Magnetodielectric effect of Mn-Zn ferrite at resonant frequency

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Abstract The dielectric properties and the magnetodielectric effect in Mn-Zn ferrite at resonant frequency have been studied in this paper. Dimensional-resonance-induced abnormal dielectric spectrum was observed at $f \approx 1$ MHz. The relatively large magnetodielectric ratio of 4500% in a magnetic field of 3.5 kOe was achieved from the Mn-Zn ferrite sample with the initial permeability of 15K at resonant frequency at room temperature. Theoretical analysis suggests that the large MD effect at resonant frequency is attributed to the enhanced magnetostriction effect.

Key words: Mn-Zn ferrite, magnetoresistance effect, magnetodielectric effect, magnetostriction effect

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1. Introduction

The modulation of the dielectric permittivity by an external magnetic field excitation, namely magnetodielectric (MD) effect, has been attracting an intense interest due to its potential application in magnetic sensor, magnetic memory and microwave resonator. [1][2][3] Some efforts have been made to research the MD effect in several material systems. Firstly, it is the multiferroic material. In multiferroics, the coupling of ferromagnetic order and ferroelectric order gives rise to the MD effect. [4] For example, Kimura reported a MD ratio of 0.6% in BiMnO_3 which is induced by a magnetic field of 90 kOe at ferromagnetic transition temperature, $T_M \approx 100$ K. [5] Secondly, it is the magnetoelectric material. With the application of the magnetic field, the magnetostrictive effect of the ferromagnet distorts the ferroelectrics, and thereby induces the MD effect. As Wei Wang reported, a strong magnetocapacitance as large as 1200% was observed in a layer composite Terfenol-D/PZT/Terfenol-D at a saturated magnetic field of 1.5 kOe. [6] Thirdly, it is the non-multiferroic material. Through the combination of the Maxwell-Wagner (M-W) effect and magnetoresistance (MR) effect, the MD effect can be achieved in the ferromagnetic material without magnetoelectric coupling. [7] Recently, Yajie Chen reported a MD ratio of 1800% in $\text{Mn}_{0.60}\text{Zn}_{0.40}\text{Fe}_{2.12}\text{O}_{4+}$ at $f = 7$ MHz in a magnetic field of 3.5 kOe. [8]

Considering the practical application, the achievement of a larger MD effect at a lower magnetic field at room temperature has been the emphasis of researches. According to reports, the MD effect is enhanced at resonant frequency compared with the one at non-resonant frequency. [6][9] However, the generation mechanism of the large MD effect at resonant frequency has not been investigated. In fact, the dispersion of permittivity at certain magnetic field is considered more complicated than the description afforded by the MD mechanisms mentioned above if there exist a dimensional resonance. Thus, in this work, we present evidences for the mechanism of the MD effect at resonant frequency and study the influence of the dimensional resonance on the MD effect for the Mn-Zn ferrite sample.

2. Experiment

Material researched in this paper is the commercial Mn-Zn ferrite with the initial permeability (μ_i) of 5K, 10K and 15K. The ferrite samples were prepared by the conventional solid-state reaction. The precursor materials of MnO, ZnO, Fe_2O_3 powders with high purity were weight to have the normal compositions of $\text{Mn}_{1-\delta}\text{Zn}_\delta\text{Fe}_2\text{O}_4$. The ferrite samples with different μ_i can be obtained by different δ . The dielectric properties were measured in cuboid samples with the dimension of $6.0 \times 6.0 \times 2.0 \text{ mm}^3$. The ferrite samples were applied with silver paste as electrodes onto both surfaces and sintered at 400°C for 2 hours. The dielectric permittivity (ϵ') and loss tangent ($\tan\delta$) were measured using an impedance analyzer (IM3570, HIOKI). The resistance was measured in cuboid samples with the dimension of $10.0 \times 6.0 \times 2.0 \text{ mm}^3$, using the standard four-prob method. The magnetization of the ferrite samples at different electric field frequency and the magnetic field dependent magnetization were measured with a vibrating sample magnetometer (VSM 7404, LakeShore). The DC magnetic field was provided parallel to the surface of the ferrite samples for the measurement of the MD, ML (magneto-loss) and MR ratios. The complex permeability was measured in toroidal samples with inner diameter of 6 mm, outer diameter of 10 mm and thickness of 5 mm. The ferrite samples were wound with 10~15 turn coils. Then, the inductance (L_s) and the AC resistance (R_s) of coils were surveyed with an impedance analyzer at $100 \text{ Hz} < f < 5 \text{ MHz}$.

According to $\mu' = L_s/L_0$ and $\mu'' = R_s/\omega L_0$, the real (μ') and imaginary (μ'') parts of the complex permeability were achieved, where L_0 was the inductance of the air core. All the measurements were proceed at room temperature.

3. Results and discussion

Fig. 1(a) shows the complex permeability spectra for the ferrite sample with $\mu_i = 15K$ at zero magnetic field. In experimental curves, the frequency dispersion of μ'' shows two peaks at $f = 10$ kHz and 1 MHz, approximately. According to T. Nakamura's report, the permeability spectra of the Mn-Zn ferrite sample contains two components, owing to domain-wall motion and spin rotation. [10] Consequently, the complex permeability can be described by [11]

$$\mu = 1 + \chi_d + \chi_s = 1 + \frac{\omega_d^2 \chi_{d0}}{\omega_d^2 + \omega + i\omega\beta} + \frac{(\omega_s + i\omega\alpha)\omega_s \chi_{s0}}{(\omega_s + i\omega\alpha)^2 - \omega^2}, \quad (1)$$

where χ_d and χ_s are the magnetic susceptibility for domain wall and spin motions, ω_d and ω_s are the resonant frequencies of domain wall and spin components, χ_{d0} and χ_{s0} are the static magnetic susceptibility for each component, α and β are damping coefficients. Based on equation (1), the theoretical curves of μ' and μ'' are calculated, as Fig. 1(a) presents. Compared the theoretical curve with the experimental curve, various parameters can be acquired, $\alpha = 3.95$, $\beta = 3.2 \times 10^5$, $\omega_d = 18.5$ kHz and $\omega_s = 1.97$ MHz. Since ω_d is less than ω_s , the peak at lower frequency corresponds to the domain-wall resonance and the one at higher frequency stems from the spin resonance in the μ'' spectrum. [10] According to reports [10][12][13], the Mn-Zn ferrite sample almost turns into a single-domain structure at $H = 1$ kOe, which means that the magnetization changes with the spin rotation rather than the domain-wall motion. Thus, the domain-wall contribution to the permeability at $H = 1$ kOe is negligible. The single peak in the frequency dispersion of μ'' at $H = 1$ kOe is attributed to the spin rotation, which is presented in Fig. 1 (b). [14]

As shown in Fig. 1(a), the theoretical curve matches the experimental curve well at $f < 1$ MHz. However, since the ferrite sample has a relatively large conductivity, the effect of the eddy current should be considered in the high frequency region. The skin depth effect of an electromagnetic wave impacts the permeability spectra at $f > 1$ MHz, which triggers the inconformity between the experimental and theoretical curves. [12]

Fig. 2(a) shows the dielectric spectra of the ferrite sample with $\mu_i = 15K$ in the fields of $H = 0$ and 3.5 kOe. The dielectric permittivity undergoes a sign reversal from positive to negative around $f = 1$ MHz. It remains negative and then reaches a valley value at $f = 1.463$ MHz for $H = 0$ (or at $f = 1.496$ MHz for $H = 3.5$ kOe), after which the dielectric permittivity starts to increase. According to reports, no magnetoelectric coupling occurs in the Mn-Zn ferrite material. [15][8] However, since the polycrystalline ferrites contain two phases with different resistance (e.g. the grains and the grain boundaries) and the grains consist of different metal ions (e.g. Fe^{2+} , Fe^{3+} , Mn^{3+} , Mn^{4+}), the behavior of the space charges plays an important role in the generation of the dielectric properties with applying an AC electric field. On the one hand, the accumulated charges at the interfaces of the grains form dipoles which lead to a large polarization and subsequently a high dielectric permittivity. On the other hand, considering the low resistance of the ferrite samples ($R = 510 \Omega \cdot cm$, $355 \Omega \cdot cm$, $300 \Omega \cdot cm$ for the ferrite samples with 5K, 10K, 15K at $H = 0$), the transport of the charges in the grains gives rise to the direct current condition but which may also leads to the polarization, such as the polarization of hopping charge-induced Fe^{2+} - Fe^{3+} dipoles.

Since the dielectric permittivity reflects the action of dipoles, the frequency dependence of the dielectric permittivity results from the superposition of the relaxation processes of different dipoles in the AC electric field (e.g. Fe^{2+} - Fe^{3+} dipoles, interfacial polarization). In practice, the displacement occurs between the dipoles and the external electric field under the influence of inertial effect. Based on the harmonic oscillator model of the dipoles, the real part (χ') of the complex dielectric susceptibility is given by

$$\chi'(\omega) = \int_0^\infty f(t) \cos(\omega t) dt = \left(\frac{\omega_p}{\omega_r} \right)^2 \frac{1 - x^2}{(1 - x^2)^2 + k^2 x^2}, \quad (2)$$

where $\omega_p = (e^2 N / \epsilon_0 m)^{1/2}$, $x = \omega / \omega_r$, N is the number of identical non-interaction dipoles, k is the damping coefficient, ω_r is the resonant frequency, ωt is the displacement between the dipoles and the external electric field, $f(t)$ is the time-domain dielectric response function. [16] Because of $\chi'(\omega) \approx \epsilon'(\omega)$, the theoretical curve of the dielectric response at resonant frequency can be achieved following equation (2), as the green solid line shown in Fig. 2(a). The theoretical and experimental curves match well at $0.993 \text{ MHz} < f < 5 \text{ MHz}$. Thus, it is speculated that for $\omega > \omega_r$ the displacement tends to reach anti-phase with the driving field which results in $\epsilon'(\omega) < 0$, due to the inertial effect. When the displacement becomes the maximum, the dielectric permittivity decreases to the minimum. However, the inconformity appears between the experimental and theoretical curves at $f < 0.993 \text{ MHz}$. Since the dipoles are generated by the space charges, it is possible that the increase of the impedance promotes larger damping coefficients for the dipoles in the ferrite sample at $f < 0.993 \text{ MHz}$. [17]

It is noticed that the magnetic field has a drastic effect on the dielectric permittivity around $f = 1 \text{ MHz}$. The frequency dependent MD effect of the ferrite sample with $\mu_i = 15\text{K}$, given as $\text{MD} = 100\% \times [\epsilon'(H) - \epsilon'(0)] / \epsilon'(0)$ at $H = 3.5 \text{ kOe}$, is shown in the inset of Fig. 2(a). The ferrite sample presents a strong resonant peak, $\text{MD} = 4500\%$, at $f = 0.989 \text{ MHz}$. According to reports [8][18], the spin-related dielectric mechanisms in the frequency region around $f = 1 \text{ MHz}$ are affected by the magnetic field, including the hopping charge polarization and the interface effect. For one thing, driven by the magnetic field, a forced spin alignment of Fe^{2+} and Fe^{3+} ions decreases the scattering of the charges and promotes the charge exchange between Fe^{2+} and Fe^{3+} ions. This enhances the Fe^{2+} - Fe^{3+} dipoles and subsequently induces the positive MD effect. For another, with the application of the magnetic field, the different MR responses of either grains or grain boundaries change the charge distribution at the sides of the interfaces. Consequently, the interfacial polarization is altered and in turn the MD effect.

Fig. 2(b) shows the loss tangent ($\tan\delta$) spectra of the ferrite sample with $\mu_i = 15\text{K}$ in the fields of $H = 0$ and 3.5 kOe . In the absence of the magnetic field, a sharp resonant peak appears at $f = 0.993 \text{ MHz}$ which reveals to be a dimensional resonance. It is known that when the wave length of electromagnetic wave is less than the double of the sample thickness, the dimensional resonance occurs in materials and absorbs electromagnetic wave energy intensively. [9] The resonant frequency is estimated in term of the equation

$$f = c / 2d \sqrt{\mu' \epsilon'}, \quad (3)$$

where d is the sample thickness, c is the speed of light, f is the resonant frequency, ϵ' is the dielectric permittivity, μ' is the permeability. [19] According to equation (3), the theoretical resonant frequency is calculated as 0.937 MHz which is very close to the experimental resonant frequency.

Furthermore, it is observed that a magnetic field of 3.5 kOe drives the resonant frequency of the loss tangent increase from 0.993 MHz to 1.07 MHz. Since the increasing magnetic field promotes the frequency shift of the complex permeability in Fig. 1, it is considered that the interaction between the loss tangent and the complex permeability exists in the ferrite sample, especially at resonant frequency. [13]

Figs. 3(a) and 3(b) show the magnetic field dependence of the MD and ML ratios for the ferrite samples with $\mu_i = 5K, 10K$ and $15K$ at resonant frequency, where the ML ratio is defined as $ML = 100\% \times [\tan\delta(H) - \tan\delta(0)] / \tan\delta(0)$. As shown in Fig. 3(a), the MD ratios of 3093%, 3569% and 4500% are measured at $H = 3.5$ kOe for the ferrite samples with $\mu_i = 5K, 10K$ and $15K$, respectively. Below the magnetic field of 0.5 kOe, the MD ratios of all samples increase rapidly. At higher fields ($0.5 \text{ kOe} \leq H < 3.5 \text{ kOe}$), the MD ratios tend toward saturation. |ML| ratios in Fig. 3(b) are less than MD ratios, but it shows similar tendency relying on the magnetic field. The magnetic field dependence of the MD ratios is consisted with the magnetization curves for the ferrite samples with $\mu_i = 5K, 10K$ and $15K$, as shown in Fig. 3(c). These results indicate that the MD effect is closed related with the magnetization process, including domain-wall motion and spin rotation. What's more, the difference in sign of variations of the MD and ML curves suggests that the dominant mechanism of the MD effect is the extrinsic effect, i.e., the combination of the M-W effect and MR effect. [7]

Fig. 3(d) shows the magnetic field dependence of the MR ratios for the ferrite samples with $\mu_i = 5K, 10K$ and $15K$, where the MR ratio is defined as $MR = 100\% \times [R(H) - R(0)] / R(0)$. The MR ratios of all ferrite samples rapidly decrease at $0 < H < 0.5 \text{ kOe}$, and tend toward saturation at $0.5 \text{ kOe} \leq H < 3.5 \text{ kOe}$. It is ascribable to spin-polarized tunneling effect at grain boundaries. [15] As domain-wall motion occurs, spin-polarized electrons are available to cross the grain boundaries with less scattering which results in the rapid decrease of the resistance, and subsequently the MR effect. [20] As the domain-wall motion diminishes, the increasing magnetic field promotes the spin rotation until the sample being a single-domain structure, which, to an outside observer, corresponds to saturated MR ratios. [8] Besides, the MR ratios of -1.39%, -1.659%, and -2.23% are observed at $H = 3.5$ kOe for the ferrite samples with $\mu_i = 5K, 10K, 15K$, respectively. Since different μ_i represents different content of Mn ions in the ferrite samples, it is reasonably speculated that the double-exchange mechanism of $Mn^{3+}-O^{2-}-Mn^{4+}$ makes contribution to the MR effect. [21][22] As the magnetic field applies, the distorted spins of Mn ions are aligned gradually. Due to the overlap between the 3d electron clouds of Mn ions and the 2p electron clouds of O^{2-} ions, the alignment of Mn ions promotes the electron transport and lower the resistance of the grains, giving rise to the negative MR ratios.

Compared Fig. 3(a) with Fig. 3(d), it is observed that the MD and MR curves show similar magnetic field dependence. This demonstrates that the mechanism of the MR-induced MD effect is reasonable for the ferrite samples. However, the MR ratios is much smaller than the MD ratios which means the MD effect is not wholly due to the simple change of the resistances. For example, for the ferrite sample with $\mu_i = 15K$, the MR ratio and the MD ratio at $H = 3.5$ kOe are -2.23% and 4500%, respectively. Since the MD ratios are measured at resonant frequency, we speculate that there is the other mechanism enhanced the large MD effect, which is affected by the dimensional resonance, such as the magnetostriction effect.

According to S. Dinesh Kumar's report, the magnetostriction (λ) and the magnetization (M) of the ferrite sample is related as $\lambda \propto M^2$. [23] Thus, the derivation of the square of the magnetization

with respect to the electrical field frequency (dM^2/dF) manifests the change of the magnetostriction at different frequencies. Fig. 4 shows the frequency dependences of M and dM^2/dF for the ferrite sample with $\mu_i = 15K$ at $H = 3.5$ kOe. A step-like increase of the magnetization is observed near $f = 0.9$ MHz which corresponds to the peak of dM^2/dF in the frequency dispersion. The experimental result demonstrates that the alignment of the spins in the ferrite sample increases dramatically at resonant frequency. Moreover, the magnetostriction is enlarged intensively at resonant frequency which results from the dimensional resonance.

To understand the microscopic mechanism of the large MD effect, it is informative to discuss the enhanced magnetostriction effect at resonant frequency. Because of the polycrystalline Mn-Zn ferrite, λ represents the average effect of the magnetostriction property of the grains. With the magnetic field applies, the spin alignment of Fe^{2+} and Fe^{3+} ions is largely enhanced at resonant frequency. Since the anisotropic Fe^{2+} electron clouds are strongly coupled to the spins via spin-orbit interaction, canting of the Fe spins causes the lattice distortion. Thus, spin rotation in an applied magnetic field should result in a redistribution of the electron clouds and thereby leads to a reorientation lattice structure, giving rise to the magnetostriction. [24] Our research shows that the MD effect is related to the magnetic domain occupancy variation, that it is likely to share a similar origin with the magnetostriction. We therefore attribute the large MD effect to a similar mechanism, in which the H -induced lattice distortion triggers the change of the electron hopping in grains, and thereby changes the Fe^{2+} - Fe^{3+} dipoles, which determines the large MD ratios.

4. Conclusion

The dielectric resonance of the Mn-Zn ferrite samples near $f = 1$ MHz is caused by the dimensional effect. The frequency shift of the loss tangent is attributed to the decrease of the complex permeability at an external magnetic field. At resonant frequency, the combination of the M-W effect and MR effect makes contribution to the MD effect, but the enhanced magnetostriction effect determines the generation of the large MD ratios.

Acknowledgements

This work was supported by the National Science Foundation of China under grand number 51277098.

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Figures

FIG. 1 The complex permeability spectra for the Mn-Zn ferrite sample with $\mu_i = 15\text{K}$ at $H = 0$ (a) and $H = 1\text{ kOe}$ (b). Solid and dash lines are calculation curves for μ' and μ'' , respectively.

FIG. 2 The frequency dependences of the dielectric permittivity (a) and the dielectric loss (b) for the Mn-Zn ferrite sample with $\mu_i = 15\text{K}$ in the fields of $H = 0$ and 3.5 kOe . Green solid line is the calculation curve for the dielectric permittivity.

FIG. 3 The magnetic field dependence of MD (a) and ML (b) ratios for the Mn-Zn ferrite samples with $\mu_i = 5\text{K}$, 10K and 15K at resonant frequency. The values of M (c) and MR ratio (d) as a function of the applied magnetic field for the Mn-Zn ferrite samples with $\mu_i = 5\text{K}$, 10K and 15K .

FIG. 4 The frequency dependences of M and dM^2/dF for the Mn-Zn ferrite sample with $\mu_i = 15\text{K}$ at $H = 3.5\text{ kOe}$.

FIG. 1

FIG. 2

FIG. 3

FIG. 4