

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

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 theory¹⁾. Accordingly, the square of the spontaneous polarization is obtained from eq. (8) as follows;

$$P_s^2 = -(u + gp)/\xi \quad (9)$$

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;

$$1/\epsilon = u + gp + 3\xi P_s^2 \quad (10)$$

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

$$1/\epsilon = -2(u + gp) \quad (11)$$

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.

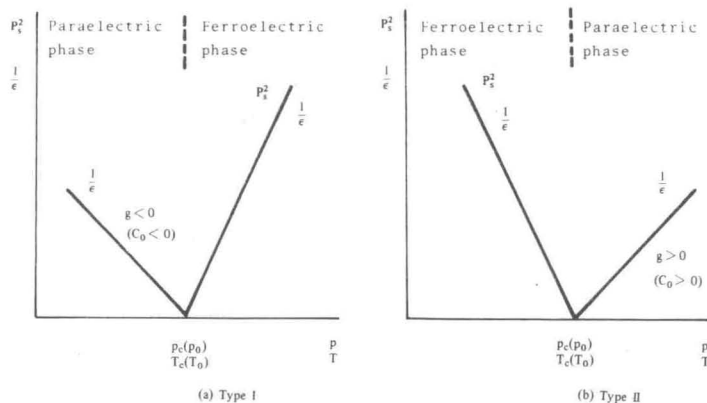


Fig. 1. Schematic temperature & pressure variations (type I, type II) of the spontaneous polarization & the reciprocal permittivity for the second order transition.

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 ξ 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 ξ 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;