Magnetodielectric effect in Z-type hexaferrite

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The authors report on the magnetodielectric (MD) effect of Z-type hexaferrite $Sr_3Co_2Fe_{24}O_{41}$ at various temperatures and frequencies. A fairly large negative MD effect was observed with a peak near room temperature and a maximum at low frequencies. Analysis suggests that the MD effect shows a quadratic dependence on magnetization. The results were discussed by considering the magnetic field induced change of transverse conical spin structure and spin-phonon coupling. This work is helpful for understanding the MD effect in materials with complicated spin structures. © *2012 American Institute of Physics*. [doi:10.1063/1.3677672]

Recently magnetodielectric (MD) effect, defined as the change of dielectric constant accompanying magnetic phase transitions or with magnetic field, has attracted much attention due to the renaissance of research on multiferroic materials which involve magnetoelectric coupling.[1–9] The study of MD effect is important regarding the fundamental interest as well as potential applications.[9] Therefore, a lot of work on MD effect has been carried out in a variety of materials both theoretically and experimentally.[1–9] The key issue in the study of MD effect is the origin of magnetic control of dielectric property of materials. Several mechanisms have been proposed to account for the MD effect.[1,3,9] One of the interesting scenarios is the correlation between change of dielectric constant and the square of magnetization ($\Delta\varepsilon = \gamma M^2$),[1] which was derived in the framework of Ginzburg–Landau theory for the second-order phase transition for ferroelectromagnet. This scenario has been used to interpret the MD effect in a number of ferromagnetic systems.[1,2,6,9] And even for antiferromagnetic system, this scenario is valid for MD effect induced by external magnetic field.[5] However, it was also shown that this scenario is not valid for Mn_3O_4 (Ref. 4), which is believed due to some complex spin-spin correlation function for the magnetically ordered phase. So, it is interesting to explore the validity of this scenario in other systems, especially those with complicated spin structures. Moreover, the study on the frequency dependence of MD effect on magnetization and temperature dependence of γ is still lacking. Recently, Kitagawa *et al.* reported that electric polarization can be induced in the Z-type hexaferrite $Sr_3Co_2Fe_{24}O_{41}$ (SCFO) with a complicated spiral spin structure by low magnetic fields at room temperature,[10] and the direction of the induced polarization can be switched through a magnetoelectric annealing procedure,[11] which suggests an unusual non-volatile and low-power memory device. It is interesting to explore the correlation between change of dielectric constant and magnetization in the Z-type hexaferrite SCFO, which has not been reported so far. In this letter, the temperature and frequency dependence of MD effect was explored in Z-type hexaferrite SCFO with different magnetizations and the results were discussed by considering the magnetic field induced change of transverse conical spin structure and spin-phonon coupling.

Polycrystalline samples with the nominal composition $Sr_3Co_2Fe_{24}O_{41}$ were prepared by the conventional solid state reaction.[10] Before high purity powders of $SrCO_3$, Co_3O_4, and Fe_2O_3 were carefully weighed in stoichiometric proportion, mixed and well ground, $SrCO_3$ and Fe_2O_3 were dried at 300 °C for 3 h. The mixture was calcined in air at 1000 °C for 16 h. Then the samples were quenched to room temperature and pulverized. The resulting powders were pressed into pellets with a 12 mm diameter under 40 MPa. The pellets were finally sintered in air at 1200 °C for 16 h and then cooled down with a cooling rate of 1 °C/s. The sintered pellets were polished into thin plates with a 0.8 mm thickness. X-ray diffraction (XRD) patterns of the samples were obtained using a Rigaku D/max-RB x-ray diffractometer with a Cu K_α radiation. Au electrodes were prepared by magnetron sputtering. The resistivities of the samples were measured at 300 K by the two-probe method using a Keithley 6517 A electrometer. Dielectric property was measured by using Precision Impedance Analyzers 6500B. A superconducting quantum interference device (SQUID) magnetometer (MPMS XL7) was used for measuring the magnetic field and temperature dependence of the magnetization and dielectric constants of the samples.

Figure 1(a) is the powder XRD patterns of SCFO. All the peaks can be indexed to the Z-type structure with the space group $P6_3/mmc$ and the lattice parameters are a = 5.87 Å, c = 52.07 Å. It was mentioned that it was very difficult to obtain single-phase SCFO (Ref. 10), which was not realized there. The electric-field dependence of current-density at 300 K is illustrated in Fig. 1(b) and the resistivity estimated from the linear characteristic is $\sim 1.22 \times 10^9\ \Omega$ cm. Surprisingly this value is 6 orders of magnitude larger than that of the samples which were also sintered in air (Ref. 10). This high resistivity is good for magnetoelectric measurements. Figure 1(c) shows the magnetization as a function of temperature with zero field cooling (ZFC) and field cooling (FC), respectively. Magnetization exhibits two drops at about 510 K and 670 K, which correspond to a transition from the phase with a cone of easy magnetization into the

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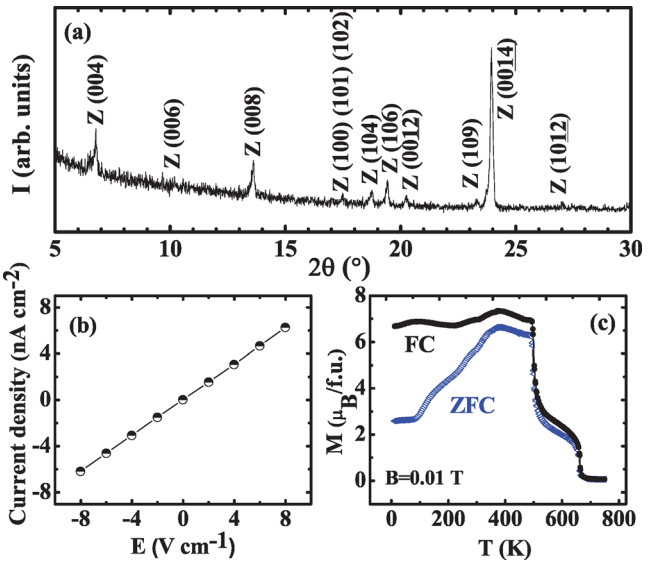

FIG. 1. (Color online) Characterizations of $Sr_3Co_2Fe_{24}O_{41}$ polycrystalline sample. (a) X-ray powder diffraction pattern. (b) The current-density versus electric-field at 300 K. (c) Temperature dependence of magnetization with FC and ZFC sequences measured at 0.01 T.

ferrimagnetic phase with Fe and Co magnetic moments parallel to the c axis, and a transition into a paramagnetic phase, respectively.[12]

Based on these high quality samples, we studied the MD effect at various temperatures. Figure 2(a) is the magnetization curves of the sample at various temperatures. It can be seen that magnetization increases in two steps up to the saturation value, similar to that of the previous report.[10] The magnetization shows a rapid increase with 0 to ~0.15 T, a slow increase with ~0.15 to ~1.3 T and then is almost saturated at around 2 T. Figure 2(b) shows the variation of MD effect $(\Delta\varepsilon(B)/\varepsilon(0) = [\varepsilon(B) - \varepsilon(0)]/\varepsilon(0))$ with magnetic field. The dielectric constant measured at 50 MHz decreases with magnetic field. The magnitude of this change shows a rapid increase from 0 to ~0.15 T, a slow increase from ~0.15 to ~1.3 T and then becomes nearly constant above ~2 T. This behavior is similar to that of the magnetization curve, suggesting a certain correlation between the MD effect and magnetization. It has been shown that SCFO has an electric polarization below 400 K even at zero magnetic field,[13] which is different from that in Y-type hexaferrite. This means that SCFO is in the ferroelectric side of the paraelectric-ferroelectric transition region. It has been shown that the dielectric constant shows a maximum around the paraelectric-ferroelectric transition induced by magnetic fields.[14] Therefore, the negative MD effect can be understood since SCFO is in the ferroelectric side of the transition region, in that the dielectric constant decreases with magnetic field.

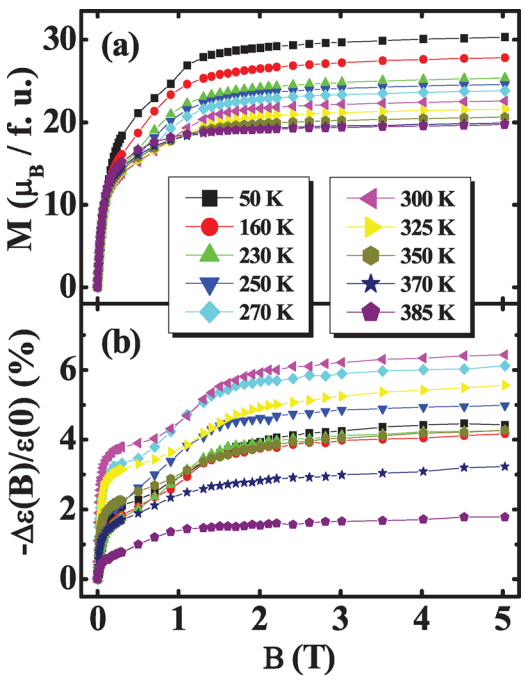

FIG. 2. (Color online) Magnetic field dependence of (a) magnetization and (b) MD effect at various temperatures.

The negative MD as a function of the square of magnetization (M^2) is shown in Fig. 3(a). It can be seen that MD changes linearly with M^2 for larger M at various temperatures. Thus, MD versus the square of M can also be expressed by $\Delta\varepsilon(B) = \gamma M^2$ for SCFO. By fitting Fig. 3(a) with this formula, the temperature dependence of γ is obtained as shown in Fig. 3(b) with the inset showing the temperature dependence of dielectric constant at zero magnetic field. Interestingly, the value of γ shows a maximum near room temperature, which is close to the paraelectric-ferroelectric transition region around T_c.[13] It should be mentioned that for the correlation between MD and M, M should be the spontaneous magnetization.[1] So it can be understood that the correlation between MD and M is not satisfied for smaller M (at low magnetic fields), considering the contribution from the change of magnetic domains to M and the disturbance of the paraelectric-ferroelectric transition region to the dielectric constant.

As mentioned before in the literature, the study on the frequency dependence of MD effect on magnetization is still lacking and most studies are related to dielectric constant measured at high frequencies. However, the MD effect at low frequencies is also an interesting topic since different mechanism is involved for low frequency dielectric property.[15] We studied the frequency dependence of MD effect

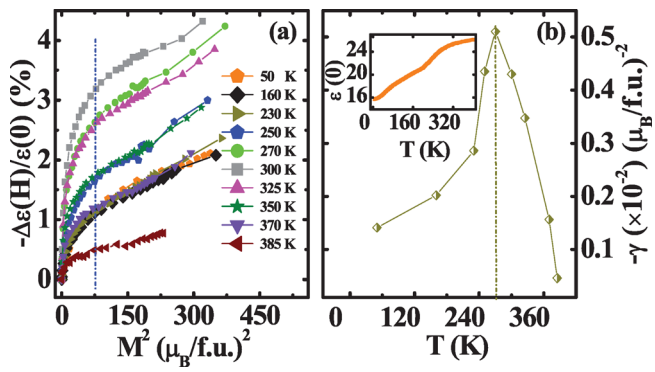

FIG. 3. (Color online) (a) M^2 dependence of the MD effect at various temperatures. (b) The absolute values of the coupling coefficient γ $(\Delta\varepsilon(B) = \gamma M^2)$ versus temperature curves. γ is the fitting value obtained from the linear region (the right region of the dotted blue line). The inset of (b) shows the temperature dependence of the dielectric constant at zero magnetic field.

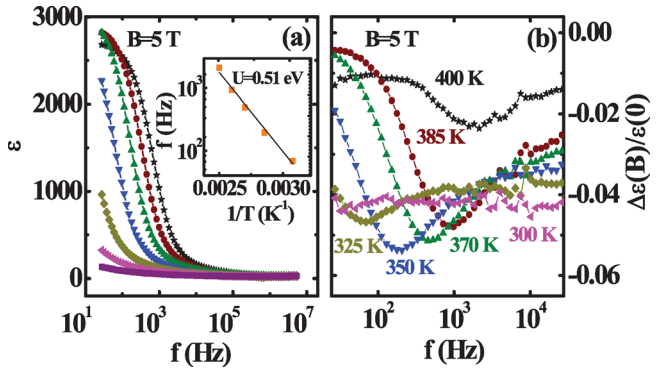

FIG. 4. (Color online) (a) Frequency dependence of dielectric constant at various temperatures at 5 T. From top to bottom, the temperatures are 400, 385, 370, 350, 325, 300, and 275 K, respectively. The inset shows 1/T dependence of the relaxation rate f. The straight line is the fit using the Arrhenius law and the activation energy is about 0.51 eV. (b) Frequency dependence of MD effect at various temperatures.

on magnetization for SCFO and the results are shown in Fig. 4. Figure 4(a) is the frequency dependence of the dielectric constant measured in a magnetic field of 5 T at different temperatures. It can be seen that the dielectric constant shows a strong frequency dependence at high temperatures below a threshold frequency f_T, which decreases with decreasing temperature. This can be accounted by some trapping and detrapping process of space charges in the sample.[16] The frequency dependence of MD is shown in Fig. 4(b). Since the frequency dependence of MD is weak for high frequencies, only the low frequency data are shown. It shows that MD is nearly frequency independent below 300 K. However, MD shows strong frequency dependence above 300 K with a maximum in magnitude at a certain frequency, which is related to the maximum slope in the ε-f curves. The peak position increases with frequency with an exponential dependence of corresponding relaxation time τ ($\sim$1/f) on 1/T, $\tau = \tau_0 \exp(\frac{U}{k_B T})$, as shown in the inset of Fig. 4(a). From this inset, we obtained the activation energy for the trapped space charges to be 0.51 eV, which is comparable to those in oxides.[16] We also plotted the normalized $\Delta\varepsilon$(B) versus M^2 for both the high and low frequency data and they overlapped (not shown), suggesting that the same mechanism is involved for MD effect at both high and low frequencies. The microscopic origin of MD effect in the Z-type hexaferrite can be understood in terms of the spin-phonon coupling scenario.[2] The real part of the dielectric constant depends on ε_s and ε_∞ as $\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\tau^2}$, where τ is the relaxation time, ε_s and ε_∞ are the static dielectric constant and dielectric constant at optical frequencies, respectively. It is well-known that ε_s and ε_∞ are related to the long wavelength longitudinal (ω_{LO}) and transverse (ω_{TO}) optic phonon frequencies through the Lyddane-Sachs-Teller relation as $\frac{\omega_{LO}}{\omega_{TO}} = \sqrt{\frac{\varepsilon_s}{\varepsilon_\infty}}$. If the phonon frequency can be changed by magnetic fields, then the MD effect is expected. In Z-type hexaferrite, magnetic field results in the change of the conical magnetic structure, which induces the change of electric polarization through the inverse Dzyaloshinskii–Moriya (DM) interaction[17] or the spin current[18] mechanism. The change of electric polarization alters the phonon frequencies, which leads to the MD effect as mentioned above.

In summary, we have investigated the MD effect of Z-type hexaferrite $Sr_3Co_2Fe_{24}O_{41}$ at various temperatures and frequencies. A fairly large negative MD effect was observed which is more remarkable near room temperature and at low frequencies. It was also shown that the MD effect shows a quadratic dependence on magnetization. These behaviors were explained by considering the magnetic field induced change of transverse conical spin structure and spin-phonon coupling. This work is helpful for understanding the MD effect in materials with complicated spin structures.

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