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# The fabrication of nanocrystalline BaTiO<sub>3</sub> ceramics under high temperature and high pressure

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## ARTICLE INFO

### Article history:

Received 27 August 2007

Received in revised form

14 April 2008

Accepted 26 April 2008

### Keywords:

High pressure

Nanocrystalline ceramics

Agglomerates

Three-step method

## ABSTRACT

The high temperature and high pressure sintering method was adopted to fabricate dense nanocrystalline BaTiO<sub>3</sub> ceramics. In the direct procedure sintering, there existed many “beams” in nanocrystalline BaTiO<sub>3</sub> ceramics. The microstructure and chemical composition of the “beam” has been investigated by scanning electron microscope, transmission electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction. The results indicated that the “beams” in nanocrystalline ceramics were caused by nano powders agglomerating. Using the three-step method sintering, i.e., two times cold pressing, and following by the high pressure and high temperature sintering, all the “beams” disappeared. Moreover, the dense BaTiO<sub>3</sub> ceramics with uniform grain sizes were obtained.

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## 1. Introduction

BaTiO<sub>3</sub> is one of the most widely used ferroelectric materials and has been extensively studied. It is well known that the crystal structures (Deng et al., 2006; Frey and Payne, 1996) and dielectric properties (Zhao et al., 2004) of BaTiO<sub>3</sub> ceramics strongly depend on the grain size. When particle size is reduced to the nanoscale, one will find some unusual physical properties and even the disappearance of ferroelectricity as compared with those of conventional polycrystalline. Recently, Gleiter (1992) and Liao et al. (1998) have widely investigated the sintering behaviors of nano powders. As is known to all, the nano powders have extremely large specific area and strongly tend to be agglomerated either during synthesis or during post-processing, especially, severely agglomerated nano powders caused great difficulties in preparing dense ceramics (Dynys and Halloran, 1984; Ferkel and Hellmig, 1999).

In addition, sintering of nano powders using the conventional method produced exaggerated grain growth, thus losing the advantages of the nanoscale grain size. In recent years, some special sintering methods, such as SPS (Deng et al., 2006; Roberta et al., 2007; Zhao et al., 2004), the doped methods (Brzozowski and Castro, 2005; Hreniak et al., 2006) and the two-step sintering (Wang et al., 2006) and the selective laser sintering (Majewski et al., 2008), were adopted to prepare the nanocrystalline BaTiO<sub>3</sub> ceramics. However, there are few reports on the details of agglomerates during the sintering course of nanocrystalline ceramics.

High pressure could significantly increase the densification. Moreover, the nucleation rate increased due to reducing the energy barrier for nucleation during high pressure sintering. Besides, due to the decreasing porosity in specimens by high pressure, the sintering activity significantly increased and therefore, it could obtain the dense ceramics (Liao et al.,

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1998). So the high-pressure-assisted sintering is expected to be an ideal approach to fabricate dense ceramics with ultra fine grain size.

In this paper, the high pressure (6 GPa) and high temperature (1000 °C) sintering method was used to fabricate dense nanocrystalline BaTiO<sub>3</sub> ceramics. The “beams” in nanocrystalline ceramics prepared by the direct procedure were investigated using different techniques. In order to eliminate the “beams”, an effective three-step high pressure sintering method was adopted.

## 2. Experimental procedure

The nano BaTiO<sub>3</sub> powders were synthesized by chemical processing (Li et al., 2002). In order to fabricate nanocrystalline BaTiO<sub>3</sub> ceramics, a straightforward high temperature and high pressure sintering method which was called the direct procedure sintering was adopted. The nano powders were uniaxially pressed into the pellets under 7 MPa at room temperature. No binder was added. The pellets with the dimension of 6 mm in diameter and 2 mm in thickness were wrapped

by Ag foils to prevent from contamination. The pellets were inserted into BN spacer tubes that were in turn put into graphite heaters, respectively. The high pressure sintering was performed using a cubic anvil type apparatus. The pyrophyllites were used as the pressure-transmitting mediums. The samples were first pressurized up to 6 GPa and then heated at 1000 °C for 5 min in air. After temperature quenching, the samples were removed by releasing the pressure slowly to one atmospheric pressure.

The microstructures of sintered samples were observed by scanning electron microscope, and there existed many “beams” in nanocrystalline BaTiO<sub>3</sub> ceramics. In order to eliminate the “beams”, a three-step high pressure sintering method was used to prepare the samples. The first step that the nano powders were pressed into the pellets was identical with that of the aforementioned direct procedure. In the second step, the pellets were cold-isostatic pressed at a pressure of 3 GPa for 10 min, then they were unloaded and ground into powders in mortars. The processed powders were repressed alike that of the first step. The process needed to be repeated several times, which is effective to prepare the nanocrystalline ceramics in the following high pressure sintering. Finally, the

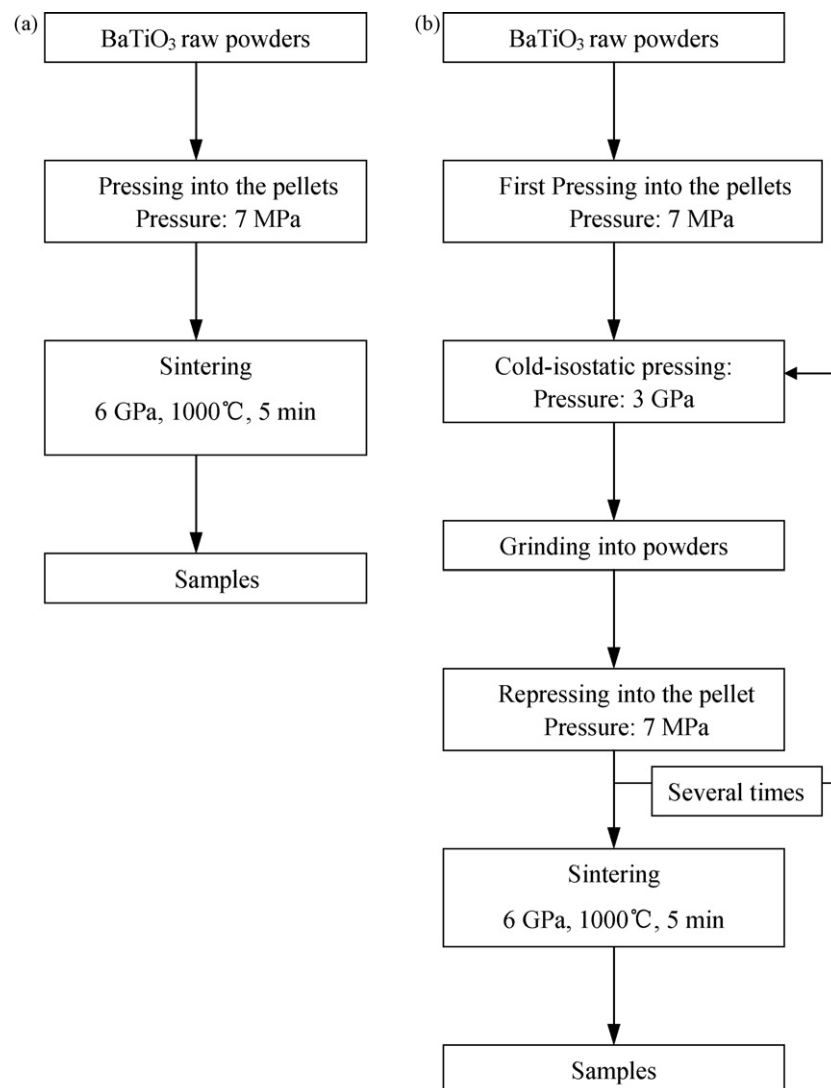


Fig. 1 – The schematic routes of high pressure sintering methods. (a) direct procedure, (b) three-step method.

pellets were sintered according to the same process as that of the direct procedure. The schematic routes of two kinds of sintering methods are shown in Fig. 1: (a) direct procedure sintering, (b) three-step method sintering.

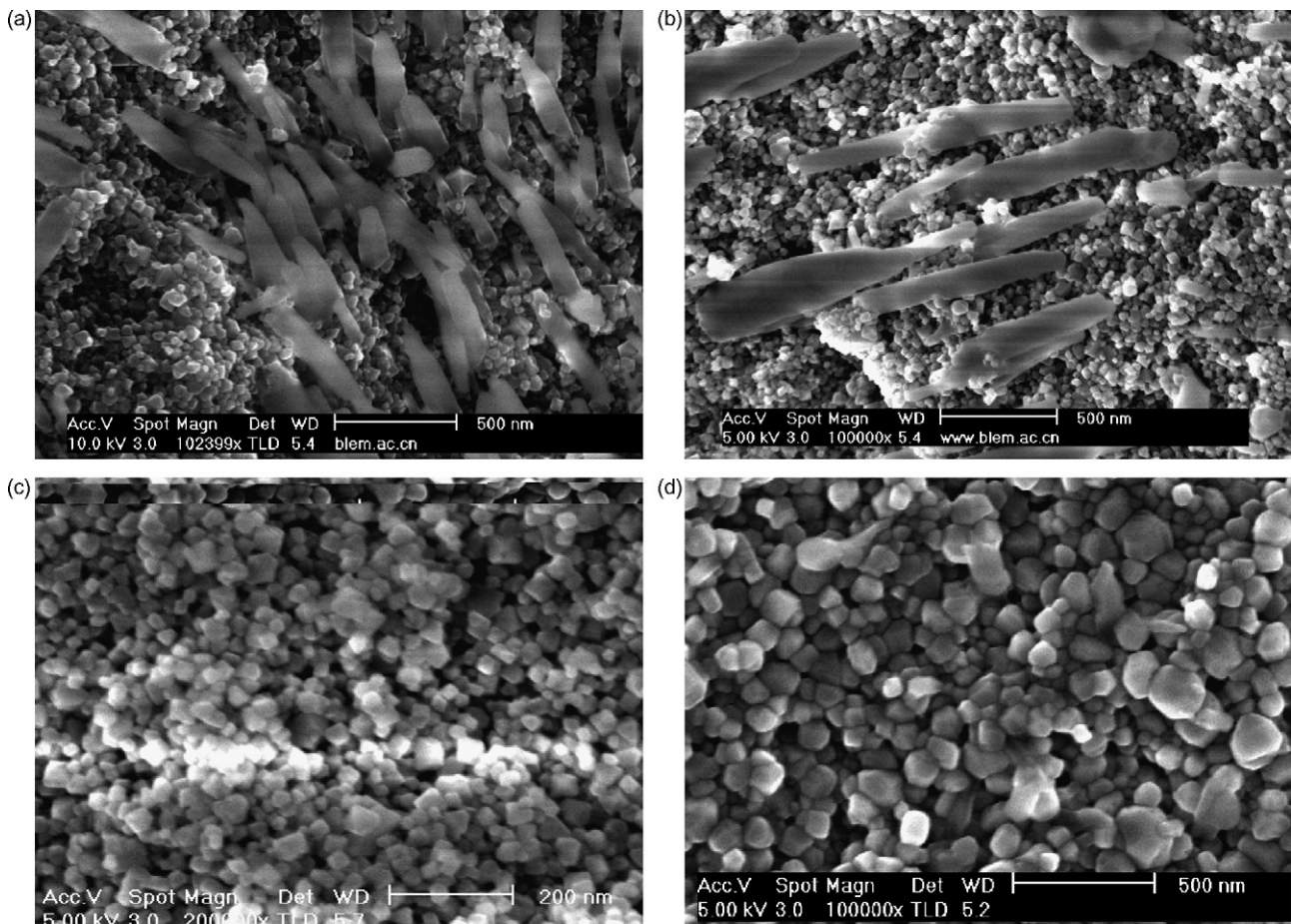
A field emission scanning electron microscope (SEM, XL30-FEG) was used to determine the particle sizes (using the linear intercept method) and the microstructures of fracture surfaces on sintered samples. Transmission electron microscopy (TEM, TECNAI F20) and the attached energy dispersive X-ray spectroscopy (EDX) were used to determine the chemical composition. The crystal structures and the grain sizes were measured by X-ray diffraction (XRD, Rigaku D/max-2500, Cu  $K\alpha$  radiation). Densities of sintered samples were measured by Archimedes' method. A value of  $6.02 \text{ g/cm}^3$  was used as the theoretical density.

### 3. Results and discussions

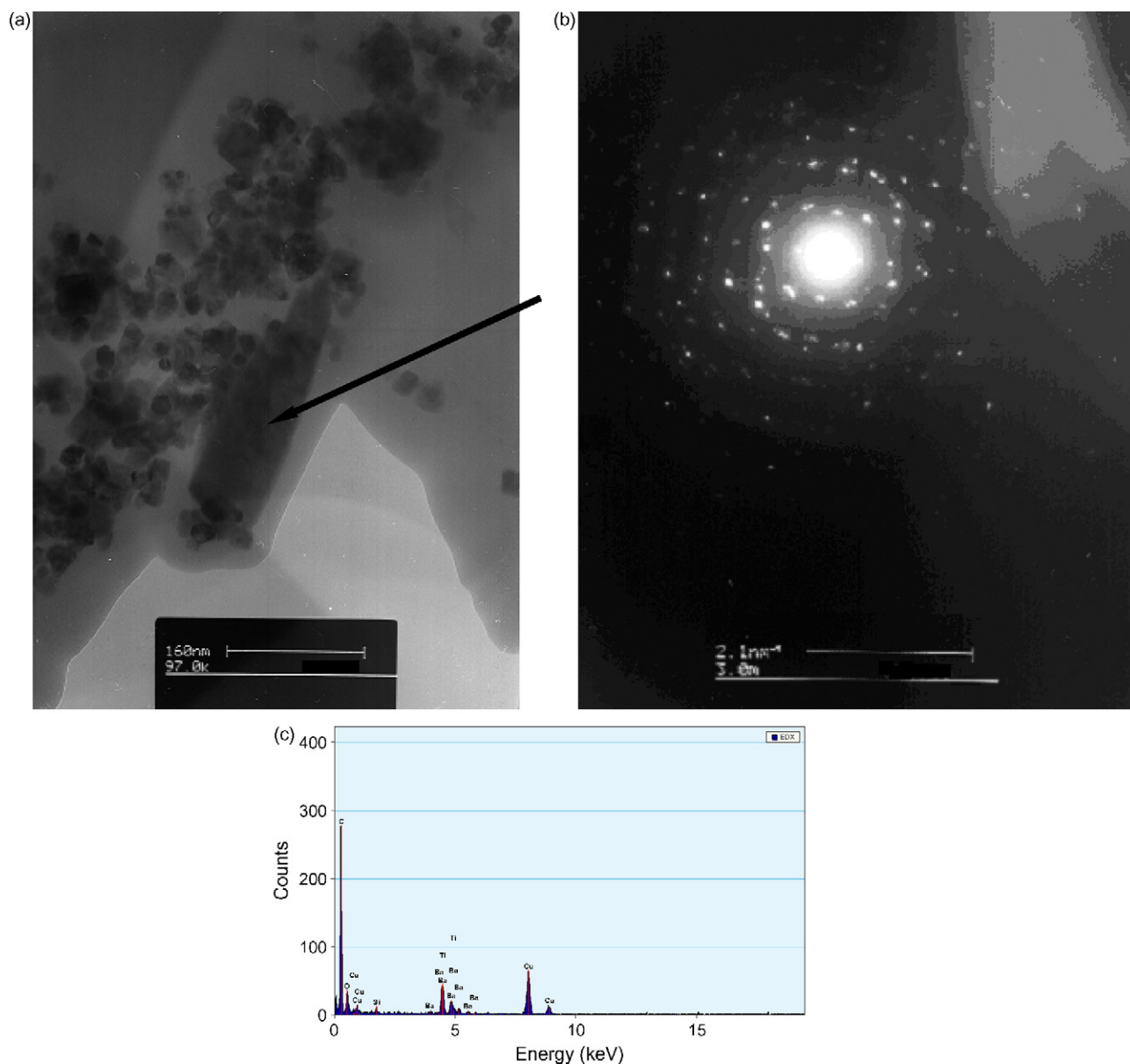
The SEM image of the sintered sample whose raw powders is 10 nm, fabricated by the direct procedure sintering, is shown in Fig. 2(a). It can be seen that the grain sizes (estimated by the intercept line method) is about 30 nm, but there exist many "beams" in sintered samples. The dimensions of the "beams" are about 250–400 nm in length and 60–120 nm in

diameter, which are far larger than that of the grains. The average densities of sintered samples are 94.5%. In order to verify the phenomenon, the same sintering produces were adopted to fabricate  $\text{BaTiO}_3$  ceramics with raw nano  $\text{BaTiO}_3$  powders, there also exist many "beams" in sintered nanocrystalline samples. For example, the SEM image of 60 nm  $\text{BaTiO}_3$  ceramics whose raw powder is 50 nm is shown in Fig. 2(b). The dimensions of the "beams" are 600–1000 nm in length and 120–400 nm in diameter.

In order to investigate the structure and chemical composition of the "beam" in 30 nm  $\text{BaTiO}_3$  ceramics, the TEM image of the "beam" is taken as shown in Fig. 3(a). There exist some agglomerates besides the "beam" in 30 nm  $\text{BaTiO}_3$  ceramics. The electron diffraction image of the "beam" is shown in Fig. 3(b). From the image, it can be seen that the structure of "beam" is crystal. EDX of "beam" is also shown in Fig. 3(c) and the result indicates that the "beam" is composed of Ba, Ti and O (the element of Cu is from the copper grid used in the TEM experiment and the elements of C and Si are from the chemisorbed  $\text{CO}_2$  and other impurities). We also tried to investigate whether the "beams" are of preferred orientation of crystal texture. XRD patterns of raw powders and  $\text{BaTiO}_3$  ceramics sintered by direct produce are shown in Fig. 4: (a) 30 nm ceramics powders, (b) 30 nm ceramics bulk. From the XRD patterns, one can see that the patterns are sim-



**Fig. 2 – The SEM images of nanocrystalline  $\text{BaTiO}_3$  ceramics. (a) 30 nm ceramics prepared by the direct procedure sintering; (b) 60 nm ceramics prepared by the direct procedure sintering; (c) 30 nm ceramics prepared by three-step method sintering; (d) 60 nm ceramics prepared by three-step method sintering.**

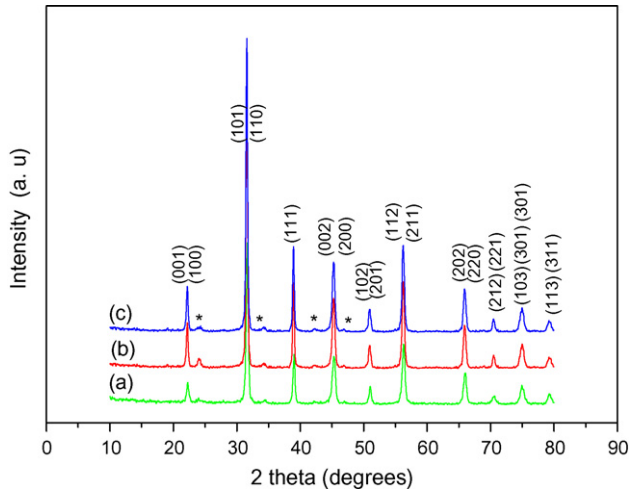


**Fig. 3 – The structure analysis of the “beam” in 30 nm BaTiO<sub>3</sub> ceramics. (a) Bright-field TEM image, the area by the arrow pointed to is the “beam”; (b) electron diffraction image of the “beam”; (c) EDX image of the “beam”.**

ilar to each other. The result reveals no preferred orientation in 30 nm BaTiO<sub>3</sub> ceramics. So the “beams” are not caused by the preferred orientation.

In order to eliminate the “beams” in nanocrystalline BaTiO<sub>3</sub> ceramics, various methods were tried. It was interesting that the “beams” in nanocrystalline BaTiO<sub>3</sub> ceramics could be eliminated when the samples were prepared using the three-step method sintering. SEM images of BaTiO<sub>3</sub> ceramics sintered by the three-step method are shown in Fig. 2(c and d). Clearly, the samples exhibit homogeneous grain size distributions and the grain sizes are about 30 and 60 nm, respectively. Using the Scherrer equation (Cullity, 1978), the average grain sizes are calculated to be 28 and 63 nm from the broadening (111) peak. The densities of 30 and 60 nm BaTiO<sub>3</sub> ceramics are about 96.1% and 97.2%, respectively. Moreover, the “beams”

in nanocrystalline BaTiO<sub>3</sub> ceramics disappeared. XRD pattern of 30 nm ceramics sintered by the three-step method is shown in Fig. 4(c). It can be seen that the pattern is also similar to that of 30 nm ceramics sintered by the direct produce, indicating there are no difference in crystal structures. The crystal structure of 30 nm BaTiO<sub>3</sub> ceramics was further refined by the Rietveld analysis of the X-ray diffraction data, a pseudo-Voigt function was chosen as a profile function among profile ones. The XRD data were measured by scanning at intervals of 0.01° in the 2θ range from 10° to 140° with graphite monochromator on a Rigaku D/max-2500 diffractometry at room temperature. A multiphase coexistence of tetragonal and orthorhombic phases was obtained in 30 nm BaTiO<sub>3</sub> ceramics at room temperature. The detailed process was shown by Xiao et al. (2008). From the above analysis, we



**Fig. 4 – XRD patterns of raw powders and sintered samples: (a) 30 nm ceramics powders (prepared by the direct procedure sintering), (b) 30 nm ceramics bulk (prepared by the direct procedure sintering), (c) 30 nm ceramics powders (prepared by the three-step method sintering). Asterisk denotes peaks assigned to  $\text{BaCO}_3$ .**

suggest that the “beams” in nanocrystalline  $\text{BaTiO}_3$  ceramics are caused by the nano powder agglomerates during the high temperature and high pressure sintering.

It is well known that the nano powders have extremely large specific area and strongly tend to be agglomerated. The bonding between the particles of these agglomerates is expected to be much stronger than the bonding between particles that are only attracted by van-der-Waals interaction. Though it is easy to break down soft agglomerates, collapsing hard agglomerates need larger forces. Before sliding these particles in strong agglomerates, the particles have to experience large shearing forces necessary for neck cleavage. If agglomerates were not broken down before sintering, these agglomerates would lead to preferential and exaggerated growth owing to stronger bonding, thus producing many “beams” in nanocrystalline ceramics. By the aid of the cold-isostatic pressing, the ultrahigh pressure brings larger shearing forces on the nanoparticles, so the plastic deformation happens to break down the agglomerates. In addition, the ultrahigh pressure would rearrange the particles to form the close packing structure (Cho et al., 1998). Thus, using an effective three-step method sintering, the “beams” disappeared and the dense nanocrystalline  $\text{BaTiO}_3$  ceramics were obtained.

#### 4. Conclusion

The high pressure sintering process has been proved to be very useful to control the grain sizes growth during nanocrystalline  $\text{BaTiO}_3$  ceramics sintering. Fabricating by the direct procedure, there exist many “beams” in nanocrystalline  $\text{BaTiO}_3$  ceramics. The “beams” were investigated by SEM, TEM, EDX and XRD techniques, the results showed that the “beams” are caused by the agglomerates in nano powders. Fabricating by the three-step method, the agglomerates in

nano powders were broken down before high pressure sintering, the “beams” disappeared and dense nanocrystalline  $\text{BaTiO}_3$  ceramics with uniform grain sizes of 30 nm was obtained.

#### 5. Acknowledgment

This work was supported by the Ministry of Sciences and Technology of China through 973 project (2002CB613301).

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