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Negative pressure effects in $SrTiO_3$ nanoparticles investigated by Raman spectroscopy

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Abstract

The size effects on $SrTiO_3$ nanoparticles have been investigated by means of Raman spectroscopy with changing the grain size in the range 10–80 nm. The intensities of the first-order polar TO_2 and TO_4 modes increase as the grain size reduces, suggesting the enhanced interaction of the surface-defect dipoles on the grain boundary. By contrast, the intensities for the first-order nonpolar TO_3 mode decrease with reducing the grain size. Further we have found that the Raman frequencies of the vibration modes are very sensitive to the variation of the grain size. The softening of the TO_2 and TO_3 modes with decreasing the grain size indicates the increase of the Ti–O bond length, which is consistent with the lattice expansion investigated by XRD. We have ascribed the size effects to the negative pressure effects due to the enhanced interaction of the surface-defect dipoles.

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Metal-oxide nanoparticles have attracted considerable attention due to their potential for applications in many technologies such as solar energy conversion, batteries and ductile ceramics [1]. Up until now, a large amount of studies concerning the structure and optical properties of these nanoparticles have demonstrated that these metal oxides have unique properties that are largely dependent on the grain size and morphology [2–4]. Recent researches [5] have also shown that the dimensional reduction into the nanoscale regime produces distinct properties in the bulk, which is thought to originate from phonon confinement, surface strain or defect centers.

$SrTiO_3$ is a perovskite-type quantum paraelectric metal oxide where large quantum fluctuations make the ferroelectric state unstable in favor of the paraelectric state. In the past few years, many investigations of $SrTiO_3$ have been conducted, which were focused on size or temperature dependence of phase transitions between the paraelectric and ferroelectric states [6,7], the variations for the optical and dielectric properties [8–11], and the characteristics for the surface layer and morphology [12,13]. It has been found that $SrTiO_3$ particles exhibit distinct properties from the bulk with the reduction of grain size into the nanoscale regime [9,14]. For example, the photoluminescence (PL) intensity [15] was observed to increase in $SrTiO_3$ nanoparticles, which was ascribed to the formation of the intrinsic surface states and defect centers in the nanoparticles. In addition, the critical temperature T_c related to quantum fluctuation was detected to increase in nanoparticles [11], implying the enhanced exchange interactions of dipoles in the $SrTiO_3$ nanoparticles. Recently, Wu et al. [4] have found the lattice expansion as the grain size of $SrTiO_3$ is reduced to the nanoscale by means of XRD spectroscopy, and attributed the lattice expansion to the negative pressure effects due to the enhanced interaction of the surface-defect dipoles.

In this work, we have employed Raman spectroscopy to investigate the size effects of $SrTiO_3$ nanoparticles in the size

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range 10–80 nm. Raman spectroscopy is one of the most sensitive probes to detect the variation of local symmetry for the surface structure. We have found that the Raman spectra of $SrTiO_3$ particles present a significant variation as the particle size reduces to nanoscale. The intensities of the first-order polar TO_2 and TO_4 modes exhibit significant increase with reducing the particle size from 80 to 10 nm. Further we have observed the decrease of the Raman frequencies of the first-order TO_2 and TO_3 modes with reducing the particle size. We have ascribed the size effects to the negative pressure effects in $SrTiO_3$ nanoparticles.

Nanocrystalline $SrTiO_3$ particles were prepared using the sol–gel method [11]. A stoichiometric mixture of $Ti(I\text{–}OC_3H_7)_4$ and $Sr(OCH_3OC_2H_4)_2$ diluted with 2-methoxyethanol was refluxed for 24 h. After gelation, the samples were heat treated for 3 h at different temperatures, i.e., 600, 700, 800 and 900 °C. The crystal structures were analyzed by a Rigaku D/max 2500 diffractometer with Cu Kα radiation and a graphite monochromator. A step scan mode was employed with a step width of $2\theta = 0.02°$ and a sampling time of 1 s. Fig. 1 shows the X-ray diffraction (XRD) powder patterns for $SrTiO_3$ nanoparticles treated at 900 °C (upper panel) and 600 °C (bottom panel). The XRD patterns indicate the cubic structure with well-crystallized character of the $SrTiO_3$ nanoparticles. The average sizes were determined from the full-width at half-maximum (FWHM) of the most intense (110) peak using Scherrer's equation, i.e., $D = 0.9\lambda/B\cos(\theta)$ [16], where D is the average grain size, λ is the X-ray wavelength, B is the FWHM of (110) peak and θ is the diffraction angle. The corresponding average sizes of the nanoparticles were obtained as 10, 40, 70, 80 nm, respectively, which are in agreement with the TEM results. The lattice parameters for the samples were calculated by using the least-squares procedure. The inset in Fig. 1 shows the diffraction (110) peak at 80 nm (solid circles) and 10 nm (open circles), in which the diffraction angle shifts from $2\theta = 32.4°$ at 80 nm to $2\theta = 32.3°$ at 10 nm, indicating the increase of lattice parameters. Fig. 2 shows that the lattice parameter a increases from 3.907 Å at 80 nm to 3.922 Å at 10 nm. In Raman experiments, the samples were excited at 514.5 nm (2.41 eV) with an argon laser in a backward configuration. To avoid the sample damage, the laser power density was kept below 40 W/cm^2. The scattered light was detected with a double monochromator (JobinYvon-U1000) equipped with a photon-counting system.

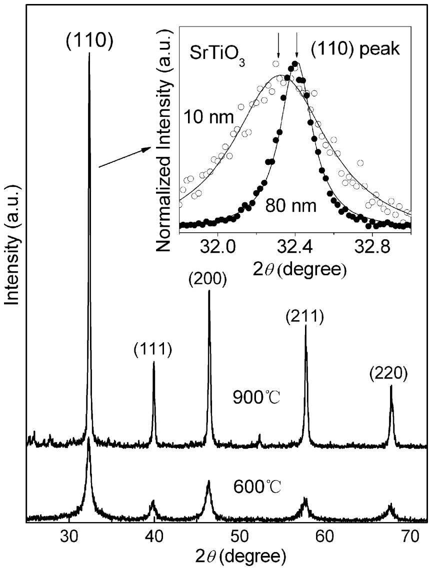

Fig. 1. X-ray diffraction (XRD) powder patterns for the $SrTiO_3$ nanoparticles treated at 900 °C (upper panel) and 600 °C (bottom panel). The inset shows the diffraction (110) peak at 80 nm (solid circles) and 10 nm (open circles). The solid curves are the best-fitted results with the Lorentzian functions.

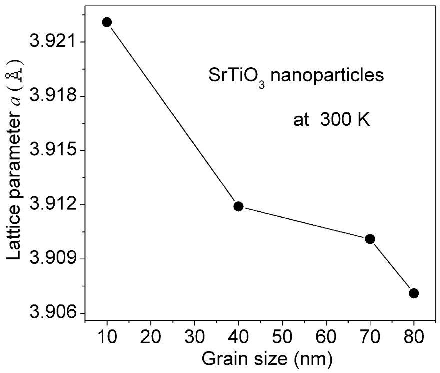

Fig. 2. Size dependence of the lattice parameter a for $SrTiO_3$ nanocrystals at 300 K.

Before describing the details of the size effects on Raman spectra, let us survey the Raman active modes of $SrTiO_3$. At room temperature, $SrTiO_3$ has an ideal cubic perovskite structure with space group *Pm3m* (O_h^1), and the vibration modes are $3F_{1u} + F_{2u}$ [17]. Neither F_{2u} nor F_{1u} modes are Raman active, and then no first-order Raman mode is expected in $SrTiO_3$ at room temperature. The first-order modes are symmetrically forbidden in bulk $SrTiO_3$ due to the phonon momentum selection rule for $q_0 = 0$ near the center of the Brillouin zone (BZ), while the second-order modes involve the creation or destruction of two first-order modes [18]. Recently, extensive studies on the Raman spectra of $SrTiO_3$ have shown that the Raman modes can be modified, especially the activation of the first-order Raman modes, by many factors like strain effects, oxygen vacancies and even external conditions [19–21]. Du et al. [19] observed the first-order modes in polycrystalline $SrTiO_3$ even at 300 K, which was ascribed to the strain effect and oxygen vacancies. In addition, presence of impurities such as Ca doping or applied external electric field was found to break the central symmetry of $SrTiO_3$ and hence the appearance of the first-order modes in bulk $SrTiO_3$ [20,21]. With decreasing temperature to 76 K, a cubic to tetragonal ($C_{4\upsilon}^1$ or *P4mm*) structural change takes place in bulk $SrTiO_3$, and each of the F_{1u} modes splits into a doubly degenerate E mode and a nondegenerate A_1 mode, while the F_{2u} mode splits into E and B_1 modes. Thus, the vibration modes are $3(A_1 + E) + E + B_1$. All the A_1 and E modes are both Raman and infrared active, while the B_1 mode is Raman active. The presence of long-range electrostatic forces further splits each of the A_1 and E modes into transverse optical (TO) and longitudinal optical (LO) modes [17]. Nilsen et al. [18] investigated the Raman spectra of bulk $SrTiO_3$ in the range 100–1000 cm^{-1}