Tunneling magnetoresistance in BaTiO$_3$/Fe$_3$O$_4$ composites

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(1-x)BaTiO$_3$-xFe$_3$O$_4$ composites were successfully prepared by conventional solid-state sintering of raw materials (BaCO$_3$, TiO$_2$, and Fe$_3$O$_4$) in the molar fraction x of Fe$_3$O$_4$ to BaTiO$_3$ at 1323 K for 5 hours under Ar gas flow. X-ray diffraction (XRD) and electron probe micro analysis (EPMA) measurements were performed for these samples and it is confirmed that the composites consist of only two phases of BaTiO$_3$ and Fe$_3$O$_4$. The largest saturation magnetization (Ms) of 73.4 emu/g was observed at x = 0.80, which was consistent with the product of the molar fraction of Fe$_3$O$_4$ and the Ms of pure Fe$_3$O$_4$. The largest MR ratio of 4.9% was observed under magnetic field of |H|>6 kOe for the x = 0.75 sample. The MR ratio is quadruple as large as that of Fe$_3$O$_4$. This result suggests that the formation of insulating BaTiO$_3$ barriers and tunneling conduction of spins between Fe$_3$O$_4$-grains cause the large MR ratio in BaTiO$_3$/Fe$_3$O$_4$ granular system.

Key words: BaTiO$_3$, Fe$_3$O$_4$, composite, tunnel magnetoresistance effect

I. Introduction

There has been an increasing interest in the tunneling magnetoresistance (TMR) effect, due to its potential application in magnetic storage devices and sensors. The TMR effect has been observed in multilayered structures separated by a thin insulating layer. Conduction tunneling junctions where ferromagnetic layers are in contact with a nonmagnetic matrix, such as Al$_2$O$_3$, AlN, Ag, AgCl, and Au, have been reported for various granular structures in magnetic storage devices and sensors. 1) The TMR effect is observed in magnetic storage devices and sensors when ferromagnetic grains tunnel through the insulating layer of a magnetic material such as Co, Ni, or Mn, and the magnetic spins in the respective ferromagnetic layers interact through the insulating layer. Similar tunneling effects have been reported for various granular structures in which ferromagnetic grains are dispersed within a nonmagnetic matrix, such as Al$_2$O$_3$, AlN, Ag, AgCl, and Au. 2) There is an advantage in using oxides for insulating oxide matrices in granular-type materials because oxide materials are easy to fabricate and to handle. 3) The MR effects in granular-type materials have been reported for several combinations of metal oxides, e.g., La$_{0.5}$Ca$_{0.5}$MnO$_3$/ZnO, 4) La$_{0.6}$Sr$_{0.4}$MnO$_3$/ZrO$_2$, 4) and Fe$_2$O$_3$/u-Fe$_3$O$_4$. 5)

The MR ratio is related to the spin polarization $P$ in the ferromagnetic grain, where $P = (N_{\uparrow}-N_{\downarrow})/(N_{\uparrow}+N_{\downarrow})$, in which $N_s$ (s = $\uparrow$ and $\downarrow$) represents the density of states at the Fermi energy for electrons with spin s. The MR ratio for a granular-type composite is expected to be MR = $P^2/(1+P^2)$. 6) Granular-type half metals with $P = 1$ should have a large MR ratio close to 50%.

Magnetite (Fe$_3$O$_4$) is a member of the spinel ferrite family $MFe_2O_4$ ($M$ = Mn, Co, Ni, Zn, Mg, etc.), of which the magnetic and electrical properties change with the cation distribution in the tetrahedral and octahedral sites. In addition, Fe$_3$O$_4$ has been known as a kind of half metal with spin polarized conduction electrons in 3d minority spin bands. 7,8) In the recent years, the large negative MR effect in low field was expected for the Fe$_3$O$_4$ thin films. 9,10) However, small negative MR ratio of 1% has been observed for polycrystalline and single crystal thin films at room temperature (R.T.) under the magnetic field of 1 T. The large MR effect can be anticipated by the TMR through the thin insulating barriers between Fe$_3$O$_4$-grains, and has been expected to realize new magnetic storage devices of magnetic random access memory (MRAM), etc. It was reported that composites of magnetite showed MR effects of 1.2%, without the use of apparent insulating barriers. 11)

On the other hand, spinel-ferrite/insulator composite materials become an attractive subject. Assuming that granular-type composite materials are prepared by using Fe$_3$O$_4$ as spinel ferrite, the large MR ratio can be enhanced as previously mentioned. In the most of composite material studies, these spinel ferrite and insulator components are separately synthesized and then composite materials are formed. 12-15) This is, however, slightly complicated since it is the sum of two syntheses for spinel ferrite and insulator materials. 15-18) In this study, previously-unreported BaTiO$_3$/Fe$_3$O$_4$ composites were prepared using a direct solid-state reaction of raw materials (BaCO$_3$, TiO$_2$, and Fe$_3$O$_4$). The magnetic behavior and MR properties are discussed in relation to the molar fraction x between Fe$_3$O$_4$ and BaTiO$_3$ in order to clarify the effect of the magnetization of the BaTiO$_3$ matrix.

2. Sample preparation

(1-x)BaTiO$_3$-xFe$_3$O$_4$ composites were prepared by a conventional ceramic method as described below. BaCO$_3$ and TiO$_2$ were mixed in the same molar...
proportion (Ba:Ti = 1:1) at 800 rpm for 5 min, by the use of a planetary mill (Fritsch, premium line P-7). The mixed powder and Fe₃O₄ were mixed again in a ball-milling pot for 24 h, so that the molar fraction x of Fe₃O₄ to BaTiO₃ was set to 0.67, 0.75, and 0.80. The mixed powder was dried, pressed into a disk, and sintered in Ar gas flow (100 mL/min.) at 1323 K for 5 h. The crystal structure was examined by powder x-ray diffraction experiments (Rigaku RINT Ultima 3) with Cu-Kα radiation. Magnetization measurements were performed with a vibrating sample magnetometer (VSM; Tamakawa TM-VSM2130HGC). MR measurements were performed by a usual 4-terminals method in dc magnetic field between -8 kOe and 8 kOe. To avoid the nonlinear effect between voltage V and current I, resistance R was measured at constant current I of 1 mA.

The surface structure and composition maps of the samples were observed by the use of a commercial electron probe micro analyzer (EPMA; JEOL JXA-8200), which applied an electron beam to a sample and detected characteristic X-rays to identify the element contained in the sample.

3. Results and discussion

X-ray diffraction patterns of (1-x)BaTiO₃-xFe₃O₄ composites with x = 0.67, 0.75 and 0.80 prepared by sintering at 1323 K for 5 h under Ar gas flow (100 mL/min.) are shown in Fig. 1. Because the diffraction peaks of raw materials and intermediate product are not detected for x = 0.67, 0.75 and 0.80 samples, these composites consist of only two phases of BaTiO₃ and Fe₃O₄. The diffraction peak positions of BaTiO₃ and Fe₃O₄ are not changed among these composites. The XRD patterns suggest that BaTiO₃/Fe₃O₄ composites are well synthesized although all of the raw materials are sintered at the same time. This simple process is different from those in most of other reports, where ferromagnetic and ferroelectric phases were separately pre-sintered and then mixed. Therefore, our results suggest the chemical stability of Fe₃O₄ and BaTiO₃, and the “inertness” between Fe₃O₄ and BaTiO₃.

Figure 2 shows the magnetization curves at room temperature for (1-x)BaTiO₃-xFe₃O₄ composites with x = 0.80 (a), 0.75 (b), and 0.67 (c) sintered at 1323 K for 5 h under Ar gas flow. Inset shows content x dependence of the magnetization.

Room temperature MR ratios are shown in Fig. 3, where the MR ratio is defined by \( \frac{R_0 - R}{R_0} \times 100 \) ( \( R_0 \) : the resistance without application of magnetic field ). The MR effect was observed in all products. The largest MR ratio of 4.9% was observed in x = 0.75.
sample at |H|>6 kOe. The x = 0.67 and 0.80 samples showed MR ratios of 3.7% and 3.1%, respectively. It was reported that compacts of FeO showed MR effects of 1.2%, without the use of apparent insulating barriers. The present results indicate that BaTiO3 components contribute to the enhancement of MR effects in this system.

Figure 4 shows the EPMA maps for Ba, Ti, and Fe in (1-x)BaTiO3-xFe3O4 composites with x = 0.75 sintered at 1323 K for 5 h under Ar. Clearly, the mapping shows two kinds of granules — one contains Ba and Ti ions and the other contains Fe ions, which indicates that BaTiO3 and Fe3O4 particles do not react with each other. A part of BaTiO3 can intervene between Fe3O4 particles. It is possible that this intervening BaTiO3 works as tunneling barriers and gives the large TMR in this sample.

4. Conclusion

(1-x)BaTiO3-xFe3O4 composites were successfully prepared by conventional solid-state sintering of raw materials (BaCO3, TiO2, and Fe2O3) in the molar fraction x of FeOx to BaTiO3 at 1323 K for 5 hours under Ar gas flow. X-ray diffraction (XRD) and electron probe micro analysis (EPMA) measurements were performed for these samples and it is confirmed that the composites consist of only two phases of BaTiO3 and Fe3O4. The largest MR ratio of 4.9% were observed under magnetic field of |H|>6 kOe for the x = 0.75 sample. The MR ratio is quadruple as large as that of FeOx. It was suggested that the formation of insulating BaTiO3 barriers were effective for the large MR ratio in this system.

References
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