{dyne}$ and $Q_{12} = -0.2 \text{ cm}^2/\text{dyne}$. There is also an unpublished estimate of Q_{11} and Q_{12} (due to Saxe and quoted by Schmidt, ref 21): $Q_{11} = 0.64 \times 10^{-12} \text{ cm}^2/\text{dyne}$ and $Q_{12} = -0.138 \times 10^{-12} \text{ cm}^2/\text{dyne}$.

We can also obtain a value of Q_{12} if we know the value of Q_{11} and also the slope of the line of inverse susceptibility versus hydrostatic pressure in the paraelectric region. The value of $\partial\chi^p/\partial p$ obtained from experimental measurements of dielectric constant versus hydrostatic pressure by Samara (ref 10) is

TABLE I. Results of Measurements

Shot	Shock pressure (kilobars)	Uniaxial strain	Inverse dielectric constant	Comments
1	4.2	-0.0021	$>8.5 \times 10^{-4}$	Aluminum elastic wave. No guard ring; 0.5-cm-thick disk
2	5.2	-0.0026	$>8.5 \times 10^{-4}$	No guard ring; 0.5-cm-thick disk
3	8.5	-0.0043	$(10 \pm 1) \times 10^{-4}$	Guard ring; 1-cm-thick disk
4	16.0	-0.0080	$(12 \pm 1) \times 10^{-4}$	Guard ring; 1-cm-thick disk
5	22.0	-0.011	$(16 \pm 1) \times 10^{-4}$	Guard ring; 1-cm-thick disk
6	26.0	-0.013	17×10^{-4}	No guard ring; 0.5-cm-thick disk

$$\frac{\partial X}{\partial P} = 2(Q_{11} + 2Q_{12}) = 0.45 \times 10^{-12} \text{ cm}^2/\text{dyne} . \quad (20)$$

This value used in conjunction with Schmidt's value for Q_{11} yields Q_{12} . From the literature (ref 31), we obtain values of the elastic compliances

$$\begin{aligned} s_{11} &= 8.7 \times 10^{-13} \text{ (cgs)} \\ s_{12} &= -2.9 \times 10^{-13} \text{ (cgs)} \end{aligned} \quad (21)$$

From the relations due to Devonshire and quoted in section 2, we have

$$g_{11} = -\frac{2}{3} \frac{Q_{11} - Q_{12}}{s_{11} - s_{12}} - \frac{1}{3} \frac{Q_{11} + 2Q_{12}}{s_{11} + 2s_{12}} .$$

Table II summarizes the various values of Q_{11} and Q_{12} and also calculated values of g_{11} .

Table II. Values of Q_{11} and Q_{12} for ceramic barium titanite and value of g_{11} calculated from these (g_{11} is dimensionless in cgs units).

$Q_{11}(\text{cm}^2/\text{dyne})$	$Q_{12}(\text{cm}^2/\text{dyne})$	Source	g_{11}
0.7×10^{-12}	-0.2×10^{-12}	Single crystal average (Jona and Shirane)	-0.86
0.64×10^{-12}	-0.14×10^{-12}	Saxe	-0.86
0.70×10^{-12}	-0.24×10^{-12}	Schmidt (above 120°C) & hydrostatic data	-0.80

The value of g_{11} is thus about -0.84. The predicted value of

$$\frac{\partial \frac{1}{\epsilon}}{\partial z} = \frac{2g_{11}}{4\pi} \text{ is } \sim \frac{-1.68}{4\pi} \sim -0.13 \text{ (cgs)}. \quad (22)$$

The value obtained by fitting a straight line to the quantitative results (between 8.5 and 26 kbars) in Table I is

$$\frac{\partial \frac{1}{\epsilon}}{\partial z} = -0.11 \pm 0.04 \text{ (cgs)}. \quad (23)$$

The experimental points and fitted line are shown in figure 5. The results from shot 1 and shot 2 were considered inadequate for reduction to numerical values of inverse dielectric constants and are discussed in the next section.

From (eq 16), the transition strain at room temperature (23°C) is given by

$$z_z = \frac{-(T - T_C)4\pi}{2g_{11}C}. \quad (24)$$

T_C is 112.5 and $C = 1.5 \times 10^5$ (ref 6). On the basis of table II, we estimate $g_{11} = -0.84$. The transition strain at room temperature is then

$$z_z = -0.0044.$$

The elastic shock velocity in BaTiO_3 is approximately 6×10^5 cm/sec and the initial density (ρ_0) is 5.5 gm/cm^3 . Using Hugoniot relations

$$p_{\text{shock}} = \rho_0 u_s u_p, \quad (25)$$

where u_s and u_p are shock and particle velocity and

$$z_z = -\frac{u_p}{u_s}. \quad (26)$$

we obtain the results that at the transition the particle velocity u_p is 2600 cm/sec and the shock pressure, 8.6 kbars.

6. CONCLUSIONS AND DISCUSSION

The agreement between the experimental and calculated value of the slope of inverse dielectric constant versus strain for the paraelectric region suggests that in the measured region between 8.5 and 26 kbars the ceramic is in a paraelectric state, and that the transition, therefore, occurs at a shock pressure equal to or below 8.5 kbars. This is consistent with the calculated shock transition pressure of about 8 kbar and also the value inferred by Doran (ref 11) on the basis of his experiments and also those of Binder. The consistency between the theory and what are now considerable experimental results support the contention that shock-induced ferroelectric-paraelectric transition occurs at about 8 kbars at room temperature. This value is quite different from the value of hydrostatic pressure producing a transition. A relation predicting the hydrostatic transition pressure at room temperature (ref 16-19) is

$$p = \frac{(T - T_C)4\pi}{2(Q_{11} + 2Q_{12})C} \quad (27)$$

It is analogous to the relation predicting the transition uniaxial strain. The relation yields the results $p = 17$ kbars where the value of $2(Q_{11} + 2Q_{12})$ is that obtained from the slope $\partial \frac{1}{\epsilon} / \partial p$ for pressures just above the transition pressure. The slope was obtained from experimental measurements of Samara (ref 10). This result is in fairly good agreement with the transition pressure 20.1 ± 0.2 (ref 9) obtained from measurements of four samples of ceramic BaTiO_3 (5-wt percent CaTiO_3) and three samples of technical grade BaTiO_3 , ceramic. It should be emphasized that the effect of the calcium additive on the transition pressure was small—the two materials exhibiting essentially the same 20-kbar transition pressure.

It should be mentioned here that the linear relation used to calculate the strain has been assumed to hold over the full range between the room temperature and the transition temperature. This assumption has been experimentally verified for the case of hydrostatic pressure (ref 6).

Examination of ϵ as a function of hydrostatic pressure (ref 6-9) indicates clearly that at the transition pressure the value of $1/\epsilon$ is relatively large. The results of the shock-compression measurements as seen in figure 5 appear inconsistent with the assumption $1/\epsilon \rightarrow 0$ at the transition. This inconsistency can be explained by assuming that the measured capacitance at a transition is the value of non-ferroelectric capacitance layer electrically in series with the capacity

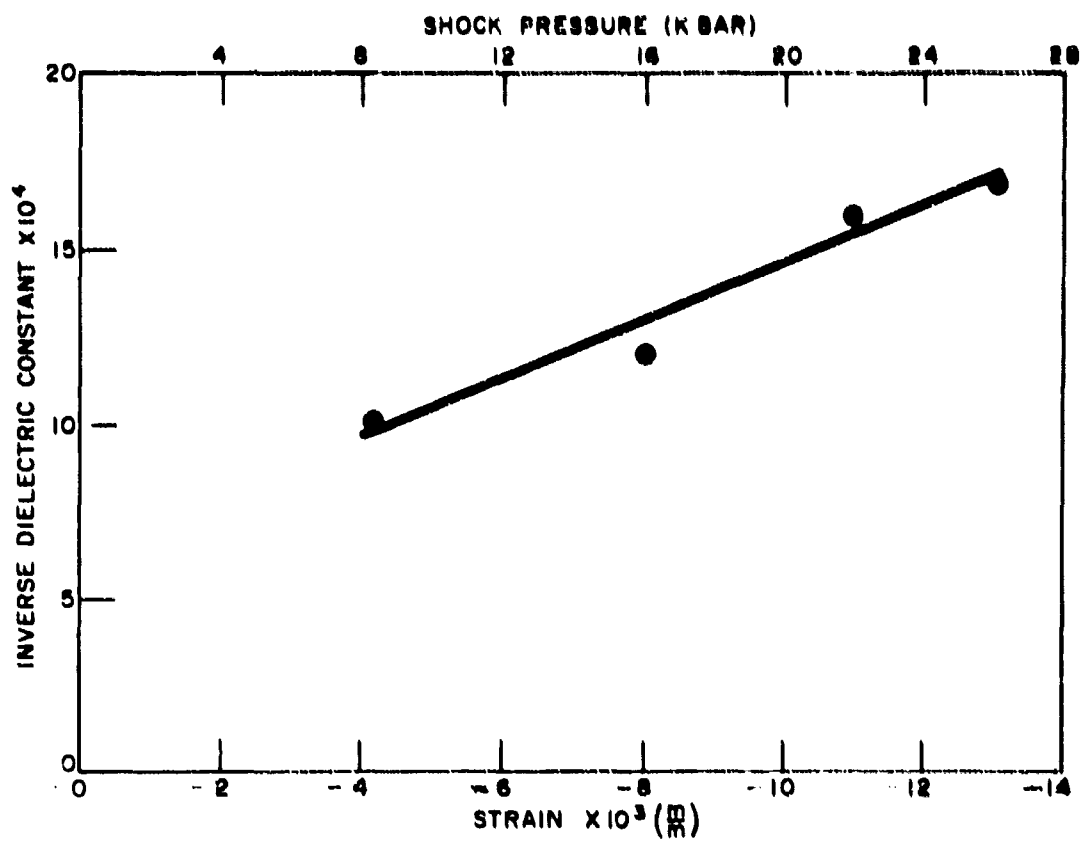


Figure 5. Inverse dielectric versus strain.

of the bulk of the material. It is also possible that the layer is ferroelectric but with transition characteristics different from that of the bulk. The capacity of such layers would be relatively independent of pressure. Thus, the measured value of d_1/dp or $d_1/d\epsilon$ would not change. The correct value for the transition pressure could then be correctly calculated by assuming $1/\epsilon \rightarrow 0$. Possible sources of such layers are not hard to find. Surface layers with properties different from that of the bulk have been observed both in ceramic and single crystals (ref 32).

That the residual value of the inverse dielectric constant at the transition results from an extraneous effect is further supported by the fact that the value of $1/\epsilon$ at the transition when produced by hydrostatic pressure, is extremely sensitive to the particular type of sample. Very different values of $1/\epsilon$ are obtained for ceramic with 5-wt percent CaTiO_3 additive, essentially pure ceramic and single crystals (ref 9). The values of the slopes and transition pressures are, however, approximately the same as would be expected in the presence of a surface layer whose dielectric constant is independent of pressure.

It would have been valuable to determine the actual minimum in the curve of inverse dielectric constant versus strain by making quantitative measurements in the range between 0 and 8 kbars--below the implied transition. Measurements in this region are difficult, because low-impact velocities are required to produce low strains and low-impact velocities produce fronts with high tilts from which it is difficult to obtain good values of inverse dielectric constant. The results obtained in shot 1 and shot 2 were thought to be too distorted relative to pulse length for reduction to quantitative values of inverse dielectric constant. The positive slopes of the wave form however clearly indicate that the inverse dielectric constant at these points is greater than the room temperature atmospheric pressure value of 8.5×10^{-4} . This is consistent with a minimum in the curve in the vicinity of 8 kbars.

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Measurements on BaTiO₃ ceramic were made of inverse dielectric constant versus uniaxial strain for values of strain ranging between 7.0043 and -0.013. The strain was produced in the region behind a shock front generated in a slab of the material by impacting it with a flying plate. The plate was accelerated in a gas gun. The slabs were disks with electrodes on the flat surfaces. The normal stress producing these strains ranged between 8.5 and 26 kbars. The dielectric constant was obtained from oscillograms of the shock-induced depolarization current through a circuit connecting the electrodes. A straight line was fitted to the curve of inverse dielectric constant versus strain. The slope of the line was -0.11 ± 0.04. Thermodynamic theory was used to calculate this slope assuming the material was in the paraelectric phase for the range of experimental shock pressures. The calculated value was -0.13. The calculated value is in agreement with the experimental value and the assumption that the material is in the paraelectric phase for shock pressures between 8.5 and 26 kbars. The agreement implies that the transition at approximately room temperature is produced by a shock pressure less than or equal to about 8.5 kbars. This is markedly different from the experimental results for hydrostatic pressure where the transition occurs at 20 kbars at room temperature, and the material is in its paraelectric phase above 20 kbars. In both cases the temperature is approximately room temperature. The		

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transition strain and shock pressure was calculated using thermodynamic theory and assuming that the transition could be approximated as a second order one. The result was a transition strain of -0.0044 and a transition shock pressure of 8.6 kbars. This is consistent with the preceding results and also supported by experimental findings by Doran who observed a discontinuity in sound velocity at that shock pressure.							

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