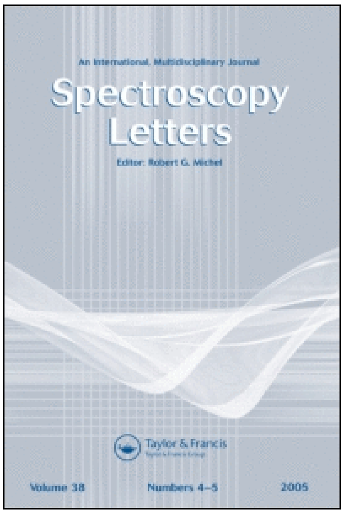

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FT-RAMAN SPECTROSCOPIC STUDY OF $Pb_{1-x}Ca_{x}TiO_3$ NANOCRYSTALS

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FT-RAMAN SPECTROSCOPIC STUDY OF $Pb_{1-x}Ca_xTiO_3$ NANOCRYSTALS

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ABSTRACT

FT-Raman Spectra of $Pb_{1-x}Ca_xTiO_3$ nanocrystals with different lanthanum amounts were measured at 288 K and 378 K. Several nanocrystals of $Pb_{0.85}Ca_{0.15}TiO_3$ with different grain size were also prepared at 288 K. The effects of the amount of lanthanum, grain size and temperature on phonon frequency were discussed in details. Furthermore, the conclusion that lattice expansion's presentation in PCT nanocrystals can be obtained by the frequency comparison of PCT nanocrystal of $x \geq 0.2$ with ceramic doped with the same amount of calcium.

Key Words: Calcium modified lead titanate; Nanocrystal; FT- Raman spectra; Phonon.

INTRODUCTION

As a ferroelectric material, $PbTiO_3$ has excellent piezoelectric and pyroelectric properties, but with a large terragonal axial ratio. When cooled down to Curie temperature, there appears to be stress cracks. additionally, owing to its easily brittle and low mechanical strength properties, it is very difficult to obtain pure phase $PbTiO_3$ as ceramics and thin films. One effective method to produce less brittle material is to modify its composition. In the lattice of $Pb_{1-x}Ca_xTiO_3$ (PCT), Ca^{2+} one can replace Pb^{2+} of the A lattice. Many modification methods have been used to prepare PCT with excellent piezoelectric anisotropy and high pyroelectric ratio of merit sufficient for potential applications in the fields of sonar and pyroelectrics. In recent years, the study of PCT pyroelectric thin films is becoming more and more important. Thin films have been made on different matrix by different methods [1–2], but when the amount of calcium is more than 20% (mol%), the composition phase with the pyrochlore structure appears easily at higher temperatures. Getting pure PCT thin film with a perovskite structure is difficult [3–4]. So present studies about PCT thin film are more superficial than that of PLT ($Pb_{1-x}La_xTiO_3$) thin films and nanocrystals. A FT-Raman spectroscopic study on PCT thin film has rarely been reported (15). In this work pure perovskite structure PCT nanocrystals with $x \geq 0.3$ have been successfully synthesized, and have been examined for unit cell constant crystal axis ratio, and grain size. The effects of the amount of calcium and grain size on the frequency of phonon properties can be detected using FT-Raman spectroscopic techniques, the results obtained can provide the guidance for this film study.

EXPERIMENT

Nanocrystals with different amounts of calcium were made using the sol-gel method. The heat treatment was under the condition of rapid increasing to 700 C, then heating at a constant temperature for one hour. The structural data for the nanocrystals prepared is shown in Table 1.

Raman spectra was measured using a BRUKER RFS100 FT-Raman spectroscopic detector. The excitation line was at 1 064 nm from a Nd:YAG laser. Nanocrystals with different quantities of calcium were tested at 15C and 105C, respectively. Different nanocrystals were tested only at room temperature. Test conditions were : 40 mW laser power; 2 cm^{-1} resolution; and 200 co-added scans

Table 1. The Structure Data of Nanocrystals from Sol-gel Method ($T = 700$ C, with Rapid Heating to Reach 700 C)

x	0	0.01	0.05	0.15	0.20	0.25	0.30
c/a	1.061 5	1.051 8	1.051 0	1.048 4	1.045 6	1.042 7	1.041 7
Dm (nm)	26.44	27.90	26.43	25.69	23.10	21.53	21.89

Note: The structural data of $Pb_{0.85}Ca_{0.15}TiO_3$ nanocrystals with different crystal grain size under different heat treatment conditions are shown in Table 2.

Table 2. The Data of $Pb_{0.85}Ca_{0.15}TiO_3$ Nanocrystals with Different Grain Size Under Different Heat Treatment Conditions

c/a	1.038 3	1.043 3	1.048 4	1.050 2	1.050 7	1.053 1
Dm (nm)	17.89	20.75	25.69	26.43	28.23	36.25

per spectrum. Gaussian line-type fitting techniques were used to divide the overlapping peaks, and to confirm the peak positions.

RESULT AND DISCUSSION

Raman spectra of nanocrystals with different amounts of calcium are shown in Figures 1a and 1b. The symmetry of each phonon frequency of nanocrystals modified by calcium was identified, comparing the data of phonon frequency with the identification result of the lead titanate single crystals [6], and the nanocrystals. Relations between each phonon frequency and the amount of calcium are shown in Figures 2a and 2b. To research the influence of the crystal grain size of nanocrystals on the phonon frequency, $Pb_{1-x}Ca_xTiO_3$ nanocrystals with different crystal grain size were measured, and the resultant identification of spectral peaks are listed in Table 3. The results indicate that the shift of phonon frequency has a closer

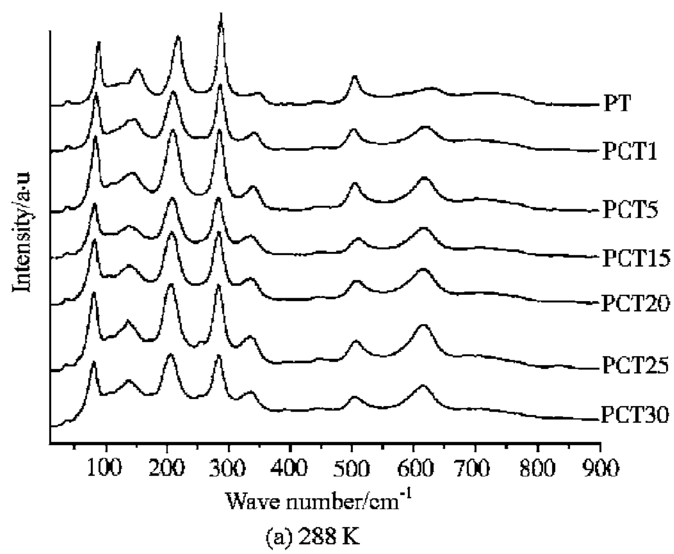

Figure 1a. FT-Raman spectra of $Pb_{1-x}Ca_xTiO_3$ nanocrystals (288 K).

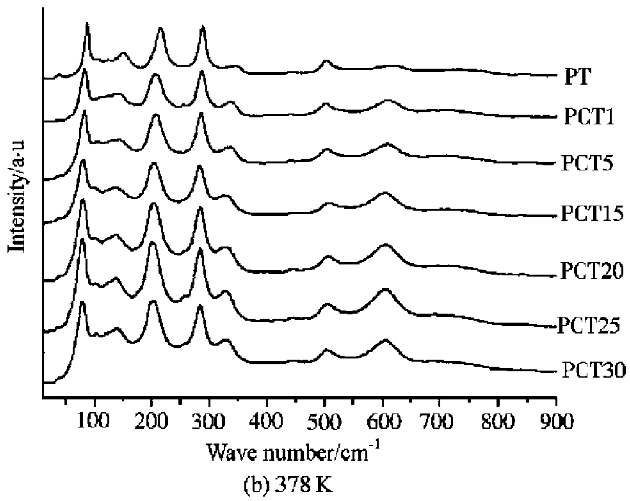

Figure 1b. FT-Raman spectra of $Pb_{1-x}Ca_xTiO_3$ nanocrystals (378 K).

relationship with the amount of calcium, the test temperature, and the crystal grain size. When doped with little calcium, each phonon frequency exhibited a trend to shift to lower positions and the frequency decreased with increasing amounts of calcium present, the (E(3TO) phonon mode excluded. But when $x \geq 0.20$, the

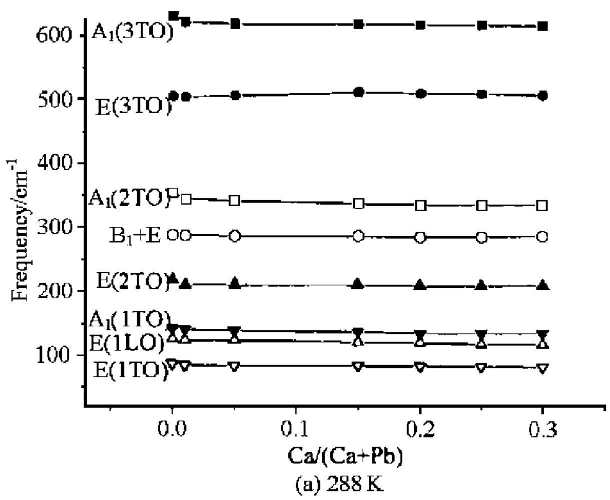

Figure 2a. Symmetry of each phonon frequency of nanocrystals (288 K).

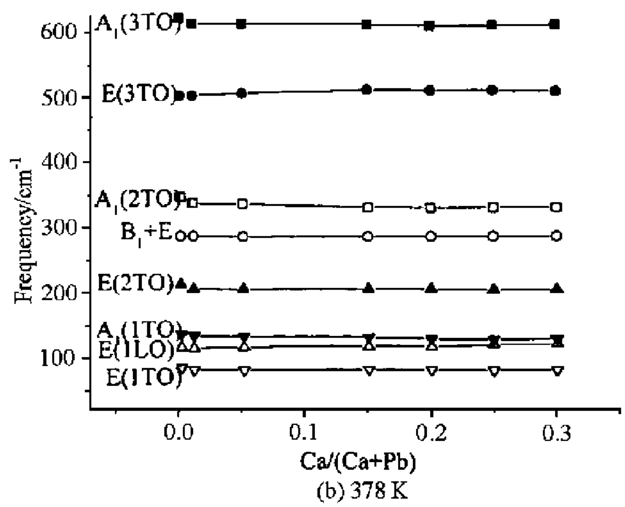

Figure 2b. Symmetry of each phonon frequency of nanocrystals (378 K).

frequency remained constant with the increasing amount of calcium. This is mainly because when Ca is substituted for Pb, the photon frequency increases following a mass effect (i.e., the mass of Ca is far lighter than that of Pb. On the other hand, r_{Ca2+}(0.99 pm) is smaller than r_{Pb2+}(120 pm), when Ca^{2+} joined the lattice, c/a

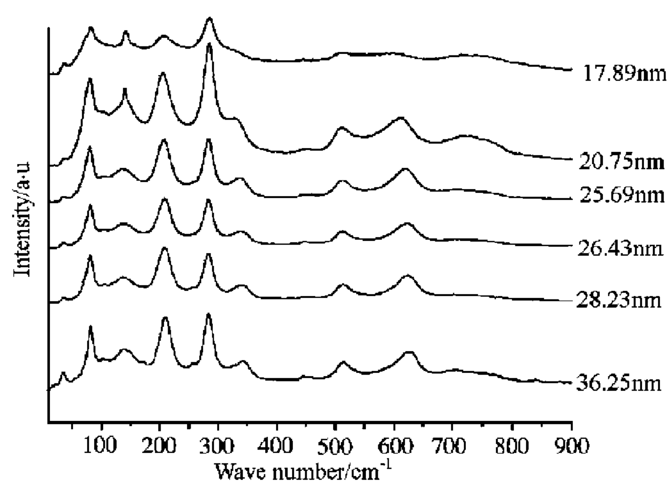

Figure 3. FT-Raman spectra of $Pb_{0.85}Ca_{0.15}TiO_3$ nanocrystal with different crystal grain sizes.

Table 3. The Phonon Frequency of $Pb_{0.85}Ca_{0.15}TiO_3$ Nanocrystal (cm^{-1})

Phonen	Dm = 17.89 c/a = 1.0383	Dm = 20.75 c/a = 1.043	Dm = 25.69 c/a = 1.0484	Dm = 26.43 c/a = 1.050 2	Dm = 28.23 c/a = 1.0507	Dm = 36.25 c/a = 1.0531
E(1TO)	72.8–83.1	82.1	82.7	83.2	83.2	83.7
E(1LO)		122.8	119.6	121.1	121.1	121.1
A1(1TO)	143.5	142.1	138.9	142.1	142.1	145.3
		138.0		130.8	130.9	129.1
	103.5	102.1	108.3	106.0	106.9	104.9
E(2TO)	208.1	206.4	209.6	211.3	211.2	212.6
B1 + E	285.3	285.3	285.3	285.3	285.3	285.3
A1(2TO)	328.8	328.8	336.8	340.0	343.2	344.8
A1(2LO) +E(2LO)		444.6	444.6	444.6	446.2	447.8
E(3TO)	507.3	510.6	510.6	510.6	512.2	512.2
A1(3TO)	610.4	610.4	616.8	623.2	624.8	629.7
E(3LO)	705.0	702.1	698.8	700.4	700.4	698.9
A1(3LO)	765.0	756.8	752.0	761.6	756.8	761.6

became small (i.e., a remains unchanged, c becames obviously smaller) with the lattice contract. But when the amount of Ca increases to a specified amount, the change of c/a is very small and the value of the contraction of the crystal exhibits equilibrium with the mass effect, thus the photon frequency becomes constant. With the temperature increasing, the photon frequency decreased, but the change of photon frequency with the amount of Ca is similar to that of the spectrum at normal temperature. When $x \geq 0.2$, the photon frequency of the nanocrystal was higher than that of ceramic materials except that of E(3TO). Research on lead titanate indicated [7] that the values of dV/dp, change photon frequency values with pressure, and that all are below zero except that of E(3TO). A pressure increase means a volume decrease of the lattice. Conversely, decreasing the photon frequency of E(3TO, means decreasing the pressure or increasing the volume of the lattice. So when $x \geq 0.2$, the volume of the PCT nanocrystal unit increases more than that of ceramic, because of far lower temperature and shorter heat treatment time of the nanocrystal compared to that of ceramic. The expansion phenomenon of lattice was also described by J. Mendiolas [5], whos researched the result of Raman spectrla measurements of $Pb_{0.76}Ca_{0.24}TiO_3$. With a decreasing crystal grain size, the peak of each photon moved to a lower frequency, except that of E(3TO), see Figure 3. Because the dipole number decreases with the decreasing of crystal grain size, the long-range stress is lower. Whereas its short-range perturbation strengthens, affecting thermal motion, and depolarization field. When the size of the crystal grain was very small (17.89 nm), the soft mode peak of E(1TO) broadened markedly, and showed a double peaks phenomenon. This meant that Ca^{2+} diffuses unequally under the low heat treatment temperature. This led to the swing between micro areas. The dispersion of the phase changing temperature was found in observation at its curie temperature.

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