

# Raman Scattering Study of Ca-Modified Lead Titanate

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**Abstract**—The paraelectric to ferroelectric phase transitions were studied by Raman scattering in Ca-doped lead titanate ceramics. The soft optic modes responsible for the ferroelectric phase transitions were clearly observed. The  $A_1(1TO)$  mode, which softens toward  $T_c$ , contains four subpeaks. The frequencies of these subpeaks depend to a great extent on the Ca content and the temperature. These behaviors are discussed on the basis of the anharmonicity of lattice vibrations.

## I. INTRODUCTION

LEAD titanate,  $PbTiO_3$  (PT), is one of the most important ferroelectric materials for basic research and industrial applications. Among perovskite oxide ferroelectric materials such as barium titanate  $BaTiO_3$  and potassium niobate  $KNbO_3$ , PT behaves close to the expected manner of an original concept of displacive-type ferroelectrics. Because the damping of soft optic modes is much smaller than that of other perovskite ferroelectrics [1], the inelastic scattering of soft optic phonons of PT has been well studied by many researchers.

In potential application among many PT-based ferroelectrics,  $(Pb_{1-x}Ca_x)TiO_3$  is a promising material for piezoelectric, pyroelectric, and electro-optical devices. On the other hand, PT-based ferroelectrics have been investigated not only for technical application but also for fundamental research due to their simple crystal structure. The  $(Pb_{1-x}Ca_x)TiO_3$  solid solution has been studied by x-ray diffraction (XRD), Raman scattering, and theoretical calculations [2]. Although there are many publications on Ca-modified  $PbTiO_3$  ceramics, detailed analysis of their lattice dynamics is still not adequate because of the lack of the low-frequency Raman scattering measurements. It is recognized that the lattice dynamic properties, especially in low-frequency regions, are important for considering the origin of ferroelectricity relative to lattice instability [3].

In this work, we have measured the temperature and Ca content dependences of Raman scattering of Ca-modified lead titanate ceramics,  $(Pb_{1-x}Ca_x)TiO_3$ , to elucidate the anharmonic properties of the soft optic mode responsible for the ferroelectric phase transition.

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## II. EXPERIMENTAL

The various forms of  $(Pb_{1-x}Ca_x)TiO_3$ :  $x = 0.19, 0.25, 0.37, 0.38, 0.41, 0.42, 0.44, 0.48,$  and  $0.50$ , where  $x$  is the molar content of Ca, were synthesized at The National Defense Academy [4]. The composition of  $(Pb_{1-x}Ca_x)TiO_3 + 1$  mol% MnO was weighed using  $PbO$  (99.5%),  $CaCO_3$  (99.6%),  $TiO_2$  (99.9%), and  $MnCO_3$  (99.3%) powders. The mixed powders were calcined at  $850^\circ C$  for 2 hours in air, and the sintering condition was  $1150^\circ C$  for 100 hours in air. The  $PbTiO_3$  used ( $x = 0.00$ ) is a powder (Furuuchi Chemical Corporation, Tokyo, Japan). Raman spectra were measured by means of a triple grating spectrometer of the additional dispersion (Jobin Yvon, T64000; Horiba, Ltd., Tokyo, Japan) with a resolution of  $3\text{ cm}^{-1}$ . The output signals were detected using a conventional photon counting system. The excited source was a green YAG laser with the wavelength  $532\text{ nm}$  and power  $100\text{ mW}$ . The temperature dependence of Raman spectra was measured by using a Linkam stage (Japan High Tech Co., Ltd., Fukuoka, Japan). The temperature of the sample was stabilized by a temperature controller.

Dielectric constants were measured by an impedance analyzer (Solartron SI 1260; Solartron Analytical, Hampshire, UK). We measured the temperature dependence of dielectric constants for all samples at  $1\text{ kHz}$  from room temperature to the temperature well above the Curie temperature,  $T_c$ , at the heating rate of  $1.0^\circ C/min$ . The temperature of a sample was controlled by a home-made high-temperature furnace with a digital temperature controller and was monitored by a chromel-alumel thermocouple. Silver was fired on the surfaces of the samples as electrodes.

## III. RESULTS AND DISCUSSION

Fig. 1 shows the temperature and Ca content dependences of the dielectric constant of  $(Pb_{1-x}Ca_x)TiO_3$  measured at  $1\text{ kHz}$ . The  $T_c$  was determined by the peak temperature. As shown in Fig. 1, the  $T_c$  decreases from  $646\text{ K}$  to  $333\text{ K}$ , i.e., the ferroelectricity decreases as Ca is added.

Fig. 2 shows the Ca content dependence of the Raman spectra. As  $x$  increases from  $0.00$  to  $0.50$ , the phonon modes change gradually. Some modes disappear above  $x = 0.42$ . In the paraelectric phase ( $T > T_c$ ), PT belongs to a cubic system with a point group  $m3m$ . At the  $\Gamma$  point in the Brillouin zone, the 12 optical phonon modes belong to the  $3T_{1u} + T_{2u}$  irreducible representations. The  $T_{1u}$  modes are triply degenerated and infrared active, while the

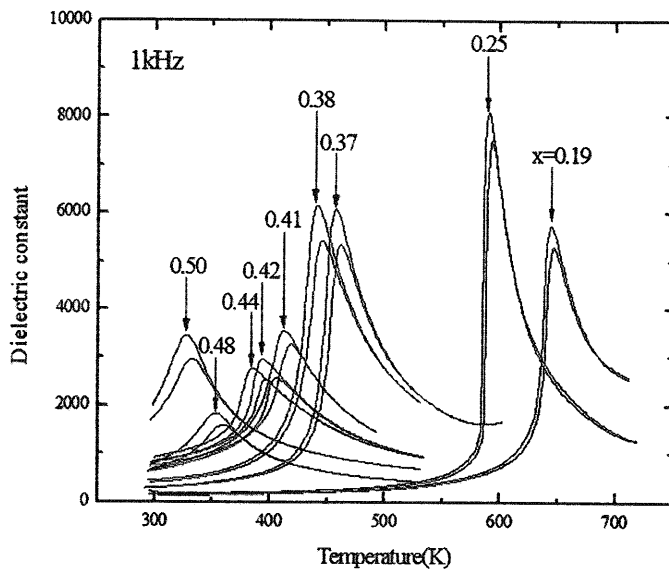


Fig. 1. The temperature dependence of the dielectric constant of  $(\text{Pb}_{1-x}\text{Ca}_x)\text{TiO}_3$  ceramics at 1 kHz.

$T_{2u}$  mode is silent, neither infrared nor Raman active. In the ferroelectric phase ( $T < T_c$ ), PT belongs to a tetragonal system with a point group 4 mm. Each  $T_{1u}$  mode splits into two modes of  $A_1(z) + E(x, y)$ , and the  $T_{2u}$  mode splits into two modes of  $B_1 + E(x, y)$  [5].

Burns and Scott reported that the  $A_1(1\text{TO})$  mode plays a dominant role in the dielectric behavior along the ferroelectric c-axis at all temperatures below  $T_c$  [1]. Thus, the  $A_1(1\text{TO})$  mode is very important for understanding PT-based ferroelectrics.  $(\text{Pb}_{1-x}\text{Ca}_x)\text{TiO}_3$  ceramics prepared by the sol-gel method were found to exhibit a decrease in tetragonality ( $c_0/a_0$  ratio) with the increase of  $x$ , and it approaches 1 where  $a_0$  and  $c_0$  are lattice constant [6]. Because the addition of Ca causes the decrease of tetragonality, the  $A_1(1\text{TO})$  mode transforms into the  $T_{1u}$  mode at  $T_c$  on heating. The  $A_1(1\text{TO})$  mode is anharmonic, as shown in Fig. 3, because the line shape deviates from the Lorentzian function.

The anharmonicity of the  $A_1(1\text{TO})$  mode was studied by analyzing the four Lorentzian peaks under the assumption of a double-well potential in a ferroelectric phase for the  $A_1(1\text{TO})$  mode [3], [5], [6]. The schematic diagram of a double-well potential and energy levels is shown in Fig. 3. We labeled the four subpeaks in the  $A_1(1\text{TO})$  mode 1, 2, 3, and 4, as indicated in the inset of Fig. 3. They correspond to the transitions from  $n = 3$  to  $n = 4$ ,  $n = 2$  to  $n = 3$ ,  $n = 1$  to  $n = 2$ , and  $n = 0$  to  $n = 1$  of the vibrational quantum states, respectively [3], [7]. When we neglect an order of anharmonicity higher than fifth order, the difference of the transition energy between two adjacent levels is given by

$$E_{n+1} - E_n = \hbar\omega_0 - \frac{3\hbar^2}{2m\omega_0^2}(n+1) \left( \frac{5c^2}{m\omega_0^2} - 2d \right) \equiv \hbar\omega_{n+1}, \quad (1)$$

where  $c$  and  $d$  are the coefficients for the third- and fourth-order terms of anharmonicity. Since  $\omega_0$  is the  $A_1(z)$  soft

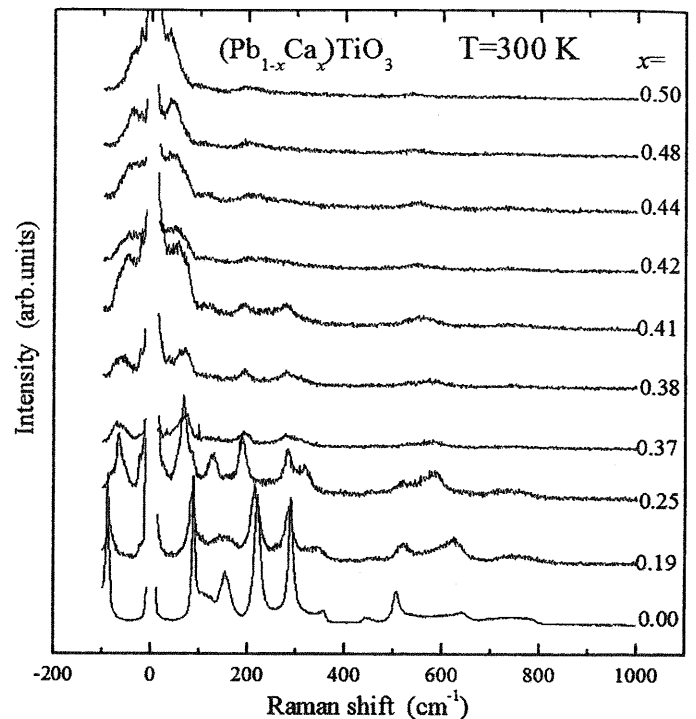


Fig. 2. The Ca content dependence of Raman spectra at 300 K.

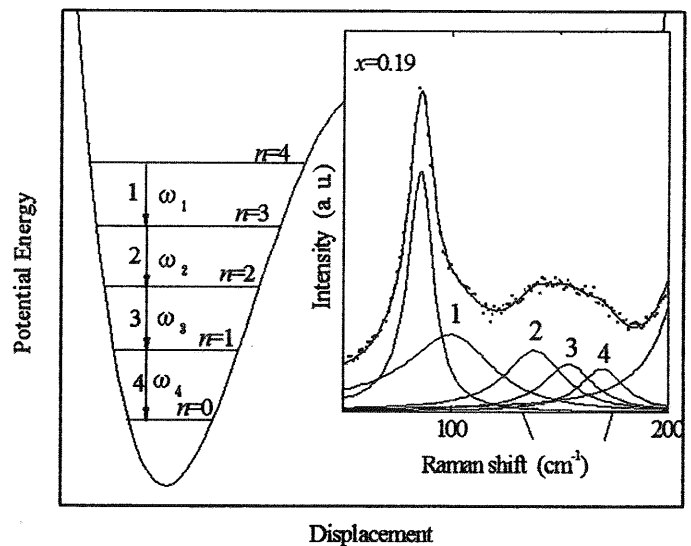


Fig. 3. Schematic diagram of a double-well potential.

mode frequency [3], [8],  $\omega_0$  is proportional to  $(T_c - T)^{0.5}$  below  $T_c$  in the mean field theory of a second-order phase transition. Eq. (1) gives the frequency of each subpeak, as indicated in Fig. 3. The difference between two adjacent vibrational transitions is given by

$$\hbar\omega_n - \hbar\omega_{n+1} = \frac{3\hbar^2}{2m^2\omega_0^2} \left( 5 \frac{c^2}{m\omega_0^2} - 2d \right). \quad (2)$$

At  $T \ll T_c$  (without anharmonic terms), one side of the double-well potential is almost harmonic. Therefore, it holds that  $\hbar\omega_n - \hbar\omega_{n+1} = 0$ , which means that the transition energy between two adjacent vibrational transitions

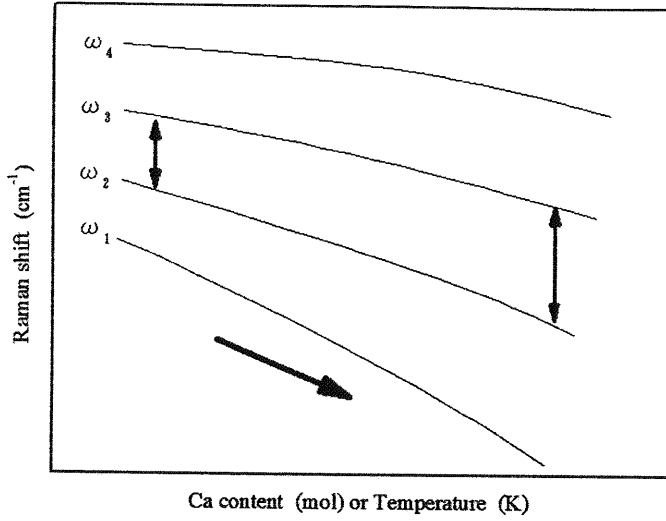
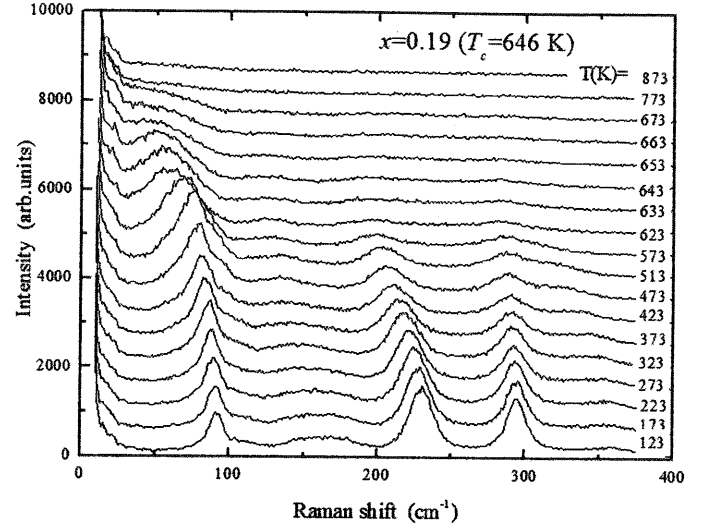
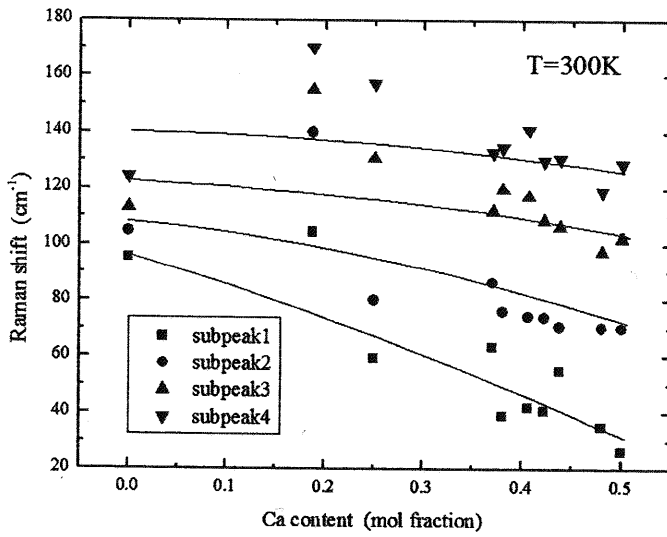
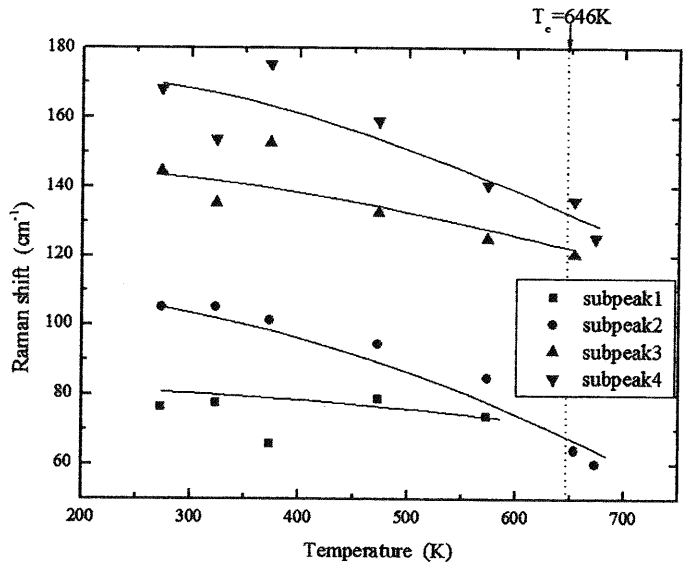


Fig. 4. The theoretical prediction of the subpeak frequencies.

Fig. 6. The temperature dependence of Raman spectra at  $x = 0.19$ .Fig. 5. The Ca content dependences of subpeak frequencies of the  $A_1(1TO)$  mode at 300 K.Fig. 7. The temperature dependence of the subpeak frequencies of the  $A_1(1TO)$  mode at  $x = 0.19$ .

is equal. At  $T \sim T_c$ , one side of the double-well potential becomes anharmonic. Consequently,  $\hbar\omega_n - \hbar\omega_{n+1} \neq 0$  and the difference between two adjacent vibrational transition becomes larger with increasing  $x$  (Fig. 4). Since  $\omega_0^2$  goes to zero as  $T$  approaches  $T_c$  or  $x$  increases below  $T_c$ , from (1) and (2), one can expect that the frequency of each subpeak to decrease and the difference of adjacent subpeak frequencies to increase as Ca is added or as the temperature is increased, as shown in Fig. 4. Fig. 5 shows the observed result on the Ca content dependence of subpeak frequencies of the  $A_1(1TO)$  mode, where solid lines are the guides to eyes. Although there is deviation from the theoretical prediction between 0.00 and 0.19, this shows reasonable behavior of (2), which implies the validity of the anharmonic model with third and fourth anharmonicity.

Fig. 6 shows the temperature dependence of the Raman spectra at  $x = 0.19$ . The  $E(1TO)$  mode ( $\sim 100 \text{ cm}^{-1}$  at

123 K) shows softening, as expected by the phenomenological theory [9]. Besides, the  $A_1(1TO)$  mode also shows softening ( $\sim 150 \text{ cm}^{-1}$  at 123 K). We fit the  $A_1(1TO)$  mode by four Lorentzians, and the temperature dependences of subpeak frequencies are shown in Fig. 7, where solid lines are the guides to eyes. From (2), it is clear that the spacing between subpeak frequencies expands as  $T_c$  increases, as shown in Fig. 4, because  $\omega_0$  decreases as the temperature increases. Since the result is not consistent with the present analysis, the anharmonic terms higher than fifth order might be important to reproduce the results.

#### IV. CONCLUSION

The phase transitions of  $(\text{Pb}_{1-x}\text{Ca}_x)\text{TiO}_3$  ceramics were investigated by Raman scattering with changing Ca con-

tent and temperature. We have discussed the second lowest soft optic mode with  $A_1(z)$  symmetry on the basis of third- and fourth-order anharmonicity. The Ca content dependences at room temperature are explained qualitatively by the perturbation theory containing third- and fourth-order terms of anharmonicity. In the temperature dependence, however, we could not reproduce the result by this theory, because the difference of adjacent subpeak frequency decreases on heating. Probably the contributions from higher-order anharmonicity cause the deviation, because the atomic motion of phonons becomes very large near  $T_c$  due to the strong lattice instability.

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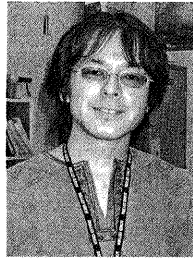
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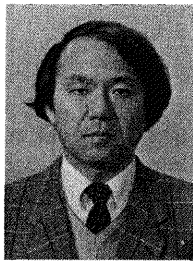
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