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High temperature properties of multiferroic $BiFeO_3$–$DyFeO_3$–$BaTiO_3$ solid solutions

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Abstract

Dielectric and magnetic properties of the xBiFeO$_3$–yDyFeO$_3$–zBaTiO$_3$ solid solution ceramics at high temperature range of RT ~600 °C have been characterized. For the more detailed understandings of the multiferroic property, the relation between the crystal structure transition, magnetic transition, dielectric transition with increasing temperature have been analyzed. Residual magnetization M_r under the low and high applied magnetic fields (H = 20 Oe, 8 kOe) and the dielectric properties, ε_r and tan δ, with varying measuring frequency and temperature have been characterized using the vibrating sample magnetometer and LCR meter, respectively. The neutron diffraction data has been collected at the temperature range of RT ~800 °C. The low DyFeO$_3$ concentration samples (y = 0, 0.025) show the magnetic transitions at temperature range of 410–430 °C, while the high DyFeO$_3$ samples ($y \geq 0.05$) show the additional transition at 250–290 °C. The magnetic transition at 410–430 °C corresponds to the crystal structural transition to the tetragonal $P4mm$ from the rhombohedral R-3c, at which the BiFeO$_3$ and the DyFeO$_3$ samples lose their antiferromagnetic ordering.

Keywords: Perovskites; Softmagnetic; Sintering; Ferroelectric property; Magnetic property

1. Introduction

The materials exhibiting multiple ferroic properties, such as ferroelectricity, ferroelasticity, and ferromagnetism (or antiferromagnetism) in one phase have been named as the multiferroics. Recently the ferroelectromagnetic materials have became widely known due to their potential applications in the memory devices, sensors, and spintronics. The nickel iodine boracite $Ni_3B_7O_{13}I$ and its derivatives are the first and indisputable ferromagnetic ferroelectrics evidenced by both the ferroelectric P–E and ferromagnetic M–H hysteresis measurements.[1,2]

The ferroelectromagnetic property has been reported in several structural types of materials such as sulfide spinel, oxide perovskite and nonperovskites.[3,4] The $BiFeO_3$ (BF) of perovskite structure has been known as ferroelectric and antiferromagnetic (G-type, T_N = 397 °C) with a cycloidal spin arrangement, and a rhombohedral structure (R-3c, a = 5.616 Å, α = 59.35°).[5] The spontaneous magnetic moment was absent in pure $BiFeO_3$ up to a 8 kOe as a consequence of the completely compensated antiferromagnetic ordering.[5] However, the epitaxial BF thin film grown by PLD on $SrTiO_3$ single crystal with $SrRuO_3$ electrode has been reported to show P_s = 50–90 μC/cm^2 and M_s = 5–150 emu/cm^3.[6] The origin of the ferroelectrictiy was ascribed to the structural distortion from the rhombohedral to tetragonal due to the coherency strain between the epitaxial thin film and the substrate.

The perovskite type materials provide the vast spectrum of electrical properties covering (anti-)ferroelectric, (anti-)ferromagnetic, metallic, semiconductor, and insulator. Hence the combination of these perovskite members could open various routes for achieving the multiferroic properties in one phase material. We had explored several combined perovskite systems such as the antiferromagnetic–ferroelectric [$BiFeO_3$(BF)–$BaTiO_3$(BT)], the weak ferromagnetic antiferromagnet–ferroelectric [$PrFeO_3$(PF) + $PbTiO_3$ (PT)], and the antiferromagnetic–weak ferromagnetic–ferroelectric [(BF)–$PrFeO_3$(PF)–$PbTiO_3$(PT), and BF-$DyFeO_3$(DF)–$BaTiO_3$(BT)] systems.[7,8]

In these previous studies,[7,8] we had obtained the ferroelectricity and ferromagnetism simultaneously in the

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ternary BF–DF–BT system with remanent polarization $P_r = 1.0–7\ \mu C/cm^2$, $M_r = 0.01–0.2$ emu/g. In these systems, the rare-earth orthoferrites $REFeO_3$ (RE = Dy, La, Pr) played an important role for producing spontaneous magnetic moments. These orthoferrites are the G-type antiferromagnets ($T_N = 372–457\ ^\circ C$) with weak ferromagnetism and electrically insulating.[9]

In this study, the crystal structures, dielectric and ferromagnetic properties in the temperature range of RT ~600 °C (~800 °C for the crystal structure) have been characterized for the detailed understanding of the multiferroism in the ternary perovskite xBF–yDyFeO$_3$(DF)–zBT ($x = 0.4–0.7$, $y = 0–0.05$, $z = 0.3–0.6$) ceramics. The origin of the weak ferromagnetism will be discussed in terms of high temperature characteristics of this perovskite system. The multiferroic properties at room temperature of these ternary ceramics had been reported in our previous report.[8]

2. Experimental

The binary and ternary ceramic samples of $(1-x)$BF–xBT ($x = 0.3–0.6$) and xBF–yDyFeO$_3$(DF)–zBT ($x = 0.4–0.7$, $y = 0.025–0.05$, $z = 0.3–0.6$) have been prepared by the conventional ceramic processing using the chemical reagents, $BaCO_3$, Dy_2O_3, TiO_2, Bi_2O_3, and Fe_2O_3. The samples were sintered at temperature range of 950–1340 °C for 0.5–10 h in air.

Residual magnetic moments at 20 Oe and 8 kOe have been measured using vibrating sample magnetometer (VSM) with increasing temperature up to 600 °C. The dielectric constant ε_r and loss tangent tan δ have been measured using impedance analyzer (10 kHz to 1 MHz) in the temperature range of RT ~550 °C. Neutron diffraction data were collected using HRPD diffractometer at HANARO in Korea Atomic Energy Research Institute. The neutrons from the HANARO reactor were monochromatized by a vertically focusing composite Ge-monochromator to a wavelength of 1.8348 Å. The crystal structure was analyzed by the rietveld profile refinement method using a version 3.2 of the program Fullprof.

3. Result and discussions

The sintered densities of the samples for P–E and M–H measurement show the 90–95% theoretical density and microstructural grain sizes of 2–4 μm. The P–E and M–H hysteresis characteristics for the binary and ternary samples in this study have been already reported in our previous study.[8] In this paper, we report the residual magnetic moments under the two levels of magnetic fields ($H = 20$ Oe and 8 kOe) and dielectric properties over the temperature range of RT ~600 °C.

At $H = 20$ Oe (Fig. 1) two types of magnetic phase transitions appear. All of the samples clearly show the magnetic transitions at around 410–430 °C. On the other hand, the high DF concentration samples (0.55BF–0.05DF–0.4BT, 0.65BF–0.05DF–0.3BT, and 0.45BF–0.1DF–0.45BT) show an additional transition at around 250–290 °C. These high DF samples (xDF = 0.05, 0.10) showed the double magnetic hysteresis similar to that of the antiferroelectrics.[8] The magnetic transition at ~400 °C corresponds to that of the spontaneous (weak) magnetization transition (T_N) of the rare earth orthoferrites ($ErFeO_3$ and $DyFeO_3$).[9] The residual magnetic moment curves in Fig. 1 show the very small humps at ~520 °C.

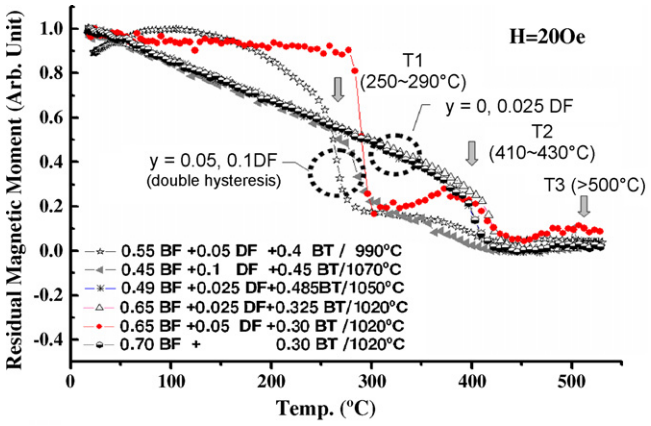

Fig. 1. Residual magnetic moments of the samples xBiFeO$_3$–yDyFeO$_3$–z BaTiO$_3$ under the low magnetic field $H = 20$ Oe with temperature.

At $H = 8$ kOe (Fig. 2) the samples also show the magnetic transition at about 410–430 °C except the 0.5BF–0.5BT sample which did not show any spontaneous magnetization in our previous study.[8] The high DF sample (xDF = 0.05) shows an additional magnetic transition at about 290–310 °C. The magnetic behavior under high magnetic field ($H = 8$ kOe) is nearly the same as those of low magnetic field ($H = 20$ Oe).

The dielectric constant ε_r and loss tangent tan δ with temperature are shown in Fig. 3 for the 0.65BF–0.05DF–0.30DF. The shape of ε_r and tan δ curves are very dependent on the measurement frequency. Three types of phase transitions can be depicted in the curves: at ~300 °C, ~400 °C, and ~520 °C. These transition temperatures correspond to the magnetic phase transition temperatures in Figs. 1 and 2.

The high temperature neutron diffraction patterns are represented in Fig. 4. The rietveld refinement results are summarized in Table 1. The two structural models, rhombohedral R-3c and tetragonal $P4mm$, are compared with the diffraction temperature. The cubic model Pm-3m showed a divergence in R-values during the refinement. Based on R-values, the crystal structure of the 0.55BF–0.05DF–0.40BT sample is the rhombohedral R-

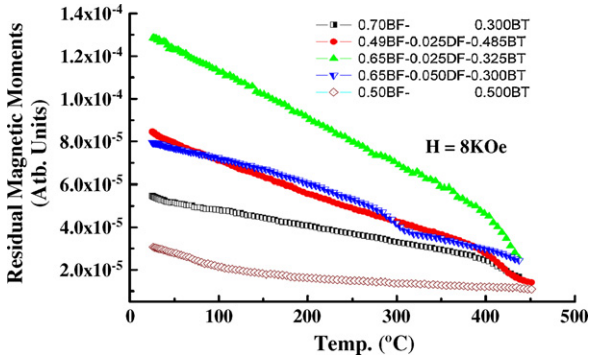

Fig. 2. Residual magnetic moments of the samples xBiFeO$_3$–yDyFeO$_3$–z BaTiO$_3$ under the high magnetic field $H = 8$ kOe with temperature.

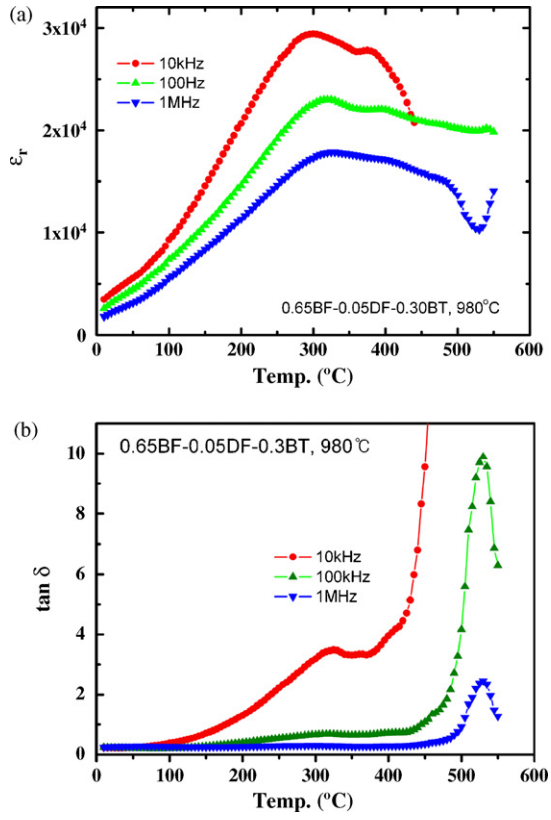

Fig. 3. Dielectric properties of the 0.65BF–0.05DF–0.30BT sample with varying measurement frequency 10 kHz to 1 MHz (a) ε_r vs. temperature (b) tan δ vs. temperature.

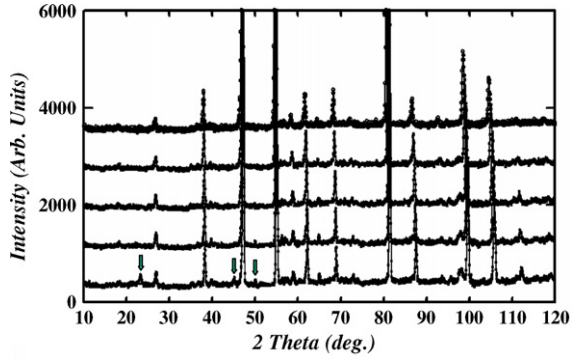

Fig. 4. High temperature neutron diffraction patterns of the 0.55BF–0.05DF–0.4BT sintered at 1050 °C for 5 h. The arrows indicate the magnetic reflections.

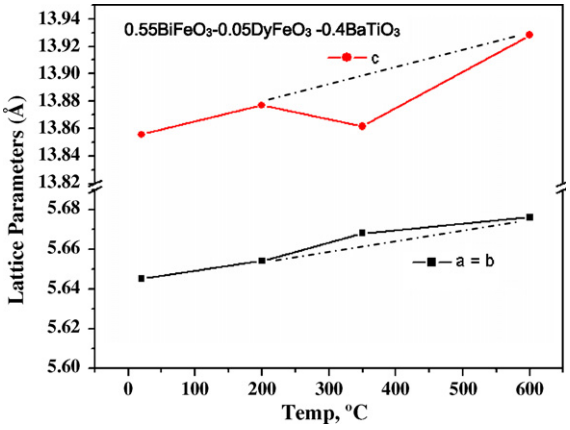

Fig. 5. Refined lattice parameters of the 0.55$BiFeO_3$–0.05$DyFeO_3$–0.4$BaTiO_3$ sample using the neutron diffraction data with the tetragonal model *P4mm* as shown in Table 1.

3*c* up to 350 °C, and changes to the tetragonal *P4mm* at 600 °C. The reflection peaks marked by the arrows in the figure originate from the magnetic ordering. These magnetic reflections partly disappear at 200 °C and completely disappear at ~350 °C.

The lattice parameter change with temperature is shown in Fig. 5. The lattice parameters of the tetragonal models in Table 1 are plotted for the comparison. The increasing rate shows a deflection at the temperature of ~350 °C. The dashed straight line is drawn to delineate the deflection in the increasing rate. This deflection temperature cannot be clearly matched to the magnetic and/or dielectric transitions shown Figs. 1 and 3 due to the insufficient diffraction measurements of temperature intervals. The crystal structure remains in the rhombohedral *R*-3*c* at 350 °C regardless of the deflection in the lattice parameter change.

Therefore, we can conclude that the magnetic transition at 410–430 °C corresponds to the crystal structural transition to the tetragonal *P4mm* from the rhombohedral *R*-3*c* at which the $BiFeO_3$ phase (G-type, $T_N = 397$ °C) and the

Table 1
Summary of structural refinements results using the neutron diffraction data of the 0.55$BiFeO_3$–0.05$DyFeO_3$–0.4$BaTiO_3$ sample

Temp. (°C)	Space group	*a* (Å)	*c* (Å)	χ^2	Rp, Rwp	Rb, Rf	Magnetic reflection
RT	*R*-3*c*	5.6453 (4)	13.8557 (19)	4.6	7.1, 9.4	9.6, 8.9	Weak
	P4mm	3.9932 (5)	3.9968 (9)	6.9	8.6, 11.6	14.6, 11.4	
200	*R*-3*c*	5.6541 (4)	13.8770 (19)	3.9	6.6, 8.7	9.1, 9.5	Very weak
	P4mm	3.9997 (4)	4.0030 (6)	4.96	7.4, 9.84	11.5, 9.2	
350	*R*-3*c*	5.6682 (6)	13.8617 (27)	3.9	6.8, 8.8	11.1, 10.9	None
	P4mm	4.005 (6)	4.009 (10)	5.4	7.7, 10.3	14.5, 12.2	
600	*R*-3*c*	5.6762 (6)	13.928 (26)	3.4	6.4, 8.2	11.1, 12.2	None
	P4mm	4.0158 (6)	4.0193 (9)	3.7	6.6, 8.6	10.4, 8.7	
850	*R*-3*c*	5.6997 (6)	13.9386 (26)	2.8	5.6, 7.4	10.4, 11.4	None
	P4mm	4.0277 (7)	4.0295 (7)	2.8	5.7, 7.5	9.6, 8.4	

rare earth orthoferrites $REFeO_3$ ($T_N = 372$–$457\,^{\circ}C$) completely lose the antiferromagnetic ordering. The magnetic transition at 250–290 °C in the high DF samples are considered that they have a different origin from those of $REFeO_3$.

4. Conclusion

The binary and ternary samples of BF–BT and BF–DF–BT show the magnetic transitions at the temperature range of 410–430 °C. The high DF concentration samples (0.55BF–0.05DF–0.4BT, 0.65BF–0.05DF–0.3BT, and 0.45BF–0.1DF–0.45BT) show an additional transition at 250–290 °C. The high temperature dielectric properties, ε_r and $\tan\delta$, of the 0.65BF–0.05DF–0.3BT sample varied substantially with the measurement frequency. Three types of broad phase transitions in the ε_r ($\tan\delta$) versus temperature curves were observed at the temperatures of ~300 °C, ~400 °C, and ~510 °C which temperatures are similar to the magnetic phase transitions. The crystal structure of the 0.55BF–0.05DF–0.40BT sample was the rhombohedral *R*-3*c* up to 350 °C, and changed to the tetragonal *P*4*mm* at higher temperature. The magnetic reflections completely disappear at ~350 °C in the neutron diffraction patterns. The magnetic transition at 410–430 °C corresponds to the crystal structural transition to the tetragonal *P*4*mm* from the rhombohedral *R*-3*c*, at which the $BiFeO_3$ and the rare earth orthoferrites $REFeO_3$ (RE = Dy, La) completely lose their antiferromagnetic ordering. The magnetic transition at 250–290 °C in the high DF samples has an unknown origin need to be studied further.

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