Microstructure and Dielectric Properties of Microwave-Sintered Barium Titanate Ceramics (Postprint)

Authors: Wan Le, Zhu Guisheng, Xu Huarui, Zhenxiao Fu, Hu Chunyuan, Zhu Guisheng

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Abstract

To improve the properties of BaTiO3 ceramics, barium titanate ceramics were prepared by microwave sintering and conventional sintering using high-tetragonal-phase barium titanate powder synthesized via solid-state method as the raw material. The samples were characterized by XRD, SEM, XPS, and LCR analyzer, and the compositional segregation differences between the ceramics prepared by the two methods were analyzed. Experimental results demonstrate that microwave-sintered barium titanate ceramics exhibit uniform grain size and reduced Ba atomic segregation at interfaces, resulting in significant enhancement of the room-temperature dielectric constant. The barium titanate ceramics microwave-sintered at 1100 ℃ for 2 h exhibit a grain size of 1 m, a room-temperature dielectric constant of 5688 at 10 kHz, and a dielectric loss of 0.021. In contrast, the fracture surface of barium titanate ceramics conventionally sintered at 1250 ℃ for 2 h shows no obvious grains, with a room-temperature dielectric constant of only 3257 at 10 kHz and a dielectric loss of 0.021.

Full Text

Study on the Microstructure and Dielectric Properties of Microwave-Sintered Barium Titanate Ceramics

Fu Zhenxiao, Zhu Guisheng, Huarui, Chunyuan

1. School of Materials Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China

2. Engineering Research Center of Electronic Information Materials and Devices, Ministry of Education, Guilin University of Electronic Technology, Guilin 541004, China
3. Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin 541004, China
4. State Key Laboratory of Advanced Materials and Processes for Electronic Components, Guangdong Fenghua High-Tech Co., Ltd., Zhaoqing 526000, China

Abstract

Using high-tetragonal-phase barium titanate powder synthesized by the solid-state method as raw material, barium titanate ceramics were prepared by both microwave sintering and conventional sintering methods. The phase composition, microstructure, and dielectric properties of the ceramics prepared by the two methods were analyzed using XRD, SEM, XPS, and LCR analyzer. The experimental results show that microwave-sintered barium titanate ceramics exhibit uniform grain size and minimal atomic segregation. Consequently, the room-temperature dielectric constant of the microwave-sintered ceramics is significantly improved, reaching 370 with a dielectric loss of only 0.021, which is substantially better than that of conventionally sintered samples.

Introduction

Barium titanate ($BaTiO_3$) is a strong dielectric material with excellent piezoelectric and dielectric properties [1-3]. $BaTiO_3$-based ceramics are widely used in multilayer ceramic capacitors (MLCC), positive temperature coefficient resistors (PTCR), sonar sensors, and other electronic devices [4-6]. With the development of the electronics industry, higher performance requirements have been proposed for ceramic components, including high capacitance and low loss [7-9]. Although the size of MLCCs has been reduced, this also results in lower breakdown voltage. Therefore, preparing high-performance, low-loss $BaTiO_3$-based ceramics remains a research hotspot.

Various preparation methods for $BaTiO_3$-based ceramics have been reported, including microwave sintering, plasma-assisted sintering [11], and cold sintering [13]. Compared with other methods, microwave sintering is a volumetric heating process that offers greater advantages in solving problems such as heterogeneous grain growth and non-uniform sintering temperature. Previous studies have reported on microwave sintering of $BaTiO_3$ ceramics. Annett et al. [14] investigated the effects of microwave sintering and conventional sintering on the microstructural stress of $BaTiO_3$ ceramics. Takahashi et al. [16-18] used cubic-phase $BaTiO_3$ powder to prepare ceramics with a room-temperature dielectric constant of [value] and studied the microwave sintering temperature. However, there are few reports on the microstructure of microwave-sintered $BaTiO_3$ ceramics, particularly regarding surface morphology and composition segregation.

In this study, using high-tetragonal-phase $BaTiO_3$ powder synthesized by the solid-state method, dense $BaTiO_3$ ceramics were prepared by both microwave sintering and conventional sintering to investigate the effects of the two sintering methods on the microstructure and dielectric properties.

Experimental Methods

Sample Preparation

High-tetragonal-phase $BaTiO_3$ powder was synthesized by the solid-state method using barium hydroxide octahydrate and metatitanic acid as starting materials. The synthesized powder exhibited a tetragonal phase with c/a = 1.010 and a particle size of 200–400 nm. A certain amount of $BaTiO_3$ powder was placed in an agate mortar, and a binder solution was added for granulation. The powder was dried in an oven and then sieved through a mesh. The samples were placed in a mold and dry-pressed under [pressure] to obtain $BaTiO_3$ ceramic green bodies. The green bodies were first placed in a muffle furnace and then transferred to a microwave sintering furnace for sintering at a heating rate of °C/min.

Characterization

The crystal structure of the $BaTiO_3$ ceramic samples was characterized by X-ray diffraction (XRD, D8/Max-2500). The microstructure and morphology were observed using scanning electron microscopy (SEM, Tecnai-450). The elemental distribution was analyzed by energy-dispersive X-ray spectroscopy (EDS, X-Max20). The chemical state was examined by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi). The density of the ceramics was measured by the Archimedes method. For dielectric property testing, silver paste was screen-printed on the ceramic surfaces and fired to form electrodes. The capacitance and dielectric loss were measured using an LCR analyzer (HP4294A) at frequencies of 30–200. The dielectric constant was calculated using the formula: $= CS/(_0 d)$, where C is the capacitance, S is the electrode area, d is the sample thickness, and $_0$ is the vacuum permittivity.

Results and Discussion

Phase Structure Analysis

The XRD patterns show that both microwave-sintered and conventionally sintered $BaTiO_3$ ceramics are single-phase. The tetragonal phase content of $BaTiO_3$ is primarily determined by the degree of splitting of the double diffraction peaks. Because microwave sintering relies on the material itself absorbing microwave energy, there is no thermal lag during heating. As the microwave sintering temperature increases, the peak splitting becomes more pronounced (Fig. 3(i), (j)), indicating that the tetragonal phase content of the $BaTiO_3$ ceramics gradually increases. In contrast, the conventionally sintered $BaTiO_3$

ceramics show lower tetragonal phase content, and the peak splitting becomes indistinct at certain temperatures. This may be due to abnormal grain growth and transgranular fracture caused by conventional sintering.

Microstructural Characteristics

The microstructure of the $BaTiO_3$ ceramics is shown in Fig. 3. At a sintering temperature of [value]°C, grain growth is not significant, with an average grain size of [value] nm. The ceramics are not fully dense, with obvious pores at grain boundaries, and the relative density is only [value]%. When the sintering temperature increases to [value]°C (Figs. 3(c), (d)), the grain size increases further, pores shrink significantly, and the relative density reaches 95.20%. At this temperature, dense $BaTiO_3$ ceramics are obtained with a grain size of about [value] nm. With continued temperature increase, the grain size in the cross-section increases noticeably, but remains consistent between surface and cross-section. The ceramic density increases slightly (Figs. 3(e)-(h)).

Chemical State and Elemental Segregation

The XPS spectra of $BaTiO_3$ ceramics show two binding energy peaks: a higher binding energy peak at 779.5 eV corresponding to Ba in the perovskite phase, and a lower binding energy peak at 778.1 eV corresponding to Ba in the surface phase, consistent with peak deconvolution results from other researchers [19-21]. The microwave-sintered $BaTiO_3$ ceramics show higher Ba content in the perovskite phase, while the conventionally sintered ceramics show higher Ba content in the surface phase. This occurs because microwave sintering couples directly with the material, resulting in uniform temperature throughout the crystal interior and surface, generating fewer defects and less atomic segregation. In contrast, conventional sintering is a surface heating method that creates temperature gradients between the interior and surface, leading to more defects during sintering. These defects create potential differences between the crystal interior and interface, driving Ba segregation to the surface phase.

To further investigate elemental segregation, EDS mapping was performed on the cross-section of $BaTiO_3$ ceramics. The results show that in microwave-sintered ceramics, elements are uniformly distributed on the grains without aggregation. In conventionally sintered ceramics, elements are not uniformly distributed—Ba content is higher at grain boundaries, indicating that Ba atoms preferentially migrate to grain boundaries during conventional sintering. This segregation can cause abnormal grain growth in $BaTiO_3$ ceramics.

Dielectric Properties

The dielectric constant of $BaTiO_3$ ceramic samples decreases with increasing frequency for both sintering methods. The temperature dependence of dielectric constant and loss was investigated at [frequency]. As the microwave sintering

temperature increases, the dielectric constant at the Curie peak gradually increases. The microwave-sintered $BaTiO_3$ ceramics with an average grain size of about [value] nm exhibit a room-temperature dielectric constant of 370, which is significantly higher than that of conventionally sintered ceramics. The dielectric loss continuously decreases with increasing temperature, while the room-temperature dielectric constant first increases and then decreases, reaching a maximum value at [temperature] with a dielectric loss of 0.021. This behavior is mainly attributed to the size effect of $BaTiO_3$ ceramics [7,22]. When the grain size is in the range of [value] nm, the ceramics exhibit the maximum room-temperature dielectric constant. The conventionally sintered $BaTiO_3$ ceramics show a lower room-temperature dielectric constant of [value] with a dielectric loss of 0.21 (likely 0.021). This is because Ba atoms segregate to grain boundaries during conventional sintering, causing abnormal grain growth and reducing the dielectric constant due to the size effect.

Conclusion

Using high-tetragonal-phase $BaTiO_3$ powder prepared by the solid-state method, microwave sintering successfully produced $BaTiO_3$ ceramics with uniform grain size and minimal atomic segregation at interfaces. The microwave-sintered ceramics exhibited a high room-temperature dielectric constant of 370 and a low dielectric loss of 0.021. This study provides a new approach for preparing high-capacitance $BaTiO_3$ ceramics for advanced electronic applications.

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Note: Figure translations are in progress. See original paper for figures.