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Fabrication and Characterization of (1-x)$BiFeO_3$-$xBaTiO_3$ Ceramics Prepared by a Solid State Reaction Method

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In this study, $BiFeO_3$-$BaTiO_3$ ceramics have been fabricated by a solid-state reaction method. The effects of $BaTiO_3$ content in the (1-x)$BiFeO_3$-$xBaTiO_3$ (x = 0.1, 0.2, 0.25, 0.3, 0.4, 0.5) system on crystal structure and magnetic, dielectric, and ferroelectric properties were investigated. Perovskite $BiFeO_3$ was stabilized through the formation of a solid solution with $BaTiO_3$. Rhombohedrally distorted structure (1-x)$BiFeO_3$-$xBaTiO_3$ ceramics showed strong ferromagnetism at x = 0.5. Dielectric and ferroelectric properties of the $BiFeO_3$-$BaTiO_3$ system also changed significantly upon addition of $BaTiO_3$. It was found that the maximum dielectric and ferroelectric properties were exhibited in the (1-x)$BiFeO_3$-$xBaTiO_3$ system at x = 0.25. This suggested the morphotropic phase boundary (MPB) with the coexistence of both rhombohedral and cubic phases of the (1-x)$BiFeO_3$-$xBaTiO_3$ system at x = 0.25.

Keywords : $BiFeO_3$, $BaTiO_3$, ferromagnetism, ferroelectric, dielectric

1. Introduction

Recently, multiferric materials, where both electric and magnetic polarizations coexist, have been extensively studied. This class of materials is considered to offer a large application potential for novel devices by taking advantage of 2 coupled ferric properties based on local off-centered crystal distortion and electron spin [1, 2]. $BiFeO_3$ is a representative material that shows ferroelectric (T_C: 1103 K) and antiferromagnetic (T_N: 643 K) properties [3-5]. The crystallographic structure of $BiFeO_3$ is a rhombohedrally distorted perovskite structure [6]. In addition, it is also known to exhibit weak ferromagnetism at room temperature due to a residual moment from a canted spin structure [7, 8]. The spontaneous polarization of $BiFeO_3$ single crystals has been reported to be 3.5 $\mu C/cm^2$ along the <100> direction and 6.1 $\mu C/cm^2$ along the <111> direction at 77 K [9]. However, the preparation of pure $BiFeO_3$ in a bulk form without traces of impurities has proven a difficult task. Therefore, $BiFeO_3$-ABO_3 solid solution systems have attracted great attention as a means to increase structural stability. Furthermore, another serious problem of $BiFeO_3$-based ceramics is their low, electrical resistivity, which affects the measurement of ferroelectric (dielectric) properties at ambient temperatures. $BaTiO_3$ is a prototype ferroelectric material with several excellent ferroelectric properties (T_C: 393 K, P_S: 26 $\mu C/cm^2$, and $\varepsilon_r > 1000$), and is expected that both ferroelectricity and ferromagnetism still coexist in the new compound formed when mixed with $BiFeO_3$.

In this work, perovskite (1-x)$BiFeO_3$-$xBaTiO_3$ (x = 0, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5) ceramics were prepared by the solid-state reaction method. Effects of $BaTiO_3$ content on crystallographic phase, magnetization behavior, and electrical properties of the resultant (1-x)$BiFeO_3$-$xBaTiO_3$ ceramics were investigated.

2. Experimental Procedure

The (1-x)$BiFeO_3$-$xBaTiO_3$ ceramics were prepared by a solid-state reaction with conventional milling and firing

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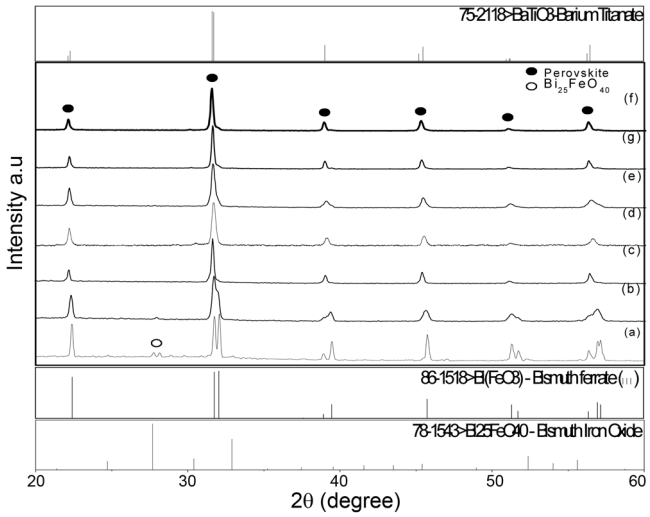

Fig. 1. XRD patterns of (1-x)$BiFeO_3$-$x$$BaTiO_3$ ceramics: (a) x = 0; (b) x = 0.1; (c) x = 0.2; (d) x = 0.25; (e) x = 0.3; (f) x = 0.4; (g) x = 0.5.

techniques. $BaCO_3$, TiO_2, Bi_2O_3, and Fe_2O_3 powders corresponding to the (1-x)$BiFeO_3$-$x$$BaTiO_3$ (x = 0.1, 0.2, 0.25, 0.3, 0.4, 0.5) were mixed by a conventional ball-milling method for 30 min. The mixtures were dried, pressed, and calcined at 900°C for 5 h at a rate of 5°C/min. The calcined samples were ground and pressed into pellets, with polyvinyl alcohol as the binder. The powder compacts were subsequently sintered at 925-1050°C for 2 h at heating and cooling rates of 5°C/min.

Crystallographic phase identification of the prepared (1-x)$BiFeO_3$-$x$$BaTiO_3$ ceramics was performed by X-ray diffraction (XRD) analysis using CuKα radiation with a monochromator. The magnetization behavior of the (1-x)-$BiFeO_3$-$x$$BaTiO_3$ powder samples was characterized using a vibrating sample magnetometer (VSM). The dielectric properties were evaluated with an impedance gain phase analyzer. The polarization-electric (P-E) hysteresis loop was also measured using the Sawyer-Tower circuit at room temperature.

3. Results and Discussion

3.1. Phase Identification

As shown in Fig. 1, XRD patterns show that (1-x)-$BiFeO_3$-$x$$BaTiO_3$ (x = 0.1, 0.2, 0.25, 0.3, 0.4, 0.5) ceramics crystallize in the perovskite single phase, without any second phase like pyrochlore. Conversely, $BiFeO_3$ (x = 0) ceramics crystallized in the perovskite $BiFeO_3$ with a small amount of $Bi_{25}FeO_{40}$ phase, as shown in Fig. 1a. Regarding $BiFeO_3$, it has proven a difficult task to prepare a pure compound because of the low structural stability of perovskite $BiFeO_3$ and its relatively low tolerance factor. However, the diffraction lines of the impurity phase disappeared by formation of a solid solution with $BaTiO_3$, as shown in Fig. 1(b)-(g). Crystallographic symmetry of $BiFeO_3$-$BaTiO_3$ changed from rhombohedral to cubic near x = 0.3. In an earlier report, the crystal structure was rhombohedral between x = 0 and 0.33, cubic between x = 0.33 and 0.925, and tetragonal over x = 0.925 [10].

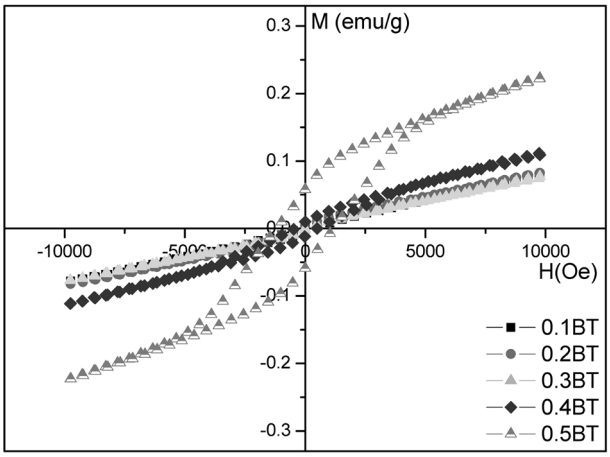

Fig. 2. M-H Hysteresis loops of (1-x)$BiFeO_3$-$x$$BaTiO_3$ ceramic powders x = 0.1-0.5.

3.2. Magnetic Properties

The magnetization behavior of perovskite (1-x)$BiFeO_3$-$x$$BaTiO_3$ was evaluated using a VSM. Fig. 2 shows the M-H hysteresis loops of (1-x)$BiFeO_3$-$x$$BaTiO_3$ (x = 0.1, 0.2, 0.3, 0.4, 0.5) crystalline powders measured at room temperature. These powders were prepared by grinding the sintered (1-x)$BiFeO_3$-$x$$BaTiO_3$ disks. The samples showed typical M-H hysteresis loops of weak ferromagnetism at x = 0.1, 0.2, and 0.3, and stronger ferromagnetism at x = 0.4 and 0.5. The usual polycrystalline $BiFeO_3$ ceramics showed M-H hysteresis loops without spontaneous magnetization [11]. The onset of ferromagnetism of the $BaTiO_3$-rich compositions is thought to depend upon the structural distortion (rhombohedrally distorted crystal structure) [12] and statistical distributions of Fe^{3+} and Ti^{4+} ions in the octahedral sites of $BiFeO_3$-$BaTiO_3$ [13].

3.3. Electrical Properties

The perovskite (1-x)$BiFeO_3$-$x$$BaTiO_3$ single-phase ceramics were obtained for x = 0.1, 0.2, 0.25, 0.3, 0.4, and 0.5 compositions, as described in 3.1. These ceramics also showed high sintered densities near 90% of the theoretical density. Dielectric properties of (1-x)$BiFeO_3$-$x$$BaTiO_3$ sintered bodies were evaluated at room temperature. However, the insulating resistance of the x = 0.1, 0.2, 0.25,

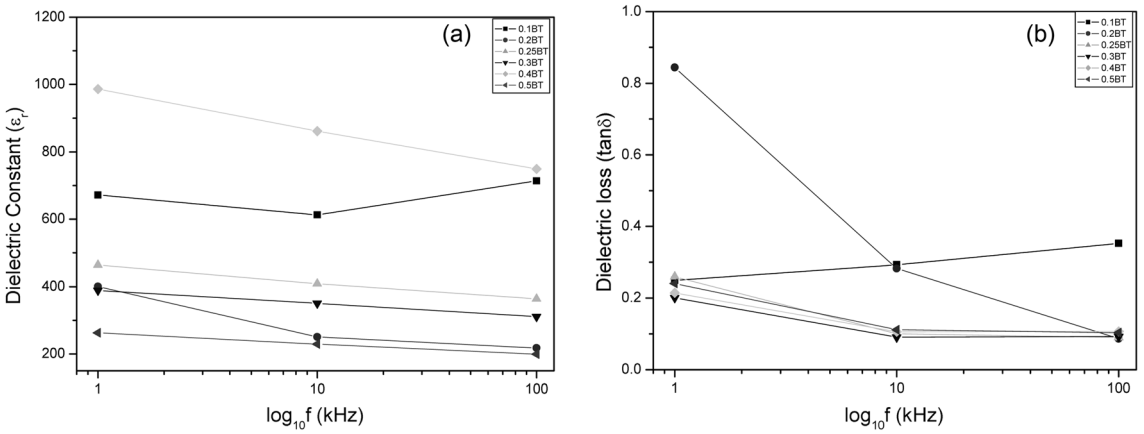

Fig. 3. (a) Dielectric constant and (b) dielectric loss of (1-x)$BiFeO_3$-$x$$BaTiO_3$ as a function of measuring frequency.

0.3, 0.4, and 0.5 samples was too low to characterize the temperature-dependent dielectric properties, regardless the amount of $BaTiO_3$. The values of dielectric loss (tanδ) of the samples were rather high over a wide frequency range. Among them, the electrical resistivity of the 0.75$BiFeO_3$-0.25$BaTiO_3$ sample was 4.7×10^3 Ω·cm.

Fig. 3 shows the frequency dependence of the dielectric constant (ε_r) and dielectric loss (tanδ) for (1-x)$BiFeO_3$-$x$$BaTiO_3$ ceramics. Higher dielectric constants (ε_r) in some composition are possibly due to high dielectric loss (tanδ). When $BaTiO_3$ was added, the dielectric constant value increased. However, at $x = 0.5$ composition the dielectric constant decreased because the ceramics were insufficiently sintered (determined from SEM micrographs not shown here and a relatively lower value in density of < 90% the theoretical density). The insulating resistance of the sample was high at 0.75$BiFeO_3$-0.25$BaTiO_3$, suggesting that 0.75$BiFeO_3$-0.25$BaTiO_3$ behaves as an acceptor

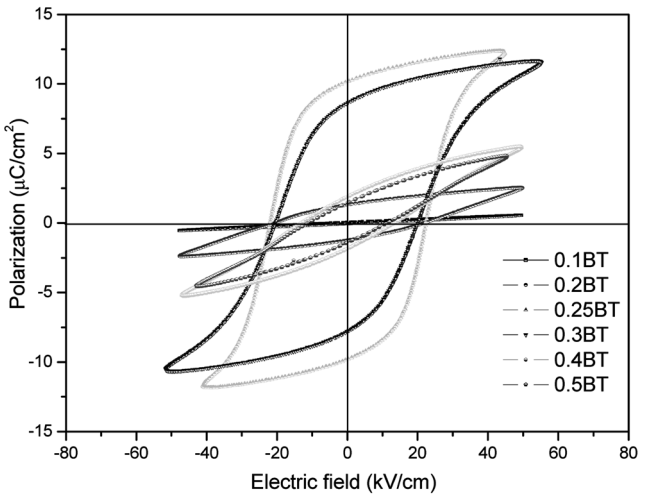

Fig. 4. P-E Hysteresis loops of the (1-x)$BiFeO_3$-$x$$BaTiO_3$ sample sintered at 925°C.

due to its multivalency and prevents electron hopping ($Fe^{3+} \rightarrow Fe^{2+}$) in (1-$x$)$BiFeO_3$-$x$$BaTiO_3$. The ε_r values of the $BiFeO_3$-$BaTiO_3$ ceramics were approximately 250-650. Higher loss of low frequency 1 kHz may be a result of surface charge conduction that increases the dielectric loss. A decrease of the dielectric properties with increasing frequency is caused by the inability of various polarization contributions to follow the change of the applied electric field, leading to lower dielectric constants and loss at higher frequencies.

Fig. 4 shows the P-E hysteresis loops of (1-x)$BiFeO_3$-$x$$BaTiO_3$ measured at a frequency of 50 kHz and room temperature. These samples showed typical ferroelectric P-E hysteresis loops at an applied field of 40-50 kV/cm. When $BaTiO_3$ was added, P-E hysteresis loops of the (1-x)$BiFeO_3$-$x$$BaTiO_3$ system could be changed. The P-E hysteresis loop at $x = 0.1$ was paraelectric. $BaTiO_3$ addition helped increase ferroelectric properties. At $x >$ 0.25, the hysteresis loops were similar to the $BaTiO_3$ ceramic, and the remnant polarization decreased, possibly due to samples incompletely sintered (observed from SEM micrographs not shown here and the density of the sinter specimen near < 90% the theoretical density). The best hysteresis loop was obtained in the 0.75$BiFeO_3$-0.25$BaTiO_3$ composition. The remnant polarization (P_r) and coercive field (E_c) (sintered at 925°C) was approximately 12 μC/cm^2 and 22 kV/cm, respectively. However, further improvement of ferroelectric properties is clearly required; therefore, optimization of the 0.75$BiFeO_3$-0.25-$BaTiO_3$ is currently under investigation.

4. Conclusions

Perovskite (1-x)$BiFeO_3$-$x$$BaTiO_3$ ceramics were successfully prepared by the solid-state reaction method. In this system, impurity peaks of a second phase disappeared by

formation of a solid solution with $BaTiO_3$. Perovskite $BiFeO_3$ was then stabilized through the formation of a solid solution with $BaTiO_3$. Rhombohedrally distorted structure $(1\text{-}x)BiFeO_3\text{-}xBaTiO_3$ ceramics showed strong ferromagnetism at $x = 0.5$. Dielectric and ferroelectric properties of the $BiFeO_3$-$BaTiO_3$ system also changed significantly with $BaTiO_3$ content. It was found that the maximum dielectric and ferroelectric properties were exhibited in the $(1\text{-}x)BiFeO_3\text{-}xBaTiO_3$ system at $x = 0.25$, suggesting the morphotropic phase boundary (MPB) (consisting of both rhombohedral and cubic phases) of the $(1\text{-}x)BiFeO_3\text{-}xBaTiO_3$ system at $x = 0.25$.

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