Magnetic properties of ZnO-doped cobalt ferrite

Jian-ping Zhou · Zhan Shi · Hong-cai He · Ce-Wen Nan

Abstract The cobalt ferrites with chemical composition $Co_{1+x}Zn_xFe_{2-2x}O_4$ (x=0.0, 0.1, 0.2, 0.4) were obtained with conventional solid reaction. The ZnO-doped samples have lower lattice constant than $CoFe_2O_4$ by adjusting Co ions to the octahedral sites. The results show that doping ZnO could extremely improve the magnetic properties. In comparison with pure $CoFe_2O_4$, the little ZnO-doped sample has higher permeability and much lower coercivity at the condition of a little decrease of magnetization saturation. Sample with x=0.1 shows evident magnetostrictive effect at the magnetic field of 30–60 mT while pure cobalt ferrite sample does not, though the saturation magnetostriction decreases. These indicate that ZnO-doping improves the magnetostrictive sensitivity of the cobalt ferrites and have potential applications in magnetoelectric devices and magnetic detector.

Keywords $CoFe_2O_4$ · ZnO-doping · Magnetics · Magnetostriction

1 Introduction

Cobalt ferrites are important in microwave industry because of their low cost, easily manufacturing and remarkable electric and magnetic properties. Their physical and chemical properties are mainly dependent on the chemical compositions as well as processing.

Electric properties of the cobalt ferrites can be modified by the addition of small amount of foreign ions, such as Li$^+$ [1], Al^{3+} [2, 3], Zn^{2+} and Mn^{2+} [4], or lanthanide ions [5]. The ferrite lattice parameters are also modified by the substitute ions. The cobalt ferrite has a largest magnetostriction among the spinel ferrites and was used in combination with the ferroelectrics to produce the magnetoelectric effects [6]. Zinc was doped to improve the magnetoelectric coefficient and sensitivity [7]. But the cobalt ferrite crystal lattice is more than twice that of the ferroelectrics, and Zn^{2+} ions commonly substitute for Co^{2+} in the tetrahedral sites [7, 8], resulting in the lattice parameter increase [7] because of the larger crystal lattice constant of $ZnFe_2O_4$. However, the smaller lattice parameter of the cobalt ferrite may be obtained by replacing Fe^{3+} in the octahedral site, such as with Al^{3+} [2] and Cr^{3+} [9].

The addition of foreign elements can modify the magnetic properties, such as coercivity and saturation magnetization [9, 10]. In this paper, we prepare the ZnO-doped cobalt ferrite with a smaller lattice parameter and study the influence of the divalent zinc ions substitution on the coercivity, saturation magnetization and magnetostriction of the cobalt ferrite.

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2 Experimental procedures

Polycrystalline spinel ferrites were prepared by the standard ceramic technique. High pure oxides Co_3O_4, ZnO and Fe_2O_3 were mixed together according to the stoichiometric composition $Co_{1+x}Zn_xFe_{2-2x}O_4$, where x=0.0, 0.1, 0.2, 0.4, assigned as sample (a), (b), (c) and (d). The mixed powder was preheated at 1000°C for 4 h. The powder was riddled

with a sifter and then pressed in a stainless-steel die under a pressure of 250 MPa. Some samples were pressed to tablets with about 1.8 mm in thickness and 10 mm in diameter and some were pressed to toroidal shapes with about 1.5 mm in thickness, 10 mm in inner diameter and 20 mm in outside diameter. Then these samples were sintered at 1100°C for 4 h in air.

The tablets were polished to a smooth surface. The phase was determined by X-ray diffractometry (XRD). The tablets were cut to different shapes of cubes and cuboids for VSM (Vibrating Sample Magnetometer) and magnetostriction measurement, respectively. The toroidal samples were for magnetic permeability investigates with an Agilent 4911A analyzer. JSM-6460LV type of Scanning electron microscopy (SEM) was used to study the cross section of the samples.

3 Results and discussion

3.1 Crystal lattice and microstructure characteristics

Figure 1 shows the XRD patterns of the samples calcined at 1100°C, and the inset shows the enlarged parts in the range of 35–38°. The XRD patterns of the samples (a)–(c) keep similar characteristics. Their peaks and relative intensities are consistent with the ASTM data cards of $FeCo_2O_4$ but move to large angle with the ZnO-doping increasing as shown in the inset, meaning that the lattice parameter decreases with ZnO doping.

$ZnFe_2O_4$, $CoFe_2O_4$ and $ZnCo_2O_4$ share the spinel structures and have very close crystal lattice parameters. For

the pure sample, it is easy to make sure the phase of $CoFe_2O_4$. But for the ZnO-doped samples, three spinel structures of $ZnFe_2O_4$, $CoFe_2O_4$ and $ZnCo_2O_4$ could form in the solids.

After preheating temperature of 1000°C, cations have enough energy for diffusion and reaction. Zn^{2+} lies in the tetrahedral sites considering its free enthalpy increment of an interchange reaction with the various atoms [11]. Then two possible spinels of $ZnFe_2O_4$ and $ZnCo_2O_4$ can be produced. Considering that $ZnFe_2O_4$ has a largest lattice constant in these spinels, it would lead to large strain energy in the solid mixture of $CoFe_2O_4$, $ZnCo_2O_4$ and Co_3O_4. The composition formula $Co_{1+x}Zn_xFe_{2-2x}O_4$ can be written as another format: $xZnCo_2O_4 \cdot (1-x)CoFe_2O_4$ (x=0.0, 0.1, 0.2, 0.4). Therefore, $CoFe_2O_4$ solid solution with $ZnCo_2O_4$ forms in the low ZnO-doped samples, resulting in a decrease in the lattice parameter because of the small lattice parameter of $ZnCo_2O_4$. After the samples were calcined at temperature of 1100°C, the samples (a)–(c) keep the same lattice characteristics as shown in the inset. This means that the lattice can be reduced by adjusting the position of ions.

With increasing ZnO and Co_3O_4, CoO appears in the sample (d), resulting in an increase in the $CoFe_2O_4$ lattice parameter after sintering at 1100°C.

The SEM micrographs of the samples (a)–(d) calcined at 1100°C are shown in Fig. 2. It is evident from the figures that the particles in the samples (b) and (c) are more homogeneous, compact and smoother than those in the sample (a) by introducing a small number of Zn^{2+}. This indicates that the incorporation of ZnO can enhance the ions mobility to form the uniform particles. But with the increase in ZnO and Co_3O_4, CoO separates from the solid, resulting in the rough particles.
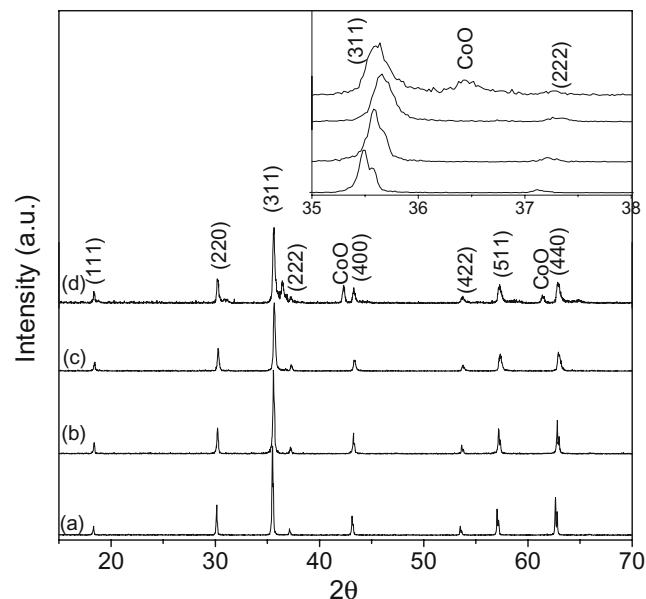
3.2 Magnetic properties

The magnetic properties of the samples were determined by a VSM. Figure 3 shows the magnetic hysteresis loops of the samples (a) and (b) sintered at 1100°C. The effect of Zn ions on the magnetic properties is obvious. Figure 4 plots the summation of saturation magnetization (M_s), coercivity (H_c) and remnant ratio (M_r/M_s) with the composition x at the maximal field of 10 kOe. In ferrites, the magnetization is commonly equal to the difference between the magnetic ions in site A and site B. Zn^{2+} ions have a preference for site A, then a low concentration of Zn should enhance the saturation magnetization of ferrites. But nonmagnetic Zn^{2+} ions have no effect on the magnetic exchange interaction. Then the exchange interaction between the trivalent ions on the B sites is so weak that the material is paramagnetic at room temperature [12]. As a result, M_s reduces with the ZnO content.

With the increase in ZnO, the coercivity drastically decreases at the cost of a little magnetization saturation as

Fig. 1 X-ray diffraction patterns of samples calcined at 1100°C. The *inset* shows the enlarged patterns in the range of 35–38°

Fig. 2 SEM micrographs of $Co_{1+x}Zn_xFe_{2-2x}O_4$ ferrite system for the samples (**a**)–(**d**) calcined at 1100°C
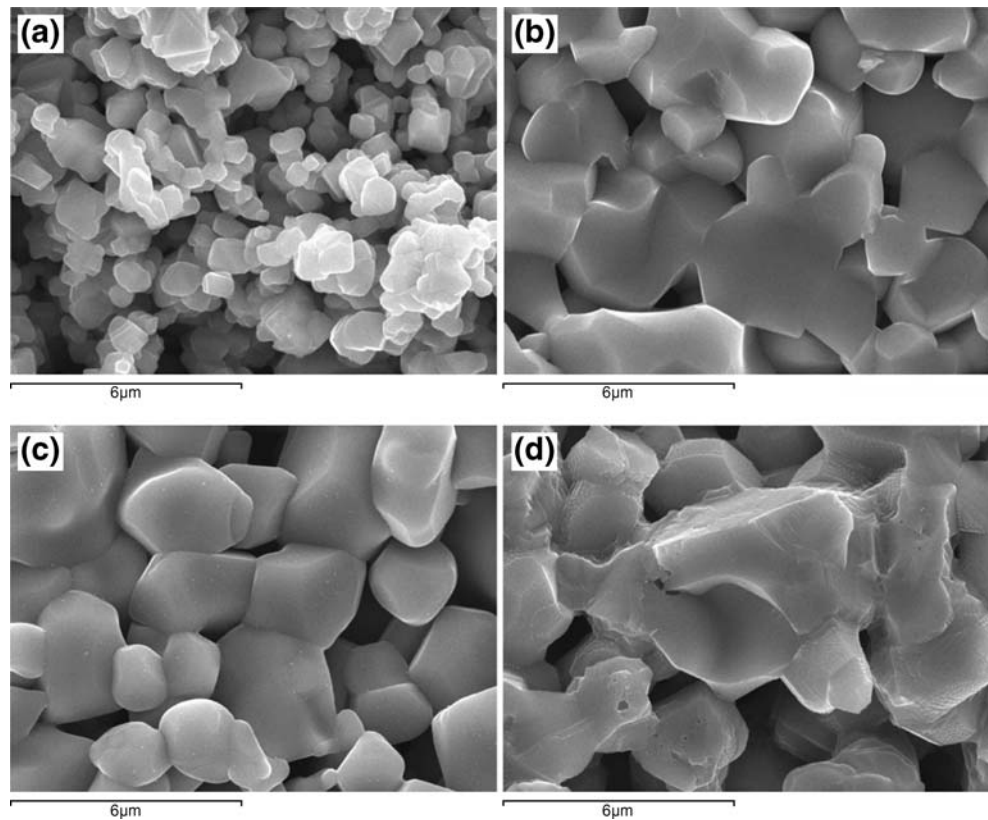
shown in Fig. 4. The coercivities of the samples (b) and (c) are as low as 68 Oe and 42 Oe, respectively. The addition of ZnO enhances mobility of the ions to form the uniform particles and increase the particle size. As a result, the strain decreases and the magnetic domains reverse easily under the external magnetic field. From

$$H_c^\sigma \propto \frac{\lambda_s \sigma}{M_s} \qquad (1)$$

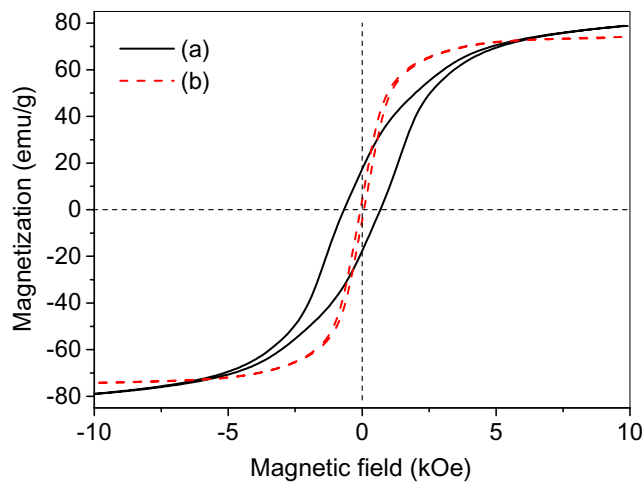where λ_s is saturation magnetostriction, H_c decreases with strain σ. The coercivity of these samples is much lower than that of the cobalt ferrites doped with Al and Ti [3].

The remnant ratio of $CoFe_2O_4$ is small. The addition of Zn^{2+} much decreases the remnant ratio as shown in Fig. 4. The remnant ratio is as low as 0.06 for the samples (b) and (c).

The magnetic permeability (μ_r) of pure $CoFe_2O_4$ is 1. H_c decreases after the addition of ZnO, and the magnetic susceptibility χ should be increase from the relation

$$\chi^\sigma \propto \frac{M_s^2}{\lambda_s \sigma} \propto \frac{M_s}{H_c} \qquad (2)$$

Fig. 3 Hysteresis loops of the samples (a) and (b) sintered at 1100°C
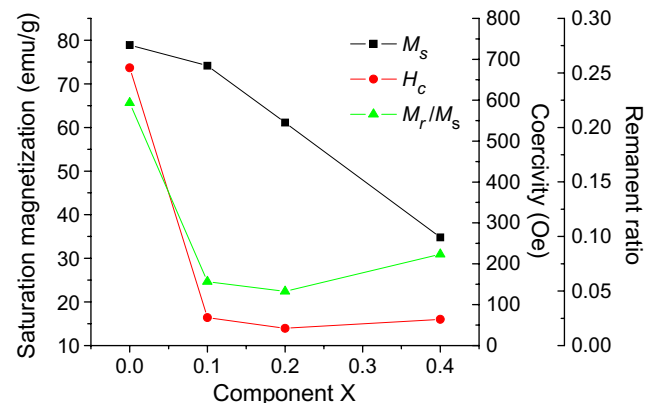

Fig. 4 Coercivity, magnetization saturation and remnant ratio as a function of the component x
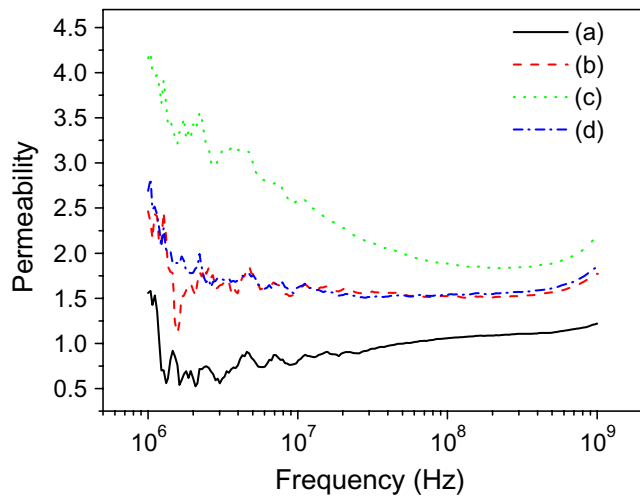
Fig. 5 The variation of magnetic permeability with frequency for the samples calcined at 1100°C

The dependence of the magnetic permeability on frequency is shown in Fig. 5. It is found that the magnetic permeability is almost independent of frequency in the range of $10^6–10^9$Hz, and μ_r of ZnO-doped samples is higher than that of the pure $CoFe_2O_4$.

3.3 Magnetostriction

The longitudinal (λ_{11}) and transverse (λ_{13}) magnetostrictions of the $Co_{1+x}Zn_xFe_{2-2x}O_4$ samples are plotted in Fig. 6. In our experiment, λ_{11} is -190×10^{-6} for the sample (a). The saturation magnetostriction is related to the coercivity by
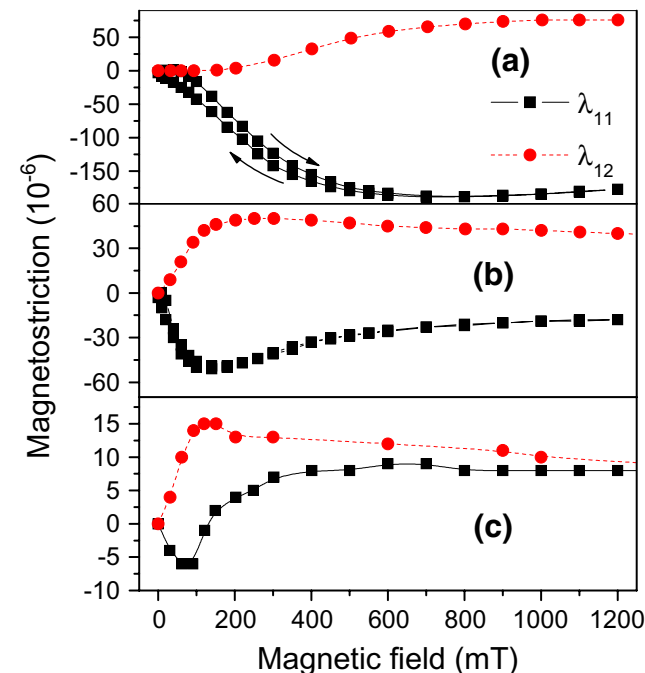

Fig. 6 Longitudinal (λ_{11}) and transverse (λ_{12}) magnetostrictions for the $Co_{1+x}Zn_xFe_{2-2x}O_4$ samples measured at room temperature
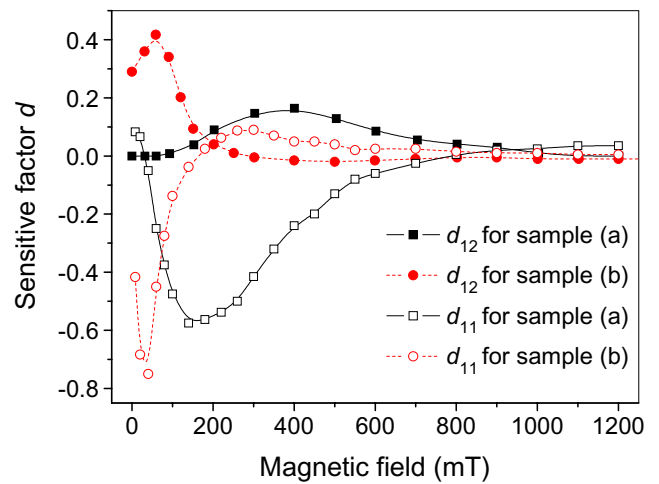

Fig. 7 Sensitive factor as a function of the magnetic field for the samples (a) and (b) calcined at 1100°C

Eq. 1. λ_{11} of the sample (b) is one quarter of that of the sample (a), but the magnetic field at the saturation magnetostriction is only 1/5 of the sample (a). What's more, at low magnetic field of 30 and 60 mT, the sample (a) does not show magnetostrictive effect while the sample (b) shows -14×10^{-6} and -30×10^{-6}, respectively. These mean that the addition of ZnO improves the sensitivity of response to the magnetic field. But the magnetostriction is weak for the sample (c) and unobvious for the sample (d) because of their weak magnetism. The cobalt ferrite is a hard magnetic material and shows a loop for the magnetostriction as shown in Fig. 6. The sample (b) shows a little loop because of its low coercivity.

The sensitive factor of the magnetostriction is defined as $d=\partial\lambda/\partial H$. Figure 7 shows the sensitive factor of samples (a) and (b). It is clear that the maximum sensitive factor of the sample (b) is larger at lower magnetic field in comparison with the sample (a).

Co^{2+} is one of the strong magnetic crystalline anisotropic ions, but Zn^{2+} is not. Once Zn^{2+} enters into the lattice of ferrite, the anisotropy of the cobalt ferrite decreases, as a result, both the saturation magnetostriction and coercivity decrease.

4 Conclusion

The cobalt ferrites with ZnO-doped have been studied. The ZnO-doping can decreases the lattice parameter of ferrites instead of increasing it as reported in the literature. The ZnO-doped samples have uniform particles in the solids. The results of magnetism and magnetostriction for the samples show that doping ZnO could extremely improve the magnetic properties. In comparison with pure $CoFe_2O_4$, the little ZnO-doping sample has higher permeability and

much lower coercivity by a loss of magnetization saturation. Although the ZnO-doping decreases saturation magnetostriction of the cobalt ferrites, it improves the magnetostrictive sensitivity and reduces the magnetic field to saturation magnetostriction. These mean that ferrites have potential applications in magnetoelectric devices and magnetic detector.

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