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Journal of Alloys and Compounds 224 (1995) 130–134

Journal of ALLOYS AND COMPOUNDS

Size effect on the Raman spectra and phase transition in $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystalline powders

Xiaohui Wang [a,*], Zichen Wang [a], Muyu Zhao [a], Jinfang Meng [b], Jiangping Li [b], Guangtian Zou [b]

[a] *Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China*
[b] *Department of Physics, Jilin University, Changchun 130023, People's Republic of China*

Received 17 October 1994

Abstract

We report a size effect on the Raman spectra of and the phase transition in $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystalline powders. The samples were synthesized by the stearic acid gel method. The average grain sizes and crystal structures were determined by X-ray diffraction. The Raman spectra of $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals have been measured under different temperatures and hydrostatic pressures. The results show that the phase transition temperature T_c shifts to a lower temperature with decreasing grain size. The possibility that the additional band occurring in the low frequency Raman spectra might be due to zone boundary transverse acoustical phonons which couple to the $q \approx 0$ soft E (transverse optical) mode is confirmed. The Raman spectra, as a function of pressure, reveal that the phase transition may be connected with a diffuse phase transition.

Keywords: Size effect; Raman spectrum; Lead zirconate titanate; Phase transitions

1. Introduction

Lead zirconate titanate (PZT) is a well-known ceramic solid solution of $PbZrO_3$–$PbTiO_3$ which offers, in bulk form, high permittivity for capacitors [1], a large electromechanical coupling coefficient for surface acoustic wave applications [2], large spontaneous polarization for non-volatile memory devices [3], and good optical properties for electro-optic devices [4]. As new ceramic devices are developed, the investigation of the dependence of their properties on grain size has become very important. Ishikawa et al. [5] studied the size effect on the ferroelectric phase transition in $PbTiO_3$ ultrafine particles, finding that, when the particle size is less than 50 nm, the transition temperature T_c, determined by Raman scattering, decreases from its bulk value (490 °C) as the grain size decreases. However, to our knowledge, study of the Raman spectra of nanocrystalline $PbZr_xTi_{1-x}O_3$ powders at high temperature and high pressure has been nonexistent. Therefore, we synthesized nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$ by the stearic acid gel method [6] and investigated the size effect on the Raman spectra and phase transition in the system.

2. Experimental details

The nanocrystalline powders were synthesized by the stearic acid gel method using lead acetate, stearic acid, zirconium oxychloride and tetrabutyl titanate as precursor materials. Firstly, newly prepared zirconium hydroxide precipitate, produced by reacting zirconium oxychloride with aqueous ammonia, was dissolved in the appropriate amount of melted stearic acid solution. Then, stoichiometric lead acetate and tetrabutyl titanate were added into the solution by stirring to form a transparent sol. Finally, the sol was cooled to room temperature slowly and solid gel was obtained. By calcining the gel at various temperatures in air, we obtained nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$ powders with different grain sizes.

The nanocrystalline structures were measured by powder X-ray diffraction with an automated Rigaku X-ray diffractometer using Cu Kα radiation with a single-crystal graphite monochromator. The average grain size was determined from the full width at half-maximum (FWHM) of the X-ray diffraction peak using

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* Present address; Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210014, China.

0925-8388/95/$09.50
SSDI 0925-8388(94)01460-4

Scherrer's equation [7,8]

$$D=K\lambda/(B\cos\theta)$$

where D is the size, λ is the wavelength, θ is the diffraction angle, B is the FWHM of a diffraction peak (101 in our case) and K is a constant which is near unity for the usual crystals. The value of B depends on three factors: the apparatus parameters, the $K\alpha_2$ line of the target and the grain size. By comparison with diffraction of a standard material (Si in our case) the width due to the apparatus can be eliminated. By use of the modified Ranchinger method, the width due to the $K\alpha_2$ line can be eliminated. Therefore, the true width induced by the grain size can be obtained and the size can be calculated using Scherrer's equation.

The Raman spectra of nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$ powders were measured by using a SPEX-1403 Raman spectrometer with a third monochromator and a standard photon counting technique. A 514.5 nm line from an argon ion laser was used as an exciting light source at an output power of 80 mW. The Raman measurements at high temperature were made using a specially designed high temperature cell with a heating rate of 5 °C min^{-1}. The backscattered Raman spectra at high pressure were measured by using a miniature diamond anvil cell at room temperature (about 20 °C). The accuracy of the pressure was ±0.12 GPa.

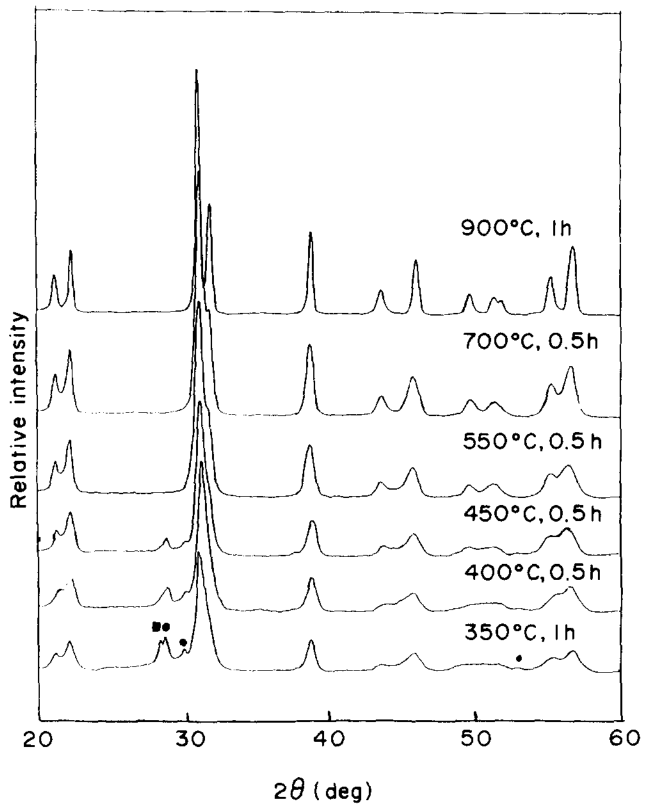

Fig. 1. The X-ray diffraction patterns of nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$ powders calcined at various temperatures: ■, monoclinic ZrO_2; ●, orthorhombic PbO.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$ powders calcined at various temperatures. It can be seen that the $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals calcined at and below 450 °C are not a single perovskite phase but contain some impure phases (PbO and ZrO_2). The Raman spectra (Fig. 2) were consistent with the powder X-ray diffraction data. In Fig. 2, peak intensities at 142 cm^{-1} and 90 cm^{-1} due to orthorhombic PbO and monoclinic ZrO_2 are observed with decreasing calcining temperature, which behaviour is different from that of pure $PbTiO_3$ but the same as that of $PbZrO_3$ synthesized by Li et al. [9]. Clearly, the calcining temperature plays an important role in the synthesis. Pure perovskite $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals were obtained at a high temperature, 550 °C. With increasing calcining temperature, the grain size increases.

The Raman spectra at room temperature of $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals with different average grain sizes reveal that with decreasing grain size the soft E (1TO)) (first-order transverse optical [10] mode shifts to the low frequency region from 74 cm^{-1} to 51 cm^{-1} as shown in Fig. 2. The softening of the soft E (1TO) mode indicates a softening of the lattice vibration and implies a lowering of the phase transition temperature with decreasing grain size.

Figs. 3(a) and 3(b) show the Raman spectra of $PbZr_{0.2}Ti_{0.8}O_3$ with average grain size of 44.5 nm at high temperatures and temperature dependences of the phonon modes respectively. It is obvious that the frequencies of the high frequency phonon modes (199, 283, and 330 cm^{-1}) decrease with increasing temperature and that, when the temperature is above 420 °C, only a very large band is observed in the region 100–420 cm^{-1}. Meanwhile, it is noted that in the low frequency region (20–100 cm^{-1}) below 420 °C, there appears an additional band centred at 50 cm^{-1} in addition to the band associated with the soft E (1TO) mode with a maximum intensity at 69 cm^{-1} in the 20 °C spectrum. The two full triangles in each Raman spectrum in Fig. 2, Fig. 3(a) and Fig. 5(a) represent the additional mode and the soft E (1TO) mode; that in the lower frequency region is for the additional mode and the other is for the soft E (1TO) mode. We should point out first that the additional mode is not caused by the size effect because its frequency does not change with different grain sizes and no additional mode is observed in the low frequency region of nanocrystalline $PbTiO_3$ [11]; on the contrary, the frequency of the additional mode is strongly dependent on neither temperature nor pressure (see Fig. 3(a) and Fig. 5(a)). It does not play an important role in the phase transition. So we have

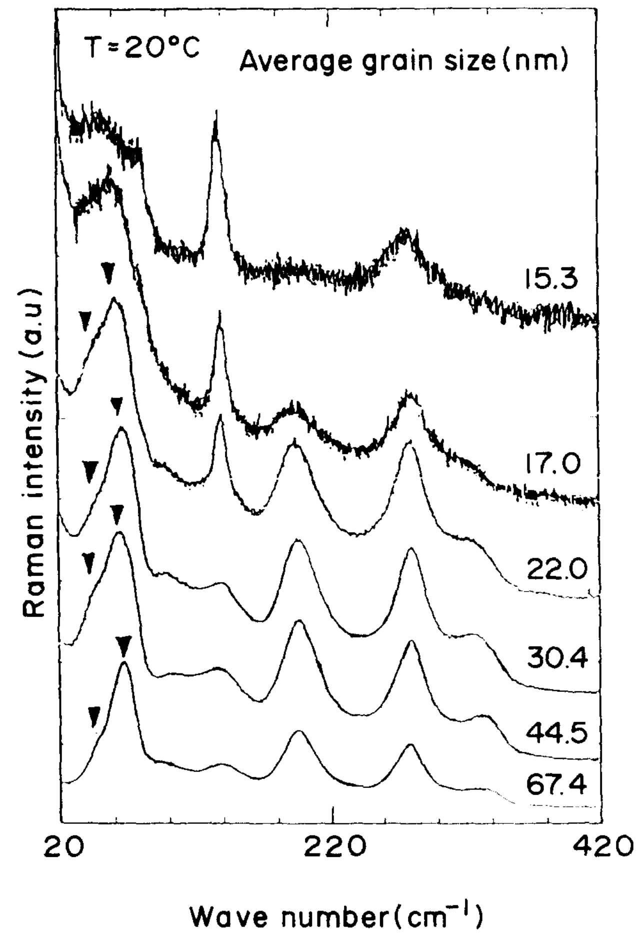

Fig. 2. The Raman spectra of $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals with different grain sizes at room temperature.

confirmed the possibility, hypothesized by Merlin et al. [12], that the additional model might originate in zone boundary transverse acoustic (TA) phonons coupled to the $q \approx 0$ soft E (TO) mode because of a lack of translational symmetry in nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$.

The phase transition is determined by two approaches. First, at 420 °C we observed that the first-order Raman modes disappear abruptly except for the Raman band at 260 cm^{-1}. This is expected since in the cubic phase the normal modes of vibration transform as the $3T_{1u}+T_{2u}$ irreducible representation of the O_h point group and are thus not Raman active. Second, the damping constants of the lowest soft TO modes diverge as T_c is approached as in $PbTiO_3$. Therefore, 420 °C is regarded as T_c of $PbZr_{0.2}Ti_{0.8}O_3$ with a grain size of 44.5 nm.

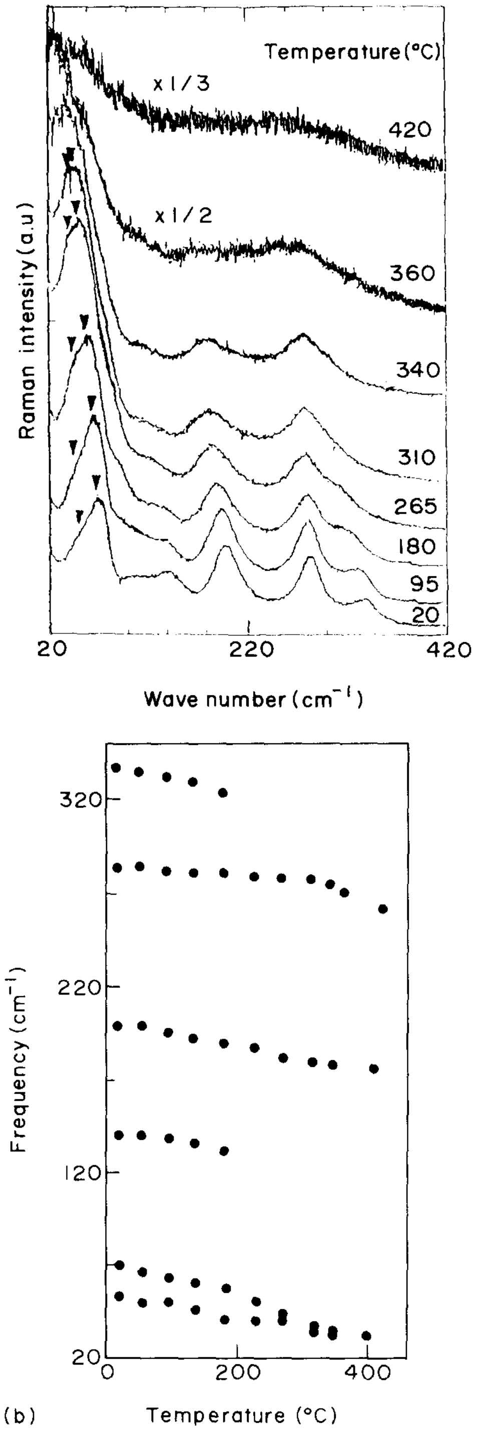

Fig. 3. (a) The Raman spectra for $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals with average grain size of 44.5 nm at high temperatures. (b) Temperature dependence of the low frequency phonon modes in $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals with average grain size of 44.5 nm.

The Raman spectra of $PbZr_{0.2}Ti_{0.8}O_3$ for the other grain sizes have been measured. The grain size dependence of the phase transition temperature T_c is shown in Fig. 4. The full curve in Fig. 4 is obtained from the following equation:

$$T_c(D) = T_c(\infty) - c/(D-13.1)$$

with $c = 807$ K nm. In this equation, $T_c(\infty)$ is the Curie temperature of the bulk $PbZr_{0.2}Ti_{0.8}O_3$ which is taken to be 723 K. If we define a critical size D_{crit} as the size at which $T_c = 0$ K, then, from the equation, $D_{crit} =$ 14.0 nm. It is found that, the smaller the grain size, the lower the phase transition temperature, which is

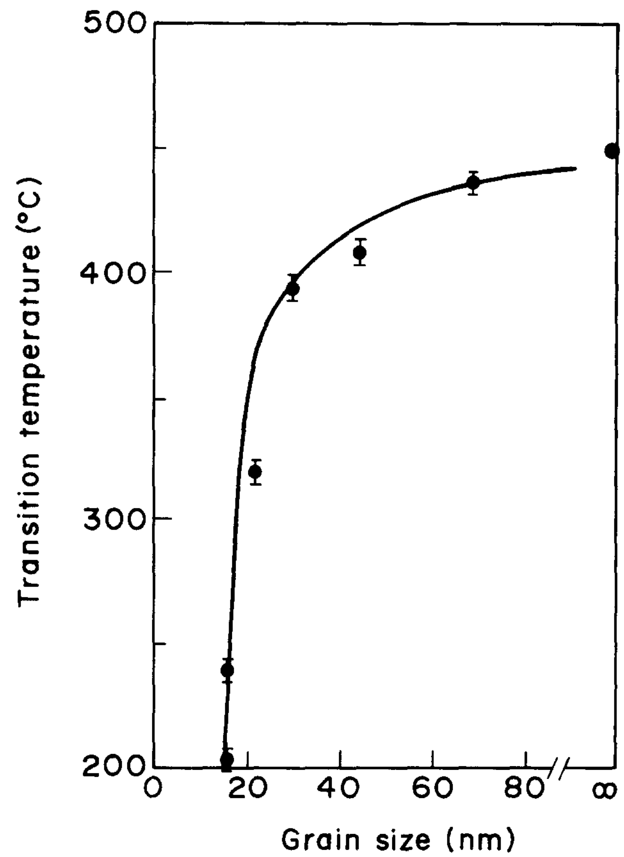

Fig. 4. The transition temperature vs. the grain size.

similar to the behaviour of $PbTiO_3$ ultrafine particles [5]. When the grain size is smaller than 14.0 nm, the structure of $PbZr_{0.2}Ti_{0.8}O_3$ can be transformed from the tetragonal ferroelectric phase into a cubic paraelectric phase. At the present stage there seems to be no general theory to describe the size effects in three-dimensional ferroelectric fine grains. However, qualitative understanding could be obtained from the soft mode picture. Ferroelectricity is intrinsically a long-range cooperative phenomenon. The "freezing out" of the soft mode depends on the balance of the short-range force and the long-range Coulomb force. The latter depends on the field E_s due to the dipole summation and the depolarization field E_d. E_s can be expressed in the simplest case as the Lorentz field: $E_s=(4\pi/3)P$, where P is the polarization. E_d is shape dependent and can be written $E_d=-\gamma P$, where γ is a constant. For the TO mode in an infinite crystal, $E_d=0$ and E_s is strong enough to balance out the short-range force. However, in small grains, E_s is weakened because the dipole summation runs over limited numbers, and $E_d \neq 0$ since the surface can no longer be neglected. When the size reaches the critical value, the long-range force cannot balance out the short-range force even at low temperature; thus ferroelectricity cannot appear.

The Raman spectra of nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$ powders with an average grain size of 44.5 nm at high pressures are shown in Fig. 5(a), and Fig. 5(b) describes the pressure dependence of the phonon modes. It is found that the frequency of the soft mode becomes constant beyond 4.78 GPa (to be considered as P_c; that of bulk material is about 9 GPa) and the line width

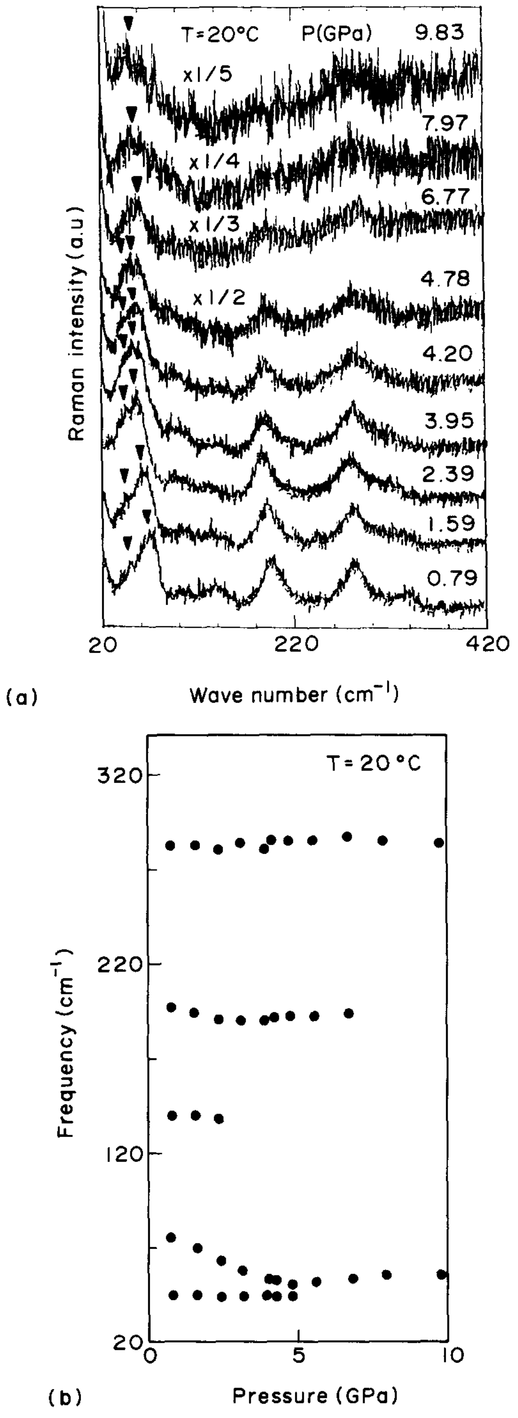

Fig. 5. (a) The Raman spectra for $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals with average grain size of 44.5 nm at high pressures. (b) Pressure dependence of the low frequency phonon modes in $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals with average grain size of 44.5 nm.

does not appear to diverge at higher pressures up to 9.83 GPa, in contrast to the behaviour of bulk material. It should be noted that the results cannot be fully caused by substitution of Zr^{4+} ions for Ti^{4+} ions because in pure nanocrystalline $PbTiO_3$ similar phenomena have been observed at hydrostatic pressures up to 12 GPa [11]. On the contrary, the widened phase transition region is very analogous to the dielectric anomalies of PZT ceramic, in which the dielectric peak becomes rather broad with decreasing grain size [13].

The concept of diffuse phase transition (DPT) is based on the existence of small microregions in the crystal or ceramic that can switch from paraelectric to ferroelectric states in a statistical way, implying that each region has or many have a different transition pressure P_c. Any factor tending to decrease V_k (the volume of these microregions) must also broaden the DPT. Such a factor includes the decrease in the average size of the crystals and the application of high hydrostatic pressure.

In the case of nanocrystalline material, every nanocrystalline grain can be regarded as a microregion. According to the structural characteristics of nanocrystals, there are many atoms with unsaturated and broken bonds on the grain surface whose dimension is as large as that of one or several unit cells. Because the zone centre ($q = 0$) soft mode responsible for the ferroelectric transition in many ABO_3 oxides consists of the vibration of the positive A and B ions against the negative oxygen ions [14], the broken bond atoms no longer contribute to the soft mode, and the soft mode softens in the nanocrystalline grain as shown in Fig. 2. The smaller the grain size, the larger the surface and interface, and thus fewer atoms take part in the soft mode phase transition, so that each grain has or may have a different transition pressure. Therefore the phase transition in nanocrystalline material is transferred from a sharp phase transition of bulk material to a broad DPT region.

In addition, we find that the line width of the soft E (1TO) mode is widened abruptly as the pressure is increased beyond 7.97 GPa. This behaviour originates mainly from the dislocation of the lattices, the breaking up of the crystal and the change in the contact zones at higher pressure [15]. The non-zero Raman bands in the "cubic phase" at high pressure and at high temperature still need further clarification and confirmation.

It is interesting that there are some discrepancies between the Raman spectra show in Fig. 3(a) and Fig. 5(a). In Fig. 3(a), as the temperature is 420 °C, the line width of the E (1TO) mode diverges and the frequency can no longer be measured, which means that the temperature-induced phase transition occurring in $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals is still a first-order transition [16]. In contrast, in Fig. 5(a), no discontinuity in the soft phonon energy is observed as a function of pressure, which indicates that the pressure-induced phase transition is second order [17].

4. Conclusion

Nanocrystalline $PbZr_{0.2}Ti_{0.8}O_3$ powders synthesized using the stearic acid gel method were characterized by X-ray diffraction and Raman spectroscopy. The pure perovskite $PbZr_{0.2}Ti_{0.8}O_3$ phase occurred at a higher crystallization temperature (550 °C) than the perovskite $PbTiO_3$ phase during this process. The additional mode occurring in the low frequency Raman spectra of $PbZr_{0.2}Ti_{0.8}O_3$ nanocrystals might be due to zone boundary TA phonons which couple to the $q \approx 0$ soft E (TO) mode. The phase transition temperature T_c decreases abruptly with decreasing grain size. The Raman spectra, as a function of pressure, reveal that the phase transition may be correlated with a DPT. Non-zero Raman bands in the high pressure as well as temperature phase may originate from broken bonds of atoms and a disordered distribution of some atoms in nanocrystalline phase.

Acknowledgements

This project was supported by the National Natural Science Foundation of China and the Doctoral Foundation of the National Committee of Education of China.

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