

## Fabrication and Properties of BiFeO<sub>3</sub>-SrTiO<sub>3</sub> Ceramics by Solid State Reaction

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Perovskite BiFeO<sub>3</sub>-SrTiO<sub>3</sub> ceramics have been prepared by the solid state reaction. The effect of SrTiO<sub>3</sub> content in BiFeO<sub>3</sub>-SrTiO<sub>3</sub> system on the crystal structure was investigated. Single phase of perovskite BiFeO<sub>3</sub>-SrTiO<sub>3</sub> ceramics were successfully fabricated, whereas pure BiFeO<sub>3</sub> ceramics contained a small amount of second phase in perovskite BiFeO<sub>3</sub>. Crystallographic symmetry of BiFeO<sub>3</sub>-SrTiO<sub>3</sub> changes from rhombohedral to cubic when the amount of SrTiO<sub>3</sub> exceeded 20 mol%. Mn doping to BiFeO<sub>3</sub>-SrTiO<sub>3</sub> is very effective in controlling the grain growth and improving the sintered density. The dielectric properties of resultant ceramics were also improved by the Mn doping. Furthermore, rhombohedrally distorted Mn-doped BiFeO<sub>3</sub>-SrTiO<sub>3</sub> show weak ferromagnetism at room temperature.

Key words: BiFeO<sub>3</sub>-SrTiO<sub>3</sub>, perovskite, Mn doping, dielectric properties, ferromagnetism

### 1. INTRODUCTION

Multiferroic materials, which exhibit a coexistence of ferroic orderings such as ferroelectricity and ferromagnetism, are considered to offer various potential applications in novel devices such as information storage memories and sensors. Among this type of materials, BiFeO<sub>3</sub> is a well-known material which has ferroelectric ( $T_C$  : 1103K) and antiferromagnetic ( $T_N$  : 643K) properties [1,2]. The crystal structure of BiFeO<sub>3</sub> is a rhombohedrally distorted perovskite [3]. In addition, it is also known to exhibit weak ferromagnetism at room temperature due to a residual moment from a canted spin structure [4,5]. The spontaneous polarization of BiFeO<sub>3</sub> single crystal has been reported to be 3.5  $\mu\text{C}/\text{cm}^2$  along the <100> direction and 6.1  $\mu\text{C}/\text{cm}^2$  along the <111> direction at 77K [6]. However, the preparation of pure BiFeO<sub>3</sub> ceramics without traces of impurities is usually a difficult task. Therefore, BiFeO<sub>3</sub>-ABO<sub>3</sub> solid solution systems have attracted great attention as a means to increase structural stability. Furthermore,

another problem of BiFeO<sub>3</sub>-based ceramics is their low electrical resistivity, which affects the measurement of dielectric (ferroelectric) properties at ambient temperatures.

This paper describes the synthesis of perovskite (1-x)BiFeO<sub>3</sub>-xSrTiO<sub>3</sub> (x=0, 0.1, 0.2) ceramics by the solid-state reaction. Effects of SrTiO<sub>3</sub> content and Mn doping on crystallographic phase, electrical and magnetic properties of resultant BiFeO<sub>3</sub>-SrTiO<sub>3</sub> ceramics were examined.

### 2. EXPERIMENTAL PROCEDURE

(1-x)BiFeO<sub>3</sub>-xSrTiO<sub>3</sub> and Mn-doped 0.9BiFeO<sub>3</sub>-0.1SrTiO<sub>3</sub> ceramic samples were prepared by a solid-state reaction that used conventional milling and firing techniques. Bi<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub> and SrTiO<sub>3</sub> powders corresponding to the (1-x)BiFeO<sub>3</sub>-xSrTiO<sub>3</sub> (x=0, 0.1, 0.2) and y mol% Mn-doped 0.9BiFeO<sub>3</sub>-0.1SrTiO<sub>3</sub> (y=0, 0.4, 0.8, 1.6) compositions with 0.75 mol% of excess Bi were weighed and thoroughly mixed using stabilized ZrO<sub>2</sub> balls in ethanol. The mixtures were dried, pressed, and calcined at 750-800°C

for 2 h at a rate of  $10^\circ\text{C}/\text{min}$ . The calcined samples were ground and pressed into pellets. In this case, polyvinyl alcohol was used as a binder. The powder compacts subsequently sintered at  $850\text{-}1000^\circ\text{C}$  for 3-10 h at a rate of  $10^\circ\text{C}/\text{min}$ .

Crystallographic phase of prepared  $(1-x)\text{BiFeO}_3\text{-}x\text{SrTiO}_3$  ceramics was characterized by X-ray diffraction (XRD) analysis using  $\text{CuK}\alpha$  radiation with a monochromator. The microstructure of the samples was observed by scanning electron microscopy (SEM). For dielectric measurements, Ag paste was fired at  $650^\circ\text{C}$  for 5 min at both surfaces of the disk. The dielectric properties were evaluated with an impedance gain phase analyzer at room temperature. The magnetization behavior of  $(1-x)\text{BiFeO}_3\text{-}x\text{SrTiO}_3$  powder samples was characterized using a vibrating sample magnetometer (VSM) at room temperature.

### 3. RESULT AND DISCUSSION

#### 3.1 Crystallographic phase of prepared $\text{BiFeO}_3\text{-SrTiO}_3$ ceramics

Figure 1 illustrates XRD patterns of  $(1-x)\text{BiFeO}_3\text{-}x\text{SrTiO}_3$  ( $x=0, 0.1, 0.2$ ) ceramics.  $(1-x)\text{BiFeO}_3\text{-}x\text{SrTiO}_3$  ( $x=0.1, 0.2$ ) were found to crystallize in the perovskite single phase without any formation of second phase like pyrochlore. On the other hand, pure  $\text{BiFeO}_3$  ( $x=0$ ) ceramics crystallizes in the perovskite  $\text{BiFeO}_3$  with a small amount of  $\text{Bi}_{36}\text{Fe}_2\text{O}_{57}$  phase as shown in Fig. 1(a). As for  $\text{BiFeO}_3$ , it has always been difficult to fabricate a pure compound because of the low structural stability of perovskite  $\text{BiFeO}_3$  with a relatively low tolerance factor. However, the diffraction lines of impurity phase disappeared by the formation of solid solution with  $\text{SrTiO}_3$  as shown in Figs. 1(b) and (c). Furthermore, crystallographic symmetry of  $\text{BiFeO}_3\text{-SrTiO}_3$  changes from rhombohedral to cubic at  $x \geq 0.2$ . From the results described above, rhombohedrally distorted  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  composition was

selected and further following investigations were performed.

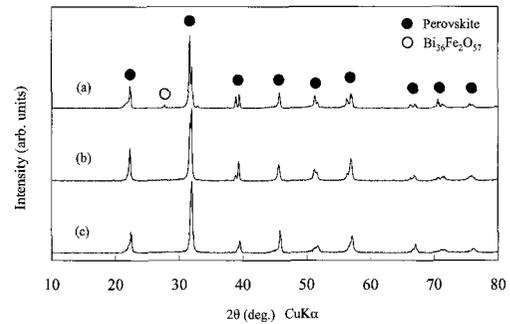


Fig. 1 XRD patterns of  $(1-x)\text{BiFeO}_3\text{-}x\text{SrTiO}_3$  ceramics, (a)  $x=0.0$ , (b)  $x=0.1$  and (c)  $x=0.2$ .

#### 3.2 Sintered density and microstructure of $\text{BiFeO}_3\text{-SrTiO}_3$ ceramics.

The sintered density of the  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics was around 90% of the theoretical value. Therefore, the  $\text{BiFeO}_3\text{-SrTiO}_3$  samples were required to improve the sintered density for the evaluation of dielectric properties. After several preliminary experiments, Mn doping was found to be quite effective in improving the sinterability of  $\text{BiFeO}_3\text{-SrTiO}_3$  ceramics. The sintered density of the Mn-doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  specimens were above 95% of theoretical. Also, these samples crystallize in the rhombohedral perovskite  $\text{BiFeO}_3\text{-SrTiO}_3$  single phase.

Figure 2 shows SEM images of  $y$  mol% Mn doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics ( $y=0, 0.4, 0.8, 1.6$ ). The optimum sintering conditions of  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ( $y=0$ ) and  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics ( $y=0.4, 0.8, 1.6$ ) were found to be  $950^\circ\text{C}$  for 5h and  $970^\circ\text{C}$  for 10h, respectively. The optimum conditions were determined to obtain the maximum densities. The  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics without Mn doping had the grain size ranged from 5 to  $10\ \mu\text{m}$ . As the content of Mn was increased from 0.4 mol% to 1.6 mol%, the average grain size decreases to  $0.5\text{-}1.0\ \mu\text{m}$  in diameter. From the results, Mn ions doped into  $\text{BiFeO}_3\text{-SrTiO}_3$  work

effectively to suppress the undesired grain growth and to improve the sintered density.

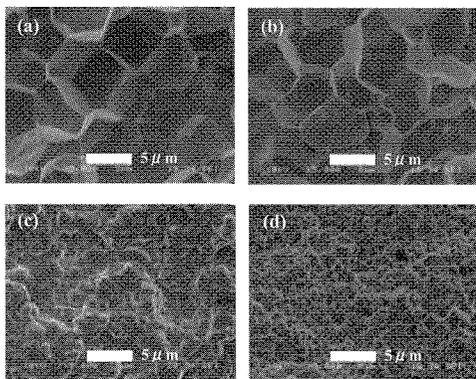


Fig. 2 SEM images of  $y$  mol% Mn-doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics, (a)  $y=0$ , (b)  $y=0.4$ , (c)  $y=0.8$  and (d)  $y=1.6$

### 3.3 Dielectric properties of $\text{BiFeO}_3\text{-SrTiO}_3$ ceramics

Figure 3 shows frequency dependence of dielectric constant ( $\epsilon_r$ ) and loss ( $\tan\delta$ ) for  $y$  mol% Mn doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics ( $y=0, 0.4, 0.8, 1.6$ ). Dielectric properties of the samples were evaluated at room temperature. The dielectric constant ( $\epsilon_r$ ) of the  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ( $y=0, 0.4, 0.8$ ) depended on the measured frequency and it decreases in high frequency region. The values of  $\epsilon_r$  of 1.6 mol% Mn doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics are constant and approximately 100 over a wide frequency range. Kumar et al. reported that the dielectric constant of pure  $\text{BiFeO}_3$  prepared by the conventional solid state reaction was approximately 70 (in 1MHz) [7]. The formation of solid solution with  $\text{SrTiO}_3$  was considered to lower the Curie temperature and affect the value of dielectric constant (higher than pure  $\text{BiFeO}_3$ ) at room temperature.

On the contrary, the dielectric loss shows a reverse trend. The values of dielectric loss ( $\tan\delta$ ) of the  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ( $y=0$ ) were 10-70% in the frequency range  $10^2 - 10^6$  Hz. However, as the amount of Mn was increased, the values of dielectric loss decreases notably in a high frequency region. 1.6 mol% Mn doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics show the lowest dielectric loss less than 5% over a wide frequency

range as shown in Fig. 3. The insulating resistance might be greatly improved by a small amount of Mn doping. This result suggests that doped Mn behaves as an acceptor due to its multivalency, and prevents the electron hopping ( $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ ) in  $\text{BiFeO}_3\text{-SrTiO}_3$  as in the case of  $\text{BiFeO}_3\text{-BaTiO}_3$  ceramics reported by the authors [8]. Since the dielectric properties were improved as described above, the evaluation of ferroelectric properties of the Mn-doped  $\text{BiFeO}_3\text{-SrTiO}_3$  are now under investigation.

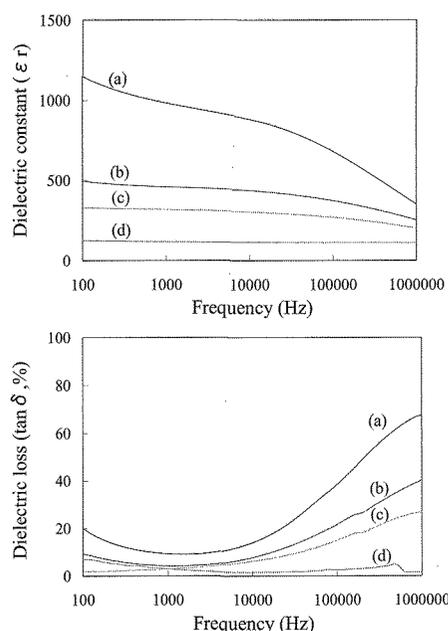


Fig. 3 Dielectric constant and loss of  $y$  mol% Mn-doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  ceramics as a function of measured frequency, (a)  $y=0$ , (b)  $y=0.4$ , (c)  $y=0.8$  and (d)  $y=1.6$

### 3.4 Magnetic properties of perovskite $\text{BiFeO}_3\text{-SrTiO}_3$

The magnetization behavior of Mn-doped  $\text{BiFeO}_3\text{-SrTiO}_3$  was evaluated using a VSM. Figure 4 shows the M-H hysteresis loops of 1.6 mol% Mn doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  crystalline powders measured at room temperature. This powder sample was prepared by grinding the sintered 1.6 mol% Mn doped  $0.9\text{BiFeO}_3\text{-}0.1\text{SrTiO}_3$  disk. In addition to the result of Fig. 4, the samples of all compositions ( $y=0, 0.4, 0.8, 1.6$ ) show typical M-H hysteresis loops of weak ferromagnetism. The concentration of Mn does not affect the shape of

M-H curves and the values of magnetization and coercive force. The onset of ferromagnetism of the BiFeO<sub>3</sub>-SrTiO<sub>3</sub> is considered to depend upon the structural distortion (rhombohedrally distorted crystal structure) [9] and the statistical distributions of Fe<sup>3+</sup> and Ti<sup>4+</sup> ions in the octahedral sites of BiFeO<sub>3</sub>-SrTiO<sub>3</sub>. However, saturated hysteresis loops were not observed for all 0.9BiFeO<sub>3</sub>-0.1SrTiO<sub>3</sub> samples even at a magnetic field of 16 kOe. The usual BiFeO<sub>3</sub> ceramics exhibits quite small magnetization and M-H hysteresis loops without spontaneous magnetization [10]. Also, BiFeO<sub>3</sub>-SrTiO<sub>3</sub> at  $x \geq 0.2$  did not show the spontaneous magnetization, because crystallographic symmetry of BiFeO<sub>3</sub>-SrTiO<sub>3</sub> changes from rhombohedral to cubic. Although further optimization of the chemical composition and processing conditions is needed, rhombohedrally distorted 0.9BiFeO<sub>3</sub>-0.1SrTiO<sub>3</sub> is found to be suitable to obtain weak ferromagnetism at ambient temperatures.

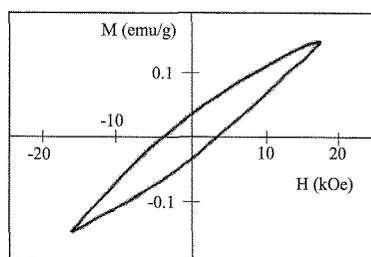


Fig. 4 M-H hysteresis loop of 1.6 mol% Mn-doped 0.9BiFeO<sub>3</sub>-0.1SrTiO<sub>3</sub> ceramic

#### 4. CONCLUSIONS

Perovskite BiFeO<sub>3</sub>-SrTiO<sub>3</sub> ceramics were successfully prepared by the solid state reaction. In this system, impurity peaks of second phase disappeared by the formation of solid solution with SrTiO<sub>3</sub>. The sintered BiFeO<sub>3</sub>-SrTiO<sub>3</sub> samples have relatively low density around 90% of the theoretical value, and these specimens exhibited high dielectric loss. The Mn doping to BiFeO<sub>3</sub>-SrTiO<sub>3</sub> is very effective in improving

the sintered density as well as the electrical properties of the resultant ceramics. The 1.6 mol% Mn-doped 0.9BiFeO<sub>3</sub>-0.1SrTiO<sub>3</sub> ceramics were found to exhibit both low dielectric loss and weak ferromagnetism at room temperature.

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