

Application of Phenomenological Analysis to Ferroelectric Stannated Lead Titanate under Hydrostatic Pressure

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Abstract

This work is concerned with the dielectric properties of stannated lead titanate $\text{Pb}(\text{Ti}+\text{Sn})\text{O}_3$ under hydrostatic pressure. The temperature and pressure dependence of the spontaneous polarization, the permittivity and the dielectric loss tangent are elucidated by applying a phenomenological theorem to $\text{Pb}(\text{Ti}+\text{Sn})\text{O}_3$.

1. Instruction

Stannated lead titanate $\text{Pb}(\text{Ti}+\text{Sn})\text{O}_3$ is a ferroelectric. Its phase transition is of first order from the ferroelectric to the paraelectric phase at atmospheric pressure with increasing temperature, and also at temperatures below a transition temperature with increasing pressure.

In this paper, the effects of temperature and hydrostatic pressure on the dielectric properties, such as the spontaneous polarization, the permittivity and the dielectric loss tangent, are explained by the application of a phenomenological theory to stannated lead titanate.

2. Phenomenological Analysis

When hydrostatic pressure p is applied to a ferroelectric which is not piezoelectric in the paraelectric phase, then if terms are taken to the sixth order in polarization, the Gibbs function for ferroelectrics with a first order transition can be expressed on the basis of the free energy function for ferroelectrics under hydrostatic pressure p as follows :

$$F = \frac{1}{2} cp^2 + W(p, P)$$

$$W = \frac{1}{2}(u + gp)P^2 + \frac{1}{4}\xi P^4 + \frac{1}{6}\zeta P^6 \dots\dots\dots (1)$$

,where W is the free energy with respect to the polarization P , and the expansion coefficients

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u , g , f , ξ and ξ are phenomenological constants which are dependent on temperature.

The electric field E in ferroelectrics is obtained from equation (1) as follows :

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

The permittivity ϵ of ferroelectrics is obtained from equation (2) as follows :

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0 \epsilon_r} = u + gp + 3\xi P^2 + 5\xi P^4 \dots\dots\dots (3)$$

because of $\epsilon \gg \epsilon_0$ for ordinary ferroelectrics, where ϵ_0 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 :

2. 1 Paraelectric phase ($P = 0$)

The permittivity ϵ and the transition pressure p_c are given by the following equations :

$$\frac{1}{\epsilon} = c_0 (T - T_0) \simeq u + gp \dots\dots\dots (4)$$

$$p_c = -u/g = p_0 \dots\dots\dots (5)$$

,where c_0 is the Curie constant, T_0 is the characteristic temperature ($= T_c$: Curie temperature), and p_0 is the characteristic pressure.

2. 2 Ferroelectric phase

The spontaneous polarization P_s , the permittivity ϵ and the dielectric loss tangent $\tan\delta$ for ferroelectrics with a first order transition are given at constant temperature by the following equations^{1),2)} :

$$P_s^2 = -\frac{\xi}{2\xi}(1 + \alpha) \dots\dots\dots (6)$$

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0 \epsilon_r} = -4(u + gp) + \frac{\xi^2}{\xi}(1 + \alpha) \dots\dots\dots (7)$$

$$\tan\delta = \tan\delta_1 \times \sqrt{1 - \frac{\xi P_0^2(2 + 5\alpha)^2}{\xi(1 + \alpha)\alpha^2 \sin^2\delta_1}} \dots\dots\dots (8)$$

,where P_0 is the induced polarization by the applied ac electric field, $\tan\delta_1$ is the dielectric loss tangent in the paraelectric phase, and

$$\alpha^2 = 1 - \frac{4\xi}{\xi^2}(u + gp) \dots\dots\dots (9)$$

The spontaneous polarization, the permittivity and the dielectric loss tangent at the transition pressure p_c ($= -u/g$) or the transition temperature T_c are given by the following equations :

$$P_{s,c}^2 = -\frac{3\xi}{4\xi} \dots\dots\dots (10)$$

$$\frac{1}{\epsilon_{c,f}} = \frac{3\xi^2}{4\xi} = \frac{4}{\epsilon_{c,p}} \dots\dots\dots (11)$$

$$\tan\delta_c = \tan\delta_1 \times \sqrt{1 - \frac{54\xi P_0^2}{\xi \sin^2\delta_1}} \dots\dots\dots (12)$$

,where $\epsilon_{c,p}(=16\xi/3\xi^2)$ is the permittivity at p_c or T_c in the paraelectric phase. The characteristic pressure p_0 is

$$p_0 = p_c - \frac{3\xi^2}{16g\xi} \dots\dots\dots (13)$$

The spontaneous polarization, the permittivity and the dielectric loss tangent at constant pressure are expressed by the following equations :

$$P_s^2 = -\frac{\xi}{2\xi}(1+\beta) \dots\dots\dots (14)$$

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_0\epsilon_r} = -4c_0(T-T_o) + \frac{\xi^2}{\xi}(1+\beta) \dots\dots\dots (15)$$

$$\tan\delta = \tan\delta_1 \times \sqrt{1 - \frac{\xi P_0^2(2+5\beta)^2}{\xi(1+\beta)\beta^2\sin^2\delta_1}} \dots\dots\dots (16)$$

,where β and the characteristic temperature T_o are

$$\beta^2 = 1 - \frac{4c_0\xi}{\xi^2}(T-T_o) \dots\dots\dots (17)$$

$$T_o = T_c - \frac{3\xi^2}{16c_0\xi} \dots\dots\dots (18)$$

The electric field E dependence of the permittivity ϵ at constant temperature and constant pressure is given as follows :

$$E = \frac{1}{5} P_1 \left\{ 4(u+gp) + 2\xi P_1^2 + \frac{1}{\epsilon} \right\} \dots\dots\dots (19)$$

$$\text{where } P_1^2 = -\frac{3\xi}{10\xi} \left\{ 1 + \sqrt{1 - \frac{20\xi}{9\xi^2} \left(u + gp - \frac{1}{\epsilon} \right)} \right\} \dots\dots\dots (20)$$

3. Preparation of Specimens and Experimental Method

Specimens $\text{Pb}(\text{Ti}+\text{Sn})\text{O}_3$ were prepared from the starting materials PbO , TiO_2 and SnO_2 (purity >99.99%, particle size <1 μm) by usual techniques, and the molar fraction of SnO_2 was 0.7, i.e. $\text{Pb}(\text{Ti}_{0.3}+\text{Sn}_{0.7})\text{O}_3$. Intimate mixtures were calcinated at 920°C for 3 hours, pulverized to fine powders (particle size <0.5 μm), and then pressed into discs. These discs

were sintered at 112°C for 2 hours in a controlled PbO atmosphere in a Pt crucible in order to prevent the loss of PbO. X-ray powder patterns of ceramic specimens showed cubic powder patterns of the perovskite type (lattice constants $a = 4.007\text{\AA}$, $c = 4.043\text{\AA}$ and a separation of the lattice planes $d = 2.048\text{\AA}$) at room temperature^{3),4)}. Sintered specimens were cut with a diamond wafering saw, and polished to the final thickness of 0.1mm. The lapped specimens were electroded with silver paste by firing at 580°C for 5 minutes. The spontaneous polarization was examined with an improved Sawyer–Tower's circuit⁵⁾. The dielectric loss tangent was measured at 1kHz 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 pyrophyllite as a pressure transmitting medium. The pressure and the temperature were measured with manganin gauges to an accuracy of $\pm 1.5\%$, and with a calibrated copper–constantan thermocouple to within $\pm 0.1^\circ\text{C}$, respectively.

4. Application of Phenomenological Theory to Experimental Results

The transition temperature T_c of ferroelectric $\text{Pb}(\text{Ti}_{0.3} + \text{Sn}_{0.7})\text{O}_3$ has been reported to be 160°C at atmospheric pressure, and to decrease with a pressure coefficient $dT_c/dp \approx -6.1^\circ\text{C}/\text{kbar}$ in the pressure range up to 20kbar^{3),4)}.

Experimental results on the temperature dependence of the relative permittivity ϵ_r (or its reciprocal $1/\epsilon_r$) and the spontaneous polarization P_s at atmospheric pressure are shown in Fig.1.

It is found from Fig.1 and equation (4) that $T_o = 160^\circ\text{C}$ and $c_0 = 2.19 \times 10^6 \text{m}/^\circ\text{C}$ in the paraelectric phase at temperatures above transition temperature $T_c = 163.7^\circ\text{C}$ at which the spontaneous polarization changes discontinuously from $P_{s,c} = 6.12 \times 10^{-2} \text{C}/\text{m}^2$ to $P_s = 0$ with increasing temperature. On substituting the above values for $P_{s,c}$ and c_0 in equations (10) and (18), $\xi = -8.65 \times 10^9 \text{m}^5/\text{FC}^2$ and $\zeta = 1.73 \times 10^{12} \text{m}^7/\text{FC}^4$ are obtained.

Figure 2 shows the pressure dependence of the relative permittivity ϵ_r and the spontaneous polarization P_s at 80°C.

It is found from Fig.2 and equation (4) that $p_0 = 12.5 \text{kbar}$, $g = 1.4 \times 10^7 \text{m}/\text{Fkbar}$ and

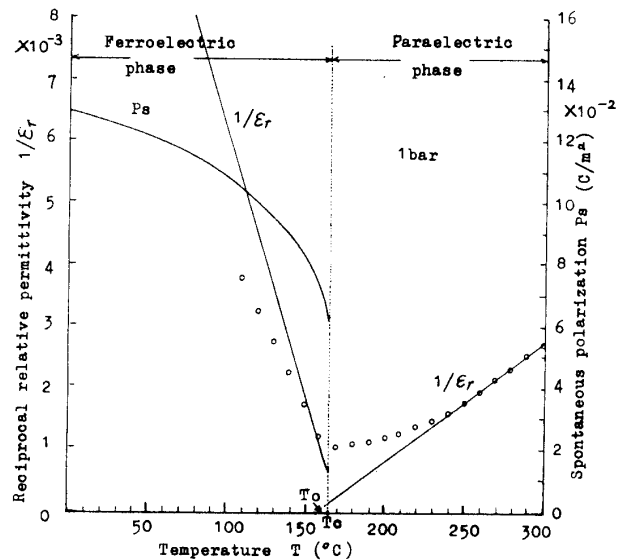


Fig.1 Reciprocal relative permittivity and spontaneous polarization as a function of temperature at 1 bar.

$u = 2.19 \times 10^6(T - 160) = -1.75 \times 10^8 \text{ m/F}$ in the paraelectric phase at pressures above transition pressure $p_c = 13.08 \text{ kbar}$ at which the spontaneous polarization changes discontinuously from $P_{s,c}$ to zero with increasing pressure.

By putting these values on u , g , ξ and ζ in equations (19) and (8), the curve of the relative permittivity ϵ_r against the dc electric field E in the ferroelectric phase at 80°C is obtained for various pressures (0, 5 and 10kbar) as seen in Fig.3.

Figure 4 shows the pressure dependence of the dielectric loss tangent in the ferroelectric phase at 80°C which is obtained by using equation (8), $P_0 = 4.1 \times 10^{-4} \text{ C/m}^2$ and $\tan\delta_1 = 1.9 \times 10^{-2}$, where the value of $\tan\delta_1$ is obtained by measuring a dielectric loss tangent at any pressure in the paraelectric phase (16kbar, for example), and the value of P_0 is calculated by putting a measured value of the dielectric loss tangent at any pressure in the ferroelectric phase (6kbar, for example) into equation (8).

The spontaneous polarization P as a function of applied electric field E (P - E hysteresis loop), and the free energy W as a function of spontaneous polarization P for various temperatures ($T = 80$ and 150°C) under various hydrostatic pressure ($p = 0$ and 10kbar) are obtained by putting the values u , g , ξ and ζ into equations (1)

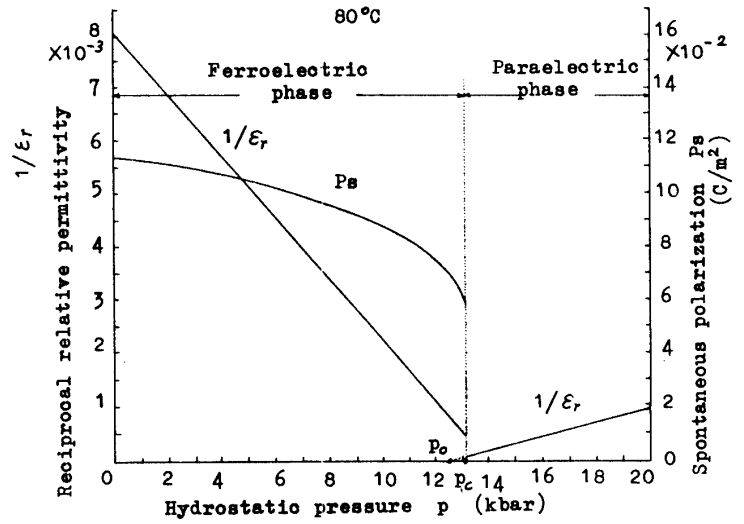


Fig.2 Reciprocal relative permittivity and spontaneous polarization as a function of hydrostatic pressure at 80°C .

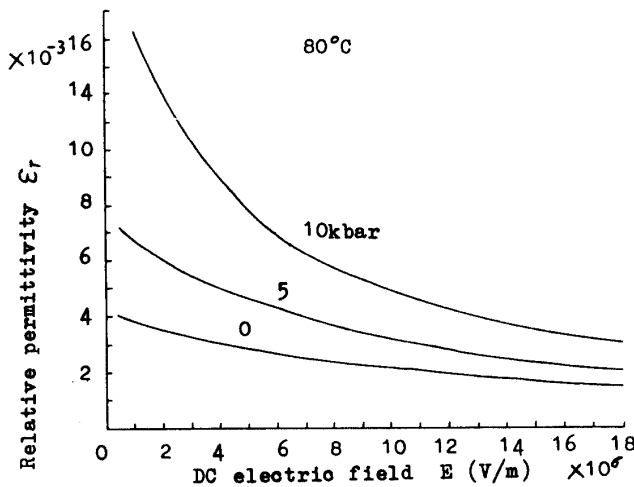


Fig.3 Effect of the electric field on the relative permittivity for various pressures (0, 5 and 10kbar) at 80°C .

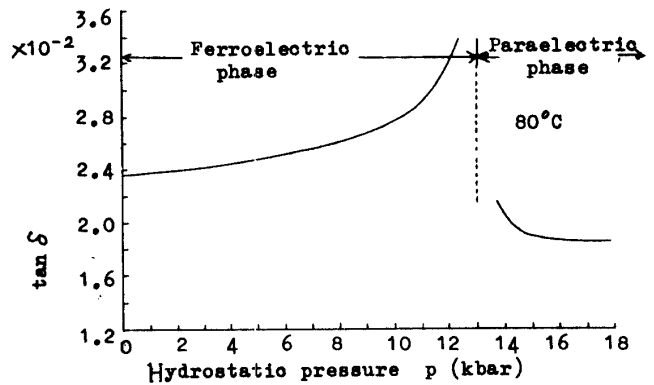


Fig.4 Effect of the hydrostatic pressure on the dielectric loss tangent ($\tan\delta$) at 80°C .

and (2) as seen in Fig.5 and Fig.6, respectively, where $u = -2.19 \times 10^7 \text{ J/m}^3$ for $T = 150^\circ\text{C}$. Maximum and minimum values of the free energy in the ferroelectric phase appear at polarizations for $E = 0$, and those of E appear at polarizations where the equation

$$u + gp + 3\xi P^2 + 5\xi P^4 = 0 \quad \dots\dots\dots (21)$$

is satisfied.

The relations between E and P , and W and P for $p = 0$ kbar at $T = 80^\circ\text{C}$ are indicated in Fig.5 by curve I and in Fig.6 by curve II, respectively. As the electric field E increases from a large and negative value, the polarization P increases along curve I in Fig.6 from point A through point B to point C, where the polarization is the limiting value P_c determined by conditions for minimum free energy ($P_c = 11.34 \times 10^{-2} \text{ C/m}^2$ at $W_m = -8.697 \times 10^5 \text{ J/m}^3$, see Fig.7). When the electric field exceeds the critical field $E_c (= 12.77 \times 10^6 \text{ V/m})$, the polarization becomes unstable, and jumps from point D where $P = -7.9 \times 10^{-2} \text{ C/m}^2$ to point K where $P = 12.1 \times 10^{-2} \text{ C/m}^2$ at E_c , and then increases with increasing electric field towards point L on curve I.

Such behaviour can also be explained from the relation between W and P or by using curve II in Fig.6. Let the points A', B', C', D', O', G', J', K' and L' on curve II in Fig.6 correspond to the points A, B, C, D, O, G, J, K and L on curve I in Fig.5, respectively. The

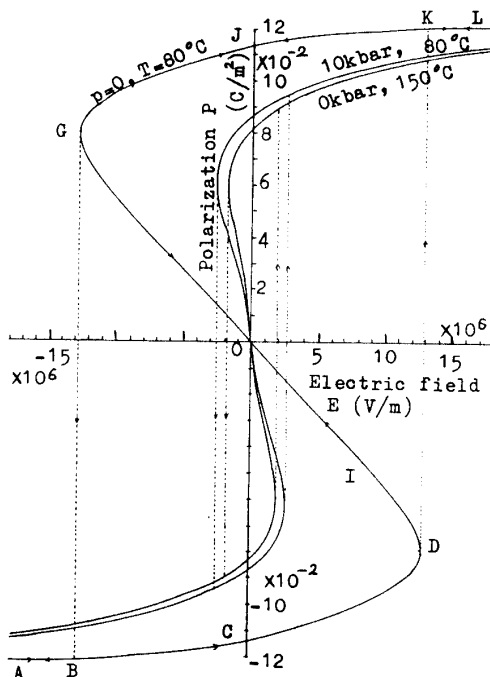


Fig.5 Relation between the polarization and the electric field (P - E hysteresis loop) for $T = 80^\circ\text{C}$ and 150°C at atmospheric pressure, and for $p = 0$ and 10kbar at 80°C .

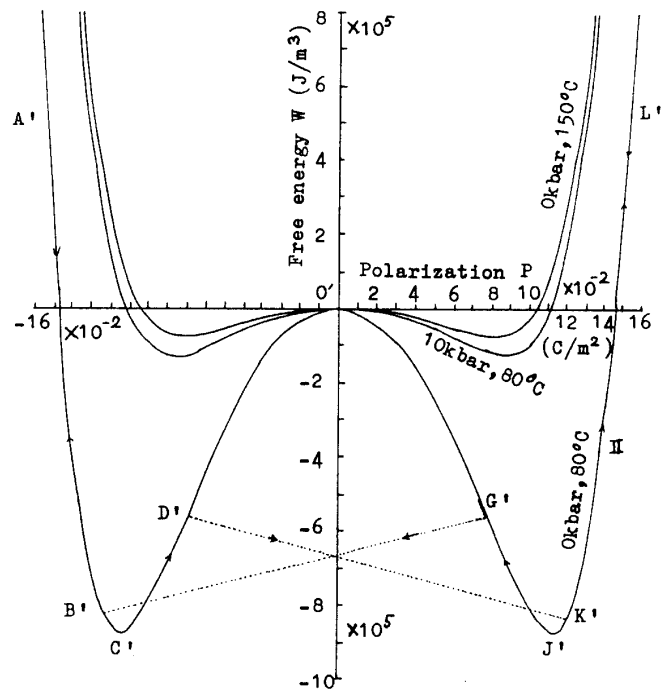


Fig.6 Free energy as a function of polarization for $T = 80^\circ\text{C}$ and 150°C at atmospheric pressure, and for $p = 0$ and 10kbar at 80°C .

reason why the polarization changes suddenly from D to K on curve I to become stable is that the free energy at point K' on curve II ($= -8.2 \times 10^5 \text{ J/m}^3$) is lower than the energy at point D' ($= -5.6 \times 10^5 \text{ J/m}^3$) for the same value of the electric field E_c ($= 12.77 \times 10^6 \text{ V/m}$).

Conversely, as the electric field decreases from a large and positive value, the polarization decreases along curve I in Fig.5 from point L through point J (where $E = 0$ and $P = 11.34 \times 10^{-2} \text{ C/m}^2$) to point G where the polarization is the lower limit of the stable state. The polarization drops from point G (where $P = 7.9 \times 10^{-2} \text{ C/m}^2$ and $E = -E_c$) to point B where the polarization is more stable and its value is $-12.1 \times 10^{-2} \text{ C/m}^2$, because the energy at B ($= -8.2 \times 10^5 \text{ J/m}^3$ as indicated by B' on curve II in Fig.6) is lower than the energy at G ($= -5.6 \times 10^5 \text{ J/m}^3$) for the same value of the electric field ($= -12.77 \times 10^6 \text{ V/m}$). After that the polarization decreases with decreasing electric field along curve I.

In this way a hysteresis loop $A \rightarrow B \rightarrow C \rightarrow D \rightarrow K \rightarrow L \rightarrow K \rightarrow J \rightarrow G \rightarrow B \rightarrow A$ is drawn as seen in Fig.5, and a theoretical path $A \rightarrow B \rightarrow C \rightarrow D \rightarrow O \rightarrow G \rightarrow J \rightarrow K \rightarrow L \rightarrow K \rightarrow J \rightarrow G \rightarrow O \rightarrow D \rightarrow C \rightarrow B \rightarrow A$ is never realized, because the polarization is unstable in the negative gradient range $D \rightarrow O \rightarrow G \rightarrow O \rightarrow D$.

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