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Role of the Grain Boundaries on the Electrical Transport Behavior of Nanocrystalline $BaTiO_3$ under High Pressure①

SANG Dan-dan　WANG Qing-lin　ZHANG Bing-yuan
WANG Wen-jun　HU Hai-quan

(School of Physical Science & Information Technology, Shandong Key Laboratory of Optical Communication Science and Technology, Liaocheng University, Liaocheng 252059, China)

Abstract　Using a diamond anvil cell, the variable-frequency alternating current impedance spectroscopy of nanocrystalline $BaTiO_3$ has been measured under high pressure up to 35 GPa. The grain and grain boundaries contribution to the total electrical transport properties are extracted. The grain boundaries show a major contribution to the total electrical transport properties in the high-pressure phases. The difference of the grain boundaries resistance magnitude among three phases results from the phase transitions that leading to the rearrangement of grain boundaries microstructure.

Key words　high-pressure; nanocrystalline $BaTiO_3$; grain boundary; impedance
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1　Introduction

As an important ferroelectric material, $BaTiO_3$ (BTO) has been extensively investigated for more than half a century and used in a variety of electronic applications, such as multilayer ceramic capacitors, positive-temperature-coefficient resistors, and transducers[1,2]. With the demand of higher integration and miniaturization in microelectronic devices, the grain size required for the BTO ceramic is down to the order of submicrons, sometimes even nanometers. A strong size effect begins to appear at such small scale that affects the physical properties of the material such as the structure, ferroelectricity and phase transition. Size effect has become one of the most important topics in physics and materials science communities.

Compared to bulk samples, nanocrystalline materials have large surface to volume ratios and fewer

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通讯作者:王庆林,男,汉族,博士,讲师,研究方向:高压下凝聚态物质的结构与电输运性质,E-mail:wangqinglin@lcu. edu. cn.

dislocations. There is lattice relaxation at grain boundaries which has a significant impact on the physical and electronic properties of the material[3]. It is therefore worthwhile exploring how the grain boundaries particularly influence the electrical transport behavior of the material under high pressure. The studies of the phase stability of nanocrystalline BTO under high pressure have attracted considerable attention in recent years. The dielectric studies of BTO by Zhu et al. showed that at room temperature the transition from the tetragonal ferroelectric phase to the cubic paraelectric should be observed at about 2.6 GPa and 2.5 GPa for bulk and 60 nm crystallites, respectively[4]. However, using high pressure X-ray powder diffraction method, Kumar et al. demonstrated that when the crystallite size decreases to 40 nm, the transition pressure increases to 4.1 GPa and the cubic phase is stable up to 52 GPa for the 40 nm crystallites and at least to 36 GPa for bulk BTO[5]. When the crystallite size further decreases to 20 nm, the tetragonal phase does not transform to the cubic phase but to the orthorhombic phase at 10.9 GPa and then to a new phase at about 19.8 GPa[6]. Li et al. have studied different particles sizes of nano-BTO ranging from 10-200 nm with energy dispersive X-ray diffraction technique at ambient temperature and reported an increase in the phase transition pressure with decrease in grain size[7]. Han et al. studied the temperature and pressure structural stability of 5 nm BTO particles and found two phase transitions at 7.5 and 17.3 GPa, respectively[8]. Zhang et al. reported a morphology-tuned structural phase transition under high pressure in the horseshoe shaped BTO nanomaterials with an average diameter of 26 ± 4 nm, and found a phase transition from the tetragonal to the cubic phase at about 7.7 GPa[9].

As mentioned above, the phase transition behaviors of nanocrystalline BTO and related mechanisms have been gradually clarified under high pressure. However, the effect of grain boundaries on the electrical transport properties of nanocrystalline BTO was scarcely tackled and this lack motivated the present work: using the variable-frequency ac impedance spectroscopy in a diamond anvil cell (DAC), we have undertaken experiments on nanocrystalline BTO under high pressure, aiming at disclosing the grain boundary role in the total impedance, the conduction mechanism involved in the electrical transport at the grain boundaries.

2 Experimental

A DAC was utilized to generate high pressure, and the anvil culet was 300 μm in diameter. Preindented T301 stainless steel was used as the gasket, and a ruby with a size of 5 μm was placed in the center of the sample chamber as the pressure calibrator. Two-electrode configuration was used for in situ electrical impedance spectroscopy measurement on DAC under high pressure. The manufacturing process of the microcircuit was similar to that described in previous works[10,11]. Solartron 1260 impedance analyzer equipped with Solatron 1296 dielectric interface was used to measure the impedance spectroscopy. A 0.1 V sine signal was input into the sample and its frequency ranged from 0.1 Hz to 1 MHz. Indoor conditions were controlled and maintained stable during all the measurements. The sample studied here was brought from Aladdin Co. with a purity of 99.9%.

3 Results and discussions

Fig. 1 shows the impedance spectra (Nyquist plot) of nanocrystalline BTO at different pressures. At low pressure region, the impedance spectra are composed of a well-defined semicircle at high frequency region and a straight line at low frequency region as shown in Fig. 1(a)-(d). The semicircle in the high frequency region represents the charge carrier transportation in the bulk; the straight line in the low frequency region is due to the space charge depletion at grain boundaries[12]. In the moderate pressure region (14.5 GPa-24.2 GPa, Fig. 1(e) and 1(f)), the semicircle disappears indicating that the grain boundaries resistance play a primary role in the total BTO impedance. When the pressure went up to 25.7 GPa, as shown in Fig. 1(g) and 1(h), the impedance spectrum shows an oblatelike arc and the size of the arc decreased with pressure increasing. We attribute the electrical conduction at this pressure range to the grain boundaries contribution. We shall come back to this point later.

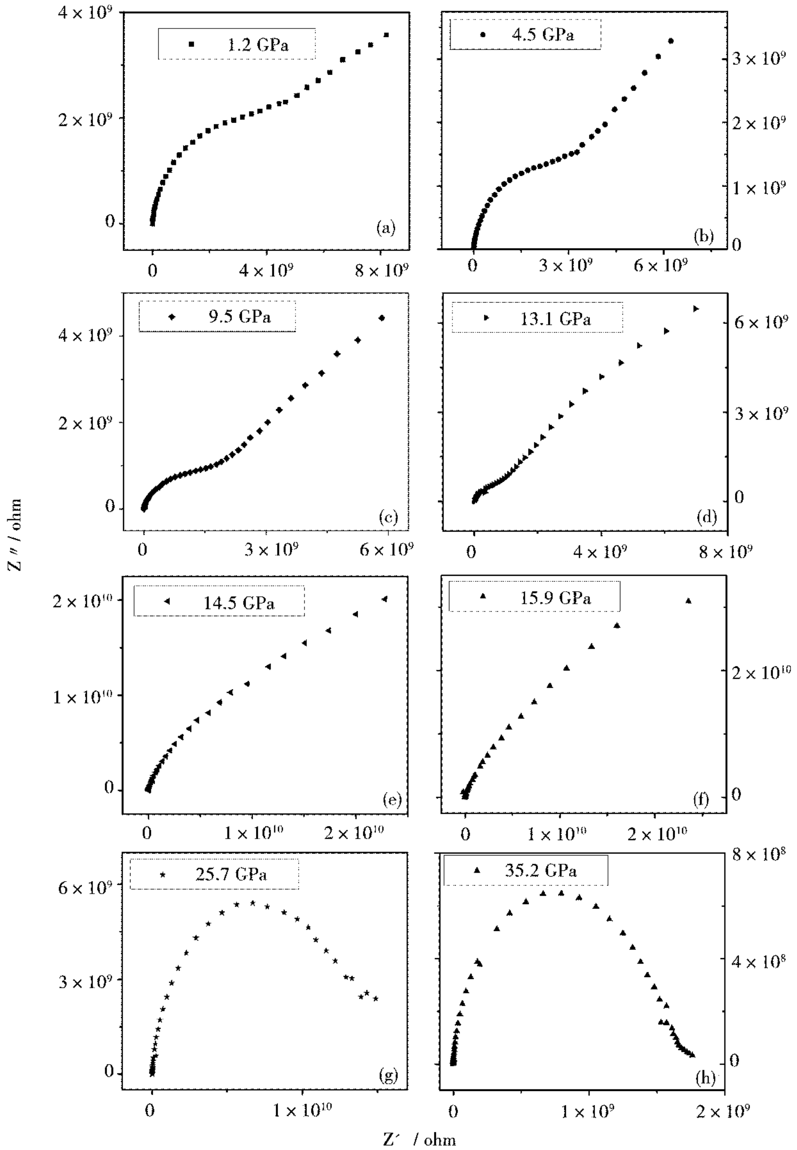

Fig. 1 Impedance of nanocrystalline $BaTiO_3$ at different pressures

According to the report of Abrantes et al. ,[13] we replotted the impedance spectra into a Z'-(Z''/f) representations, as shown in Fig. 2. From the report of Abrantes et al. , we know that, in low frequency region ($f \ll f_{gb}$)

$$Z' \approx R_b + R_{gb} + (Z''/f) f_{el} , \tag{1}$$

where b and gb represent the bulk and grain boundary, respectively, f_{el} is the electrode relaxation frequency. In the moderate frequency region, $f_{gb} \ll f \ll f_b$, we have

$$Z' \approx R_b + (Z''/f) f_{gb} . \tag{2}$$

From Eqs. (1) and (2) we obtained the bulk resistance and grain boundary resistance under high pressure, as shown in Fig. 3, and three distinct segments can be observed as marked I, II, and III. In segment (I), the bulk resistance decreased with increasing pressure but the grain boundary resistance increased with pressure increasing which can be explained as follows: because of its small size and large specific surface area for nanoparticles, the surface atoms make a large proportion in the total number of atoms. The unsaturated coordinated surface atoms leave the original equilibrium position, resulting in the number of unsaturated coordinated surface atoms and the surface energy increased and leading to the ability of capturing carriers enhancing and the number of carriers that crossing the interface decreasing. As a consequence, the grain boundary resistance increased with pressure increasing.

In segment (Ⅱ), the grain boundaries show a major contribution to the total conduction. The value of grain boundaries resistance increased by one order of magnitude compared with in segment (Ⅰ) and decreased with pressure increasing. According to the high-pressure Raman study of 20 nm nanocrystalline BTO, there is a phase transition from tetragonal phase to orthorhombic phase at 10.9 GPa[6]. Li et al. have studied different particles sizes of nanocrystalline BTO ranging from 10-200 nm with energy dispersive X-ray diffraction technique at ambient temperature and reported an increase in the phase transition pressure with decrease in grain size[7]. We hereby speculate that a structural phase transition happened at 14.5 GPa. The phase transition will generate new grain boundaries structure and that is the reason why the grain boundaries resistance become larger. In this segment, the resistance of the material comes mainly from the contribution of the grain boundaries, the grains become high-conductivity phase and yield a large amount of carriers, resulting in the saturation of carrier capturing by grain boundaries. Therefore, the grain boundaries resistance decreased with pressure increasing.

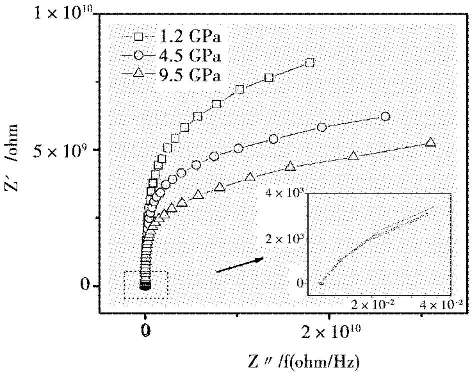

Fig. 2　**Z'-Z''/f plots of nanocrystalline BTO under high pressure. Inset: the enlargement of the left arc**

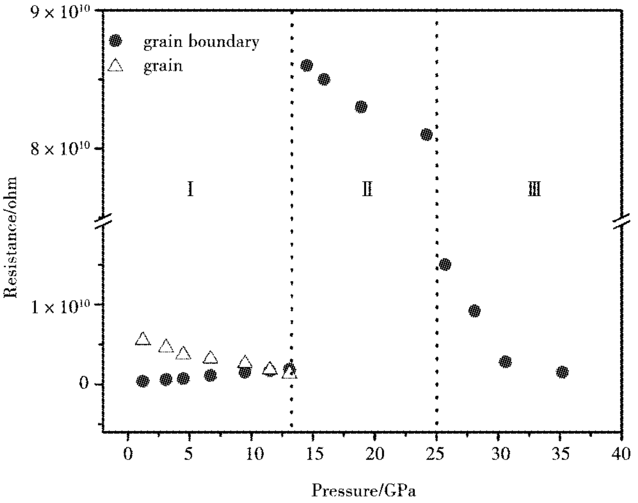

Fig. 3　**Pressure dependence of R_b and R_{gb} of nanocrystalline BTO**

As mentioned above, in segment (Ⅲ), we attribute the electrical conduction to the grain boundaries contribution. According to the formula $M^* = j\omega C_0 Z^*$[14] (where ω is the angular frequency $2\pi f$, C_0 is the vacuum capacitance of the measuring cell and electrodes with an air gap in place of the sample, $C_0 = \varepsilon_0 A/d$, where ε_0 is the vacuum permittivity, A is the area and d is the thickness of the sample), the impedance data can be analyzed much better by re-plotting them in the modulus formalism, as shown in Fig. 4(a). It shows two semicircular arcs with very small semi-circle at high frequency and large semi-circular arc in the low frequency region, which represent the grain and grain boundaries contribution, respectively. A direct comparison of Z'' and M'' spectroscopic plots (Fig. 4(b)) shows two peaks in M'' (the one at high frequency is not obvious), whereas in Z'' only one, corresponding to the lower frequency of the two M'' peaks, appears. This is because the impedance plots give most emphasis to those elements in the corresponding equivalent circuit with the largest resistance, whereas modules plots highlight those with the smallest capacitances[15]. Furthermore, the modulus spectrum shows a change in the shape with rise in pressure suggesting a probable change in the capacitance value of the material as a function of pressure. It is worthwhile to note that the grain boundaries resistance in this segment is lower than in segment (Ⅱ) by about one order of magnitude, which may be resulted from another phase transition leading to new grain boundaries structure appeared. The result is in consistent with Ref[5]. that there is a phase transition from orthorhombic phase to a new phase at about 19.8 GPa. The transition pressure in this work (25.7 GPa) is higher which can be caused by size effect.

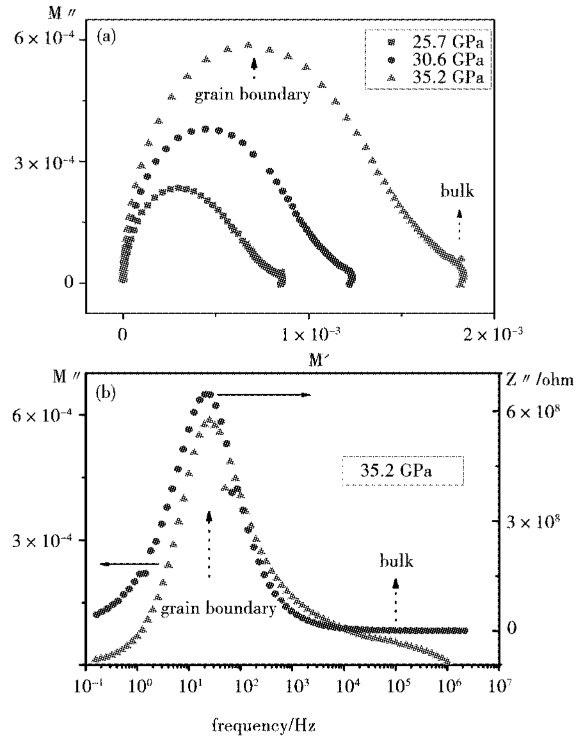

Fig. 4 Complex modulus plot (M'' vs. M') at different pressures and variation of M'' and Z'' with frequency at 35.2 GPa

4 Conclusions

In summary, we have conducted in-situ impedance measurements on nanocrystalline BTO under high pressure. The grain boundary effect was investigated for each phase. In segment (Ⅰ), the bulk resistance decreased with increasing pressure but the grain boundary resistance increased with pressure increasing due to the decreased number of carriers that crossing the interface. In segment (Ⅱ), the grain boundaries show a major contribution to the total conduction. The grain boundaries resistance in segment (Ⅲ) is lower than in segment (Ⅱ) by about one order of magnitude, which may be resulted from structural phase transition leading to rearrangement of grain boundaries microstructure. The study could shed light on the grain boundary design and control in nano ceramics.

References

[1] Dawber M, Rabe K M, Scott J F. Physics of thin-film ferroelectric oxides[J]. Rev Mod Phys, 2005, 77(4): 1083-1130.

[2] Haertling G H. Ferroelectric ceramics: history and technology[J]. J Am Ceram Soc, 1999, 82(4): 797-818.

[3] Wang Z W, Saxena S K, Pischedda V, et al. X-ray diffraction study on pressure-induced phase transformations in nanocrystalline anatase/rutile (TiO$_2$)[J]. J Phys Condens Mat, 2001, 13: 8317-8323.

[4] Zhu J L, Jin C Q, Cao W W, et al. Phase transition and dielectric properties of nanograin BaTiO$_3$ ceramic under high pressure[J]. Appl Phys Lett, 2008, 92: 242901.

[5] Kumar R S, Cornelius A L, Nicol M F. Equation of state of nanocrystalline BaTiO$_3$ up to 52 GPa at room temperature[J]. Phys Status Solidi B, 2007, 244: 290-296.

[6] Zhang W W, Chen L C, Jin C Q, et al. High pressure Raman studies of dense nanocrystalline BaTiO$_3$ ceramic[J]. J Electroceram, 2008, 21: 859-865.

[7] Li F Y, Jin CQ, You S J, et al. Pressure-induced phase transition in BaTiO$_3$ nanocrystals[J]. Chin Phys Lett, 2006, 23: 1249-1256.

[8] Han W, Zhu J L, Zhang S J, et al. Phase transitions in nanoparticles of BaTiO$_3$ as functions of temperature and pressure[J]. J Appl Phys, 2013, 113: 193513.

[9] Zhang H F, Cheng B Y, Li Q J, et al. Morphology-tuned phase transitions of horseshoe shaped BaTiO$_3$ nanomaterials under high pressure[J]. J Phys Chem C, 2018, 122(9): 5188.

[10] Wang Q L,Sang D D,Jiao H,et al. Ionic transport and dielectric properties in $NaNbO_3$ under high pressure[J]. Appl Phys Lett,2017,111:152903.

[11] Wang Q L,Liu C L,Gao Y,et al. Mixed conduction and grain boundary effect in lithium niobate under high pressure[J]. Appl Phys Lett,2015,106:132902.

[12] Tuller H L. Ionic conduction in nanocrystalline materials[J]. Solid State Ionics,2000,131:143-150.

[13] Abrantes J C C,Labrincha J A,Frade J R. An alternative representation of impedance spectra of ceramics[J]. Mater Res Bull,2000,35:727-735.

[14] Sinclair D C,West A R. Impedance and modulus spectroscopy of semiconducting $BaTiO_3$ showing positive temperature coefficient of resistance[J]. J Appl Phys,1989,66:3850-3856.

[15] Qin T R,Wang Q L,Yue D H,et al. High-pressure dielectric behavior of polycrystalline CaMoO4: The role of grain boundaries[J]. J Alloys Compd,2018,730:1-7.

高压下晶界对 $BaTiO_3$ 纳米晶电输运行为的影响

桑丹丹　王庆林　张丙元　王文军　胡海泉

（聊城大学 物理科学与信息工程学院、山东省光通信科学与技术重点实验室，山东 聊城 252059）

摘　要　利用金刚石对顶砧装置，测量了 $BaTiO_3$ 纳米晶高压下（最高压力达 35GPa）的交流阻抗谱. 给出了晶粒和晶界各自对电输运性质的贡献. 在高压相，晶界对总的电输运性质起主导作用. 三个结构相晶界电阻的差异源于结构相变引起的晶界微结构重组.

关键词　高压；$BaTiO_3$ 纳米晶；晶界；阻抗

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The new Criteria for Determining Nonsingular *H*-tensors

ZHANG Yun-cui[1]　WANG Ming-hui[1]　WANG Guang-bin[2]

(1. School of Mathematical Sciences,Qingdao University of Science and Technology,Qingdao 266100,China;2. School of Science and Information Science,Qingdao Agricultural University,Qingdao 266109,China)

Abstract　*H*-tensor is a newly developed concept in tensor analysis,and it is also an extension of *M*-tensor. In recent years,*H*-tensor has applied many aspects of mathematics and physics. The definitions、theorems and inferences used in this paper are given first,then the new criterion for the determination of nonsingular *H*-tensors are given,and at last two numerical examples are given.

Key words　*H*-tensor;generalized diagonally dominant;*M*-tensor