

Dielectric and magnetic properties of ZnO-doped cobalt ferrite

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A series of cobalt ferrites with the chemical composition $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.4$) were obtained by a conventional ceramic method. The ZnO-doped samples have a smaller lattice constant than that of CoFe_2O_4 by adjusting part of the cobalt ions to the octahedral sites. Doping with ZnO could greatly improve the dielectric and magnetic properties. AC dielectric properties show that the samples had semiconductor characteristics for an electron exchange between ions with a different chemical valence. The dielectric constant of the ZnO-doped ferrites is mainly enhanced by Maxwell-Wagner polarization and a Koops mechanism. In comparison with pure CoFe_2O_4 , the sample with small amounts of ZnO-doping has a higher permeability and a much lower coercivity with the condition of a small decrease in magnetization saturation, and it shows an obvious magnetostrictive effect at a magnetic field of <60 mT while the pure cobalt ferrite sample does not, although the saturated magnetostriction decreases. These results indicate that ZnO doping improves the magnetostrictive sensitivity of cobalt ferrites.

Key words: CoFe_2O_4 , ZnO-doping, dielectrics, magnetics.

Introduction

Cobalt ferrites are of importance in the microwave industry because of their low cost, easy manufacturing and remarkable electric and magnetic properties. Their physical and chemical properties are mainly dependent on the chemical composition and processing. The magnetic and dielectric properties of cobalt ferrites can be modified by doping with a small amount of foreign ions, such as Li^+ [1, 2], Al^{3+} [3] and lanthanide ions [4]. The ferrite lattice parameters are also modified by the substitute ions. Cobalt ferrite is a well-known hard magnetic material with a coercivity as high as 2 kOe [5, 6]. Some studies have been focused on increasing its coercivity [4, 7]. Another important characteristic of cobalt ferrite is that it has the largest magnetostriction among the spinel ferrites, which has been used with ferroelectrics (e. g. PZT) to produce magnetoelectric effects [8]. Zinc has been doped to improve the magnetoelectric coefficient and sensitivity [9]. But the cobalt ferrite crystal lattice is more than twice that of ferroelectrics, and Zn^{2+} ions commonly substitute for Co^{2+} in tetrahedral sites [10], resulting in an increase in the lattice parameter [9] because of the larger crystal lattice constant of ZnFe_2O_4 . However, a smaller lattice parameter of cobalt ferrite may be obtained by replacing the Fe^{3+} in octahedral sites with ions such as Al^{3+} [3].

Studying the AC electrical properties is a convenient technique for understanding the mechanisms involved in the dielectric structure, temperature and frequency. In

this paper, we describe the preparation of the ZnO-doped cobalt ferrites with a smaller lattice parameter and study the influence of divalent zinc ions substitution on the dielectric and magnetic properties of cobalt ferrites.

Experimental

A series of polycrystalline spinel ferrites were prepared using a conventional ceramic method. Pure oxides Co_3O_4 , ZnO and Fe_2O_3 were mixed together according to the chemical composition $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_{2-2x}\text{O}_4$, with $x = 0.0, 0.1, 0.2, 0.4$, assigned as samples (a), (b), (c) and (d). The mixtures were ground in a satellite mill for about 6 hours to obtain a homogeneous mixture of fine powder. The powder was pre-fired at 1000°C for 4 hours and then slowly cooled down to room temperature in the furnace. Then the powder was pressed into different shapes for the studies. Tablets 1.5–2 mm in thickness and 10 mm in diameter were used for dielectric measurements. Toroids 1.5 mm in thickness, 10 mm in inner diameter and 20 mm in external diameter were used for magnetic permeability measurements. The samples were sintered at 1000°C and 1100°C for 4 hours. Then some of the tablets were polished to a uniform parallel surface. Silver paste was coated on their surfaces acting as good electrical contacts for measuring electrical and dielectric properties. Some of the tablets were cut to different shapes of cubes and cuboids. The cubes were about $1.8 \times 1.8 \times 1.8 \text{ mm}^3$ for VSM (vibrating sample magnetometer) measurements. The cuboids about $4 \times 4 \times 1.8 \text{ mm}^3$ were used for magnetostriction studies.

The AC electrical properties were measured at different temperatures using an HP4192 complex impedance

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analyzer in the frequency range of 10^3 - 10^6 Hz, and at room temperature by using an HP4194 complex impedance analyzer in the frequency range of 10^2 - 10^7 Hz. The VSM was employed to determine the hysteresis loops. Magnetostriction was measured under a magnetic field up to 1.5 T using a static strain gauge. The high frequency permeability was investigated with an Agilent 4911A meter on the toroidal samples in the frequency range of 10^6 - 10^9 Hz. A JSM-6460LV type of SEM (scanning electron microscope) was employed for analysis of the cross sections of the samples.

Results and Discussion

Structural characteristics

Fig. 1 shows the X-ray diffraction (XRD) patterns of the samples calcined at 1100 °C together with sample (d) calcined at 1000 °C, and the inset shows the blown-up parts in the range 29.5~39°. The XRD patterns of samples (a)-(c) calcined at 1100 °C and 1000 °C (not shown here) showed similar characteristics. Their lines and relative intensities resemble the ASTM data cards of FeCo_2O_4 but move slightly to a larger angle with an increase of dopant content as shown in the inset.

ZnFe_2O_4 , CoFe_2O_4 and ZnCo_2O_4 share the spinel structure and have very similar crystal lattice parameters. For the pure sample, it is easy to be sure that the phase is CoFe_2O_4 . But for the ZnO-doped samples, three spinel structures of ZnFe_2O_4 , CoFe_2O_4 and ZnCo_2O_4 perhaps coexist in the solid.

At a preheating temperature of 1000 °C, cations have enough energy for diffusion and reaction. Zn^{2+} lies in tetrahedral sites considering its free enthalpy increment from an interchange reaction with the various atoms [11,

12]. Then two possible spinels ZnFe_2O_4 and ZnCo_2O_4 can be produced. But ZnFe_2O_4 has the largest lattice constant of these spinels, resulting in a large strain energy in the solid mixture of CoFe_2O_4 , ZnCo_2O_4 and Co_3O_4 . The composition formula $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_{2-2x}\text{O}_4$ can also be written as $x\text{ZnCo}_2\text{O}_4 \cdot (1-x)\text{CoFe}_2\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.4$). Therefore, a CoFe_2O_4 solid solution with ZnCo_2O_4 forms in the low ZnO-doped samples, as a result, the lattice parameter decrease with ZnO-doping [13]. After the samples were calcined at temperatures of 1100 °C and 1000 °C, samples (a)-(c) retained the same lattice characteristics as shown in Fig. 2. The line for ZnCo_2O_4 separates from that of CoFe_2O_4 in sample (d) calcined at 1000 °C because of extensive Zn-doping, and after sintering at 1100 °C, CoO appears in the sample, resulting in the CoFe_2O_4 lattice parameter increase.

The mean radius of the cations at tetrahedral sites (A sites) R_A and octahedral sites (B sites) R_B were calculated from [14]:

$$R_A = \sqrt{3}(\mu - 0.25)a - R(\text{O}^{2-}) \quad (1)$$

$$R_B = (0.625 - \mu)a - R(\text{O}^{2-}) \quad (2)$$

where a is the lattice parameter of ferrite, $R(\text{O}^{2-}) = 1.26 \text{ \AA}$ is the radius of the oxygen ion, and $\mu = 0.381$ is the oxygen parameter.

The calculated R_A and R_B as a function composition are also shown in Fig. 2, which shows that both R_A and R_B decrease with increasing Zn-doping, similar to the lattice parameters discussed above. The decrease in R_A and R_B indicates that part of the Fe^{3+} and Co^{2+} ions are distribution over A and B positions, taking into account their ionic radii. The cation distribution for $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_{2-2x}\text{O}_4$

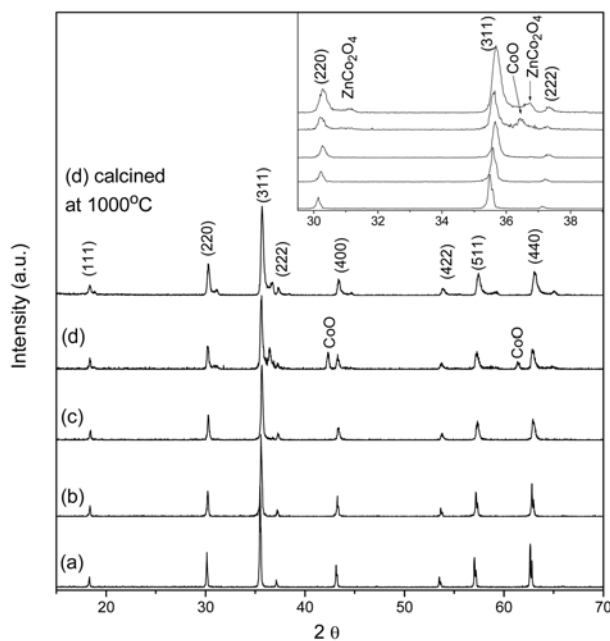


Fig. 1. X-ray diffraction patterns of samples. The inset shows the blown-up patterns in the range of 29.5~39°.

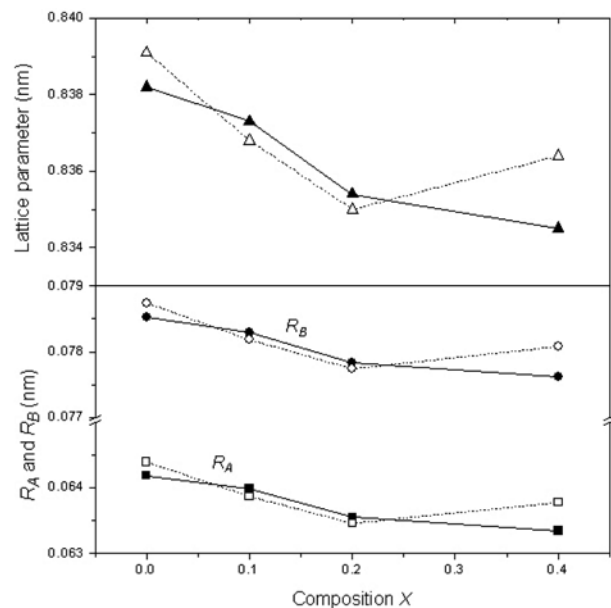


Fig. 2. The composition dependence of the lattice parameter and mean radius of ions at calcining temperatures of 1000 °C (solid line) and 1100 °C (dash line).

was estimated according to Eqs. (1) and (2), together with the cation distribution expression of the ferrite system [14]:

$$\text{Co}_8\text{Fe}_{1-\delta}[\text{Co}_{1-\delta}\text{Fe}_{1+\delta}]\text{O}_4 \quad (3)$$

where the cations on B sites are in brackets, and δ determines the cation distribution. Here we only consider the CoFe_2O_4 part for Zn-doped samples. The mean radius of ions at tetrahedral sites can be expressed simply as linear relationship:

$$R_A = \delta R(\text{Co}^{2+}) + (1-\delta)R(\text{Fe}^{3+}) \quad (4)$$

where $R(\text{Co}^{2+}) = 0.72 \text{ \AA}$ and $R(\text{Fe}^{3+}) = 0.63 \text{ \AA}$ [14]. From Eqs. (1) and (4), δ can be obtained. The estimated cation distribution for $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_{2-2x}\text{O}_4$ is given in Table 1.

The composition formula $x\text{ZnCo}_2\text{O}_4 \cdot (1-x)\text{CoFe}_2\text{O}_4$ indicates that Co^{2+} and Co^{3+} exist in the solids, what is more, Fe^{3+} ions in B sites have a strong preference for A sites becoming Fe^{2+} ions.

Microstructure and density

The SEM micrographs of samples (a)~(d) calcined at 1000 °C and 1100 °C are shown in Fig. 3 and Fig. 4, respectively. It is evident from these figures that the particle size of sample (b) and (c) is more uniform, compact and smooth than that of sample (a), indicating that the addition of ZnO can enhance the diffusion to form uniform particles [13]. But with an increase in ZnO and Co_3O_4 , CoO or ZnCo_2O_4 separates and the particles become rough. When the sintering temperature rises to 1100 °C, the grains grow larger and become more compactly stacked.

The density of the samples determined by Archimedes's method is listed in Table 2. The density results are in agreement with the microstructure observed by SEM. Addition of ZnO improves the densities of the cobalt ferrites.

AC dielectric measurements at room temperature

Fig. 5 shows the variation of the dielectric constant

Table 1. The estimated cation distribution (Sample (d) is not shown because it is two phases)

Composition	Samples sintered at 1000 °C		Samples sintered at 1100 °C	
	A site	B site	A site	B site
(a) CoFe_2O_4	$\text{Co}_{0.132}\text{Fe}_{0.868}$	$\text{Co}_{0.868}\text{Fe}_{1.132}$	$\text{Co}_{0.155}\text{Fe}_{0.845}$	$\text{Co}_{0.845}\text{Fe}_{1.155}$
(b) $\text{Co}_{1.1}\text{Zn}_{0.1}\text{Fe}_{1.8}\text{O}_4$	$\text{Zn}_{0.1}\text{Co}_{0.169}\text{Fe}_{0.731}$	$\text{Co}_{0.931}\text{Fe}_{1.069}$	$\text{Zn}_{0.1}\text{Co}_{0.156}\text{Fe}_{0.744}$	$\text{Co}_{0.944}\text{Fe}_{1.056}$
(c) $\text{Co}_{1.2}\text{Zn}_{0.2}\text{Fe}_{1.6}\text{O}_4$	$\text{Zn}_{0.2}\text{Co}_{0.180}\text{Fe}_{0.620}$	$\text{Co}_{1.020}\text{Fe}_{0.980}$	$\text{Zn}_{0.2}\text{Co}_{0.170}\text{Fe}_{0.630}$	$\text{Co}_{1.030}\text{Fe}_{0.97}$

*Co ions include Co^{2+} and Co^{3+} at B site.

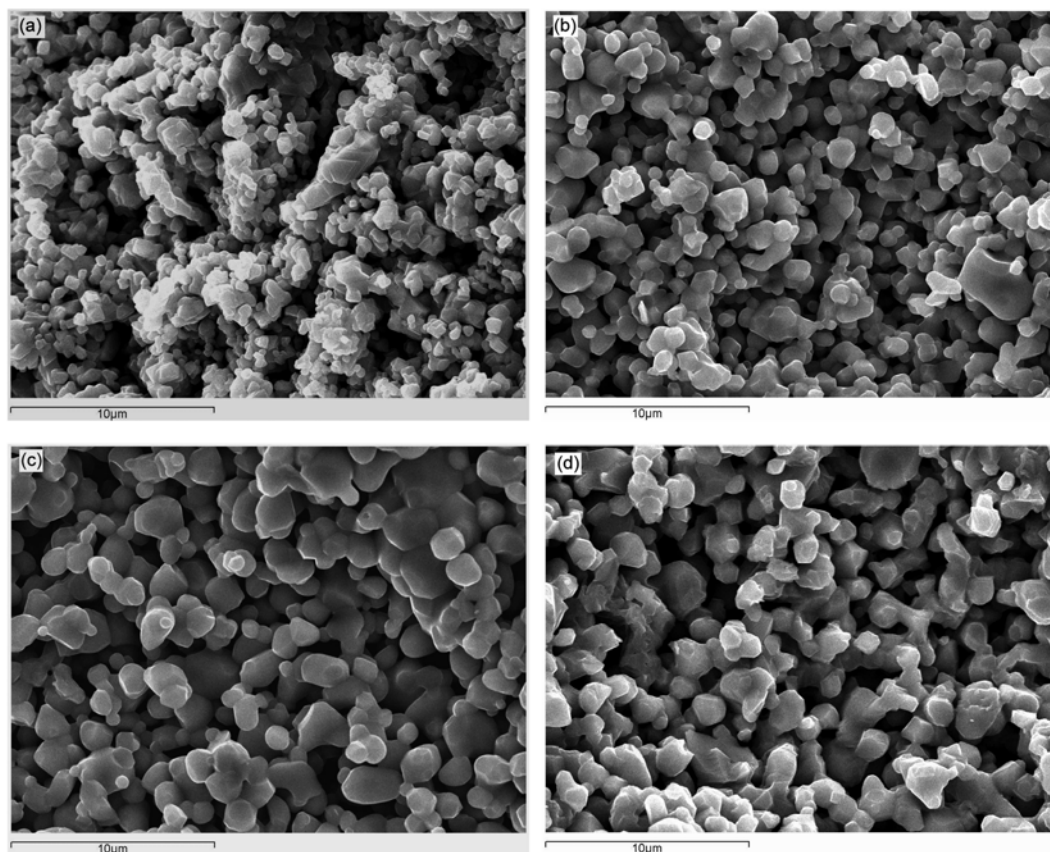


Fig. 3. SEM micrographs of $\text{Co}_{1+x}\text{Zn}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite system for samples (a) ~ (d) calcined at 1000 °C.

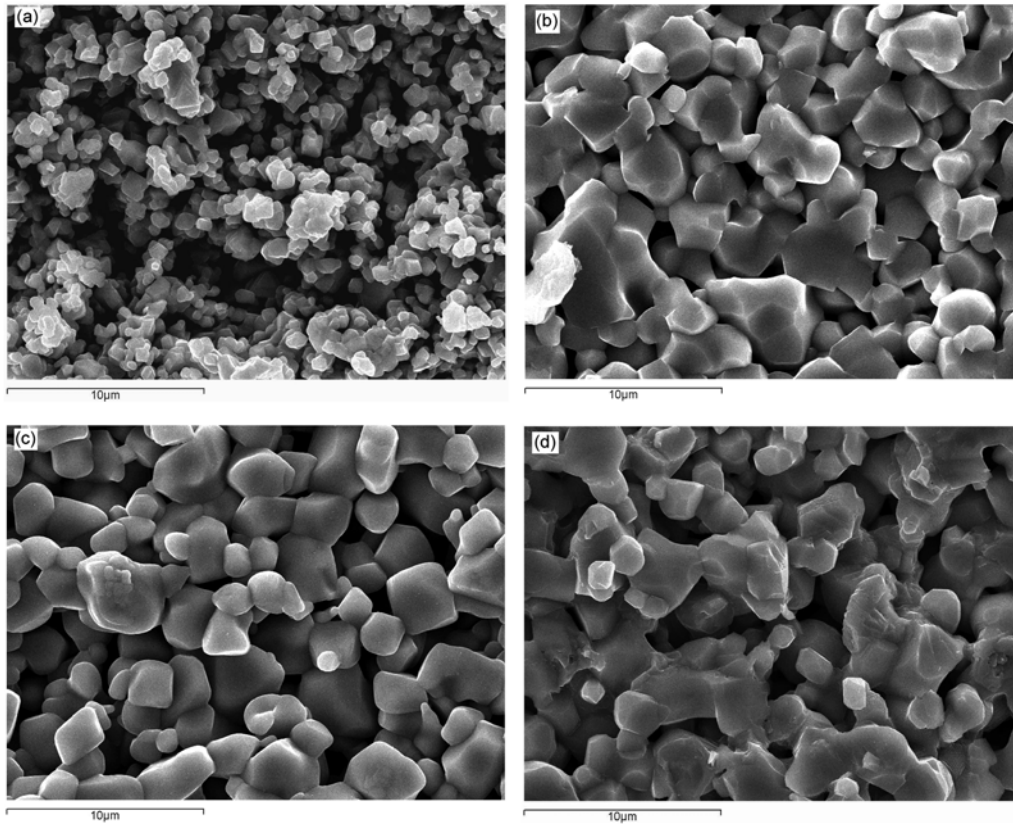


Fig. 4. SEM micrographs of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-2x}\text{O}_4$ ferrite system for samples (a) ~ (d) calcined at 1100 °C.

Table 2. The densities of the samples sintered at 1000 °C and 1100 °C (g/cm^3)

T_s	(a) $x = 0$	(b) $x = 0.1$	(c) $x = 0.2$	(d) $x = 0.4$
1000 °C	3.91	4.67	4.45	3.99
1100 °C	4.43	5.14	4.87	4.89

(ϵ), dielectric loss tangent ($\tan\delta$) and resistivity (ρ) for the pure and ZnO-doped samples calcined at 1000 °C and 1100 °C. It can be seen that the frequency dependence of the dielectric constant, dielectric loss tangent and resistivity of the samples calcined at 1000 °C resembles that of those calcined at 1100 °C. A comparison of the dielectric constant, dielectric loss tangent and resistivity at different frequencies for the samples indicates that ZnO-doping modifies their parameters extensively. The dielectric dispersion in ferrites can be explained on the basis of space charge polarization by the Maxwell-Wagner model. The applied voltage on the sample drops mainly across the grain boundaries, causing localized accumulation of charge under the influence of an electric field. The space charge in ferrites comes predominantly from the electron hopping between Fe^{2+} and Fe^{3+} [15]. Zn-doping can enhance the ionic mobility [13] and increase the space charge, not only of the electron transfer between Fe^{2+} and Fe^{3+} , but between Co^{2+} and Co^{3+} pairs of ions as well. In ferrites the solids consist of well-conducting grains separated by poorly conducting grain boundaries [16]. The electrons reach the grain boundaries by hopping and if

the resistance of the grain boundary is high enough, electrons pile up and produce polarization at these places. With an increase of the frequency of the applied field, the electrons reverse their direction more often, even the electron exchange between Fe^{2+} and Fe^{3+} , Co^{2+} and Co^{3+} ion pairs cannot follow the change of the external applied field above a certain frequency. These effects result in a decrease in the probability of electrons reaching the grain boundaries and reducing the polarization of electrons. Therefore both the dielectric constant ϵ' and resistivity decrease with an increase of the frequency.

The dielectric loss tangent $\tan\delta$ curves of samples (b) and (d) exhibit a peak, which is related to a strong correlation between the conduction and the dielectric behavior in the ferrite. In this case, the peak appears when the hopping frequency of the electrons between the ions with different chemical valence is close to that of the external electric field. The different peak position of sample (d) at different sintering temperatures of 1100 °C and 1000 °C is caused by the different phases in the sample.

The addition of small amounts of dopant ($x = 0.1$) brought about a progressive increase in the dielectric constant and a corresponding decrease in resistivity, indicating there are many mobile ions in the solids. The Cole-Cole diagrams of real and imaginary part of the impedance for samples sintered at 1100 °C are shown in Fig. 6, which clearly illustrate the charges in the insulating matrix of dielectrics. The left end of the circle stands for the grain resistance,

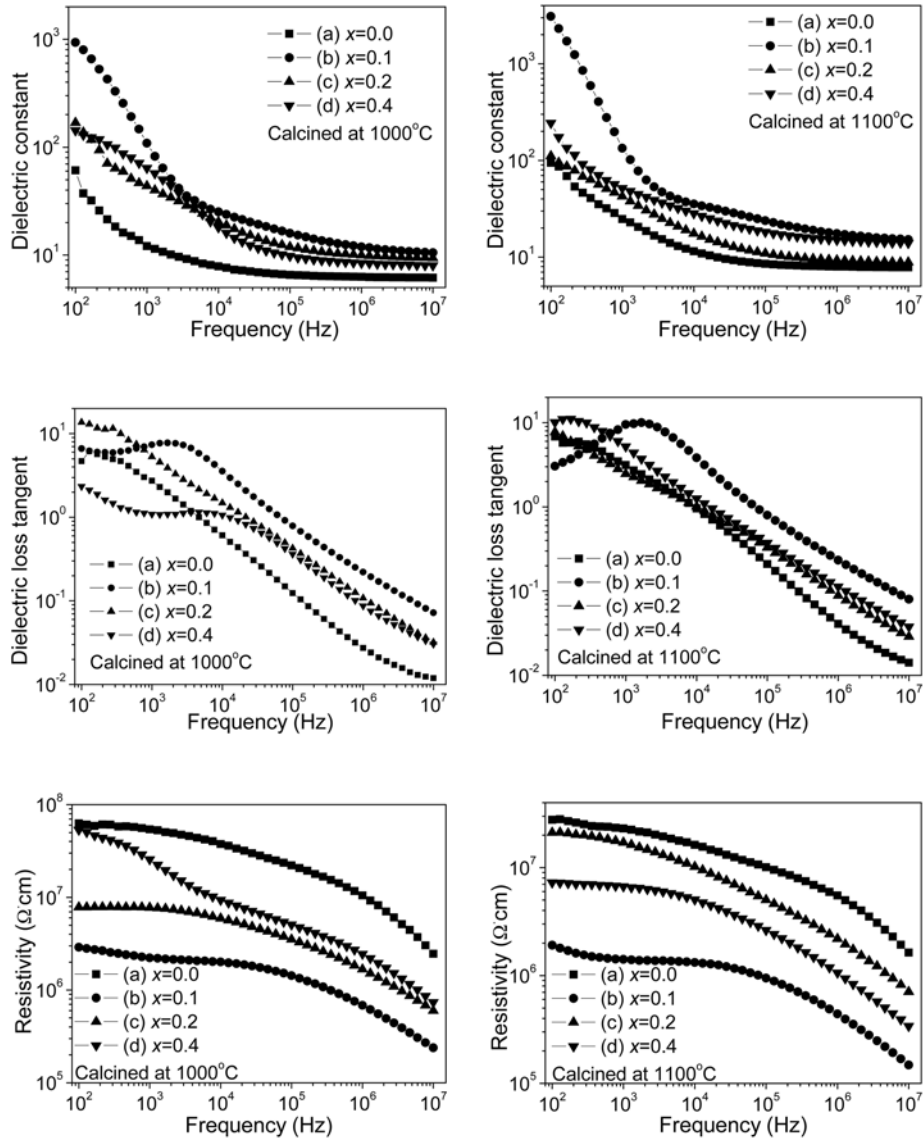


Fig. 5. The frequency dependence of the dielectric constant, dielectric loss tangent and resistivity for the samples calcined at 1000 °C and 1100 °C.

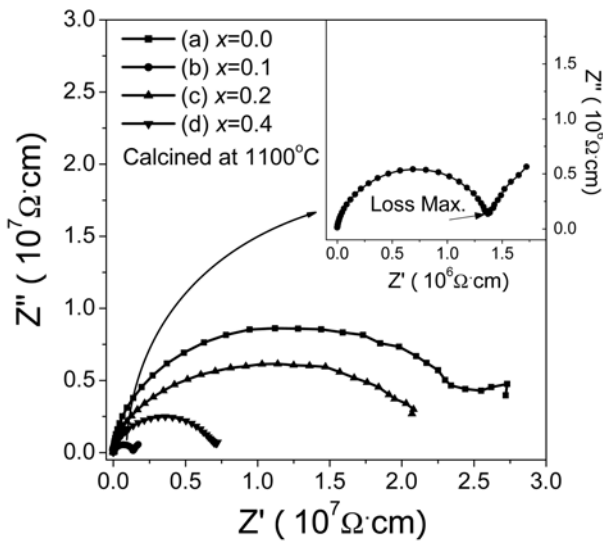


Fig. 6. Cole-Cole diagrams for the samples sintered at 1100 °C

while the right one stands for the whole resistance of the grains and grain boundaries. ZnO-doping in solids gives no clear difference in the grain resistance, but contributes a remarkable decrease of grain boundary resistance, especially for sample (b). This is achieved by the more uniform particles and smaller gaps between the grains after ZnO doping as shown in Fig. 4. The tail at the right end of the circle for the low frequency agrees with the Debye formulae [17]:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + i\omega\tau} - i\frac{\sigma}{\omega} \quad (5)$$

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + (\omega\tau)^2}$$

$$\varepsilon'' = \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + (\omega\tau)^2} \omega\tau + \frac{\sigma}{\omega}$$

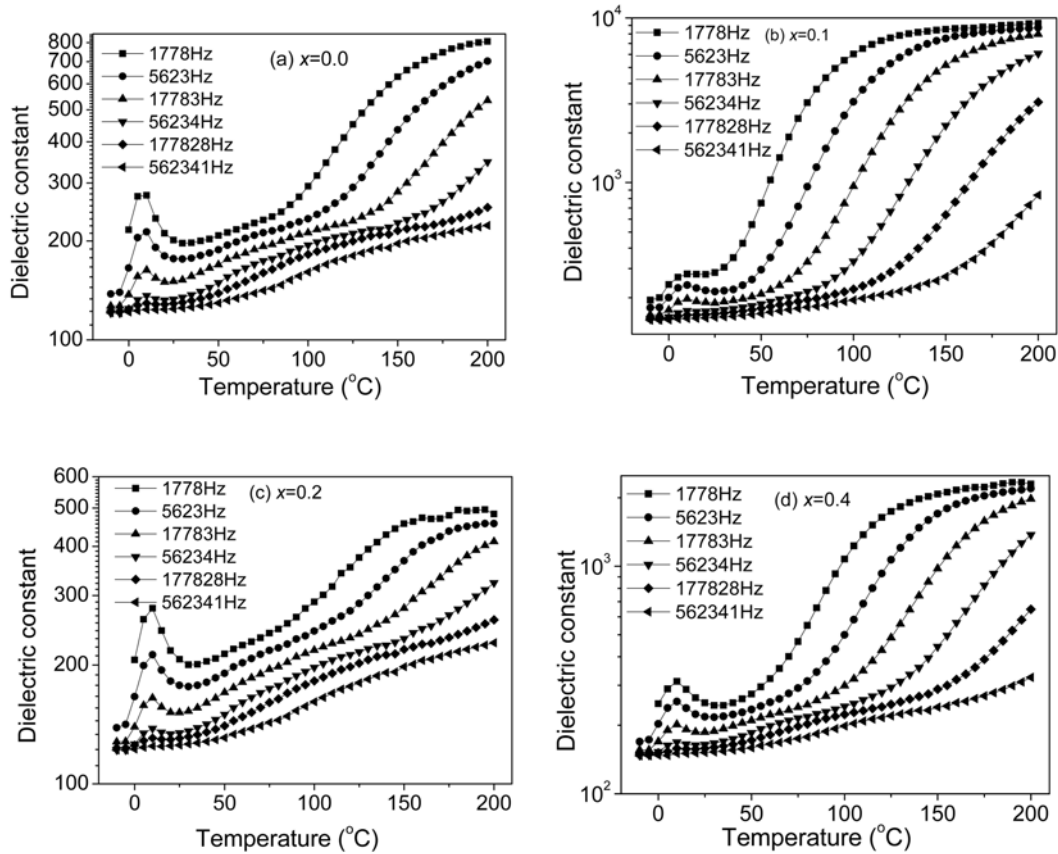


Fig. 7. The temperature dependence of the dielectric constant at six frequencies for samples calcined at 1100 °C

where ϵ' describes the stored energy and ϵ'' the dissipated energy. The result can be approximately described by a set of RC equivalent circuits, which consist of one capacitor and one resistor in parallel.

Temperature dependence of dielectric properties

Because of the similar dielectric behavior of the samples calcined at 1000 °C and 1100 °C, we choose the samples calcined at 1100 °C for a more detailed analysis of the temperature dependence. Fig. 7 shows the dielectric constant vs. temperature at different selected frequencies for the samples. It is seen that the four samples show similar behavior. The dielectric constant shows a peak at about 285 K, and then continuously increases with temperature until a maximum, which shifts towards higher temperature with increasing frequency. The electron hopping between different chemical valences of cobalt and iron ions due to the external field will produce holes in the bulk of the samples. Then both n and p type carriers take part in the conduction. Increasing the temperature will excite more charge carriers from their trapping centers. This in turn enhances their contribution to the polarization, resulting in an increase in the dielectric constant ϵ' of samples [18]. The hopping probability in the case of the pure cobalt ferrite sample (a) is smaller than those with nonmagnetic ions [19], leading to a larger ϵ' of the ZnO-doped samples.

Fig. 8 illustrates the variation of the AC conductivity σ with temperature at six selected frequencies for the samples calcined at 1100 °C. The conductivity σ increases with increasing temperature, reaches a maximum at about 285 K, corresponding to the dielectric maximum shown in Fig. 7. Then σ decreases with the temperature, and reaches a minimum around 310 K, and finally increases continuously. This characteristic was interpreted as the transition from the ferromagnetic phase to the paramagnetic phase at the Curie temperature [20, 21]. But for our samples, the Curie temperature of cobalt ferrites is usually in the range of 700-800 K, which is much higher than the slope transition in these experiments. The conductivity σ change with temperature exhibits a typical semiconductor characteristic, which is caused by the behavior of the different carriers shown at different temperature ranges. At relatively high temperatures, the AC conductivity curves stack together. The AC conductivity σ can be expressed as [3]:

$$\sigma = \sigma_{DC} + \sigma_{AC} \quad (6)$$

where the first term is the DC electric conductivity which is dependent on the temperature, and the second term is dependent on the frequency and the temperature. σ_{DC} is related to the drift mobility of the free charge carriers, while σ_{AC} to the dielectric relaxation of bound charge

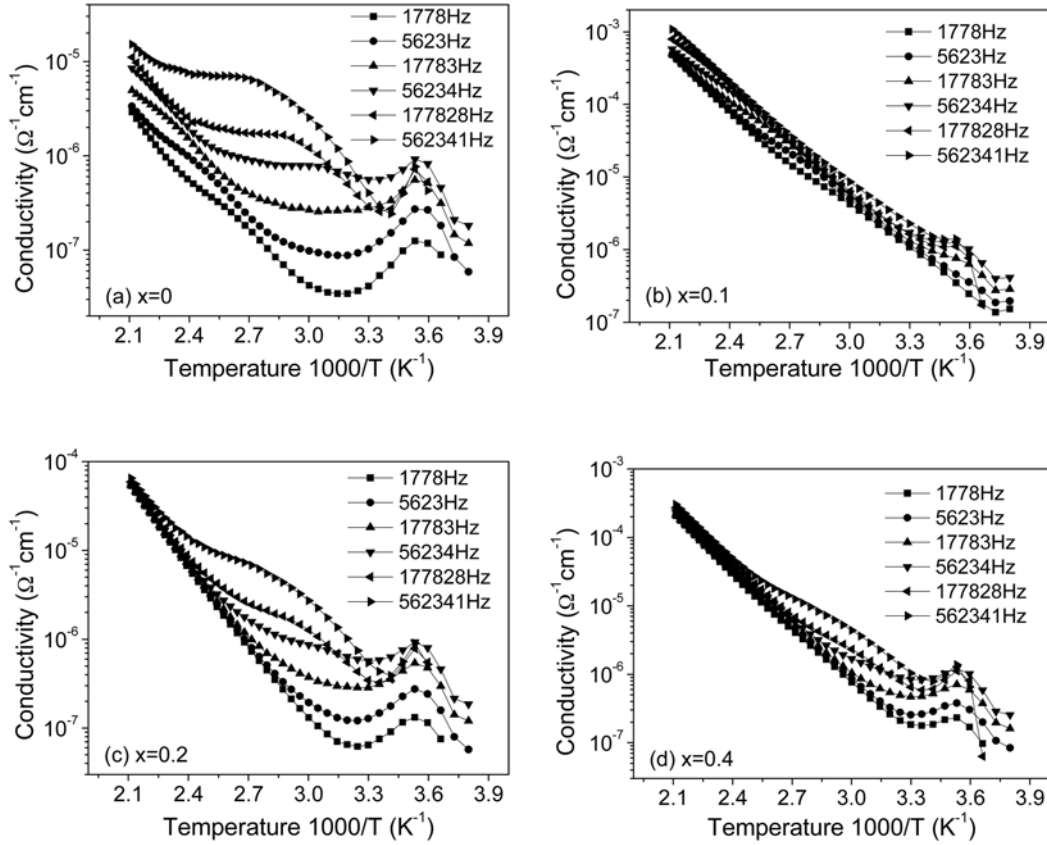


Fig. 8. The variation of the AC conductivity vs. temperature for the samples calcined at 1100 °C.

carriers. σ_{DC} is predominant at low frequency and high temperature, and reverse is true for σ_{AC} . The frequency dependence of σ_{AC} can be written as:

$$\sigma_{AC} = A\omega^n \quad (7)$$

where A is a constant with the units of conductivity and the exponent n is a dimensionless parameter. The temperature dependence of δ_{DC} obeys the theory of a band semiconductor and can be written as:

$$\sigma_{DC} = \sigma_0 \exp(-E/k_B T) \quad (8)$$

where σ_0 is a pre-exponential constant, k_B the Boltzmann constant and E the activation energy for conduction. At a low frequency and high temperature, the activation energy E and σ_0 can be estimated on the assumption that σ_{AC} is independent of temperature. The obtained values of E and σ_0 are summarized in Table 3. It can be seen that the activation energy E does not vary greatly but σ_0 increases a hundred times, indicating that the addition

of Zn ions increases the charge carrier concentration and enhances their mobilities, as a consequence, the conductivity increases as shown in Fig. 8.

The temperature dependence of $\tan\delta$ for the samples is shown in Fig. 9. All these curves share similar behavior with the corresponding conductivity curves. The maximum position of samples (a), (c) and (d) at temperature around 285 K are related to the position of the maximum conductivity. These data mean that the dielectric loss is mainly caused by the conductivity. The temperature maxima in the curves of sample (b), corresponding to the slope transition in the conductivity curves, shift towards higher temperatures with an increase in the frequency, indicating a dipolar relaxation mechanism [15].

Considering the fact that the conductivity and dielectric loss vary with temperature in a typical semiconductor manners, the electron hopping between Fe^{2+} and Fe^{3+} , Co^{2+} and Co^{3+} ions contributes to the conductivity loss tangent, and plays a dominant role in the dielectric behavior by a Maxwell-Wanger polarization and Koops mechanism.

Magnetic properties

The magnetic properties of the samples have been determined with a vibrating sample magnetometer. Fig. 10 shows the change of saturation magnetization (M_s) and coercivity (H_c) with the composition x in a maximum field of 10 kOe. The data show that M_s decrease with an increasing addition of ZnO. In ferrites, the magnetization

Table 3. Conduction activation energy E and σ_0 for the samples calcined at 1100 °C

Component	(a) $x = 0$	(b) $x = 0.1$	(c) $x = 0.2$	(d) $x = 0.4$
σ_0 ($\Omega^{-1} \cdot \text{cm}^{-1}$)	3.61	330	780	722
E (eV)	0.554	0.526	0.656	0.597

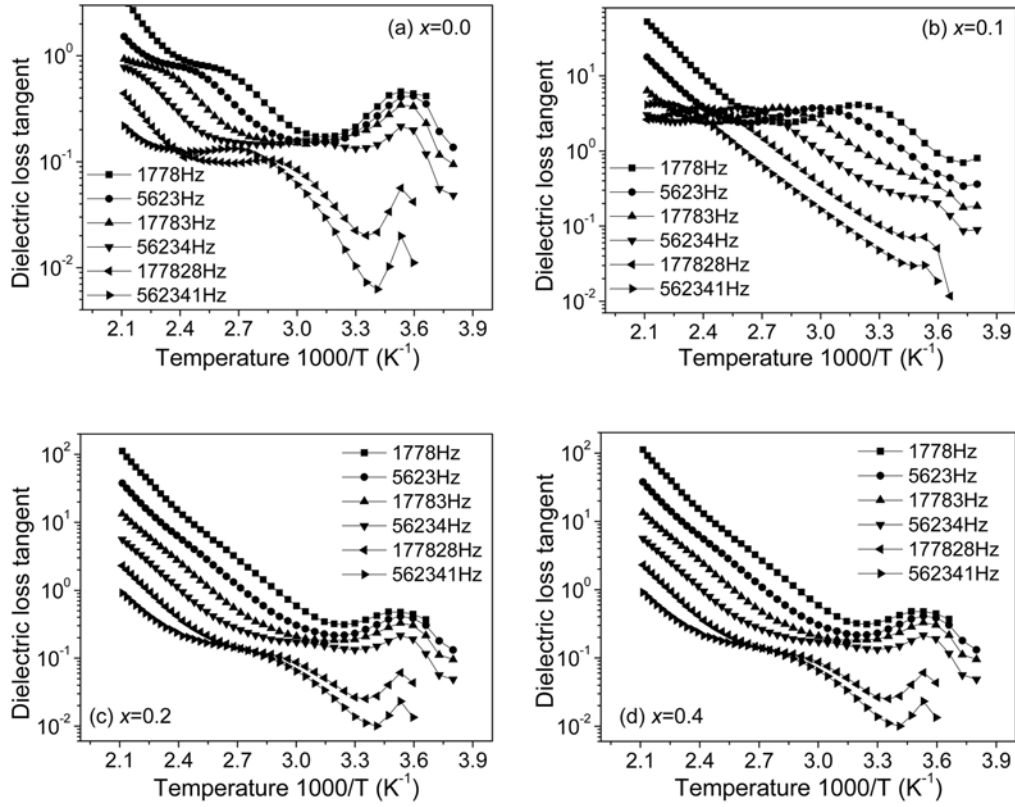


Fig. 9. Dielectric loss tangent as a function of temperature for the samples calcined at 1100 °C.

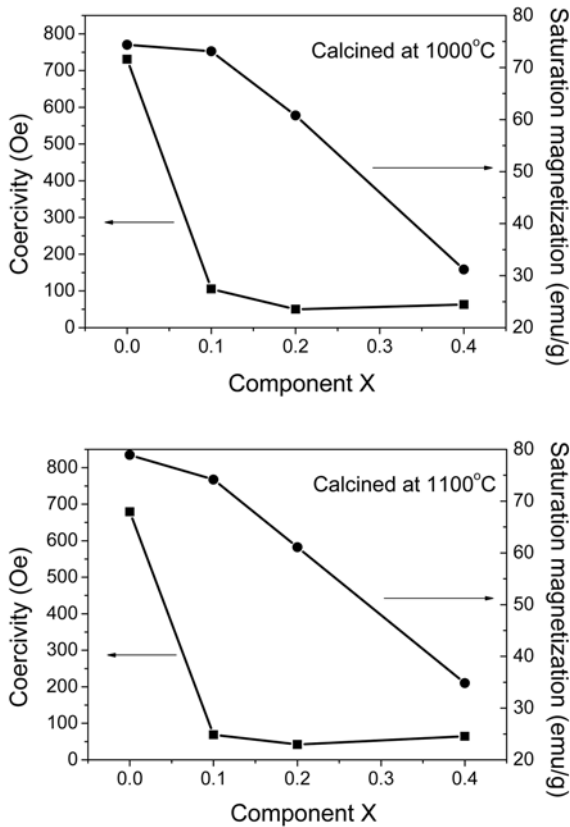


Fig. 10. Coercivity and magnetization saturation as a function of the component x at sintering temperatures of 1000 °C and 1100 °C.

is commonly equal to the difference between the magnetic ions of A and B sites. Zn^{2+} ions have a preference for the A sites and 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 too weak so that the material is paramagnetic at room temperature [22]. As a result, M_s reduces with the ZnO content. The saturation magnetization of the samples calcined at 1100 °C is larger than that of the corresponding samples calcined at 1000 °C, owing to the larger particle size after the process at a high sintering temperature.

With an increase of the addition of ZnO, the coercivity drastically decreases as shown in Fig. 10. After calcining at 1100 °C, the coercivity of samples (b) and (c) is as low as 68 Oe and 42 Oe, respectively, with the condition of a small decrease of magnetization saturation. There are many factors influencing H_c . In our experiments, the addition of ZnO enhances the mobility of the ions to form 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:

$$H_c^\sigma \propto \frac{\lambda_s \sigma}{M_s} \quad (9)$$

where λ_s is saturation magnetostriction, H_c decreases

with strain σ . On the other hand, a larger grain size is helpful to decrease H_c . Therefore, the H_c of the samples calcined at 1100 °C is lower than that of the corresponding samples calcined at 1000 °C. The coercivity of these samples is much lower than that of cobalt ferrites doped with Al and Ti [23].

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 increase from the relation:

$$\chi \propto \frac{M_s^2}{\lambda_s \sigma} \propto \frac{M_s}{H_c} \quad (10)$$

The dependence of the magnetic permeability on frequency is shown in Fig. 11. It is found to be almost independent of frequency in the frequency range of 10^6 - 10^9 Hz, and the μ_r of ZnO-doped samples is higher than that of the pure CoFe_2O_4 .

Magnetostriction

The longitudinal λ_{11} and transverse λ_{12} magnetostrictions of the $\text{Co}_{1+x}\text{Zn}_x\text{Fe}_{2-2x}\text{O}_4$ samples are shown in Fig. 12. The saturation magnetostriction of polycrystalline ferromagnetics is described by:

$$\lambda_s = \frac{2}{5}\lambda_{100} + \frac{3}{5}\lambda_{111} \quad (11)$$

and it is about -200×10^{-6} for the pure cobalt ferrite. In

our experiments, λ_{11} is -115×10^{-6} for the sample calcined at 1000 °C and -190×10^{-6} for the sample calcined at 1100 °C, owing to the complete reaction and particle growth after sintering at high temperature.

The saturation magnetostriction is related to the coercivity by equation (9). By comparing sample (b) with (a), λ_{11} is one quarter of sample (a), but the magnetic field at saturation magnetostriction is only 1/5 of sample (a). What is more, at low magnetic fields of 30 and 60 mT, sample (a) does not show a magnetostrictive effect while sample (b) shows -11×10^{-6} and -26×10^{-6} , respectively.

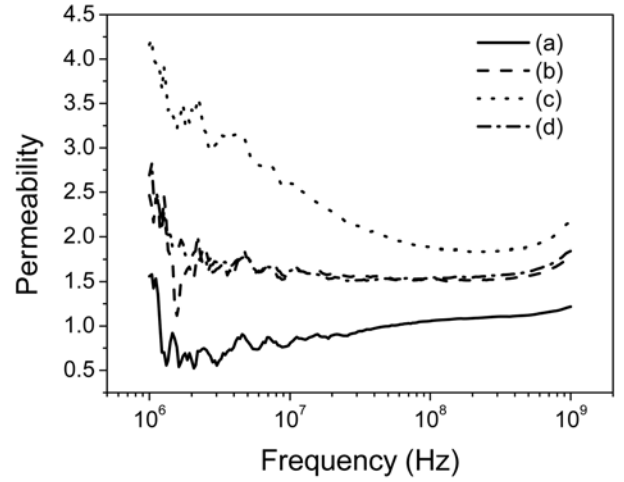


Fig. 11. The variation of the magnetic permeability with frequency for samples calcined at 1100 °C.

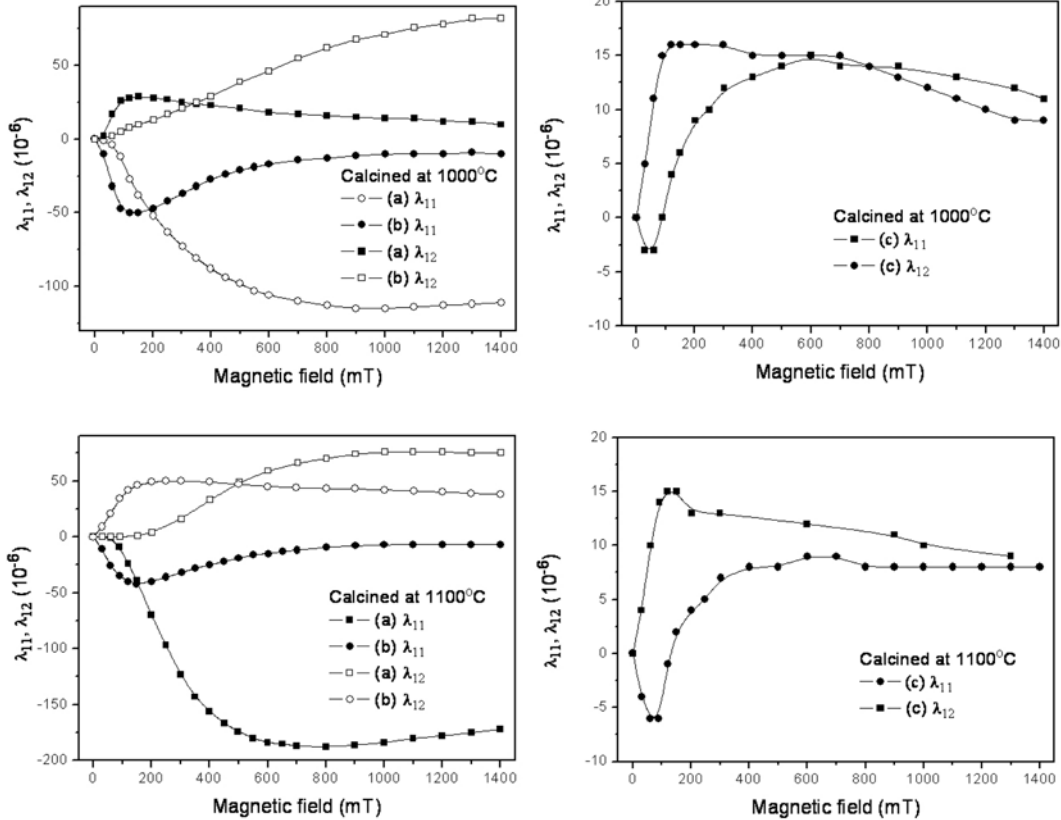


Fig. 12. Longitudinal λ_{11} and transverse λ_{12} magnetostrictions for the $\text{Co}_{1+x}\text{Zn}_x\text{Fe}_{2-2x}\text{O}_4$ samples measured at room temperature.

At a magnetic field of 90 mT, λ_{11} for sample (b) is 4 times higher than that for sample (a). These data mean the addition of ZnO improves the sensitivity of the response to the magnetic field. Sample (d) does not show an obvious magnetostrictive effect for its weak magnetism.

The magnetostriction of samples (b) does not shows a clear difference after calcining at 1000 °C and 1100 °C, which is attributed to the catalytic effect of Zn^{2+} . The addition of ZnO decreases the reaction temperature and forms uniform particles at a low temperature as shown in Figs. 3 and 4.

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

Conclusions

Pure- and ZnO-doped cobalt ferrites have been studied. The samples doped with a small amount of ZnO have a smaller lattice constant than that of CoFe_2O_4 by adjusting some cobalt ions to the octahedral sites. But with an increase of ZnO and Co_3O_4 , a new phase separates from solids. The electrical properties have been studied for the samples obtained. The conductivity variation with temperature shows typical semiconductor characteristics for the electron exchange between the ions with different chemical valence. The electron hopping between ions with different chemical valence plays a dominant role in the dielectric behaviors by a Maxwell-Wagner polarization and Koops mechanism. The increasing dielectric constant of the ZnO-doped ferrites is attributed to the nonmagnetic ions. Although the saturation magnetization reduces a little, a small amount of ZnO-doping decreases the coercivity of the sample markedly, and improves the magnetostrictive sensitivity of cobalt ferrites. These data mean that ZnO-doped ferrites have potential applications in magnetoelectric devices.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 50772065).

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