Ceramic **Processing Research**

Microstructures and dielectric properties of bismuth ferrite ceramics prepared using two sintering methods

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Bismuth ferrite (BiFeO₁) ceramics are sintered using conventional (CS) and microwave (MS) methods. The average grain size of BiFeO₃ ceramics sintered using a microwave oven is smaller than that obtained using the conventional method. When the temperature is above 80 °C, the dielectric constant of BiFeO₃ ceramics prepared by CS is larger than that obtained by MS which may results from the larger grain sizes produced by conventional sintering. At -20 °C, an obvious peak is observed in the dielectric loss-temperature curve of the microwave-sintered sample. The remanent polarization of the BiFeO₃ ceramics prepared by CS is much smaller than that obtained by MS, and the coercive electric fields of BiFeO₃ ceramics prepared by two sintering methods are almost identical.

Key words: Bismuth ferrite, Ceramic, Ferroelectric, Microwave sintering.

Introduction

Multiferroic materials, which simultaneously feature ferroelectric and magnetic orders, have attracted considerable interest because of their novel applications in spintronic devices and storage media [1-3]. Several single-phase multiferroic materials have recently been investigated. However, bismuth ferrite (BiFeO₃) is the only multiferroic material known to express coupling between ferroelectric and magnetic orders at room temperature [4-6]. Spin ordering with a $T_{\rm N}$ of 643 K and polarization ordering with a high $T_{\rm C}$ of 1103 K are simultaneously observed in BiFeO₃ [7-9].

Reports on microwave-sintered ceramics have increased [10-12]. The microwave sintering (MS) method can reportedly refine the microstructure and enhance properties. For example, the density of microwave-sintered alumina ceramics is up to 98.5% of the theoretical value [10]. Microwave-sintered lead zirconate titanate ceramics show fine microstructures and improved piezoelectric properties [11].

In this work, BiFeO₃ ceramics were prepared using conventional (CS) and microwave (MS) sintering processes. The crystal structures, surface morphologies, and dielectric and ferroelectric properties of the BiFeO3 ceramics prepared using the two methods were compared.

Experiments

Preparation

BiFeO₃ ceramics were prepared by CS and MS. High-

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purity ferric nitrate nanohydrate $[Fe(NO_3)_3 \cdot 9H_2O_3]$ \geq 98.5%], bismuth nitrate [Bi(NO₃)₃ · 8H₂O, \geq 99.0%], nitric acid (HNO₃, \geq 99.5%), acetic acid (CH₃COOH, \geq 99.5%), and ethylene glycol (HOCH₂CH₂OH, \geq 99.5%) were used as raw materials to prepare a precursor solution. First, an Fe precursor solution was prepared by adding HOCH2CH2OH and CH3COOH as solvents into $Fe(NO_3)_3 \cdot 9H_2O$. The Fe content in the solution was $0.5 \text{ mol} \cdot \text{L}^{-1}$. After continuous stirring at 60 °C for 30 min, Bi(NO₃)₃ · 8H₂O was dissolved in HOCH₂CH₂OH and CH₃COOH to form a Bi precursor solution. The Bi content of this precursor solution was $0.525 \text{ mol} \cdot \text{L}^{-1}$. The Fe solution was then added dropwise to the Bi solution. Continuous stirring of the mixture was performed at 80 °C for 1 h to form the parent solution. After aging at room temperature for 24 h, the solution was heated at 105 °C in an oven and then calcined at 600 °C for 2 h to obtain powders. The calcined powders were mixed with nitric acid and unwanted ferric oxide was eliminated by filtering. The powders were dried thrice in an oven at 105 °C. Finally, the powders were mixed with 6 wt.% paraffin wax and pressed into cylindrical slices at 20 MPa. The diameter and thickness were 10.0 and 1.0 mm, respectively. The slices were split into two series. One set of green slices was conventionally sintered at 800 °C for 3 h in air. The other set of pellets was sintered at 3 kW for 35 min in air using a microwave oven (WLD3S-09, China).

Characterization

The phase of the samples was identified using X-ray diffraction (XRD, DX2700, China) using Cu Ka radiation $(\lambda = 0.1541 \text{ nm})$ at room temperature. Scanning electron microscopy (S3700, Hitachi, Japan) was performed to

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Fig. 1. XRD patterns of the BiFeO3 ceramics prepared by CS and MS.





(b)

Fig. 2. Scanning electron micrographs of the $BiFeO_3$ ceramics sintered using different methods: (a) 800 °C for 3 h in air by CS and (b) 3 kW for 35 min in air by MS.

determine the grain sizes of the BiFeO₃ ceramics.

The dielectric properties of the ceramics were measured using an Agilent E4980A inductance, capacitance, and resistance meter at $1 \text{ V} \cdot \text{mm}^{-1}$ and temperature range of -60 °C to 160 °C ($0.5 \text{ °C} \cdot \text{min}^{-1}$). The polarization hysteresis curves were measured using a TF2000 FE-HV ferroelectric test unit (aix-ACCT Inc., Germany).

Results and Discussions

Crystal structure

Fig. 1 shows the XRD patterns of the BiFeO₃ ceramics prepared by CS and MS. After sintering



Fig. 3. Temperature dependence of the (a) dielectric constant and (b) dielectric loss of the BiFeO₃ ceramics sintered by CS and MS.

the pellets at 800 °C for 3 h in air by CS or at 3 kW for 35 min in air by MS, $BiFeO_3$ and some $Bi_2Fe_4O_9$ particles are formed. Based on the standard XRD spectrum, the crystal structures of the samples are determined to correspond to the distorted perovskite structure of diamond and belong to the R3c (161) group.

Surface morphology

Fig. 2 shows typical scanning electron micrographs of the BiFeO₃ ceramics sintered using different methods. An evident difference in the grain sizes of the ceramics may be observed. The average grain size of BiFeO₃ ceramics sintered at 800 °C for 3 h by CS is approximately 20 μ m, as shown in Fig. 2a. By contrast, Fig. 2b shows that the average grain size of BiFeO₃ ceramics sintered at 3 kW for 35 min by MS is smaller than 5 μ m.

Dielectric properties

The dielectric constant-temperature curves of the BiFeO₃ ceramics is given in Fig. 3a. No obvious peaks are observed, indicating that the Curie temperature ($T_{\rm C}$) of the samples is beyond the measuring temperature range. The dielectric constant of the samples gradually increases with increasing temperature from -60 °C to

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Fig. 4. Hysteresis loops of the BiFeO₃ ceramics at room temperature and 1 kHz.

160 °C. When the temperature is above 80 °C, the dielectric constant of the conventionally sintered BiFeO₃ ceramics is larger than that of the microwave-sintered samples, which may be caused by the larger grain sizes of the former compared with the latter (Fig. 2). However, at temperatures ranging from -35 °C to 75 °C, the dielectric constant of BiFeO₃ ceramics prepared by CS is smaller than that obtained by MS, possibly because the polarization mechanism varies with temperature.

The dielectric loss-temperature curves of the BiFeO₃ ceramics is given in Fig. 3b. When the temperature is above 50 °C, the dielectric loss of all samples increases with increasing temperature. This result may be due to the increase in leakage current density with increasing temperature. Moreover, an obvious peak is observed in the curve of the sample prepared by MS at -20 °C. Why the curve of this set of samples shows an apparent peak is unknown but we believe that this result may be due to the smaller grain size of the sample.

Ferroelectric properties

Fig. 4 shows the electric field dependence of the polarization of BiFeO₃ ceramics at 1 kHz and room temperature. Well-behaved hysteresis loops are observed in all samples, which suggests that BiFeO₃ ceramics sintered using the two methods exhibit the ferroelectric structure at room temperature. This result is agreement with the XRD results and dielectric constant-temperature curves.

Based on Fig. 4, we can calculate the remanent polarization $(2P_r)$ and coercive electric field $(2E_C)$ of BiFeO₃ ceramics. The remanent polarization $(0.060 \,\mu\text{C/cm}^2)$ of BiFeO₃ ceramics prepared by CS is much smaller than that $(0.104 \,\mu\text{C/cm}^2)$ obtained by MS. However, no obvious differences are observed between the coercive electric fields of both types of BiFeO₃ ceramics. This odd phenomenon may be due to the many factors influencing ferroelectric properties,

such as crystalline structure, grain size, and domain configuration. As shown in Fig. 2, the grains of the conventionally sintered ceramics are larger than those of the microwave-sintered ceramics, resulting in larger remanent polarization and a lower coercive electric field. However, the microwave-sintered ceramics have better domain alignment [11].

Conclusions

The samples exhibit the distorted perovskite structure of diamond. The average grain sizes of the BiFeO₃ ceramics obtained by MS are smaller than those obtained by CS. In addition, the dielectric constant increases with increasing temperature. The remanent polarization of BiFeO₃ ceramics prepared by CS is much smaller than that obtained by MS. No obvious differences are observed in the coercive electric fields of the samples.

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