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参考文献

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Introduction

Tunneling magnetoresistance (MR) has attracted much attention because of its application in magnetic storage devices and sensors. 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 and also in sintered compacts. Most of their combinations were ferromagnetic metals with nonmagnetic oxide insulator. There is a big advantage in oxide combinations to reduce the interface reaction in their preparation and also in their operation. Some examples can be found on La2/3Ca1/3MnO3/Al2O3, La0.8Sr0.2MnO3/ZrO2. The MR effect was recently found out on sintered compacts of spinel ferrite mixtures with α-Fe2O3.

Barium hexaferrite; BaFe12O19 (hereafter denoted as BaM) is one of the most famous ferromagnetic materials. It has magnetoplumbite-type structure with space group of P63/mmc (a = 0.589 nm and c = 3.291 nm), 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. This value is 35 times smaller than that of the BaM magnet (~ 430 kA/m). Their reported saturation magnetization values are 72 Am²/kg for BaM and 76 Am²/kg for Co2W. 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-Fe2O3 and Co2W/α-Fe2O3 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.

Experimental procedure

BaM/α-Fe2O3 and Co2W/α-Fe2O3 composites were prepared in two steps. First, the pure BaM and Co2W were prepared in solid state reactions between α-Fe2O3 (99.9%, Kanto Chemical Co., Inc.), BaCO3 (99.9%, Wako Pure Chemical Ind., Ltd.) and Co3O4 (99.9%, Kanto Chemical Co., Inc.). Their stoichiometric amounts were well mixed in an agate mortar to be obtained in a similar procedure to the above. 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-Fe2O3 in the amounts of (1−x)BaM (or Co2W)/(x)α-Fe2O3 (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-
ing sample magnetometer (Riken Denshi Co., Ltd., BHV-50). Electrical resistivity ($\rho$) in a magnetic field of up to $\pm398$ kA/m was measured by the van der Pauw method (Toyo Corp., Resistest8300). The MR ratio was defined by the following formula: $MR = \frac{\rho(0 \text{ kA/m}) - \rho(398 \text{ kA/m})}{\rho(0 \text{ kA/m})}$. 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 $\alpha$-Fe$_2$O$_3$ mixture

Figure 1(a) shows a diffraction pattern calculated using the structural data estimated from BaFe$_{12}$O$_{19}$ single crystal. 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/$\alpha$-Fe$_2$O$_3$ 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 $\alpha$-Fe$_2$O$_3$ in a whole compositional range of $0 < x < 70$ mol%. The XRD analysis suggested that the sintered bodies were simple mixtures of BaM and $\alpha$-Fe$_2$O$_3$. Magnetic measurements showed ferromagnetic hysteresis behavior in both pure BaM and its composite in the magnetic field of $\pm1193$ kA/m. Their magnetization was almost saturated above the magnetic field of $\pm600$ 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 $\alpha$-Fe$_2$O$_3$ in the composites as shown in Fig. 2. The diffusion intensity for $\alpha$-Fe$_2$O$_3$ increased in the composite product of Co$_2$W/$\alpha$-Fe$_2$O$_3$ ($x = 60$ mol%) as shown in Fig. 3(b). There was no extra diffusion except for those of Co$_2$W and $\alpha$-Fe$_2$O$_3$. The samples of Co$_2$W and Co$_2$W/$\alpha$-Fe$_2$O$_3$ ($x = 60$ 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 $\alpha$-Fe$_2$O$_3$ and were diluted from 65 Am$^2$/kg for the Co$_2$W to 45 Am$^2$/kg for the Co$_2$W/$\alpha$-Fe$_2$O$_3$ ($x = 60$ mol%). The magnetic behavior of Co$_2$W was comparable to that reported in ref. 17. Their electrical resistivity also gradually increased from $10^3$ Ωm.

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$_2$Fe$_{16}$O$_{27}$ and its $\alpha$-Fe$_2$O$_3$ mixture

W-type barium cobalt ferrite crystallized with a small amount of $\alpha$-Fe$_2$O$_3$ 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 $\alpha$-Fe$_2$O$_3$ increased in the composite product of Co$_2$W/$\alpha$-Fe$_2$O$_3$ ($x = 60$ mol%) as shown in Fig. 3(b). There was no extra diffusion except for those of Co$_2$W and $\alpha$-Fe$_2$O$_3$. The samples of Co$_2$W and Co$_2$W/$\alpha$-Fe$_2$O$_3$ ($x = 60$ 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 $\alpha$-Fe$_2$O$_3$ and were diluted from 65 Am$^2$/kg for the Co$_2$W to 45 Am$^2$/kg for the Co$_2$W/$\alpha$-Fe$_2$O$_3$ ($x = 60$ mol%). The magnetic behavior of Co$_2$W was comparable to that reported in ref. 17.
annealed BaCo$_2$Fe$_{16}$O$_{27}$ at 1000°C.

Fig. 4. Field dependences of magnetization in BaCo$_2$Fe$_{16}$O$_{27}$ (a), BaCo$_2$Fe$_{16}$O$_{27}$/α-Fe$_2$O$_3$ composite with $x = 60$ mol% (b) and the post annealed BaCo$_2$Fe$_{16}$O$_{27}$ at 1000°C for 5 h in Ar (c).

The 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$_{12+}$Fe$_{3+}$O$_{19}$. It was assumed as a conduction induced by the mixed valency between Fe$^{3+}$ and Fe$^{2+}$, because the Fe$^{3+}$ substitution with Co$^{2+}$ enhanced the conductivity.$^{18}$ All iron ions are trivalent in BaCo$_2$Fe$_{16}$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$_2$W with a small amount of α-Fe$_2$O$_3$ 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$_2$O$_3$ slightly increased. There were no trace amounts of FeCo alloy and Fe$_2$O$_3$ reported to be present after the annealing of Co$_2$W and Fe$_2$O$_3$ 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 $10^4$ 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 0.86%.

The reduced composite showed the field dependence of its electrical resistivity corresponding to the MR effect of 0.86%.

Fig. 5. Magnetic field dependence of electrical resistivity in the post annealed BaCo$_2$Fe$_{16}$O$_{27}$ at 1000°C for 5 h in Ar. The MR ratio was defined by the following formula: $MR = (\rho(0 \text{ kA/m}) - \rho(398 \text{ kA/m}))/\rho(0 \text{ kA/m})$.

4. Conclusion

Polycrystalline samples of magnetoplumbite-type BaFe$_{12}$O$_{19}$ and W-type BaCo$_2$Fe$_{16}$O$_{27}$ ferrites were prepared by using the solid state reaction. Even after sintering of their mixture with α-Fe$_2$O$_3$ at 1250°C for 5 h, the products were simple mixtures of either ferromagnetic BaFe$_{12}$O$_{19}$ or BaCo$_2$Fe$_{16}$O$_{27}$ with an insulating α-Fe$_2$O$_3$. Their magnetizations were decreased with an increase in the amount of α-Fe$_2$O$_3$. 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$_2$Fe$_{16}$O$_{27}$ composite mixture with a small amount of α-Fe$_2$O$_3$ impurity from $10^3$ to 0.36 Ωm. The

References