Magnetoplumbite and W-type barium ferrites as magnetic mixture with hematite

Yuji MASUBUCHI,† Ryoji SAITO and Shinichi KIKKAWA

Graduate School of Engineering, Hokkaido University, N13, W8, Kita-ku, Sapporo 060–8628

Magnetic properties were studied on polycrystalline composite mixtures of magnetoplumbite-type $BaFe_{12}O_{19}$ and W-type $BaCo_2Fe_{16}O_{27}$ ferrites with α-Fe_2O_3. The respective ferrite mixtures were prepared with hematite in 0 to 70 mol% using solid state reaction. X-ray diffraction (XRD) analysis and magnetic measurement suggested the products were simple mixtures of the ferromagnetic $BaFe_{12}O_{19}$ or $BaCo_2Fe_{16}O_{27}$ with α-Fe_2O_3 even after sintering at 1250°C. Their magnetization decreased with the increasing contents of α-Fe_2O_3. Their electrical resistivities of higher than 10^2 Ωm were too large to observe their magnetic field dependence, magnetoresistance (MR) effect. Electrical resistivity decreased to 0.36 Ωm by the post annealing of the as prepared $BaCo_2Fe_{16}O_{27}$ with a small amount of α-Fe_2O_3 in Ar at 1000°C for 5 h. The improved electrical conductivity in 4 orders of magnitude showed the MR effect of 0.86% on the post annealed $BaCo_2Fe_{16}O_{27}$ product.

Key-words : Magnetoresistance, $BaFe_{12}O_{19}$, $BaCo_2Fe_{16}O_{27}$, α-Fe_2O_3, Polycrystalline composite, Solid state reaction

[Received September 2, 2008; Accepted October 16, 2008]

1. Introduction

Tunneling magnetoresistance (MR) has attracted much attention because of its application in magnetic storage devices and sensors.[1] Large tunneling MR effect has been observed in the multilayered tunneling junction. Ferromagnetic (FM) materials sandwich an insulating layer (I) in nanometer thickness to form FM/I/FM stacking in the junction. The MR effect can also be observed in granular type composites. FM grains are dispersed in an insulating matrix to be surrounded by insulating grain boundary. This type of MR has been reported in polycrystalline films[2)–5)] and also in sintered compacts.[6),7)] Most of their combinations were ferromagnetic metals with nonmagnetic oxide insulator. There is a big advantage in oxide combinations to reduce their interface reaction in their preparation and also in their operation. Some examples can be found on $La_{2/3}Ca_{1/3}MnO_3/Al_2O_3$,[8)] Fe_3O_4/α-Fe_2O_3[9)] and $La_{0.8}Sr_{0.2}MnO_3/ZrO_2$.[10)] The MR effect was recently found out on sintered compacts of spinel ferrite mixtures with α-Fe_2O_3.[11)]

Barium hexaferrite; $BaFe_{12}O_{19}$ (hereafter denoted as BaM) is one of the most famous ferromagnetic materials. It has magnetoplumbite-type structure with space group of $P6_3/mmc$ (a = 0.589 nm and c = 2.32 nm).[12)] The structure is described as an alternative stacking of spinel block consisting of iron oxide and a barium layer in rock salt type structure.[12)] It has been widely used as permanent magnet since the 1950s.[13),14)] There are several kinds of its analogues named as ferroxplana-type hexagonal ferrites such as W, Y, Z, X and U-types. Their way of stacking is different between the spinel and the rock salt blocks. They have been investigated in their crystal structure, especially in their spin orientation,[15)] and magnetic resonance in the high frequency range.[16)] Their general formula is $m(Ba, Me^{2+})\cdot nFe_2O_3$ (Me = Mn, Fe, Co, Ni, Cu, Mg and Zn). W-type barium cobalt ferrite with a chemical composition of $BaCo_2Fe_{16}O_{27}$ (hereafter denoted as Co_2W) has a hexagonal lattice (a = 0.590 nm and c = 3.291 nm),[15)] which is closely related to the magnetoplumbite structure. Its barium layer is interleaved by every two-spinel blocks containing iron and cobalt oxide, although every one-spinel block alternatively stacks with barium layer in BaM. It is ferromagnetic with a relatively low coercive force of about 12 kA/m.[17)] This value is 35 times smaller than that of the BaM magnet (≈ 430 kA/m).[13)] Their reported saturation magnetization values are 72 Am^2kg^{-1} for BaM and 76 Am^2kg^{-1} for Co_2W.[17)] They are comparable to the largest value for the manganese ferrite among the spinel ferrites. The relatively large magnetization may contribute to enhance the MR ratio.

In this study, both BaM/α-Fe_2O_3 and Co_2W/α-Fe_2O_3 composites were prepared by changing the mixing ratio and firing condition in a conventional solid state sintering method. Their magnetic behavior and magnetoresistance property was discussed in relation to their electrical resistivity.

2. Experimental procedure

BaM/α-Fe_2O_3 and Co_2W/α-Fe_2O_3 composites were prepared in two steps. First, the pure BaM and Co_2W were prepared in solid state reactions between α-Fe_2O_3 (99.9%, Kanto Chemical Co., Inc.), $BaCO_3$ (99.9%, Wako Pure Chemical Ind., Ltd.) and Co_3O_4 (99.9%, Kanto Chemical Co., Inc.). Their stoichiometric amounts were well mixed in an agate mortar in the presence of acetone. The mixtures were calcinated at 1250°C for 5 h in air. After grinding, they were uni-axially pressed in 25 MPa to discs, and then sintered at 1250°C for 12 h in air. Some of them were annealed at 1000°C for 5 h in Ar flow to reduce their electrical resistivity. The pure products were mixed again with α-Fe_2O_3 in the amounts of $(1-x)$BaM (or Co_2W)/$(x)\alpha$-Fe_2O_3 (x = 0 to 70 mol%). Their sintered bodies were obtained in a similar procedure to the above. Their sintering conditions were at 1250°C for 5 h.

Powder X-ray diffraction (XRD) patterns were recorded with a diffractometer with monochromatized Cu Kα radiation (PANalytical, X'pert-MPD). Magnetic hysteresis was studied in a field of up to ± 1193 kA/m at room temperature using a vibrat-

† Corresponding author: Y. Masubuchi; E-mail: yuji-mas@eng.hokudai.ac.jp

ing sample magnetometer (Riken Denshi Co., Ltd., BHV–50). Electrical resistivity (ρ) in a magnetic field of up to ± 398 kA/m was measured by the van der Pauw method (Toyo Corp., Resistest8300). The MR ratio was defined by the following formula: MR = [ρ(0 kA/m) – ρ(398 kA/m)]/ρ(0 kA/m). Copper lead wires were ultrasonically soldered to the sample tablets 10 mm in diameter using a SUNBONDER (ASAHI Glass Co., USM-III).

3. Results and discussion

3.1. Magnetoplumbite-type $BaFe_{12}O_{19}$ and its α-Fe_2O_3 mixture

Figure 1(a) shows a diffraction pattern calculated using the structural data estimated from $BaFe_{12}O_{19}$ single crystal.[12] Single phase of BaM was obtained after firing at 1250°C for 12 h in air as shown in Fig. 1(b). The fired mixture of BaM/α-Fe_2O_3 with x = 44 mol% was also their mixture as represented in Fig. 1(c). There was no trace of other crystalline phase derived from a decomposition or a reaction of BaM and α-Fe_2O_3 in a whole compositionalrange of $0 < x < 70$ mol%. The XRD analysis suggested that the sintered bodies were simple mixtures of BaM and α-Fe_2O_3. Magnetic measurements showed ferromagnetic hysteresis behavior in both pure BaM and its composite in the magnetic field of ± 1193 kA/m. Their magnetization was almost saturated above the magnetic field of ± 600 kA/m. BaM sintered compact had the value of 63.0 Am^2/kg at 1193 kA/m and its coercive force of 118 kA/m. The magnetization decreased with increasing the content of the antiferromagnetic α-Fe_2O_3 in the composites as shown in **Fig. 2**. The ferrimagnetism of BaM was diluted by antiferromagnetic α-Fe_2O_3 with T_N = 950 K. Their electrical resistivity gradually increased from 10^2 Ωm for pure BaM to 10^4 Ωm for the composite of x = 70 mol%. There was no systematical change in the electrical resistivity against the applied magnetic field. The MR effect was not observed in the all BaM/α-Fe_2O_3 composites. Their electrical resistivity was probably so high that the conduction electron could not migrate through a ferromagnetic grain and spin polarization could not tunnel between the neighboring grains. After annealing in Ar flow, their electrical conductivity did not change significantly. The broadening on their diffraction peak was observed in the annealed samples; therefore they might be slightly decomposed by the annealing.

3.2. W-type $BaCo_2Fe_{16}O_{27}$ and its α-Fe_2O_3 mixture

W-type barium cobalt ferrite crystallized with a small amount of α-Fe_2O_3 impurity after the firing of the stoichiometric starting mixture at 1250°C for 12 h in air as represented in **Fig. 3**(b). The relative diffraction intensity for α-Fe_2O_3 increased in the composite product of Co_2W/α-Fe_2O_3 (x = 60 mol%) as shown in Fig. 3(c). There was no extra diffraction except for those of Co_2W and α-Fe_2O_3. The samples of Co_2W and Co_2W/α-Fe_2O_3 (x = 60 mol%) composite showed ferromagnetic hysteresis curves with coercive force of about 14 kA/m as shown in **Fig. 4**. Their magnetizations were easily saturated. Their values at the magnetic field of 1193 kA/m decreased with an increase in the content of α-Fe_2O_3 and were diluted from 65 Am^2/kg for the Co_2W to 45 Am^2/kg for the Co_2W/α-Fe_2O_3 (x = 60 mol%). The magnetic behavior of Co_2W was comparable to that reported in ref. 17. Their electrical resistivity also gradually increased from 10^3 Ωm

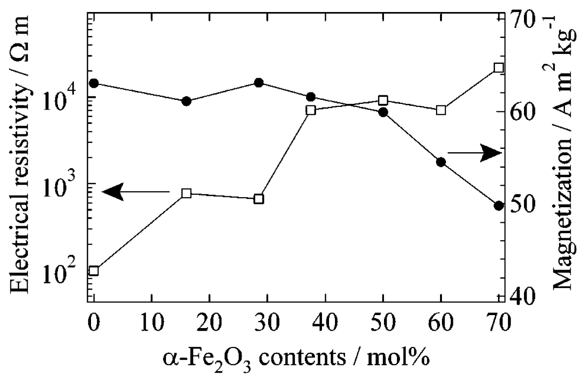

Fig. 2. Magnetization and electrical resistivity against the α-Fe_2O_3 contents in $(1-x)BaFe_{12}O_{19}/(x)\alpha$-$Fe_2O_3$ composites.

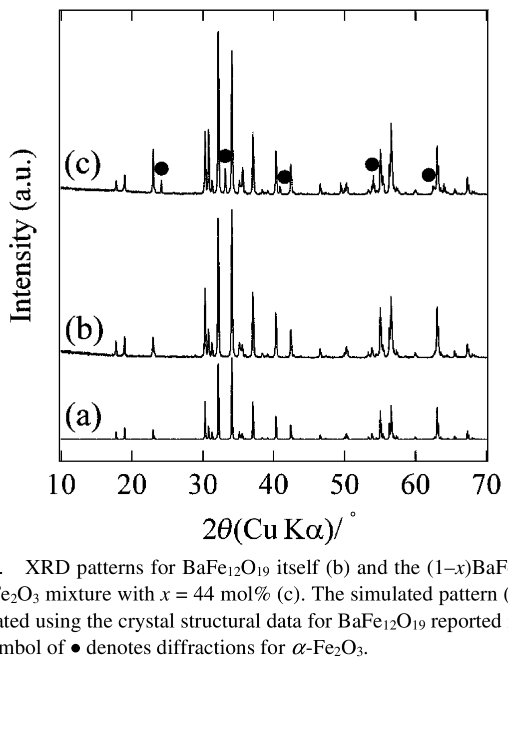

Fig. 1. XRD patterns for $BaFe_{12}O_{19}$ itself (b) and the $(1-x)BaFe_{12}O_{19}/(x)\alpha$-$Fe_2O_3$ mixture with x = 44 mol% (c). The simulated pattern (a) was calculated using the crystal structural data for $BaFe_{12}O_{19}$ reported in Ref. 12. Symbol of • denotes diffractions for α-Fe_2O_3.

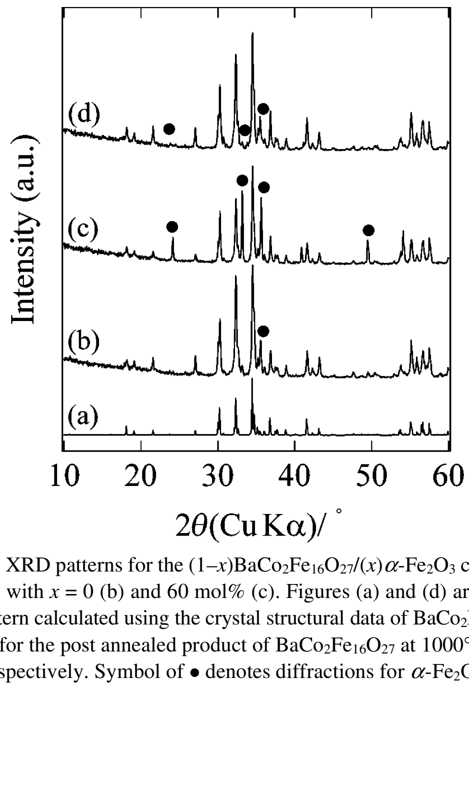

Fig. 3. XRD patterns for the $(1-x)BaCo_2Fe_{16}O_{27}/(x)\alpha$-$Fe_2O_3$ composite mixtures with x = 0 (b) and 60 mol% (c). Figures (a) and (d) are a simulated pattern calculated using the crystal structural data of $BaCo_2Fe_{16}O_{27}$[15] and that for the post annealed product of $BaCo_2Fe_{16}O_{27}$ at 1000°C for 5 h in Ar, respectively. Symbol of • denotes diffractions for α-Fe_2O_3.

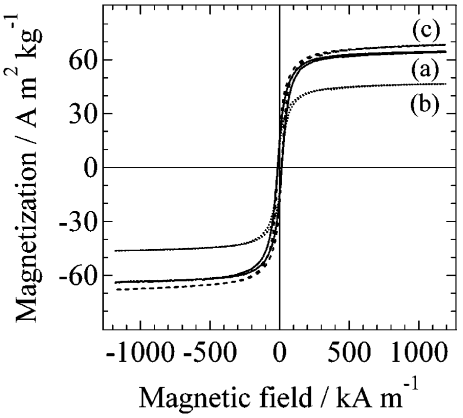

Fig. 4. Field dependences of magnetization in $BaCo_2Fe_{16}O_{27}$ (a), $BaCo_2Fe_{16}O_{27}/\alpha$-$Fe_2O_3$ composite with x = 60 mol% (b) and the post annealed $BaCo_2Fe_{16}O_{27}$ at 1000°C for 5 h in Ar (c).

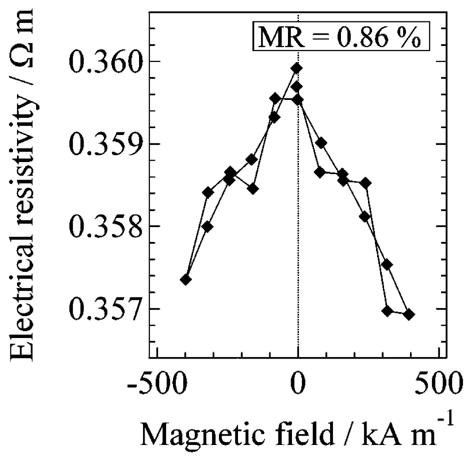

Fig. 5. Magnetic field dependence of electrical resistivity in the post annealed $BaCo_2Fe_{16}O_{27}$ at 1000°C for 5 h in Ar. The MR ratio was defined by the following formula: MR = [ρ(0 kA/m) − ρ(398 kA/m)]/ρ(0 kA/m).

(x = 0 mol%) to 10^4 Ωm (60 mol%), similar to the BaM/α-Fe_2O_3 composites. Its electrical resistivity was again too high to change against the applied magnetic field.

Electrical conduction has been reported on the W-type hexagonal barium ferrite $BaFe^{2+}{}_2Fe^{3+}{}_{16}O_{27}$. It was assumed as a conduction induced by the mixed valency between Fe^{2+} and Fe^{3+}, because the Fe^{2+} substitution with Co^{2+} enhanced the conductivity.[18)] All iron ions are trivalent in $BaCo_2Fe_{16}O_{27}$. Reduction of its electrical resistivity can be expected by a partial reduction of its Fe^{3+} to Fe^{2+}. The as prepared Co_2W with a small amount of α-Fe_2O_3 impurity was post annealed in Ar flow at 1000°C for 5 h. XRD patterns were almost the same before and after the annealing as shown in Fig. 3(d). The amount of α-Fe_2O_3 slightly increased. There were no trace amounts of FeCo alloy and Fe_3O_4 reported to be present after the annealing of Co_2W and Fe_2O_3 in hydrogen atmosphere.[8),19)] The field dependence of magnetization did not change so much as shown in Fig. 4. The electrical resistivity drastically decreased from 10^3 Ωm to 0.36 Ωm by the post annealing. It changed with the applied magnetic field as shown in **Fig. 5**. Its MR ratio can be calculated to be 0.83%. The reduction of electrical resistivity in the barium ferrite composite was very important to observe the MR effect. This is the first report on the MR effect of Co_2W/α-Fe_2O_3 polycrystalline composite. Polycrystalline composites with another kind of ferroxplana-type ferrite may improve the MR effect.

4. Conclusion

Polycrystalline samples of magnetoplumbite-type $BaFe_{12}O_{19}$ and W-type $BaCo_2Fe_{16}O_{27}$ ferrites were prepared by using the solid state reaction. Even after sintering of their mixture with α-Fe_2O_3 at 1250°C for 5 h, the products were simple mixtures of either ferromagnetic $BaFe_{12}O_{19}$ or $BaCo_2Fe_{16}O_{27}$ with an insulating α-Fe_2O_3. Their magnetizations were decreased with an increase in the amount of α-Fe_2O_3. Their electrical resistivity was too high to show their change against the applied magnetic field. Post annealing at 1000°C for 5 h in Ar flow reduced the electrical resistivity of the $BaCo_2Fe_{16}O_{27}$ composite mixture with a small amount of α-Fe_2O_3 impurity from 10^3 to 0.36 Ωm. The reduced composite showed the field dependence of its electrical resistivity corresponding to the MR effect of 0.86%.

References

1) R. L. Comstock, *J. Mater. Sci., Mater. Electron.*, 13, 509–523 (2002).
2) C. Wang, X. Xiao, Y. Rong and T. Y. Hsu, *J. Mater. Sci.*, 41, 3873–3879 (2006).
3) Y. Kawaai, A. Yamada, T. Takeda and S. Kikkawa, *Jpn. J. Appl. Phys.*, 43, 5671–5672 (2004).
4) S. Kikkawa, K. Sakon, Y. Kawaai and T. Takeda, *Adv. Sci. Technol.*, 52, 70–74 (2006).
5) D. Tripathy, A. O. Adeyeye and C. B. Boothroyd, *J. Appl. Phys.*, 99, 08J105 (2006).
6) C. S. Xiong, Q. P. Huang, Y. H. Xiong, Z. M. Ren, L. G. Wei, Y. D. Zhu, X. S. Li and C. L. Sun, *Mater. Res. Bull.*, 43, 2048–2054 (2008).
7) P. Chen, D. Y. Xing, Y. W. Du, J. M. Zhu and D. Feng, *Phys. Rev. Lett.*, 87, 107202 (2001).
8) L. E. Hueso, J. Rivas, F. Rivadulla and M. A. Lopez-Quintela, *J. Non-Crystal. Solids*, 287, 324–328 (2001).
9) A. C. Sun, P. C. Kuo, C. Y. Chou, S. C. Chen, C. T. Lie, M. H. Lin, J. W. Chen and H. L. Huang, *J. Magn. Magn. Mater.*, 272–276, 1776–1777 (2004).
10) W. J. Lu, Y. P. Sun, X. B. Zhu, W. H. Song and J. J. Du, *Mater. Lett.*, 60, 3207–3211 (2006).
11) Y. Masubuchi, M. Minoya, T. Takeda and S. Kikkawa, *J. Am. Ceram. Soc.*, in preparation.
12) X. Obradors, A. Collomb, M. Pernet, D. Samaras and J. C. Joubert, *J. Solid State Chem.*, 56, 171–181 (1985).
13) F. E. Luborsky, *J. Appl. Phys.*, 37, 1091–1094 (1966).
14) A. Cochardt, *J. Appl. Phys.*, 37, 1112–1115 (1966).
15) A. Collomb, P. Wolfers and X. Obradors, *J. Magn. Magn. Mater.*, 62, 57–67 (1986).
16) C. Surig, K. A. Hempel, R. Muller and P. Gornert, *J. Magn. Magn. Mater.*, 150, 270–276 (1995).
17) R. Muller, *J. Magn. Magn. Mater.*, 120, 61–63 (1993).
18) Z. Simsa, A. V. Zalesskij and K. Zaveta, *Phys. Stat. Sol.*, 14, 485–490 (1966).
19) C. Sudakar and T. R. N. Kutty, *J. Electron. Mater.*, 33, 1280–1288 (2004).