

# High pressure Raman studies of dense nanocrystalline BaTiO<sub>3</sub> ceramic

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**Abstract** High pressure Raman spectra have been measured on 20 nm BaTiO<sub>3</sub> ceramic from atmospheric pressure to 36.7 GPa. It was found that most of tetragonal phase has transformed to orthorhombic phase at about 10.9 GPa, and a new phase appeared at about 19.8 GPa. Raman modes still persisted up to 36.7 GPa. The phase transition was reversible.

**Keywords** High pressure · Raman spectra · BaTiO<sub>3</sub>

## 1 Introduction

Perovskite BaTiO<sub>3</sub> is extensively used in electronic industry for the fabrication of multilayer ceramic capacitors, piezoelectric transducers, pyroelectric elements and ferroelectric memories. With the fast development of microelectric, higher integration and miniaturation demand smaller grain size ceramic. Grain size has dramatic effect on the structure, ferroelectricity and phase transition, and so size effect has been a hot issue [1–3] for nanocrystalline BaTiO<sub>3</sub> ceramic studies now. There is scanty data available for dense nanocrystalline BaTiO<sub>3</sub> ceramic with grain size smaller than 50 nm, which is mainly related to the difficulty

to produce fully dense ceramic meanwhile keeping small grain size.

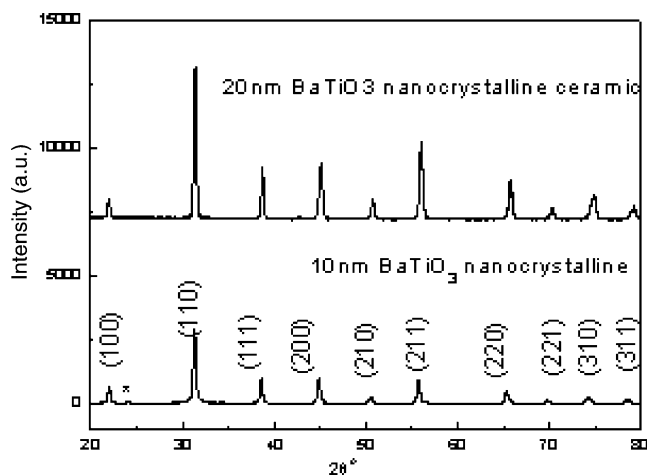
Raman spectroscopy is a powerful tool to investigate the relationship between ferroelectricity and structure. From the Raman spectra at high pressure, we could determine its structure evolution and ferroelectricity evolution. High-pressure Raman studies of BaTiO<sub>3</sub> polycrystalline show that it transforms from tetragonal phase to cubic phase at 2 GPa, and to a new phase at 5 GPa [4]. To investigate size effect on BaTiO<sub>3</sub> pressure behavior, in this paper, we have studied the in-situ high pressure Raman spectra of 20 nm BaTiO<sub>3</sub> ceramic. Our data showed evidence for two structural phase transformations; one was at about 10.9 GPa, which corresponded to the transformation to orthorhombic phase, the other was at about 19.8 GPa, which corresponded to the unknown new phase. After releasing high pressure, the BaTiO<sub>3</sub> ceramic was recovered to the initial state.

## 2 Experimental

Dense nanocrystalline BaTiO<sub>3</sub> ceramic sample with grain size of 20 nm was obtained from Tsinghua University. The sample was prepared as the following step: firstly, ultrafine pure BaTiO<sub>3</sub> powders were produced by chemical method [5]. The main impurities contained in the powders were as follows: 0.04 wt% Sr, 0.02 wt% Na, and 0.006 wt% K. Then the BaTiO<sub>3</sub> nanocrystalline ceramic was prepared from the powders by the spark plasma sintering (SPS) method [6, 7]. Figure 1 showed the X-ray diffraction pattern of 20 nm ceramic and 10 nm BaTiO<sub>3</sub> ultrafine powder. The sample was confirmed to be the tetragonal phase and the orthorhombic phase coexistence. In previous paper [7], the preparation process and the properties of

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**Fig. 1** XRD patterns of 10 nm BaTiO<sub>3</sub> ultrafine powder and 20 nm nanocrystalline BaTiO<sub>3</sub> ceramic at room temperature. The peak signed with asterisk comes from BaCO<sub>3</sub> impurity

ultrafine BaTiO<sub>3</sub> powders and ceramic had been reported in detail.

Pressure was produced with a Mao–Bell type diamond-anvil cell. 4:1 methanol–ethanol mixture served as the hydrostatic pressure medium, and the pressure was calibrated by the standard ruby fluorescence method.

Raman spectra were collected in backscattering geometry at room temperature by a Jobin Yvon T64000 triple spectrometer equipped with a cooled charge-couple device. In the spectrometer a long focus objective of 20× magnification was used to focus the laser beam on the sample surface and to collect the scattered light. Raman spectra were excited with 532.0 nm radiation from a Coherent solid-state laser. The laser power at the focus spot of about 1 μm in diameter was kept about 4.8 mW to obtain high quality spectra and prevent laser-induced damage to the samples. A spectral resolution better than 1 cm<sup>-1</sup> was obtained for our experimental configuration.

### 3 Results and discussion

Perovskite BaTiO<sub>3</sub> has five atoms (one formula unit) per unit cell; therefore, there are 12 optical vibrational modes. In the cubic phase of *m3m* symmetry, the optical modes belong to  $3F_{1u} + F_{2u}$  irreducible representations. Each of the  $F_u$  modes is triply degenerate, and all of them are Raman inactive. Upon transition to the tetragonal phase of *4mm* symmetry, the  $F_{1u}$  modes split into  $A_1$  and  $E$  modes, and the  $F_{2u}$  phonon gives rise to  $B_1$  and  $E$  modes. Thus,

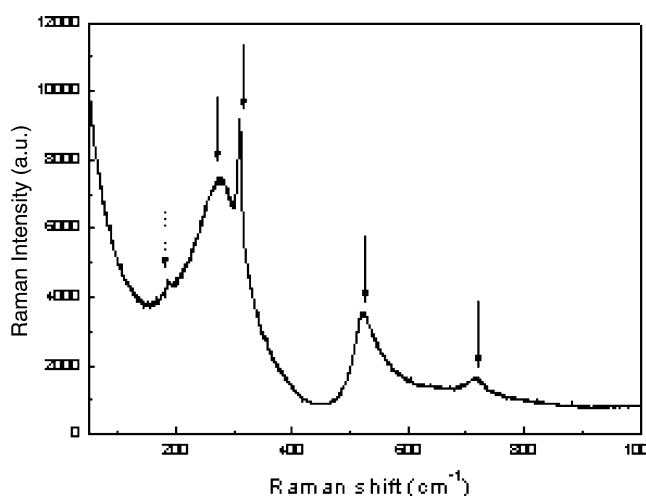
$$\Gamma_{C_{4v}}^{\text{optic}} = 3(A_1 + E) + E + B_1.$$

All the  $A_1$  and  $E$  modes are both Raman and infrared active and the  $B_1$  mode is only Raman active. The presence

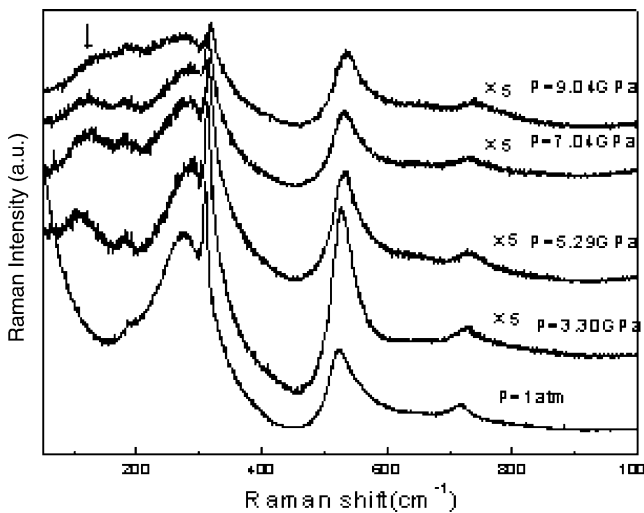
of long-range electrostatic forces further splits each of the  $A_1$  and  $E$  modes into transverse and longitudinal optical (TO and LO) modes. For the  $E$  modes, transverse and longitudinal optical (TO and LO) modes are doubly degenerate because of small drive force. In the orthorhombic phase of *mm2* symmetry, the optical vibrations belong to  $A_1$ ,  $A_2$ ,  $B_1$ , and  $B_2$  symmetry and all of them are Raman active. In the rhombohedral phase of *3m* symmetry, the modes originating from the cubic  $F_{1u}$  phonons are split into  $A_1$  and  $E$  modes, while the  $F_{2u}$  vibrations produce  $A_2$  and  $E$  modes. The symmetric  $A_1$  and  $E$  modes are Raman active.

Figure 2 showed unpolarized Raman spectrum of nanocrystalline BaTiO<sub>3</sub> ceramic at room temperature. It consisted Raman bands from two phases, tetragonal and orthorhombic phase, denoting with solid arrows and dash arrow respectively. Comparing to Raman spectrum of the single crystal BaTiO<sub>3</sub> [8–10], we assigned the spectrum as follows, a weak peak at 187.2 cm<sup>-1</sup> [ $A_1$  (LO<sub>1</sub>)] originated from orthorhombic symmetry; the other peaks, 267.8 cm<sup>-1</sup> [ $A_1$  (TO<sub>1</sub>)], 522.1 cm<sup>-1</sup> [ $A_1$  (TO<sub>2</sub>)], 715.6 cm<sup>-1</sup> [ $A_1$  (LO<sub>2</sub>)] and 308.6 cm<sup>-1</sup> [ $E$  (TO)], were the common character of tetragonal and orthorhombic symmetry. The phonon assignment was given inside square brackets. So the sample was the orthorhombic and the tetragonal coexistence.

Figure 3 showed the room temperature Raman spectra of nanocrystalline BaTiO<sub>3</sub> ceramic from 1 atm to 9.04 GPa, as the applied pressure was increased, the intensity of Raman spectra reduced quickly. The  $A_1$  (TO<sub>1</sub>) phonon peak shifted towards higher frequency slightly up to 3.3 GPa, and then shifted to lower frequency. At the same time, a new peak emerged at about 105.4 cm<sup>-1</sup>. Comparing to the Raman

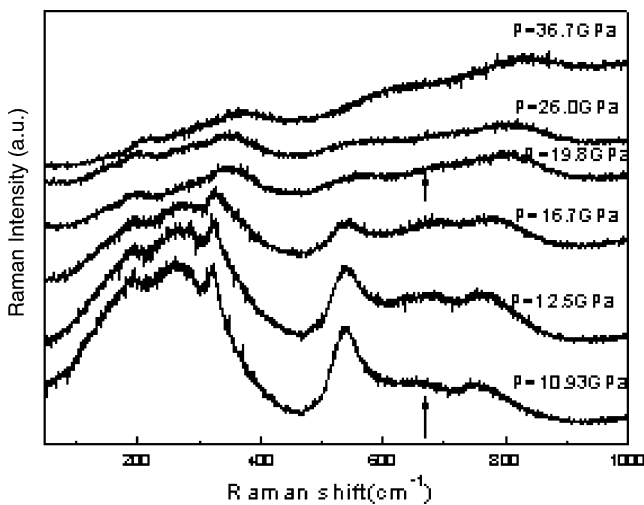


**Fig. 2** Raman spectrum of BaTiO<sub>3</sub> nanocrystalline ceramic recorded at room temperature and ambient pressure. The solid arrow represented the vibrations from tetragonal and orthorhombic phase, and the dashed arrow represented the vibrations from only orthorhombic phase

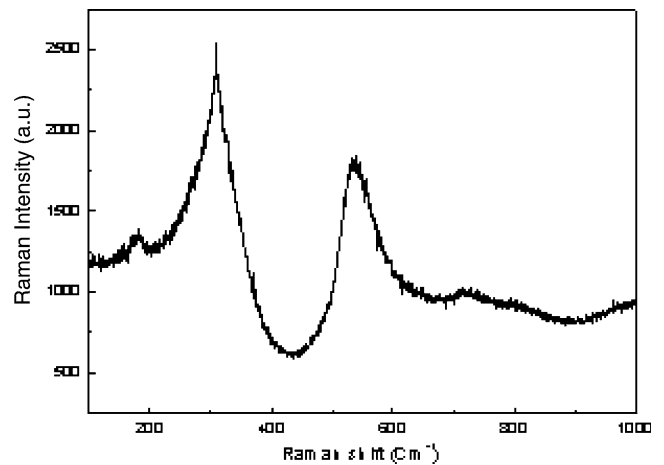


**Fig. 3** Unpolarized Raman spectra of BaTiO<sub>3</sub> nanocrystalline ceramic for selected pressure from atmospheric pressure to 9.04 GPa recorded at room temperature. A peak at about 105.4 cm<sup>-1</sup> appeared and shifted towards high frequency with pressure shown by arrow. The intensity reduced quickly with the increment of pressure. In order to comparing to data at atmospheric pressure, the high pressure spectra data were multiplied by five times

data of BaTiO<sub>3</sub> up to now, the new peak could not be assigned as a mode from any known phase. This new peak was particular in BaTiO<sub>3</sub> nanocrystalline ceramic and has not been reported before. We speculated that it might stem from the phonon interference between the certain tetragonal modes and the certain orthorhombic modes, like the dip [11] near 186 cm<sup>-1</sup> in pure tetragonal BaTiO<sub>3</sub> phase. The phonon interference induced a lattice distortion at 3.3 GPa.



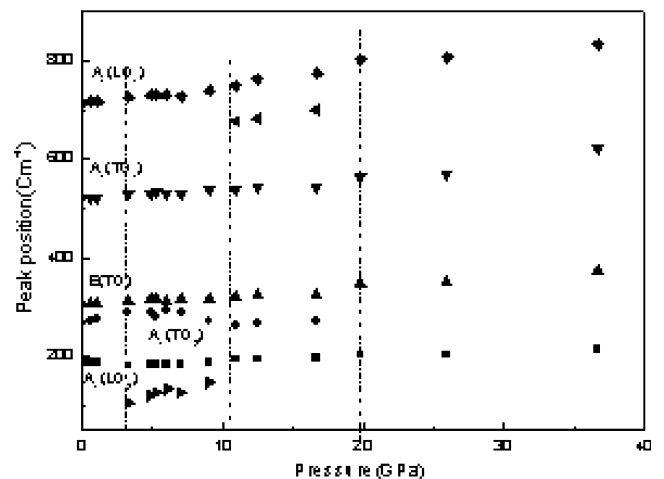
**Fig. 4** Unpolarized Raman spectra of BaTiO<sub>3</sub> nanocrystalline ceramic from 10.93 to 36.7 GPa recorded at room temperature. A peak at about 676 cm<sup>-1</sup> appeared and shifts towards high frequency with pressure shown by arrow. Up to 19.8 GPa, the new peak disappeared, and the Raman line shape changed



**Fig. 5** The Raman spectrum of BaTiO<sub>3</sub> ceramic released from 36.7 GPa

The new peak shifted towards higher frequency with the increment of pressure and then disappeared at 10.93 GPa (Fig. 4). Simultaneously, the other new peak appeared at about 676 cm<sup>-1</sup>. This peak should originate from orthorhombic *mm2* symmetry [4]. It was weaker than the other peaks, but it was seldom mentioned in published papers. At atmospheric pressure, the peak did not appear on account of little proportion of the orthorhombic phase. The intensity of 676 cm<sup>-1</sup> Raman peak enhanced with the increment of pressure. At 19.8 GPa, there was a significant change in the line shape of the whole wave number range. We inferred that it came from another unknown phase. BaTiO<sub>3</sub> nanocrystalline ceramic kept crystallization state in our experimental pressure range.

Figure 5 showed the Raman spectrum of the sample released from 36.7 GPa. Comparing to the basic profile of



**Fig. 6** Frequency of the Raman peaks plotted as a function of pressure for nanocrystalline BaTiO<sub>3</sub> ceramic

Fig. 2, we concluded the phase transition was reversible. The pressure dependences of the Raman peaks were shown in Fig. 6, in which the phase transition process was displayed more clearly.

#### 4 Conclusions

We investigated the high pressure Raman spectra of 20 nm BaTiO<sub>3</sub> ceramic up to 36.7 GPa. Lattice distortions induced by phonon interference occurred at 3.3 GPa, and two phase transitions have been found in the studied pressure range. One occurred at around 10.9 GPa, in which most of sample has transformed to orthorhombic phase; the other occurred at 19.8 GPa, in which the sample has transformed to a new unknown phase.

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