Raman spectra and structural phase transition in nanocrystalline lead lanthanum titanate

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The effects of particle size on the structure and Raman spectra of lead lanthanum titanate nanocrystalline particles are investigated. Samples with different particle sizes were prepared by the sol–gel process using different calcination temperatures. The sizes of the crystallites of particles were determined by x-ray diffraction with the aid of Scherrer's equation. Raman vibration modes of samples with various particle sizes were also studied by Raman scattering at room temperature. The results show that the tetragonal distortion of the unit cell apparently decreases with decreasing particle size: the soft $A_1(1TO)$ phonon mode which is related to the spontaneous polarization of ferroelectric materials shifts toward lower frequency, and other peaks exhibit broadening and intensity changes with decreasing particle size. These are attributed to a phase transformation from the ferroelectric tetragonal to the paraelectric cubic phase. The above phenomena are related to a grain size-induced structural phase transition. © *2001 American Institute of Physics.*
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I. INTRODUCTION

Due to the advance in nanoparticle synthesis techniques, some researchers have come to realize that nanomaterials possess many new characteristics with different sizes,[1–3] and there has been great interest in the application of nanocomposites to electronic devices as ultrasonic transducers and pyroelectric infrared sensors. These applications include both fabrication of the fine ferroelectric particles of nanometer size and understanding nanoparticle properties. Therefore, the study of size effects on the structural phase transition of ferroelectric nanocrystalline particles has recently become very important because of their potential applications.

The effects of particle size on the physical properties of ferroelectric materials have been investigated theoretically[4] and experimentally.[5,6] Frey *et al.*[5] and McCauley *et al.*[6] studied the effect of particle size on the crystal structure and dielectric properties of $BaTiO_3$; and Ishikawa *et al.*[7] investigated the effect of particle size on the Curie temperature in $PbTO_3$ (PT). However, the origin of the size effect and structural phase transition in ferroelectric materials has not been clarified, and there have been few reports on the size effects for the structure and ferroelectric properties of lead lanthanum titanate $(Pb_{1-x}La_x)TiO_3$ ($x = 10$ mol %). This material was reported to have very good pyroelectric properties,[8] hence it was incorporated into a pyroelectric vinylidene

fluoride/trifluoroethylene copolymer [P(VDF-TrFE)] matrix to form 0–3 nanocomposites.[9]

In this study, a nanocrystalline system PLT was prepared by the sol–gel process. The average crystallite size was calculated from x-ray diffraction (XRD) data using the Scherrer equation, the particle size and morphology were observed in a transmission electron microscope (TEM), and the tetragonal distortion and Raman phonon modes were investigated. The mechanism of a grain size-induced structural phase transformation will be discussed.

II. EXPERIMENTAL PROCEDURES

Nanocrystalline $(Pb_{0.90}La_{0.10})TiO_3$ powders, denoted PLT10, were prepared by the sol–gel process from a stoichiometric mixture of lead (II) acetate, lanthanum (III) nitrite, and tetrabutyl (IV) titanate as the raw materials.[10] First, lead acetate trihydrate was dissolved in 2-methoxyethanol $(C_3H_8O_2)$ in a reaction flask at 80 °C, and then the solution was heated to 118 °C to remove residual water. When the temperature of the vapor reaching the top of the reflux condenser rose from 100 to 124 °C, residual water had been completely removed. After cooling to 80 °C, a stoichiometric amount of tetrabutyl titanate was added to the lead acetate solution and the solution was refluxed at 124 °C for 3 h. After cooling the Pb–Ti complex alkoxide solution to room temperature, a stoichiometric amount of lanthanum nitrate dissolved in $C_3H_8O_2$ was added and the solution was

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stirred at room temperature for 2 h, thereby forming a Pb–La–Ti complex alkoxide solution. By controlling the hydrolysis condition of the solution and adjusting the pH value of the solution was about 11 during the polymerization and precipitation of metal alkoxide, the gel was then dried at a designated temperature and time. This dry gel was subjected to differential thermal analysis (DTA) and thermogravimetric analysis (TGA), and the formation temperature for PLT10 was thereby found to be about 500 °C. PLT nanocrystalline powder with various crystallite sizes was obtained by calcining the gel powder at different temperatures between 400 and 900 °C.

Structure and phase transformation analyses were investigated by XRD using a Philips X′Pert diffractometer with Cu $K\alpha$ radiation in the range of 20°–60° (scan speed of 0.2° min^{-1}). The average crystallite size was calculated from the full width at half maximum (FWHM) of the diffraction lines using Scherrer's relation which assumes the small crystallite size causes line broadening,[11]

$$d=(K\lambda)/(B\cos\theta),\qquad(1)$$

where d is the crystallite diameter, λ the x-ray wavelength, θ the diffraction angle, B the FWHM of the diffraction peak, and K the Scherrer constant which is 0.89 for a Gaussian distribution. By comparing with the widths of the diffraction peaks of a standard material (Si), the width due to the instrument can be evaluated, and the true width of the finite crystallite size can be obtained. The morphology of the particles was observed by a JEOL-100c$\times$ TEM. The powder was dispersed in ethanol using an ultrasonic bath, and the solution was dropped onto a carbon film evaporated on a microgrid supported by a copper mesh. The average particle size was calculated by computer simulation.

The Raman vibrational modes of powders with different grain sizes were measured by a SPEX-1403 double spectrometer at room temperature. An Ar-ion laser with wavelength of 514.5 nm in a backscattering configuration was used as an exciting light. The spectrum was scanned from 100 to 1000 cm^{-1}.

III. RESULTS AND DISCUSSIONS

The crystallization process of the PLT gel powder was monitored by XRD at various annealing temperatures, shown in Fig. 1. The samples annealed below 450 °C exhibit the typical amorphous pattern, showing broad peaks around 30°; when the annealing temperature reaches 500 °C, crystalline diffraction peaks appear. This indicates that the sample has been transformed into a crystalline phase. The (002) and (200) peaks of the PLT powder appear clearly split while the annealing temperature reaches 850 °C. The average crystallite size of the powder was calculated using Eq. (1). Figure 2 shows the variation of the grain size with annealing temperature. In general, the growth mechanism of grains under different annealing temperatures has mainly two stages, the first stage includes the removal of internal stress and the interface structure relaxation at lower temperature; the second is
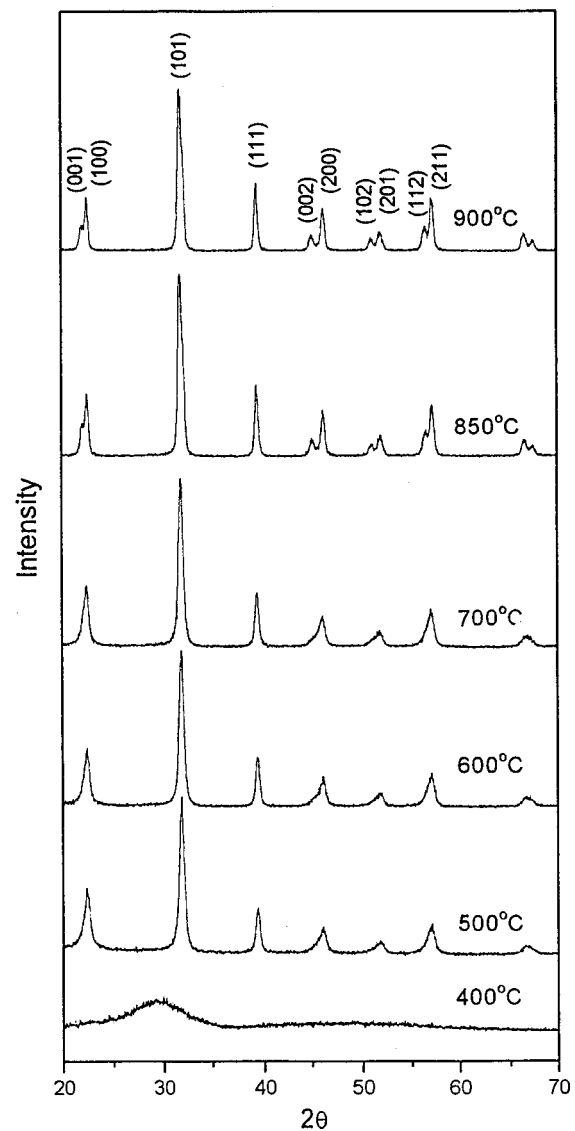

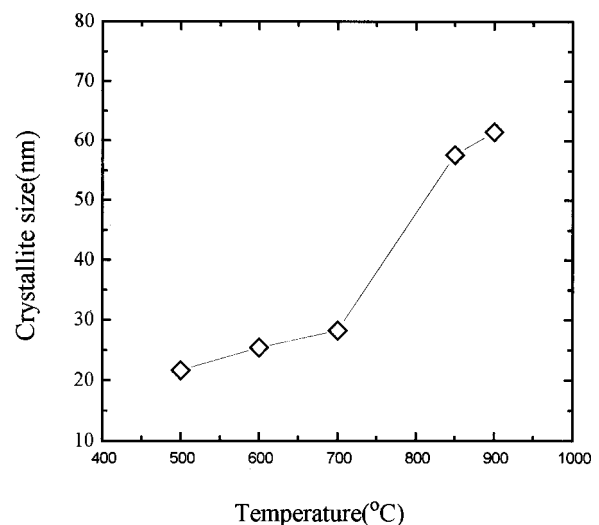FIG. 1. XRD patterns of PLT gel powder annealed at various temperatures for 1 h.

FIG. 2. Variation of the grain size with the annealing temperature.

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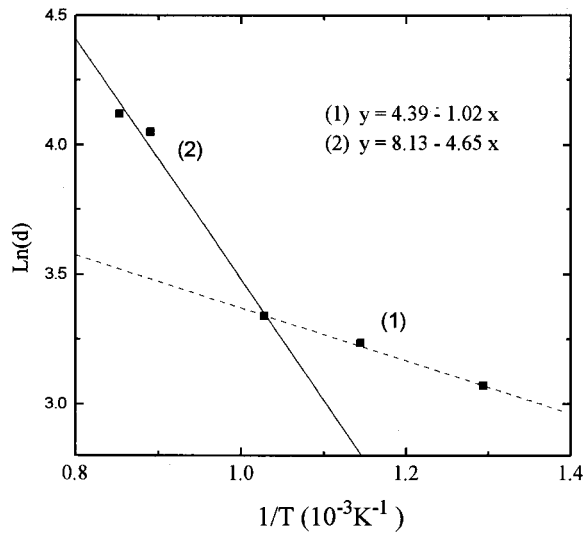
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FIG. 3. Relation of the grain size on a log scale with the inverse of the calcined temperature.

mainly the growth of grains at high temperature. The energy for the interface structure relaxation is usually smaller than that for the growth of the grains, so the grains grow slowly at low annealing temperature. On the other hand, the grains grow rapidly at high annealing temperature. The growth of grains is also described by the following equation:[12]

$$d = d_0 \exp(-E_a/k_B T), \tag{2}$$

where d is grain size, d_0 a constant, E_a the activation energy, and k_B the Boltzmann constant. The activation energy can be calculated from Eq. (2) using the data in Fig. 2. Figure 3 shows the grain size on a log scale with the inverse of the calcined temperature. The growth process of grains can evidently be divided into two stages. The activation energy of the sample can be obtained by linear regression, shown as curves (1) and (2) of Fig. 3. Results show that E_{a1} is 0.46 eV when the annealing temperature of the sample is below 750 °C and E_{a2} is 2.35 eV when the temperature is over 750 °C, respectively.

Figure 4(a) shows a TEM micrograph of the sample annealed at 850 °C. The magnification is 80 k, and the nanocrystalline PLT particles are nearly spherical. Figure 4(b) shows the distribution of the particle size obtained from Fig. 4(a) by computer simulation. The average particle size is about 54 nm. Hence, the particle size determined by TEM is in fairly good agreement with the crystallite size determined by XRD if the annealing temperature is not very high and the soft agglomeration of particles is dispersed. On the other hand, the particle size measured by TEM is larger than the crystallite size measured by XRD if agglomeration exists or if multidomain grains have formed.

The lattice constants of PLT10 particles were calculated using a peak profile analysis from the XRD data in Fig. 1. Figure 5 shows the variation of the lattice constants a and c with grain size at room temperature. It is seen that the lattice constant c decreases and a increases with decreasing grain size, and that c is nearly equal to a when the grain size is 20 nm. Meanwhile, the tetragonal distortion c/a decreases rap-
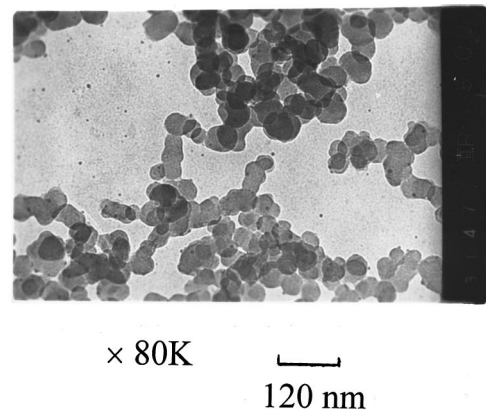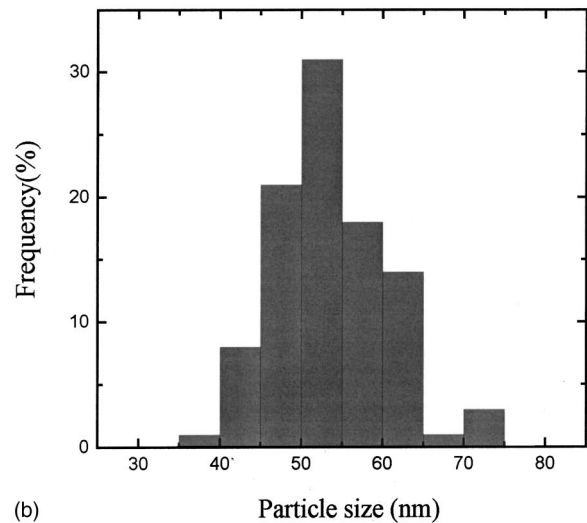
FIG. 4. (a) TEM micrograph of PLT annealed at 850 °C for 1 h. (b) Distribution of the diameter of PLT particles.

idly when the particle size is below about 57 nm, shown in Fig. 6. In the case of random grain orientation, the diffraction intensity of XRD from both (200) and (020) crystal planes is about twice the intensity from elongated (002) planes. When lattice constant c is near a, the (002) and (200)
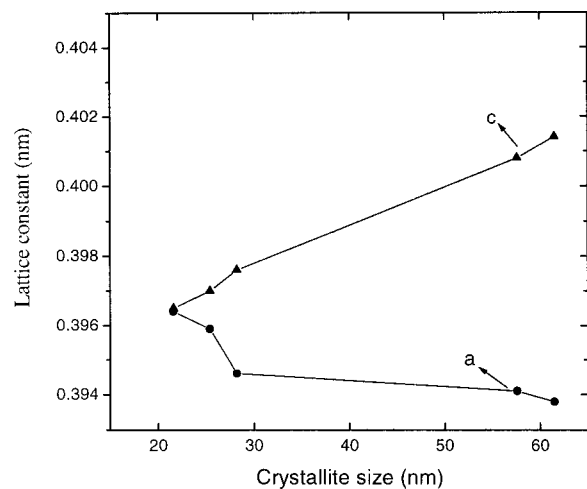

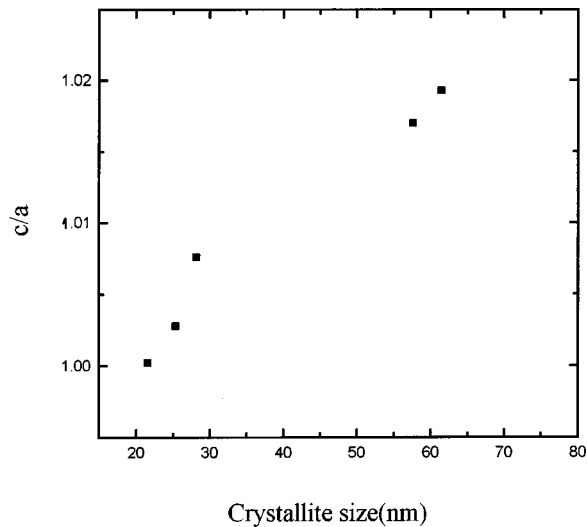FIG. 5. Particle size dependence of lattice constants a and c of PLT at room temperature.

FIG. 6. Relation of tetragonal distortion c/a with the particle size of PLT.

FIG. 7. Raman spectra of PLT with different grain sizes at room temperature: (a) 21.6, (b) 25.4, (c) 28.2, and (d) 57.6 nm.

diffraction peaks appear to overlap. On the other hand, when a is smaller evidently than c in which the grain size is larger, shown in Fig. 5, the (200) and (002) diffraction peaks appear to split, and this is confirmed by XRD. From Fig. 6, the tetragonality factor (c/a ratio) was 1.02 when the crystalline size was about 60 nm; this value is smaller than that of bulk tetragonal $PbTiO_3$ (1.063). It was shown that the crystallite structure of PLT10 powder was strongly influenced by doping with La, and the tetragonality factor (c/a) decreased with decreasing grain size. The lattice constant c is equal to a when the grain size is below 20 nm of PLT powder. The results suggest that the transformation from tetragonal phase to cubic phase will occur at room temperature when the grain size is smaller than 20 nm. Similar results in a PCLT system were also observed in previous work.[13]

Raman spectroscopy is one of the powerful tools available to experimental condensed matter physics.[14] It is well known that spontaneous polarization (P_s) and spontaneous strain are related to the ferroelectric crystal c/a ratio in the perovskite system. According to mean-field as well as to self-consistent phonon model calculations.[15–17] The frequency of the $A_1(1TO)$ mode is thought to be proportional to an order parameter which is the spontaneous polarization P_s for a ferroelectric.[18] Fontana *et al.*[19] assigned the $A_1(1TO)$ phonon mode as a result of polarization characteristics. The softening of this mode of $A_1(1TO)$ phonon is believed to be indicative of the displacive nature of the phase transition. However, almost nobody has given any explanation of the nanocrystalline size induced structure phase transformation of the $A_1(1TO)$ soft mode. Thus, it is very important to explore the relationship between the grain size and structure phase transformation by Raman scattering.

Figure 7 shows the Raman spectra of PLT samples with various grain sizes at room temperature. It is obvious that particle size has a significant effect on the Raman vibrational modes. The soft mode $A_1(1TO)$ shifts downwards in low frequency as the grain size decreases, shown in Fig. 8. The intensity of the $A_1(1TO)$ phonon mode weakens when the grain size is smaller, and the peak wave number of about 150
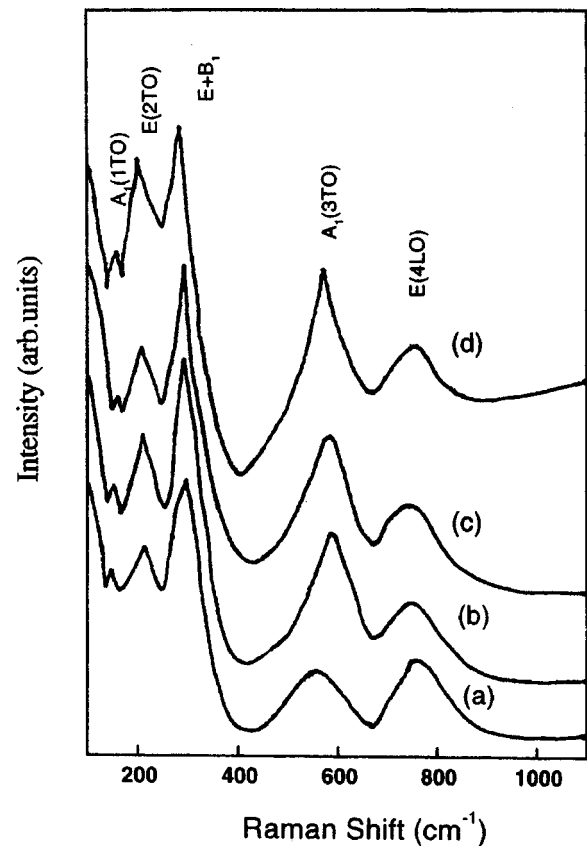
cm^{-1} at a grain size of 57 nm is in good agreement with our previous result of tetragonal PT.[20] However, the main differences in the $A_1(1TO)$ phonon mode between PT and PLT are the intensity changes with grain sizes; its intensity in PT is larger than in PLT with similar grain size. This is because the $A_1(1TO)$ phonon mode at $k \cong 0$ in the tetragonal perovskite system corresponds to vibrations of the lead ion with respect to the slightly distorted TiO_6 octahedra in which the
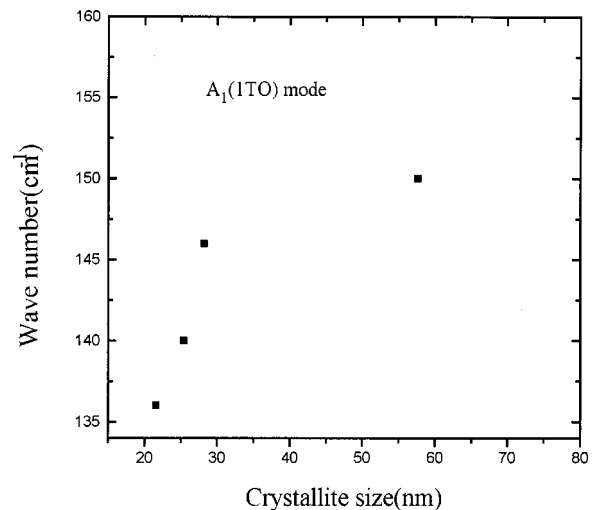

FIG. 8. Peak frequency of the $A_1(1TO)$ phonon mode as a function of grain size.

displacement polarization is determined by the tetragonal distortion (c/a).[21] In PT, c/a of 1.063 is one of the largest in ferroelectric materials, however, c/a of PLT decreases (see Fig. 6) after Pb^{+2} is replaced by La^{+3} in La-doped PT, and its structure will be transformed from tetragonal phase to cubic phase with increasing La content.[22] Thus, the $A_1(1TO)$ mode of PLT is very sensitive to the addition of La and grain size. Frantti *et al.*[21] suggested the soft-mode character of the $A_1(1TO)$ line of Nd-doped PZT thin films as an explanation for the disappearance of the mode at about 135 cm^{-1} at higher temperature, and confirmed the mode relative to the addition of Nd to replace Pb in Nd-doped PT. Foster *et al.*[23] found that the line shape of the $A_1(1TO)$ peak broadens with increasing temperature to a superposition of many subpeaks as a consequence of the anharmonic nature of the lattice in PT.

Figure 7 also shows that there is an evident change in the relative intensity of $A_1(3TO)$ and $E(4LO)$ phonon modes with particle size. The intensity of $A_1(3TO)$ is smaller than that of the $E(4LO)$ phonon mode when the grain size is about 20 nm. It indicates that the $A_1(3TO)$ phonon mode is also sensitive to the grain size of the sample. Meanwhile, the peaks evidently broaden with decreasing size. Richer *et al.*[24] also observed Raman peak broadening in a small grain size silicon film prepared by the plasma transport method. They chose a Gaussian attenuation factor $\exp(-2r^2/L^2)$ near at the boundary of the spherical microcrystal with a diameter L. The calculation result indicated that the existence of the broader mode in smaller crystalline particles is caused by finite size effects. Liu *et al.*[25] suggested that the Gaussian phonon confinement function with an amplitude of exp $(-4\pi^2)$ at the boundary of a spherical crystallite yields consistent results for nanocrystallite ZrO_2 particles. The low frequency shifts and broadening with a decrease in grain size are caused by the size-dependent relaxation of the $q=0$ selection rule due to the phonon confinement in a grain.

It is almost impossible to measure ferroelectric properties of nanocrystalline powder directly. However, we may observe directly the second harmonic generation (SHG) signal of PLT samples with different sizes. A Nd:YAG Q switched pulse laser with a wavelength of 1.06 μm, a pulse duration of 10.8 ns, and a single pulse energy of 100 mJ was used. It was observed that the SHG signal intensity evidently decreases with decreasing grain size. The green light begins to disappear when the grain size is about 20 μm in PLT powder. According to the literature,[26] the SHG signal can be expressed as

$$I = NdP_s^2, \tag{3}$$

where N is the concentration of ferroelectric crystallites, d the grain size, and P_s spontaneous polarization. Since the intensity depends on the square of P_s, a weak SHG signal indicates that P_s is very small. This phenomenon was observed by SHG and is in good agreement with above results. So we chose the PLT powder with grain size of about 57 nm which has good ferroelectric properties to fabricate a 0–3 nanocomposite pyroelectric sensor to elicit good properties in our previous experiment.[9]

As we know, there is not yet a completely quantitative theory to calculate the grain size effect in nanocrystalline ferroelectric particles. However, we may quantitatively understand the mechanism of nanocrystalline particles using previous experimental data and theory. Ishikawa *et al.*[7] observed that the Raman $E(1TO)$ soft mode of PT shifts toward a low frequency region and that the Curie temperature (T_c) decreases from its bulk value as the size decreases. The relation of the temperature T_c with critical size is described by an empirical expression from experimental data. Zhong *et al.*[27] observed that the phase transition temperature of PT decreases and diffused as the particle size decreases using a specific-heat method, and also gave an empirical formula between T_c and the grain size. Chattopadhyay *et al.*[28] showed that the T_c of PT decreases gradually and the transition becomes increasingly diffused with decreasing size by dielectric measurements. These results indicate that small size will induce a phase transition. In the perovskite ferroelectrics, phase transformations are usually from ferroelectric tetragonal phase to paraelectric cubic phase when the grain size is very small, as shown by our results above. It will cause the T_c to shift toward low temperature. Therefore, we suggest that the size effect on the nanocrystalline particle will directly induce its structural distortion and phase transformation.

In general, ferroelectricity is intrinsically a long-range cooperative process. The existence of a ferroelectric soft depends on the balance of the short-range force and the long-range Coulomb force,[27] in which the short-range force will cause the unable of soft mode. The long-range force depends on the field E_s due to the dipole summation and the depolarization field E_d. In the simple case, E_s and E_d can be expressed, respectively, as $E_s = 4\pi P/3$, where P is the polarization and $E_d = -\gamma P$, where γ is a constant. For an infinite crystal, E_d is near 0, and E_s is much larger than that of the short-range force, so the ferroelectric phase is stable. However, for nanocrystalline particles, E_s is greatly weakened because the numbers of dipoles decreases, E_d is not equal to 0, and the short-range force is greatly strengthened because of the increase in surface atoms. Both E_d and the short-range force directly destroy the ordering of the dipoles, so ferroelectricity disappears even at low temperature because of the size effect induced structural phase transition.

IV. CONCLUSIONS

We have studied the structural change and Raman scatting of nanocrystalline PLT particles with different grain sizes. The results show the tetragonal distortion apparently decreases with decreasing size. The activation energy of grain growth is obtained for two different growth stages. The XRD results show that the transformation from tetragonal phase to cubic phase will occur at room temperature when the grain size is smaller than 20 nm. The $A_1(1TO)$ phonon mode, which is related to the spontaneous polarization, shifts toward lower frequency with decreasing grain size. An evident change in the relative intensity of the $A1(3TO)$ and $E(4LO)$ phonon modes with particle size is also observed. Finally, the mechanism of the grain size induced structural

phase transition was also discussed. The research has shown that it is necessary to choose optimized nano-sized powder to fabricate 0–3 nanocomposite materials for pyroelectric sensor applications.

ACKNOWLEDGMENTS

[1] H. Gleiter, Prog. Mater. Sci. **33**, 223 (1989).

[2] U. Herr, J. Ting, R. Rirring, U. Gonser, and H. Glerter, Appl. Phys. Lett. **50**, 472 (1987).

[3] R. S. Katiyar and J. F. Meng, Ferroelectrics **226**, 79 (1999).

[4] W. Kanzig, Phys. Rev. **98**, 549 (1955).

[5] M. H. Frey, Z. Xu, P. Han, and D. A. Payne, Ferroelectrics **206**, 337 (1998).

[6] D. McCauley, R. E. Newnham, and C. A. Randall, J. Am. Ceram. Soc. **81**, 979 (1998).

[7] K. Ishikawa, K. Yoshikawa, and N. Okada, Phys. Rev. B **37**, 5852 (1988).

[8] T. Futakachi and K. Tanino, Jpn. J. Appl. Phys., Part 1 **33**, 5294 (1994).

[9] Q. Q. Zhang, H. L. W. Chan, Q. F. Zhou, and C. L. Choy, Chin. Sci. Bull. **43**, 111 (1998).

[10] Q. F. Zhou, H. L. W. Chan, and C. L. Choy, Appl. Phys. A: Mater. Sci. Process. **70**, 293 (2000).

[11] L. S. Birks and H. Friedman, J. Appl. Phys. **17**, 687 (1946).

[12] K. Ishikawa, N. Okada, K. Takada, T. Nomura, and M. Hagino, Jpn. J. Appl. Phys., Part 1 **33**, 3495 (1994).

[13] X. G. Tang, Q. F. Zhou, and J. X. Zhang, J. Appl. Phys. **86**, 5194 (1999).

[14] M. Cardona, *Light Scattering in Solids* (Springer, New York, 1975).

[15] J. Feder and E. Pytte, Phys. Rev. B **1**, 4803 (1970).

[16] N. S. Gillis and T. R. Koehler, Phys. Rev. B **5**, 1925 (1972).

[17] E. Pytte, Phys. Rev. B **5**, 3758 (1972).

[18] G. Burns and B. A. Scott, Phys. Rev. B **7**, 3088 (1973); Phys. Rev. Lett. **25**, 167 (1970).

[19] M. D. Fontana, H. Idrissi, G. E. Kugel, and K. Wojcik, J. Phys.: Condens. Matter **3**, 8695 (1991).

[20] Q. F. Zhou, J. X. Zhang, H. L. W. Chan, and C. L. Choy, Ferroelectrics **195**, 211 (1997).

[21] C. J. Frantti, V. Lantto, and J. Lappalainen, J. Appl. Phys. **79**, 1065 (1996).

[22] G. A. Rossetti, L. E. Cross, and J. P. Cline, J. Mater. Sci. **30**, 24 (1995).

[23] C. M. Foster, Z. Grimsditch, Z. Li, and V. G. Karpov, Phys. Rev. Lett. **71**, 1258 (1993).

[24] H. Richter, Z. P. Wang, and L. Ley, Solid State Commun. **39**, 625 (1981).

[25] F. X. Liu, J. L. Ying, and T. P. Zhao, Phys. Rev. B **55**, 8847 (1997).

[26] M. Yanovskaya *et al.*, J. Mater. Sci. **23**, 395 (1988).

[27] W. L. Zhong, B. Jiang, P. L. Zhang, J. M. Ma, H. M. Cheng, Z. H. Yang, and L. X. Li, J. Phys.: Condens. Matter **5**, 2619 (1993).

[28] S. Chattopadhyay, P. Ayyub, V. R. Palker, and M. Multani, Phys. Rev. B **52**, 13177 (1995).