

Magnetic and Electric functionalities of magnet-ferroelectrics $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($0 \leq x \leq 0.5$)

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Magnetic and electric properties of $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ system have been observed in order to investigate the correlation between ferroelectric and ferromagnetic transition. Polycrystalline oxides with the formula $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$, ($0 \leq x \leq 0.5$), are prepared. The X-ray diffraction patterns of the pre-heated sample reveal that the starting substances are obtained as single phase. In this study, the lattice parameters are refined, while magnetic and electric properties of the samples were measured. We observed that ferromagnetic region in anti-ferromagnetic matrix is introduced by Mn substitution. Mössbauer spectroscopy was carried out and the hyperfine structure is discussed at room temperature. The Mössbauer parameters of the one six-line sub spectrum agree to usually found for octahedral trivalent iron in oxides.

Key words: BiFeO_3 , BiMnO_3 , magnet-ferroelectrics, Mössbauer spectroscopy, antiferromagnet

1. Introduction

One of the methods to obtain ferroelectric-ferromagnets is to prepare solid solutions of ferroelectric and magnetic materials. Bismuth ferrite, BiFeO_3 is known to have two types of long-range order: The G-type anti-ferromagnetic ordering of the Fe magnetic moments, below $T_N=643\text{K}$, and the ferroelectric ordering, with a high Curie temperature at 810K [1]. It is well known that BiFeO_3 forms solid solutions with a number of other ABO_3 type perovskite materials. It reported in literature that when BiFeO_3 formed solid solutions, the sample exhibits weak ferromagnetism and ferroelectricity at the same time. For example $\text{BiFeO}_3\text{-BaTiO}_3$, $\text{BiFeO}_3\text{-PbTiO}_3$, $\text{BiFeO}_3\text{-Pb}(\text{Fe}_{0.5}\text{Nb}_{0.5}\text{O}_3)$, and $\text{BiFeO}_3\text{-PLZT}$ have been reported to be ferroelectric-ferromagnetic solid solutions [2-7]. Although, there are many reports about ferroelectric materials and BiFeO_3 solid solution systems, there is no report on substituting BiFeO_3 with ferromagnetic material. We have chosen BiMnO_3 , as the perovskite material to substitute, because it originally possesses ferromagnetic properties under 105K . When ferromagnetism and ferroelectricity coexist in a material, novel phenomena such as magneto-electric effect are expected due to the interaction between the magnetization and electric polarization.

Our interest in material is to make a new material that exhibits ferromagnetism and ferroelectricity at the same time. Therefore, in this work, we synthesized and investigated magnetic and electric properties of $\text{BiFeO}_3\text{-BiMnO}_3$ new solid solution system to understand the basic magnetic and electrical nature of these materials.

2. Experimental procedures

2.1 Material

$\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ samples were prepared in air for $x=0$,

0.1, 0.2, 0.3, 0.4, and 0.5 by solid state reaction. Dry Bi_2O_3 , Fe_2O_3 and MnO_2 powders with purities of 99.9% or better were mixed in the atomic ratios of $\text{Bi:Fe:Mn}=1:(1-x):x$ by grinding and then pre-heated in air to 770°C ($x=0$) or 820°C (except for $x=0$) for 15h. The X-ray diffraction pattern of the pre-heated samples reveals that the starting substances had reacted. The pre-heated mixture are ground again and pressed into pellets with diameters of 2cm. The pellets of $x=0$ is sintered in air at 820°C for 15h, and samples with $x=0.1, 0.2, 0.3, 0.4, 0.5$ are heated in air at 850°C for 35h. All the samples are finally cut off into small pieces in order to measure X-ray powder diffraction, magnetic and electric properties, and Mössbauer effect.

2.2 Measurement

X-ray powder diffraction is undertaken at room temperature on a Rigaku Rint2000 diffractometer with $\text{CuK}\alpha$ radiation. In order to eliminate the systematic errors, the silicon powder of a purity of 99.9999% is used as an external standard reference material. The diffraction peak positions of silicon calculated from its lattice constant are employed to calibrate the measured diffraction peak positions of silicon and further to calibrate the diffraction peak positions of the $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ samples.

Magnetization measurements are carried out on a vibration sample magnetometer. (VSM: Toei VSM-5SC-5HF) Temperature dependence of magnetization is measured from liquid helium temperature to 700K under magnetic field of 1000Oe and magnetic ordering temperature is determined. Field dependence of magnetization is measured at 20K and room temperature for all of the samples.

Electric conductivity is measured by using FLUKE 111 multimeter at room temperature. Electric properties, (impedance, dielectric constant) are measured in the temperature range of room temperature to 523K by

using an impedance analyzer (HP4192a). Dielectric constant is measured using 10 MHz frequencies for all composition.

Mössbauer effect measurements are performed at room temperature for $x=0, 0.1, 0.2,$ and 0.3 in the standard transmission geometry using a source of ^{57}Co in a Rh matrix. The spectra are collected by multi-channel analyzer and fitted using a least-square refinement program. The velocity of the Mössbauer spectrometer is calibrated using pure $\alpha\text{-Fe}$ absorber.

3. Results and discussion

3.1 X-Ray diffraction

The preparation of BiFeO_3 in the poly-crystal bulk form, without any traces of impurity had been a very difficult task. For $x=0$ and 0.1 samples, a slight impurity peak of $\text{Bi}_2\text{Fe}_4\text{O}_9$, which has been reported by Sosnowska et al. [8] is observed. For other samples, ($x=0.2, 0.3, 0.4, 0.5$) single phase is obtained.

The X-Ray diffraction patterns reveal that all of the samples are rhombohedrally distorted perovskite structure, with space group $R3c$ unrelated to the Mn concentration. As the Mn concentration increases, unevenness stresses inside the particle also increase and the XRD peaks become broader. It has been reported that BiMnO_3 can be synthesized only under high pressure [9]. In this work, all of the samples are prepared under ambient pressure, so random distortions are expected to exist inside or between crystals which result in the distribution of interplanar spacing.

Refined lattice parameters on this material with hexagonal unit cell are shown in Fig.1. Although two cations' six coordinated ionic radius are nearly the same ($\text{Fe}^{3+}:0.55 \text{ \AA}$, $\text{Mn}^{3+}:0.58 \text{ \AA}$), as the Mn concentration increases, the lattice parameters decrease. We observe non-linear concentration dependence of a-axis and c-axis. Compared with a-axis, c-axis is more composition sensitive at room temperature.

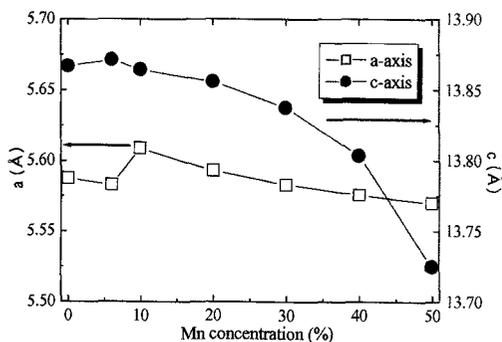


Fig.1 Concentration variation of lattice parameter with hexagonal unit cell.

3.2 Magnetic measurement

Concentration variation of magnetic ordering temperature (T_N : Neel temperature) is determined by the temperature dependence of magnetization and is shown in Fig.2. The data for $x=0, 0.1$ and 0.2 already reported by Sosnowska et al. [10] are also shown, which are in good agreement with our sample. While BiFeO_3 has high Neel temperature, the Curie temperature of

ferromagnetic BiMnO_3 is reported to be 105K [9]. The mixed property of their solid solution linearly decreases when increasing Mn concentration. From these linear dependences, it is presumed that the solid solution of BiFeO_3 and BiMnO_3 is successfully achieved in this concentration range. BiMnO_3 has low magnetic ordering temperature, so increasing the ratio of BiMnO_3 in solid solution probably let the ordering temperature decreases.

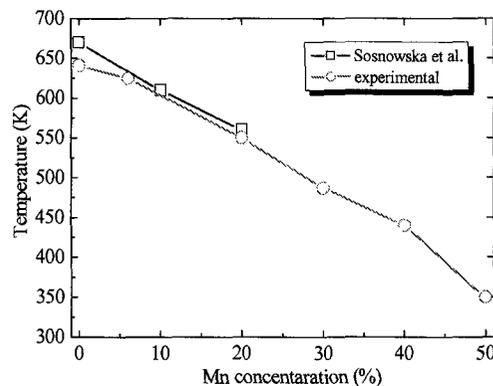


Fig.2 Concentration variation of Magnetic ordering temperature for $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($0 \leq x \leq 0.5$)

All of the samples do not show any ferromagnetic property (don't write magnetic hysteresis loop) at room temperature. An interesting phenomenon at low temperature range is observed for the temperature dependence of magnetization. (Fig.3(a)) The doping effect of BiFeO_3 with Mn ions introduces a certain amount of disorder and ferromagnetic region is introduced among anti-ferromagnetic matrix frustrated anti-ferromagnetic interactions, and this leads to unusual temperature in case of magnetization. Ferromagnetic like behavior for the $x=0.5$ sample observed at 20K is shown in Fig.3 (b). The sample draw a hysteresis loop and then, remnant magnetization was estimated to be 0.16 (emu/g). The sample of $x=0.4$ also draw the loop but the magnitude of the value of remnant magnetization is smaller than that of $x=0.5$. As the Mn concentration increases, the magnetic interaction shifts towards to ferromagnetic and the frustration increases.

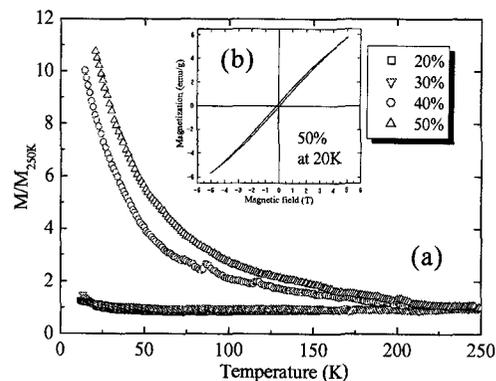


Fig.3 (a) Temperature variation of magnetizations under 1000Oe magnetic field for $x=0.2, 0.3, 0.4, 0.5$ (b) M-H curve for $x=0.5$ at 20K

3.3 Electric measurement

We have measured DC electric conductivity at room temperature. The value of the conductivity of our Mn contain sample is very high and that is not insulator ($\sigma \cong 10^{-8} \Omega^{-1} \text{cm}^{-1}$) but semiconductor ($10^{-8} \leq \sigma \leq 10^3 \Omega^{-1} \text{cm}^{-1}$) region. Substitution Fe of Mn lineally induces electric conductivity at room temperature.

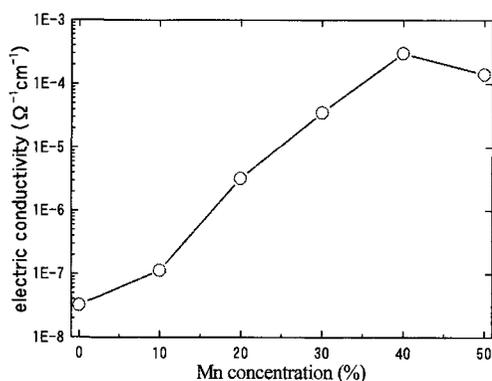


Fig.4 Concentration variation of DC conductivity at room temperature.

The value of AC impedance also decreases with Mn substitution. No electric transition is observed in this measurement. From R.T. to 523K, impedance decreases as temperature increased. Every frequency, for all composition, the value of the impedance is also same above 523K.

The real part of dielectric constant is shown in Fig.5. All composition has peak over 523K and that has concentration dependence. The magnitude of dielectric constant is lower than 40 (that of BiFeO_3) for all Mn concentration [6]. It is reported that electric Curie temperature of BiFeO_3 is 810K [1]. It reveals that all of our samples possess ferroelectricity under that peak. Dielectric loss drastically increases in high temperature range, so that we can't measure dielectric constant over 523K.

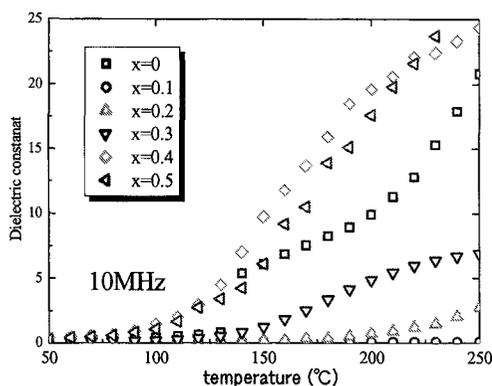


Fig.5 Temperature dependence of dielectric constant for $\text{BiFe}_{1-x}\text{Mn}_x\text{O}_3$ ($0 \leq x \leq 0.5$)

3.4 Mössbauer measurement

Mössbauer spectroscopy is carried out for the samples $x=0, 0.1, 0.2$ and 0.3 at room temperature. The sample $x=0.4$ and 0.5 can't obtain good Mössbauer effect spectra because of reduction of ^{57}Fe ion in the sample. ^{57}Fe Mössbauer spectra of the sample with $x=0$ is fitted with two component and shown in Fig.6.

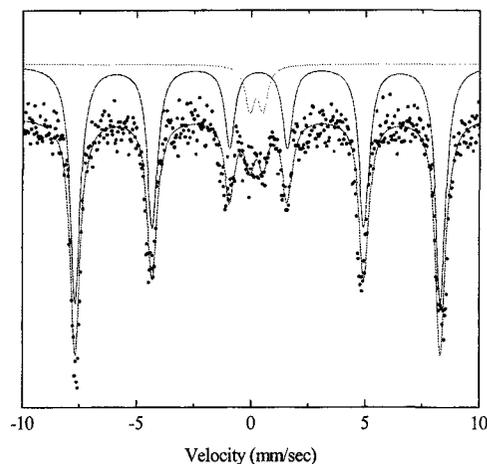


Fig.6 The Mössbauer spectra of BiFeO_3 at R.T.

Mössbauer spectra for all of the measured samples can be fitted with one six-line and one double-line sub-spectra like the $x=0$ sample. This indicates that our samples possess two magnetic sites. As our samples are single phase that the double-line site can be attributes to diminish of magnetic moment due to the particle size effect. Mössbauer parameters of the six-line site are summarized in Table1.

Table1 Mössbauer parameters

Mn	0%	10%	20%	30%
Q.S. (mm/sec)	0.129	0.132	0.137	0.282
I.S. (mm/sec)	0.295	0.274	0.265	0.260
H.F.F. (T)	49.8	49.6	46.2	43.6
Line width	0.504	0.507	0.881	1.081
Six-line (%)	92.3	91.6	95.3	90.3

The Mössbauer parameters of the one six-line sub spectrum agree to those usually found for octahedral trivalent iron in oxides. Magnetic site that appeared in $\text{BiFeO}_3\text{-SrTiO}_3$ [11] system do not appears in our solid solution system. In that system, oxygen deficiency makes tetrahedral trivalent iron in oxide. As x increases from 0 to 0.3, the isomer shift of this sample decreases slightly from 0.295 to 0.260. The magnitude of negative quadropole splitting increases with increasing Mn content. The doping effect of BiFeO_3 with Mn ions induces hyper fine field and isomer shift, but it doesn't make another magnetic site like other solid solution system.

4. Conclusion

A solid solution $(1-x)\text{BiFeO}_3-x\text{BiMnO}_3$ ($0 \leq x \leq 0.5$) with rhombohedrally distortion has been formed by conventional ceramic technique. The lattice parameters are refined by XRD in hexagonal unit cell and shown in Fig1. Although two cations' ionic radiuses are nearly the same, as the Mn concentration increases, the lattice parameters decrease.

Magnetic ordering temperature lineally decreases with increasing Mn concentration. Although, magnetic measurement indicates that all of our samples do not have ferromagnetic property at room temperature, Mn substitution increases ferromagnetic like behavior that occurs in low temperature range. As the Mn concentration increases, the magnetic interaction shifts towards to ferromagnetic and the frustration increases.

The value of DC conductivity at room temperature is not insulator but near semiconductor's region. Mn substitution induces conductivity towards $x=0.4$ and then saturated. Real part of dielectric constant is lower than that of BiFeO_3 . It has peak around 523K. It reveals that our sample possess ferroelectricity. Dielectric loss drastically increases in high temperature range.

Mössbauer parameters of six-line sites are suitable for octahedral trivalent iron in oxides. The doping effect of BiFeO_3 with Mn induces hyper fine field and isomer shift, in other hand, quadropole splitting decreases.

5. Acknowledgments

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6. References

- [1] I. Sosnowska, R. Przenioslo, P. Fischer, V.A. Murrashov, *J. Magn. Magn. Matter.* 160 (1996) 384.
- [2] G.A. Gehring, *Ferroelectrics* 161 (1994) 275.
- [3] K. Siratori, K. Kohn, E. Kita, *Acta Phys. pol.*, A81 (1992) 431.
- [4] P. Fischer, M. Polomska, I. Sosnowska, M. Szymanski, *J. Phys. C* 13 (1980) 1931.
- [5] A.I. Kashlinskii, V.I. Chechernikov, Yu.N. Venevtsev, *Sov. Phys. Solid State* 8 (1969) 2074.
- [6] M. Mahesh Kumar, S. Srinath, G.S. Kumar, S.V. Suryanarayana, *J. Magn. Magn. Mater.* 188 (1998) 203.
- [7] T. Kanai, S. Ohkoshi, A. Nakajima, T. Watanabe, K. Hashimoto, *Adv. Mater.* 13 (2001) 487
- [8] I. Sosnowska, T. Peterlin-Neumaier, E. Steichele, *J. Phys. C* 115 (1982) 4835
- [9] T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, and Y. Shono *Journal of Solid State Chemistry* 145, 639-642 (1999)
- [10] I. sosnowska, W. Achafer, W. Kockelmann, I.O. Troyanchuk, *Applied Physics A* 74, S1040-S1042 (2002)
- [11] J. Li, Y. Duan, H. He, D. Song, *Journal of Alloys and Compounds* 315 (2001) 259-264