

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

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 ξ & ζ 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

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

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 ξ & ζ 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.) & NaNO_3 which belong to the second order transition, and of 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.

		$\text{LiH}_3(\text{SeO}_3)_2$	NaNO_3	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 NaNO_3 obtained by recrystallization. (Crystal)	Melting method, using KF as a flux. (Crystal)	Press and calcination of the mixture of 75 % SnO_2 and 25 % TiO_2 , using PbO as a flux. (Ceramic)
Di- mension	Thickness d (mm)	0.5 - 1.0	0.28	0.5	0.2
	Area S (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)⁵. 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

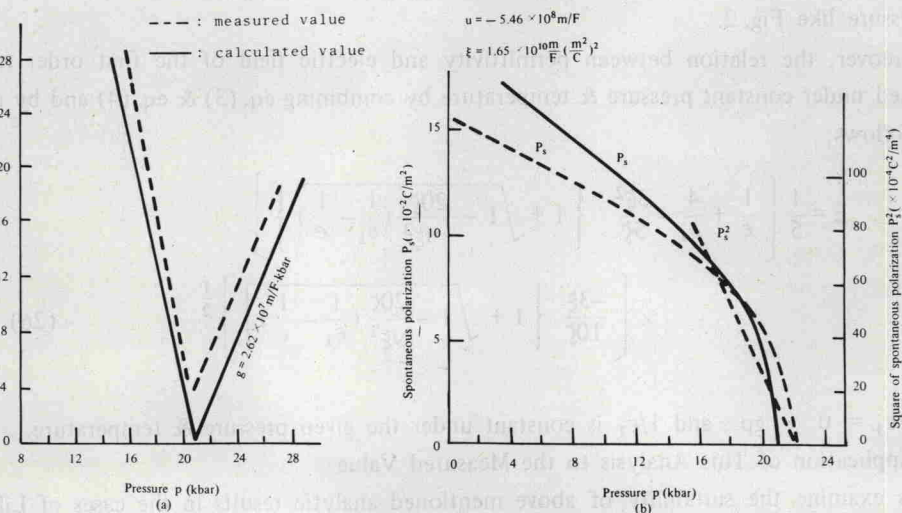


Fig. 3. (a) The pressure dependence of the reciprocal relative permittivity of $\text{LiH}_3(\text{SeO}_3)_2$ at 23°C . (b) The pressure dependence of the spontaneous polarization & the square of spontaneous polarization of $\text{LiH}_3(\text{SeO}_3)_2$ at 22°C .