

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

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 PbO as a flux. (Ceramic) |
| Di-<br>mension             | Thickness<br>d (mm)         | 0.5 - 1.0  | 0.28   | 0.5  | 0.2  |
|                            | Area<br>S ( $\text{cm}^2$ ) | 0.3 - 0.7  | 0.3  | 0.2 - 0.6  | 0.5 - 0.6  |
| Space group                |                             | $\text{P}2_1/\text{n}$<br>(Peraelectric phase)<br>Centrosymmetry   | R3C<br>(Peraelectric phase)<br>Centrosymmetry  | $\text{Pm}3\text{m}$<br>(Peraelectric phase)<br>Centrosymmetry | (Ceramic)  |
| High pressure<br>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  $p$

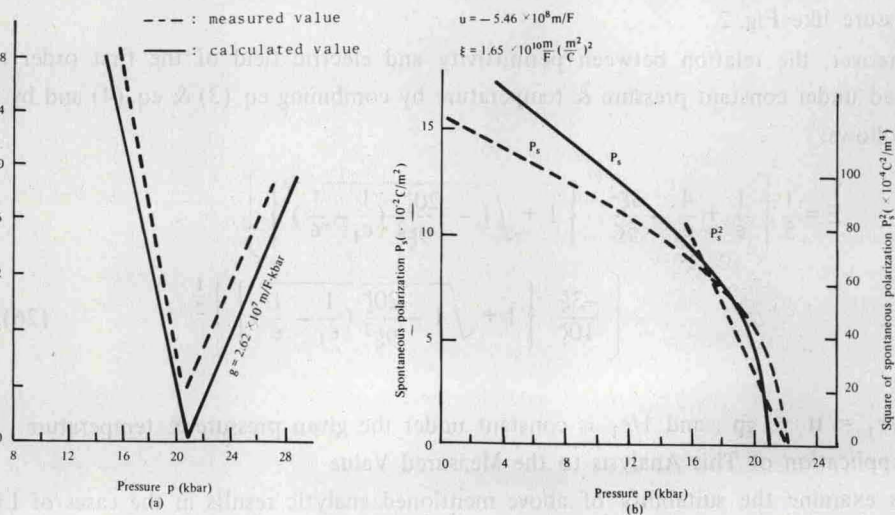


Fig. 3. (a) The pressure dependence of the reciprocal relative permittivity of  $\text{LiH}_3(\text{SeO}_3)_2$  at  $23^\circ\text{C}$ . (b) The pressure dependence of the spontaneous polarization & the square of spontaneous polarization of  $\text{LiH}_3(\text{SeO}_3)_2$  at  $22^\circ\text{C}$ .