Ferroelectric Phase Transitions in Nanocrystalline ABO₃ System at High Pressure*

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Ferroelectric phase transitions of nanocrystalline ABO₃ type materials, PbTiO₃, PbZrO₃, Pb_{1-x}Sr_xTiO₃, PbZr_xTi_{1-x}O₃, Pb_{1-x}Ba_xO₃, Pb_{1-x}La_xO₃, have been researched by Raman scattering and x-ray diffraction at different conditions. The phase transition from FE to PE is driven by the softening of the lowest phonon mode E(TO). The difference between nanocrystalline materials and its' bulk one under high pressure has been discussed.
[ferroelectric, phase transition, soft mode]

1. Introduction

ABO₃ type materials, such as PbTiO₃(PT), PbZrO₃(PZ), PbZr_{1-x}Ti_xO₃ (PZT), Pb_{1-x}La_xTiO₃ (PLT), Pb_{1-x}Sr_xTiO₃ (PST), Pb_{1-x}Ba_xTiO₃ (PBT) etc. are of interest due to their excellent piezoelectric, pyroelectric, ferroelectric, dielectric and optical-electric properties. These characteristics facilitate applications in many areas, including hydrophones, thermal imaging, nonvolatile memories, surface acoustic wave generators, and gas sensors. It is well known that enhanced piezoelectric effects exist, such as high maximum electromechanical coupling coefficient and dielectric susceptibility, for compositions near the morphotropic phase boundary (MPB) between the tetragonal and rhombohedral ferroelectric phases in the PZT solid solution system. This makes PZT the most useful piezoelectric ceramic for preparing some advanced devices. Recently, most efforts have been concentrated on PT and PZT solid-solution compositions near MPB using various experimental methods, such as Raman scattering, the calculations for the ionic polarizabilities in PZT compositions; the thermodynamic theory and the statistical model for the MPB etc. Size effects in ferroelectric materials have become a subject of increasing interest recently. Decreasing dimensions in microelectronic devices requires knowledge of material properties below a critical size. Especially, effects of grain size are well known to play an important role in changing ferroelectric properties and phase transitions in ABO₃ perovskite oxides. Behavior of nanocrystalline ABO₃ materials under high pressure is also a interesting research field.

2. Experimental

Nanocrystalline PT, PZ, PZT, PST, PLT and PBT powders were prepared using a sol-gel process. Chemical phase analysis was done by powder XRD measurements. The average grain size (d_{grd}) was calculated from the full width at half maximum (FWHM) of the (111) diffraction peak by the Scherrer equation $d_{\text{grd}} = K\lambda / \beta(\theta) \cos(\theta)$, where λ is the x-ray wavelength, $\beta(\theta)$ is the FWHM of the diffraction line, θ is the angle of diffraction.

The back scattering Raman spectra were performed on a Jobin-Yvon T64000 Spectrophotometer with a 514.5 nm radiation line from Ar-ion laser. A Mao-Bell type diamond anvil was used to produce high pressure. A 16:3:1 methanol-ethanol-water mixture was served as the pressure transmitting medium, and the fluorescence of a small ruby chip as the pressure calibration.

3. Results and discussion

3.1. Pressure-induced FE - PE Phase Transition for PbTiO₃ with Various Grain Size

The Raman spectra of bulk PbTiO₃ material at room temperature and hydrostatic pressure up to 11.63 GPa reveal that the E(TO₁) phonon linewidth is nearly pressure independent over a wide frequency range (88-30 cm⁻¹) and appear to diverge

Fig. 1. The pressure dependence of low frequency phonon modes for PbTiO₃ with a grain size of 50.5 nm.

near the phase transition. The hydrostatic Raman spectra for PbTiO₃ of grain size 200 nm, 50.5 nm, 36.6 nm and 30.0 nm were measured, respectively[1]. These results show that for grain size 50.5nm the E(TO₁) mode and A₁(TO₁) mode are well separated at low pressure. Fig. 1 shows the pressure dependence of each phonon mode of PbTiO₃ with a grain size of 50.5 nm. The results demonstrate that with increasing pressure up to 6.7 GPa the 'silent' mode at 286 cm⁻¹ is still pressure independent as in bulk PbTiO₃ materials; the E(TO₂) mode starts to disappear; the A₁(TO₁) and E(TO₁) modes firstly soften with increasing pressure and appear to be pressure independent as the pressure increases beyond 6.7GPa. Thus it is probable that the structure of PbTiO₃ with grain size of 50.5 nm begins to be changed at 6.7 GPa. However, it should be pointed out that, the smaller the grain size, the more difficult measuring the E(TO₁) mode frequency exactly. In fact, when the grain size is sufficiently small (< 7 nm[2]) the softening of E(TO₁) mode can no longer be observed.

Fig. 2. The pressure dependence of the square of the soft mode $E(TO_1)$ frequency for $PbTiO_3$ (50.5 nm).

Fig. 2 shows the pressure dependence of the square of the soft $E(TO_1)$ mode frequency (50.5 nm). The data show a non-straight-line dependence of against P , or non-Curie-Weiss behavior obviously at high pressure. This means that the phase transition is not in agreement with that of bulk $PbTiO_3$ materials, where, as a function of pressure the soft $E(TO_1)$ mode softens to zero and all other modes disappear at 11.63 GPa.

The pressure dependence of the linewidth of the $E(TO_1)$ mode is shown in Fig. 3 (50.5 nm). It should be noted that the linewidth does not diverge at high pressures. This is also different from that of bulk materials, where as a function of temperature or pressure the linewidth follow $t^{-1/2}$ ($t = (T_c - T)/T_c$ is the reduced temperature, $p = (P_c - P)/P_c$ is the reduced pressure) respectively or appears to be singularly damped at T_c or P_c . So, according to the above experimental facts, it is reasonable to suggest the phase transition occurring nanocrystalline $PbTiO_3$ may be a diffused phase transition from tetragonal to cubic with the property changing from ferroelectric to paraelectric.

Fig. 3. The pressure dependence of the linewidth of the soft $E(TO_1)$ mode: circles for $PbTiO_3$ of grain size 50.5 nm; filled circles for bulk $PbTiO_3$ materials.

3. 2. Pressure - Induced AFE - FE - PE Phase Transition for Nanocrystalline $PbZrO_3$

The hydrostatic pressure Raman spectra for $PbZrO_3$ with grain size of 94 nm indicate that low Raman peaks 34, 43, 49 and 56 cm^{-1} can be assigned for cation (ZrO_2) lattice modes[3].

Fig. 4. The Raman spectra for $PbZrO_3$ with grain size of 94 nm at high pressure and room temperature

Some features of these Raman spectra, as a function of pressure, can be described as follows: The most remarkable features in the the spectra is that none of the peaks has a large softening with increasing pressure, and only the peaks 56 cm^{-1} and 132 cm^{-1} are observed to have a small decrease in frequency. The spectra between 0.21 and 0.53 GPa are essentially identical to the room temperature spectra at zero pressure, in the pressure region from 0.53 to 0.79 GPa, a small region, the peak at 34 and 43 cm^{-1} strongly decrease in intensity, in comparison with the remaining Raman peaks. The peak 56 cm^{-1} is nearly pressure independent as pressure is beyond 0.79 GPa, but its frequency reduces with pressure up to 4 GPa. As pressure is beyond 4 GPa, only a peak can be observed in the frequency region 20-60 cm^{-1} . It is also observed that energies of some phonon modes seem to be discontinuous between 0.53 and 0.79 GPa as well as between 3.82 and 4.12 GPa. Comparing these experiment results with the high temperature Raman data of the $PbZrO_3$ bulk material[4], we conclude that there are three pressure phases for $PbZrO_3$ with grain size of 94 nm: (1) the antiferroelectric orthorhombic phase (AFE) below 0.79 GPa, (2) the ferroelectric rhombohedral phase (FE) between 0.79 and 4.12 GPa, (3) the cubic paraelectric (PFE) above 4.12 GPa, see fig. 4. The large FE phase region in nanocrystalline case originate from the effect of broken bond Pb and O atoms (or Pb and O vacancies) on crystal interfacial areas.

3. 3. Pressure-Induced Phase Transition for Nanocrystalline $PbTiO_3$ with Doping Ba, Zr, La and Sr Ions

A. Nanocrystalline $Pb_{1-x}Ba_xTiO_3$ at High Pressure

High pressure micro Raman spectra for $Pb_{0.8}Ba_{0.2}TiO_3$ (PBT20) with grain size of 60 nm is shown in Fig. 4. The soft mode reveals "softening" behavior with increasing pressure. It is very different from the case of bulk $PbTiO_3$. Several phonon modes at 7.41 GPa differ from those at 0.65 GPa. For example,

the modes $E(\text{LO}_3)$ and $A_1(\text{LO}_3)$ coalesce into one mode. Similar behavior is observed between modes $E(\text{TO}_3)$ and $A_1(\text{TO}_3)$, modes $A_1(\text{TO}_2)$ and B_1+E . The mode $E(\text{LO}_2)$ disappears at 7.41 GPa. These features should be attributed to a phase transition occurring at 7.41 GPa. However, this phase transition has been still considered to be driven by "softening" of the soft mode. The soft mode frequency can result from a coupling between the soft mode and a lowest phonon mode above 7.41 GPa. For PBT60, a similar pressure-induced phase transition is also observed, indicating a lower phase transition pressure of 4.22 GPa. This illustrates that for the same grain size, the phase transition pressure is still reduced with increasing Ba ion content.

B. Nanocrystalline $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ at High Pressure

The grain size dependence of the frequency of the lowest soft mode appears as a red shift, the linewidth is widened and the intensity of the Raman band weakens with decreasing grain size. The smaller the grain size, the lower the phase transition temperature, which is as in PbTiO_3 , but when the grain size is smaller than 16.8 nm, $\text{PbTi}_{0.75}\text{Zr}_{0.25}\text{O}_3$ (PTZ25) structure can be transformed from FE (tetragonal) into a nonferroelectric phase. It is not in agreement with that in PTZ25, in which Curie temperature increases with decreasing grain size.^[5] The frequency of the soft mode $E_1(\text{TO})$ begins to remain unchangeable beyond 4.78 GPa (9 GPa for its bulk material) and the linewidth does not appear to diverge up to 9.8 GPa, which is different from that of its bulk material. The phase transition of nanocrystalline $\text{PbTi}_{0.75}\text{Zr}_{0.25}\text{O}_3$ may be a diffused phase transition, which is similar to that in PbTiO_3 nanocrystals.

The additional mode has been observed in the low frequency region and the possibility that the mode might result from the zone boundary coupled to the $q \sim 0$ soft mode $E_1(\text{TO})$ had been further confirmed.

Fig. 5. Raman spectra for $\text{Pb}_{0.8}\text{Ba}_{0.2}\text{TiO}_3$ with grain size of 60 nm at different pressure.

C. Nanocrystalline $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ at High Pressure

For $x = 0.1, 0.2, \dots, 1$ with different grain size, the soft phonon mode $E_1(\text{TO})$ can be observed only for $x \leq 0.4$. MPB occur at $x_0 = 0.57$ and 0.69 for 30 nm and bulk $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$, respectively. The temperature induced phase transition of $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (PST20) with grain size of 37 and 27 nm are also

a soft mode phase transition from FE to NFE(cubic) at 355°C and 275°C respectively. No additional mode at $20 \sim 80 \text{ cm}^{-1}$ region was observed for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$, which is very different from $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ and $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$. For PST20 with 60 nm grain size, pressure-induced phase transition occurs at 7.86 GPa and the phase transition is considered as a second order one. This phase transition behavior is the same as that of bulk PbTiO_3 . With decreasing grain size of PST20, the phase transition pressure and temperature decrease too. There is a critical grain size of 15 nm for PST20 at room temperature and ambient pressure for phase transition.

D. Nanocrystalline $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ at High Pressure

For $x = 0.06, 0.08, 0.10, 0.12, 0.14$ and 0.20 , with different grain size, the Raman spectra of La-doped titanate at high pressure and high temperature reveal that the pressure and temperature of phase transition from tetragonal to cubic shift to a lower one with decreasing grain size of the samples. The variation of crystal tetragonality (c/a) at room temperature and ambient pressure as a function of La concentration x for PLT with grain size is obtained. The phase transition from tetragonal FE to cubic PE for PLT14 with grain size 54 nm and 35 nm driven by a soft mode has been observed at 5.6 and 4.8 GPa respectively. It should be noted that this is not a diffused phase transition, the phase boundary is sharp. It is a second order phase transition[6].

3. 4. Determination of Phase Boundaries in doped ABO₃

A. Nanocrystalline PZT

Typical Raman spectra for nanocrystalline ceramics in the $\text{PbTi}_{1-x}\text{Zr}_x\text{TiO}_3$ system having $x=0, 0.1, 0.2, \dots, 1.0$ were measured. As x reaches 0.4, the soft mode displays a very weak intensity and an unmeasurable frequency position. On increasing x further, its intensity begins to increase reversibly up to $x=0.7$, above which the soft mode exhibits a more quick increase in intensity all the way up to $x=1.0$. Another low frequency mode, occurring at 50 cm^{-1} for $x=0.1$, is considered to be an additional phonon mode, as determined in bulk PZT ceramics. A similar Zr content dependence with respect to the $E(\text{TO}_1)$ soft mode is found to occur in the additional mode at $\sim 50 \text{ cm}^{-1}$. In addition, it should be noted that the spectrum at $x=0.8$ basically corresponds to that of PbZrO_3 , especially for the soft mode and the additional phonon mode. The Raman spectra for PbZrO_3 nanocrystalline powder is the same as that of the bulk materials, which means that it still in an antiferroelectric phase. Thus, noticeable changes occur in Raman spectra of nanocrystalline powder crossing two Zr concentrations of 0.4 and 0.7. New phase regions for nanocrystalline PZT with the grain size of 60 nm have been obtained and compared with the phase regions of bulk PZT.

It should be pointed out that the soft mode frequency does not reduce to zero at the MPB, due to a level repulsion with the mode at 10 cm^{-1} . The non-zero soft mode frequency does not originate from a possible coupling between the soft mode and the additional phonon mode at $\sim 50 \text{ cm}^{-1}$, because the two modes have an analogous Zr content dependence. The interesting phenomenon differs from previous reports in bulk PZT system[4].

The experimental results suggest that the changes in the short-range harmonic interaction, when Zr^{4+} ions replace Ti^{4+} ions in the nanocrystalline PZT system, determine the 'softening' of the $E(TO_1)$ phonon mode, as shown in the case of bulk PZT materials. Thus, this shift of the MPB with decreasing grain size may result from an additional effect of stress caused by small particle size on the changes in short-range forces in the system. In fact, as the particle size of materials is decreased, there will appear some small particle distribution. Apparently, the smaller the average particle size, the smaller the spherical particle, and then the larger the stress on the surfaces of particles. Finally, the stress will act on atoms inside particles and produce an additional effect similar to an external pressure. Thus, the observed frequency decreases and linewidth of the soft mode can result from the additional effect. In addition, in the case of bulk materials, the softening of the soft mode is well known to be connected with a delicate balance of short-range forces favoring the cubic state and long range forces favoring the ferroelectric tetragonal states. For nanocrystalline PZT system, therefore, it is reasonably thought that the additional stress effect plays a key role in the balance of these forces. The phenomenological analysis of the effect of hydrostatic pressure on the phase stability of morphotropic PZT compositions shows some expected results, i. e., the rhombohedral-tetragonal phase boundary is rather sensitive to the elastic boundary conditions. A ferroelectric tetragonal to ferroelectric rhombohedral phase transition can be induced in the morphotropic PZT compositions by the application of a relatively small hydrostatic pressure.

B. Nanocrystalline $Pb_{1-x}Sr_xTiO_3$

Raman Spectra in nanocrystalline PST with grain size of 60 nm shows the softening of the $E(TO_1)$ mode with increasing Sr composition. For Sr contents above 0.7, it becomes very difficult to measure the soft mode frequency. Moreover, anomalous change of the other phonon modes is also seen. For example, the phonon modes at 180 and 260 cm^{-1} become weak in intensity and begin to coalesce a wide band for above $x=0.7$. These striking differences of Raman spectra suggest that a phase transition from the tetragonal ferroelectric of $PbTiO_3$ to the cubic paraelectric state of $SrTiO_3$ occurs at $\sim$ Sr concentration of 0.7. (Fig. 5)

C. Nanocrystalline $Pb_{1-x}Ba_xTiO_3$

Raman spectra of $Pb_{1-x}Ba_xTiO_3$ (PBT) with grain size of 60 nm for $x=1.0$ (BT) show a very wide Raman band from 100 to 300 cm^{-1} and three phonon modes at 518 at 638 and 723 cm^{-1} , reveals that $BaTiO_3$ with grain size of 60 nm should have a cubic structure, rather than a tetragonal one described in bulk BT at room temperature.

On increasing Ba concentration from $x=0$, the $E(TO)$ mode at 74 cm^{-1} for nanocrystalline PT widens and its frequency decreases to about 45 cm^{-1} at $x=0.7$, at which a discontinuous change in the phonon energy is observed. This implies that PBT is reasonably considered to undergo a phase transition at $x \sim 0.7$ and the $E(TO)$ mode at 74 cm^{-1} still plays an important role in the phase transition. On the other hand, three modes at 120, 144 and 198 cm^{-1} coalesce into a band at 133 cm^{-1} as x is increased to 0.5, and then the band disappears at $x \sim 0.7$. The mode at 289 cm^{-1} called as a 'silent' mode, exhibiting a very weak intensity at $x \sim 0.7$, is found to merge into a very wide band with

other modes below 350 cm^{-1} for Ba concentrations above 0.7. Obviously, the above mentioned Ba concentration

Fig. 6. Powder X-ray diffraction for PBT system with grain size of 60 nm

dependence of the phonon modes at 74, 120, 144, 198 and 289 cm^{-1} , different from those in bulk PBT, can be thought as evidence responsible for the phase transformation at $x \sim 0.7$. Powder X-ray diffraction for PBT system with grain size of 60 nm are exhibited in Fig. 6. In order to confirm the phase transition occurring in nanocrystalline PBT system. The spectrum at the bottom, corresponding to pure $PbTiO_3$, displays the features of the tetragonal phase, including 12 diffraction peaks. With increasing Ba content, the double peaks at (001) and (100), (101) and (110), (002) and (200), (201) and (210), (112) and (211) coalesce respectively into several signal peaks at 110, 110, 200, 210 and 211 at $x=0.7$. For Ba contents above 0.4, it can be easily seen that all x-ray diffraction peaks change little up to $x=1.0$ ($BaTiO_3$). This means that PBT reaches a cubic structure of $BaTiO_3$ at $x=0.7$. From the Raman

Table 1. Phase boundary of doped ABO_3 .

Materials	Phase boundary of nanocrystalline	Phase boundary of bulk materials
$Pb_{1-x}Sr_xTiO_3$ (30nm)	$0 \leq x < 0.7$ Tetragonal $0.7 \leq x \leq 1.0$ Cubic	----
$Pb_{1-x}Ba_xTiO_3$ (60 nm)	$0 \leq x < 0.7$ Tetragonal $0.7 \leq x \leq 1.0$ Cubic phase	----
$PbTi_{1-x}Zr_xO_3$ (96 nm)	$0.0 \leq x < 0.4$ Tetragonal $0.4 \leq x \leq 0.5$ Rhombohedral I $0.5 < x \leq 0.7$ Rhombohedral II $x > 0.7$ Antiferroelectric Orthorhombic	$0.0 \leq x < 0.52$ Tetragonal $0.52 \leq x \leq 0.64$ Rhombohedral I $0.64 < x \leq 0.94$ Rhombohedral II $x > 0.94$ Antiferroelectric Orthorhombic

spectra and x-ray diffraction, it is concluded that a phase transition induced by the "softening" of the $E(\text{TO}_1)$ mode occurs at $x \sim 0.7$. The summary of the phase boundary of doped nanocrystalline ABO_3 materials is listed in Table 1.

3. 5. Effect of Pressure, Temperature, Grain Size and Dopant Concentration on the Soft Mode

It has been found that all experiments of ABO_3 type materials as mentioned above have the same regularity of lowest frequency phonon mode (soft mode $E(\text{TO})$). The red shift of the frequency and the width of frequency peak of Raman spectra, with decreasing the grain size, increasing pressure, temperature and dopant concentration.

For PLT14, Fig.7 shows the variation of $E(\text{TO})$ frequency square with various reduced parameters, $D = x/x_c$, d_c/d , P/P_c , T/T_c , where D expresses reduced doping concentration,

Fig. 7. The variation of $E(\text{TO})$ frequency square with various reduced parameters D . 1. $D = x/x_c$. 2. $D = d_c/d$. 3. $D = P/P_c$. 4. $D = T/T_c$.

reduced grain size, reduced pressure and temperature respectively. The results indicate that the relation of the frequency of $E(\text{TO})$ with critical grain size and concentration, phase transition pressure and temperature is a linear one.

$$\begin{aligned}\omega^2 &\propto (d-d_c) & (d_c < d) \\ \omega^2 &\propto (x-x_c) & (x_c < x) \\ \omega^2 &\propto (P-P_c) & (P_c < P) \\ \omega^2 &\propto (T-T_c) & (T_c < T)\end{aligned}$$

Here $x_c = 0.2$, $d_c = 19\text{nm}$, $P_c = 5.6\text{ GPa}$, $T_c = 180^\circ\text{C}$ for PLT14. All the relation agree with the result predicted by the mean field theory[1].

But for PT nanocrystals the relation between the square of the soft mode frequency and pressure dose not satisfy the mean field theory. It is a nonlinear one obviously, as discussed before (see Fig. 2).

3. 6. Discussions of Pressure-Induced Phase Transition

According to the results mentioned above, grain size and different dopants are found to have an obvious effect on

ferroelectric phase transitions in ABO_3 . For PbTiO_3 , as grain size is decreased, the phase transition transferred from a normal second order phase transition to diffused one. For PBT20 and PZT20, similar phase transition behavior seems to be found. Because the phase transition occurring in PT is a typical soft mode phase transition, effects of grain size and doping ions on phase transitions are attributed to those on the soft mode. However, the pressure-induced phase transitions in nanocrystalline PLT20 and PST20 are the same as those of bulk PT, indicating obvious decrease in phase transition pressure. The decrease of transition pressure can be explained by a stress model of spherical nanocrystalline particles. The smaller the grain size, the more the stress on atoms inside every spherical particle. And then the additional stress will lead to the soft mode more sensitivity to pressure. Finally, the phase transition pressure is reduced with decreasing grain size (for example PLT20, PST20). For real diffused phase transition behavior, transition pressures cannot be exactly determined. What we can observe is only a phase transition region. According to the several nanocrystalline materials mentioned above, for PbTiO_3 with smaller grain sizes (for 36.6 and 30.0nm), it is very difficult indeed to determine their phase transition pressure from the pressure dependence of the soft mode. This means that these phase transitions are to approach exact diffused. On the other hand, for PBT20 and PZT20, their phase transitions may be quasi-diffused. Mechanism responsible for diffused phase transition have not been understood clearly. In the case of nanocrystalline materials, the behavior of diffused phase transitions may result from distribution of some broken-bond atoms on the surfaces of spherical particles. However, why do the phase transition for PLT20 display a normal phase transition, rather than a diffused one. The different pressure-induced phase transition behavior among PBT20, PZT20, PLT20, PST20, may come from different chemical properties of Sr, La, Ba, Zr. This problem is in progress.

4. Conclusion

1. The phase transitions from tetragonal FE to Cubic PE for PT, PST, PBT, PLT and from orthorhombic AFE to rhombohedran FE to cubic PE for PZ, PZT can be reached by changing the grain size, temperature, pressure and dopant concentration separately.

2. The phase boundaries between FE and PE for materials researched move to lower doping concentration, temperature and pressure in this paper with decreasing its grain size. There is a critical grain size in every material mentioned above, ferroelectric phenomenon will disappear as the grain size of the sample is less than its critical grain size.

3. The phase transition from FE to PE in above ABO_3 materials concerns the softening of the lowest phonon mode $E(\text{TO})$, which dues to changing of the short range force. The grain size induced phase transition can be explained by a stress model. The relations of the lowest frequency square of mode $E(\text{TO})$ to the grain size, temperature, pressure and doping concentration satisfy the mean filed theory for the secondary phase transition, such as for nanocrystalline PLT, but it does not satisfy the mean field theory for the diffused phase transition, such as for nanocrystalline PT.

4. The widening of the lowest E(TO) phonon mode with the changing of reduced parameter depend on not only some bulk factors but also the disordering of atoms in boundary.

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