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Giant magnetodielectric effect and magnetic field tunable dielectric resonance in spinel MnZn ferrite

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The sensitive response of the dielectric permittivity under the application of magnetic fields in $Mn_{0.60}Zn_{0.40}Fe_{2.12}O_{4+\delta}$ polycrystalline ferrite is presented. A magnetic field of 3.5 kOe induced a giant magnetodielectric $\{MD=[\varepsilon'(H)-\varepsilon'(0)]/\varepsilon'(0)\}$ response, of 1800% at $f=7$ MHz, at room temperature. The ferrite exhibits a large magnetic field-induced frequency response of 180 Hz/Oe. We suggest that this effect arises primarily from a spin-dependent space charge polarization mechanism in response to the application of dc magnetic fields. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3095498]

Since the 1960s, it has been a longstanding goal of solid-state chemists, condensed matter physicists, and materials scientists to develop multifunctional materials, including those having magnetoelectric coupling. In very recent years, this research has been revitalized by the so-called multiferroic (MF) effect, in which materials show simultaneous ferroelectric and magnetic ordering.[1–4] Subsequently, MF materials have attracted a great deal of interest for both their unusual physical properties as well as their potential as key enabling materials in such applications as memory devices, electric field-controlled microwave resonance devices, low frequency magnetic field sensors, etc.[5,6]

MF materials are classified as either single phase or multiphase materials. The former includes $BiFeO_3$, $LuFeO_4$, $CdCr_2s_4$, etc.,[7–9] which present intrinsic MF properties, whereas the latter usually consists of two or more components in the form of superlattices, laminated structures (or heterostructures), and/or composites.[10–13] Very recently, Castel and Brosseau[14] reported a large magnetodielectric (MD) effect (i.e., $\Delta\varepsilon'/\varepsilon'=10\%$ at 2 kOe and $\Delta\varepsilon''/\varepsilon''=300\%$ at 5 kOe) near the dielectric resonance frequency in the $BaTiO_3-Ni$ nanocomposite. The magnetoelectric effect induced in these materials is not intrinsic to any one component material but rather arises from the interplay between granular and intergranular phases. Notwithstanding, this research may lead to many opportunities in the design of practical materials, heterostructures, and devices.[15,16]

In this letter, we address a class of MD materials that can give rise to a *giant* dielectric response to applied magnetic fields. This kind of material, a polycrystalline MnZn-ferrite, consists of conductive grains separated by highly resistive grain boundary regions. Catalan[17] predicted that some polycrystalline materials may exhibit a magnetocapacitance (or MD) phenomenon without coupling between magnetic and electric parameters. A few previous reports have supported this prediction.[18,19] Obviously, these materials should not be classified as true MFs but nonetheless the MD effect observed in such simple structures provides an avenue to explore magnetoelectric devices. More importantly, we demonstrate here a *giant* room temperature MD effect in response to low magnetic fields in this spinel ferrite. These results are of significance in research of both fundamental physics as well as in the development of magnetic field-tuned electronic devices.

In the experiments reported here, polycrystalline MnZn ferrite, having a composition $Mn_{0.60}Zn_{0.40}Fe_{2.12}O_{4+\delta}$, was prepared using conventional hot-press sintering ceramic techniques. X-ray diffraction analyses indicated that all diffraction peaks were indexed to the spinel ferrite phase (space group: $Fd\text{-}3m$) with a lattice constant of 8.565 Å. The composition was verified by energy dispersive x-ray spectroscopy. For the dielectric measurements, silver-paint contacts were applied to rectangular platelike samples ($8.42\times8.42\times2.0$ mm^3). This sample geometry and measurement methodology was similar to those previously reported.[9,20] Room temperature resistivity was determined to be about 200 Ω cm. The ratio of grain-to-grain boundary resistivity ranged from approximately 1/10 to 1/50, as determined by means of the Cole–Cole analysis technique. A toroid sample of dimension $\Phi7.8\times3.9\times1.5$ mm^3 (outer diameter, inner diameter, and thickness) was prepared for frequency-dependent measurement of permeability. The dielectric constant, permeability, and loss tangent were measured using an Agilent 4294A impedance analyzer over a frequency range of 40 Hz–110 MHz.

Figure 1(a) presents the frequency dependence of initial permeability for the MnZn ferrite sample. A primary resonance frequency appears at 1.3 MHz, while a minor resonance occurs at about 7 MHz. The low frequency resonance arises from domain wall motion, whereas the high frequency peak corresponds to spin rotation resonance.[21,22] Quantitatively, the dispersion of permeability can be described by[23]

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

where χ_d, and χ_s are the magnetic susceptibilities for domain wall and gyromagnetic spin motion, respectively, ω_d and ω_s are the resonance frequencies for domain wall and spin motion, respectively, and α and β denote damping coefficients

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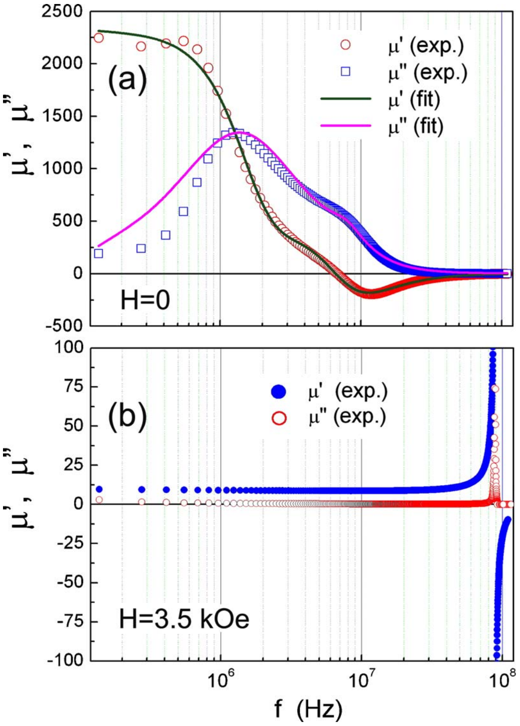

FIG. 1. (Color online) (a) The frequency dependence of initial permeability without an external field for MnZn-ferrite. Solid lines denote the fit results to Eq. (1) (see text). (b) Measured results for the frequency dependence of initial permeability with an external field of 3.5 kOe.

of wall motion and spin rotation, respectively. Figure 1(a) additionally shows the fitting curves to Eq. (1). The fit data yields $\alpha=0.3$ and $\beta=7.7\times10^7$, which are comparable to values previously reported.[24]

One notices that when the spin rotation resonance dominates, the permeability drops precipitously under the application of a dc magnetic field. Since a magnetic field of 3.5 kOe is high enough to complete the domain wall process, the contribution of domain wall motion to permeability is largely negligible.[22] As a result, a permeability (μ') of 10 and a spin rotation resonance frequency of ~88 MHz were measured, as illustrated in Fig. 1(b). The physical mechanism was interpreted by Smith and Wijn[21] and Kramar and Panova[25] in terms of magnetization rotation and domain wall dynamics.

Dielectric measurements were performed over a frequency range of 1 kHz–20 MHz, as depicted in Fig. 2. In the absence of applied magnetic fields, the dispersion of the dielectric permittivity obeys the Debye relaxation expression.[26] However, since the ferrite consists of two phases, having different conductivity (i.e., the grains and the grain boundary regions), the charge carriers readily transverse the grains but are impeded at the grain boundary region. This causes a buildup of charges at the interface which, to an outside observer, corresponds to a large polarization and subsequently a high dielectric constant. This polarization results in part from the heterogeneity of the sample and is particularly remarkable for the semiconducting MnZn ferrite, in which the electrical conductivity is appreciable.

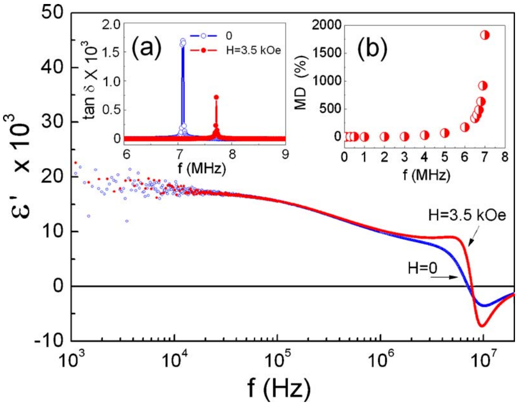

FIG. 2. (Color online) Measured frequency dependence of the real part of effective permittivity for MnZn-ferrite. Hollow circles correspond to zero applied magnetic field measurements, whereas solid circles represent the measurement at $H=3.5$ kOe. Inset (a) shows the variation of loss tangent angle with frequency (Symbols denote experimental data, and the solid lines represent guides to the eye.) Inset (b) is the measured MD effect with frequency at $H=3.5$ kOe.

Since under the application of an ac electric field, the space charge accumulates at the interface between the grain and boundary regions. For this situation, the Maxwell–Wagner (MW) space charge polarization model adequately describes the dielectric relaxation process. We express the dispersion of permittivity for this structure in terms of Eqs. (2a) and (2b),[17]

$$\varepsilon'(\omega)=\frac{1}{C_0(R_g+R_{gb})}\,\frac{\tau_g+\tau_{gb}-\tau+\omega^2\tau_g\tau_{gb}\tau}{1+\omega^2\tau^2}, \tag{2a}$$

$$\varepsilon''(\omega)=\frac{1}{\omega C_0(R_g+R_{gb})}\,\frac{1-\omega^2\tau_g\tau_{gb}+\omega^2\tau(\tau_g+\tau_{gb})}{1+\omega^2\tau^2}, \tag{2b}$$

where subindices g and gb denote the grain and grain boundary phases, respectively, and R, C, and ω represent resistance, capacitance, and angular frequency, respectively. $\tau_g=C_gR_g$, $\tau_{gb}=C_{gb}R_{gb}$, $\tau=(\tau_gR_{gb}+\tau_{gb}R_g)/(R_g+R_{gb})$, $C_0=\varepsilon_0A/t$, A is the area of the capacitor, and t is the thickness. In Eqs. (2a) and (2b), permittivity varies with the ratio of R_g/R_{gb}, rather than the absolute value of either R_g or R_{gb}.

However, measurements reveal the dielectric resonance to be a dimensional resonance. The resonance frequency is estimated in terms of the equation, $f_r=c/\lambda\sqrt{\mu_e\varepsilon_e}$, $d=\lambda/2$, where d is the sample width.[20] Here, our focus is the frequency dependence of the permittivity upon an external magnetic field. Not only does the dielectric permittivity increase upon the application of a magnetic field but also the resonance frequency shifts toward higher frequencies. From inset (a) of Fig. 2, one observes that a field of 3.5 kOe increases the resonance frequency from 7.08 to 7.71 MHz, a frequency of 0.63 MHz or a frequency tunability of 180 Hz/Oe. We attribute the frequency shift to the decrease in magnetic permeability under external magnetic fields,[22,23] which in turn affects the permeability dispersion, especially the effective permeability near resonance. On the other hand, the effect of the magnetic field on the permittivity sensitively depends upon frequency, most notably at frequencies greater than 1 MHz. When the frequency is below ~1 MHz, both permeability and permittivity vary slowly with frequency with or without the application of a magnetic field. Inset (b) of Fig. 2 demonstrates a frequency dependence of the MD effect, $\mathrm{MD}=[\varepsilon'(H)-\varepsilon'(0)]/\varepsilon'(0)$ at $H=3.5$ kOe. The MD effect is dramatically enhanced by increasing frequency from 4 to 7 MHz. In particular, the sample exhibits a giant MD effect, MD=1800%, at $f=7$ MHz. It is noticed that there is a significant change in permittivity as frequency approaches

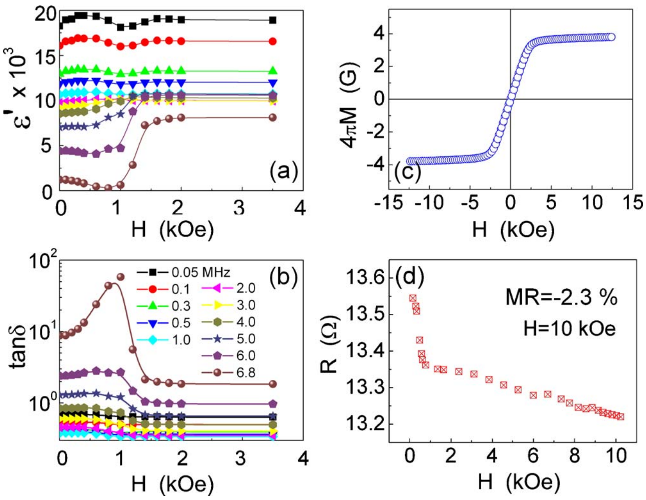

FIG. 3. (Color online) (a) Magnetic field dependence of the real part of effective permittivity at different frequencies for MnZn-ferrite, (b) magnetic field dependence of loss tangent at different frequencies, (c) magnetic hysteresis loop, and (d) variation of dc resistance with magnetic field. All of symbols denote measured data whereas solid lines in (a) and (b) represent guides to the eye.

dielectric dimensional resonance frequency. Similarly, permeability changes dramatically as frequency nears the domain wall resonance even in the absence of a magnetic field. These results indicate that the giant MD effect not only reflects the correlation of charge relaxation in magnetic fields but also represents the dependence of spin relaxation upon magnetic field. These figures of merit are far beyond those previously reported in materials systems measured in the vicinity of resonance frequencies.[27] In addition, inset (b) of Fig. 2 indicates a “magnet-loss” tangent,[17] $[\tan\delta(H)-\tan\delta(0)]/\tan\delta(0)$, of -68%.

Figure 3(a) presents the field dependence of real permittivity at different frequencies for the MnZn ferrite. At low frequencies, far from the resonance frequency, permittivity varies insensitively with magnetic field strength and frequency. At a field of 3.5 kOe and frequencies of <1 MHz, we still noticed a $\sim 1\%-5\%$ MD effect.

However, the variation of the real part (ε') of permittivity with magnetic field strength is nonlinear, which is more remarkable at a high frequency, such as $f=6.8$ MHz. We notice that the permittivity has a dip at about $H=1$ kOe, and drastically increases to a saturation value as the magnetic field approaches 2 kOe. From Fig. 3(b), the loss tangent, $\tan\delta$, also demonstrates a similar trend as that seen in $\varepsilon'(H)$. These reflect the trend observed in the magnetic hysteresis curve of the sample, as depicted in Fig. 3(c). We conjecture that the MD effect originates from both the MW space charge effect and magnetoresistance (MR).[17] Any changes in resistance of either grain or grain boundary phase induce polarization, and in turn the MD effect. We also measured a field dependence of resistance, revealing a kink in the $R(H)$ at $H\sim 1$ kOe, as presented in Fig. 3(d). This corresponds to a field strength signaling the end of the domain wall displacement magnetization. Therefore, the MD effect is attributed in part to the MR effect that may arise from the spin-polarized tunneling across grain boundaries, although MR effect is merely about -1.5% at $H=3.5$ kOe. This spin-dependent polarization, likely influenced by the interfaces between grains, is fundamentally different from the giant magnetocapacitance effect previously reported in single crystal samples.[7,9] In fact, the dispersion of permittivity is more complicated than the description afforded by the MW model if there exist a dimensional resonance within the frequency range of interest. This resonance may affect both the permittivity and permeability simultaneously, as well as change the overall relaxation process.

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