Application of Phenomenological Analysis to Ferroelectric Stannated Lead Titanate under Hydrostatic Pressure (Part II)

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Abstract

This work is concerned with the dielectric properties of stannated lead titanate Pb(Ti+Sn)O_3 under hydrostatic pressure. The pressure dependence of the permittivity and the spontaneous polarization, and the electric field dependence of the permittivity under hydrostatic pressure are elucidated by applying a phenomenological theorem to Pb(Ti+Sn)O_3.

1. Introduction

Stannated lead titanate Pb(Ti,$_{0.3}$+Sn,$_{0.7}$)O_3 undergoes a phase transition from the paraelectric to the ferroelectric phase at 163.7°C at atmospheric pressure with decreasing temperature, and at a transition pressure with decreasing pressure. Its transition is of first order[1,2].

In this paper,the effects of the hydrostatic pressure and the electric field on the dielectric properties such as the permittivity and the spontaneous polarization are shown. The curves of the electric field against the polarization and of the polarization against the free energy for various pressures at various temperatures in the ferroelectric phase are also shown. The above results are explained on application of a phenomenological theory to stannated lead titanate.

2. Phenomenological Theory

When the hydrostatic pressure p is applied to a ferroelectric which is not piezoelectric in the paraelectric phase, the Gibbs function (free energy) with respect to the polarization P for ferroelectrics with a first order transition is given by the following equation[3].

$$W = (u+gp)P^2/2 + \xi P^4/4 + \zeta P^6/6 \cdots\cdots(1)$$

where the expansion coefficients u, g, ξ and ζ are phenomenological constants which are depend on temperature T.

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The electric field E in ferroelectrics and the permittivity ε of ferroelectrics are obtained from equation (1) as follows :

$$E = (u + gp + \xi P^2 + \zeta P^4)P \cdots\cdots(2)$$

$$1/\varepsilon = 1/\varepsilon_o \varepsilon_r = u + gp + 3\xi P^2 + 5\zeta P^4 \cdots\cdots(3)$$

because of $\varepsilon >> \varepsilon_o$ for ordinary ferroelectrics, where ε_o is the vacuum permittivity and ε_r is the relative permittivity.

By using the above equations, the following relations are obtained for the paraelectric and the ferroelectric phases.

(A) Paraelectric phase

$$\left. \begin{array}{ll} 1/\varepsilon = c_o(T - T_o) & \text{at constant pressure} \\ 1/\varepsilon \simeq u + gp & \text{at constant temperature} \end{array} \right\} \cdots\cdots(4)$$

$$p_o = -u/g \cdots\cdots(5)$$

where c_o is the reciprocal of the Curie constant, T_o is the characteristic temperature and p_o is the characteristic pressure.

(B) Ferroelectric phase

$$P_s^2 = -(1 + \alpha)\xi/2\zeta \cdots\cdots(6)$$

$$1/\varepsilon = -4(u + gp) + (1 + \alpha)\xi^2/\zeta \cdots\cdots(7)$$

$$p_c = p_o + 3\xi^2/16g\zeta \cdots\cdots(8)$$

at constant temperature, where P_s is the spontaneous polarization, p_c is the transition pressure and

$$\alpha^2 = 1 - 4(u + gp)\zeta/\xi^2 \cdots\cdots(9)$$

The spontaneous polarization $P_{s,c}$ at p_c is

$$P_{s,c}^2 = -3\xi/4\zeta \cdots\cdots(10)$$

The transition temperature at constant pressure is

$$T_c = T_o + 3\xi^2/16c_o\zeta \cdots\cdots(11)$$

The relation between the electric field and the permittivity at constant temperature and constant pressure is expressed as follows :

$$E = [4(u + gp) + 2\xi P_1^2 + 1/\varepsilon]P_1/5 \cdots\cdots(12)$$

where

$$P_1^2 = -[1 + \sqrt{1 - 20(u + gp - 1/\varepsilon)\zeta/9\xi^2}]3\xi/10\zeta \cdots\cdots(13)$$

3. Specimen and Experimental Method

Specimens were prepared from the starting materials PbO, TiO_2 and SnO_2 by usual techniques, and the molar fraction of SnO_2 was 0.7, i.e. $Pb(Ti_{,0.3} + Sn_{,0.7})O_3$. Intimate mixtures were calcinated at 920°C for 3 hours, pulverized to fine powders, and then pressed into discs.

These discs were sintered at 1120°C for 2 hours in a controlled PbO atmosphere in a Pt crucible in order to prevent the loss of PbO. Sintered specimens were cut out with a diamond cutter, and polished to the final thickness of 0.1mm. The spontaneous polarization was examined with an improved Sawyer-Toewr's circuit[4]. The permittivity was measured at 10kHz with a field of less than 5V/cm using an ac bridge. The pressure apparatus applying hydrostatic pressure to the specimen was an anvil type 700-ton hexahedral press employing pyrophillite as a pressure transmitting medium[5].

4. Application of Phenomenological Theory to Pb(Ti+Sn)O₃

The transition temperature T_c of Pb(Ti,$_{0.3}$+Sn,$_{0.7}$)O₃ has been reported to be 163.7°C at atmospheric pressure, and to variate with a slope $\mathrm{d}T_c/\mathrm{d}p \simeq -6.1°\mathrm{C/kbar}$ in the pressure range up to 20kbar[1,2,5]. From the experimental results on the dependence of the permittivity on the pressure and of the spontaneous polarization on the pressure at atmospheric pressure, $T_o = 160°\mathrm{C}$, $c_o = 2.19 \times 10^6 \mathrm{m/F°C}$ and $P_{s,c} = 0.061\mathrm{C/m^2}$.[5]

On putting the above values into equations (10) and (11), $\xi = -8.65 \times 10^9 \mathrm{m^5/FC^2}$ and $\zeta = 1.73 \times 10^{12} \mathrm{m^9/FC^4}$ are obtained.

Figure 1 shows experimental results on the dependence of the reciprocal of relative permittivity and the spontaneous polarization P_s on the pressure at 60°C. It is found from Figure 1 and equation (4) that $p_o = 15.1\mathrm{kbar}$, $p_c = 15.7\mathrm{kbar}$, $P_{s,c} = 0.07\mathrm{C/m^2}$, $g = 1.45 \times 10^7 \mathrm{m/Fkbar}$ and $u = 2.19 \times 10^6 (T-160) = -2.19 \times 10^8 \mathrm{m/F}$.

On putting the values u, g, ξ and ζ into equations (12) and (13), the curves of the relative permittivity ε_r against the dc electric field E at 60 and 80°C in the ferroelectric phase are obtained for various pressures (0, 5 and 10kber) as seen in Figure 2. The permittivity decreases with increasing electric field, and this slope becomes steeper as the pressure and the temperature increase.
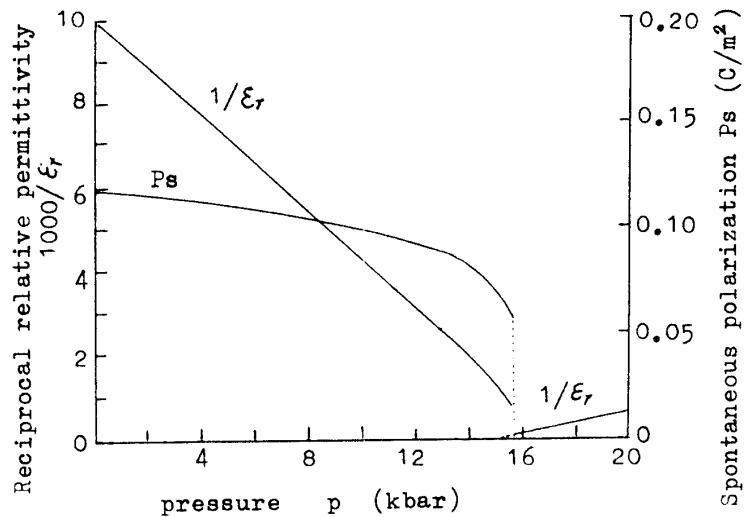
The spontaneous polarization

Fig.1 Reciprocal relative permittivity $1/\varepsilon_r$ and spontaneous polarization P_s as a function of hydrostatic pressure p at 60°C.

P as a function of applied electric field E (P-E hysteresis loop), and the free energy W as a function of polarization P for various temperatures ($T = 60$ and $100°C$) and various hydrostatic pressures ($p = 0, 5$ and 10kbar) are obtained by putting the values u, g, ξ and ζ into equations (1) and (2) as shown in Figures 3 and 4, respectively, where $u = -1.31 \times 10^8 m/F$ for $T = 100°C$. The points A', B', C', D', O', G', J', K' and L' on a curve in Figure 4 correspond to the points A, B, C, D. O, G, J, K and L on the curve in Figure 3, respectively. As the electric field E increases from point A to point C, where the polarization is the limiting value P_c determined by conditions for
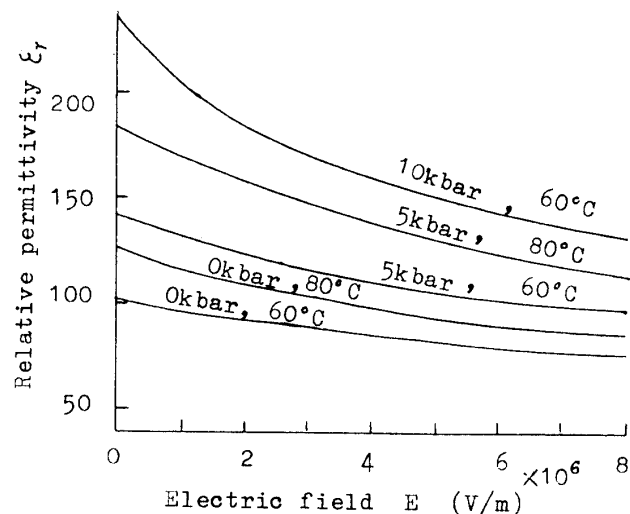

Fig.2 Effect of the electric field E on the relative permittivity ε_r for various pressures (0, 5 and 10kbar) at 60 and 80°C.
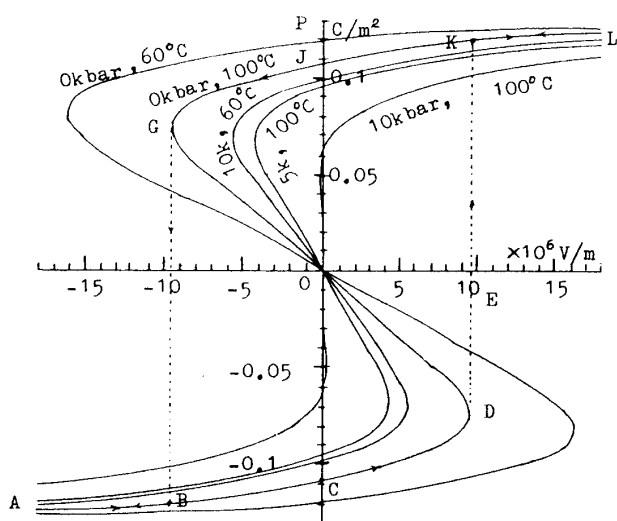

Fig.3 Relation between the polarization P and the electric field E (P-E hysteresis loop) for various pressures (0 , 5 and 10kbar) at 60 and 100°C.
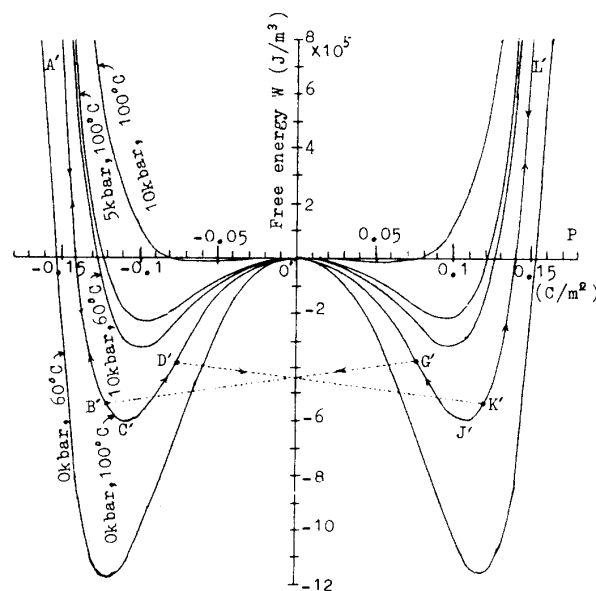

Fig.4 Relation between the free energy W and the polarization P for various pressures (0, 5 and 10kbar) at 60 and 100°C.

minimum free energy W_m ($P_c = -0.107C/m^2$, $W_m = -6 \times 10^5 J/m^3$ at 0 kbar and 100°C, for example). When the electric field exceeds the critical field E_c, the polarization becomes unstable, and jumps from point D to point K ($P = -0.074$ and $0.117C/m^2$ at $E_c = 9.5 \times 10^6 V/m$, and then increases with increasing electric field towards point L. The reason why the polarization jumps from D to K is that the free energy W at point K' ($-5.7 \times 10^5 J/m^3$) is lower than the energy at point D' ($-3.8 \times 10^5 J/m^3$) for the same value of the electric field E_c.

Conversely, as the electric field decreases from a large and positive value, the polarization decreases from point L, and drops from point G to point B where the polarization is more stable, because the energy at B is lower than the energy at G for the same value of the electric field (see points G' and B' in Figure 4).

In this way a hysteresis loop A→B→C→D→K→L→K→J→G→B→ A is drawn as seen in Figure 3, and a theoretical path A→B→C→D→O→G→J→K→L→K→J→G→O→D→C→B→ A is never realized, because the polarization is unstable in the negative gradient range D→ O→G.

5. Summary

$Pb(Ti_{,0.3} + Sn_{,0.7})O_3$ is ferroelectric at pressures below 15.7kbar at 60°C, and the permittivity decreases with increasing electric field. These results and the P−E hysteresis loop are explained in terms of the phenomenological theory.

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