Pressure and Temperature Dependences of the Dielectric Properties of the Perovskites BaTiO$_3$ and SrTiO$_3$†

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The dielectric properties of single-crystal and ceramic BaTiO$_3$ and of single-crystal SrTiO$_3$ were investigated as functions of hydrostatic pressure to 25 kbar and temperature to 150°C. The Curie point of BaTiO$_3$ decreased linearly with increasing pressure, but at a rate which varied from -4.6 to -5.9°C/kbar for different samples. Its spontaneous polarization P_s decreased slowly ($<2\%$ per kbar) up to the transition pressure, where it dropped rapidly. This change in P_s is primarily due to the displacement of the Curie point to lower temperatures. At constant temperature, the dielectric constant ϵ in the cubic phase of both compounds obeys the relationship $\epsilon = C^*/(p-p_0)$. At 25°C, $C^* = 2.8 \times 10^4$ kbar and $p_0 = 18.5$ kbar for pure single-crystal BaTiO$_3$, and $C^* = 1.2 \times 10^4$ kbar and $p_0 = -40$ kbar for single-crystal SrTiO$_3$. Both C^* and p_0 change with temperature. Similarly, the Curie-Weiss constant C and temperature T_0 change with pressure. The temperature dependence of ϵ is separated into volume-dependent and volume-independent contributions, and it is shown that the change of the infrared polarizability with temperature at constant volume is the predominant factor in determining the change in ϵ.

I. INTRODUCTION

THIS paper deals with the effects of hydrostatic pressure and temperature on the dielectric properties of the two perovskites, barium titanate (BaTiO$_3$) and strontium titanate (SrTiO$_3$). BaTiO$_3$ is a well-known ferroelectric,[1] but the question of ferroelectricity in SrTiO$_3$ is still unresolved. SrTiO$_3$ has the cubic perovskite structure down to 110°K where recent x-ray-diffraction[2] and resonance[3] work has established a small distortion of the lattice to tetragonal symmetry ($c/a \simeq 1.00056$) and domain structure has been observed.[2] However, there is no anomaly in the dielectric constant at the transition and no measurable spontaneous polarization below it.

There is a wealth of data in the literature on the temperature dependence of the dielectric properties of both BaTiO$_3$ and SrTiO$_3$.[1] Little has been reported on the pressure dependence of these properties. The variations of these properties with decreasing volume (increasing pressure), at constant temperature, are of practical and theoretical interest. Of particular interest is the Curie-Weiss behavior of the dielectric constant ϵ in the cubic paraelectric phase. This behavior has been attributed to anharmonic contributions to the potential energy[4,5] and more recently related to the temperature dependence of a long-wave-length transverse optical mode of the lattice.[6,7]

A number of authors have investigated the effect of pressure on the Curie point of BaTiO$_3$.[8-11] These investigations were carried out below 12 kbar and showed considerable disagreement among the various authors. Moreno and Gränicher,[12] in a brief note, reported on the pressure dependence (to <2 kbar) of the dielectric constants of BaTiO$_3$ and SrTiO$_3$ as did Bosman and Havinga[13] in measurements to 5 kbar. Samara and Giardini[14] reported on the pressure dependence of the dielectric constant of SrTiO$_3$ to 50 kbar.

In the present work a detailed investigation was made of the effects of hydrostatic pressure (to 25 kbar) and temperature (to 150°C) on the polarization, dielectric constant, and Curie point of BaTiO$_3$ using both single-crystal and ceramic samples. The pressure and temperature dependences of the dielectric constant of single-crystal SrTiO$_3$ were also investigated. In Sec. II, a brief account of the experimental techniques is given. The results are presented in Sec. III and discussed in Sec. IV. Section V summarizes the over-all results and conclusions.

II. EXPERIMENTAL TECHNIQUES

The experiments were performed in a 30-kbar hydrostatic pressure system using a 50-50 mixture of normal pentane and isopentane as the pressure fluid. A description of the apparatus and general experimental procedures including pressure calibration has been given

† This work was supported by the U. S. Atomic Energy Commission.

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[10] S. Minomura, T. Kawakubo, T. Nakagawa, and S. Sawada, J. Appl. Phys. (Japan) **3**, 562 (1964).

[11] G. G. Leonidova and I. N. Polandov, Fiz. Tverd. Tela **4**, 2613 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1916 (1963)].

[12] M. Moreno and H. Gränicher, Helv. Phys. Acta **37**, 625 (1964).

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TABLE I. Curie points T_c and Curie-Weiss temperature and constant, T_0 and C, respectively, and their pressure derivatives for each of the BaTiO₃ samples investigated.

Sample No.	T_c (°C)	dT_c/dp (°C/kbar)	T_0 (°C)	dT_0/dp (°C/kbar)	C (°K)	dC/dp (°K/kbar)
1	118.0	−5.5	101.0	−4.8	3.08×10^5	-3.8×10^3
2^a	113.5	−5.9	97.0	−5.4	1.34×10^5	-0.9×10^3
3^b	114.0	−5.0	98.5	−4.4	1.61×10^5	-1.3×10^3
4^c	112.5	−4.7	97.5	−5.7	1.50×10^5	-0.3×10^3
5^d	113.0	−5.1	103.0	−6.1	1.23×10^5	-2.0×10^3
6	120.0	−4.95	⋯	⋯	⋯	⋯
7	111.0	−4.83	102.0	⋯	1.40×10^5	⋯
8	122.5	−4.63	⋯	⋯	⋯	⋯

^{a} Pb doped (1 mole % PbTiO₃ added to flux during crystal growth).
^{b} Fe doped (0.5 mole % Fe₂O₃ added to flux during crystal growth).
^{c} Ceramic sample with 5 mole % CaTiO₃. Density =5.65 g/cm³.
^{d} Ceramic sample (pure BaTiO₃). Density =5.75 g/cm³.

elsewhere.[15] The polarization of BaTiO₃ was measured from both low-frequency (manual) and 60-cycle hysteresis loops using conventional circuitry. Capacitance and dissipation factor were measured at 1 kc/sec with a transformer ratio-arm bridge having an accuracy of ±0.01%.

The BaTiO₃ single crystals used were in the form of thin plates about 0.5-mm thick ×0.2–0.6 cm². Most of them were selected from various batches grown at this laboratory. Because the available crystals were quite thin, all the measurements were made with the field applied along the tetragonal c axis. The ceramic samples were in the form of thin plates 0.5–1-mm thick ×0.5–0.8 cm². The SrTiO₃ samples were thin plates 0.5-mm thick ×0.4–0.7 cm² cut parallel to one of the cube faces from a large boule purchased from the National Lead Company. Silver electrodes were applied to the samples by either vapor coating or by painting and firing.

III. EXPERIMENTAL RESULTS

A. BaTiO₃

Measurements of the dielectric constant ϵ and the loss tangent-δ were made on several single crystals and two ceramic samples. Two of the crystals were slightly doped (see Table I), and one ceramic sample contained 5 mole% CaTiO₃. The various samples are identified and listed in Table I.

Figure 1 shows isobars of the dielectric constant along the c axis, ϵ_c, measured as a function of temperature for sample No. 1. The other single crystals exhibited similar behavior, but there were considerable differences in the values of the shifts of the Curie points. In all cases, the Curie point T_c decreased linearly with pressure. The results are summarized in Table I.

Figure 2 shows isobars of the dielectric constant versus temperature for the pure ceramic, sample No. 5. There is a very striking difference between these curves and those in Fig. 1. Whereas for single crystals the value of the dielectric constant in the immediate

[15] G. A. Samara, J. Phys. Chem. Solids **26**, 121 (1965).
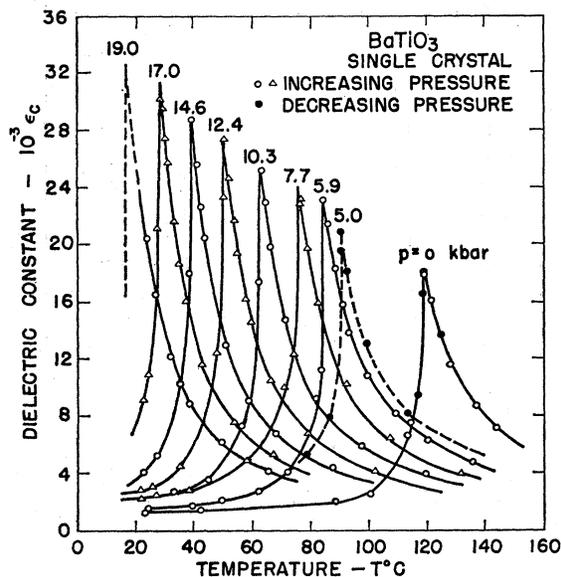
FIG. 1. The temperature dependence of the dielectric constant of single-crystal BaTiO₃ (sample No. 1) measured along the c axis at various hydrostatic pressures.

vicinity of the peak increased by 50–65% in 15 kbar, it decreased by over 50% in this case for the same pressure range. The other ceramic sample exhibited similar changes with pressure.

Figure 3 shows ϵ_c-versus-pressure isotherms for two single crystals. The 23°C isotherm is for sample No. 6, and the 60 and 85°C isotherms are for sample No. 7. It is interesting to note the very close resemblance between these isotherms and the corresponding isobars in Fig. 1.
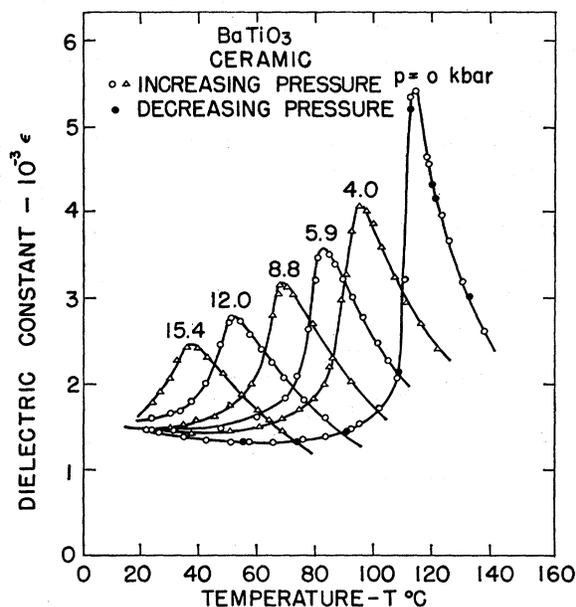
FIG. 2. The temperature dependence of the dielectric constant of pure ceramic BaTiO₃ (sample No. 5) at various hydrostatic pressures.

FIG. 3. The pressure dependence of the dielectric constant of single-crystal BaTiO₃ measured along the c axis at various temperatures. The 23°C isotherm is for sample No. 6 and the 60 and 85°C isotherms are for sample No. 7.

In analogy to the Curie point T_c there is a transition pressure p_c taken as the pressure corresponding to the peak value of ϵ. Above p_c ϵ decreases monotonically with increasing pressure as it does with increasing temperature above T_c. The ceramic samples exhibited qualitatively similar behavior.

Hysteresis-loop measurements were made on several single crystals. There were some quantitative differences, but the qualitative features were all the same. The changes in the loop with pressure closely resemble the more familiar changes observed with increasing temperature at 1 bar. Small decreases in polarization and coercive field occurred up to the transition pressure where the polarization decreased sharply and a "kinking" at the center of the loop, indicating the appearance of a double hysteresis loop, was observed. Figure 4 shows the pressure dependence of the spontaneous and remanent polarizations (P_s and P_r) of sample No. 8 at 23°C. Also shown is the change of P_s of sample No. 3 at 45°C. This sample had a P_s of 22 μC/cm² at 1 bar and 25°C.

When a dc biasing field is applied, the transition pressure increases with field strength at a rate of $\simeq$0.3
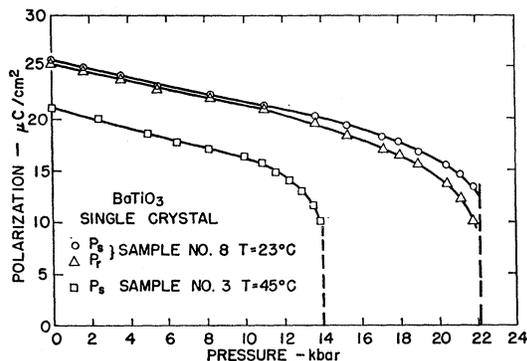
FIG. 4. Pressure dependence of the spontaneous (P_s) and remanent (P_r) polarizations of single-crystal BaTiO₃.

kbar cm/kV at 25°C. The increase of the transition temperature with field strength $\simeq$1.4°C cm/kV at 1 bar.

B. SrTiO₃

The variation of the dielectric constant ϵ with temperature and pressure is shown in Fig. 5. ϵ decreases monotonically with both increasing temperature and pressure as is observed for the cubic phase of BaTiO₃.

IV. DISCUSSION

A. Transition Temperatures of BaTiO₃

Figure 6 shows the shift of the Curie point with pressure for two of the samples and compares the results with those of other workers. Table I summarizes our
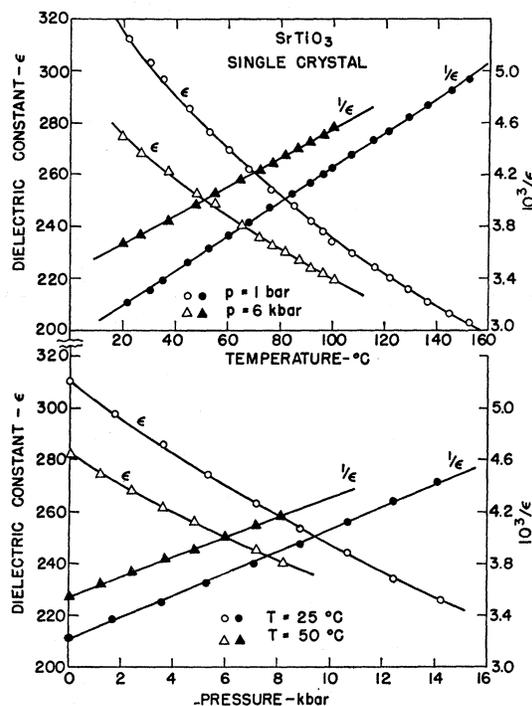
FIG. 5. Temperature and pressure dependences of the dielectric constant of single-crystal SrTiO₃.

results. The decrease in T_c with increasing pressure is expected from a consideration of the strains introduced into the lattice at the onset of spontaneous polarization. These strains consist of an elongation along the polar c axis and contractions along the a axes resulting in a small increase in unit-cell volume. Since pressure favors the smaller volume, a stabilization of the cubic phase, or a decrease in T_c, is expected and observed.

The three transitions in BaTiO₃ are first-order phase transformations, and thus obey the Clausius-Clapeyron equation

$$dT_c/dp = T_c \Delta V/Q, \tag{1}$$

where p is the pressure and ΔV and Q are the transition

volume and latent heat, respectively. Approximate values of ΔV and Q are given by Shirane and Takeda[16] for ceramic $BaTiO_3$. Using their values for the cubic-tetragonal transition, namely, $\Delta V = -0.062$ Å^3/unit cell and $Q = 50$ cal/mole, and a value of 120°C for T_c, a decrease in the Curie point of 7° C/kbar is calculated. This is in reasonable agreement with the measured shifts.

As can be seen from Table I, the magnitude of dT_c/dp varies considerably from sample to sample. Literature values show an even wider spread, with the initial slope varying from -3.5 to -6.7°C/kbar.[8–11] The cause of this variation is not known, but contributing factors may be the presence of impurities and the quality (e.g. domain structure) of the sample. The results on the two ceramic samples suggest a possible trend: The magnitude of the shift increases with the size of the solute ion substituted for the A cation in the general perovskite formula ABO_3 and with the tetragonality (i.e. c/a ratio) of the lattice. $CaTiO_3$ forms solid solutions with $BaTiO_3$ with Ca occupying Ba sites and decreasing the lattice parameters and c/a. It may be pointed out here that preliminary results on $PbTiO_3$, which is more highly tetragonal than $BaTiO_3$ ($c/a = 1.06/1.01$), indicate a considerably larger shift (~ -7.5°C/kbar) than that for $BaTiO_3$.[17] For the $BaTiO_3$ single crystals, standard x-ray powder patterns showed no measurable differences in lattice parameters among the various samples, and thus, for these samples the variation in dT_c/dp may be associated with domain structure. The amounts of doping in the Fe- and Pb-doped crystals were insufficient to establish any definite trends. There was evidence that dT_c/dp depends somewhat on whether the pressure is varied while the crystal is above or below the Curie point, the slope being larger when, for a given crystal, pressure is always varied above the Curie point.

Up to ~ 3 kbar, there is general agreement between the present results and those in the literature. Above 3 kbar, the continued linear dependence of T_c on pressure observed in this work is in agreement with the observation of Minomura et al.[10] but disagrees with the results of Klimowski[9] and Leonidova and Polandov.[11] We observed no sharp change in slope around 3.5 kbar nor the irreversible pressure effect reported by Klimowski. Furthermore, our results showed no evidence of the sudden decrease in capacitance at ~ 11 kbar and 20°C reported by Leonidova and Polandov.

For the tetragonal-orthorhombic transition near 5°C, Merz[8] measured a decrease of the transition temperature of 3°C/kbar up to 1.5 kbar followed by an increase of 3°C/kbar between 1.5 and 3 kbar. If Merz's data are extrapolated, the transition is predicted to occur at room temperature and 10 kbar. A special effort was made to detect the dielectric anomaly associated with

[16] G. Shirane and A. Takeda, J. Phys. Soc. Japan **7**, 1 (1952).
[17] G. A. Samara, Bull. Am. Ceram. Soc. **44**, 638 (1965).
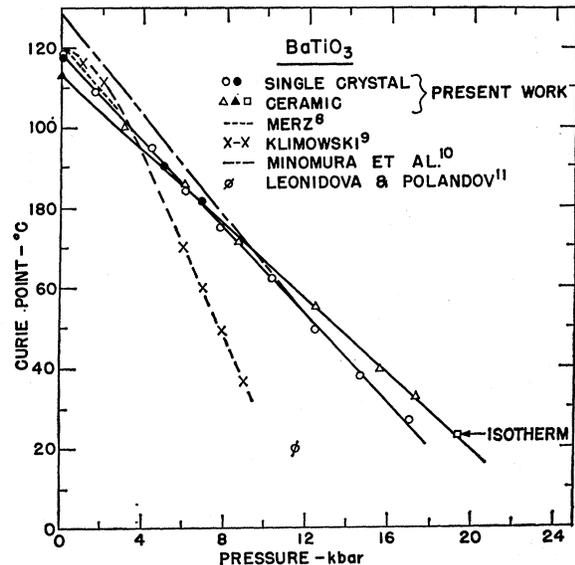
FIG. 6. Shift of the Curie point of BaTiO₃ with pressure. Present results are compared with literature values.

this transition for three of the single-crystal samples studied, but no such anomaly was observed even at pressures up to 20 kbar. Recently Minomura et al.[10] studied this transition up to 4.5 kbar and observed a linear decrease in transition temperature of 2.8°C/kbar. On the basis of the thermodynamic data for this transition[16] ($Q = 22$ cal/mole and $\Delta V = -0.014$ Å^3/unit cell), a shift of -2.6°C/kbar is predicted.

No measurements have been made on the orthorhombic-rhombohedral transition. In this case, the thermodynamic data ($Q = 8$ cal/mole and $\Delta V = +0.006$ Å^3/unit cell) yield an increase in the transition temperature of ~ 2°C/kbar.

On the basis of the above discussion, a tentative pressure-temperature phase diagram for $BaTiO_3$ is given in Fig. 7. It is seen that the range of stability of the orthorhombic phase decreases with increasing
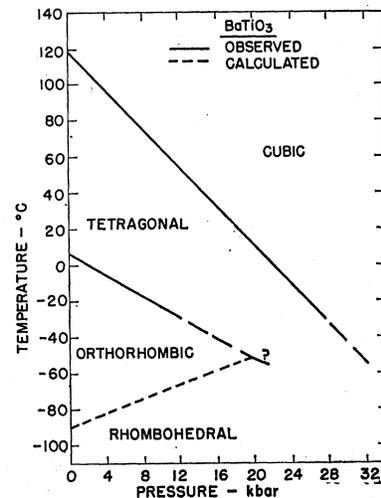
FIG. 7. Temperature-pressure phase diagram for BaTiO₃.

FIG. 8. The spontaneous polarization of single-crystal $BaTiO_3$ (sample No. 6) as a function of the reduced temperature $(T-T_c)$ for various hydrostatic pressures.

pressure and may vanish at a triple point at ~ 19 kbar and $\sim -50°C$. It would be of interest to extend the measurements to lower temperature in order to examine the behavior in this region.

B. Spontaneous Polarization of $BaTiO_3$

As shown in Sec. III, the spontaneous polarization P_s of $BaTiO_3$ in the tetragonal phase decreases with increasing pressure in the same manner as with increasing temperature. Since the Curie point decreases with pressure, one may inquire as to whether or not the pressure dependence of P_s is the result of the simple displacement of the P_s-versus-T curve along the temperature axis. Figure 8 shows four isobars of P_s versus the reduced temperature $(T-T_c)$ for sample No. 6. These results clearly indicate that the major part of the change of P_s with pressure is caused by the shift of T_c. There is only a small decrease of the dipole moment with pressure. This is not too surprising if the dipole moment is indeed associated with the Ti-O interaction along the c axis, and in view of the fact that the compressibility of the c axis[18] is only $\sim 4 \times 10^{-4}$ kbar^{-1}. It is interesting to note here that earlier results on Rochelle salt[15] and triglycine sulfate[19,20] also indicate no appreciable pressure effect on the magnitudes of the dipole moments of these two compounds.

The variations of the polarization and dielectric constant with pressure establish the pressure dependence of the piezoelectric coefficients d_{31} and d_{33}. The relations are[21]

$$d_{31}(\text{or } d_{33}) \propto \chi_c P_s, \tag{2}$$

where χ_c is the dielectric susceptibility $[= (\epsilon_c - 1)/4\pi]$. Referring to Figs. 3 and 4, it is seen that χ_c increases fairly rapidly with pressure while P_s decreases rather slowly up to near the transition. Thus d_{31} and d_{33} should

[18] S. S. Kabalkina, L. F. Vereshchagin, and B. M. Shulenin, Dokl. Akad. Nauk SSSR **144**, 1019 (1962) [English transl.: Soviet Phys.—Doklady **7**, 527 (1962)].

[19] F. Jona and G. Shirane, Phys. Rev. **117**, 139 (1960).

[20] G. A. Samara (to be published).

[21] W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 47.

increase with increasing pressure and drop sharply to zero at the transition.

C. Dielectric Constant—Cubic Phase

1. Curie-Weiss Behavior

At atmospheric pressure, the dielectric constant in the cubic paralectric phase of both compounds varies with temperature according to the Curie-Weiss law

$$\epsilon = C/(T - T_0), \tag{3}$$

where C and T_0 are the Curie-Weiss constant and temperature, respectively. Here we wish to make the distinction between T_0, the Curie-Weiss temperature, and T_c, the Curie point. T_c is taken as the temperature corresponding to the peak value of ϵ. T_0 is the temperature at which $1/\epsilon$ extrapolates to zero on a $1/\epsilon$-versus-T plot.

Values of C and T_0 for the $BaTiO_3$ samples investigated and their pressure derivatives are given in Table I. Both C and T_0 decrease with increasing pressure. The decrease in C varied between <0.5 to $>1\%$ per kbar for the various samples. T_0 decreased linearly for all samples. For single crystals, T_0 decreased at a lower rate than did T_c, while for ceramic specimens, the reverse was true (see Table I). These effects are related to the fact that the peak value of ϵ, ϵ_{max}, rises sharply with pressure in the case of single crystals but decreases for ceramics. This can be easily seen by remembering that ϵ_{max} occurs at $T = T_c$ and writing Eq. (3) as

$$\epsilon_{max} = C/(T_c - T_0). \tag{4}$$

Thus, a smaller $\Delta T(= T_c - T_0)$ is associated with a higher ϵ_{max} and vice versa. (The small change in C with pressure has been neglected in this argument.)

The striking difference in the pressure dependence of ϵ in the immediate vicinity of the peak between single-crystal and ceramic $BaTiO_3$ (Figs. 1 and 2) may be related to the pressure dependence of the dielectric constant along the a axis which has not been measured. For the single crystals, ϵ was measured along the c axis. Since this axis decreases with pressure at a faster rate than the a axis,[18] pressure may switch some c domains to a domains, thus leading to a higher ϵ_c (lower ϵ_a). In ceramics, of course, it is the average value of ϵ that is measured. It should be pointed out that the denser of the two ceramics (sample No. 5) exhibited a larger decrease of ϵ, so that porosity is not an important factor in the explanation of the effect.

Figure 5 shows $1/\epsilon$-versus-T isobars for $SrTiO_3$. At 1 bar, $C = 8.27 \times 10^4 °K$ and $T_0 = 36°K$. Here C increases with pressure at a rate of $\sim 2\%$ per kbar. T_0 decreases with pressure as in the case of $BaTiO_3$ but at a much faster rate $(\sim -14°K/kbar)$. Thus, T_0 becomes negative above ~ 3 kbar.

The present results show that the pressure dependence of ϵ in the cubic phase follows a relationship similar to

Eq. (3) expressed in terms of pressure,[22] i.e.,

$$\epsilon = C^*/(p-p_0),\qquad (5)$$

where at a given temperature, C^* and p_0 are constants corresponding to C and T_0, respectively.

Figure 3 shows $1/\epsilon_c$-versus-p isotherms for single-crystal BaTiO₃. C^* and p_0 vary from sample to sample (as do C and T_0). C^* is $\sim 2.8 \times 10^4$ kbar and decreases with increasing temperature. p_0 is around 1–2 kbar lower than the transition pressure p_c and decreases linearly with increasing temperature. Table II summarizes the results on samples Nos. 6 and 7.

Moreno and Gränicher[12] measured ϵ versus p of BaTiO₃ up to 1.5 kbar in the temperature range 125–157°C. No details of the experiment were given and their result is reported as $d(1/\epsilon)/dp\,(=1/C^*) = 2.6\times 10^{-5}$ kbar^{-1}. Bosman and Havinga[13] obtained the same slope in measurements up to 5 kbar, but the temperature at which the experiment was performed was not stated (presumably it was over 120°C). This value is considerably smaller than that obtained in the present work, namely $\sim 3.5\times 10^{-5}$ kbar^{-1}. A possible explanation for this discrepancy is obtained by examining the data in Fig. 3. It is seen that the results deviate from the $1/\epsilon$-versus-p lines over a region of pressure close to the transition. The data in this region can also be represented by Eq. (5) but with different constants C^* and p_0. This is indicated by the lightly dashed lines in Fig. 3. The slopes of these lines, $d(1/\epsilon)/dp$, in units of 10^{-5} kbar^{-1} are 2.63, 2.76, and 2.90 for the 23, 60, and 85°C isotherms, respectively. These values are in close agreement with the earlier measurements. It is also seen from Fig. 3 that the pressure range over which this behavior occurs increases with increasing temperature. At 100°C it should be 4–5 kbar. The earlier low-pressure measurements thus appear to have been performed in this region. At higher pressures the data obey Eq. (5) over a much wider pressure range.

Figure 5 shows $1/\epsilon$-versus-p isotherms for SrTiO₃. At 25°C, $d(1/\epsilon)/dp = 8.3\times 10^{-5}$ kbar^{-1}, $C^* = 1.2\times 10^4$ kbar, and $p_0 = -40.3$ kbar. These values are in good agreement with earlier results.[12–14]

2. Phenomenological Treatment

The linear dependence of $1/\epsilon$ versus T at any given pressure can be arrived at, to a first-order approximation, from Devonshire's phenomenological theory.[4] In this theory, the free energy A of the crystal is expanded as a function of strain $\mathbf{x}$ and polarization $\mathbf{P}$. For the purpose of the present work, we need the free-energy expansion in terms of stress $\mathbf{X}$ and $\mathbf{P}$. The transformation has been carried out by Forsbergh[23] and leads to the following expression for the free energy in terms of

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[22] It should be noted here that Eq. (5) is an empirical relationship, and one should not attach to it the same type of physical interpretation as for the Curie-Weiss law, Eq. (3).

[23] P. W. Forsbergh, Jr., Phys. Rev. **93**, 686 (1954).

TABLE II. Transition pressure p_c and the various quantities in Eq. (5) for single crystals of BaTiO₃ and SrTiO₃.

Sample	T (°C)	p_c (kbar)	p_0 (kbar)	C^* (kbar)
BaTiO₃ No. 6	23.0	19.6	18.0	2.77×10^4
BaTiO₃ No. 7	60.0	10.4	9.6	2.90×10^4
BaTiO₃ No. 7	85.0	5.5	4.9	2.75×10^4
SrTiO₃	23.0	$\cdots$	−40.3	1.20×10^4

hydrostatic pressure p, polarization P, and temperature T:

$$A(p,P,T) = \Lambda p^2 + [(2\pi/C)(T-T_0)+\Omega p]P^2 \\ + \tfrac{1}{4}\xi P^4 + \tfrac{1}{6}\zeta P^6. \qquad (6)$$

Here Λ and Ω are functions of the elastic and electrostrictive constants. The coefficients ξ and ζ are weak functions of temperature.

From the thermodynamic relations $(\partial A/\partial \mathbf{P}) = \mathbf{E}$ and $(\partial \mathbf{E}/\partial \mathbf{P}) = (\partial^2 A/\partial \mathbf{P}^2) = 1/X$, where $\mathbf{E}$ is the electric field and $X = (\epsilon-1)/4\pi \simeq \epsilon/4\pi$ for $\epsilon \gg 1$ is the dielectric susceptibility, it follows that the reciprocal of the susceptibility of the nonpolar cubic phase, i.e.,

$$\left(\frac{\partial^2 A}{\partial \mathbf{P}^2}\right)_{P=0} = \frac{1}{X} \simeq \frac{4\pi}{\epsilon} = 2\left[\frac{2\pi}{C}(T-T_0)+\Omega p\right],\qquad (7)$$

is a linear function of temperature at any given pressure. The Curie-Weiss law is obeyed but with a different C and T_0 for each pressure.

Equation (7) also establishes the pressure dependence of the transition temperature. A linear dependence is predicted only if the pressure dependences of Ω and C are negligible or if their effects cancel, which is the case if ΩC is independent of pressure. As noted earlier, C decreases with pressure at a rate of ~ 0.5 to 1% per kbar so that Ω probably increases. Ω is a function of the elastic and electrostrictive constants and is given by[23]

$$\Omega = -\frac{(g_{11}+2g_{12})c_{11}+(g_{11}-2g_{12})c_{12}}{(c_{11}-c_{12})(c_{11}+2c_{12})},\qquad (8)$$

where the g terms and c terms are electrostrictive and elastic constants, respectively. Unfortunately, the pressure dependences of these constants are not known.

3. Polarizability and Internal Field

One of the difficulties encountered in the theoretical treatment of dielectric properties is the relationship between the dielectric constant and the polarizability. Directly related to this, of course, is the question of the value of the internal field at a given point in the lattice. The effective field $\mathbf{F}$ at a given lattice site i is generally given by

$$\mathbf{F}_i = \mathbf{E} + \mathbf{E}_{\text{int}} = \mathbf{E} + 4\pi \sum_j \phi_{ij} \mathbf{P}_j,\qquad (9a)$$

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where E is the applied field, and E_{int} is the internal field acting on the ion i due to the other ions j and is expressed in terms of the polarization. ϕ_{ij} is the internal-field coefficient, which is a dimensionless quantity that depends on the position of the ion in the lattice. In diagonal cubic crystals, i.e., crystals in which all ions have cubic environments, the Lorentz internal field is applicable and $\phi_{ij} = \frac{1}{3}$. In the perovskite lattice this is not the case (the oxygens do not have cubic surroundings), and the field at each site has to be computed. This has been done, and the results are summarized in the article by Slater.[5]

Once the internal field at each lattice site is known, an expression for the dielectric constant in terms of the individual polarizabilities of the ions can be obtained. However, it is not possible to discuss the present results on the atomic scale described above, for to do so requires a knowledge of the temperature and pressure dependences of the electronic and ionic polarizabilities of each ion. Such data are not available. It is instructive, however, to treat the results on a macroscopic scale. Equation (9a) can then be written as

$$F = E + 4\pi\phi P. \tag{9b}$$

This effective field combined with the two defining relationships

$$P = (\alpha/V)F, \tag{10}$$

and

$$\epsilon = 1 + 4\pi P/E, \tag{11}$$

leads to the following relationship for the dielectric constant:

$$(\epsilon - 1)/[1 + \phi(\epsilon - 1)] = 4\pi(\alpha/V), \tag{12}$$

where α is the total polarizability of a macroscopic element of the material of volume V. In the Lorentz-field approximation, $\phi = \frac{1}{3}$, and Eq. (12) yields the well-known Clausius-Mossotti relationship which is applicable in its macroscopic form to cubic or isotropic materials such as the perovskites above their Curie points.[24] Von Hippel et al.,[25] on the basis of semi-empirical arguments, have indicated that, for the perovskites, ϕ is much smaller than the Lorentz factor of $\frac{1}{3}$, and, in particular, $\phi \simeq 2.8 \times 10^{-3}$ for BaTiO$_3$ and 4.5×10^{-4} for SrTiO$_3$. These values are arrived at by assuming for the polarizability a temperature dependence of the form

$$(\alpha/V) = c/T, \tag{13}$$

where c is a constant. Such a dependence can be easily shown to lead to a Curie-Weiss behavior for the susceptibility with the result

$$X = (T_0/\phi)/(T - T_0). \tag{14}$$

ϕ is then evaluated from $1/X$-versus-T plots.

[24] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, England, 1949), Appendix 3, p. 169.
[25] A. von Hippel et al., Technical report 178, Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1963 (unpublished).

The applicability of such small values of ϕ for the perovskites seems somewhat doubtful. Slater[5] had earlier argued against the above temperature dependence for α. Instead, he, as did Devonshire,[4] assumed a slow decrease of (α/V) with temperature of the form

$$(4\pi/3)(\alpha/V) = 1 - c'(T - T_0). \tag{15}$$

This linear temperature dependence of α is obtained by introducing anharmonic terms into the potential energy of the lattice, and it also leads to a Curie-Weiss behavior $(\phi = \frac{1}{3})$ for X.

Differentiating Eq. (12) with respect to temperature at constant pressure (assuming ϕ is independent of temperature) we get

$$\frac{1}{(\epsilon - 1)[1 + \phi(\epsilon - 1)]}\left(\frac{\partial \epsilon}{\partial T}\right)_p = \gamma\left(\frac{\partial \ln\alpha}{\partial \ln V}\right)_T$$

$$-\gamma + \left(\frac{\partial \ln\alpha}{\partial T}\right)_V, \tag{16}$$

where γ is the volume coefficient of thermal expansion defined by

$$\gamma = (\partial \ln V/\partial T)_p. \tag{17}$$

The first term on the right-hand side of Eq. (16) represents the change in the polarizability of a given number of particles with change in volume. The second represents the change of the dielectric constant with increasing temperature due to the decrease in the density of polarizable particles. These two terms constitute the total contribution due to volume expansion. The third term is the change of the polarizability with temperature at constant volume.

One would now like to know the relative contribution of each of these three terms to the temperature dependence of ϵ in the cubic phase. In Eq. (16), the left-hand side is known from the measurement of ϵ versus T. γ can be calculated from the known temperature dependence of the lattice parameters. There are two unknowns remaining: $(\partial \ln\alpha/\partial \ln V)_T$ and $(\partial \ln\alpha/\partial T)_V$. The first of these unknowns can be calculated from the measured pressure dependence of ϵ and the compressibility as follows. Differentiating Eq. (12) with respect to pressure at constant temperature (assuming ϕ is independent of pressure) we get

$$\frac{1}{(\epsilon - 1)[1 + \phi(\epsilon - 1)]}\left(\frac{\partial \epsilon}{\partial p}\right)_T$$

$$= \left(\frac{\partial \ln\alpha}{\partial p}\right)_T + \beta = -\beta\left(\frac{\partial \ln\alpha}{\partial \ln V}\right)_T + \beta, \tag{18}$$

where β is the compressibility of the material defined by

$$\beta = -(\partial \ln V/\partial p)_T. \tag{19}$$

TABLE III. The various contributions to the temperature dependence of the dielectric constants of BaTiO₃ and SrTiO₃ [defined by Eq. (16)] calculated for two cases of the internal-field coefficient ϕ. Various quantities appearing in Eqs. (16) and (18) are also listed.

Compound	T (°C)	ϵ	$(1/K)(\partial\epsilon/\partial p)_T{}^a$ (kbar⁻¹)	β (kbar⁻¹)	$(\partial\ln\alpha/\partial\ln V)_T$	$(1/K)(\partial\epsilon/\partial T)_p$ (°K⁻¹)	$\gamma(\partial\ln\alpha/\partial\ln V)_T$ (°K⁻¹)	$-\gamma$ (°K⁻¹)	$(\partial\ln\alpha/\partial T)_V$ (°K⁻¹)
Case (i): $\phi=\frac{1}{3}$									
BaTiO₃	150	2920	-10.8×10^{-5}	78×10^{-5}	1.13	-2.0×10^{-5}	5.65×10^{-5}	-5.0×10^{-5}	-2.65×10^{-5}
SrTiO₃	25	307	-24.6×10^{-5}	57×10^{-5}	1.43	-3.6×10^{-5}	4.30×10^{-5}	-3.0×10^{-5}	-4.90×10^{-5}
Case (ii): $\phi=2.8\times10^{-3}$ for BaTiO₃ and 4.5×10^{-4} for SrTiO₃									
BaTiO₃	150	2920	-11.4×10^{-3}	0.78×10^{-3}	15.6	-2.10×10^{-3}	0.78×10^{-3}	-0.05×10^{-3}	-2.83×10^{-3}
SrTiO₃	25	307	-22.0×10^{-3}	0.57×10^{-3}	39.5	-3.30×10^{-3}	1.19×10^{-3}	-0.03×10^{-3}	-4.46×10^{-3}

ᵃ $K = (\epsilon-1)[1+\phi(\epsilon-1)]$.

In Table III we tabulate the various quantities in Eqs. (16) and (18) for BaTiO₃ and SrTiO₃ for two different cases of the internal-field coefficient ϕ: (i) $\phi=\frac{1}{3}$ and (ii) ϕ as empirically evaluated by von Hippel et al.[25] The compressibility of SrTiO₃ is from the recent measurements of Poindexter et al.[26] The compressibility of the cubic phase of BaTiO₃ is not known, but it would not be expected to be much different from that of the tetragonal phase at room temperature. This latter value was calculated from the x-ray data of Kabalkina et al.[18] The volume-expansion coefficients were calculated from the x-ray data of Kay and Vousden[27] for BaTiO₃ and Lytle[2] for SrTiO₃.

The results in Table III show that the change in polarizability with temperature at constant volume, i.e., $(\partial\ln\alpha/\partial T)_V$, is the predominant factor in determining the the temperature dependence of the dielectric constant. This conclusion is not strongly affected by the value of the internal-field coefficient chosen. The two volume contributions $\gamma(\partial\ln\alpha/\partial\ln V)_T$ and $-\gamma$ have opposite signs and for the case $\phi=\frac{1}{3}$ are of comparable magnitude. For the case of small ϕ, the thermal-expansion contribution $-\gamma$ is negligible.

As mentioned earlier, α is the total macroscopic polarizability of the material. It can be separated into two components,

$$\alpha=\alpha_{\rm op}+\alpha_{\rm ir}. \qquad (20)$$

The optical, or high-frequency, contribution, $\alpha_{\rm op}$, arises from displacements of the electronic charge distributions of the ions relative to the nuclei. The infrared, or low-frequency contribution $\alpha_{\rm ir}$, arises from the combined effects of the displacements of the ions and the resulting displacement of the electronic charge distributions.

With increasing pressure the ions in the lattice get closer together, and, as a result, the elastic restoring forces increase. Therefore, $\alpha_{\rm ir}$ can be expected to decrease. A priori, the pressure dependence of $\alpha_{\rm op}$ is more difficult to predict since the amount of overlap between electronic wave functions is quite sensitive to changes in interatomic distance.

$\alpha_{\rm op}$ is related to the high-frequency dielectric constant n^2 ($n=$ refractive index) by a relationship similar to Eq. (12) with ϵ replaced by n^2 and α by $\alpha_{\rm op}$, and similarly for the temperature and pressure coefficients in Eqs. (16) and (18). The change of n with temperature at atmospheric pressure is known for both BaTiO₃ and SrTiO₃. No data is available on the pressure dependence of n of BaTiO₃; however, the change of n of SrTiO₃ with pressure up to 1 kbar has been recently measured by Waxler and Weir.[28] Their results yield $(\Delta n/\Delta p)_{25^\circ\rm C} = -12\times10^{-5}$ (kbar)⁻¹. The temperature coefficient is[29] $(\Delta n/\Delta T)_{1\,\rm bar} = -6.2\times10^{-6}$°K⁻¹. From these slopes and the known values of n ($=2.41$), γ and β we get for SrTiO₃

$$(\partial\ln\alpha_{\rm op}/\partial p)_{25\,\rm C} = -61.6\times10^{-5}\ \rm kbar^{-1},$$

$$(\partial\ln\alpha_{\rm op}/\partial T)_V = -0.48\times10^{-5}\ {}^\circ\rm K^{-1}.$$

Now from Eq. (20) we have

$$\left(\frac{\partial\ln\alpha}{\partial T}\right)_V = \frac{\alpha_{\rm op}}{\alpha}\left(\frac{\partial\ln\alpha_{\rm op}}{\partial T}\right)_V + \frac{\alpha_{\rm ir}}{\alpha}\left(\frac{\partial\ln\alpha_{\rm ir}}{\partial T}\right)_V. \qquad (21)$$

The ratios $\alpha_{\rm op}/\alpha$ and $\alpha_{\rm ir}/\alpha$ can be calculated from the known values of ϵ, n, and Eqs. (12) and (20) and the analogous equations in terms of n^2. At 1 bar and 25°C the results are $\alpha_{\rm op}/\alpha=0.62$ and $\alpha_{\rm ir}/\alpha=0.38$ based on $\phi=\frac{1}{3}$. All the quantities in Eq. (21) are known except $(\partial\ln\alpha_{\rm ir}/\partial T)_V$, for which we get by substitution

$$(\partial\ln\alpha_{\rm ir}/\partial T]_V = -12.1\times10^{-5}\ {}^\circ\rm K^{-1}$$

From the above considerations it is clear that the change in $\alpha_{\rm ir}$ is the important factor in determining the temperature and pressure dependences of the dielectric constant of SrTiO₃. The change in $\alpha_{\rm op}$ has a much smaller effect. The situation is undoubtedly similar for BaTiO₃ and other perovskites. Here again, it can be easily shown that this conclusion is not strongly affected by the choice of ϕ.

4. Lattice-Dynamical Approach

The large infrared contribution to the temperature dependence of the dielectric constant is important in

[26] E. H. Poindexter, A. A. Giardini, and G. A. Samara (unpublished).
[27] H. F. Kay and P. Vousden, Phil. Mag. **40**, 1019 (1949).
[28] R. M. Waxler and C. E. Weir (private communication).
[29] F. Gaydon, Travail de diplome, École Fédérale Polytechnique, Zurich, 1955 (unpublished).

relation to the theory of Cochran[6] and Anderson[7] which considers the paraelectric-ferroelectric transition in the perovskites to be the result of an instability of the lattice against a transverse optic mode of long wavelength at $k=0$ caused by the near cancellation of short-range and Coulomb interactions. The Curie-Weiss behavior of ϵ in the cubic phase is associated with the temperature dependence of the frequency of this mode according to the relationship

$$\omega_T{}^2 \propto (T-T_0) \propto 1/\epsilon. \tag{22}$$

At the critical temperature T_0, $\omega_T \rightarrow 0$ and the lattice displacements associated with this mode become unstable and the crystal distorts to the ferroelectric phase. Experimental support for the above T dependence of ω_T has come from far ir dielectric dispersion[30,31] and inelastic-neutron-scattering[32] studies.

In analogy with Eq. (22), the pressure dependence of ϵ in the cubic phase suggests that ω_T may vary with pressure according to the empirical relationship

$$\omega_T{}^2 \propto (p-p_0) \propto 1/\epsilon. \tag{23}$$

There are at present no available data on the pressure dependence of ω_T to check the validity of Eq. (23). A number of severe experimental difficulties have to be surmounted before such a measurement becomes possible.

V. SUMMARY AND CONCLUSIONS

The results of this work can be summarized as follows:

1. The Curie point of $BaTiO_3$ decreased linearly with increasing hydrostatic pressure, but at a rate which varied from -4.6 to $-5.9°C/kbar$ for different samples.

Contributing factors for this variation are believed to be impurities and domain structure.

2. The spontaneous polarization of $BaTiO_3$ decreases slowly with increasing pressure up to the transition pressure, where it drops rapidly. It is shown that this change in P_s is primarily due to the displacement of the Curie point to lower temperatures. However, a small decrease in the magnitude of the dipole moment with increasing pressure is suggested by the data.

3. At constant pressure, the dielectric constant of the nonpolar cubic phase of both compounds obeys the Curie-Weiss law $\epsilon=C/(T-T_0)$. Both C and T_0 are functions of pressure.

4. At constant temperature, the dielectric constant of the cubic phase of both compounds obeys the relationship $\epsilon=C^*/(p-p_0)$. Both C^* and p_0 are functions of temperature.

5. The temperature dependence of the dielectric constant of the cubic phase is separated into volume-dependent and volume-independent contributions. This is done for two different values for the internal-field coefficient. It is shown that the variation of the total macroscopic polarizability with temperature at constant volume is the predominant effect.

6. The total polarizability is separated into an optical and an infrared contribution, and it is shown that the change of the ir polarizability with temperature and pressure is the important factor in determining the change in ϵ. This result is related to the lattice-dynamical theory which associates the Curie-Weiss behavior of ϵ with the temperature dependence of a low-frequency transverse optic mode of the lattice.

[30] A. S. Barker, Jr., and M. Tinkham, Phys. Rev. 125, 1527 (1962).
[31] W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, Phys. Rev. 126, 1710 (1962).
[32] R. A. Cowley, Phys. Rev. Letters 9, 159 (1962).