Effect of Zn doping on the magnetoresistance of sintered Fe$_3$O$_4$ ferrites

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Abstract

The Zn doped Fe$_3$O$_4$ ferrites were prepared by mixing ZnO with Fe$_3$O$_4$ powder and then sintering in argon atmosphere at 1100°C for 3 h. The effects of Zn content and sintering temperature on the magnetoresistance (MR) and microstructure of sintered samples were investigated. From the analysis of Fe$^{2+}$ and Fe$^{3+}$ ions contents, X-ray diffraction, and scanning electron microscopy, we found that the nonstoichiometric phases of Fe$_3$O$_4$ and ZnFe$_2$O$_4$ coexisted in a sintered sample and Zn ions were dispersed uniformly in the sample. From the measurement of electrical resistivity at temperatures between 80K and room temperature, the relationship between log $\rho$ and $T^{-1/2}$ is linear, which means that the dominant MR effect is spin-dependent tunneling. The sample with Zn=0.86 at% has the highest MR which is about 7% at room temperature under a magnetic field of 8 kOe. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sintered Fe$_3$O$_4$ ferrites; Magnetoresistance; Zn doped Fe$_3$O$_4$ ferrites

1. Introduction

Recently, research was focused on the transport properties of the ferrimagnets Fe$_3$O$_4$ and CrO$_2$ [1–3] in view of potential applications. These magnetic materials are half metallic and therefore ideal candidates for the emergence of oxide spin electrons. However, the intrinsic magnetoresistance (MR) of these compounds is small. The MR of pure Fe$_3$O$_4$ thin films has been intensively investigated [3–6]. The epitaxial Fe$_3$O$_4$ films show no MR in low fields, whereas the polycrystalline film exhibits an MR of 1.7% at room temperature, indicative of spin-polarized tunneling between the adjacent grains. The MR behavior of Fe$_3$O$_4$ in polycrystalline thin film, powder compact, and single-crystal has been compared by Coey et al. [4], but not in the sintered sample. The MRs of Fe$_3$O$_4$ are still too low in these studies to be used at room temperature. Therefore, developing a suitable fabrication process and modifying the composition of Fe$_3$O$_4$ in order to increase its MR at room temperature is necessary.

In this study, the mechanism of the magnetotransport properties of sintered Fe$_3$O$_4$ ferrite and the effects of Zn doping on its MR were investigated.

2. Experiment

The samples were prepared by the conventional ceramic method. The starting materials are high-purity ZnO and Fe$_3$O$_4$ powder. According to the formula of (ZnO)$_x$(Fe$_3$O$_4$)$_{100-x}$ (where $X = 0–25$), each starting material was weighted, added into acetone and ball mill to complete mixing. The mixed powder was compressed into a pellet shape (10 mm diameter, 1 mm thick) under a pressure of 53.3931 lb/in$^2$ and then sintered in Ar atmosphere at 1100°C for 3 h.

The crystalline structure of sintered samples was examined by X-ray diffractometer (XRD) with a Cu-K$_{\alpha}$ radiation and their microstructures were observed with a scanning electron microscopy (SEM). The chemical composition was analyzed by energy disperse...
spectrometer (EDX). The Fe\(^{2+}\) and Fe\(^{3+}\) ion contents of the sintered sample were examined by the method of chemical titration [7]. The magnetic properties were measured by vibrating sample magnetometer (VSM) at room temperature with a maximum applied field of 12 kOe. The MR of the sintered sample was measured at room temperature with the four-probe method and the applied field was parallel to the direction of current, the maximum applied field was 9 kOe. The electric resistivity \(\rho\) was measured by the four-probe method at temperatures between 80 K and room temperature.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the sintered samples with various amounts of ZnO powder (2–25 mol\%) in mixed powder. The sintering temperature \(T_s\) is 1100 \(\degree\)C. We can observe that the two phases of Fe\(^3\)O\(_4\) and ZnFe\(^2\)O\(_4\) coexisted in all sintered samples. This indicates that the ZnO oxide will react with a part of Fe\(^3\)O\(_4\) to form ZnFe\(^2\)O\(_4\) ferrite during sintering. The X-ray diffraction peaks of ZnFe\(^2\)O\(_4\) ferrite are quite close to that of Fe\(^3\)O\(_4\) and almost overlapped. The peaks of ZnFe\(^2\)O\(_4\) ferrite phase are not easy to identify separately as the ZnO powder content in mixed powder is <5 mol\%. Table 1 shows the ZnO powder contents of various mixed powder samples and the measured Zn contents in these samples after sintering.

From the examination of Fe\(^{2+}\) and Fe\(^{3+}\) ion contents in the sample by the chemical titration method, the (Fe\(^{2+}\)/total Fe) value is about 27 mol\% which is lower than that of pure Fe\(^3\)O\(_4\) (33 mol\%). This means that some Fe\(^3\)O\(_4\) are oxidized to Fe\(^2\)O\(_3\) during sintering. After ZnO is added, we inferred that ZnO would combine with Fe\(^2\)O\(_3\) or a part of Fe\(^3\)O\(_4\) ferrite to form ZnFe\(^2\)O\(_4\) ferrite or nonstoichiometric ZnFe\(^2\)O\(_4\)\(_{1-\delta}\) ferrite during sintering, because Fe\(^2\)O\(_3\) peaks did not appear in the X-ray diffraction patterns. We speculate that the content of Fe\(^2\)O\(_3\) is small and cannot be detected by X-ray diffraction. Fig. 2 shows the SEM micrographs of the sintered samples with various Zn contents and their Zn mapping. The average grain sizes of all samples are almost the same (it is about 3 \(\mu\)m) and we can observe some pores dispersed in the grain boundary. The sintering density of all these samples is about 4.93 g/cm\(^3\), that is, about 94\% of the theoretical density. By comparing between Zn mapping and the corresponding SEM micrograph, it is revealed that Zn ions disperse uniformly in the grain. We believe that the Zinc-rich component may be ZnFe\(^2\)O\(_4\) ferrite or nonstoichiometric ZnFe\(^2\)O\(_4\)\(_{1-\delta}\) ferrite, but it is difficult to determine the \(\delta\) value.

We investigated the relationship between \(\log \rho\) and \(T^{-1/2}\) of various samples with different Zn contents, as shown in Fig. 3. It shows good linear relationship between \(\log \rho\) and \(T^{-1/2}\) in all samples. This implies that the transport of electrons is in tunneling mode, where the electrons flow through barriers (e.g. Fe\(^2\)O\(_3\), Zn ferrite, etc.) between the two magnetic Fe\(^3\)O\(_4\) phases [8]. On the other hand, the Zn ions are uniformly distributed within the sample and grains (see Fig. 2), which also confirms this tunneling mechanism.

### Table 1

The ZnO powder content in the mixed powder of various samples and the measured Zn content in these samples after sintering

<table>
<thead>
<tr>
<th>ZnO content in mixed powder (mol%)</th>
<th>Zn content in sintered sample (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>0.47</td>
</tr>
<tr>
<td>5</td>
<td>0.86</td>
</tr>
<tr>
<td>10</td>
<td>1.72</td>
</tr>
<tr>
<td>15</td>
<td>2.55</td>
</tr>
<tr>
<td>25</td>
<td>4.16</td>
</tr>
</tbody>
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Fig. 1. X-ray diffraction patterns of the sintered samples with various amounts of ZnO powder in mixed powder, sintered at 1100 \(\degree\)C.
the MR curve of the sintered Fe\textsubscript{3}O\textsubscript{4} ferrite. When the applied field increases, the value of negative MR increases rapidly with \(H\); the solid arrows indicate the increase of \(H\) and the dotted arrows indicate the decrease of \(H\). The MR value of this sintered Fe\textsubscript{3}O\textsubscript{4} ferrite at room temperature is about 5.4\% as \(H = 8\) kOe. The \(H_c\) value of this sample is small and about 30 Oe as shown in the \(M-H\) loop of Fig. 4(b).

Fig. 5 shows the relationship between MR value and Zn content in sintered samples. The maximum MR value is about 7\% as Zn content is 0.86 at\%. The amount of ZnFe\textsubscript{2}O\textsubscript{4} ferrite or ZnFe\textsubscript{2}O\textsubscript{4-\delta} ferrite affects the MR value obviously, that was controlled by the doping amount of Zn. The ZnFe\textsubscript{2}O\textsubscript{4} ferrite or ZnFe\textsubscript{2}O\textsubscript{4-\delta} ferrite provides the tunneling barrier for enhancing the MR value. As the doping amount of Zn is more than 0.86 at\%, the length of spin-dependent tunneling barrier becomes very large and the MR value is decreased with increasing Zn content, as shown in Fig. 5.

4. Conclusions

The effect of Zn doping on the MR of sintered Fe\textsubscript{3}O\textsubscript{4} ferrite was studied. It was demonstrated that a little amount of Zn doping improves the MR value of Fe\textsubscript{3}O\textsubscript{4}
The maximum MR value at room temperature is about 7% when the Zn content is 0.86 at%. The dominant MR effect is spin-dependent tunneling. From the analysis of Fe$^{2+}$ and Fe$^{3+}$ ion contents, X-ray diffraction, and scanning electron microscopy, it was found that the nonstoichiometric phases of Fe$_3$O$_4$ and ZnFe$_2$O$_4$ coexisted in the sintered sample and Zn ions were dispersed uniformly in the sample.

Fig. 5. Relationship between MR value and Zn content in sintered sample. The sintering temperature is 1100°C.

References