

## Preparation and properties of multiferroic bismuth iron oxides

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**Abstract** The compositional dependence of bismuth iron oxides and effect of La-substitutions in the structure of BiFeO<sub>3</sub> compounds were investigated, which compounds were synthesized by conventional ceramic processing. It is shown that some of bismuth iron oxides including BiFeO<sub>3</sub> show the narrow single phase region. The effect of La-doping in BiFeO<sub>3</sub> was presented as disappearance of many impurity phases of Bi-Fe-O compounds. The lower electrical resistivity was obtained as those compositions of Fe deficient region and La-doped BiFeO<sub>3</sub>. The saturation magnetization of La-doped BiFeO<sub>3</sub> was increased with La content. The dielectric dispersion was also observed for those Bi-Fe-O compounds with Fe deficient and La-doped BiFeO<sub>3</sub> at low frequencies under 1 kHz.

**Key words** BiFeO<sub>3</sub>, Canted orthoferrite, Multiferroic oxide, Dielectric dispersion

### 1. Introduction

Magnetoelectric multiferroics have drawn increasing interest due to their unique coupling behavior between ferroelectricity, ferromagnetism and ferroelasticity and also because of the potential application for devices in spintronics, information storage, sensing and actuation. In the coexistence of two ferroic orders among the above three parameters, an external field can make the electric polarization and also changes in magnetization resulted in the magnetoelectric (ME) effect. The ferroelectric-antiferromagnetic ME coupling below room temperature is found usually in most multiferroic materials including BiFeO<sub>3</sub> [1, 2]. The orthoferrite BiFeO<sub>3</sub> with rhombohedrally distorted perovskite structure is an interesting material due to their higher ferroelectric Curie temperature ( $T_C \sim 830^\circ\text{C}$ ) and antiferromagnetism below Néel temperature ( $T_N \sim 370^\circ\text{C}$ ). In general, BiFeO<sub>3</sub> is defined as magnetic ferroelectrics such as YMnO<sub>3</sub> and BiMnO<sub>3</sub>. These materials have potential applications for use in magnetoelectric devices and sensors with the typical property of polarization and magnetization as coupled both [3, 4].

On the other hand, those bulky BiFeO<sub>3</sub> ceramics exhibits weak ferromagnetism at room temperature due to residual moment from the canted spin structure generated by the second or impurity phase. The large leakage current due to the low resistivity of the BiFeO<sub>3</sub>

system leads to difficulties in the measurement of ferroelectric hysteresis. The formation of single phase BiFeO<sub>3</sub> is normally difficult and other impurity phases are appeared because of its narrow range for single phase region in phase diagram. Therefore, the cation-modified compositions of BiFeO<sub>3</sub> ceramics can be attracted to study the physical properties of the ferromagnetic interaction observed in ferroelectric BiFeO<sub>3</sub>. These BiFeO<sub>3</sub> ceramics could be useful for potential applications with multiferroic property, but some of researches on microscopic structures and physical properties related to dielectric loss are still requested for further work on the multiferroic applications. While many studies have been reported on these Bi-Fe-O systems, their investigations for application are not successful yet due to the formation of impurity phases and difficulties in controlling the microstructures of single phase BiFeO<sub>3</sub>.

In this paper, we aimed to study the effect of composition in bismuth iron oxides, the properties of Bi-Fe-O ceramics including La-doped solid solution and the development of various microstructures of conventionally sintered ceramics, identification of various crystalline phases, magnetic properties, and frequency-dependent dielectric behavior.

### 2. Experiments

BiFeO<sub>3</sub> samples Bi<sub>1-x</sub>Fe<sub>1+x</sub>O<sub>3</sub> ( $x = -0.2 \sim 0.2$ ) and Bi<sub>1-y</sub>La<sub>y</sub>FeO<sub>3</sub> ( $y = 0.1 \sim 0.3$ ) were synthesized by the conventional solid-state reaction process with stoichiometric mixing of Bi<sub>2</sub>O<sub>3</sub> (99.99%), Fe<sub>2</sub>O<sub>3</sub> (99.99%), La<sub>2</sub>O<sub>3</sub> (99.99%)

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using ethyl alcohol and ground by ball-milling. The mixtures of raw materials were calcined at 500°C for 3 h in air and sintered at 750°C for  $\text{Bi}_{1-x}\text{Fe}_{1+x}\text{O}_3$  system, 850°C for  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  system, respectively. The crystalline phase was identified by X-ray diffraction (XRD, 2311-B/Rigaku) and microscopic images of the sintered samples were observed by Field-Emission Scanning Microscope (FE-SEM, JSM 6700F/Jeol). The electrical resistivity measured at 50~100 V using a High Resistance Meter (Agilent, 4339B). The dielectric constant was measured by Impedance Analyzer (Agilent, 4294A) in 40 Hz~10 MHz range. The magnetization was measured using Vibrating Sample Magnetometer (VSM, Lakeshore) at room temperature.

### 3. Results and Discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of  $\text{Bi}_{1+x}\text{Fe}_{1-x}\text{O}_3$  samples. As shown in Fig. 1, those impurity phases including  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Bi}_{12}(\text{Bi}_{0.5}\text{Fe}_{0.5})\text{O}_{19.5}$ , and  $\text{Bi}_2\text{Fe}_4\text{O}_9$  in Fig. 1(c) are found for all samples of  $x = -0.2 \sim +0.2$ . The presence of those impurity phases is affected by the inhomogeneous materials processing with insufficient reaction time. The effect of La-doping in Bi-Fe-O system is clearly defined from XRD analysis as shown in Fig. 2. As the increasing of La content ( $y$ ) in  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  samples, it is found that those impurity phases are almost disappeared, but still remains as very tiny peaks of the impurity phases.

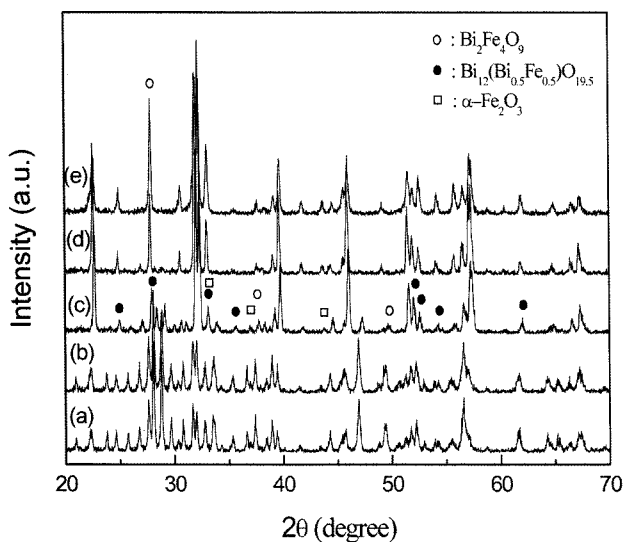


Fig. 1. X-ray diffraction patterns of  $\text{Bi}_{1+x}\text{Fe}_{1-x}\text{O}_3$  samples; (a)  $x = -0.2$ , (b)  $x = -0.1$ , (c)  $x = 0$ , (d)  $x = 0.1$ , and (e)  $x = 0.2$ , respectively [●: impurity phases,  $\text{Bi}_{12}(\text{Bi}_{0.5}\text{Fe}_{0.5})\text{O}_{19.5}$  defined at the JCPDS number 77-0865 and 72-2035].

In general, the electrical property of Bi-Fe-O ceramics is dependent on the presence of impurity phases as shown in Fig. 1 and Fig. 2. Fig. 3 shows the result of

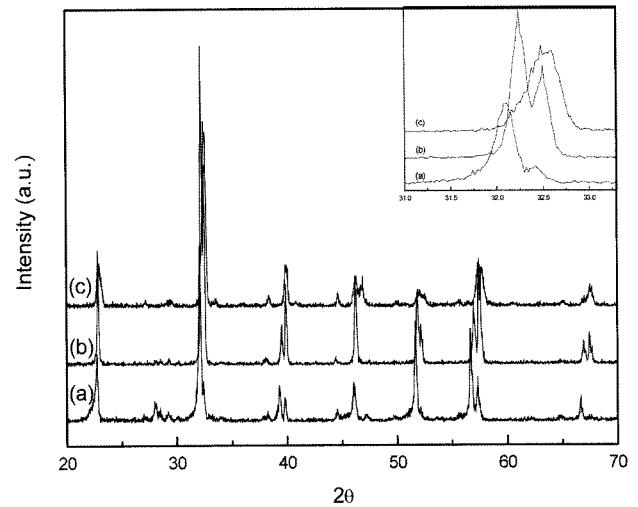


Fig. 2. X-ray diffraction patterns of  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  ceramics; (a)  $y = 0.1$ , (b)  $y = 0.2$ , and (c)  $y = 0.3$ , respectively.

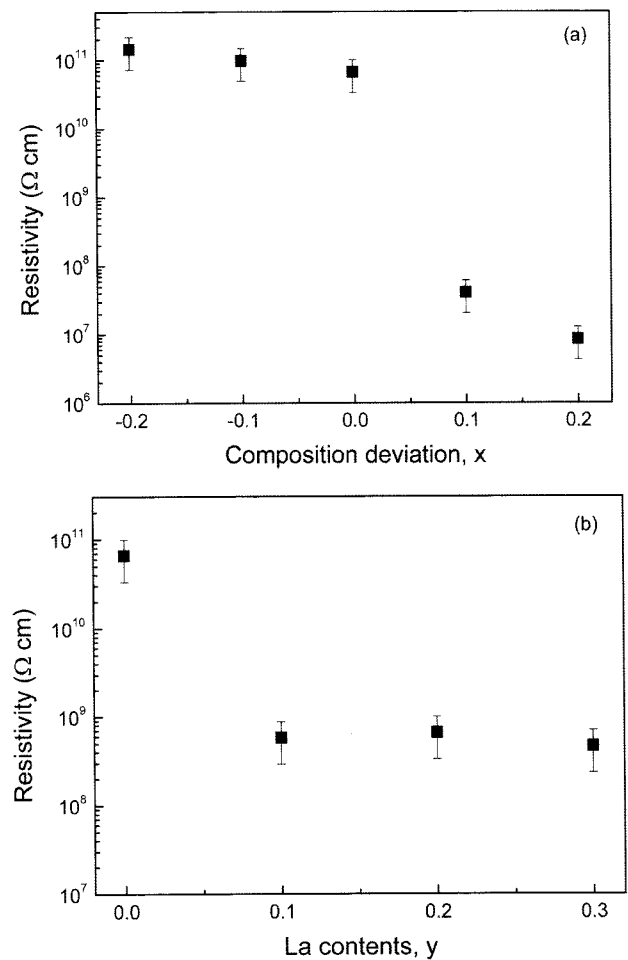


Fig. 3. Variation of the electrical resistivity of Bi-Fe-O ceramics; (a)  $\text{Bi}_{1+x}\text{Fe}_{1-x}\text{O}_3$  samples, (b)  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  samples, respectively.

electrical resistivity of  $\text{Bi}_{1+x}\text{Fe}_{1-x}\text{O}_3$  and  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  samples. The upper value of electrical resistivity (at 100 V) is obtained as about  $6.6\text{--}14 \times 10^{10} \Omega\text{-cm}$  for compositions of  $x = -0.2\text{--}0$ , while the other multi-phase samples ( $x = 0.1\text{--}0.2$ ) have slightly decreased values of about  $8.48\text{--}40.5 \times 10^6 \Omega\text{-cm}$  due to the existence of those impurity phases as shown in Fig. 1. Furthermore, the results in Fig. 3(a) indicate the lower electrical resistivity value is related to the formation of  $\text{Fe}^{2+}$  ions in the Fe-deficient composition [2].

The composition of La-doped samples ( $y = 0.1\text{--}0.3$ ) shows the lower range of electrical resistivity ( $\sim 5.8 \times 10^8 \Omega\text{-cm}$ ) compared to La-free  $\text{BiFeO}_3$  ( $\sim 6.6 \times 10^{10} \Omega\text{-cm}$ ). The reduced electrical resistivity in Bi-Fe-O system is usually related with the porosity in multi-phase samples and leads to a higher conductivity [2]. In order to reduce the leakage current for multiferroic materials and obtain the optimized condition for high polarization, the electrical resistivity value of  $10^8\text{--}10^9 \Omega\text{-cm}$  should be enough to be polarized [5].

Fig. 4 shows the variation of saturation magnetization ( $M_S$ ) of  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  samples. Recently, it has been reported that the rare earth  $\text{La}^{3+}$ -substitution for  $\text{Bi}^{3+}$  ion in  $\text{BiFeO}_3$  composition can modify the rhombohedrally distorted perovskite structure [6]. The  $\text{La}^{3+}$ -ion shows an electron configuration of  $5d^1 6s^2$  and related to the collapse of canted antiferromagnetic order with space-modulated spin structure of  $\text{BiFeO}_3$  [7, 8]. The increase in  $M_S$  with La content ( $y$ ) seems to be related to the modified spin structure of  $\text{BiFeO}_3$  after  $\text{La}^{3+}$ -doping.

The variations of the dielectric constant as a function of frequency in the range of 40 Hz–10 MHz for  $\text{Bi}_{1+x}\text{Fe}_{1-x}\text{O}_3$

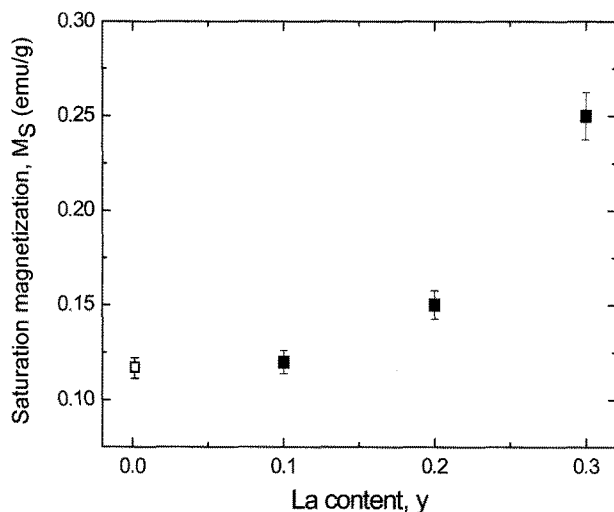


Fig. 4. Saturation magnetization ( $M_S$ ) of  $\text{Bi}_{1+y}\text{La}_y\text{FeO}_3$  samples (□: sintered at 750°C, ■: sintered at 850°C).

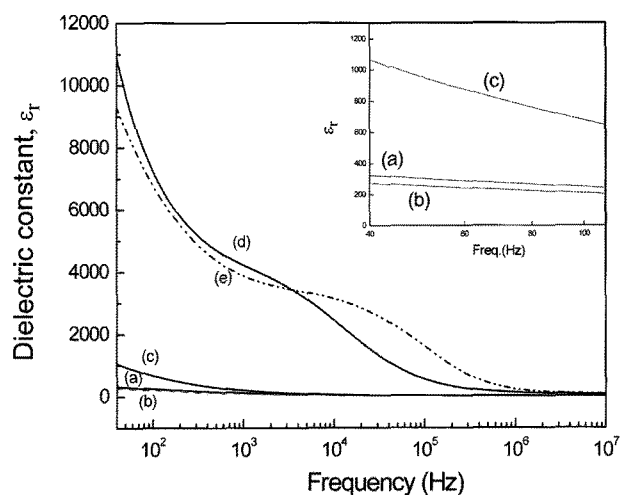


Fig. 5. Variation of the dielectric permittivity of  $\text{Bi}_{1+x}\text{Fe}_{1-x}\text{O}_3$  samples; (a)  $x = -0.2$ , (b)  $x = -0.1$ , (c)  $x = 0$ , (d)  $x = 0.1$ , and (e)  $x = 0.2$ , respectively.

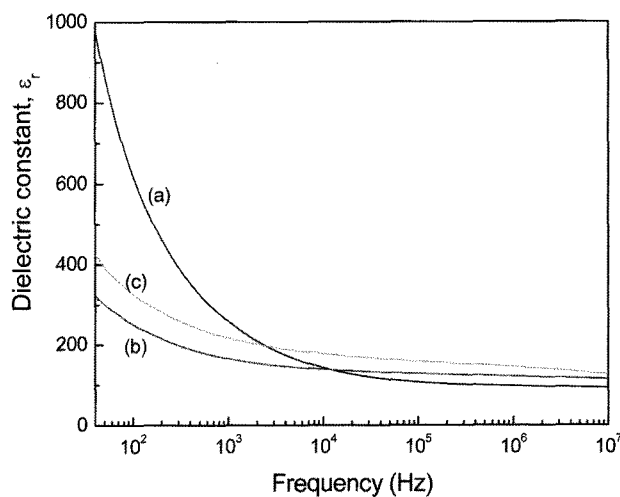


Fig. 6. Variation of the dielectric permittivity of  $\text{Bi}_{1+y}\text{La}_y\text{FeO}_3$  samples; (a)  $y = 0.1$ , (b)  $y = 0.2$ , and (c)  $y = 0.3$ , respectively.

and  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  were shown in Fig. 5 and Fig. 6, respectively. Those Fe deficient composition of  $x = 0.1\text{--}0.2$  in Fig. 5 presented a large dielectric dispersion and nearly constant at high frequencies of over 1 MHz. This kind of behavior can be estimated in terms of the space charge relaxation at a low frequency range under 1 kHz [9].

On the other hand, a large dielectric dispersion is not appeared in the composition of La-doped  $\text{BiFeO}_3$  as shown in Fig. 6. It is clearly found that the frequency-dependent dielectric behavior is not same between  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  and  $\text{BiFeO}_3$ . The cation substitution in  $\text{Bi}^{3+}$  site by  $\text{La}^{3+}$  has presented an enhanced property for multiferroic materials. At below 100 Hz, the vacancies ( $\text{V}_O^{2-}$ ,  $\text{V}_{\text{Bi}}^{3+}$ ) may be affected by frequency and resulted in

higher value of dielectric constant [10]. Above the frequency range of 100 Hz, the dielectric behavior shows the weak dependence on frequency due to the contribution of electron and domains [2, 10].

#### 4. Conclusion

The present investigation of  $\text{Bi}_{1+x}\text{Fe}_{1-x}\text{O}_3$  and  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$  samples has revealed that the cation substitution in  $\text{BiFeO}_3$  may have the effective solutions for an enhanced properties of multiferroic ceramics, which seems to be a promising and adopted as a possible material for improving the multiferroic properties. The compositional change in bismuth iron oxides is strongly related to the crystalline phase transformation accompanying the change in magnetic structure in  $\text{Bi}_{1-y}\text{La}_y\text{FeO}_3$ .

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