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DIELECTRIC AND PYROELECTRIC CHARACTERISTICS AND FERROELECTRIC SOFT MODES IN $PbTiO_3$ POLYCRYSTALS DOPED WITH Ca^{2+}

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The effects of Ca^{2+} ions on the structure and dielectric and pyroelectric characteristics of $PbTiO_3$ polycrystals were investigated. With increasing content of Ca, a decrease in tetragonal axial ratio (c/a) was observed as a consequence of shrinkage of the lattice parameter c. The dielectric constant and pyroelectric coefficient increase and Curie temperature (T_C) shifts toward lower temperature with increasing content of Ca. The theory of ferroelectric soft mode has been developed to illuminate the relationship between the structure and properties of the polycrystal.

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I. INTRODUCTION

Lead titanate ($PbTiO_3$) has a perovskite crystal structure. It is an ideal piezoelectric and pyroelectric material widely used as transducers and infrared sensors because of its relatively high Curie point of 490 °C, high spontaneous polarization, low dielectric constant and good piezoelectric properties. However, polycrystalline $PbTiO_3$ is easy to disintegrate into powders when cooled down through the Curie point, because of the large c/a ratio(1.063) of the low-temperature tetragonal phase. Much attention has been focused on the modification for $PbTiO_3$ by doping. Substitution of other cations for Ti at B site in $PbTiO_3$ has been extensively studied and lead zirconate titanate ($Pb(Ti_{1-x}Zr_x)O_3$ or PZT) is a typical example of solid solutions with good piezoelectric properties.[1−3] Ichinose[4] and Prasad[5] investigated the dielectric and pyroelectric characteristics of $(Pb_{1-x}Ca_x)$ (W,Cd,Ti)O_3, and

$(Pb_{1-x}Ca_x)(Mn, W, Ti)O_3$ for different x, respectively, in which the substitution of A site cations is achieved. However, there have been few works on this kind of substitution responsible for the phase transition.

In 1940, Raman and Nedungadi seem to be the first to have observed a soft mode in a structural phase transition. In 1959, Cochran[6] and Anderson[7] suggested that the phase transitions in certain ferroelectrics might result from an instability of one of the normal vibrational modes of the lattice. In this theory, the frequency of the relevant soft phonon decreases on approaching the critical temperature T_C and the restoring force for the mode displacements tends to zero until the phonon has condensed out at the stability limit. The static atomic displacements occur on going from the paraelectric to the ferroelectric phase. More specifically, it can be considered that a "ferroelectric ordering" involves the instability of a phonon at the Brillouim zone centre. Since then,extensive experimental and theoretical studies on this subject have been reported. There have been few works on the relationship between structure and properties of solid solutions in terms of the theory of soft mode.

In the present paper, the effects of Ca^{2+} ions on the structure and dielectric and pyroelectric characteristics of $PbTiO_3$ polycrystals are investigated and the ferroelectric soft mode theory is developed to explain the experimental results.

II. EXPERIMENTAL PROCEDURE

The sample composition was $(Pb_{1-x}Ca_x)[(Co_{1/2}W_{1/2})_{0.04}Ti_{0.96}]O_3 + 1$ mol % $MnCO_3$ +0.8 mol %NiO, where x=0.05–0.30. The starting materials were reagent chemicals PbO(99.5 %), TiO_2 (98.0 %), and $CaCO_3$ (99.0 %). The powders were mixed by ball milling for 4 h and drying and, pressed into pellets with 10 mm in diameter and 1 mm in thickness at a pressure of 1000 kg/cm^2. These pellets were sintered at 1140°C for 1.5 h. Phase structure and degree of reaction were checked by X-ray diffraction (XRD). Silver paste was fired on both faces of the pellets at 550°C to serve as electrodes for dielectric measurements.

XRD was carried out with a D/max-IIIA diffractometer using Cu$K\alpha$ radiation(λ = 0.1542 nm) in the 2θ range 10°–70° at a 2θ scanning rate of 2°/min. The dielectric and pyroelectric properties of the samples were measured by using HP-936 computer -controlled HP4274A, HP4275A and HP4192 LCR measurement system and HP-4140B micro-current meter, respectively.

III. RESULTS

A. Phase structure and lattice parameters

XRD patterns indicated that all specimens were of single-phase tetragonal perovskite structure at room temperature, belonging to the point group 4mm. It was found that the $(Pb_{1-x}Ca_x)TiO_3$ solid solution was formed by doping with Ca^{2+} for $x < 0.30$, and Ca^{2+}

ions occupied the site of Pb^{2+} ions(A site),as shown in Fig.1. The lattice parameters of the $(Pb_{1-x}Ca_x)TiO_3$ polycrystalline samples were calculated by using Nelson extrapolation procedure in order to find the relevant interplanar spacing, d, and Miller indexes, h and k, corresponding to l=0 from the XRD data, then a series of values of the lattice parameter,

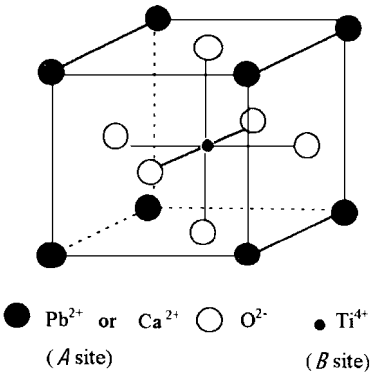

Fig.1. Schematic diagram of perovskite type structure.

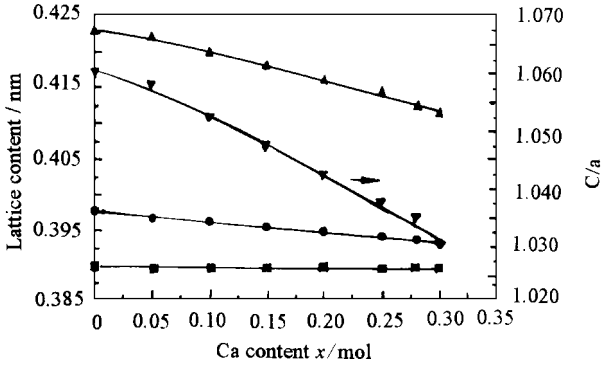

Fig.2. Variation of lattice parameters versus Ca content at 25℃. ■ —a; ● —$\sqrt[3]{a^2c}$; ▲ —c; ▼ —c/a.

a, were obtained by using the relation $\frac{l}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$ and a series of $f(\theta)$, where $f(\theta) = \frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}$. Extrapolating the linear relation of $a - f(\theta)$ up to $f(\theta)$=0, the accurate value of the lattice parameter, a, could be determined. Similarly, the lattice parameter, c, was obtained. The changes in lattice parameters and the axial ratio (c/a) of the tetragonal structure for different contents of Ca are shown in Fig.2; the values of a, c and c/a for pure $PbTiO_3$ are also shown in the figure for comparison. With increasing content of Ca a decrease in tetragonality (c/a) was observed as a consequence of shrinkage of the c-axis. The result is considered to be due to two factors. First, because the Ti—O covalent bond in $PbTiO_3$ along the a-axis is stronger than that along the c-axis,so that a-axis is not easy to change. Second, because the radius of Ca^{2+} ions (0.099 nm) is smaller than that of Pb^{2+} ions(0.121 nm) and the difference of the electronegativity of Ca—O binding (2.5) is much larger than that of Pb—O binding (1.7)the binding force of Ca—O is stronger than that of Pb—O.

B. Dielectric and pyroelectric properties

Figure 3 shows the temperature dependence of the dielectric constant, ε,in the range from−50 to 300 °C under 10 kHz for different content of Ca, x=0–0.30. As a typical one of normal ferroelectrics, the dielectric constant increases gradually with increasing temperature below the Curie point, T_C. Also, it is seen that with increasing content of Ca, the value of ε increases and the Curie point shifts toward lower temperature. Figure 4 shows the variation

of the pyroelectric coefficient, p, with temperature(20–110°C) for the different content of Ca,x=0–0.28. It is found that the value of p increases with increasing temperature and content of Ca. As a result, the dielectric constant and the pyroelectric coefficient will be increased by doping with Ca^{2+} ions in $PbTiO_3$.

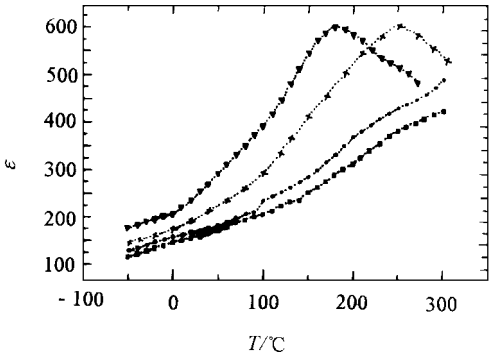

Fig.3. Temperature dependence of the dielectric constant, ε at 10 kHz ■ —x=0; ● —x = 0.10; ▲ —x = 0.25; ▼ -x = 0.30.

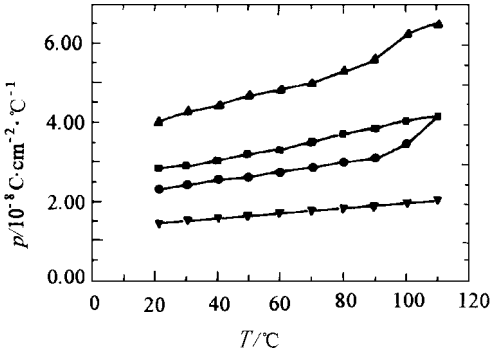

Fig.4. Temperature dependence of the pyroelectric coefficient,p. ▼ —x = 0; ● —x = 0.15;■ —x = 0.20; ▲ —x = 0.28.

Figure 5 shows the variation of the reciprocal of the dielectric constant of $(Pb_{1-x}Ca_x)TiO_3$ with temperature for x=0.25, 0.28 and 0.30. It is seen that the changes of the dielectric constant with temperature still have the characteristics of first-order phase transition of displacive type of ferroelectrics. With increasing content of Ca, the Curie point, T_C, the limiting temperature of ferroelectric phase, T_0, and the Curie-Weiss constant, C, exhibit a falling tendency.

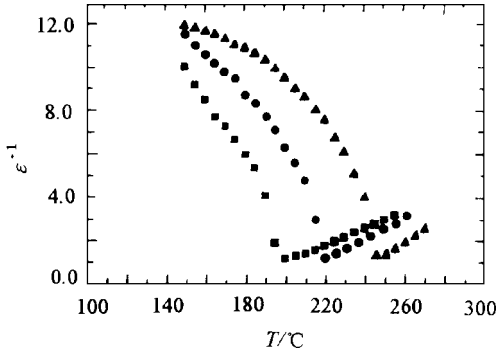

Fig.5. Reciprocal of dielectric constant of $(Pb_{1-x}Ca_x)TiO_3$ versus temperature. ▲ —x=0.25; ● —x = 0.28 and ■ —x = 0.30.

IV. THEORY OF FERROELECTRIC SOFT MODE AND DISCUSSION

It is known that when the ferroelectric phase transition takes place in ferroelectrics, generally it is only related to the rearrangement of a few atoms in the unit cell, whereas

the positions of all other atoms remain unchanged. For the displacive type of ferroelectrics, $PbTiO_3$, it may be regarded as the relative displacement of the Ti^{4+} ions with respect to O^{2+} ions in oxide octahedra of the perovskite structure. In treating the soft mode, from the dynamics of this system we suppose that Ti^{4+} ions are active particles in the lattice, the rest of the crystal lattice are regarded as hot-pool. The model Hamiltonian describing the structural phase transition, which will then depend only on this local normal coordinate, Q_l, and the corresponding momentum P_l in $(Pb_{1-x}Ca_x)TiO_3$, can be written as

$$H = \sum_l H_l^{(\mathrm{s})} + H^{(\mathrm{int})} = \sum_l \left[\frac{1}{2M}P_l^2 + V(Q_l)\right] - \frac{1}{2}\sum_{ll'} v_{ll'}Q_lQ_{l'}\,. \tag{1}$$

Here,$V(Q_l)$ is the potential energy of a singleparticle contributed by the simple harmonic and quartic anharmonic interaction items which can be written as follows:

$$V(Q_l) = \frac{1}{2}M\Omega_{\mathrm{s}_0}^2 Q_l^4 + \frac{1}{4}\gamma Q_l^4\,. \tag{2}$$

In Eqs.(1) and (2), Q_l is the local normal coordinate which is used to describe the displacement of ions in the lth cell, γ the coefficient of quartic anharmonic force, P_l the canonically conjugate momentum, M the effective mass, $v_{ll'}$ the harmonic coefficient which is used to describle the interaction among the ions in the different unit cells, and Ω_{s_0} is the simple harmonic fequency of the singleparticle.

As far as the properties of the system described by the Hamiltonian in Eq.(1), they strongly depend on the shape of the single-particle potential $V(Q_l)$. In displacive ferroelectrics, we assume $\Omega_{\mathrm{s}_0}^2 > 0$ and $\gamma > 0, V(Q_l)$ is only slightly anharmonic, and has a single minimum at Q_l=0. If the interactions are strong enough, they can lead to a destabilization of the position at Q_l=0. In this case, a harmonic instability and a displacive phase transition take place, which is connected with the condensation of a soft phonon, as the ferroelectric state is characterized by a macroscopic spontaneous polarization.

By using the molecular field approximation (MFA) and the random phase approximation(RPA), the spontaneous polarization, P_{s}, and the dynamic electric susceptibility, χ, as functions of temperature, T, and the thermal average value of the normal coordinate $< Q_l >$, which measures the distortion from the high-temperature structure, can be obtained by the following formulas:

$$P_{\mathrm{s}}^2 \propto < Q_l > = \frac{1}{4\gamma}\left[\nu_0 - 2M\Omega_{\mathrm{s}_0}^2 + \sqrt{3(\nu_0 - 2M\Omega_{\mathrm{s}_0}^2)^2 - 24k_{\mathrm{B}}\gamma T}\right], \tag{3}$$

$$\varepsilon^{-1} \cong \chi^{-1} = \frac{1}{2}\left[\nu_0 - 2M\Omega_{\mathrm{s}_0}^2 + \sqrt{3(\nu_0 - 2M\Omega_{\mathrm{s}_0}^2)^2 - 24k_{\mathrm{B}}\gamma T}\right] + (\nu_0 - \nu_q) - M\omega^2\,, \tag{4a}$$

where ω is the angular frequency of the electric field applied, k_{B} is boltzmann constant, $\nu_0 \sum_l \nu_{ll'}$ and $\nu_q = \sum_{l'} u_{ll'} \mathrm{e}^{-\boldsymbol{q}\cdot(\boldsymbol{R}_l - \boldsymbol{R}_{l'})}$ are Fourier transforms of the harmonic interaction between the primitive cells. However, in the case of the paraelectric state, $T > T_{\mathrm{C}}, < Q_l > =$

0. The dielectric constant as a function of temperature obeys Curie-Weiss law, which can be written in the form

$$\varepsilon^{-1} \cong \chi^{-1} = \frac{3\gamma k_{\mathrm{B}}}{2\nu_q - M\Omega_{\mathrm{s_0}}^2}(T - T_{\mathrm{C}}) + (\nu_0 - \nu_q) - M\omega^2 = \frac{1}{C}(T - T_0) + (\nu_0 - \nu_q) - M\omega^2, \quad (4\mathrm{b})$$

where $T_{\mathrm{C}} = \dfrac{\nu_0(2\nu_0 - M\Omega_{\mathrm{s_0}}^2)}{3\gamma k_{\mathrm{B}}}$ is the characteristic temperature, generally referred to as Curie point, and is related to the structure of the materials; C is Curie-Weiss constant which is about $1.5 \times 10^5\,\mathrm{K}$. When the displacive phase transition from the ferroelectric to the paraelectric phase takes place, the vibration mode will be softened by anharmonic interaction which is beneficial to the stabilization of the paraelectric phase. From this, it is considered that anharmonic interaction will lead to a low Curie point.

By using Eq.(3), the pyroelectric coefficient can be obtained as the following:

$$p^2 \propto \left[\frac{\mathrm{d} < Q_l >}{\mathrm{d}T}\right]^2 = \frac{9k_{\mathrm{B}}^2\gamma}{(\alpha + \sqrt{\beta - 24k_{\mathrm{B}}\gamma T})(\beta - 24k_{\mathrm{B}}\gamma T)}, \quad (5)$$

where $\alpha = \nu_0 - 2M\Omega_{\mathrm{s_0}}^2, \quad \beta = (3\nu_0 - 2M\Omega_{\mathrm{s_0}}^2)^2$.

In practice, the value of p/ε is an important parameter used to describe the pyroelectric effect of the materials. Combining Eq.(4a) with Eq. (5), the value of p/ε has the following form

$$\frac{p^2}{\varepsilon^2} \propto \frac{9k_{\mathrm{B}}^2\gamma}{4(\beta - 24k_{\mathrm{B}}\gamma T)} + \frac{9k_{\mathrm{B}}^2\gamma[2(\nu_0 - \nu_q) - 2M\omega^2]^2}{4(\alpha + \sqrt{\beta - 24k_{\mathrm{B}}\gamma T})(\beta - 24k_{\mathrm{B}}\gamma T)}. \quad (6)$$

By using Eqs.(4), (5)and (6), the pyroelectric coefficient p/ε and the dielectric constant ε as functions of temperature have been calculated. The results are shown in Fig.6. Compared with the experimental results, the regularity is similar. It is clear that the model is suitable to illuminate the pyroelectric and dielectric properties of $(\mathrm{Pb}_{1-x}\mathrm{Ca}_x)\ \mathrm{TiO}_3$ solid solutions. In addition, we found that the values of p/ε and ε are related not only to the temperature but also to the parameters of $M\Omega_{\mathrm{s_0}}^2, \gamma$ and $\nu_{ll'}$. As mentioned above, we know that the lattice constants decrease with increasing content of Ca in lead titanate, which implies that the moving spaces of Ti^{4+} ions are narrowed and then the interaction between the ion displacements is enhanced to a certain extent when the particles in the lattice are drawing near each other. As a result of this structural change, the potential function and the Hamiltonian function of Ti^{4+} ions will be changed. In this case, the coefficients of $M\Omega_{\mathrm{s_0}}^2, \gamma$ and $\nu_{ll'}$, especially γ, in the equations will increase with the decrease of the lattice constant. Assuming that the coefficient of $M\Omega_{\mathrm{s_0}}^2$ and $\nu_{ll'}$ are not in change at a certain temperature when the lattice constant decreases with increasing content of Ca, the parameters p and ε are regarded as functions of γ.

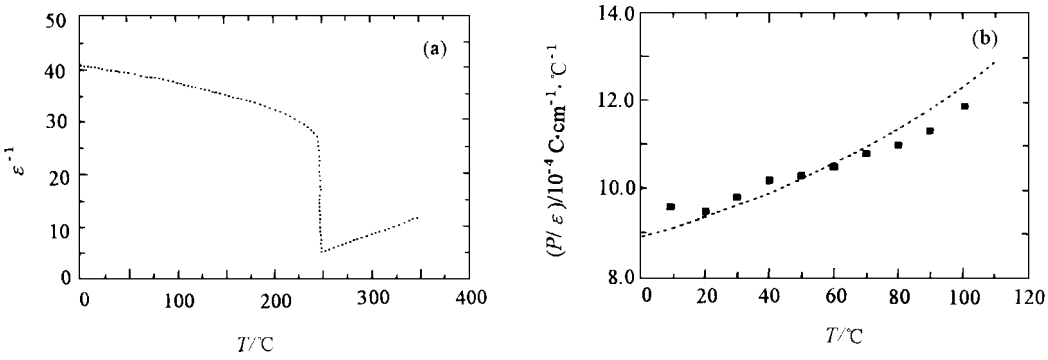

Fig.6. Calculated value of the reciprocal of the dielectric constant ε^{-1} (a),and the pyroelectric coefficient p/ε (b), as functions of temperature. ■ denotes the experimental value at x=0.10.

Figure 7 shows the theoretical and experimental values of p and ε versus the change of γ and the content of Ca according to Eqs.(4) and (5). It is obvious that the lattice constants decrease with increasing content of Ca, which results in the increase of the coefficient of quartic anharmonic force γ, and in turn the increase of the pyroelectric coefficient p/ε and the dielectric constant ε.

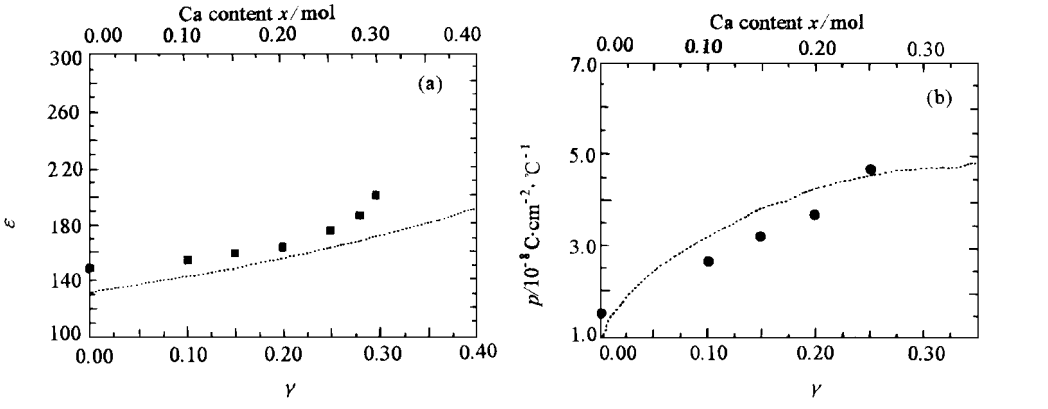

Fig.7. The theoretical and experimental values of ε (a),and p(b)versus the change of γ and the content of Ca. ■—the experimental value of ε at 0°C; ●—the experimental value of p at 30°C.

V. CONCLUSION

1. Doping with Ca^{2+} ions in lead titanate polycrystals causes the decrease of tetragonality (c/a) as a consequence of shrinkage of the unit cell along the c-axis. It is considered that the Ti—O covalent binding of $PbTiO_3$ along the a-axis is stronger than along the c-axis, and the binding force of Ca—O is stronger than that of Pb—O.

2. The lattice dynamic theory of ferroelectric soft modes in Ca–doped $PbTiO_3$ has been developed. It is indicated that the decrease of the lattice constants in $PbTiO_3$ is attributed to the enhancement of anharmonic force in the lattices due to doping with Ca^{2+} ions. As a result, the value of dielectric constant and pyroelectric coefficient increases and the Curie point shifts toward lower temperature with increasing content of Ca.

3. It has been verified by the experimental results that the lattice dynamic theory of ferroelectric soft modes can be used to explain the relation between the structure and properties of $PbTiO_3$ with the substitution of A site.

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