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Microwave sintering of lead-free barium titanate piezoelectric ceramics from barium titanate powders synthesized by a hydrothermal method

Kongjun Zhu*, Jinhao Qiu, Hongli Ji and Yuansheng Chen

The Key Lab for Smart Materials & Structures, College of Aerospace Engineering, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

In this study, three types of $BaTiO_3$ powder with different particle sizes synthesized by a hydrothermal method were used to fabricate the lead-free barium titanate piezoelectric ceramics. The $BaTiO_3$ ceramics from these three types of $BaTiO_3$ powders were sintered at different temperatures (1100 and 1150 °C) using a microwave sintering method, and their piezoelectric properties were investigated and compared. The results indicate that all The $BaTiO_3$ piezoelectric ceramics exhibit higher d_{33} value (above 330 pC/N, the highest is about 370 pC/N). The reasons were also investigated by comparing the properties of the three types of $BaTiO_3$ powders, sintering temperature and method.

Key words: Barium Titanate, Hydrothermal method, Microwave sintering, Lead-free, Ceramics, Piezoelectric property.

Introduction

Lead zirconium titanate (PZT) ceramics are high-performance piezoelectric materials, which are widely used in sensors, actuators and other electronic devices [1]. PZT ceramics contain more than 60 weight percent lead. Because of the toxicity of lead oxide, however, there is a rising concern about recycling and disposal of devices containing PZT, especially those used in expendable such as cars, various types of smart systems and sound generators. The facts that lead oxide vaporizes during processing, that lead stays for a long time in the environment and that it accumulates in organisms and cause damage to the brain and nervous system, have lead to strict legislations in many countries. In addition, there is a trend of developing biocompatible piezoelectric materials for using as sensors and actuators which was directly implanted into living tissue, including human body. Thus, there is an increasing tendency to find alternative lead-free piezoelectric materials.

Saito *et al* [2]. reported that most of the piezoelectric properties of lead-free ceramics are comparable to those of PZT, which leads us to develop candidate materials for environmentally - friendly piezoelectric devices. Many lead-free piezoelectric materials have been developed recently, which include $Bi_{0.5}(Na_{1-x}K_x)_{0.5}TiO_3$ [3], $(Bi_{0.5}Na_{0.5})TiO_3$-$BaTiO_3$ [4], $SrBi_4Ti_4O_{15}$ [5, 6], $Ba(Ti_{1-x}Zr_x)O_3$ [7], (0.97-x) $(Bi_{0.5}Na_{0.5})TiO_3$- 0.03$NaNbO_3$-x$BaTiO_3$ [8], Bi_3TiNbO_9-$BaBi_2Nb_2O_9$ [9], (K,Na)(Nb,Ta)O_3 [10]. Barium titanate ($BaTiO_3$: BT) is well known as a lead-free piezoelectric material. However, the low piezoelectric properties of BT ceramics have been the main obstacle to their wider applications as actuators and sensors.

In order to improve the piezoelectric properties of lead-free ceramics, many novel sintering methods have been developed. For example, microwave sintering [11], hybrid sintering process [12], spark plasma sintering [13, 14] etc. In addition, the synthesis method of the starting powders is also very important for fabrication of piezoelectric ceramics. It is well known that the hydrothermal method is a wet-chemical technique for directly forming complex oxide powders [15]. In our former study [16], BT powders synthesized by hydrothermal method were used to fabricate piezoelectric ceramics using a traditional sintering method. The results indicate that the BT powders synthesized by a hydrothermal method improved the piezoelectric property greatly. However, the growth of the particles resulted in a decrease of the piezoelectric properties of BT ceramics.

In this study, three types of $BaTiO_3$ powder with different particle sizes synthesized by a hydrothermal method were used to fabricate lead-free barium titanate piezoelectric ceramics. The $BaTiO_3$ ceramics from these three types of $BaTiO_3$ powders were sintered at different temperatures (1100 and 1150 °C) using a microwave sintering method, and their piezoelectric properties were investigated and compared.

Experimental Procedure

The BT powders used in this study were commercial powders BT01, BT03 and BT05 made by the Sakai Chemical Industry Co. Ltd, which were synthesized by the hydrothermal method. The particle sizes of these powders were about 0.1, 0.3 and 0.5 m, respectively. The BT powders (0.75 g for each particle size) were mixed with polyvinyl

*Corresponding author:
Tel : +86-25-84893466-190
Fax: +86-25-8489-1123
E-mail: kjzhu@nuaa.edu.cn

alcohol (1 wt%) and formed into discs 15 mm in diameter and 1.2 mm in thickness by die pressing at a pressure of 200 MPa. The binder was burned out at 700 °C. The temperature of specimens was raised from room temperature to the sintering temperature at a rate of 873 $K \cdot h^{-1}$, maintained for 30 minutes and then cooled at the same rate as that of the rising rate.

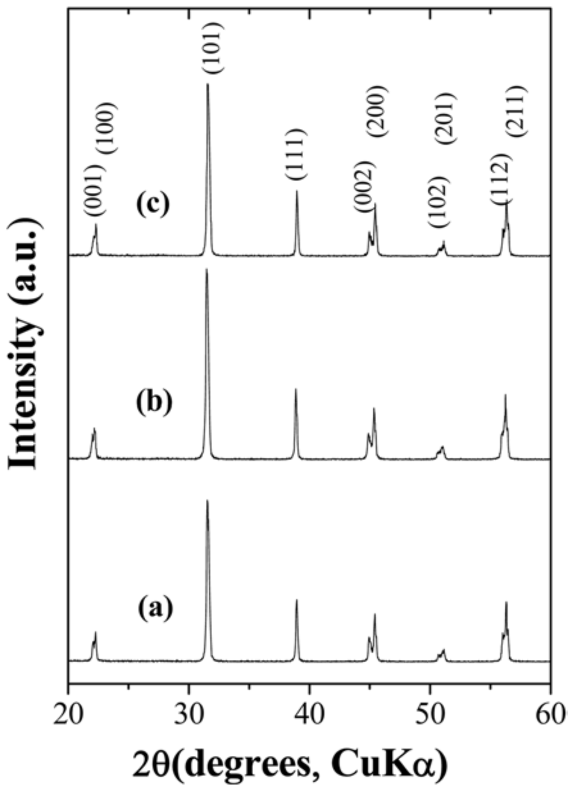

Fig. 1. XRD patterns of BT ceramics sintered at 1150 °C for 30 minutes from three types of BT powders (a) BT01 (b) BT03 (c) BT05.

The BT specimens were characterized by powder X-ray diffraction (XRD; Model RTP-300RC, Rigaku Co. Japan) with Cu Kα radiation (36 kV and 20 mA). The density and porosity of the specimens obtained were measured by the Archimedes technique using water. The microstructure was observed by a scanning electron microscope (SEM; JSM551, JEOL, Japan). Electrodes were formed on the specimens by sputtering gold on both surfaces. The specimens were then polarized in a silicon oil bath under a DC field of 1 kV/mm at 110 °C for 10 minutes. The dielectric properties of the specimens were measured at a frequency of 1 kHz using an HP4194A precision impedance analyzer (Agilent, Palo Alto, CA). The value of d_{33} was measured using a d_{33} meter (Model ZJ-3D, Institute of Acoustic Academia Sinica, China). The polarization versus electric field (*P-E*) hysteresis loops was observed using a precision workstation (RT6000HVS, Radiant technology, Inc).

Results and Discussion

Phase, microstructure and density

Fig. 1 shows the X-ray diffraction patterns of BT specimens sintered by a microwave sintering method at 1150 °C for 30 minutes from three types of BT powders. There was only the tetragonal perovskite BT phase in all of these BT specimens. This indicates that the phase of the BT01 was changed from the cubic in the powder to the tetragonal phase in the specimen obtained after sintering, while the phase of BT03 and BT05 was still tetragonal after sintering according to the results in our former study [16].

The SEM micrographs of the BT specimens sintered by the microwave sintering method at 1100 °C and 1150 °C from three types of BT powders are shown in Fig. 2. A dense microstructure was obtained in all of the specimens sintered from three types of BT powders, small and

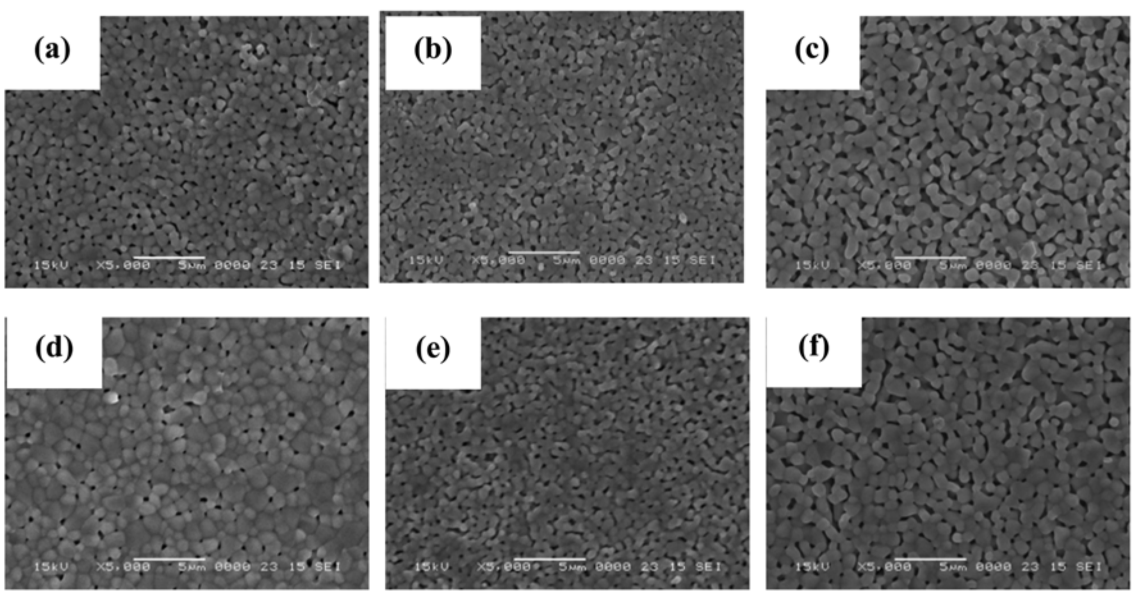

Fig. 2. SEM micrograph of BT ceramics sintered at different temperatures (a) BT01 1100 °C (b) BT03 1100 °C (c) BT05 1100 °C (d) BT01 1150 °C (e) BT03 1150 °C (f) BT05 1150 °C.

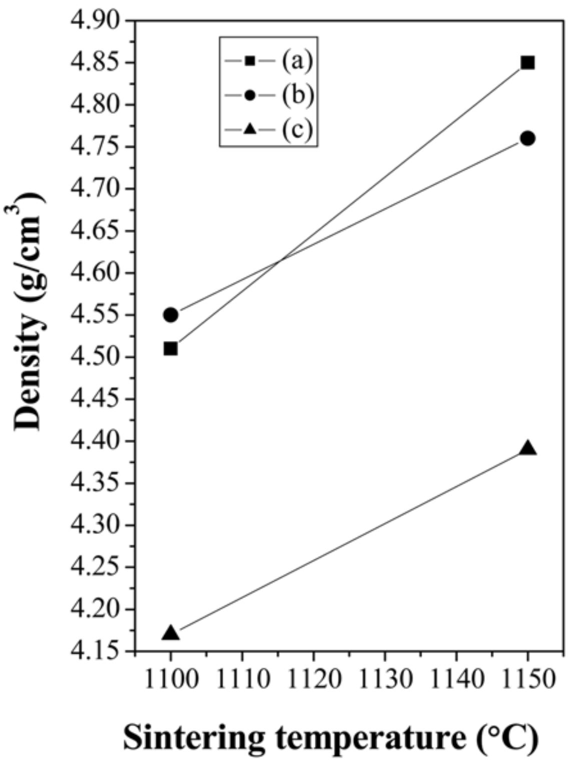

Fig. 3. The density of BT specimens sintered by the microwave sintering method at different temperatures from three types of BT powders (a) BT01 (b) BT03 (c) BT05.

homogeneous grains were observed in all of the specimens. But the grains in the BT01 ceramic grew substantially with an increase of the sintering temperature. It may be considered that BT01 powder is easily sintered because the particle size of BT01 is the smallest in the three BT powders according to the results in our former study [16].

Fig. 3 shows the density of the specimens sintered by the microwave sintering method at different temperatures from three types of BT powders. The density of the BT specimens are all increased with an increase of the sintering temperature. The density of the BT01 ceramic sintered at 1150 °C is the largest, and the density of the BT05 ceramic sintered at 1150 °C is the lowest. However, the density of the BT01 ceramic sintered at 1100 °C is lower than that of the BT03 ceramic sintered at 1100 °C. This may be explained by the sinterability of BT powders with different particle sizes. The BT01 powder with OH^- defects was synthesized by the hydrothermal method at a low temperature, and the particle size is the smallest. Thus, the density of BT01 is lower than that of BT03 sintered at 1100 °C due to more ignition loss, and the density of the BT01 ceramic sintered at 1150 °C is the largest.

Table 1. The piezoelectric properties of BT ceramics sintered by the microwave sintering method at different temperatures

	1100 °C			1150 °C		
	BT01	BT03	BT05	BT01	BT03	BT05
Cap (nF)	2.34	1.85	1.07	3.72	2.62	2.58
tan (%)	0.80	0.92	1.20	3.49	1.12	1.35
r	1600	1250	1200	2500	1570	1580
d_{33} (pC/N)	345.1	340.9	335.1	365.2	373.9	359.6

Measurement of electrical properties

The electrical properties were measured (Table 1). In general, the dielectric properties were affected by not only the sintered density but also the crystalline phase, chemical composition and microstructure. In this study, BT01, BT03 and BT05 have the same crystalline phase and chemical composition, the microstructure is also very similar due to microwave sintering. So the dielectric properties depended mainly on the density of BT ceramics. With a decrease of particle size and an increase of the sintering temperature, the density of BT ceramics increased. Therefore, the dielectric properties increased with the decrease of particle size of the BT powders and an increase of the sintering temperature.

In this study, all specimens have a large piezoelectric constant due to the homogeneous grains grown after microwave sintering. In our former study, only the BT03 specimen with homogeneous grains in the structure had a large piezoelectric constant (d_{33} is about 350 pC/N). In particular large grains were grown in the structure of BT03 and BT05 specimens sintered by the traditional sintering method, which resulted in a decrease of the piezoelectric constant. This comparison indicates that microwave sintering is very useful to enhance the dielectric properties of BT ceramics.

Measurement of P-E hysteresis loops and displacement

In order to characterize the ferroelectricity, the *P-E* Hysteresis loops of BT ceramics were measured. The results are shown in Fig. 4. This indicates that the polarization value of BT-1100 is less than it of BT-1150 at all coercive

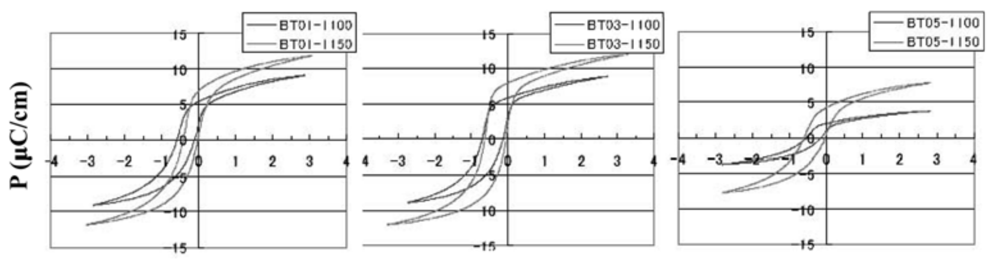

Fig. 4. *P-E* hysteresis loops of BT ceramics sintered by the microwave sintering method at different temperatures.

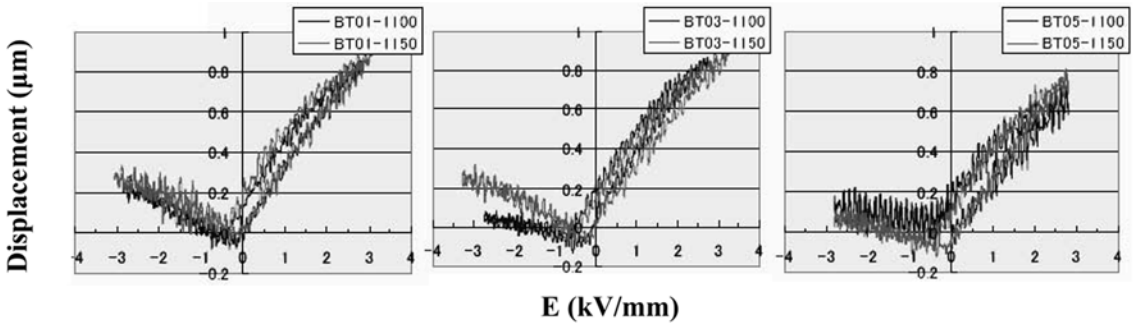

Fig. 5. The displacement versus electric field for BT ceramic sintered by the microwave sintering method at different temperatures.

fields, and the Pr value increased with an increase of the sintering temperature. The hysteresis loops of BT01 and BT03 are very similar. The hysteresis loop of BT05 is smaller than the others. The results are in agreement with the measurements of the piezoelectric constants.

An experiment was designed to measure the displacement characteristics of BT ceramics. A laser sensor was used to measure the displacement of the BT ceramic. A mirror was used to reflect the laser light. The displacement versus electric field for BT ceramics are shown in Fig. 5. This was measured at 0.5 Hz with a triangular wave. It can be seen that the BT01 and BT03 samples can give 0.8 m at 3 kV/mm, while the displacement of BT05 is smaller. This also shows that the displacement of BT-1100 is close to BT-1150 with a positive electric field, but they are different with a negative electric field.

Conclusions

BT ceramics with dense microstructure and homogeneous grains were sintered by a microwave sintering method from three types of BT powders with different particle sizes synthesized by a hydrothermal method. The dielectric properties depended mainly on the density of BT ceramics, and increased with an increase of the density. All BT piezoelectric ceramics have higher d_{33} value (over 330 pC/N, the highest is about 370 pC/N). The Pr values of all BT ceramics increased with an increase of the sintering temperature. The hysteresis loops of BT01 and BT03 are very similar. The hysteresis loop of BT05 is smaller than the others. All specimens show a high displacement, BT01 and BT03 can give 0.8 m at 3 kV/mm, while the displacement of BT05 is smaller.

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