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Dielectric and magnetic properties of $BiFeO_3$ ceramics prepared by hydrothermal synthesis

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Abstract

Single-phase $BiFeO_3$ powders were prepared at a temperature of 200 °C by a hydrothermal synthesis. $BiFeO_3$ ceramics were prepared with the powders by a conventional ceramic process. The $BiFeO_3$ ceramics with no impurity phase were prepared at the sintering temperature of 650–800 °C. The dense microstructure was observed in the $BiFeO_3$ ceramics sintered at a temperature of 700 °C and higher. $BiFeO_3$ ceramics show linear M–H curves in low H, which are antiferromagnetic behaviors. The dielectric dispersion was observed at the frequency range of 10 kHz to 1 MHz in the $BiFeO_3$ ceramic sintered at 700 °C or lower. The dielectric constant and loss of the $BiFeO_3$ ceramics sintered at 750 °C or higher were about 85 and 0.4 at 100 kHz, respectively.

Keywords: A. Powders: chemical preparation; A. Sintering; Dielectric properies; C. Magnetic properties

1. Introduction

Multiferroic materials show two or more properties among ferroelectric, (anti)ferromagnetic and ferroelastic property and have attracted considerable attention due to the fascinating fundamental physics underlying their behavior and potential applications for novel magnetoelectric devices [1]. $BiFeO_3$ is a multiferroic material with a rhombohedrally distorted perovskite structure (space group *R3c*). It shows both ferroelectric and antiferromagnetic properties simultaneously at room temperature. Its phase transition temperatures are high ($T_N = 640$ K, and $T_C = 1100$ K), which makes it very attractive from an application point of view [2,3].

The $BiFeO_3$ ceramics can be fabricated by a conventional solid-state reaction [4,5]. However, it has reported that impurity phases would be easily formed with the $BiFeO_3$ phase because of the volatilization of some reactants and/or phase decompositions at high temperature. There have been many reports to stabilize the perovskite phase and enhance the electrical properties of $BiFeO_3$ by adding various dopants, like La, Nb and so on [6,7] or forming solid solution with other perovskites, like $BaTiO_3$ [8]. Recently, some researchers have attempted to prepare phase pure $BiFeO_3$ via a variety of routes, including a rapid thermal annealing [9,10], a sol–gel method [11,12] a hydrothermal method [13–16], and others [17]. The hydrothermal synthesis of $BiFeO_3$ powders has many advantages among various fabrication techniques because the $BiFeO_3$ crystalline particles could be formed at a reaction temperature around 200 °C without a further calcination step. Such a low processing temperature prevents the volatilization of reactants and phase decompositions at high temperature.

In this work, single-phase $BiFeO_3$ powders were prepared at a temperature of 200 °C by a hydrothermal synthesis. With the hydrothermally synthesized powders, $BiFeO_3$ ceramics were prepared at various sintering temperatures by a conventional ceramic process. We explored the phase evolution, microstructure development and densification of $BiFeO_3$ ceramics. Magnetic and dielectric properties of single-phase $BiFeO_3$ ceramics sintered at various temperatures were investigated.

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2. Experimental

Equi-molar mixtures of bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were dissolved in distilled water. After adding 8 M potassium hydroxide (KOH) and 0.025 M cetyl tri-methylammonium bromide (CTAB), the mixed solution was stirred for 30 min and poured into an autoclave. The hydrothermal treatments were conducted under autogenic pressure at 200 °C for 10 h. The produced powders were collected at the bottom of the autoclave after cooling to room temperature. The products were washed several times by repeated cycles of centrifugation in distilled water, and redispersed in ethanol by sonicating for 30 min. Subsequently, powders were obtained by evaporating ethanol in a mortar heated at 80 °C. The detailed process and characteristics were reported in other publication [16].

$BiFeO_3$ ceramics were prepared by using a conventional ceramic process with hydrothermally synthesized $BiFeO_3$ powders. The $BiFeO_3$ powder was heat-treated at 600 °C for 2 h in order to evaporate residual ions such as $(NO_3)^-$, $(OH)^-$, and so on. And the powders were ball-milled with 1 wt.% polyvinyl alcohol (PVA). The mixtures were pressed uniaxially into disk-shaped pellets, and sintered at temperatures from 650 °C to 800 °C for 3 h in air. The crystal structures of the sintered samples were analyzed by using an X-ray diffractometer (XD-D1; Shimadzu, Japan). The scanning electron micrographs (SEM: Quanta 200, FEI) of the samples were taken to observe the microstructures. Ag electrodes were applied on both $BiFeO_3$ surfaces for dielectric measurements. The dielectric constant and the loss tangent were measured by using an impedance analyzer (HP4192A). Magnetization hysteresis (M–H) measurements were carried out at room temperature by using a vibrating sample magnetometer (VSM).

3. Results and discussion

Hydrothermal route at 200 °C for 10 h provided single phase $BiFeO_3$ powder with plate- or polyhedron-shaped morphology of the size ranging from several hundred nanometers to several micrometers [16]. The XRD pattern and the morphology of the $BiFeO_3$ powder were little changed after annealing as-synthesized powders at 600 °C for 1 h. Fig. 1 illustrates XRD patterns of the $BiFeO_3$ ceramics sintered at 650–800 °C for 3 h in air. $BiFeO_3$ single phase is observed with no second phase in all samples. It has been reported that impurity phases are usually formed along with a $BiFeO_3$ phase in the solid state reaction process. Fig. 1 indicates that a hydrothermal synthesis is an effective method to prepare a pure $BiFeO_3$ ceramic. The surface morphologies of the $BiFeO_3$ ceramics sintered at various temperatures are shown in Fig. 2. The $BiFeO_3$ ceramics sintered at the temperature above 650 °C show dense microstructures while the $BiFeO_3$ ceramic sintered at 650 °C has many pores at grain boundaries. The linear shrinkages of the $BiFeO_3$ ceramics sintered at 650–800 °C are shown in Table 1. The shrinkage increased a lot when the sintering temperature increased from 650 °C to 700 °C and became saturated when the sintering temperature increased above 700 °C as shown in Table 1. This coincides with the surface morphologies as shown in Fig. 2. The dense microstructure of the $BiFeO_3$ ceramic sintered at 700 °C is comparable with that sintered at 800 °C and higher in other reports [4–7]. The average grain size increased when the sintering temperature rose from 650 °C to 700 °C and little changed when the sintering temperature increased from 700 °C to 750 °C, and then increased abruptly when the sintering temperature increased from 750 °C to 800 °C. The average grain sizes are summarized with linear shrinkages and dielectric properties in Table 1.

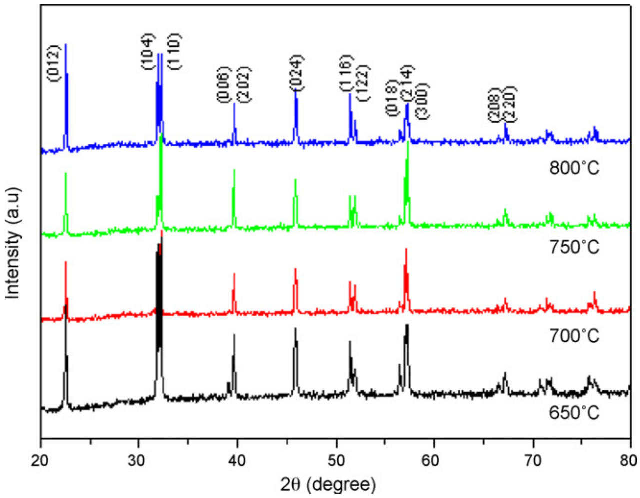

Fig. 1. X-ray diffraction patterns of the $BiFeO_3$ ceramics sintered at 650–800°C.

Fig. 3 displays magnetic M–H hysteresis characteristics of the $BiFeO_3$ ceramics sintered at 650–800 °C. All samples show the linear M–H curve within the magnetic field of 15 kOe, which indicates the $BiFeO_3$ ceramics are antiferromagnetics. Dielectric properties of the $BiFeO_3$ ceramics sintered at

Table 1
Physical properties of the $BiFeO_3$ ceramics sintered at 650–800 °C.

Sintering temperature (°C)	Linear shrinkage (%)	Average grain size (μm)	Dielectric constant (ε_r) at 100 kHz	Dielectric Loss (tan δ) at 100 kHz
650	10.9	5.5	3152	0.761
700	15.2	11.9	3046	0.681
750	16.1	10.3	84	0.423
800	16.4	68.0	83	0.418

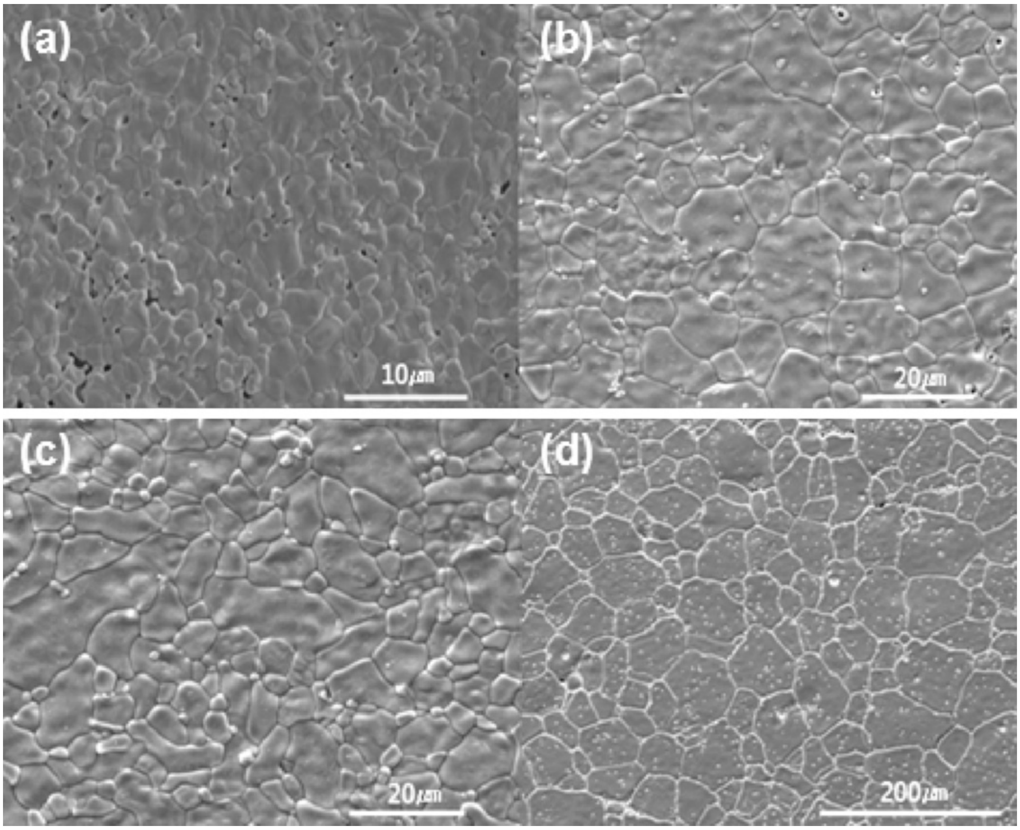

Fig. 2. SEM micrographs of the $BiFeO_3$ ceramics sintered at (a) 650, (b) 700, (c) 750, and (d) 800 °C.

650–800 °C are illustrated in Fig. 4. The $BiFeO_3$ ceramic sintered at 700 °C or lower displays a dielectric dispersion at the frequency range from 10 kHz to 1 MHz. The dielectric dispersion has been reported at similar frequency with Fig. 4 in ferrite ceramics and claimed to be caused by a peculiar microstructure; semiconducting grains surrounded by grain boundaries with a relatively high resistances [18]. The dielectric behaviors in Fig. 4 could be explained with the same origin. It has been reported that many impurity ions such as $(OH)^-$, $(NO_3)^-$, and so on are included during a hydrothermal reaction of $BiFeO_3$ in a aqueous solution [14,16]. The ionic defects like oxygen vacancies would be remained or created after evaporating the impurity ions by annealing at 600 °C for 1 h. It has been reported that a part of trivalent irons (Fe^{3+}) change into divalent irons (Fe^{2+}) for electric compensation when oxygen vacancies are formed [17,18]. A small amount of divalent iron ions, which makes the $BiFeO_3$ conductive by electron hopping between Fe^{2+} and Fe^{3+}, could be involved in $BiFeO_3$ ceramics, even though most iron ions are trivalent as confirmed by X-ray diffraction pattern shown in Fig. 1. When the $BiFeO_3$ samples are sintered in an air atmosphere, the grain boundary area would be more completely oxidized during sintering than the inner parts of grains. This microstructure is thought to result in the dielectric dispersions shown in Fig. 4. The $BiFeO_3$ ceramic sintered at 750 °C or higher does not display such a dielectric dispersion but a similar dielectric behavior with the $BiFeO_3$ ceramics reported in other papers which were prepared by solid state reaction at 800 °C or higher. Faster oxygen diffusion at the higher sintering temperature would bring about more uniform microstructure. The dielectric constant and loss decreased gradually in the $BiFeO_3$ ceramics sintered at 750 °C or higher when the frequency increased from 1 kHz to 1 MHz and were about 85 and 0.4 at 100 kHz.

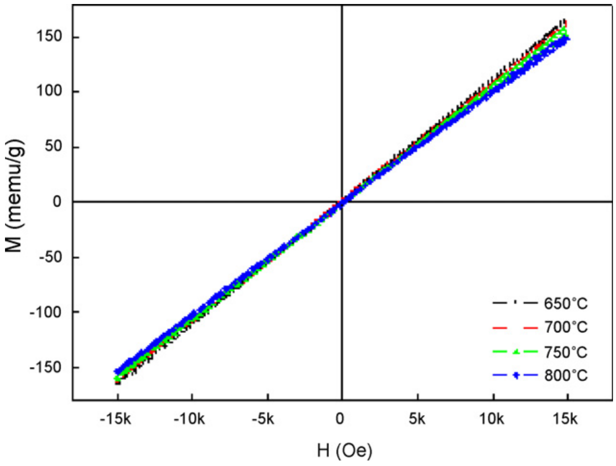

Fig. 3. M–H hysteresis of the $BiFeO_3$ ceramics sintered at 650–800°C.

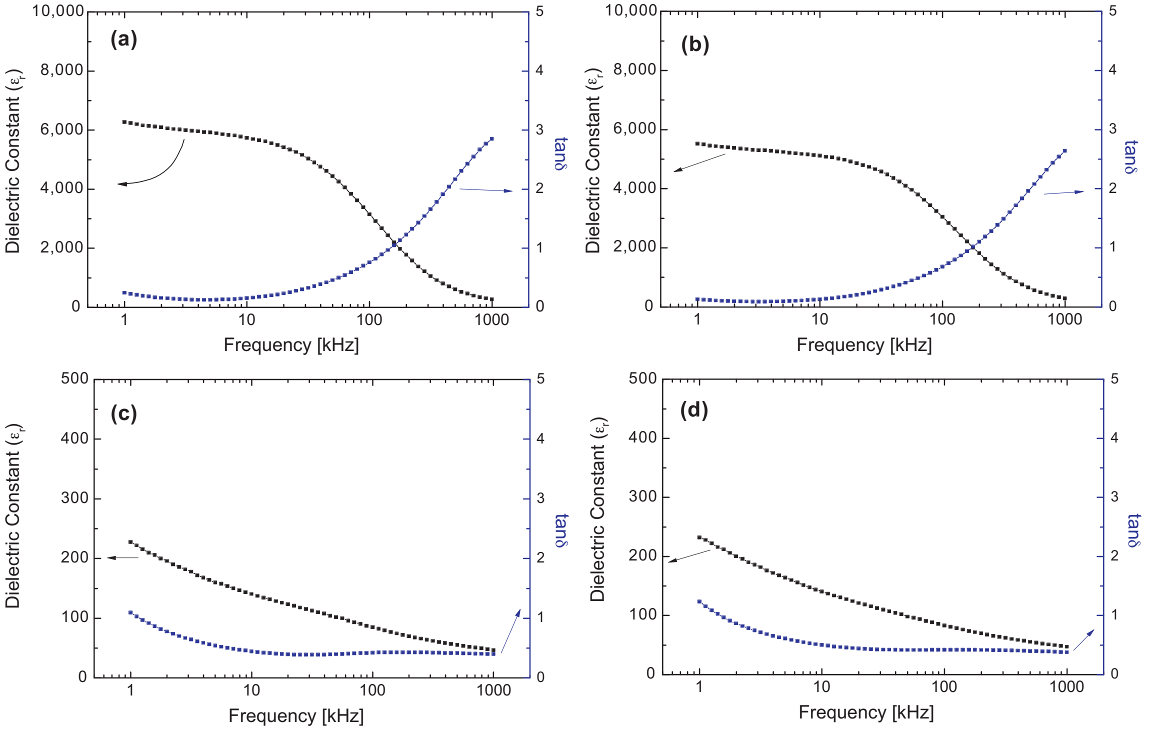

Fig. 4. Dielectric properties of the $BiFeO_3$ ceramics sintered at (a) 650, (b) 700, (c) 750, and (d) 800 °C as a function of a measuring frequency.

4. Conclusion

The $BiFeO_3$ ceramics were prepared with single phase $BiFeO_3$ powders synthesized at 200 °C via hydrothermal route. Phase pure $BiFeO_3$ phase was observed with no impurity phase in ceramics sintered at a temperature up to 800 °C. Dense ceramics with several micron-sized grains were fabricated at the sintering temperature of 700 °C, which was lower than that of a $BiFeO_3$ ceramic prepared by a solid state reaction by 100 °C or more. $BiFeO_3$ ceramics show linear M–H curves in low H, which are antiferromagnetic behavior. The dielectric dispersion was observed at the frequency range of 10 kHz to 1 MHz in the $BiFeO_3$ ceramic sintered at 700 °C or lower. The dielectric constant and loss of the $BiFeO_3$ ceramics sintered at 750 °C or higher were about 85 and 0.4 at 100 kHz, respectively.

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