

# Effect of Zn doping on the magnetoresistance of sintered $\text{Fe}_3\text{O}_4$ ferrites

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## Abstract

The Zn doped  $\text{Fe}_3\text{O}_4$  ferrites were prepared by mixing ZnO with  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions contents, X-ray diffraction, and scanning electron microscopy, we found that the nonstoichiometric phases of  $\text{Fe}_3\text{O}_{4+\alpha}$  and  $\text{ZnFe}_2\text{O}_{4-\delta}$  coexisted in a sintered sample and Zn ions were dispersed uniformly in the sample. From the measurement of electrical resistivity  $\rho$  at temperatures between 80 K 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  $\text{Fe}_3\text{O}_4$  ferrites; Magnetoresistance; Zn doped  $\text{Fe}_3\text{O}_4$  ferrites

## 1. Introduction

Recently, research was focused on the transport properties of the ferrimagnets  $\text{Fe}_3\text{O}_4$  and  $\text{CrO}_2$  [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  $\text{Fe}_3\text{O}_4$  thin films has been intensively investigated [3–6]. The epitaxial  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  are still too low in these studies to be used at room temperature. Therefore, developing a suitable fabrication process

and modifying the composition of  $\text{Fe}_3\text{O}_4$ , in order to increase its MR at room temperature is necessary.

In this study, the mechanism of the magneto-transport properties of sintered  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  powder. According to the formula of  $(\text{ZnO})_X(\text{Fe}_3\text{O}_4)_{100-X}$  (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 53 393 lb/in<sup>2</sup> 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  $\text{Cu-K}_\alpha$  radiation and their microstructures were observed with a scanning electron microscopy (SEM). The chemical composition was analyzed by energy disperse

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spectrometer (EDX). The  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  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°C. We can observe that the two phases of  $\text{Fe}_3\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  coexisted in all sintered samples. This indicates that the ZnO oxide will react with a part of  $\text{Fe}_3\text{O}_4$  to form  $\text{ZnFe}_2\text{O}_4$  ferrite during sintering. The X-ray diffraction peaks of  $\text{ZnFe}_2\text{O}_4$  ferrite are quite close to that of  $\text{Fe}_3\text{O}_4$  and almost overlapped. The peaks of  $\text{ZnFe}_2\text{O}_4$  ferrite phase are not easy to identify separately as the ZnO powder content in mixed powder

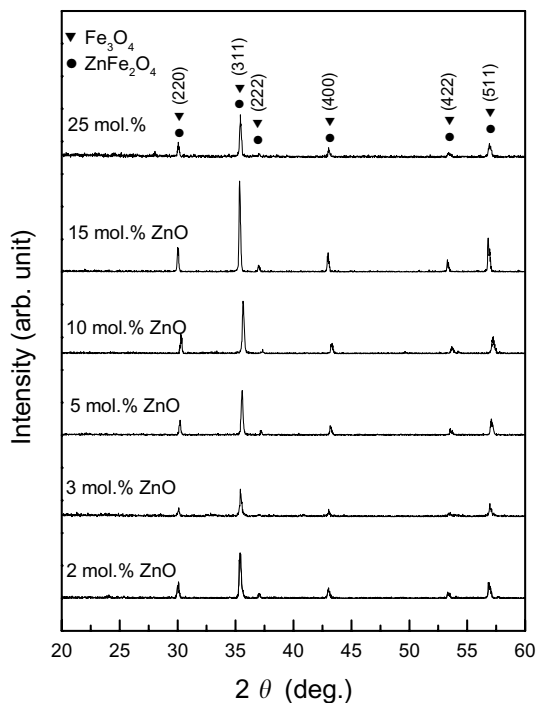


Fig. 1. X-ray diffraction patterns of the sintered samples with various amounts of ZnO powder in mixed powder, sintered at 1100°C.

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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ion contents in the sample by the chemical titration method, the ( $\text{Fe}^{2+}/\text{total Fe}$ ) value is about 27 mol% which is lower than that of pure  $\text{Fe}_3\text{O}_4$  (33 mol%). This means that some  $\text{Fe}_3\text{O}_4$  are oxidized to  $\text{Fe}_2\text{O}_3$  during sintering. After ZnO is added, we inferred that ZnO would combine with  $\text{Fe}_2\text{O}_3$  or a part of  $\text{Fe}_3\text{O}_4$  ferrite to form  $\text{ZnFe}_2\text{O}_4$  ferrite or nonstoichiometric  $\text{ZnFe}_2\text{O}_{4-\delta}$  ferrite during sintering, because  $\text{Fe}_2\text{O}_3$  peaks did not appear in the X-ray diffraction patterns. We speculate that the content of  $\text{Fe}_2\text{O}_3$  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  $\mu\text{m}$ ) and we can observe some pores dispersed in the grain boundary. The sintering density of all these samples is about 4.93  $\text{g}/\text{cm}^3$ , 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  $\text{ZnFe}_2\text{O}_4$  ferrite or nonstoichiometric  $\text{ZnFe}_2\text{O}_{4-\delta}$  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.  $\text{Fe}_2\text{O}_3$ , Zn ferrite, etc.) between the two magnetic  $\text{Fe}_3\text{O}_4$  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.

The MR was defined as  $\text{MR}(\%) = (R_H - R_0)/R_0$ , where  $R_H$  is the resistance in applied magnetic field  $H$  and  $R_0$  is the resistance in zero-field. Fig. 4(a) shows

Table 1

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

ZnO content in mixed powder (mol%)	Zn content in sintered sample (at%)
0	0
2	0.42
3	0.47
5	0.86
10	1.72
15	2.55
25	4.16

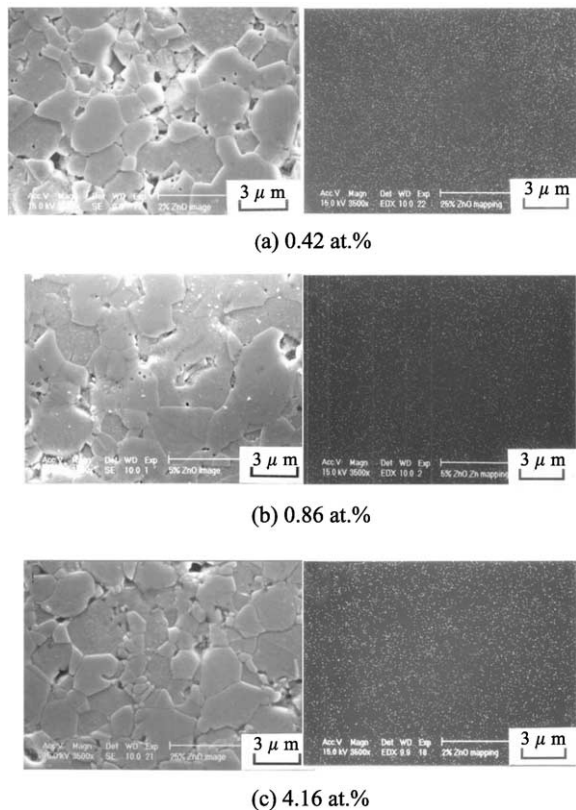


Fig. 2. SEM micrographs of the sintered samples with various Zn contents and their Zn mapping. The Zn content of (a) is 0.42 at.%, (b) is 0.86 at.%, and (c) is 4.16 at.%.

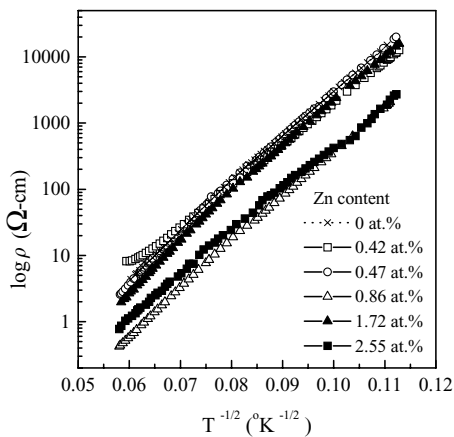


Fig. 3.  $\log \rho$  vs.  $T^{-1/2}$  of various samples which were sintered at 1100°C.

the MR curve of the sintered  $\text{Fe}_3\text{O}_4$  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

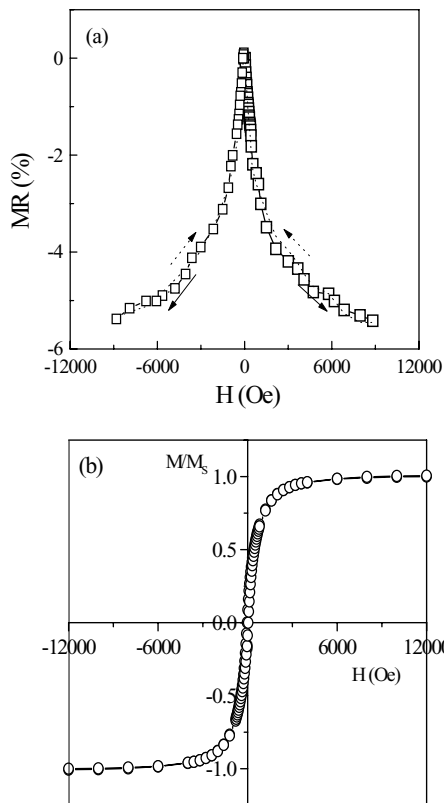


Fig. 4. (a) The magnetoresistance curve and (b)  $M-H$  loop at room temperature of the  $\text{Fe}_3\text{O}_4$  ferrite which is sintered at 1100°C.

decrease of  $H$ . The MR value of this sintered  $\text{Fe}_3\text{O}_4$  ferrite at room temperature is about 5.4% as  $H = 8 \text{ kOe}$ . 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  $\text{ZnFe}_2\text{O}_4$  ferrite or  $\text{ZnFe}_2\text{O}_{4-\delta}$  ferrite affects the MR value obviously, that was controlled by the doping amount of Zn. The  $\text{ZnFe}_2\text{O}_4$  ferrite or  $\text{ZnFe}_2\text{O}_{4-\delta}$  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  $\text{Fe}_3\text{O}_4$  ferrite was studied. It was demonstrated that a little amount of Zn doping improves the MR value of  $\text{Fe}_3\text{O}_4$

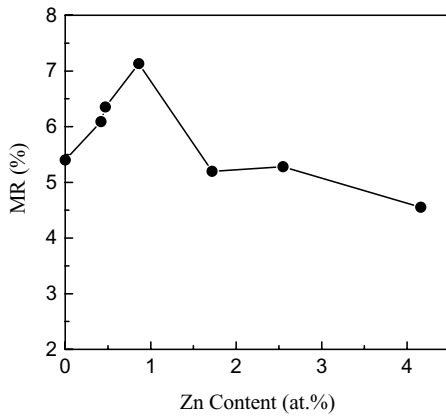


Fig. 5. Relationship between MR value and Zn content in sintered sample. The sintering temperature is 1100°C.

ferrite. 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  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ion contents, X-ray diffraction, and scanning electron microscopy, it was found that the nonstoichiometric phases of  $\text{Fe}_3\text{O}_{4+\alpha}$  and  $\text{ZnFe}_2\text{O}_{4-\delta}$  coexisted in the sintered sample and Zn ions were dispersed uniformly in the sample.

## References

- [1] S. Sundar Manoharan, D. Elefant, G. Reiss, J.B. Goodenough, *Appl. Phys. Lett.* 72 (1998) 984.
- [2] J.B. Goodenough, *Proc. Solid State Chem.* 5 (1972) 141.
- [3] S.B. Ogale, K. Ghosh, R.P. Sharma, R.L. Greene, R. Ramesh, T. Venkatesan, *Phys. Rev. B* 57 (1998) 7823.
- [4] J.M.D. Coey, A.E. Berkowitz, L.I. Balcells, F.F. Putris, F.T. Parker, *Appl. Phys. Lett.* 72 (1998) 734.
- [5] G.Q. Gong, A. Gupta, G. Xiao, W. Qian, V.P. Dravid, *Phys. Rev. B* 56 (1997) 5096.
- [6] X.W. Li, A. Gupta, G. Xiao, G.Q. Gong, *J. Appl. Phys.* 83 (1998) 7049.
- [7] P.C. Kuo, T.S. Tsai, *J. Appl. Phys.* 65 (1989) 4349.
- [8] Ping Sheng, B. Abeles, Y. Arie, *Phys. Rev. Lett.* 31 (1973) 44.