Theory on the Effect of Hydrostatic Pressure on the Permittivity and Curie Point of Single Crystal Barium Titanate

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The effect of hydrostatic pressure on the permittivity and Curie point of single crystal of barium titanate has been investigated from phenomenological thermodynamic theory. In all previous studies, such correlation has been made in the para-electric state where the reciprocal permittivity is linear with temperature. In contrast, the present paper predicts the variation of permittivity of the material with pressure both in the para-electric and in the ferroelectric state. The change in Curie point under hydrostatic pressure has also been computed. The predicted variation of both the permittivity and the Curie point with pressure are compared with the earlier experimental data and are in reasonably good agreement.

§ 1. Introduction

There are a number of experimental papers on the effect of hydrostatic pressure on the permittivity and the Curie point of single crystal barium titanate.[1-5] However, not a single publication is known which can predict the complete experimental behavior. In a few papers,[2] attempt has been made to correlate the experimental data on permittivity in the paraelectric state where the reciprocal permittivity is linear with temperature. The present investigation is an attempt to predict the permittivity variation of barium titanate single crystal with hydrostatic pressure at any temperature, *i.e.*, in both the paraelectric and in the ferroelectric state, and the change in Curie point with hydrostatic pressure.

§ 2. Theoretical Approach

It has been shown elsewhere[6,7] that the high permittivity and its two-dimensional pressure effect of fine grain ceramic barium titanate could be explained from phenomenological thermodynamic theory if the Devenshire's[8,9] free energy function in strain and polarization is expressed in terms of stress and polarization, the constants of the free energy function are slightly modified from the most recent experimental data on single crystal, and the internal stress model is considered. It will be seen that by using the same modified free energy function, the variation of permittivity and Curie temperature with hydrostatic pressure could be satisfactorily explained.

The free energy function in terms of stress and polarization is given by:

$$
\begin{aligned}
G_1 - G_{10} = & -\frac{1}{2}s_{11}(X_x{}^2 + Y_y{}^2 + Z_z{}^2) - s_{12}(X_x Y_y + Y_y Z_z + Z_z X_x) \\
& -\frac{1}{2}s_{44}(X_y{}^2 + Y_z{}^2 + Z_x{}^2) + (Q_{11}X_x + Q_{12}Y_y + Q_{12}Z_z)P_x{}^2 \\
& + (Q_{12}X_x + Q_{11}Y_y + Q_{12}Z_z)P_y{}^2 + (Q_{12}X_x + Q_{12}Y_y + Q_{11}Z_z)P_z{}^2 \\
& + Q_{44}(X_y P_x P_y + Y_z P_y P_z + Z_x P_z P_x) + A(P_x{}^2 + P_y{}^2 + P_z{}^2) \\
& + B(P_x{}^4 + P_y{}^4 + P_z{}^4) + C(P_x{}^6 + P_y{}^6 + P_z{}^6) \\
& + D(P_x{}^2 P_y{}^2 + P_y{}^2 P_z{}^2 + P_z{}^2 P_x{}^2) \\
& + G(P_x{}^2 P_y{}^4 + P_x{}^4 P_y{}^2 + P_y{}^2 P_z{}^4 + P_y{}^4 P_z{}^2 + P_z{}^2 P_x{}^4 + P_z{}^4 P_x{}^2)
\end{aligned}
\tag{1}
$$

where

X_x, Y_y, Z_z are the normal stress components.

Y_z, Z_x, X_y are the shear stress components,

s_{11}, s_{12}, s_{44} are the elastic compliances,

P_x, P_y, P_z are the components of polarization,

Q_{11}, Q_{12}, Q_{44} are the electrostrictive coefficients,

and A, B, C, D, G are the constants of the free

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energy function, G_{10} being the same function for an unpolarized and unstressed crystal.

The field components may be readily obtained from the free energy function by

$$
\left.
\begin{aligned}
E_x &= \frac{\partial G_1}{\partial P_x} \\
E_y &= \frac{\partial G_1}{\partial P_y} \\
E_z &= \frac{\partial G_1}{\partial P_z} .
\end{aligned}
\right\} \quad (2)
$$

The permittivities in the tetragonal state are given by

$$
\left.
\begin{aligned}
\frac{4\pi}{\varepsilon_a} &= \frac{4\pi}{\varepsilon_{xx}} = \frac{\partial^2 G_1}{\partial P_x{}^2} \\
\frac{4\pi}{\varepsilon_a} &= \frac{4\pi}{\varepsilon_{yy}} = \frac{\partial^2 G_1}{\partial P_y{}^2} \\
\frac{4\pi}{\varepsilon_c} &= \frac{4\pi}{\varepsilon_{yy}} = \frac{\partial^2 G_1}{\partial P_z{}^2} .
\end{aligned}
\right\} \quad (3)
$$

The constants of the free energy function are given by:

$$
\left.
\begin{aligned}
& A = 3.7 \times 10^{-5} \ (T\text{-}108) \ \text{cgs} \\
& B = 0.58 \times 10^{-14}(T\text{-}120) - 2.5 \times 10^{-13} \ \text{cgs} \\
& C = -7.41 \times 10^{-25}(T\text{-}120) + 3.7 \times 10^{-23} \ \text{cgs} \\
& D = 4.0 \times 10^{-13} \ \text{cgs} \\
& G = 6.0 \times 10^{-23} \ \text{cgs} \\
& T = \text{temperature in } °C \\
& Q_{11} = 1.23 \times 10^{-12} \ \text{cgs} \\
& Q_{12} = -0.45 \times 10^{-12} \ \text{cgs} \\
& Q_{44} = 2.7 \times 10^{-12} \ \text{cgs} \\
& s_{11} = 0.87 \times 10^{-12} \ \text{cm}^2/\text{dyne} \\
& s_{12} = -0.335 \times 10^{-12} \ \text{cm}^2/\text{dyne} \\
& s_{44} = 0.89 \times 10^{-12} \ \text{cm}^2/\text{dyne}
\end{aligned}
\right\} \quad (4)
$$

For hydrostatic pressure,

$$
\left.
\begin{aligned}
X_x &= Y_y = Z_z = -\sigma \\
X_y &= Y_z = Z_x = 0 .
\end{aligned}
\right\} \quad (5)
$$

For the spontaneous polarization in the Z-axis, i.e., in the tetragonal state,

$$
E_z = \frac{\partial^2 G_1}{\partial P_z{}^2} = 0 . \quad (6)
$$

From (1), (5) and (6), we readily obtain

$$
P_s{}^2 = \frac{-B + \sqrt{B^2 - 3AC - 0.97119 \times 10^{-6}\sigma C}}{3C} \quad (7)
$$

$$
\frac{4\pi}{\varepsilon_a} = \frac{\partial^2 G_1}{\partial P_x{}^2} = 2A + 0.6476 \times 10^{-6}\sigma + 2DP_s{}^2 + 2GP_s{}^4 \quad (8)
$$

$$
\frac{4\pi}{\varepsilon_c} = \frac{\partial^2 G_1}{\partial P_z{}^2} = 2A + 0.6476 \times 10^{-6}\sigma + 12BP_s{}^2 + 30CP_s{}^4, \quad (9)
$$

where σ is the pressure in kg/cm^2.

Temperature variation of ε_a and ε_c is affected by constants A, B and C which are temperature dependent, and their pressure variation is influenced by the term containing σ.

P_s can be determined from (7) for a certain value of σ. With this calculated P_s and for the same value σ, ε_a and ε_c were calculated from (8) and (9) respectively.

In the paraelectric state, $P_s = 0$, and $\varepsilon_a = \varepsilon_b = \varepsilon$ so that

$$
\frac{4\pi}{\varepsilon} = 2A + 0.647616 \times 10^{-6}\sigma . \quad (10)
$$

Since the constants A, B and C are temperature dependent, one can compute the permittivity at any temperature for a range of pressure in the ferroelectric state from (8) and (9), and in the paraelectric state from (10).

The variation of the Curie point with pressure can be obtained by imposing to P_s the condition that above the Curie point, P_s ceases to become real, i.e., the square root in the expression for P_s in (7) should be zero.

$$
i.e., \quad B^2 - 3AC - 0.97119 \times 10^{-6}\sigma C = 0
$$

$$
i.e., \quad \sigma = \frac{B^2 - 3AC}{0.97119C} . \quad (11)
$$

§3. Results and Discussion

The permittivity value ε_c at 20°C, 95°C, and 150°C, and the Curie temperature T_c were calculated for various values of hydrostatic pressure.

Figure 1 is a graphical plot of ε_c vs. pressure at 20°C. At this temperature, no experimental data are available except those of Leonidova and Polanov, and unfortunately their data appear inaccurate as demonstrated by Cross and Goswami[10] and by Minomura and Sawada.[11] The experimental values of capacitance vs. pressure of Leonidova and Polanov are also presented in this figure. The apparent disagreement is probably due to the fact that Leonidova's sample lost contact during the measurement.

Figure 2 shows the variation of ε_c at 95°C and 150°C with hydrostatic pressure. Theoretical curves are compared with the corresponding experimental curves of Klimowski and Pietrazak. The agreement is very reasonable.

Figure 3 gives the variation of Curie temperature with pressure. The experimental data of