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Temperature-induced phase transition and morphotropic phase boundary in the nanocrystalline $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system

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Abstract. The Raman spectra in the nanocrystalline $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ system show that the morphotropic phase transition from the tetragonal phase to the cubic structure occurs at $x_c = 0.57$ and it can be associated with 'softening' of the lowest-frequency E(TO) phonon mode. The phase transition temperature in $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ decreases with decreasing grain size. The disappearance of the ferroelectric phase of $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ has been discussed as a function of grain size. The correlation between the temperature-induced and the Sr-concentration-induced phase transition in nanocrystalline $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ has been observed.

1. Introduction

It is well known that PbTiO_3 and SrTiO_3 are very typical perovskite materials and they have been extensively investigated. In the case of bulk materials, the phase transitions occurring in PbTiO_3 and SrTiO_3 were revealed by Raman scattering [1–3] and it can be correlated with 'softening' of the lowest TO phonon mode with temperature or pressure. The experimental results on $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ (PST) demonstrated the Sr concentration dependence of lattice modes but did not indicate the morphotropic phase boundary [4]. Recently, Ishikawa *et al* have reported that the phase transition temperature in PbTiO_3 shifts to a lower temperature with decrease in grain size [5]. However, so far, investigations of nanocrystalline PST have been found to be rather scarce. Hence, in this paper, we shall report some experimental data and try to reveal the effects of the grain size of the sol-gel-prepared PST materials on the Raman spectra and the phase transition.

2. Experimental details

Powders of $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x = 0.0, 0.1, 0.2, \dots, 1.0$, where the experimental uncertainty in x is ± 0.015) of small grain size were synthesized by the sol-gel method using high-purity stearic acid, lead acetate, tetrabutyl titanate, etc as raw materials. From the sol-gel process, we obtained nanocrystalline PST powder. The grain size of the sample increased with increase in the calcining temperature. Similar experimental details can be found in [6]. The average grain size D (its experimental uncertainty is ± 0.024) of the sample was determined from the full width at half-maximum of the x-ray diffraction peak. The lattice constants were calculated by means of a least-squares computer refining program, according

to the data of the angular position of all reflections measured between 20 and 60° under the following experimental conditions: equatorial divergence slit, 1°; receiving slit, 0.6 mm; step width, 0.02°; time constant, 10 s.

The Raman spectra of the samples were measured using the spectrum system described in [7], which includes a Spex-1403 Raman spectrometer with a double monochromator, a standard photon-counting technique and an Ar⁺ ion laser with an output power of 200 mW. During measurement of the high-temperature Raman spectra, a thermocouple was used to monitor the temperature of the sample.

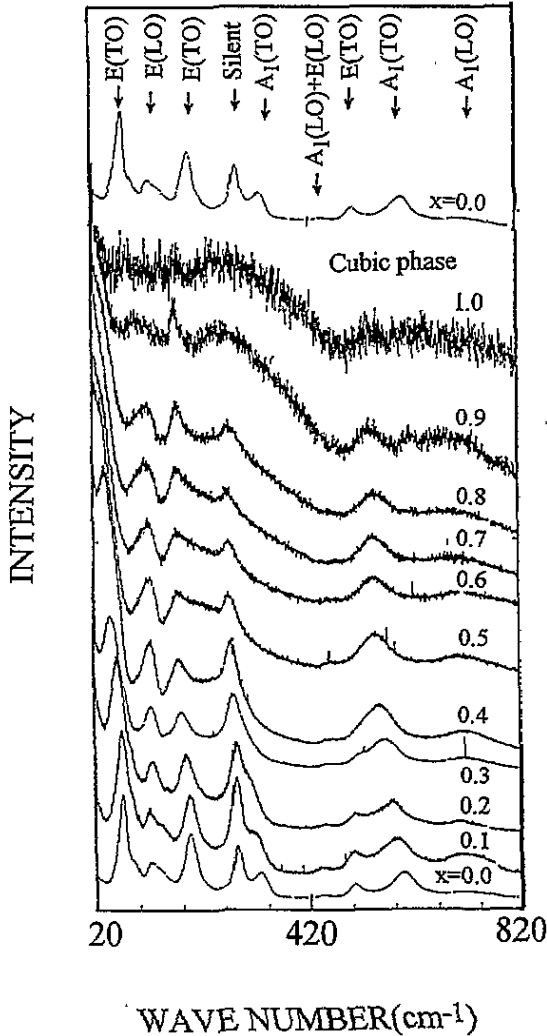


Figure 1. Raman spectra for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ of grain size 30 nm at room temperature and ambient pressure.

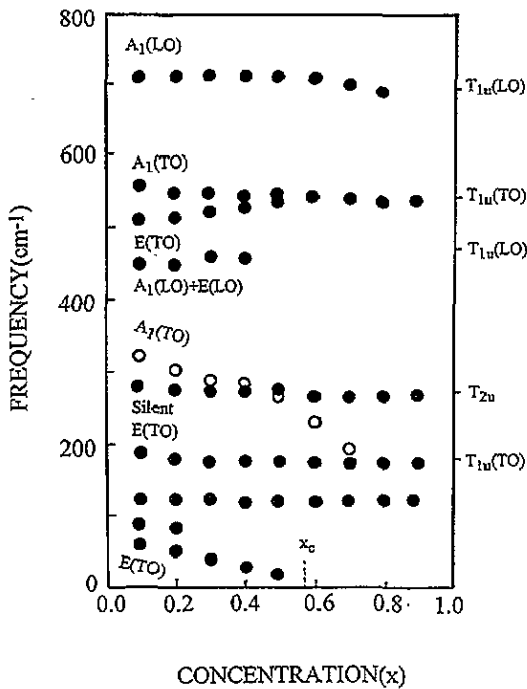


Figure 2. The Sr concentration x dependence of each phonon mode of $Pb_{1-x}Sr_xTiO_3$ at room temperature and ambient pressure.

3. Results and discussion

Typical Raman spectra for PST of grain size 30 nm at room temperature and ambient pressure as a function of Sr concentration x are shown in figure 1. The Sr concentration dependence and the symmetry of each phonon mode are given in figure 2. From figures 1 and 2 the lowest TO phonon mode (considered as the 'soft' mode) is found to 'soften' and its linewidth to increase with increasing x as in the corresponding bulk materials [4]. The 'softening' can be observed up to $x = 0.4$. For $x > 0.4$, the soft mode frequency becomes unmeasurable. It can also be seen that the other modes change very smoothly with x . For example, the $A_1(TO)$ mode at 560 cm^{-1} and the $E(TO)$ mode at 510 cm^{-1} approach each other very smoothly as x increases, and their frequencies extrapolate finally to the $T_{1u}(TO)$ mode frequency in cubic $SrTiO_3$. The 'silent' mode at 280 cm^{-1} in the tetragonal phase is at about the same frequency as the silent T_{2u} mode in the cubic phase. The presence of such a spectrum in the cubic phase could perhaps be related to defects [8]. It should be noted that for $x = 0.5$ a wide band between 180 and 260 cm^{-1} is abruptly formed. When combined with the features of the 'soft' mode x , this suggests that the cubic structure in PST of grain size 30 nm has been formed for $x \geq 0.5$. This conclusion can be further confirmed by the x-ray diffraction of the sample in figure 3. The x-ray diffraction peaks of the samples corresponding to $x \geq 0.5$ are found to possess features of the $SrTiO_3$ cubic structure.

In order to confirm the change in the structural symmetry of PST of grain size 30 nm as a function of x , the x -dependence of its tetragonality c/a has been measured and is indicated in figure 4. It is obvious that, in the case of nanocrystalline material, the c/a -value (1.0355) for $PbTiO_3$ of grain size 30 nm is smaller than that (1.064) of the corresponding bulk material.

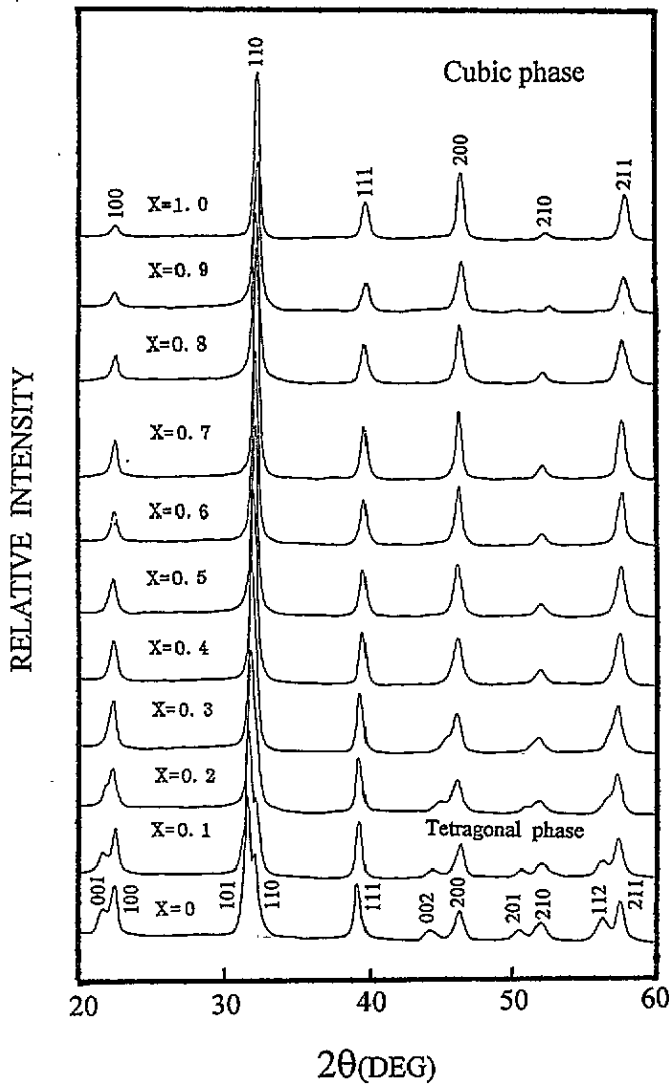


Figure 3. Powder x-ray diffractions for $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ of grain size 30 nm at room temperature and ambient pressure.

The c/a -value for $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ is 1.0032, which approaches the value ($c/a = 1$) of the cubic structure very closely.

In figure 5 we plot the Sr concentration dependence of the square ω^2 of the 'soft' mode frequency for PST of grain size 30 nm and bulk PST (the data are from [4]). According to figure 5, their morphotropic phase boundaries should occur at $x_c = 0.57$ and 0.69, respectively. This means that the morphotropic phase boundary in PST shifts to a lower Sr concentration with decreasing grain size. It is noted that the dependence of ω^2 on x can be described by a linear relation between $\omega^2(x)$ and x given by

$$\omega^2(0) - \omega^2(x) = x\omega^2(0)/x_c \quad (1)$$

where $\omega(0) = 72 \text{ cm}^{-1}$ is the frequency of the soft $q \simeq 0 \text{ E}(\text{TO})$ phonon for PbTiO_3 of grain

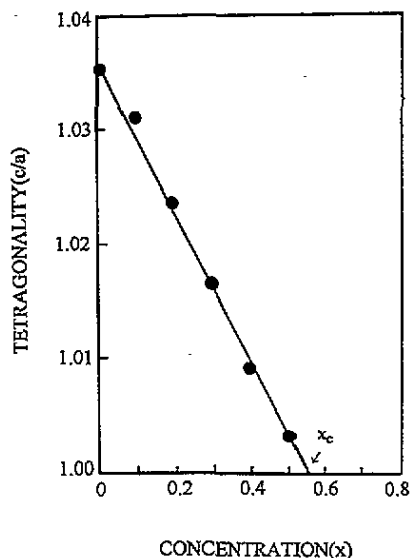


Figure 4. The Sr concentration dependence of the tetragonality c/a for $Pb_{1-x}Sr_xTiO_3$ of grain size 30 nm.

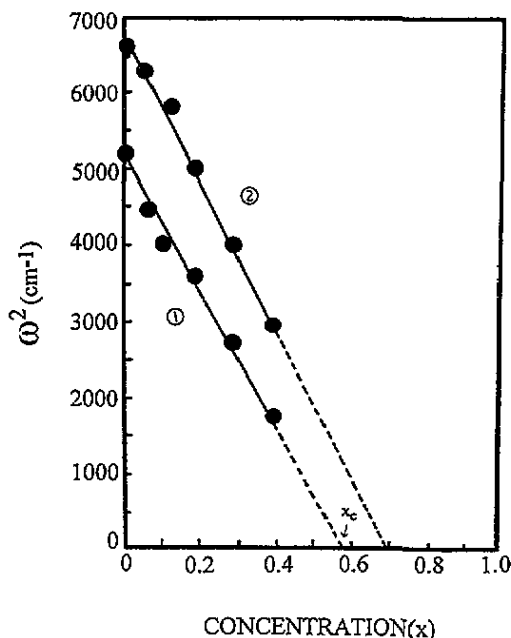


Figure 5. The Sr concentration dependence of the square of the lowest phonon mode frequency: line (1), for $Pb_{1-x}Sr_xTiO_3$ of grain size 30 nm at ambient pressure and room temperature; line (2), for bulk $Pb_{1-x}Sr_xTiO_3$ at ambient pressure and room temperature.

size 30 nm at 23 °C. On the basis of the theoretical considerations for $PbZr_xTi_{1-x}O_3$ (PZT) [9], the right-hand side of equation (1) can be associated with the change in the short-range force. This means that the morphotropic phase transition at $x_c = 0.57$ can also be correlated with an instability of the 'soft' phonon, resulting from the change in short-range force as in PZT. On the other hand, the apparent large stress of crystal interfacial areas due to the decrease in grain size, as in $Pb_{1-x}La_xTiO_3$ [10], can lead to a change in the short-range force between atoms inside the crystal grain. Therefore, as the grain size is decreased, the morphotropic phase boundary will shift to a lower Sr concentration.

The Raman spectrum for $Pb_{0.8}Sr_{0.2}TiO_3$ (PST20) of grain sizes 37 and 27 nm at high temperatures are plotted in figures 6(a) and 6(b), respectively. Figure 7 shows the temperature dependence of the phonon modes in figure 6(a). The lowest E(TO) phonon mode (considered to be a soft mode) is found to decrease in frequency and its linewidth to increase the temperature dependence of each phonon mode in the tetragonal phase is highly analogous to that of the bulk $PbTiO_3$, e.g. the lowest TO phonon mode that is connected with the phase transition softens with increasing temperature, the 'silent' mode at 290 cm^{-1} is nearly temperature independent and so on [1]. It is seen that, for temperatures of 335 and 275 °C, the features of the whole Raman band are the same as those of the cubic $SrTiO_3$. In addition, the results in figure 1 reveal that the low-temperature phase in PST20 is tetragonal. Thus, these facts suggest that PST20 of grain sizes 37 and 27 nm undergoes a temperature-induced soft-mode phase transition from the tetragonal (ferroelectric) to the cubic phase (non-ferroelectric phase) at 335 °C and 275 °C, respectively. The ferroelectricity

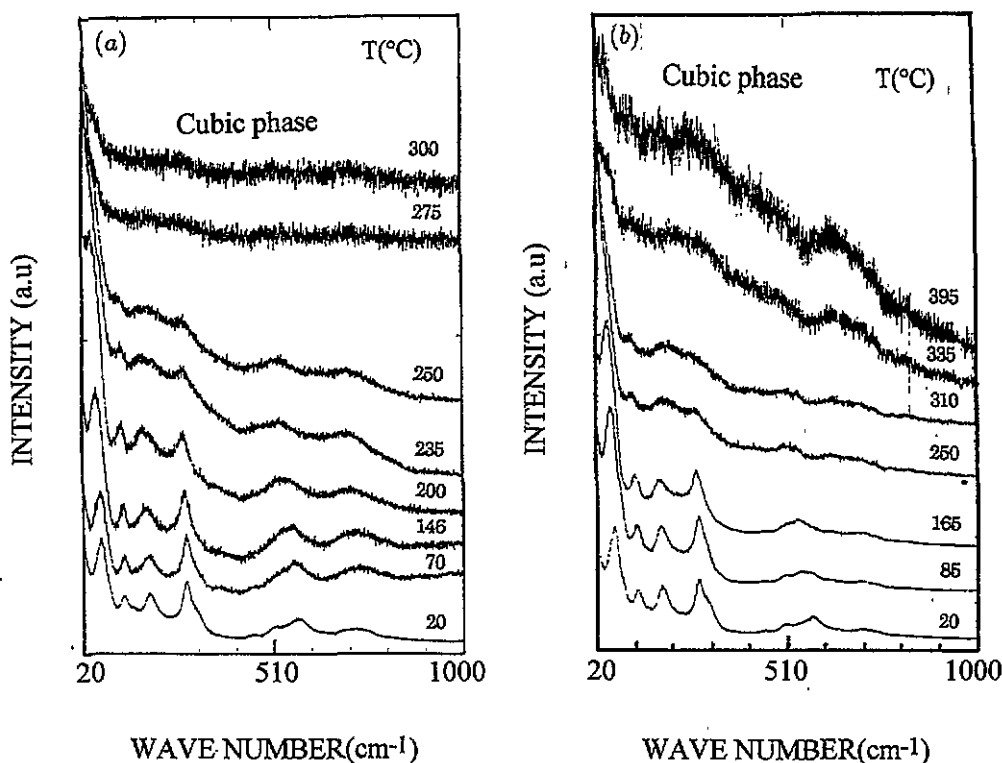


Figure 6. (a) Raman spectra for $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ of grain size 27 nm at high temperature and ambient pressure (a.u., arbitrary units), (b) Raman spectra for $\text{Pb}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ of grain size 37 nm at high temperature and ambient pressure (a.u., arbitrary units).

of the sample is closely connected with the change in its structure. It should be pointed out that non-zero Raman spectra in the cubic phase for PST20 can result from disorder distributions of some broken-bond atoms on the interfacial area [11]. On the other hand, in our experiments on both PST and PST20, no additional mode at 20–80 cm^{-1} was observed. This is very different from that of the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ and $\text{Pb}_{1-3/2x}\text{La}_x\text{TiO}_3$ systems, in which an additional phonon mode in the low-frequency region was found and it was considered to be a Brillouin boundary phonon mode and the phase transition occurring in $\text{Pb}_{0.85}\text{La}_{0.1}\text{TiO}_3$ and $\text{PbZr}_{0.25}\text{Ti}_{0.75}\text{O}_3$ is directly correlated with the coupling between the soft mode and the additional phonon mode [12, 13]. In addition, in our high-pressure Raman scattering experiments for $\text{Bi}_{1.8}\text{La}_{0.2}\text{Ti}_4\text{O}_{11}$ and $\text{Bi}_{1.8}\text{Yb}_{0.2}\text{Ti}_4\text{O}_{11}$, similar results have been observed [14].

In order to investigate the effects of grain size on the phase transition in PST20 further, the high-temperature Raman spectra for PST20 of grain sizes 17, 20 and 44 nm have been measured. The grain size dependence of T_c has been obtained and is plotted in figure 8. Obviously, with decreasing grain size, the T_c of PST20 will decrease. As the grain size is sufficiently small, e.g. D is less than the critical grain size of 15 nm, PST20 at room temperature and ambient pressure will be in the cubic phase. At the same time, the PST20 structure no longer changes with increasing temperature because of the disappearance of the

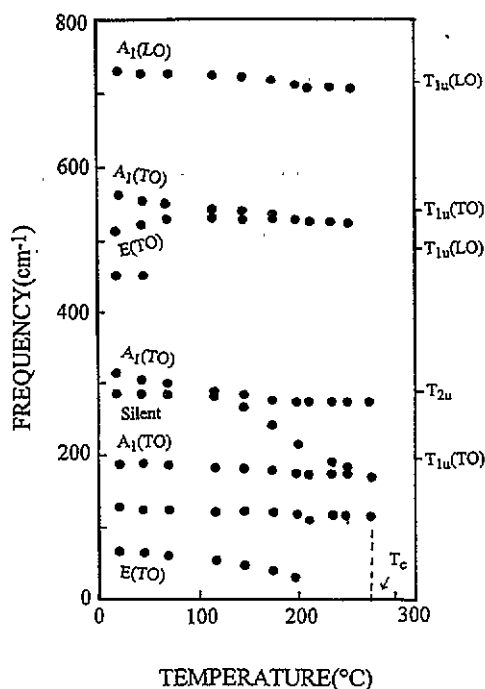


Figure 7. The temperature dependence of each phonon mode for $Pb_{0.8}Sr_{0.2}TiO_3$ of grain size 27 nm at ambient pressure.

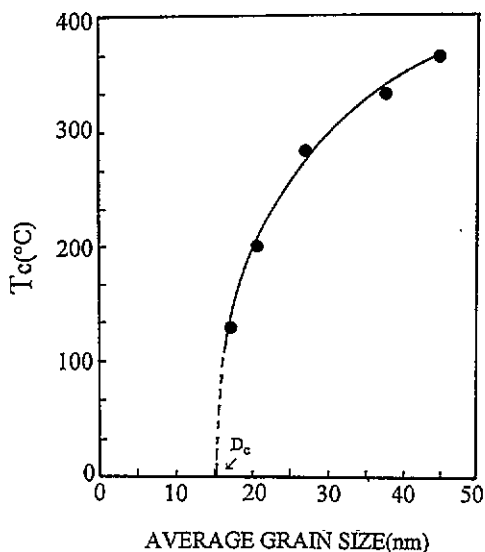


Figure 8. The grain size dependence of the phase transition temperature for $Pb_{0.8}Sr_{0.2}TiO_3$.

ferroelectric phase transition. In the previous experiment on $BaTiO_3$, it was observed that the critical grain size at which the transition from the tetragonal to the cubic phase occurs is 120 nm at room temperature and ambient pressure [15]. In fact, it may be possible that there are small grains in which the Coulomb interaction length is comparable with the sample size. All the ferroelectric soft modes are of TO type because the depolarization field associated with LO phonons suppresses the local field. However, in grains smaller than the Coulomb interaction length, the depolarization field should work also in the TO phonon mode. This obscures the increase in the local field due to the Lorentz field. The Lorentz correction term should contribute less in smaller grains because the dipole summation runs over a limited volume. Hence, these factors will lead to the disappearance of the ferroelectric phase transition. At hydrostatic pressures the similar disappearance of the ferroelectric phase was observed earlier in ABO_3 ferroelectrics, e.g. the temperature dependence of the static dielectric constant of $K_{0.72}Na_{0.28}TaO_3$ at various pressures showed that there is no transition above 1 GPa [16]. So, the effects of grain size on the phase transition temperature in the present experiment seem to be very similar to those of hydrostatic pressure.

The decrease in the phase transition temperature with increasing grain size in PST_{20} , which is the same as that in $PbZr_{0.25}Ti_{0.75}O_3$ [17] can be explained by the stress model [18] but, for $PbZr_{0.5}Ti_{0.5}O_3$ [19] and $Pb_{0.9}La_{0.09}(Ti_{0.35}Zr_{0.65})_{0.98}O_3$ [15], some opposite results were obtained, where the phase transition temperature shifts to a higher temperature with decreasing grain size. These contradictory results need to be clarified still further.

When the results in figure 1 are combined with those in figure 4, it is very interesting to find that the x -dependence of each phonon mode is very similar to the temperature

dependence. In figure 7 the $A_1(\text{TO})$ mode at 570 cm^{-1} and the $E(\text{TO})$ mode at 510 cm^{-1} also appear to approach each other at $T = 275^\circ\text{C}$. In particular, the mechanism of the softening of the lowest phonon mode in both cases seems to agree, where the change in short-range force plays an important role in the phase transition. These correlations between the vibration modes and the phase transition are similar to some experimental results, for instance for the $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ system ($x \leq 0.5$) [12, 13], the $\text{Bi}_{2-x}\text{Nd}_x\text{Ti}_4\text{O}_{11}$ system ($x \leq 0.4$) and the $\text{Bi}_{2-x}\text{Sb}_x\text{O}_{11}$ system ($x \leq 0.3$) [14]. However, this cannot be considered as a general conclusion; for example, in the high-temperature Raman spectra of $\text{Bi}_{1.8}\text{La}_{0.2}\text{Ti}_4\text{O}_{11}$, although the softening of the lowest phonon mode with increasing temperature was observed, no 'soft' mode occurred in the Raman spectra of the $\text{Bi}_{2-x}\text{La}_x\text{Ti}_4\text{O}_{11}$ system [14].

In summary, for the PST system of grain size 30 nm, the morphotropic phase transition from the tetragonal to cubic phase is found to occur at $x_c = 0.57$ and it can be associated with the 'softening' of the lowest $E(\text{TO})$ phonon mode. This 'softening' can arise from changes in short-range harmonic forces with increasing x . The T_c of PST20 shifts to a lower temperature on decrease in the grain size. A sufficiently small grain size will lead to disappearance of the ferroelectric phase. The mechanism of the Sr-concentration-induced phase transition in PST seems to be similar to that of the temperature-induced phase transition in PST20.

Acknowledgments

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