Available online at www.sciencedirect.com
ScienceDirect
Journal of Physics and Chemistry of Solids 68 (2007) 311–314
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

The phase transitions and ferroelectric behavior of dense nanocrystalline $BaTiO_3$ ceramics fabricated by pressure assisted sintering

C.J. Xiao[a], Z.H. Chi[a], W.W. Zhang[a], F.Y. Li[a], S.M. Feng[a], C.Q. Jin[a,*], X.H. Wang[b], X.Y. Deng[b], L.T. Li[b]

[a]Beijing National Lab for Condensed Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing 100080, China
[b]State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Received 26 June 2006; received in revised form 28 September 2006; accepted 21 November 2006

Abstract

Dense nanocrystalline $BaTiO_3$ ceramics with uniform grain sizes of 30 nm was obtained by pressure assisted sintering. The phase transitions were investigated by Raman scattering at temperatures ranging from −190 to 200 °C. With increasing temperature, similar to 3 μm $BaTiO_3$ normal ceramics, the successive phase transitions from rhombohedral to orthorhombic, orthorhombic to tetragonal, tetragonal to cubic were also observed in 30 nm $BaTiO_3$ ceramics. Especially, the coexistence of ferroelectric tetragonal and orthorhombic phases was found at room temperature. The ferroelectric behavior was further characterized by P–E hysteresis loop. The experimental results indicate that the critical grain size of the disappearance of ferroelectricity in nanocrystalline $BaTiO_3$ ceramics fabricated by pressure assisted sintering is below 30 nm.

Keywords: A. Nanocrystalline ceramics; C. Raman spectroscopy; D. Ferroelectricity

1. Introduction

Barium titanate ($BaTiO_3$) is one of most widely used ferroelectric materials and has been extensively studied. It is a typical perovskite-type material with a variety of crystal structure modifications. With decreasing temperature, $BaTiO_3$ crystal undergoes three successive phase transitions from a cubic phase (*Pm3m*) to a tetragonal phase (*P4mm*) at 130 °C, then to an orthorhombic phase (*Amm2*) at 5 °C, finally to a rhombohedral phase (*R3m*) at −90 °C [1]. The cubic phase is paraelectric and the other phases are ferroelectric. The grain size has a significant effect on the structure and phase transitions of $BaTiO_3$ crystal [2–4]. When particle size is reduced to the nanoscale, one will find some unusual physical properties and even the disappearance for ferroelectricity as compared with those of conventional polycrystallines. Zhong et al. predicted theoretically that the critical size of retaining ferroelectricity is about 44 nm for $BaTiO_3$ particles [2]. By spark plasma sintering, dense nanocrystalline $BaTiO_3$ ceramics with grain sizes of 50 and 20 nm were obtained, respectively [4–7]. The successive phase transitions were observed in 50 and 20 nm $BaTiO_3$ ceramics [4,5]. The critical size was proved to be below 20 nm by piezoresponse hysteresis loop [5]. A progressive reduction of tetragonal distortion, heat of transition, Curie temperature, and relative dielectric constant with grain size decreasing from 1200 to 50 nm was found, and that the critical size was evaluated to be in the range 10–30 nm by extrapolating the experimental trends [7]. Because it is difficult to fabricate dense nanocrystalline ceramics by the conventional method, there are only few data available on structural, dielectric, and ferroelectric behavior of $BaTiO_3$ ceramics at this scale.

High pressure can significantly increase the densification. Further, during the high pressure assisted sintering, the nucleation rate is increased due to reduced energy barrier and the growth rate is suppressed due to the decreased

*Corresponding author.
E-mail address: Jin@aphy.iphy.ac.cn (C.Q. Jin).

0022-3697/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2006.11.014

diffusivity [8]. Thus high pressure enables the specimen to be fabricated under relatively lower temperature and shorter sintering period that assures to obtain dense nanocrystalline ceramics.

Raman spectroscopy has a better resolution for the local microstructure than X-ray powder diffraction, so it is a suitable technique to study phase transitional characteristics of ferroelectrics [9]. In addition, the evolution of Raman spectrum with grain size is characterized by an intensity decrease, a broadening of the line width, a frequency shift, and the disappearance of the Raman mode [10]. Therefore Raman spectroscopy is a very sensitive method to detect the structure evolution of $BaTiO_3$ nanocrystalline ceramics.

In this paper, dense $BaTiO_3$ ceramics with uniform grain sizes of 30 nm was obtained by a novel densification method, i.e. the three-step pressure assisted sintering. The phase transitions and ferroelectric behavior of 30 nm $BaTiO_3$ ceramics were investigated.

2. Experimental

In order to obtain dense nanocrystalline materials, very fine non-agglomerated powder with a narrow particle size distribution and an appropriate densification method to minimize the grain growth are required. In our experiment, the raw $BaTiO_3$ powder with a grain size of 10 nm was synthesized by chemical processing [11]. In order to densify the sample and inhibit the grain growth, a three-step pressure assisted sintering was adopted. The raw powder was pressed into a pellet uniaxially at 7 MPa. The pellet was pressed under 3 GPa at ambient temperature and then it was unloaded and ground into powder. This procedure was repeated several times that was found to be effective to eliminate nano grain agglomeration. The processed powder was repressed into a pellet and the pellet was wrapped by Ag foil to prevent from contamination and then was inserted into a BN spacer tube that was in turn put into a graphite heater. The high pressure experiment was performed using a cubic anvil type apparatus. The pyrophyllite was used as the pressure-transmitting medium. The sample was first pressurized up to 6 GPa and then heated at 1000 °C for 5 min in air. After temperature quenching, the sample was obtained by releasing the pressure slowly to one atmospheric pressure.

The microstructure of the sample was observed by scanning electron microscope (SEM, XL30-FEG) on fresh fracture surface. The grain size was calculated by X-ray diffraction (XRD) using CuK_α radiation on a Rigaku D/max-2500 diffractometry with a scan step size of 0.02°, a step time of 5 s. The phase transitions as a function of temperature were characterized by Raman spectroscopy. The Raman experiments were performed on a Renishaw RM2000 Confocal Raman Spectrometer equipped with microscope optics function. The excited laser line is 633 nm of He–Ne laser. The scattered light was colleted with a liquid-nitrogen-cooled charge-coupled device (CCD) detector. The ferroelectric behavior was characterized by polarization vs. applied electric field hysteresis loop using TF2000 axiACCT Analyzer FE at 1 kHz.

3. Results and discussion

The microstructure of the sintered sample is shown in Fig. 1. From the SEM image, the sample exhibits a uniform grain size distribution and the grain size is estimated to be about 30 nm by the intercept line method. The average grain size is calculated to be 28 nm from the full width at half maximum (FWHM) of the broadening (1 1 1) peak using Scherrer equation. It is in agreement with the SEM result. The sample is dense and the relative density is above 96% (theoretical density: 6.02 g/cm^3).

In order to detect the phase transitions as a function of temperatures for the 30 nm $BaTiO_3$ ceramics, we compare its Raman spectra with those of 3 μm normal ceramics sintered by conventional method under variable temperatures. Fig. 2(a) shows the Raman spectra of 3 μm $BaTiO_3$ ceramics at temperatures ranging from −150 to 200 °C. The main spectral features for 3 μm $BaTiO_3$ ceramics are: (a) two intense broad bands at 526 cm^{-1} [A_1(TO)] and 245 cm^{-1} [A_1(TO)], (b) a broad and weak band at 715 cm^{-1} [A_1(LO)], (c) a sharp band at 309 cm^{-1} [B_1, E(TO + LO)], (d) two weak bands at 174 cm^{-1} [A_1(TO)] and 184 cm^{-1} [A_1(LO)], (e) a weak bands at 487 cm^{-1} [E(TO)] present only in rhombohedral and orthorhombic phases. With increasing temperature, a gradual softening of the main mode together with the peak broadening and the decrease of the intensity is observed. The clear changes attributed to the phase transitions, which are highly similar to those reported in the rhombohedral, orthorhombic, tetragonal and cubic phases of $BaTiO_3$ crystal [12,13].

The corresponding Raman spectra of 30 nm $BaTiO_3$ ceramics are shown in Fig. 2(b) at temperatures ranging from −190 to 200 °C. Compared with those of 3 μm $BaTiO_3$ ceramics, it shows that, on the one hand, the main

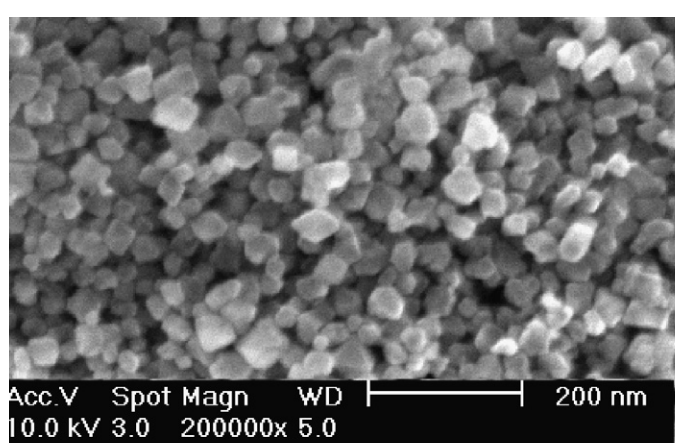

Fig. 1. SEM image of 30 nm $BaTiO_3$ ceramics sintered by the high pressure assisted method.

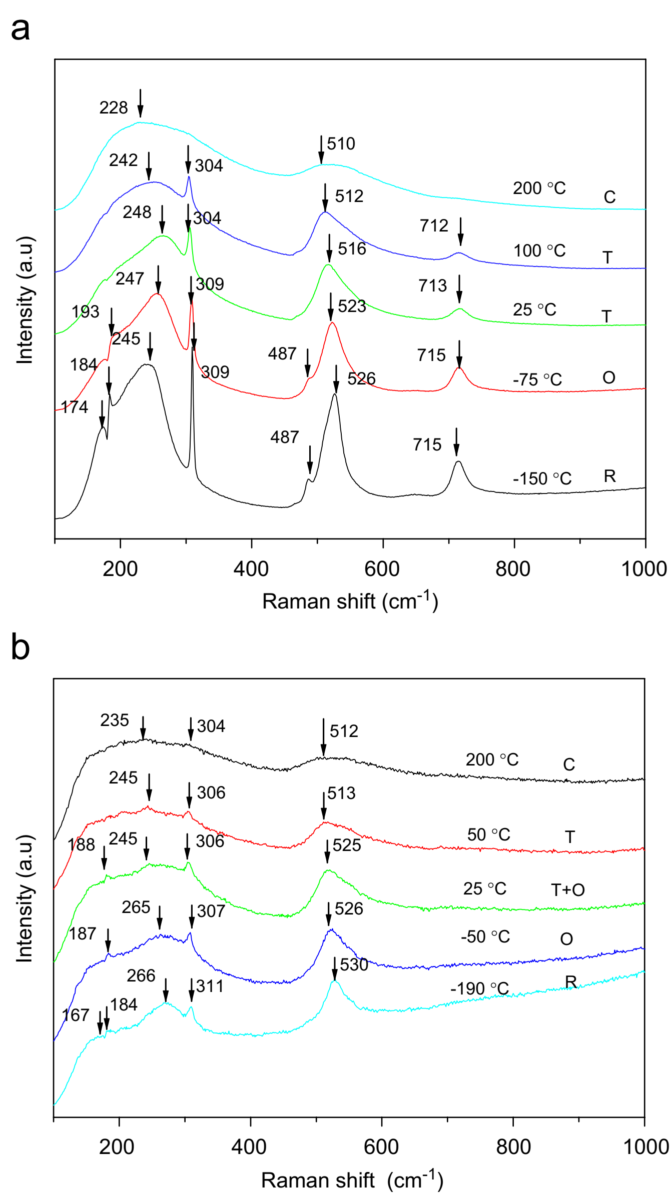

Fig. 2. Raman spectra of (a) 3 μm and (b) 30 nm $BaTiO_3$ ceramics at various temperatures. The different phases are marked as C, cubic; T, tetragonal; O, orthorhombic; and R, rhombohedral phase, respectively.

characteristics of the Raman activity are similar; on the other hand, due to the grain size decreasing, there are some differences: the intensity of Raman bands weakened, the line width broadened and the bands at near 487 and 715 cm^{-1} disappeared. Now we discuss a little detail the evolution of Raman spectra of 30 nm $BaTiO_3$ ceramics with increasing temperature. At −190 °C, except for the bands disappearing at 487 and 715 cm^{-1}, the Raman spectra features are similar to those of 3 μm $BaTiO_3$ ceramics at −150 °C. So it is concluded to be a rhombohedral phase. With increasing temperature from −190 to −50 °C, the band at 167 cm^{-1} disappeared and the band at 184 cm^{-1} shifted to 187 cm^{-1} which are similar to those of 3 μm $BaTiO_3$ ceramics from −150 to −75 °C. These changes are indicative of the rhombohedral-to-orthorhombic phase transition. When the sample was heated to 50 °C, the most noticeable change is that the band at 187 cm^{-1} disappeared, which indicates the orthorhombic-to-tetragonal phase transition occurred. At 25 °C, the frequencies of bands at 245 and 306 cm^{-1} are the same as those of at 50 °C and the band at 188 cm^{-1} still exists. So it is inferred that the orthorhombic and tetragonal phases coexist above room temperature. When further heated to 200 °C, the Raman features are two broader bands at 235 and 515 cm^{-1} which are of similar features to those of 3 μm $BaTiO_3$ ceramics, so the sample is a cubic phase. Moreover, a very weak band at 306 cm^{-1} still persisted, which disappeared in 3 μm $BaTiO_3$ ceramics. This is mainly due to the broken translation symmetry by the boundaries, defects or by possible short-range polar order regions existing in the cubic state [4,14]. From the Raman analysis, it is clear that the successive phase transitions occurred. Especially, the coexistence of ferroelectric tetragonal and orthorhombic phases was observed in 30 nm $BaTiO_3$ ceramics at room temperature.

The coexistence of tetragonal and orthorhombic phases at room temperature was also observed in fine-grained $BaTiO_3$ ceramics [4,5,15]. Using a modified Ginsburg–Landau–Devonshire thermodynamic theory, Lin et al. [16] described theoretically this phenomenon. The multiphase coexistence at room temperature can be explained by the following causes. During the ferroelectric transformation, the internal stress developed. In coarse-grained ceramics, the localized shear stress at the grain boundaries, which hindered the transformation, can be relieved by formation of 90° domains, while in dense nanocrystalline ceramics, the stress cannot be relieved owing to the absence of 90° domains [17,18]. Moreover, it seems that contribution of the shear stress may increase with decreasing grain size [16]. In order to minimize strain energy, twinning along {1 1 0} planes (90° twinning) took place in a constrained grain. Compared with the tetragonal structure, the orthorhombic unit cell, whose polar axis parallels to a face diagonal, i.e. (0 1 1) direction, was characterized by a shear deformation of the cubic perovskite cell. In terms of the stress-relieving twinning mechanisms, the orthorhombic structure can more efficiently minimize transformation stress, so its stability enhanced [3]. Therefore, the orthorhombic phase inclined to exist in $BaTiO_3$ together with the tetragonal phase upon reducing grain size at room temperature.

The Raman results revealed that the ferroelectric phases existed in 30 nm $BaTiO_3$ ceramics at room temperature, but it was not sufficient to prove the existence of ferroelectric behavior. In order to further investigate the ferroelectric characteristics, the polarization vs. applied electric field experiment was performed. Fig. 3 shows that there is a typical polarization hysteresis loop at room temperature at 1 kHz, which indicates that the ferroelectricity really retains in dense 30 nm $BaTiO_3$

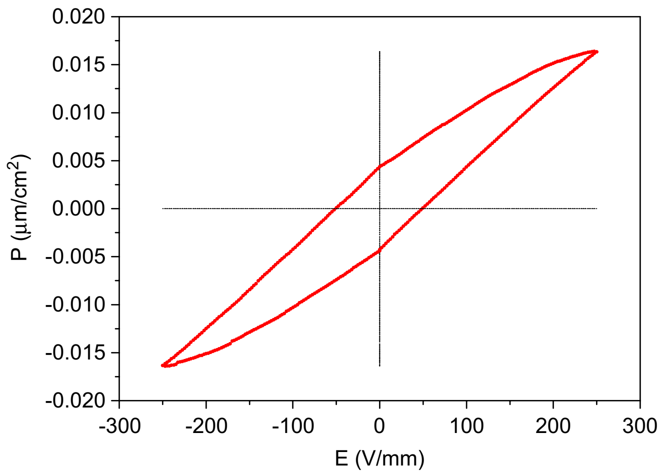

Fig. 3. Polarization vs. applied electric field hysteresis loop of 30 nm $BaTiO_3$ ceramics at 1 kHz at room temperature.

ceramics. The observed polarization value is remarkably lower than those reported for $BaTiO_3$ single crystal as a result of the reduced ferroelectric polarization related to the lower average tetragonality [4].

4. Conclusion

High pressure significantly increases the densification and dramatically suppresses the grain growth. Thus dense $BaTiO_3$ ceramics with uniform grain sizes of 30 nm can be fabricated by pressure assisted sintering. The successive phase transitions from rhombohedral to orthorhombic, orthorhombic to tetragonal, tetragonal to cubic occurred and with increasing temperature the coexistence of ferroelectric tetragonal and orthorhombic phases above room temperature was found in 30 nm $BaTiO_3$ ceramics. The ferroelectric behavior was further characterized by P–E hysteresis loop. The experimental results indicate the critical grain size of the disappearance for ferroelectricity is below 30 nm in nanocrystalline $BaTiO_3$ ceramics fabricated by pressure assisted sintering.

Acknowledgment

This work was supported by the Ministry of Sciences and Technology of China through research project (2002CB613301).

References

[1] K.-H. Helwege, A.M. Helwege (Eds.), Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Group III, vol. 16, Springer, New York, 1981, p. 67.

[2] W.L. Zhong, Y.G. Wang, P.L. Zhang, B.D. Qu, Phenomenological study of the size effect on the phase transitions in ferroelectric particles, Phys. Rev. B 50 (1994) 698–703.

[3] M.H. Frey, D.A. Payne, Grain-size effect on structure and phase transformations for barium titanate, Phys. Rev. B 54 (1996) 3158–3168.

[4] V. Buscaglia, M.T. Buscaglia, M. Viviani, T. Ostapchuk, I. Gregora, J. Petzelt, L. Mitoseriu, P. Nanni, A. Testino, R. Calderone, C. Harnagea, Z. Zhao, M. Nygren, Raman and AFM piezoresponse study of dense BaTiO3 nanocrystalline ceramics, J. Eur. Ceram. Soc. 25 (2005) 3059–3062.

[5] X.Y. Deng, X.H. Wang, H. Wen, A.G. Kang, Z.L. Gui, L.T. Li, Phase transitions in nanocrystalline barium titanate ceramics prepared by spark plasma sintering, J. Am. Ceram. Soc. 89 (2006) 1059–1064.

[6] L. Mitoseriu, C. Harnagea, P. Nanni, A. Testino, M.T. Buscaglia, V. Buscaglia, M. Viviani, Z. Zhao, M. Nygren, Local switching properties of dense nanocrystalline BaTiO3 ceramics, Appl. Phys. Lett. 84 (2004) 2418–2420.

[7] Z. Zhao, V. Buscaglia, M. Viviani, M.T. Buscaglia, L. Mitoseriu, A. Testino, M. Nygren, M. Johnsson, P. Nanni, Grain-size effects on the ferroelectric behavior of dense nanocrystalline $BaTiO_3$ ceramics, Phys. Rev. B 70 (2004) 024107-1–024107-8.

[8] S.-C. Liao, Y.-J. Chen, B.H. Kear, W.E. Mayo, High pressure/low temperature sintering of nanocrystalline alumina, Nanostruct. Mater. 10 (1998) 1063–1079.

[9] D. Fu, H. Suzuki, K. Ishikawa, Size-induced phase transition in $PbTiO_3$ nanocrystals: Raman scattering study, Phys. Rev. B 62 (2000) 3125–3129.

[10] Y.L. Du, M.S. Zhang, Q. Chen, Z. Yin, Investigation of size-driven phase transition in bismuth titanate nanocrystals by Raman spectroscopy, Appl. Phys. A 76 (2003) 1099–1103.

[11] B.R. Li, X.H. Wang, L.T. Li, Synthesis and sintering behavior of $BaTiO_3$ prepared by different chemical methods, Mater. Chem. Phys. 78 (2002) 292–298.

[12] C.H. Perry, D.B. Hall, Temperature dependence of the Raman spectrum of $BaTiO_3$, Phys. Rev. Lett. 15 (1965) 700–702.

[13] U.D. Venkateswaran, V.M. Naik, R. Naik, High-pressure Raman studies of polycrystalline $BaTiO_3$, Phys. Rev. B 58 (1998) 14256–14260.

[14] Z.G. Ye, Relaxor ferroelectric complex perovskites: structure, properties and phase transitions, Key Eng. Mater. 155–156 (1998) 81–122.

[15] G. Arlt, D. Hennings, G.D. With, Dielectric properties of fine-grained barium titanate ceramics, J. Appl. Phys. 58 (1985) 1619–1625.

[16] S. Lin, T.Q. Lü, C.Q. Jin, X.H. Wang, Size effect on the dielectric properties of $BaTiO_3$ nano ceramics, Phys. Rev. B 74 (2006) 134115–1341110.

[17] G. Arlt, The influence of microstructure on the properties of ferroelectric ceramics, Ferroelectrics 104 (1990) 217–227.

[18] K. Kyoichi, A. Yamaji, Grain-size effects on dielectric properties in barium titanate, J. Appl. Phys. 47 (1976) 371–373.