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The study on high temperature conductivity of nanocrystalline $BaTiO_3$ ceramics

Aiguo Kang*, Longtu Li, Xiangyun Deng, Xiaohui Wang

State Key Laboratory of New Ceramics and Fine Processing, Department of Material Science and Engineering, Tsinghua University, Beijing 100084, China

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Abstract

The un-doped nanocrystalline $BaTiO_3$ (BT) ceramics samples with different grain size were prepared and its electrical properties were measured. It was found that the conductivity of samples decreases with increasing temperature at some high frequency. The activation energy of carriers is calculated experimentally and theoretically for different samples. The results show that the accumulation of charges at grain boundary is the chief factor at high frequency, which lead to the decrease of conductivity with increasing temperature.

Keywords: $BaTiO_3$ ceramics; High temperature conductivity; Activation energy

1. Introduction

$BaTiO_3$ (BT) ceramics is one of the most important dielectric materials that have been used widely in various fields. The nanocrystalline ceramics, which have many new properties that are different from those with coarse grains, have been developed largely in the last few years. The ferroelectricity and dielectric constant all are weakened with reducing grain size, and the conductivity is enhanced. These results may imply a different structural and physical mechanism of grain size effects for nanocrystalline BT ceramics [1–5].

It is supposed [6,7] that nanocrystalline BT consists of ferroelectric grains and nonferroelectric grain boundary (GB), and it presumes a pseudocubic structure even at room temperature owing to the high volume fraction of GB. It is also proposed [8] that the acceptor-doped BT shows a p-type conductivity in neutral to oxidizing atmospheres.

In this paper, the high temperature complex impedance of nanocrystalline BT ceramic was measured. The influence of grain and GB on resistivity of samples was analyzed by comparing the differences of high temperature conductivity at high or low frequency. The activation energy of carriers was calculated in order to better understand the type of conductivity.

2. Experiments and results

The BT samples with different grain sizes (GS) were made by the method of spark plasma sintering (SPS). Two samples of which GS is 50 and 90 nm, are selected in our experiment. The thickness of samples is 2 and 1 mm, respectively. The GS is attested by the method of XRD and TEM. The DC resistivity of samples was measured with HP4194A and HP4140B. Hysterisis loops were measured with Radiant RT6000 High Voltage System. High temperature impedances were measured with Agilent 4294A Precision Impedance Analyzer. Temperature range selected in experiments is 573–1023 K, which step is 50 K. Frequency range is 40 Hz–100 MHz.

The impedance spectra of samples are shown in Fig. 1. The high temperature conductivity of two samples at low (40 Hz) and high frequency (1 MHz) are shown in Figs. 2 and 3. Because some data are too large to be shown in one figure and the resonance occurs after certain frequency, so the arcs are not complete. Even so, it still shows a changing rule that the semicircle of complex impedance shrinks with increasing temperature for sample of 90 nm. But for sample of 50 nm, the case is a little different. The high temperature conductivity of two samples increase with

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* Corresponding author. Tel.: +86 10 62792632.
E-mail address: kag@mail.tsinghua.edu.cn (A. Kang).

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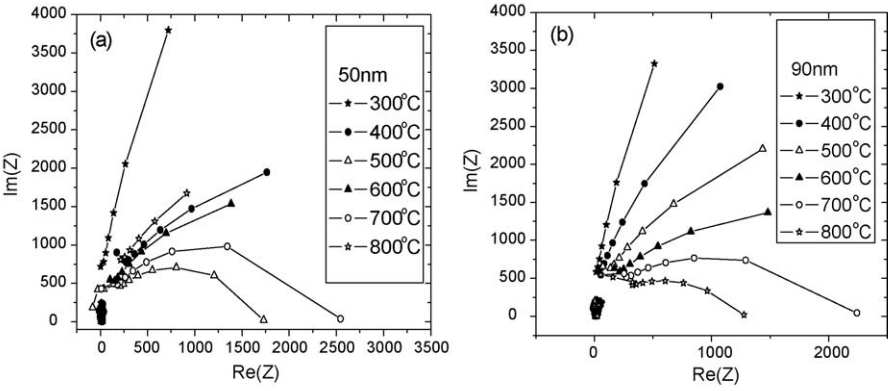

Fig. 1. The high temperature impedance spectra of samples with GS of (a) 50 nm and (b) 90 nm.

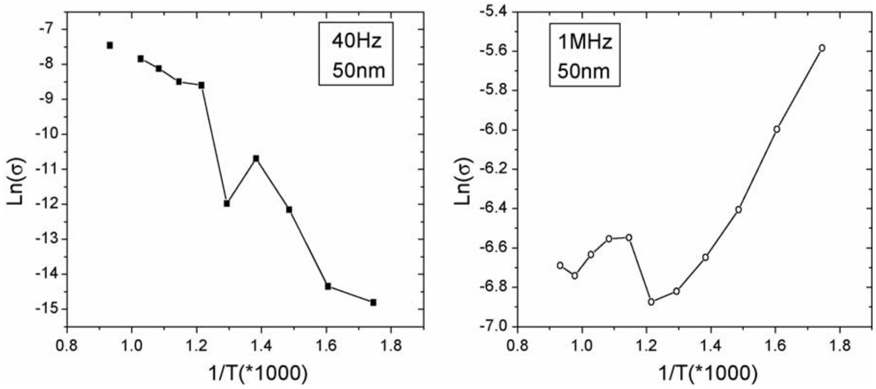

Fig. 2. The high temperature conductivity of 50 nm sample at low and high frequency.

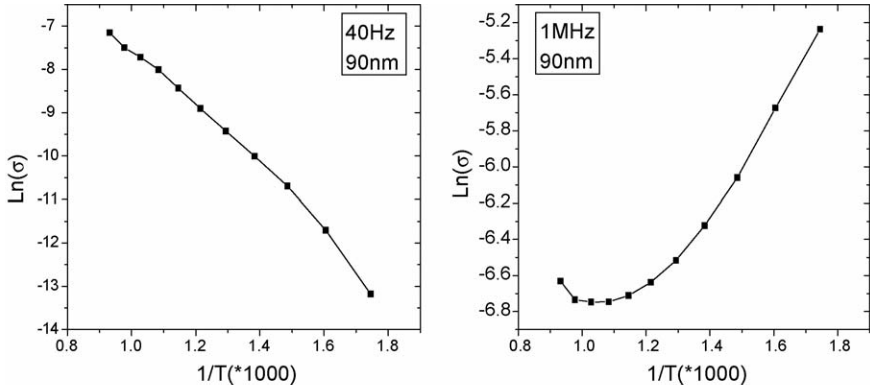

Fig. 3. The high temperature conductivity of 90 nm sample at low and high frequency.

increasing temperature at low (40 Hz) frequency, but it decreases with increasing temperature at high frequency (1 MHz).

3. Discussion

In the experiments, the capacities of samples at different frequencies are also measured in order to study the influences of grains and grain boundaries. It is shown that grains have a chief contribution to capacities at low frequencies and grain boundaries are dominating at high frequencies. The results may be analyzed by other methods. In this paper, we only want to analyze the questions in conductivity.

3.1. The ionic conductivity at low frequency

Though part of complex impedance curve at low frequency has not been shown, there still is a semicircle orderliness that can be seen in Fig. 1. The curve in Figs. 2 and 3 meet approximatively the following classical relation of ionic or electronic conductivity [9]:

$$\sigma_1 = \sigma_{10} \exp\left(-\frac{E_{g1}}{kT}\right) \quad \text{or} \quad \sigma_2 = \sigma_{20} \exp\left(-\frac{E_{g2}}{2kT}\right) \qquad (1)$$

where E_{g1} is the activation energy of ions and E_{g2} is the band gap. The activation energy of carriers and the band gap