

# PHENOMENOLOGICAL TREATMENT OF FERRO- ELECTRICITY UNDER HYDROSTATIC PRESSURE

Sanji FUJIMOTO and Naohiko YASUDA  
Electrical Engineering Dept., Gifu University

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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.<sup>1)</sup> 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<sup>2,3)</sup>. 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<sub>3</sub>, LiH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> & NaNO<sub>3</sub>, 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<sup>4)</sup>;

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

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 ( $P_i, P_j, \dots, P_m, P_n$ ) ( $i=1-3, j=1-3, \dots, n=1-3$ ),  $P_1, P_2$  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  $U_{ij}^x, \xi_{ijkl}^x$  &  $\zeta_{ijklmn}^x$  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) ( $i, j=1\sim 3$ ) 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 BaTiO<sub>3</sub>, 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) ( $i, j=1\sim 3$ ) 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  $P^6$ ;

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

Here,  $C$  is new elastic constant,  $g$  is new electrostrictive constant and  $u, \xi$  &  $\zeta$  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 ( $P$ );

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

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

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

Here, the permittivity  $\epsilon = \epsilon_0 \epsilon_r = \kappa + \epsilon_0$ , therefore,  $\kappa \approx \epsilon$  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;

$$1/\epsilon \approx u + gp \quad (5)$$

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 obtained from eq. (5) as follows;

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

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;

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

, 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 obtained by putting zero into  $E$  and by putting  $P_s$  into  $P$  in eq. (3);

$$(u + gp + \xi P_s^2 + \zeta P_s^4)P_s = 0 \tag{8}$$

Now, let's consider dielectric phenomena in the case of the second order transition and the first order one by using eq. (8).

2.2.1 Second order transition

If the phase transition is the second order, free energy(F) is considered till the term of  $P^4$  and then the  $P^6$  term of the right hand side in eq. (3), eq. (4) & eq. (8) is negligible, based on the Devonshire's phenomenological theory<sup>1)</sup>. Accordingly, the square of the spontaneous polarization is obtained from eq. (8) as follows;

$$P_s^2 = -(u + gp)/\xi \tag{9}$$

The eq. (9) indicates that the square of the spontaneous polarization is proportional to pressure at constant temperature. The pressure where the spontaneous polarization becomes zero is defined the transition pressure( $p_c$ ), that is,  $p_c = -u/g$  from eq. (9). If the transition is the second order, the  $p_c$  is equal to  $p_0$  by comparison with eq. (6). Still more, the reciprocal permittivity is obtained from eq. (4) as follows;

$$1/\epsilon \doteq u + gp + 3\xi P_s^2 \tag{10}$$

By eliminating  $P_s$  from eq. (9) & eq. (10),  $1/\epsilon$  becomes the following expression;

$$1/\epsilon = -2(u + gp) \tag{11}$$

The eq. (11) shows that the reciprocal permittivity is a linear function of pressure with the slope of  $-2g$  at the given temperature, and its slope is twice of that in paraelectric phase in comparison with eq. (5). The spontaneous polarization( $P_s$ ) and the reciprocal permittivity  $1/\epsilon$  in ferroelectric phase are zero at the transition pressure  $p_c (=p_0) = -u/g$  from eq. (9) & eq. (10). In paraelectric phase, the spontaneous polarization is not present and the reciprocal permittivity is zero at the transition pressure  $p_c (=p_0)$  from eq. (5). Accordingly, the spontaneous polarization and the reciprocal permittivity are shown to vary continuously with pressure at the transition pressure under constant temperature, and then its transition is considered to belong to the second order.

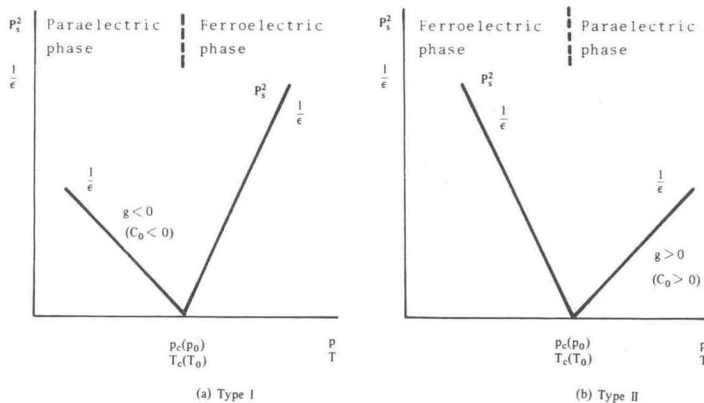


Fig. 1. Schematic temperature & pressure variations (type I, type II) of the spontaneous polarization & the reciprocal permittivity for the second order transition.

The schematic pressure dependence of the square of the spontaneous polarization & the reciprocal permittivity in the state of ferroelectric phase above the transition pressure ( $p_c$ ) is shown in Fig. 1(a), while that in the state of ferroelectric phase below the transition pressure ( $p_c$ ) is shown in Fig. 1(b). If ferroelectric phase is present in the state of  $p > p_c = p_0 = -u/g > 0$ , the slope  $g$  must be negative in paraelectric phase like Fig. 1(a). Therefore, the relation  $u + gp < 0$  holds good in ferroelectric phase because of  $u > 0$  that is,  $-gp > u$  from above condition. On the other hand, if ferroelectric phase is present in the state of  $p < p_c = p_0 = -u/g > 0$ , the slope  $g$  must be positive in paraelectric phase like Fig. 1(b). Accordingly, the relation  $u + gp < 0$  also holds good in ferroelectric phase because of  $u < 0$ , that is,  $pg < -u$ . Moreover, the value of the right hand side of eq. (9) must be positive. These conditions require  $\xi > 0$ , which is the condition of the second order transition.

The square of the spontaneous polarization is obtained under constant pressure by putting eq. (7) into eq. (9) as follows;

$$P_s^2 = -C_0(T-T_0)/\xi \quad (12)$$

The reciprocal permittivity is obtained under constant pressure by putting eq. (7) into eq. (10) and by using eq. (12) as follows;

$$1/\epsilon = -2C_0(T-T_0) \quad (13)$$

If the temperature dependence of the coefficient  $\xi$  is assumed to be negligible, the square of the spontaneous polarization & the reciprocal permittivity are proportional to temperature from eq. (12) & eq. (13), respectively. The slope of the reciprocal permittivity to temperature in ferroelectric phase is twice of that in paraelectric phase from eq. (13) in comparison with eq. (7). In ferroelectric phase, the spontaneous polarization & the reciprocal permittivity are zero at the transition temperature  $T_c (=T_0)$  under constant pressure from eq. (12) & eq. (13). In paraelectric phase, the spontaneous polarization is not present and the reciprocal permittivity is zero at the transition temperature  $T_c (=T_0)$  from eq. (7). Therefore, the spontaneous polarization & the reciprocal permittivity change continuously at the transition temperature  $T_c (=T_0)$ . Above facts confirm that the transition is the second order.

The schematic temperature dependence of the square of the spontaneous polarization & the reciprocal permittivity is shown too, in Fig. 1. When ferroelectric phase is present at temperature  $T > T_c (=T_0)$ , the slope  $C_0$  must be negative in paraelectric phase like Fig. 1(a). Therefore, the relation  $-C_0(T-T_0) > 0$  holds good in ferroelectric phase. When ferroelectric phase is present at the temperature of  $T < T_c (=T_0)$ , the slope  $C_0$  must be positive in paraelectric phase like Fig. 1(b). Therefore, the relation  $-C_0(T-T_0) > 0$  holds good in this case, too. Accordingly, the relation  $\xi > 0$  is required from eq. (12). If the transition is the second order, the coefficient  $\xi$  must be positive as well as in the case of pressure.

Furthermore, the electric field in ferroelectric phase is obtained from eq. (3) as follows;

$$E = (u + gp)P_s + \xi P_s^3 \quad (14)$$

The dielectric hysteresis loop can be predicted under constant pressure, because the electric field is expressed as the equation of 3th power of  $P_s$ . The relation between the electric field and the permittivity is obtained by combining eq. (14) and eq. (10) and by eliminating  $P_s$  as follows;

$$E = \frac{1}{3} \left( \frac{1}{\epsilon} + \frac{2}{\epsilon_2} \right) \left\{ \frac{1}{3\xi} \left( \frac{1}{\epsilon} - \frac{1}{\epsilon_2} \right) \right\}^{\frac{1}{2}} \quad (15)$$

Here

$$1/\epsilon_2 = u + gp = g(p - p_0) \quad (16)$$

$1/\epsilon_2$  is constant under the given temperature & pressure. The eq. (15) indicates the electric field dependence of the permittivity in ferroelectric phase under constant pressure, and it is found that the permittivity decreases with increasing electric field. In the special case, the permittivity at no electric field is expressed by putting zero into  $E$  of eq. (15) and by using eq. (16) as follows;

$$\epsilon = -\epsilon_2/2 = 1/2g(p_0 - p)$$

Therefore, the permittivity at no electric field depends on pressure & coefficient  $g$ .

### 2.2.2 First order transition

When the following two conditions are satisfied in the case of the first order transition, the spontaneous polarization is present at the transition pressure ( $p_c$ ).

(I) The free energy of ferroelectric phase must be equal to that of paraelectric phase at the transition pressure ( $p_c$ ). Accordingly, from eq. (2), the relation

$$\left[ F(p, P) \right]_{\substack{p=p_c \\ P=P_s=0}} = \left[ F(p, P) \right]_{\substack{p=p_c \\ P=P_s}}$$

must be satisfied. That is,

$$u + gp_c + \frac{1}{2} \xi P_s^2 + \frac{1}{3} \zeta P_s^4 = 0 \quad (17)$$

holds good.

(II) The free energy of ferroelectric phase must have the minimized value with polarization. Accordingly, from eq. (2), the relation

$$\left[ \partial F / \partial P \right]_{\substack{p=p_c \\ P=P_s}} = 0$$

must be satisfied. That is,

$$u + gp_c + \xi P_s^2 + \zeta P_s^4 = 0 \quad (18)$$

holds good. Combining eq. (17) and eq. (18), and eliminating  $(u + gp_c)$ , the square of the spontaneous polarization at the transition pressure is expressed as follows;

$$P_s^2 = -3\xi/4\zeta > 0, \quad \text{therefore } \xi\zeta < 0 \quad (19)$$

On the other hand, the spontaneous polarization in paraelectric phase does not exist. Hence, the spontaneous polarization changes discontinuously at the transition pressure. This is the character of the first order transition. The following expression is obtained by putting the  $P_s^2$  of eq. (19) into that of eq. (17);

$$p_c = p_0 + 3\xi^2/16g\zeta \quad (20)$$

Here, the  $p_0$  is given by  $p_0 = -u/g > 0$ , and  $p_c$  is the transition pressure as mentioned above.

Schematic pressure variation of  $P_s$  &  $1/\epsilon$  for the first order transition is shown in Fig. 2.

Fig. 2(a) corresponds to the transition from paraelectric phase to ferroelectric phase at  $p_c$  with increasing pressure, and Fig. 2(b) corresponds to the transition from ferroelectric phase to paraelectric phase. In Fig. 2(a), the following conditions exist;  $p_0 > p_c$ ,  $g < 0$  from paraelectric phase and  $u > 0$  because of  $p_0 = -u/g > 0$ . By putting these relations into eq. (20), the relation  $\xi > 0$  is obtained and then  $\xi < 0$  is obtained from eq. (19). In Fig. 2(b), the following conditions exist;  $p_c > p_0$ ,  $g > 0$  from paraelectric phase and  $u < 0$  because of  $p_0 = -u/g > 0$  (corresponding to, for example,  $\text{BaTiO}_3$ ). By putting these relations into eq. (20), the relation  $\xi > 0$  is obtained and then  $\xi < 0$  is obtained from eq. (19), too. Therefore, in the case of the first order transition, these relations  $\xi > 0$  &  $\xi < 0$  hold good.

Let's obtain the spontaneous polarization in ferroelectric phase under above conditions. The square of the spontaneous polarization is obtained from eq. (8) &  $P_s \neq 0$  as follows;

$$P_s^2 = -\frac{\xi}{2\xi} \left\{ 1 + \sqrt{1 - \frac{4\xi}{\xi^2}(u + gp)} \right\} \quad (21)$$

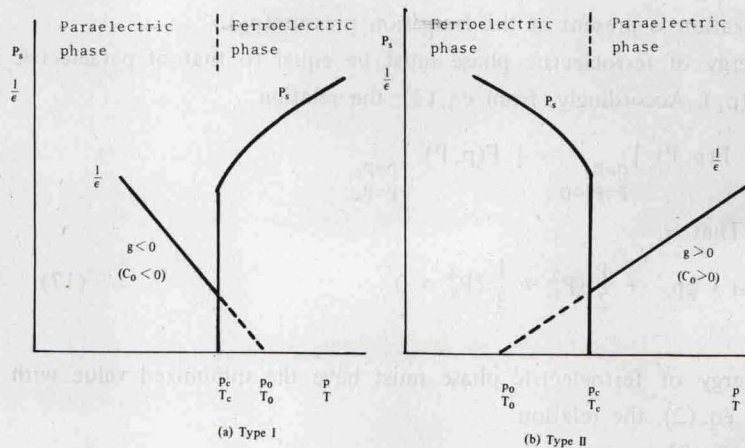


Fig. 2. Schematic temperature & pressure variations (type I, type II) of the spontaneous polarization & the reciprocal permittivity for the first order transition.

The eq. (21) shows the fact that the square of the spontaneous polarization varies according to irrational function with pressure. The reciprocal permittivity is obtained by putting  $P_s^2$  of eq. (21) into that of eq. (4);

$$\frac{1}{\epsilon} = -4(u + gp) + \frac{\xi^2}{\xi} \left\{ 1 + \sqrt{1 - \frac{4\xi}{\xi^2}(u + gp)} \right\} \quad (22)$$

The value of the reciprocal permittivity  $1/\epsilon_{cf}$  in ferroelectric phase at the transition pressure ( $p_c$ ) is expressed by putting  $p_c$  of eq. (20) into  $p$  of eq. (22);

$$1/\epsilon_{cf} = 3\xi^2 / 4\xi$$

The value of the reciprocal permittivity  $1/\epsilon_{cp}$  in paraelectric phase at the transition pressure is obtained by putting  $p_c$  of eq. (20) into  $p$  of eq. (5);

$$1/\epsilon_{cp} = 3\xi^2 / 16\zeta$$

The temperature dependence of the spontaneous polarization and the reciprocal permittivity is expressed by putting eq. (7) into eq. (21) & eq. (22) respectively as follows;

$$P_s^2 = -(\xi/2\zeta) \left\{ 1 + \sqrt{1 - (4\zeta C_0/\xi^2)(T - T_0)} \right\} \quad (23)$$

$$1/\epsilon = -4C_0(T - T_0) + (\xi^2/\zeta) \left\{ 1 + \sqrt{1 - (4\zeta C_0/\xi^2)(T - T_0)} \right\} \quad (24)$$

From eq. (23), when the temperature dependence of the coefficients  $\xi$  &  $\zeta$  is negligible, the square of the spontaneous polarization varies with temperature according to irrational function.

The value of the spontaneous polarization at the transition temperature ( $T_c$ ) is obtained in the same manner as in the case of the transition pressure. Therefore, the following relations are obtained from the expressions

$$[F(T, P)]_{\substack{T=T_c \\ P=P_s=0}} = [F(T, P)]_{\substack{T=T_c \\ P=P_s}} \quad \text{and} \quad [\partial F/\partial P]_{\substack{T=T_c \\ P=P_s}} = 0$$

by putting eq. (7) into eq. (2);

$$C_0(T_c - T_0) + (1/2)\xi P_s^2 + (1/3)\zeta P_s^4 = 0$$

$$C_0(T_c - T_0) + \xi P_s^2 + \zeta P_s^4 = 0$$

By eliminating  $(T_c - T_0)$  from above two formulas, the same formula as eq. (19) is obtained for the spontaneous polarization at  $T_c$ , and the transition temperature ( $T_c$ ) is obtained by putting it into  $P_s^2$  of above formula;

$$T_c = T_0 + 3\xi^2/16C_0\zeta \quad (25)$$

The sign of the coefficients  $\xi$  &  $\zeta$  in this case is determined similarly as in the case of pressure for the first transition by substituting  $T, T_0, T_c$  &  $C_0$  for  $p, p_0, p_c$  &  $g$  respectively in the case of pressure like Fig. 2.

Moreover, the relation between permittivity and electric field of the first order transition is obtained under constant pressure & temperature by combining eq. (3) & eq. (4) and by eliminating  $P$  as follows;

$$E = \frac{1}{5} \left[ \frac{1}{\epsilon} + \frac{4}{\epsilon_1} - \frac{3\xi^2}{5\zeta} \left\{ 1 + \sqrt{1 - \frac{20\zeta}{9\xi^2} \left( \frac{1}{\epsilon_1} - \frac{1}{\epsilon} \right)} \right\} \right] \times \left[ \frac{-3\xi}{10\zeta} \left\{ 1 + \sqrt{1 - \frac{20\zeta}{9\xi^2} \left( \frac{1}{\epsilon_1} - \frac{1}{\epsilon} \right)} \right\} \right]^{\frac{1}{2}} \quad (26)$$

Here  $1/\epsilon_1 = u + gp$ , and  $1/\epsilon_1$  is constant under the given pressure & temperature.

### 3. Application of This Analysis to the Measured Value

Let's examine the suitability of above mentioned analytic results in the cases of  $\text{LiH}_3(\text{SeO}_3)$  (briefly L. H. S.) &  $\text{NaNO}_3$  which belong to the second order transition, and of  $\text{BaTiO}_3$  &  $\text{Pb}(\text{Ti} + \text{Sn})\text{O}_3$  which belong to the first order transition. The details of these samples are shown in table 1.



Table 1. Samples and high pressure apparatus.

		$\text{LiH}_3(\text{SeO}_3)_2$	$\text{NaNO}_3$	$\text{BaTiO}_3$	$\text{Pb}(\text{Ti}+\text{Sn})\text{O}_3$
Preparation		Evaporation from saturated water solution of L.H.S. (Crystal)	Bridgman's method, using powder $\text{NaNO}_3$ obtained by recrystallization. (Crystal)	Melting method, using KF as a flux. (Crystal)	Press and calcination of the mixture of 75 % $\text{SnO}_2$ and 25 % $\text{TiO}_2$ , using $\text{PbO}$ as a flux. (Ceramic)
Di- mension	Thickness d (mm)	0.5 - 1.0	0.28	0.5	0.2
	Area S ( $\text{cm}^2$ )	0.3 - 0.7	0.3	0.2 - 0.6	0.5 - 0.6
Space group		$\text{P}2_1/\text{n}$ (Paraelectric phase) Centrosymmetry	$\text{R}3\text{C}$ (Paraelectric phase) Centrosymmetry	$\text{Pm}3\text{m}$ (Paraelectric phase) Centrosymmetry	(Ceramic)
High pressure apparatus		a 30-kbar hydrostatic pressure apparatus, liquid pressure transmitting medium (a 50-50 mixture of normal pentane and isopentane)	a 100-kbar six-anvil cubic press, solid pressure transmitting medium (Pyrophyllite)	The same as in the case of L.H.S.	(Atmospheric pressure)

### 3.1 Second order transition

(i) The pressure dependence of the permittivity and the spontaneous polarization; The pressure dependence of the reciprocal permittivity of L. H. S. obtained by G. A. Samara is shown as a dotted line in Fig. 3(a), and the pressure dependence of the spontaneous polarization ( $P_s$ ) & the square of  $P_s$  is shown as a dotted line in Fig. 3(b)<sup>5</sup>. The L. H. S. belongs to type II in Fig. 1(b), and then the second order transition. Above the transition pressure  $p_c (= p_0) = 20.8$  kbar, L. H. S. belongs to  $\text{P}2_1/\text{n}$  in the space group, and is centrosymmetry and paraelectric phase. Below the transition pressure, L. H. S. is ferroelectric phase. The  $g$  is obtained from the slope of  $1/\epsilon$  to  $p$

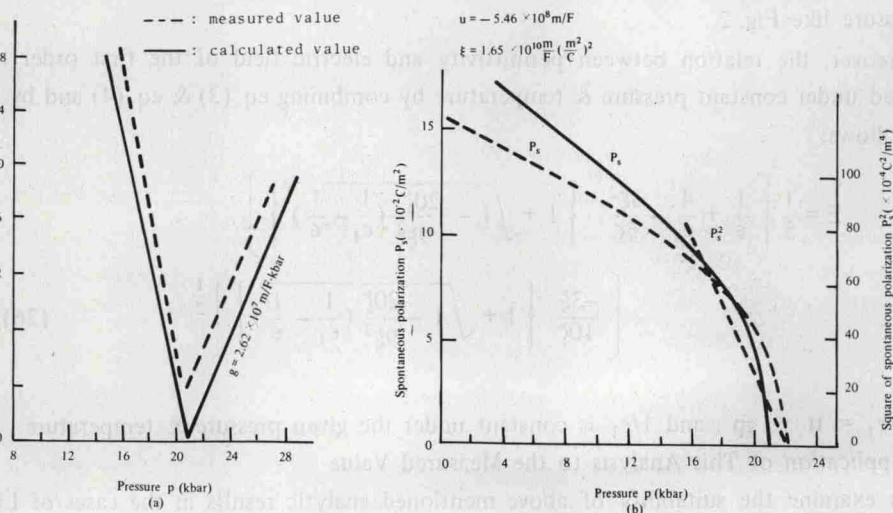


Fig. 3. (a) The pressure dependence of the reciprocal relative permittivity of  $\text{LiH}_3(\text{SeO}_3)_2$  at  $23^\circ\text{C}$ . (b) The pressure dependence of the spontaneous polarization & the square of spontaneous polarization of  $\text{LiH}_3(\text{SeO}_3)_2$  at  $22^\circ\text{C}$ .

in paraelectric phase above the transition pressure in Fig. 3(a);  $g = 2.62 \times 10^7$  m/F · kbar or  $1.85 \times 10^{-5}$ /kbar CGSesu. The  $u$  is obtained by eq. (6);  $u = -5.46 \times 10^8$  m/F or  $-3.85 \times 10^{-4}$  CGSesu. The  $\xi$  is given by putting the value of the square of  $P_s$  which is obtained at arbitrary pressure from Fig.3(b) and the values of  $g$  &  $u$  into eq. (9);  $\xi = 1.65 \times 10^{10} \text{ m}^5/\text{F} \cdot \text{C}^2$  or  $1.29 \times 10^{-13} \text{ cm}^4/\text{esu}^2$  CGSesu. The calculated curve of the pressure dependence of the reciprocal relative permittivity is obtained by putting above values into eq. (11), and is expressed as a solid line in Fig. 3(a). The solid line coincides approximately with the dotted line which stands for the measured value. While the slope  $g$  of  $1/\epsilon$  to  $p$  in ferroelectric phase should be twice of that in paraelectric phase by comparing eq. (11) with eq. (5), the value in measurement is 2.4 times from Fig. 3(a). The calculated curve of  $P_s$  versus  $p$  obtained by putting above values of  $g$ ,  $u$  &  $\xi$  into eq. (9) is shown as a solid line in Fig. 3(b). From this figure, it is found that the measured value which is shown as the dotted line follows to eq. (9) approximately.

(ii) The electric field dependence of the permittivity; Below the transition pressure,  $\text{NaNO}_3$  belongs to  $R\bar{3}C$  in the space group, and is centrosymmetry and shows paraelectric phase. However, above the transition pressure, the crystal structure of  $\text{NaNO}_3$  changes to  $R3C$  and non-centrosymmetry and then  $\text{NaNO}_3$  shows ferroelectric phase. Therefore, it belongs to the type I in Fig. 1(a). The pressure dependence of the reciprocal relative permittivity of  $\text{NaNO}_3$  is shown in the paper reported by the authors<sup>2,3</sup>) and is expressed as the straight line which passes through the coordinates of ( $p=37$  kbar,  $1/\epsilon_r=0.093$ ) & ( $45$  kbar,  $0.019$ ) in paraelectric phase. The values of  $g$  &  $u$  are obtained similarly as in the case of L. H. S. from these data;  $g = -8.81 \times 10^8$  m/F · kbar,  $u = 4.14 \times 10^{10}$  m/F. Furthermore, the value of  $\xi$  is calculated from eq. (9) by using  $P_s = 2.15 \times 10^{-2} \text{ C/m}^2$  at  $p=60$  kbar from the pressure dependence of the spontaneous polarization<sup>2,3</sup>);  $\xi = 2.48 \times 10^{13} \text{ m}^5/\text{F} \cdot \text{C}^2$ . Here, since the transition pressure from paraelectric phase to ferroelectric phase in the case of  $\text{NaNO}_3$  is very high, liquid medium like in the case of L. H. S. can't be used as a pressure transmitting medium. In this case, solid medium called pyrophyllite is used as a pressure transmitting medium and then ideal hydrostatic pressure can't be strictly applied to the sample  $\text{NaNO}_3$ . Therefore, the measured values in the case of  $\text{NaNO}_3$  don't coincide with the calculated values

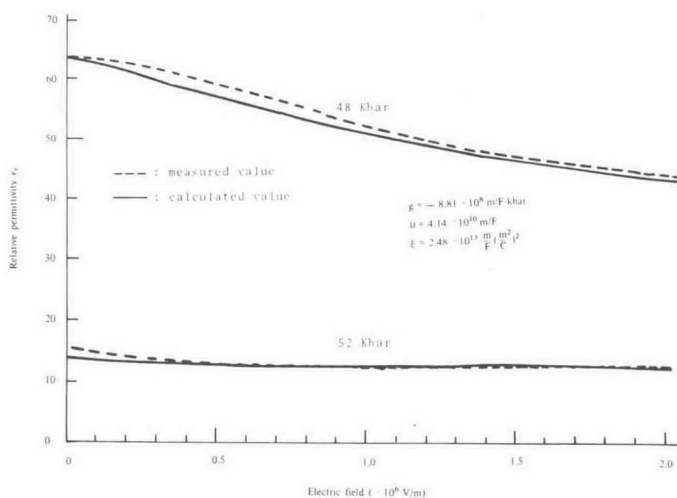


Fig. 4. Effect of external electric field on the relative permittivity of powder  $\text{NaNO}_3$  under various pressures.

so well as in the case of L. H. S. The measured dc-electric field dependence of the relative permittivity of the sample  $\text{NaNO}_3$  with the thickness  $d=0.28$  mm is expressed as a dotted line in Fig. 4 whose curves are at  $p=48$  kbar &  $p=52$  kbar in ferroelectric phase<sup>2,3</sup>). The calculated curve of dc-electric field  $E=V/d$  dependence of the relative permittivity is obtained by putting above values of  $g$ ,  $u$  &  $\xi$  into eq. (15). This curve is shown as a solid line in Fig. 4 and coincides almost with the dotted line which shows the measured value.

Subsequently, the dc-electric field dependence of the relative permittivity ( $\epsilon_r$ ) at  $p=48$  kbar, constant  $g$  and constant  $u$  under various  $\xi$ 's, that is,  $\xi_1$ ,  $10\xi_1$  &  $10^2\xi_1$  etc. is shown in Fig. 5(a) from eq. (15). The decreasing rate of  $\epsilon_r$  with increasing electric field  $E$  increases with increasing value of  $\xi$ , and the value of  $\epsilon_r$  at constant  $E$  decreases with increasing value of  $\xi$  from Fig. 5(a).

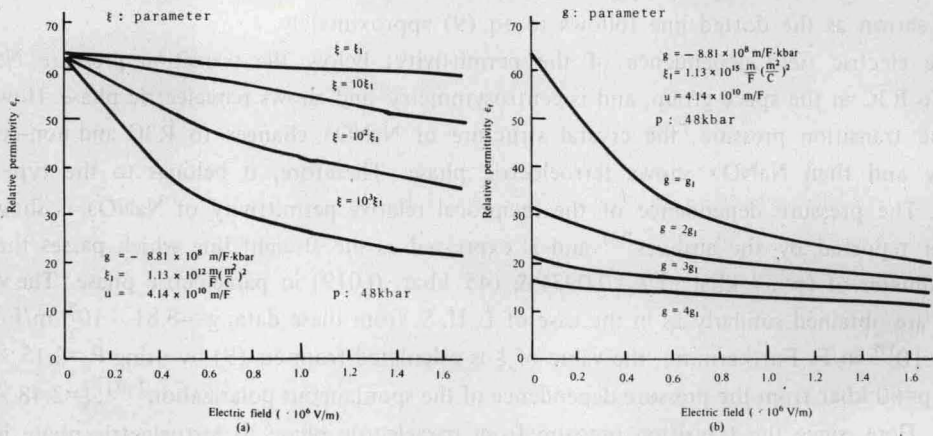


Fig. 5. Effect of external electric field on the relative permittivity under various  $\xi$ 's (a) &  $g$ 's (b).

The dc-electric field dependence of the relative permittivity ( $\epsilon_r$ ) at  $p=48$  kbar, constant  $u$  and constant  $\xi$  under various  $g$ 's, that is,  $g_1$ ,  $2g_1$  &  $3g_1$  etc. is shown in Fig. 5(b) from eq. (15). The decreasing rate of  $\epsilon_r$  with increasing electric field  $E$  increases with decreasing value of  $g$ , and the value of  $\epsilon_r$  at constant  $E$  decreases with increasing of the value of  $g$ .

### 3.2 First order transition

(i) The pressure dependence of the permittivity and the spontaneous polarization; The pressure dependence of the reciprocal relative permittivity at  $T=23$  °C,  $60$  °C &  $85$  °C and the pressure dependence of the spontaneous polarization at  $T=23$  °C &  $45$  °C of  $\text{BaTiO}_3$  given by G.A.Samara are shown as a dotted line in Fig. 6(a) & (b) respectively<sup>6</sup>).  $\text{BaTiO}_3$  shows ferroelectric phase below the transition pressure( $p_c$ ) and paraelectric phase above  $p_c$  and then belongs to type II in Fig. 2 (b). The value of  $g$  is obtained from the curve at  $T = 23$  °C in paraelectric phase in Fig. 6(a);  $g=2.82 \times 10^6$  m/F-kbar. The value of  $u$  is calculated from eq. (6) by using the characteristic pressure  $p_0=18$  kbar which is the measured value and the above value of  $g$ ;  $u=-5.08 \times 10^7$  m/F. Moreover, the values of  $\xi$  &  $\zeta$  are calculated by putting the value of  $P_s$  at arbitrary pressure (in this case, the value of  $P_s$  at the transition pressure) of the curve at  $T=23$  °C in Fig. 6(b) into eq. (19), and simultaneously putting  $p_0=18$  kbar &  $p=20$  kbar into eq. (20);  $\xi=-1.33 \times 10^9$  m<sup>5</sup>/F·C<sup>2</sup> &  $\zeta=5.93 \times 10^{10}$  m<sup>9</sup>/F·C<sup>4</sup>. The calculated curves of  $1/\epsilon_r$  versus  $p$  &  $P_s$  versus  $p$  are obtained by putting above values of  $g$ ,  $u$ ,  $\xi$  &  $\zeta$  into eq. (22) & eq. (21) and are shown as a solid line of  $T=23$  °C in Fig. 6(a) & (b) respectively.

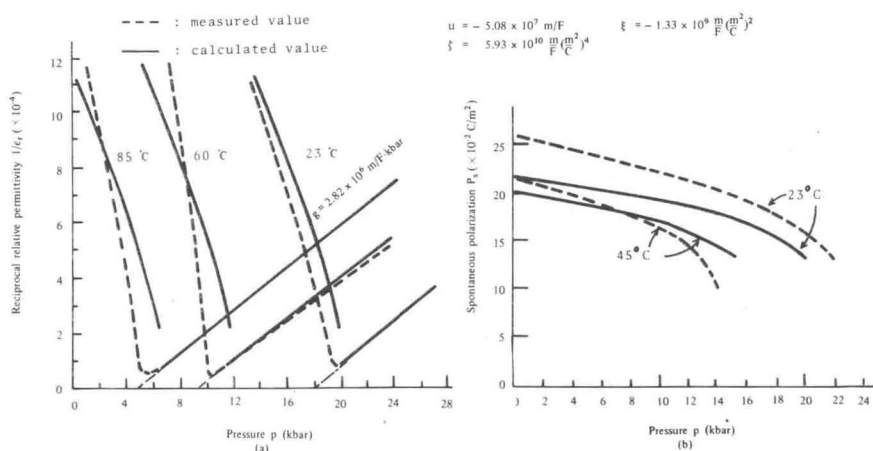


Fig. 6. The pressure dependence of (a) the reciprocal relative permittivity & (b) the spontaneous polarization of single crystal  $\text{BaTiO}_3$  with temperature parameter.

A little difference is seen between the calculated value and the measured one, and this reason is considered to be as follows;

(1) Though the value of  $1/\epsilon_r$  must be minimized value at the transition pressure and the spontaneous polarization  $P_s$  must be zero at this pressure theoretically, the pressure where  $1/\epsilon_r$  is minimized value is 20 kbar and the pressure where  $P_s$  is zero is 22 kbar as shown as a dotted line in Fig. 6(a) & (b), then the difference between these values is 2 kbar.

(2) The coefficients  $u$ ,  $g$ ,  $\xi$  and  $\zeta$  are assumed to be independent of pressure analytically here. However, practically, these coefficients will depend on pressure more or less.

Anyway, the experimental error could not be escaped even if modern equipments were used in such a measurement.

Let's examine the temperature dependence of the coefficients  $u$  &  $g$ . The coefficient  $g$  is considered to be independent of temperature, because the slope  $g$  of  $1/\epsilon_r$  to  $p$  in paraelectric phase is constant under various temperatures. The temperature dependence of the coefficient  $u$  will be

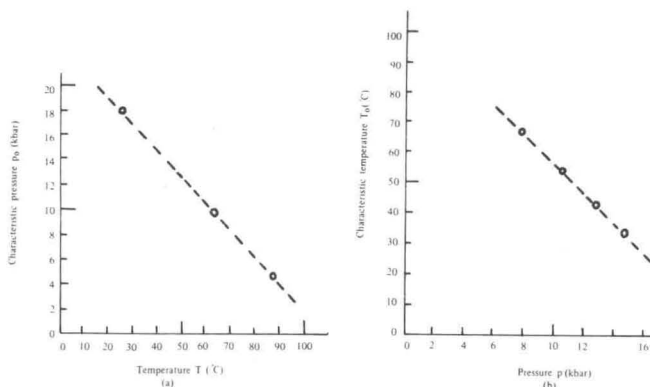


Fig. 7. (a) The temperature dependence of the characteristic pressure  $P_0$  & (b) the pressure dependence of the characteristic temperature  $T_0$  of single crystal  $\text{BaTiO}_3$ .

found by investigating the temperature dependence of the characteristic pressure ( $p_0$ ) by using eq.(6). The characteristic pressure ( $p_0$ ) versus temperature is obtained by replotting from Fig.6(a), and Fig.7(a) shows these relations. From Fig.7(a), it is noticed that the characteristic pressure decreases linearly with increasing temperature. Therefore, by reminding the relation  $u = -gp_0$ , the coefficient  $u$  is expressed as follows;

$$u = -g(a_1 - \beta_1 T) \quad (27)$$

where  $a_1 = 22.8$  kbar &  $\beta_1 = 0.217$  kbar/°C from Fig. 7(a). By putting eq.(27) into  $u$  of eq. (21) & eq. (22),

$$\frac{1}{\epsilon_r} = 4 \left\{ g(a_1 - \beta_1 T) - gp \right\} + \frac{\xi^2}{\zeta} \left[ 1 + \sqrt{1 + \frac{4\zeta}{\xi^2} \{g(a_1 - \beta_1 T) - gp\}} \right] \quad (28)$$

and

$$P_s^2 = -\frac{\xi}{2\zeta} \left[ 1 + \sqrt{1 + \frac{4\zeta}{\xi^2} \{g(a_1 - \beta_1 T) - gp\}} \right] \quad (29)$$

are obtained, and then the effect of temperature is added to eq. (22) & eq. (21) respectively. The curves of  $1/\epsilon_r$  versus  $p$  &  $P_s$  versus  $p$  at  $T = 60^\circ\text{C}$  &  $85^\circ\text{C}$  calculated from eq. (28) & eq. (29) are shown as a solid line in Fig. 6(a) & (b) respectively.

The temperature versus reciprocal relative permittivity with pressure parameter and the temperature versus spontaneous polarization with pressure parameter are shown as a dotted line in Fig. 8(a)

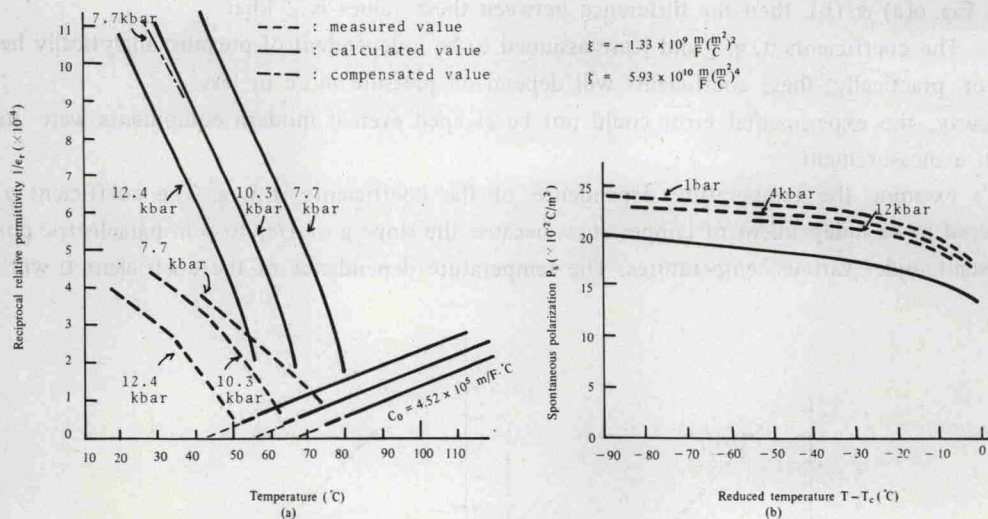


Fig. 8. The temperature dependence of (a) the reciprocal relative permittivity & (b) the spontaneous polarization of single crystal  $\text{BaTiO}_3$  with pressure parameter.

& (b) respectively. In order to consider the pressure dependence of the spontaneous polarization shown in eq. (23) and the relative permittivity shown in eq. (24), first, the pressure dependence of  $C_0$  &  $T_0$  must be examined. The slope  $C_0$  of  $1/\epsilon_r$  to  $T$  in paraelectric phase above the transition temperature ( $T_c$ ) in Fig. 8(a) is constant under various pressure parameters, that is,  $C_0 = 4.52 \times 10^5$  m/F·°C and then is independent of pressure. On the other hand, the characteristic temperature ( $T_0$ )

under  $1/\epsilon_r=0$  versus pressure is obtained by replotting from Fig. 8(a) as shown in Fig. 7(b), then it is found that the characteristic temperature( $T_0$ ) decreases linearly with increasing pressure. Accordingly,  $T_0$  is expressed as follows;

$$T_0 = a_2 - \beta_2 p \quad (30)$$

where  $a_2=104^\circ\text{C}$  &  $\beta_2=4.92^\circ\text{C/kbar}$  from Fig. 7(b). By putting eq. (30) into  $T_0$  of eq. (23) & eq. (24), the following formulas are obtained;

$$\frac{1}{\epsilon_r} = -4C_0(T - a_2 + \beta_2 p) + \frac{\xi^2}{\zeta} \left\{ 1 + \sqrt{1 - \frac{4\zeta C_0}{\xi^2} (T - a_2 + \beta_2 p)} \right\} \quad (31)$$

$$P_s^2 = -\frac{\xi}{2\zeta} \left\{ 1 + \sqrt{1 - \frac{4\zeta C_0}{\xi^2} (T - a_2 + \beta_2 p)} \right\} \quad (32)$$

The temperature dependence of  $1/\epsilon_r$  at pressure parameter  $p=7.7, 10.3$  &  $12.4$  kbar is expressed as a solid line in Fig. 8(a) by putting the previous values of  $\xi$  &  $\zeta$  at  $T=23^\circ\text{C}$  and above values of  $C_0, a_2$  &  $\beta_2$  into eq. (31). The temperature dependence of  $P_s$  is also expressed similarly as a solid line in Fig. 8(b) from eq. (32). Here, since the abscissa in Fig. 8(b) is the reduced temperature ( $T - T_c$ ), the characteristic curves with each pressure parameter overlap as a one line. Comparable large difference between the measured value and the calculated one is observed in Fig. 8(a). This cause is considered to be based on the temperature & pressure dependence of the coefficients  $C_0, \xi$  &  $\zeta$ . Let's consider this effect subsequently. The pressure dependence of the transition temperature( $T_c$ ) must be same as that of the characteristic temperature( $T_0$ ) from eq. (25). However, the paper reports that there is some difference between  $dT_c/dp=-5.5^\circ\text{C/kbar}$  and  $dT_0/dp=-4.8^\circ\text{C/kbar}$  in experimental value<sup>6</sup>). Furthermore, though all curves which are the reduced temperature ( $T-T_c$ ) versus spontaneous polarization with pressure parameters must overlap as a one line, the value of  $P_s$  decreases gradually with increasing pressure parameter like a dotted line (or the measured value) in Fig. 8(b). These facts suggest that the coefficients  $C_0, \xi$  &  $\zeta$  depend on pressure a little. However, the temperature dependence of the coefficient  $\zeta$  of higher order of  $P_s$  in the expansion formula of the free energy is considered to be extremely small, and therefore, the pressure dependence of the coefficient  $\zeta$  is also assumed to be extremely small. The slope  $C_0$  is known to be independent of pressure from experimental results. Consequently, in this case, the pressure dependence of the coefficient  $\xi$  should be considered. Here, let's add the little quantity  $\Delta\xi$  to the value of  $\xi$  to compensate  $\xi$ . In order to obtain the value of  $\Delta\xi$ , the following method is performed, that is, from eq. (21),

$$dP_s/dp = -g\zeta/2P_s \sqrt{\xi^2 - 4\zeta(u + gp)} \quad (33)$$

still more, by substituting  $\xi + \Delta\xi$  for  $\xi$  in eq. (33)

$$dP_s/dp = -g\zeta/2P_s \sqrt{(\xi + \Delta\xi)^2 - 4\zeta(u + gp)} \quad (34)$$

First, let's put  $p=7.7$  kbar and the previous values of  $u, g, \xi$  &  $\zeta$  at  $T=23^\circ\text{C}$  into eq. (33) & eq. (34), and put simultaneously the values of  $dP_s/dp$  obtained from the slope of the experimental curve (or the dotted line) & the calculated one (or the solid line) at  $p=7.7$  kbar &  $T=23^\circ\text{C}$  in Fig. 6(b), that is,  $dP_s/dp=3.80 \times 10^{-3} \text{ C/m}^2 \cdot \text{kbar}$  (or the measured value) &  $dP_s/dp=3.13 \times 10^{-3} \text{ C/m}^2 \cdot \text{kbar}$  (or the calculated value) into eq. (34) & eq. (33) respectively. Next, let's take the ratio eq. (34) to eq. (33) in order to find the value of  $\Delta\xi$ ;  $\Delta\xi=0.373 \times 10^9 \text{ m}^5/\text{F} \cdot \text{C}^2$ . The compensated curve of  $1/\epsilon_r$  versus  $T$  obtained by calculation is shown as a dot-dash-line in Fig. 8(a) by putting

$\xi + \Delta\xi = -0.96 \times 10^9 \text{ m}^5/\text{F}\cdot\text{C}^2$  into  $\xi$  of eq. (24). In this case, the compensated quantity  $\Delta\xi$  is 28% of the previous value of  $\xi$ , and the calculated value of  $1/\epsilon_r$  approaches to the measured value by about 36% in comparison with the previous case.

(ii) The electric field dependence of the permittivity; The temperature dependence of the reciprocal relative permittivity of the ceramic ( $\text{PbTiO}_3 25\% + \text{PbSnO}_3 75\%$ ) at atmospheric pressure obtained by the authors is shown as a dotted line in Fig. 9(a). The slope  $C_0$  of  $1/\epsilon_r$  to T in

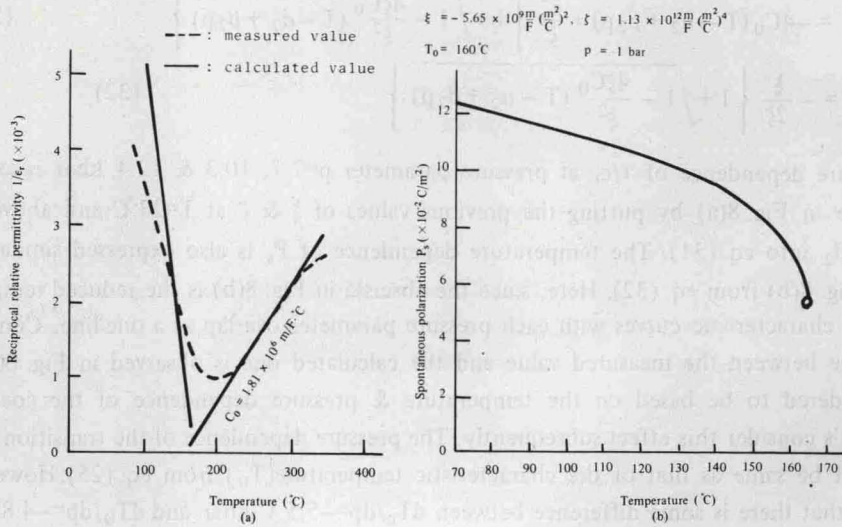


Fig. 9. The temperature dependence of (a) the reciprocal relative permittivity & (b) the spontaneous polarization of  $\text{Pb}(\text{Ti}(25\%)+\text{Sn}(75\%))\text{O}_3$  at 1 bar.

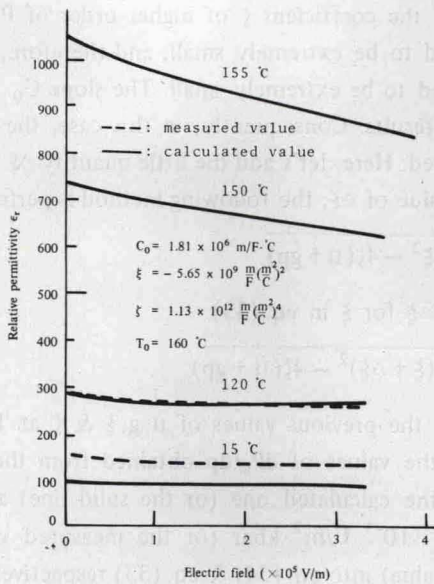


Fig. 10. Effect of external electric field on the relative permittivity of  $\text{Pb}(\text{Ti}(25\%)+\text{Sn}(75\%))\text{O}_3$  under various temperatures.

paraelectric phase and the characteristic temperature  $T_0$  are obtained from Fig. 9(a);  $C_0=1.81 \times 10^6$  m/F·°C &  $T_0=160^\circ\text{C}$ ). As the measured value of  $P_s$  at  $T_c=163^\circ\text{C}$  is  $5.33 \times 10^{-2}$  C/m<sup>2</sup>, the values of  $\xi$  &  $\zeta$  are obtained by putting above values of  $C_0, T_0, T_c$  &  $P_s$  at  $T_c$  into eq. (19) & eq. (25);  $\xi=-5.65 \times 10^9$  m<sup>5</sup>/F·C<sup>2</sup> &  $\zeta=1.13 \times 10^{12}$  m<sup>9</sup>/F·C<sup>4</sup>. On the other hand, the applied electric field dependence of the relative permittivity at  $T=15^\circ\text{C}$  &  $120^\circ\text{C}$  measured by the authors is expressed as a dotted line in Fig. 10<sup>7</sup>). By putting above values of  $C_0, T_0, \xi$  &  $\zeta$  into eq. (26), the applied electric field dependence of the relative permittivity is shown as a solid line in Fig. 10. The measured value follows to the calculated value approximately and then the suitability of eq. (26) is confirmed. Here, the solid lines at  $T=150^\circ\text{C}$  &  $155^\circ\text{C}$  in Fig. 10 are merely the calculated curve from eq. (26). Moreover, by putting the previous values into eq. (24) & eq. (23), the temperature dependence of  $1/\epsilon_r$  &  $P_s$  are obtained like a solid line in Fig. 9(a) & (b). From Fig. 9(a), it is found that the measured value in ferroelectric phase coincides almost with the calculated value, and then it is predicted that the temperature dependence of  $P_s$  should be like a solid line in Fig. 9(b).

#### 4. Dielectric Loss Tangent

The electric field  $E$  and the dielectric constant in ferroelectric phase are given by eq. (3) and eq. (4), respectively. The polarization  $P$  in ferroelectric phase written here is expressed as the sum of spontaneous polarization  $P_s$  and induced polarization  $P_E$ , namely

$$P = P_s + P_E \quad (35)$$

When the electric field  $Ee^{j\omega t}$  with angular frequency  $\omega$  is applied to the sample, the polarization induced in the sample by the field is expressed to be  $P_E=P_0e^{j(\omega t-\delta_1)}$ , where  $\delta_1$  is the phase delayed from the phase of the applied field, and  $P_0$  is the magnitude of the induced polarization.

As the coefficients  $u, g, \xi$  &  $\zeta$  in eq. (3) & eq. (4) must be complex number, the coefficients  $u^*, g^*, \xi^*$  &  $\zeta^*$  should be substituted for those. Then, when the field  $Ee^{j\omega t}$  is impressed in the sample, the eq. (3), eq. (4) & eq. (35) must be written respectively as follows;

$$Ee^{j\omega t} = (u^* + g^*P)P^* + \xi^*P^{*3} + \zeta^*P^{*5} \quad (36)$$

$$1/(\epsilon^* - \epsilon_0) = u^* + g^*P + 3\xi^*P^2 + 5\zeta^*P^4 \quad (37)$$

$$P^* = P_s + P_E^* = P_s + P_0e^{j(\omega t-\delta_1)} \quad (38)$$

By putting  $P^*$  given by eq. (38) into  $P^*$  in eq. (36), the eq. (36) is expressed as follows;

$$\begin{aligned} Ee^{j\omega t} = & (u^* + g^*P_s)P_s + \xi^*P_s^3 + \zeta^*P_s^5 + P_0e^{j(\omega t-\delta_1)} ( u^* + g^*P_s + 3\xi^*P_s^2 \\ & + 5\zeta^*P_s^4 ) + P_0^2e^{j2(\omega t-\delta_1)} (3\xi^*P_s + 10\zeta^*P_s^3) + P_0^3e^{j3(\omega t-\delta_1)} (\xi^* + 10\zeta^*P_s^2) \\ & + P_0^4e^{j4(\omega t-\delta_1)} \cdot 5\zeta^*P_s + P_0^5e^{j5(\omega t-\delta_1)}\zeta^* \end{aligned}$$

Provided that the phases of  $u^*, g^*, \xi^*$  &  $\zeta^*$  are all  $\delta_1$ , furthermore, as  $P_s$  in ferroelectric phase exists under  $E=0$  and then  $P_0=0$ , the  $P_s$  satisfies the equation derived from the eq. (36)

$$u^* + g^*P_s + \xi^*P_s^2 + \zeta^*P_s^4 = 0 \quad (39)$$

The above equation becomes the following form by putting  $A$  into  $P_0/P_s$ , namely  $A=P_0/P_s$ , and using the eq. (39);



$$Ee^{j\omega t} = A \{ (2\xi P_s^3 + 4\zeta P_s^5) e^{j\omega t} + A(3\xi P_s^3 + 10\zeta P_s^5) e^{j(2\omega t - \delta_1)} \\ + A^2(\xi P_s^3 + 10\zeta P_s^5) e^{j(3\omega t - 2\delta_1)} + A^3 5\zeta P_s^5 e^{j(4\omega t - 3\delta_1)} \\ + A^4 \zeta P_s^5 e^{j(5\omega t - 4\delta_1)} \}$$

Where since  $A$  is the ratio of the induced polarization to the spontaneous polarization, the relationship  $A \ll 1$  holds good. By using this condition and neglecting the higher term than the second one in the right hand side of the above equation, it is clear that the phase of the left hand side of the above equation is equal to that of the right hand side. Furthermore, when the complex dielectric constant is expressed to be  $\epsilon = \epsilon_1 - j\epsilon_2$ , the loss tangent ( $\tan \delta$ ) is shown to be  $\tan \delta = \epsilon_2 / \epsilon_1$ . On the other hand, the reciprocal dielectric constant in paraelectric phase is expressed to be  $1/(\epsilon^* - \epsilon_0) = u^* + g^*p = (u + gp)e^{j\delta_1}$  from eq. (37) because of including no higher terms than the second power of  $P^*$ . In general, because of  $\epsilon_1 \gg \epsilon_0$  for ferroelectrics, the loss tangent in paraelectric phase is shown to be  $\tan \delta = \epsilon_2 / \epsilon_1 \doteq \tan \delta_1$  from above relationship. Therefore, the loss tangent in paraelectric phase corresponds to that in normal dielectrics.

By the above two facts, it is confirmed to be appropriate that phases of the coefficients  $u^*$ ,  $g^*$ ,  $\xi^*$  &  $\zeta^*$  have been determined to be all  $\delta_1$ .

The complex dielectric constant  $\epsilon^*$  in ferroelectric phase can be obtained by substituting eq. (35) & eq. (39) for eq. (37) as follows;

$$\frac{1}{\epsilon^* - \epsilon_0} = (2\xi P_s^2 + 4\zeta P_s^4) e^{j\delta_1} + A(6\xi P_s^2 + 20\zeta P_s^4) e^{j\omega t} \\ + A^2(3\xi P_s^2 + 30\zeta P_s^4) e^{j(2\omega t - \delta_1)} + A^3 \cdot 20\zeta P_s^4 e^{j(3\omega t - 2\delta_1)} \\ + A^4 \cdot 5\zeta P_s^4 e^{j(4\omega t - 3\delta_1)}$$

By comparing the real & imaginary parts of the right hand side with those of the left hand side with those of the left hand side of the above equation, the following relationships can be obtained;

From the real part,

$$\frac{\epsilon_1 - \epsilon_0}{(\epsilon_1 - \epsilon_0)^2 + \epsilon_2^2} = 2(\xi + 2\zeta P_s^2) P_s^2 \cos \delta_1 + 2A(3\xi + 10\zeta P_s^2) P_s^2 \cos \omega t \\ + 3A^2(\xi + 10\zeta P_s^2) P_s^2 \cos 2(\omega t - \delta_1/2) + O(A^3),$$

where  $O(A^3)$  stands for the small quantity including the higher terms than the third power of  $A$  ( $A \ll 1$ ).

From the imaginary part,

$$\frac{\epsilon_2}{(\epsilon_1 - \epsilon_0)^2 + \epsilon_2^2} = 2(\xi + 2\zeta P_s^2) P_s^2 \sin \delta_1 + 2A(3\xi + 10\zeta P_s^2) P_s^2 \sin \omega t \\ + 3A^2(\xi + 10\zeta P_s^2) P_s^2 \sin 2(\omega t - \delta_1/2) + O'(A^3)$$

, where  $O'(A^3)$  stands for the small quantity as well as  $O(A^3)$ . By putting above relationships into  $\tan \delta = \epsilon_2 / \epsilon_1$ , the loss tangent in ferroelectric phase can be obtained as follows;

$$\tan \delta \doteq \tan \delta_1 + \frac{3\xi + 10\zeta P_s^2}{(\xi + 2\zeta P_s^2) \cos \delta_1} A \sin \omega t + O''(A^2)$$

, where  $O''(A^2)$  stands for the small quantity. Then the root mean square of  $\tan \delta$  with time can be obtained as follows;

$$\begin{aligned} \langle \tan \delta \rangle &\doteq \left\{ \tan^2 \delta_1 + \frac{1}{2} A^2 \frac{(3\xi + 10\xi P_s^2)^2}{(\xi + 2\xi P_s^2)^2 \cos^2 \delta_1} \right\}^{1/2} \\ &= \tan \delta_1 \left\{ 1 + \frac{1}{2} A^2 \frac{(3\xi + 10\xi P_s^2)^2}{(\xi + 2\xi P_s^2)^2 \sin^2 \delta_1} \right\}^{1/2} \end{aligned} \quad (40)$$

The  $\tan \delta_1$  is based on the fact that the phase of induced polarization  $P_E$  lags behind that of the applied electric field, and corresponds to the loss tangent of normal dielectrics.

Now, let's deal with two kinds of transition by using above relationships:

(I) The second order transition

In the case of the second order transition, putting the relation  $\zeta=0$  into eq.(40),

$$\langle \tan \delta \rangle \doteq \sqrt{\tan^2 \delta_1 + 9A^2/2 \cos^2 \delta_1} \quad (41)$$

By using relations  $A=P_0/P_s$  and eq. (9), eq. (41) is rewritten as follows;

$$\langle \tan \delta \rangle \doteq \sqrt{\tan^2 \delta_1 - \frac{9}{2} P_0^2 \frac{\xi}{(u + gp) \cos^2 \delta_1}} \quad (42)$$

The above equation shows the pressure dependence of  $\tan \delta$ . As the relationship between the spontaneous polarization  $P_s$  and the applied electric field  $E$  can be got by putting zero into  $\zeta$  and  $P_s$  into  $P$  in eq. (3) and the relationship between the spontaneous polarization and the loss tangent is shown in eq. (41), the dc-electric field dependence of  $\tan \delta$  can be obtained by combining these relationships as follows; under  $\tan^2 \delta_1 < 1$ ,

$$E = \left\{ u + gp + \xi \left( \frac{3}{\sqrt{2}} \frac{P_0}{\sqrt{\tan^2 \delta - \tan^2 \delta_1}} \right)^2 \right\} \frac{3}{\sqrt{2}} \frac{P_0}{\sqrt{\tan^2 \delta - \tan^2 \delta_1}} \quad (43)$$

To get the temperature dependence of  $\tan \delta$ , let us put eq. (12) into  $A^2=(P_0/P_s)^2$  in the eq. (41), then the following equation can be obtained.

$$\langle \tan \delta \rangle \doteq \sqrt{\tan^2 \delta_1 - \frac{9}{2} P_0^2 \frac{\xi}{C_0(T - T_0) \cos^2 \delta_1}} \quad (44)$$

Moreover, the dc-electric field dependence of  $\tan \delta$  is calculated by modifying eq. (43), namely;

$$E = \left\{ C_0(T - T_0) + \xi \left( \frac{3}{\sqrt{2}} \frac{P_0}{\sqrt{\tan^2 \delta - \tan^2 \delta_1}} \right)^2 \right\} \frac{3}{\sqrt{2}} \frac{P_0}{\sqrt{\tan^2 \delta - \tan^2 \delta_1}}$$

(II) The first order transition

The pressure dependence of  $\tan \delta$  in the case of the first order transition is shown in eq. (40). The value of  $\tan \delta$  at the transition pressure and temperature in the first order transition is given by putting  $[P_s^2]_{T_c} = -3\xi/4\zeta$  into  $P_s$  of eq. (40);

$$[\tan \delta]_{T_c, pc} \doteq \sqrt{\tan^2 \delta_1 - 54P_0^2 \zeta / \xi \cos^2 \delta_1} \quad (45)$$

and the pressure dependence of  $\tan \delta$  can be obtained by substituting eq. (21) for  $P_s$  of eq. (40);

$$\langle \tan \delta \rangle \doteq \left[ \tan^2 \delta_1 - P_0^2 \frac{\zeta}{\xi} \frac{\{2 + 5\sqrt{1 - (4\xi/\xi^2)(u + gp)}\}^2}{\{1 + \sqrt{1 - (4\xi/\xi^2)(u + gp)}\} \{1 - (4\xi/\xi^2)(u + gp)\} \cos^2 \delta_1} \right]^{1/2} \quad (46)$$

Furthermore, the temperature dependence of  $\tan \delta$  is exhibited by modifying eq. (46) as follows;

$$\langle \tan \delta \rangle \equiv \left[ \tan^2 \delta_1 - P_0^2 \frac{\xi}{\xi} \frac{\{2 + 5 \sqrt{1 - (4C_0 \xi / \xi^2)(T - T_0)}\}^2}{\{1 + \sqrt{1 - (4C_0 \xi / \xi^2)(T - T_0)}\} \{1 - (4C_0 \xi / \xi^2)(T - T_0)\} \cos^2 \delta_1} \right]^{1/2} \quad (47)$$

Now, let us apply the above mentioned analytical results to the experimental results of  $\text{NaNO}_3$  which belongs to the second order transition and those of  $\text{BaTiO}_3$  which belongs to the first order transition.

(1) The case of  $\text{NaNO}_3$

The pressure dependence of  $\tan \delta$  is shown in Fig. 11. The loss tangent is not almost affected by the pressure in paraelectric phase, increases rapidly at the transition pressure and increases with pressure in ferroelectric phase. The loss tangent in ferroelectric phase decreases gradually with the dc-electric field as shown in Fig. 12.

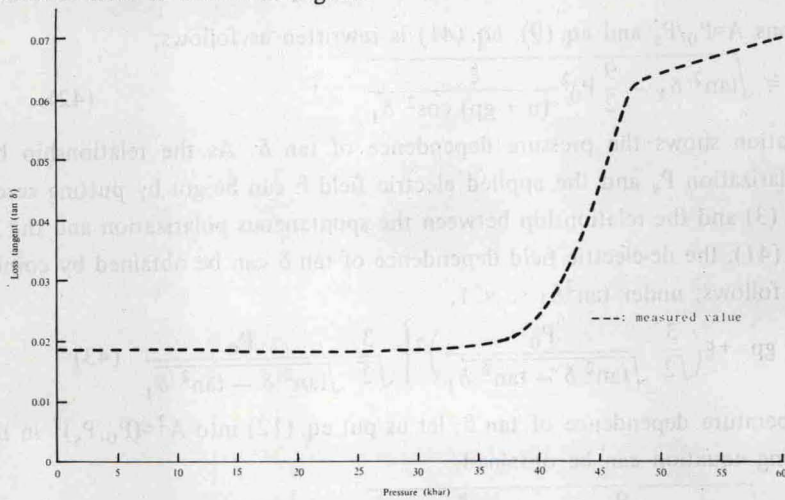


Fig. 11. The pressure dependence of the loss tangent ( $\tan \delta$ ) of powder  $\text{NaNO}_3$ .

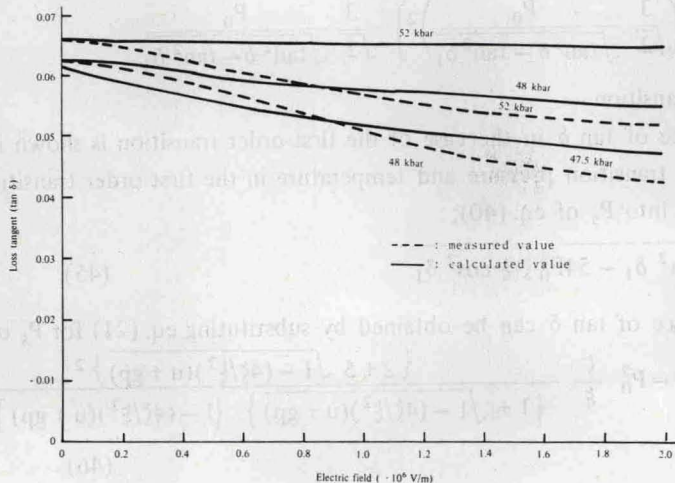


Fig. 12. Effect of external electric field on the loss tangent ( $\tan \delta$ ) of powder  $\text{NaNO}_3$  under various pressures.

To explain the loss tangent phenomenologically, eqs. (42) & (43) must be picked up. The value of  $\tan \delta_1$  which corresponds to the loss tangent in paraelectric phase is 0.018 from Fig. 11. The parameter  $P_0$  is calculated by putting the value of  $\tan \delta$  (0.062) at  $p=48$  kbar in Fig. 11 into  $\tan \delta$  of eq. (42), and its value is  $P_0=1.673 \times 10^{-4} \text{ C/m}^2$ . Here,  $u=4.14 \times 10^{10} \text{ m/F}$ ,  $g=-8.81 \times 10^8 \text{ m/F}\cdot\text{kbar}$  &  $\xi=2.48 \times 10^{13} \text{ m}^5/\text{F}\cdot\text{C}^2$  were used for the values of  $u$ ,  $g$ ,  $\xi$  &  $\zeta$  in eq. (42) as shown in the case of the dc-electric field dependence of the dielectric constant.

The dc-electric field dependence of  $\tan \delta$  at  $p=48$  kbar is obtained by substituting above values for those of eq. (43), and is shown as a solid line in Fig. 12. The value of the ratio of  $P_0$  to  $P_s$ , namely  $A$ , is the order of  $10^{-2}$ .

In this case, if the parameter  $P_0$  is entirely independent of pressure, the loss tangent in ferroelectric phase obtained from eq. (42) decreases with pressure, but such a behavior of the loss tangent is inconsistent with Fig. 11. On the contrary, if the parameter  $P_0$  increases with pressure as shown in Fig. 13, the pressure dependence of  $\tan \delta$  in ferroelectric phase is exhibited as adotted

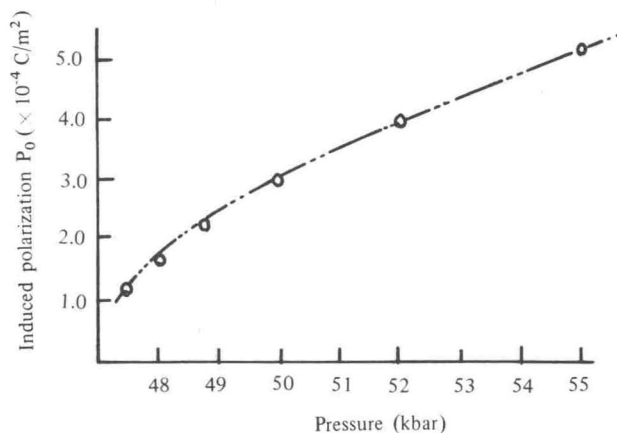


Fig. 13. The pressure dependence of the induced polarization of powder  $\text{NaNO}_3$ .

line in Fig. 11, and this fact is reasonable.

The dc-electric field dependence of  $\tan \delta$  calculated at  $p=47.5$  kbar & 52 kbar is exhibited as a solid line in Fig. 12 by using eq. (43) and the parameter  $P_0$  shown in Fig. 13.

The loss tangent decreases with the dc-electric field, and furthermore, the rate of the decrease of  $\tan \delta$  with the dc-electric field decreases with increasing pressure.

From above facts, it will be concluded that this phenomenological treatment of  $\tan \delta$  is appropriate to explain experimental results.

## (2) The case of $\text{BaTiO}_3$

The temperature dependence of  $\tan \delta$  with pressure reported by G.A.Samara is shown in Fig. 14 for  $\text{BaTiO}_3$ . Let us apply eq. (45) & eq. (47) to the results of above experiment. As the value of  $\tan \delta$  at the transition temperature is given by eq. (45), the values of parameter  $P_0$  in ferroelectric phase are determined by eq. (45) and Fig. 14. The  $\tan \delta_1$  corresponds to the loss tangent in paraelectric phase, and its value is 0.01 from Fig. 14.

In this case, the loss tangent in paraelectric phase is almost independent of pressure. It is seen

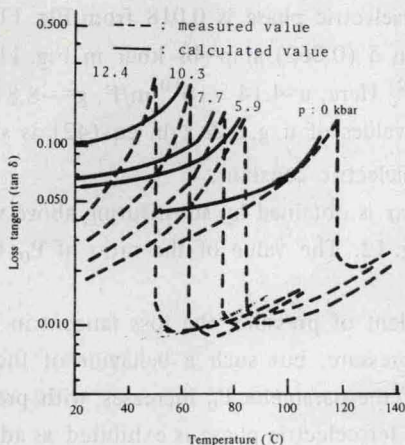


Fig. 14. The temperature dependence of the loss tangent ( $\tan \delta$ ) of single crystal  $\text{BaTiO}_3$  with pressure parameter.

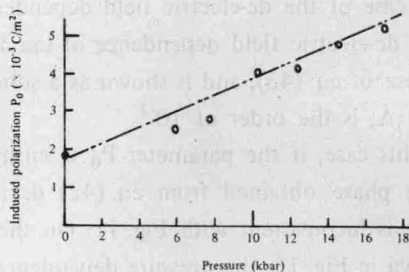


Fig. 15. The pressure dependence of the induced polarization of single crystal  $\text{BaTiO}_3$ .

that the value of  $\tan \delta$  at the transition temperature increases with increasing pressure from Fig. 14. The pressure dependence of parameter  $P_0$  obtained by eq. (45) is shown in Fig. 15 and it is found that the value of  $P_0$  increases with pressure. This behavior of parameter  $P_0$  with  $\text{BaTiO}_3$  is similar to that with  $\text{NaNO}_3$ .

The temperature dependence of  $\tan \delta$  calculated by using eq. (46) and the value of  $P_0$  given in Fig. 15 is shown as a solid line in Fig. 14. The value of  $\tan \delta$  increases with temperature and rapidly near the transition temperature. Here,  $\xi = -0.96 \times 10^9 \text{ m}^5/\text{F} \cdot \text{C}^2$ ,  $\zeta = 5.93 \times 10^{10} \text{ m}^9/\text{F} \cdot \text{C}^4$  &  $C_0 = 4.52 \times 10^5 \text{ m}/\text{F} \cdot \text{C}$  were used for the values of  $\xi$ ,  $\zeta$  &  $C_0$  in eqs. (45) & (46) as shown in the previous section.

In this case, the pressure dependence of  $\tan \delta$  shown in Fig. 14 is based on that of the characteristic temperature  $T_0$  in eq. (47), that is;

$$T_0 = 104 - 4.92 p \quad (p \text{ in kbar \& } T_0 \text{ in } ^\circ\text{C})$$

The value of the ratio of  $P_0$  to  $P_s$  is also the order of  $10^{-2}$  for  $\text{BaTiO}_3$ .

Thus, the analytical loss tangent derived from free energy is given in forms of both the dc-electric field and temperature dependence including the pressure in the case of the first and the second order transition, and follows experimental results on  $\tan \delta$ .

And eq. (40) gives the relationship between  $P_s$  and  $\tan \delta$ , and seems to show that the domain motion will contribute to the dielectric loss.

## 5. Conclusion

Based on this analysis which is obtained by modifying Devonshire's free energy for the bound crystal, when the hydrostatic pressure is applied to the crystal which has the centrosymmetry in paraelectric phase, the ferroelectric phenomena, for example, the pressure dependence of the permittivity & the spontaneous polarization with temperature parameter and the temperature dependence of the permittivity & the spontaneous polarization with pressure parameter etc., are explained very clearly. Especially, the analysis for the pressure characteristics of ferroelectric phase

which is one of the undeveloped fields becomes easy. In fact, it is confirmed that the results of the analysis in this paper coincides with the experimental results of the pressure dependence of ferroelectric phenomena up to this time. Therefore, the analysis of this paper seems to be useful on developing the study of this field.

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