PHENOMENOLOGICAL TREATMENT OF FERRO-ELECTRICITY UNDER HYDROSTATIC PRESSURE

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1. Introduction

Many papers have treated ferroelectric phenomena as a function of temperature, and the dielectric properties with temperature, namely the ferroelectric transition, the spontaneous polarization and hysteresis phenomena, etc. with temperature, have been dealt with in them. It is well known that these phenomena can be explained clearly by Devonshire's theory.[1] Recently, it was discovered by a few researchers including authors that the crystal phase of some dielectric materials was changed from paraelectric phase to ferroelectric phase at the pressure above transition.point under constant temperature by the variance of their atomic distances[2,3]. However, the analysis of this field has been scarcely seen. The purpose of this paper is to explain various dielectric phenomena with pressure successfully by using the expansion formula of the modified Devonshire's free energy with pressure. Namely, this paper treats analytically how dielectric materials behave and exhibit ferroelectricity, when hydrostatic pressure is applied to them. In such a way, the authors elucidated the pressure dependence of the permittivity & the spontaneous polarization and the electric field dependence of the permittivity under constant pressure, etc. in the case of the second order transition & the first order transition concretely. Simultaneously, the authors tried to apply this analysis to the experimental results obtained recently for $BaTiO_3$, $LiH_3(SeO_3)_2$ & $NaNO_3$, etc., and confirmed that this analysis was very useful.

2. Phenomenological Analysis

When the ferroelectric materials whose nature is not piezoelectric in paraelectric phase have been strained by applied stress and then have polarization(P), its free energy(F) is expanded as a function of strain(x) and polarization(P), according to modified Devonshire's theory as follows[4];

$$F(x,P) = \frac{1}{2}\sum_{ij} C_{ij}^P x_i x_j + \frac{1}{2}\sum_{ij} U_{ij}^x P_i P_j + \frac{1}{2}\sum_{ijk} g_{ijk} x_i P_j P_k + \frac{1}{4}\sum_{ijk\ell} \xi_{ijk\ell}^x P_i P_j P_k P_\ell$$
$$+ \frac{1}{6}\sum_{ijk\ell mn} \zeta_{ijk\ell mn}^x P_i P_j P_k P_\ell P_m P_n + \cdots \cdots \cdots \quad (1)$$

Here, as for strain (x_i, x_j) (i, j=1−6), the x_1, x_2 and x_3 are linear strains of x, y and z directions. The x_4, x_5 and x_6 are shear strains. As for polarization $(P_i, P_j, \cdots, P_m, P_n)$ (i=1−3, j=1−3, $\cdots$, n=1−3), P_1, P_2 and P_3 are x, y and z components of polarization. The C_{ij}^P's are the tensor of elastic constant under the condition of constant polarization, and the g_{ijk} is the tensor of electrostrictive constant. The U_{ij}^x, $\xi_{ijk\ell}^x$ & $\zeta_{ijk\ell mn}^x$ are also the tensors of phenomenological coefficients concerning temperature under the condition of constant strain. Under strain(x) being induced by hydrostatic pressure, the following assumptions are satisfied ;

(1) Applied stress is ideally hydrostatic pressure and the strain induced by hydrostatic pressure is proportional to pressure. Therefore, the expressions $x_4 = x_5 = x_6 = 0$ and $x_i = a_1 p$ & $x_j = a_2 p$ or

$x_i = a_3 x_j$ (where a_1, a_2 & a_3 are constant) (i, j=1~3) are assumed.

(2)　The strain is proportional to the square of·polarization for the crystal where the crystal structure in paraelectric phase is centrosymmetry, as is observed for BaTiO3, etc.. Therefore, the relations $x_i = b_1 P_i^2$ & $x_j = b_2 P_j^2$ or $P_i^2 = b_3 P_j^2$ (where b_1, b_2 & b_3 are constant) (i, j=1~3) are assumed.

In order to transform $F(x, P)$ into $F(p, P)$, the following relation is obtained by putting above assumptions into eq. (1) and by neglecting the term less than P^6;

$$F(p, P) = \frac{1}{2} Cp^2 + \frac{1}{2}(u + gp)P^2 + \frac{1}{4}\xi P^4 + \frac{1}{6}\zeta P^6 \qquad (2)$$

Here, C is new elastic constant, g is new electrostrictive constant and u, ξ & ζ are new phenomenological coefficients concerning temperature presented by deriving eq. (2).

First, the electric field(E) in the ferroelectrics is obtained by partially differentiating free energy(F) whose expression is given by eq. (2) with polarization(P);

$$E = \partial F/\partial P = (u + gp)P + \xi P^3 + \zeta P^5 \qquad (3)$$

And still more, dielectric susceptibility(κ) is obtained by partially differentiating electric field whose expression is given by eq. (3) with polarization;

$$1/\kappa = \partial E/\partial P = u + gp + 3\xi P^2 + 5\zeta P^4 \qquad (4)$$

Here, the permittivity $\epsilon = \epsilon_0 \epsilon_r = \kappa + \epsilon_0$, therefore, $\kappa \doteqdot \epsilon$ because of $\epsilon \gg \epsilon_0$ in ordinary ferroelectrics. Let's obtain various dielectric phenomenological equations in paraelectric and ferroelectric phase by using these equations.

2.1　Paraelectric phase

Since the crystal structure in paraelectric phase is centrosymmetry and then the spontaneous polarization does not exist, putting zero into P in eq. (4), the following equation is easily obtained;

$$1/\epsilon \doteqdot u + gp \qquad (5)$$

The eq. (5) predicts that the reciprocal permittivity is proportional to hydrostatic pressure at the given temperature. Here, the pressure(P_0) under $1/\epsilon = 0$ which is called characteristic pressure is obtianed from eq. (5) as follows;

$$p_0 = -u/g \qquad (6)$$

When the permittivity varies with temperature according to Curie-Weiss' law at the given pressure, the reciprocal permittivity is expressed as follows; $1/\epsilon = C_0(T-T_0)$, where C_0 is Curie constant and T_0 is characteristic temperature. If the transition is the second order, T_0 is equal to transition temperature(T_c). Combining this relation and eq. (5), the reciprocal permittivity is expressed as follows;

$$1/\epsilon = C_0(T-T_0) = u + gp \qquad (7)$$

, where C_0 & T_0 are function of pressure and u & g are function of temperature in general.

2.2　Ferroelectric phase

The spontaneous polarization(P_s) exists even when applied electric field is removed away, because the crystal in ferroelectric phase is polar. Therefore, the spontaneous polarization is obtianed by putting zero into E and by putting P_s into P in eq. (3);