Synthesis and magnetic properties of $M^{2+}Ti^{4+}$ substituted $Ba_{12}Fe_{28}Ti_{15}O_{84}$

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We investigated the synthesis conditions and magnetic properties of M-Ti substituted $Ba_{12}Fe_{28}Ti_{15}O_{84}$ with initial compositions of $Ba_{12}Fe_{28-2x}Ti_{15+x}M_xO_{84}$ ($M = Zn, Mg, Ni, Cu, \text{ and } Co$) sintered at 1100-1300°C. The highest substitution amounts of M-Ti for Fe were consistent with the Ti-ion preference of each transition metal site reported before, suggesting that substituted Ti ions also preferred the sites with high Ti-ion occupancies. The spontaneous magnetizations and Curie temperatures were decreased as the substitution amount x was increased, which means that the substitution weakened the super-exchange interactions between Fe-O-Fe. The highest Zn-Ti substitution rate was lower than the other M-Ti substitution rates, which implies that Zn ions tend to enter specific M(2) and M(14) sites in $Ba_{12}Fe_{28}Ti_{15}O_{84}$. The sweep of the magnetic field from 0 to 80 kOe changed the relative dielectric constant of $Ba_{12}Fe_{28}Ti_{15}O_{84}$ by 0.283%. This variation of the dielectric constant caused by the application of magnetic fields is not negligible, showing that this compound should be categorized as a multiferroic material.

Key words: Ferrimagnetic iron oxides (ferrite), multiferroics, $Ba_{12}Fe_{28}Ti_{15}O_{84}$.

1. Introduction

Multiferroic materials with both magnetic and dielectric properties are attracting much interest.¹⁻⁴⁾ They have potential applications in next-generation devices such as memory devices and sensors.

A barium-iron oxide, $BaFe_{12}O_{19}$, has high saturation magnetization and high coercivity, widely used as permanent magnets and microwave absorbers.^{5), 6)} On the other hand, another barium-titanium oxide, $BaTiO_3$ (BTO), is a typical ferroelectric material, widely used as a dielectric material or a piezoelectric component. These conventional materials encouraged expectation for Ba-Fe-Ti oxides as multiferroic materials, which led to an extensive investigation of the Ba-Fe-Ti oxides system.⁷⁾ Siegrist *et al.* showed the existence of at least 16 different compounds.⁷⁾ Our attempts to prepare these compounds corresponding to their stoichiometry often

produced multiple phases, indicating the difficulty in the synthesis. This paper focuses on one of the oxides, $Ba_{12}Fe_{28}Ti_{15}O_{84}$.

$Ba_{12}Fe_{28}Ti_{15}O_{84}$ has monoclinic $C2/m$ symmetry with the unit cell parameters of $a = 9.988 \text{ \AA}$, $b = 17.298 \text{ \AA}$, $c = 19.17 \text{ \AA}$, and $\beta = 99.33^\circ$.⁸⁾ Curecheriu *et al.* reported that this material has the saturation magnetization of 12.5 emu/g at room temperature and the Curie temperature of $T_C = 420 \text{ K}$.⁹⁾ The crystal structure consists of spinel-like and BTO-like building blocks along the c -axis direction, as shown in Fig. 1. Tetrahedral M(2) and M(14) sites are emphasized for discussion later. The indispensable role that spinel blocks play in the magnetism of $BaFe_{12}O_{19}$, combined with the ferroelectric BTO structure blocks, has led to the expectation for multiferroic properties for $Ba_{12}Fe_{28}Ti_{15}O_{84}$. In addition, the magnetic properties of the M-type hexaferrite can also be changed by the substitution of M^{2+} and Ti^{4+} cations for $2Fe^{3+}$ cations where M^{2+} is a divalent transition-metal cation.¹⁰⁻¹⁴⁾ However, there is a limited number of publications about other hexaferrites with this substitution, possibly due to the less stability of non-M-type hexaferrites.^{15), 16)} Although $Ba_{12}Fe_{28}Ti_{15}O_{84}$ has a structural similarity with these hexaferrites that the stacking of spinel and other blocks forms, no previous study has investigated the substitution effect on $Ba_{12}Fe_{28}Ti_{15}O_{84}$. The specific objective of this study was to synthesize $M^{2+}Ti^{4+}$ substituted $Ba_{12}Fe_{28}Ti_{15}O_{84}$ samples for controlling multiferroic characteristics because this substitution increases the titanium content in the BTO-like blocks in the structure of $Ba_{12}Fe_{28}Ti_{15}O_{84}$.

2. Experimental procedure

Samples were prepared by a conventional ceramic method. We used $BaCO_3$, $\alpha\text{-Fe}_2O_3$, TiO_2 , ZnO , MgO , NiO , CuO , and CoO as starting materials. They were mixed in

Fig. 1 Structure of $Ba_{12}Fe_{28}Ti_{15}O_{84}$. The red ions are O^{2-} , and the pink ones are Ba^{2+} . The yellow and light blue ones are transition metal cations, where the majority is Fe^{3+} for yellow and Ti^{4+} for light blue.

a desired proportion, $\text{Ba}_{12}\text{Fe}_{28-2x}\text{Ti}_{15+x}\text{M}_x\text{O}_{84}$ ($\text{M} = \text{Zn}, \text{Mg}, \text{Ni}, \text{Cu}, \text{or Co}$) in a planetary micro mill (Fritsch, PULVERISETTE 7) for 10 minutes at the rate of 1100 r.p.m. The mixed powders were pressed into disks and then sintered at 1100-1300°C in air for 5 h. Finally, the products were ground into powders in a mortar.

The crystal structures were examined by powder X-ray diffraction (XRD) with Cu-K α radiation. The magnetizations were measured with a vibrating sample magnetometer (Tamakawa, TM-VSM2130HGC), and a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-XL). The relative dielectric constant was calculated from capacitance. The capacitance was measured by a three-terminal capacitance method with a capacitance bridge (ANDEEN-HAGERLING, AH 2500A).

3. Results and discussion

Figure 2 shows the X-ray diffraction patterns of $\text{Ba}_{12}\text{Fe}_{28-2x}\text{Ti}_{15+x}\text{M}_x\text{O}_{84}$ at highest substitution x_{max} for each element. Most of the samples were sintered at 1300 °C except for the highest Cu-Ti substituted sample sintered at 1100°C. These samples exhibited single phase of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$, demonstrating the success in the M-Ti substitution. The lattice constants of each sample showed slight changes within 0.1 %, even at the maximum substitution.

These maximum substitution values of x_{max} are found to be lower than 4, which suggests possible preference of Ti ions for specific sites in the unit cell. Arranging the transition metal sites in the order of Ti-ion occupancies, we can find that there is a large difference between the fifth-highest M(15) site and the sixth-highest M(11) site. Assuming that the substituted Ti ions occupy the sites from the first to the fifth, the substitution amount can be estimated to be $x = 4.0$. The values of x_{max} of Co-Ti, Mg-Ti, Ni-Ti, and Cu-Ti substituted samples are consistent

Fig. 2 XRD patterns of the highest M-Ti substituted samples of $\text{Ba}_{12}\text{Fe}_{28-2x}\text{Ti}_{15+x}\text{M}_x\text{O}_{84}$

with this estimation.

Figure 3 shows spontaneous magnetization of $\text{Ba}_{12}\text{Fe}_{28-2x}\text{Ti}_{15+x}\text{M}_x\text{O}_{84}$ at $T=5$ K as a function of M-Ti substitution amount x . The spontaneous magnetization was estimated by linear extrapolation of each magnetization curves from a high field region. Although both Zn and Mg are nonmagnetic ions, Zn-Ti substitution decreased the spontaneous magnetization steeper than Mg-Ti substitution. Since Zn ions are generally apt to prefer tetrahedral sites,^{17), 18)} Zn ions likely sit at just two sites (M(2) and M(14) shown in Fig. 1) in the unit cell of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$, which possibly leads to the lower substitution limit than those of the other M-Ti substituted samples. Therefore, it is reasonable to assume that Fe ions at these tetrahedral sites align in

Fig. 3 M-Ti substitution dependence of spontaneous magnetization of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$

Fig. 4 M-Ti substitution dependence of Curie temperature of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$

Fig. 5 M - H loops of Co-Ti substituted samples at (a) $x=3.5$ and (b) $x=2.0$

Fig. 6 M-Ti substitution dependence of coercivity of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$

the up-spin direction. The spontaneous magnetizations of Co-Ti substituted samples were smaller than those of the other substituted samples because of the relatively higher magnetic susceptibilities of the Co-Ti substituted samples at high magnetic fields from which the spontaneous magnetizations were derived by extrapolation.

Figure 4 shows Curie temperature of $\text{Ba}_{12}\text{Fe}_{28-2x}\text{Ti}_{15+x}\text{M}_x\text{O}_{84}$ as a function of x . These linear decreases in the spontaneous magnetization and the Curie temperature with increasing x imply that M and Ti cations were successfully substituted for Fe cations in $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$, which weakened the super-exchange interactions between Fe-O-Fe. The Curie temperature of Zn-Ti substituted samples more sharply decreased than those of other M-Ti substituted samples with increasing x . This result suggests that Zn ions tend to enter the sites of significant importance in magnetic interactions between Fe-O-Fe.

Figure 5 shows the M - H loops of the Co-Ti substituted samples at (a) $x=3.5$ and (b) $x=2.0$ measured at $T=5$ K. Former sample at $x=3.5$ exhibited a large coercivity of 11 kOe and latter sample at $x=2.0$ also showed a large coercivity of 6.7 kOe. These results mean that the higher substitution of Co resulted in the higher coercivity, possibly due to the anisotropy of Co cations in contrast with the soft magnetic properties accompanying the other divalent-cation-substituted samples as shown in Fig. 6. Furthermore, these Co-Ti substituted samples had two different slopes in their magnetization curves. The temperature dependence of magnetization of each sample clearly showed just one Curie temperature, as shown in Fig. 7, demonstrating the existence of a single magnetic phase. Therefore, it is reasonable to assume the coexistence of two kinds of spin components that respond to magnetic field differently even in the same crystal

Fig. 7 Temperature dependences of magnetization of Co-Ti substituted samples at $x=3.5$, $x=2.0$, and $x=0$.

lattice. These coercivities were not observed at 300 K. It seems likely that the rise in temperature weakened the anisotropy one of the two spin components possessed and decreased the coercivity, which is consistent with the absence of anomaly in the temperature dependence of magnetization except for the Curie temperature.

Figure 8 shows the field dependence of the relative dielectric constant of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$ at $T=1.6$ K. We first applied a magnetic field up to 80 kOe, decreased it to -20 kOe, and swept it back to zero. The relative dielectric constant was calculated by the formula $C=\epsilon_0\epsilon_r S/d$ (C : capacitance, ϵ_0 : vacuum permittivity, ϵ_r : relative permittivity, S : the area of the sample, d : the thickness of the sample). The change in permittivity was about 0.283% between $H=0$ kOe and 80 kOe. This change in the dielectric constant may come from magnetostriction that depends on magnetization processes. However, the magnetization process in Fig. 9 shows a less steep increase above 20 kOe than that at low magnetic fields in spite that the dielectric constant was still significantly changed above 20 kOe as shown in Fig. 8. This variation of the dielectric constant cannot be simply explained by magnetostriction. Therefore, this compound is a possible candidate as a multiferroic material because a magnetic field can control the dielectric constant. The other sintered bulk samples with M-Ti substitutions were brittle or fragile, which prevented us from measuring their dielectric properties in magnetic fields except for the starting material of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$. Further synthesis research should be carried out to measure the dielectric properties of other substituted samples.

4. Conclusion

We successfully synthesized M-Ti substituted samples of $\text{Ba}_{12}\text{Fe}_{28-2x}\text{Ti}_{15+x}\text{M}_x\text{O}_{84}$ ($M = \text{Zn, Mg, Ni, Cu, or Co}$) by a conventional ceramic method. The highest substitution amounts of x_{max} were 2.5 (Zn-Ti), 3.5 (Mg-Ti), 4.0 (Ni-Ti), 3.0 (Cu-Ti), and 3.5 (Co-Ti).

The spontaneous magnetizations and Curie temperatures were decreased as x increased. It indicates that this substitution weakened the super-exchange interactions between Fe-O-Fe.

The highest substitution amounts of M-Ti for Fe were consistent with the Ti-ion preference of each transition metal site reported before, suggesting that substituted Ti ions also preferred the sites with high Ti-ion occupancies.

Zn ions possibly sit at just two sites (M(2) and M(14)) in the unit cell of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$, which can lead to the lower substitution limit than those of other M-Ti substituted samples. It is possible that Fe ions at these tetrahedral sites align in the up-spin direction.

The Co-Ti substituted samples showed large coercivities at 5 K. The magnetization curves implied the coexistence of two kinds of spin components that responded to applied magnetic field differently, even in the same crystal lattice.

Fig. 8 Field dependence of relative dielectric constant of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$

Fig. 9 M - H curve of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$

We measured the field dependence of relative permittivity of $\text{Ba}_{12}\text{Fe}_{28}\text{Ti}_{15}\text{O}_{84}$. Applying a magnetic field from 0 kOe to 80 kOe decreased the relative permittivity by 0.283%. Thus, this compound is a possible candidate as a multiferroic material because of the ability to change the dielectric property by application of a magnetic field.

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