Multiferroic properties of BiFeO$_3$–BaTiO$_3$ based ceramics

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Perovskite single-phase ceramics of Mn-doped (1 − $x$)BiFeO$_3$–xBaTiO$_3$ with a wide range of composition ($x = 0.1$–1.0) were prepared using the solid-state reaction. Remanent polarization $P_r$ was observed for (1 − $x$)BiFeO$_3$–xBaTiO$_3$ ($x = 0.15$–1.0) and remanent magnetization $M_r$ was observed for (1 − $x$)BiFeO$_3$–xBaTiO$_3$ ($x = 0.15$–0.8). The maximum value of $P_r$ was 39 μC/cm$^2$ was obtained at $x = 0.33$ with a high Curie temperature $T_C$, of 420°C. The maximum value of $M_r$ was 0.18 emu/g was obtained at $x = 0.33$ with a high magnetic Curie temperature $T_{CM}$, of 360°C. A multiferroic phase diagram is constructed from the $T_C$ and $T_{CM}$ observed for the samples. A multiferroic state is maintained to a high temperature up to 250°C in the wide range of $x = 0.15$–0.55.

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1. Introduction

Magnetoelastic multiferroics with both ferroelectric and ferromagnetic ordering have attracted attention because they are considered to provide potential for novel devices, such as multi-value memory and multi-tunable devices.¹² BiFeO$_3$ is a typical multiferroic material, in which ferroelectricity (Currie temperature, $T_C$: 830°C and antiferromagnetism (Néel temperature, $T_N$: 370°C) are both present at room temperature.³ BiFeO$_3$ thin films have been reported to exhibit a very large remanent polarization $P_r$ of 102 μC/cm$^2$.⁴ In the (1 − $x$)BiFeO$_3$–xBaTiO$_3$ system, a structural phase boundary from the rhombohedral to cubic structure exists at around $x = 0.33$, where anomalies in the dielectric and magnetic susceptibilities have been reported.³ The (1 − $x$)BiFeO$_3$–xBaTiO$_3$ ceramics with $x = 0.20$ and $x = 0.33$ exhibited relatively large $P_r$ of 40 and 35 μC/cm$^2$, respectively.⁵ The ferroelectric properties and microdomain structures in the cubic phase of $0.33 < x < 0.5$ were investigated using transmission electron microscopy.⁷ These ceramics have nano-scaled polar domains and $P_r$ decreases with an increase of $x$ in this region.

The doping of Mn has been reported to be effective to reduce the DC conductivity and improve the ferroelectric and piezoelectric properties.⁸ Mn-doped 0.67BiFeO$_3$–0.33BaTiO$_3$ ceramics exhibit a $P_r$ of 15.2 μC/cm$^2$ and a piezoelectric constant $d_{33}$ of 70 pm/V under a small electric field, and a piezoelectric strain constant of 327 pm/V at a high electric field strength of 60 kV/cm measured from a strain-electric field curve, and a high $T_C$ around 400°C.⁹ Ternary systems of BiFeO$_3$–BaTiO$_3$–Bi(Mg$_{1/2}$Ti$_{1/2}$)$_2$O$_3$ have been investigated with an aim to improve the ferroelectric properties.¹⁰ BiFeO$_3$–BaTiO$_3$ based thin films have been prepared using pulsed laser deposition for piezoelectric microelectromechanical system (MEMS) applications.¹¹ In addition, BiFeO$_3$–BaTiO$_3$ based thick films have been prepared using screen printing for piezoelectric actuators.¹² The remanent magnetization $M_r$ of (1 − $x$)BiFeO$_3$–xBaTiO$_3$ has been reported for $x = 0.1$ and 0.2,¹³,¹⁴ and for $x = 0.2$ and 0.33,¹⁵ $M_r$ up to $x = 0.5$ was reported due to field induced ordering of the magnetic moment and large $M_r > 0.32$ emu/g was obtained under an applied field of 50 kOe.¹⁵ Mn-doping was reported to cause an increase of spontaneous magnetization in the BiFeO$_3$ thin film.¹⁶ The possibility of room temperature magnetoelectric coupling has been reported for (1 − $x$)BiFeO$_3$–xBaTiO$_3$ at around $x = 0.25$.

In this study, solid-solution ceramics of Mn-doped (1 − $x$)BiFeO$_3$–xBaTiO$_3$ were prepared and the ferroelectric and ferromagnetic properties were investigated. A wide range of ferromagnetism is expected in addition to improvement of the dielectric and ferroelectric properties by Mn-doping. Measurement of the $M_r$ dependence on the temperature was conducted for the first time, as to the best of our knowledge. From the results, we present a multiferroic phase diagram for the (1 − $x$)BiFeO$_3$–xBaTiO$_3$ system.

2. Experimental procedure

The solid-solution series of (1 − $x$)BiFeO$_3$–xBaTiO$_3$ with 0.5 wt % MnO were prepared by the solid-state reaction method. Bi$_2$O$_3$, Fe$_2$O$_3$, MnO (Kojundo Chemical Lab. Co., Ltd., 99.9%) and BaTiO$_3$ (Sakai Chemical Industry Co., Ltd., 99.9%) were selected as starting materials. After appropriate proportions of the oxide powders were weighed and mixed, calcination was performed at 700–1100°C for 2 h in a closed alumina crucible. The MnO dopant was added in the form of 0.5 wt % with respect to BiFeO$_3$ to reduce the DC conductivity. The calcined products were crushed and ground using a planetary ball mill for 2 h with a zirconia vessel and balls. The ground powder was then granulated with an aqueous polyvinyl alcohol solution as a binder. The granulated powder was pressed into 13 mm diameter and 1 mm thick disks. Prior to sintering, the binder was decomposed at 500°C for 1 h in air. The disks were fired at 850–1300°C for 2 h in a closed alumina crucible.

X-ray diffraction (XRD; Rigaku Co., Smart Lab) with Cu-Kα radiation was employed to analyze the crystalline phase of the samples. The as-fired surfaces of the sintered bodies were observed using scanning electron microscopy (SEM; Jeol Ltd., JSM-6301F). For electrical measurements, the disk samples were polished down to 0.4 mm thick and electrodes were fabricated on both surfaces by screen printing silver paste and then firing at 850°C for

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10 min. $P_r$ and the coercive field were measured from the $P−E$ curve at 1 Hz using a ferroelectric test system (Toyo Corporation, FCE-1). The dielectric properties of the samples were measured using an impedance analyzer (Agilent, 4294A) at 100 kHz from room temperature to 720°C. The magnetization behavior and the temperature dependence of $M_r$ were evaluated using a vibrating sample magnetometer (VSM; Toei Industry Co., Ltd., VSM-5).

3. Results and discussion

3.1 Microstructure and crystallographic phase

**Figure 1** shows SEM micrographs of as-fired surfaces of $(1−x)BiFeO_3−xBaTiO_3$ ceramics. The optimum firing temperatures to obtain the maximum density for $x = 0, 0.05, 0.15, 0.25, 0.33, 0.4, 0.5, 0.6, 0.7, 0.8$ and $0.9−1.0$ were 850, 925, 975, 1025, 1050, 1075, 1100, 1150, 1175, 1200 and 1300°C, respectively. Dense microstructures were obtained for all samples. Large grain growth of 5 to 10 μm was observed for $x = 0.33$ and 0.4. The sintered density of the $x = 0−0.05$ and $0.15−1.0$ ceramics were 93% and >95% of the theoretical density, respectively.

**Figure 2** shows XRD patterns with Cu-Kα radiation of the $(1−x)BiFeO_3−xBaTiO_3$ ceramics. All compositions were crystallized with a perovskite type structure and no secondary phases were evident. The crystallographic phase changes from rhombohedral ($x = 0−0.25$) to tetragonal ($x = 1.0$) across a pseudo-cubic
structure \((x = 0.33 - 0.9)\) with increasing \(x\).

### 3.2 Ferroelectric and dielectric properties

**Figure 3** shows polarization–electric field \((P-E)\) curves for the \((1-x)\)BiFeO\(_3\)–xBaTiO\(_3\) \((x = 0.25, 0.33, \text{and } 0.40)\) ceramics. The \(P-E\) curve for \(x = 0.25\) was not saturated at 60 kV/cm because of the large coercive field. A typical ferroelectric \(P-E\) curve with a square-like shape was obtained for \(x = 0.33\). As \(x\) increases to 0.4, the \(P-E\) curve becomes tighter with a relaxor-like shape. **Figure 4** shows \(P_r\) for the \((1-x)\)BiFeO\(_3\)–xBaTiO\(_3\) ceramics as a function of composition \(x\). The maximum \(P_r\) was at 39 \(\mu\)C/cm\(^2\) for \(x = 0.33\), which is around the boundary of the rhombohedral and pseudo-cubic phases. \(P_r\) decreases with increasing \(x\) above \(x = 0.33\) and then increases at \(x > 0.8\), which corresponds to the change to tetragonal phase. The ferroelectric properties are influenced by the crystallographic phase.

**Figure 5** shows the dielectric constants of the \((1-x)\)BiFeO\(_3\)–xBaTiO\(_3\) ceramics as a function of \(x\) at 25°C. The dielectric constant increases with \(x\) and has a maximum of 3830 at \(x = 0.9\). The temperature dependence of the dielectric constant for the \((1-x)\)BiFeO\(_3\)–xBaTiO\(_3\) ceramics is shown in **Fig. 6**; all compositions had a dielectric constant peak. In this study, the temperature for the dielectric constant peak was defined as the corresponding Curie temperature, \(T_C\). \(T_C\) for the samples increase with increasing \(x\) until \(x = 0.9\), and then increases again above \(x = 0.9\). A dielectric peak maximum of 15,300 and a \(T_C\) of 420°C were obtained for \(x = 0.33\).

### 3.3 Magnetic properties

The magnetization behavior was evaluated by measuring the variation of magnetization \(M\), as a function of the applied magnetic field \(H\), between -10 to 10 kOe using a VSM. **Figure 7** shows \(M-H\) curves for the \((1-x)\)BiFeO\(_3\)–xBaTiO\(_3\) ceramics. Linear responses of the magnetization to the applied magnetic
field were observed for \( x = 0 \) and 0.05, due to antiferromagnetic ordering. With further increase in \( x \), a small remanent magnetic field was observed at \( x = 0.15 \). Typical magnetic hysteresis loops were observed for the \( x = 0.25 - 0.7 \) samples, which indicates that a ferromagnetic moment appears in the \((1-x)\text{BiFeO}_3-x\text{BaTiO}_3\) ceramics. Very small \( M_r \) and coercive magnetic field were again observed at \( x = 0.8 \). The appearance of ferromagnetism is due to canting of the antiferromagnetic ordering chain caused by the structural distortion. The ferromagnetism changes into the paramagnetic state with a linear response of the magnetization to the applied magnetic field at \( x = 0.9 \). Figure 8 shows \( M_r \) for the \((1-x)\text{BiFeO}_3-x\text{BaTiO}_3\) ceramics as a function of \( x \). A maximum \( M_r \) of 0.18 emu/g was obtained at \( x = 0.33 \), which then decreases with an increase of \( x \) above \( x = 0.33 \). This is ascribed to a decrease of \( \text{Fe}^{3+} \) ions. Moreover, \( M_r \) was observed over a wide range of the \((1-x)\text{BiFeO}_3-x\text{BaTiO}_3\) \( (x = 0.15-0.8) \) system. This may be due to the \( \text{Mn}^{3+} \) ion doping, which is changed from \( \text{MnO} \) during the firing. This mechanism can be understood by modification of the long range spiral antiferromagnetic ordering. The ferroelectric properties were affected by the ordering of magnetic ions, which can be modified throughout the solid-solution series. The temperature dependence of \( M_r \) for the \((1-x)\text{BiFeO}_3-x\text{BaTiO}_3\) ceramics is shown in Figure 9. \( M_r \) decreases with increasing temperature and becomes zero at the corresponding magnetic Curie temperature \( T_{CM} \), which decrease with increasing \( x \). A high magnetic Curie temperature of 360°C was obtained for \( x = 0.33 \).
3.4 Multiferroic phase diagram

A multiferroic phase diagram, constructed from the $T_C$ and $T_{CM}$ data for the $(1-x)$BiFeO$_3$–xBaTiO$_3$ ceramics as a function of $x$, is shown in Fig. 10, where AF-M, F-M and P-M represent antiferromagnetic, ferromagnetic and paramagnetic, respectively. F-E and P-E represent ferroelectric and paraelectric, respectively. The multiferroic state is maintained at a high temperature of around 250°C for the wide range of $x = 0.15$–0.55. These compositions have promising potential for information storage applications such as multi-value memory devices. We suggest that the significant magnitude of magnetoelectric coupling required for multi-tunable devices may be obtained at around $x = 0.4$, due to of the almost equivalent $T_C$ and $T_{CM}$, in addition to the reported composition $x = 0.25$.18

4. Conclusions

Perovskite single-phase ceramics of $(1-x)$BiFeO$_3$–xBaTiO$_3$ were successfully prepared by solid-state reaction with Mn-doping. Remanent polarization $P_r$ was observed for $(1-x)$BiFeO$_3$–xBaTiO$_3$ in the range of $x = 0.15$–1.0 and remanent magnetization $M_r$ was observed for $(1-x)$BiFeO$_3$–xBaTiO$_3$ in the range of $x = 0.15$–0.8. The maximum $P_r$ of 39 μC/cm$^2$ was obtained at $x = 0.33$ with a high Curie temperature $T_C$ of 420°C. The maximum $M_r$ of 0.18 emu/g was obtained at $x = 0.33$ with a high magnetic Curie temperature $T_{CM}$ of 360°C. The multiferroic state is maintained at a high temperature of around 250°C for the wide range of $x = 0.15$–0.55. These compositions have promising potential for information storage applications such as multi-value memory devices.

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