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Influence of nickel-zinc ratio on microstructure, magnetic and dielectric properties of $Ni_{(1-x)}Zn_xFe_2O_4$ ferrites

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 $Ni_{(1-x)}Zn_xFe_2O_4$ (x = 0 - 1.0) ceramics were synthesized by a conventional solid-state reaction method. The samples have been investigated for their structures, microstructures, dielectric and magnetic properties in detail. A pure spinel crystal structure was obtained in the sintering temperature range of 1150-1250 °C. The dielectric properties of part samples present a Debye relaxation phenomenon. The Curie temperature reduces linearly with the zinc concentrations. The magnetic permeability and saturation magnetization increase firstly to high values and then reduce with the zinc concentration. But the coercivity shows a different behavior. It increases at first and then decreases for the samples sintered at 1200 °C while it descends monotonically with the zinc concentration for the samples sintered at 1250 °C.

Key words: Ni-Zn ferrites, dielectrics, permeability, Curie temperature, magnetization. PACS: 75.50.Gg, 91.60.Np, 71.45.Gm, 75.30.Kz

Introduction

Ni-Zn ferrites are very important magnetic materials, due to their high resistivity, high saturation magnetization, high effective permeability, low magnetic coercivity and low eddy current loss [1-4]. The zinc concentration in a ferrite has a decisive influence on the material's microstructure, dielectric and magnetic properties [5-7]. A spinel-type ferrite is a natural superlattice, which has a tetrahedral A site and an octahedral B site in an AB₂O₄ crystal structure. The different cations in the A site and B site can change the super-exchange interactions among A-O-A, B-O-B and A-O-B bonds. A high zinc concentration can lower the super-exchange interaction between A-O-B bonds, which have the strongest super-exchange interaction among the three interactions. Due to the different compositions and cation distributions, a Ni-Zn ferrite shows various magnetic properties [4, 8]. The dielectric property is also an important characteristic for Ni-Zn ferrites [9], which changes with the zinc concentration. Although there are some reports about Ni-Zn ferrites, a systemic investigation about the magnetic and electric properties is lacking. This is a disadvantage for understanding the general properties of Ni-Zn ferrites. In this study, we investigated the magnetic and dielectric properties of nickel-zinc ferrites in detail.

Experimental

Ni-Zn ferrites were synthesized using a conventional

solid-state reaction method. Oxide powders NiO (99%), ZnO (99%) and Fe₂O₃ (99%) were used as raw materials to prepare the chemical composition Ni_(1-x)Zn_xFe₂O₄, where x = 0, 0.3, 0.5, 0.544, 0.6, 0.7, 0.8 and 1. The mixtures with different compositions were ground in a satellite mill for 6 hours to obtain a uniform mixture of fine ferrite powders. The powders were prefired at 970 °C for 5 hours to obtain a pure ferrite phase and then pressed into tablets and toroids under a pressure of about 200 MPa for dielectric and magnetic measurements. The green samples were sintered at 1150 °C, 1200 °C and 1250 °C for 5 hours with 3 K·minute⁻¹ heating rate and 2 K·minute⁻¹ cooling rate to 700 °C, then slowly cooled down to room temperature in the furnace.

The sample phases were identified by X-ray diffraction (D/Max2550V/PC, Rigaku, Japan) analysis in the range of 15°-85°. The microstructures were characterized using a scanning electron microscope (Quanta 200 SEM, FEI CO, Eindhoven, Netherlands). The toroidal samples were wrapped with 10-turns Cu wire for the measurement of magnetic permeability, performed with a 4294A precision impedance analyzer in the frequency range of 100 Hz-200 MHz at room temperature. The temperature dependence of the magnetic permeability was measured by an Agilent E4980A at 100 kHz to determine the Curie temperature. Magnetic hysteresis loops at room temperature were measured using a vibrating sample magnetometer (VSM, BHV-525). The tablet samples were polished to uniform parallel surfaces. Silver paste was coated on their surfaces to act as good electrical contacts for measuring dielectric properties, which were made with an Agilent E4980A complex impedance analyzer in the frequency range of 100 Hz-2 MHz.

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Results and Discussion

Structural characteristics

Fig. 1(a) shows the X-ray diffraction (XRD) patterns of the Ni-Zn ferrites Ni_(1-x)Zn_xFe₂O₄ with x = 0-1.0 sintered at 1250 °C for 5 hours. The XRD patterns of samples sintered at 1150 °C and 1200 °C share similar characteristics, which are not shown here. The XRD peaks match well with the ferrite standard card, indicating the formation of a pure spinel structure in the sintering temperature range of 1150-1250 °C. The diffraction peaks shift towards lower 20 values as the zinc concentration increases. Then, the lattice parameters were calculated by refining the XRD patterns with the MDI Jade 6.5 program (reliability factor around 7.5%) and are shown in Fig. 1(b). The lattice parameter linearly increases with the zinc concentration, which can be attributed to the greater ionic radius of Zn²⁺ (0.74 Å) compared with the radii of Ni²⁺ (0.69 Å) and



Fig. 1. (a) X-ray diffraction patterns of the samples sintered at 1250 °C and (b) variation of the lattice parameter of the samples with the zinc concentration. The line is a linear fit from the lattice parameters

 Fe^{2+} (0.61 Å) [4]. Similar results were observed by other authors [2, 4].

Microstructures

Fig. 2 shows SEM micrographs of fractured surfaces for the Ni-Zn ferrites sintered at 1250 °C. The grain size gradually increases with the zinc concentration because a zinc addition can enhance the diffusion of elements and cause the particles to grow large [10]. Fig. 3 shows SEM micrographs of Ni_{0.5}Zn_{0.5}Fe₂O₄ samples sintered at 1150 °C and 1200 °C and 1250 °C. It is clearly that the grain size increases with the sintering temperature. During the sintering process, the thermal energy drives the grain boundaries growing through pores, decreasing the pore volume and densifying the material. The ferrite ceramics sintered at 1150 °C has more porosities and so we discuss the magnetic and electric properties of the samples sintered at 1200 °C and 1250 °C in the next sections.

Saturation magnetization and coercivity

Fig. 4 shows the magnetic hysteresis loops for part samples sintered at 1200 °C and 1250 °C. The thin loops for Ni-Zn ferrites illustrate a soft magnetic characteristic and $ZnFe_2O_4$ represent an antiferromagnetic behavior. The variations of saturation magnetization and coercivity with the zinc concentration are summarized in Fig. 5. The saturation magnetization of samples sintered at 1200 °C



Fig. 2. Scanning electron micrographs of fractured surfaces for the Ni_(1-x)Zn_xFe₂O₄ ceramics sintered at 1250 °C. (a) x = 0, (b) x = 0.3, (c) x = 0.5, (d) x = 0.7, (e) x = 1.0.



Fig. 3. Scanning electron micrographs of Ni_{0.5}Zn_{0.5}Fe₂O₄ ceramics sintered at (a) 1150 °C, (b) 1200 °C, and 1250 °C.



Fig. 4. Hysteresis loops of part samples sintered at (a) 1200 $^{\circ}\text{C}$ and (b) 1250 $^{\circ}\text{C}.$

and 1250 °C shares the same behavior, i.e., it enhances firstly with the zinc concentration (x = 0 - 0.5), reaches a maximum around x = 0.5, and then declines, similar to a previous report [2]. In the spinel structure, cations occupy two sites : a tetrahedral site (A site) and an octahedral site (B site). According to the Goodenough-Kanamori rules, both the A and B sublattices have super-exchange interactions for transition metal ions with partially filled 3*d* shells. Then, the cation moments on the A and B sublattices are in an antiparallel arrangement, which is connected by the straight A-O-B bonds. An effective ferromagnetism is the result of a competition between the ions in the two sublattices, resulting in that the properties are highly sensitive to stoichiometry and ordering. Most ferrites are in a half metallic state, so



Fig. 5. Variations of saturation magnetization and coercivity with the zinc concentration for the ceramics sintered at (a) 1200 °C and (b) 1250 °C.

the total spin magnetization per unit cell is constrained to be an integer with first-principles investigations [11]. We tried to calculate the spin magnetization of the Ni-Zn ferrite with Materials Studio, but the total spin moments per unit cell are the same to be an integer for different zinc concentrations. Then we can understand the high saturation magnetization of a nickel ferrite after adding zinc with a simple illustration. The high temperature phase of the nickel ferrite is known to have an inverse spinel structure, where Fe³⁺ ions prefer to be at the A sites while Ni²⁺ and Fe³⁺ ions equally populate the B sites. The spin magnetic moments of the Fe³⁺ (A site), Ni²⁺ (B site) and Fe³⁺ (B site) are $-4.11\mu_B$, $1.57\mu_B$ and $4.11\mu_B$, respectively . When Zn²⁺ ions substitute for Ni²⁺ ions and enter into the ferrite lattice, they have a higher preference to occupy the A sites than Fe³⁺ and Ni²⁺ ions, leading to part of the Fe³⁺ ions on the A sites transferring to the B sites. Therefore, a Ni-Zn ferrite has a mixed normal-inverse spinel structure with a general formula $(Zn_xFe_{1-x})[Ni_{1-x}Fe_{1+x}]O_4$, where the term in parenthesis indicates a tetrahedral site while the term in square brackets indicates an octahedral site. The net magnetic moment in the spinel structure is the different moments from the tetrahedral and octahedral sites. The zinc ions do not have magnetic moment, so the net magnetic moment in the spinel structure is enhanced with the zinc concentration. However, when the zinc concentration rises to a certain value, the nonmagnetic zinc ions weaken the super-exchange interaction between the magnetic ions, resulting in a decline of the saturation magnetization. Finally, ZnFe₂O₄ represents an antiferromagnetic characteristic.

The coercivities of samples sintered at 1200 °C and 1250 °C reveal different behaviors. The coercivity of samples sintered at 1200 °C first increases with the zinc concentration and then decreases while that of samples sintered at 1250 °C monotonically reduces with the zinc concentration. This can be explained by:

$$H_c = 2K/(\mu_0 M_s) \tag{1}$$

where *K* is the magnetocrystalline anisotropy, μ_0 is the magnetic permeability of free space, M_s is the saturation magnetization and H_c is the coercivity of the sample [2, 13]. M_s first enhances then declines with the zinc concentration. The value of *K* is different for different materials, and an increase in the zinc concentration of Ni-Zn ferrites can reduce the value of *K* [14]. Therefore, the total value of H_c decreases with the zinc concentration for samples sintered at 1250 °C. Another important factor affecting the coercivity is the grain size and defects [7]. The relationship between the coercivity and grain size can be written as:

$$H_C \propto \frac{1}{D}$$
 (2)

where D represents the grain diameter. The samples sintered at 1200 °C have smaller grain size and more defects than those sintered at 1250 °C, As a result, the samples sintered at 1200 °C have a higher coercivity.

Magnetic permeability

Fig. 6 shows the magnetic permeability of the samples sintered at 1200 °C and 1250 °C. It is obvious that the Ni_{0.3}Zn_{0.7}Fe₂O₄ sample has the highest permeability in these results. The permeability almost remains unchanged at a low frequency and then drops sharply when the frequency gets to a certain high value, which is called the cut-off frequency. The magnetic permeability at 10 kHz is summarized in Fig. 7. The change is nearly the same for the samples sintered at 1200 °C and 1250 °C. The magnetic permeability firstly increases with the zinc concentration until x = 0.7 and then falls rapidly. The magnetic permeability and cut-off frequency f_0 confirm



Fig. 6. Variation of magnetic permeability with frequency for the samples sintered at (a) 1200 °C and (b) 1250 °C.



Fig. 7. Dependence of Magnetic permeability at 10 kHz on the zinc concentration for the samples sintered at $1200 \text{ }^{\circ}\text{C}$ and $1250 \text{ }^{\circ}\text{C}$.

the Snoek's relation [15-17]:

$$\mu_i f_0 = \text{Constant} \tag{3}$$

It is then difficult to achieve both a high permeability and a high cut-off frequency. The magnetic permeability of samples sintered at 1250 °C is slightly higher than those sintered at 1200 °C. This is because samples sintered at 1250 °C have a larger grain size and a lower coercivity than that sintered at 1250 °C.

It is well known that the permeability of a polycrystalline

ferrite is related to two different magnetizing mechanisms : spin rotation and domain wall motion, described as :

$$\mu_i = 1 + \chi_{\rm dom} + \chi_{\rm spin} \tag{4}$$

where χ_{dom} is the domain wall susceptibility and χ_{spin} is the intrinsic rotational susceptibility [6, 18]. χ_{dom} and χ_{spin} may be written as :

$$\chi_{\rm dom} = 3\pi M^2 {}_{\rm s} D/4\gamma \tag{5}$$

$$\chi_{\rm spin} = 2\pi M^2 {}_{\rm s}/K_{\rm a}$$

where M_s is the saturation magnetization, D is the grain diameter, γ is the domain wall energy, and K_u is the total anisotropy. Thus, the domain wall motion is improved with an increase in the grain size. Zinc can reduce the sintering temperature and strengthen the sintering density [17], so the grain size increases with the zinc concentration, which is observed from the SEM images in Fig. 3. A domain wall is easier to move with magnetization or demagnetization for the samples with a large grain size. Therefore, these samples are expected to have a low coercivity (H_c) and a high magnetic permeability. A sample with more inner domain walls has a greater permeability. The saturation magnetization is found to increase with the grain size. Zinc is known to increase the density and grain size and reduce the magnetocrystalline anisotropy [8], as a result, enhancing the magnetic susceptibility. Thus, the magnetic permeability of Ni-Zn ferrites increases firstly with the zinc concentration and then declines. ZnFe₂O₄ is an antiferromagnetic material and its permeability is obviously much lower than the ferromagnetic ferrites.

Curie temperature

The temperature dependence of the magnetic permeability is a very simple way to determine Curie temperature. The magnetic permeability as a function of temperature was measured at 100 kHz. Fig. 8 shows the variation of magnetic permeability with temperature for part samples (x = 0, x = 0.3, x = 0.5, x = 0.7) sintered at 1250 °C. The magnetic permeability falls abruptly when the magnetic state of the ferrite changes from the ferromagnetic ferrite to the paramagnetic state. The transition temperature T_c was calculated by drawing a tangent at the inflexion of the curve that drops sharply. The point of intersection with the temperature axis is determined as the Curie temperature [6]. The Curie temperature strongly depends on the zinc concentration. The magnetization increases with temperature close to the Curie temperature and have a well-defined maximum just below the Curie temperature, which is known as the Hopkinson effect [20, 21]. The crystal anisotropy normally decreases to zero with increasing temperature. Since crystal anisotropy decreases faster than magnetization on heating, the magnetic permeability, tends to infinity just below the T_c due to $\mu_i = M_s^2 / (\sqrt{K_1})$, where K_1 is the crystal anisotropy. Fig. 9 shows the



Fig. 8. Temperature dependence of magnetic permeability measured at 100 kHz for $Ni_{(1-x)}Zn_xFe_2O_4$ (x = 0, 0.3, 0.5, 0.7) sintered at 1250 °C.



Fig. 9. Variation of Curie temperature with the zinc concentration for samples sintered at $1200 \,^{\circ}$ C and $1250 \,^{\circ}$ C. The lines are the linear fits from the Curie temperature data.

variation of Curie temperature of Ni-Zn ferrites with the zinc concentration. It is obvious that the Curie temperature for the samples sintered at both temperatures descends linearly with the zinc concentration. The linear decrease in the Curie temperature with the zinc concentration may be explained by a modification of the A-O-B superexchange interaction due to the change of the Fe³⁺ distribution between A and B sites. The large distance between the magnetic ions in A and B sites, resulting from the linear augment of lattice parameters with zinc concentration as shown in Fig. 1(b), weakens the superexchange interaction between the magnetic ions in A and B sites. The weaker super-exchange interaction has a weaker ability to endure thermal motion, resulting in a linear decrease in the Curie temperature with the zinc concentration.

Dielectric properties

Fig. 10 shows the variation of dielectric constant and tangent loss with frequency at room temperature for the samples sintered at 1200 °C and 1250 °C. The dielectric constant decreases slightly then rapidly with frequency.

When the dielectric constant reaches to its half value, the dielectric tangent loss gets its highest value at a special frequency for different samples. Part samples do not show the loss peak, which may be at a low frequency out of the measurement range because the corresponding dielectric constant monotonically declines and is not dielectric flat.

The diversification of the dielectric constant with the frequency is the normal dielectric behavior of polycrystalline spinel ferrites, which is also observed in other investigations [5, 21, 22]. A change of the dielectric constant can be explained by the Maxwell-Wagner interfacial polarization with Koops phenomenological theory [23]. The highly conducting grains and the relatively poor conducting grain boundaries compose the dielectric structure. Due to this composite structure, charges accumulate under the influence of an electric field, resulting in an interfacial polarization [21]. When the frequency reaches a certain high value, the electric charge exchange between Fe²⁺ and Fe³⁺ ions can not follow the alteration of the electric field, resulting in the decrease in a dielectric constant above this high frequency.

The phenomenon of dielectric loss peak is a typical dielectric relaxation at a certain frequency, where the dielectric constant reduces to its half value [24]. The tangent loss is given by:



Fig. 10. The dielectric constant and tangent loss of the Ni_(1-x)Zn_xFe₂O₃ samples sintered at (a) 1200 °C and (b) 1250 °C.

$$tg\delta = \frac{\varepsilon''(w)}{\varepsilon'(w)} = \frac{(\varepsilon_s - \varepsilon_x)\omega\tau}{\varepsilon_s + \varepsilon_x\omega^2\tau^2}$$
 (6)

where $\omega = 2\pi f$ is the angle frequency, ε_s and ε_{∞} are the dielectric constant at $\omega \to 0$ and $\omega \to \infty$, respectively, and τ is the relaxation time. When the angle frequency $\omega = \omega_m = 1/\tau \sqrt{\varepsilon_s/\varepsilon_{\infty}}$, the tangent loss comes to a maximum.

Conclusions

In conclusion, we prepared a series of Ni-Zn ferrites with a conventional solid-state reaction method. The XRD patterns show the formation of a pure Ni-Zn spinel structure, and the lattice parameter extends with the zinc concentration. SEM images show that the grain size gets larger with the zinc concentration and sintering temperature. The saturation magnetization and magnetic permeability of Ni-Zn ferrites firstly increases and then reduces with the zinc concentration for samples sintered at both temperatures. Also the maximum permeability of 1760 is observed in the Ni_{0.3}Zn_{0.7}Fe₂O₃ sample. The magnetic permeability and cut-off frequency for the samples keep to the Snoke's relation. The coercivity decreases with a higher Zn²⁺ substitution for Ni²⁺ for the samples sintered at 1250 °C, but for the samples sintered at 1200 °C, the coercivity increases at first and then decreases due to lattice defects. The Curie temperature of $Ni_{(1-x)}Zn_xFe_2O_4$ samples reduces linearly with the zinc concentration. The saturation magnetization and Curie temperature are intrinsic properties only relative to the ratio of nickel and zinc. The coercivity and magnetic permeability are relative to the ratio of nickel and zinc and the preparation process. Thus, we can choose a sample with suitable properties for practical applications of Ni-Zn ferrites. The dielectric behavior exhibits a relaxation phenomenon: the dielectric constant decreases at a certain frequency, where the dielectric tangent loss comes to a maximum.

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