Fujimoto and Yasuda : Phenomenological Treatment of Ferroelectricity Under Hydrostatic Pressure

67

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(T₀) decreases linearly with increasing pressure. Accordingly, T₀ is expressed as follows;

$$T_0 = a_2 - \beta_2 p \tag{30}$$

where $a_2=104$ °C & $\beta_2=4.92$ °C/kbar from Fig. 7(b). By putting eq. (30) into T₀ of eq. (23) & eq. (24), the following formulas are obtained;

$$\frac{1}{\epsilon_{\rm r}} = -4C_0 \left({\rm T} - a_2 + \beta_2 {\rm p} \right) + \frac{\xi^2}{\zeta} \left\{ 1 + \sqrt{1 - \frac{4\zeta C_0}{\xi^2} \left({\rm T} - a_2 + \beta_2 {\rm p} \right)} \right\}$$
(31)
$$P_{\rm s}^2 = -\frac{\xi}{2\zeta} \left\{ 1 + \sqrt{1 - \frac{4\zeta C_0}{\xi^2} \left({\rm T} - a_2 + \beta_2 {\rm p} \right)} \right\}$$
(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 °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 $dT_c/dp=-5.5$ °C/kbar and $dT_0/dp=-4.8$ °C/kbar in experimental value⁶⁾. 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 ζ 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 ζ is also assumed to be extremely small. The slope C₀ is known to be independent of pressure from experimental results. Consequently, in this case, the pressure dependence of the coefficient ξ should be considered. Here, let's add the little quantity $\Delta \xi$ to the value of ξ to compensate ξ . In order to obtain the value of $\Delta \xi$, the following method is performed, that is, from eq. (21),

$$dP_{\rm s}/dp = -g\zeta/2P_{\rm s}\sqrt{\xi^2 - 4\zeta(u+gp)}$$
(33)

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

$$dP_{\rm s}/dp = -g\xi/2P_{\rm s}\sqrt{(\xi + \Delta\xi)^2 - 4\zeta(u + gp)}$$
(34)

First, let's put p=7.7 kbar and the previous values of u,g, $\xi \& \zeta$ at T=23 °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 °C in Fig. 6(b), that is, dP_s/dp=3.80 ×10⁻³ C/m²·kbar (or the measured value) & dP_s/dp=3.13 ×10⁻³ C/m²·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 $\Delta\xi$; $\Delta\xi$ =0.373×10⁹ m⁵/F·C². 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

 $\xi + \Delta \xi = -0.96 \times 10^9 \,\mathrm{m^5/F \cdot C^2}$ into ξ of eq. (24). In this case, the compensated quantity $\Delta \xi$ is 28% of the previous value of ξ , 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 (PbTiO₃25% + PbSnO₃75%) 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





The temperature dependence of (a) the reciprocal relative permittivity & (b) the spontaneous polarization of Pb(Ti(25%)+Sn (75%)) O₃ at 1 bar.





68