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Temperature and frequency dependent giant magnetodielectric coupling in $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$

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Abstract

Perovskite DyMn_{0.33}Fe_{0.67}O₃ experiences a paramagnetism-antiferromagnetism transition at 450K and spin reorientation at 290 K. Magnetodielectric properties were studied around the spin reorientation transition. Both giant positive and giant negative magnetodielectric coupling (MDC) were observed near room temperature. The MDC shows strong temperature and frequency dependence, and the sign changes from positive to negative when magnetic state transits from a canted antiferromagnetic state to a collinear antiferromagnetic state. Possible mechanisms are proposed based on the Maxwell-Wagner model, phase transition, the magnetoresistance effect, and spin-phonon coupling.

Keywords

dependent, frequency, temperature, coupling, magnetodielectric, giant, dymn0, 67o3, 33fe0

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Temperature and frequency dependent giant magnetodielectric coupling in $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$

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Perovskite $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$ experiences a paramagnetism-antiferromagnetism transition at 450 K and spin reorientation at 290 K. Magnetodielectric properties were studied around the spin reorientation transition. Both giant positive and giant negative magnetodielectric coupling (MDC) were observed near room temperature. The MDC shows strong temperature and frequency dependence, and the sign changes from positive to negative when magnetic state transits from a canted antiferromagnetic state to a collinear antiferromagnetic state. Possible mechanisms are proposed based on the Maxwell-Wagner model, phase transition, the magnetoresistance effect, and spin-phonon coupling. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4736543>]

I. INTRODUCTION

Dielectric materials are common materials which have wide applications in energy storage, electronic switches, sensors, and actuators. To develop next generation multifunctional devices, effective control of more degrees of freedom beyond electric charge should be given a priority. Considerable work has been done to control the dielectric property by magnetic methods,^{1–4} the so-called magnetodielectric coupling (MDC) effect. Most MDC effects appear around the magnetic phase transition temperature, at which dielectric abnormality can be observed and modified by external magnetic fields. These effects are notably found in some manganites. In BiMnO_3 , the dielectric constant is suppressed around 100 K, where ferromagnetic (FM) ordering occurs⁵ and a giant negative MDC effect could be induced. For spin frustrated perovskite TbMnO_3 (*Pbnm* space group),⁶ an obvious peak in the temperature dependence of the *c*-axis dielectric constant is found at 27 K, where the sinusoidal antiferromagnetic (AFM) magnetic modulation wave vector is locked at a constant value. Magnetic field can shift the dielectric peak slightly around 27 K and induce an extra dielectric peak at lower temperature. In metastable orthorhombic HoMnO_3 and YMnO_3 ,⁷ the MDC effect occurs below their incommensurate AFM transition temperature of 42 K. Apart from these manganites, the MDC effect can be found in other systems, such as SeCuO_3 ,⁸ TeCuO_3 ,⁸ MnCr_2O_4 (Ref. 9) (*M*=Mn, Co, and Ni), and $\text{Bi}_2\text{Mn}_{4/3}\text{Ni}_{2/3}\text{O}_6$,¹⁰ although their MDC values are very small. Colossal magnetoresistance (MR) materials, such as EuNbO_2N (Ref. 11) and HgCr_2S_4 ,¹² also show significant magnetodielectric response at low temperature. To achieve practical applications, it would be ideal to find materials with MDC effects near room temperature. In addition, the MDC effect should be strong. Here, we present both giant positive and giant negative MDC in perovskite $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$ near room temperature, 290 K, at which spin reorientation occurs.

II. EXPERIMENT

Polycrystalline sample of $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$ was made by the traditional solid state reaction method with Dy_2O_3 (99.9%), MnCO_3 (99.9%), and Fe_2O_3 (99.9%) powder bought from Sigma-Aldrich. Stoichiometric amounts of raw oxide powder were weighed carefully and mixed in an agate mortar, followed by pressing into pellets 15 mm in diameter at 20 MPa. Samples were calcined at 950 °C for 10 h and sintered at 1440 °C for 6 h. The crystal structure of the sample was examined by x-ray diffraction (XRD, Model: GBC MMA), using Cu *K* α radiation at $\lambda = 1.54056$ Å. The Rietveld refinement calculations were conducted via FULLPROF software. The magnetic measurements were carried out using a 14 T physical properties measurement system (PPMS), equipped with a vibrating sample magnetometer (VSM), in magnetic fields up to 5 T, over a wide temperature range from 5 to 340 K in standard mode, and from 310 K to 750 K in oven mode. Pt electrodes were deposited on both sides of the thin pellet by magnetic scattering coating for dielectric measurement. An Agilent 4294 A impedance analyser was employed for dielectric property measurements, scanning from 1 kHz to 1 MHz, while the temperature and applied magnetic fields were controlled by PPMS. A room temperature resistance measurement was carried out with a multimeter, and it showed resistivity of $\sim 10^7$ Ω cm.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray powder diffraction pattern and Rietveld refinement results at room temperature. All diffraction peaks can be assigned to the single phase orthorhombic structure with space group *Pnma*, and no detectable impurity phase is present. The quality of refinement is determined by refinement parameter $R_p = 10.2\%$ and variance $\chi^2 = 1.9$. The calculated lattice parameters are $a = 5.6237(10)$ Å, $b = 7.5602(13)$ Å, and $c = 5.2912(9)$ Å.

The temperature dependence of the magnetic moment of $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$ is shown in Figure 2(a). There are two transitions that can be clearly identified. One is the transition from paramagnetism (PM) to canted AFM, with a weak

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FIG. 1. XRD refinement result of $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$ with $R_p = 9.9\%$ (star symbols, measured, and solid line, fitted). The difference between the measured and Rietveld refined spectra is plotted with a slight downshift for clarity. The short vertical solid lines are guides for the eyes to mark the corresponding Bragg positions.

ferromagnetic (WFM) component around 450 K, while the other is the transition from a canted AFM (WFM) to a collinear AFM around 290 K as the temperature decreases. Curie-Weiss fitting was conducted above 450 K, as displayed in Figure 2(b), where the sample shows intrinsic paramagnetic features, giving a Curie-Weiss temperature of -79 K, Curie constant of 15.6, and effective moment of $11.2 \mu_B$. The negative Curie-Weiss temperature suggests the antiferromagnetic transition around 450 K. The theoretical value of maximum moment for $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$ is $11.4 \mu_B$ if all ions are in the high spin state ($4.9 \mu_B/\text{Mn}^{3+}$, $5.9 \mu_B/\text{Fe}^{3+}$, and $9.9 \mu_B/\text{Dy}^{3+}$). The close values of the theoretical and the experimental moments indicate that all magnetic ions are in the high spin state. The increasing moment below this transition indicates that the antiferromagnetism is not pure but has a weak ferromagnetic component. Generally, in G-type antiferromagnetic order, a WFM component could be induced along the c axis because of the Dzyaloshinsky-Moriya interaction, if spins are normal to b axis in the ab plane.¹³ The possibility of FM clusters can be easily excluded because the magnetic hysteresis loop measured at 5 K shows typical paramagnetic/antiferromagnetic behaviour. A similar antiferromagnetic transition can also be observed in DyFeO_3 .¹⁴ The sudden decrease in the magnetic moment at 290 K is likely to be the result of the disappearance of the WFM component. Below it, the sample is in the pure AFM state, as confirmed by the magnetic hysteresis loop at 5 K. Hence, this transition is a spin reorientation caused by the change in the highly temperature sensitive magnetic anisotropy, which is similar to the case of DyFeO_3 .¹⁴ The continuous increase in the magnetic moment at low temperature is due to paramagnetic behaviour of Dy^{3+} . The magnetic property is consistent with the previous work.¹⁵

To investigate coupling between the magnetic field and the dielectric property, dielectric constants and loss were collected in different magnetic fields at 310 K, 285 K, and 250 K, respectively, as shown in Figures 3(a), 3(b), and 3(c). Obvious up/down shifts in the dielectric constant can be observed in the frequency dependence of the dielectric constants when measurements were carried out in various magnetic fields, indicating the occurrence of magnetodielectric coupling. The strength of magnetodielectric coupling is determined by the MDC constant in the form of $(\epsilon_H - \epsilon_{H=0})/\epsilon_{H=0}$, which is calculated and given in Figures 4(a)–4(c). It is clear that the MDC is extremely significant, especially in high magnetic field. At 310 K, we found a positive MDC constant as large as 53% (0.53) around 2×10^4 Hz. At the low frequency range, the MDC constant approaches zero when the frequency decreases, indicating that mobile charge does not contribute to the MDC effect too much. Just below the spin reorientation temperature, at 285 K, an opposite MDC effect occurs, giving a large value of -35% around 1×10^4 Hz. The MDC constant also approaches zero when the frequency is close to 0 Hz, confirming the negligible effect of mobile charge on MDC. Maximum MDC can be observed at the conductivity cut-off frequency $1/RC$ (where R and C are the resistance and capacitance of the equal circle, respectively).¹⁶ When the temperature cools down from the spin reorientation temperature, this negative MDC effect becomes much stronger, reaching -70% around 5×10^3 Hz at 250 K, as shown in Figure 4(c). Hence, the MDC effect is strongly temperature dependent. On the other hand, clear frequency dependence of MDC can be well observed.

Up to now, there are three proposed mechanisms to explain the MDC effect. One is based on intrinsic multiferroic relaxor behaviour,¹⁷ one is based on the Maxwell-Wagner model,¹⁶ and one is based on spin-phonon interaction. Although DyMnO_3 and DyFeO_3 also show multiferroic features, their multiferroic properties can only appear at very low temperature, below 18 K (Ref. 18) and 3.5 K,¹⁹ because of the inverse Dzyaloshinsky-Moriya interaction and exchange striction, respectively. Hence, near room temperature, the multiferroic relaxor based mechanism is not appropriate for our result. However, the giant MDC can be tentatively explained by the Maxwell-Wagner model at low frequency range below the cut-off frequency $1/RC$. To better understand these unique phenomena, we present the frequency dependence of the dynamic magnetoloss (ML), $\text{ML} = (\text{Loss}_H - \text{Loss}_{H=0})/\text{Loss}_{H=0}$, as shown in Figures 4(a)–4(c). The significant change of ML can be observed as increasing frequency, and the ML shows the opposite tendency to that of MDC. Considering the ML effect and

FIG. 2. (a) Temperature dependence of magnetic moment from 10 K to 600 K (black closed triangles: standard mode; red closed circles: oven mode). Inset: magnetic hysteresis loop measured at 5 K. (b) Inverse DC susceptibility versus temperature as measured in an external field of 1000 Oe for the paramagnetic state of $\text{DyMn}_{0.33}\text{Fe}_{0.67}\text{O}_3$ above 450 K (dashed line: Curie-Weiss fit; triangles: the inverse curve from experimental data).

FIG. 3. Frequency dependence of dielectric constant, loss at 310 K, 285 K, and 250 K, respectively.

FIG. 4. Frequency dependence of MDC constant and dynamic ML at 310 K, 285 K, and 250 K, respectively.

the result in Ref. 16, we could assign this MDC effect to the MR related MDC effects. Above the spin reorientation temperature of 290 K, such as at 310 K, the material shows WFM, but the applied magnetic field suppresses the spin fluctuation in the WFM state.^{20,21} This results in a negative MR and favours a positive MDC effect according to the Maxwell-Wagner model, similar to the positive MDC effect that occurs in EuNbO_2N below the ferromagnetic transition temperature.¹¹ During our experiment measurement, dynamic frequency dependent resistances were obtained. Figure 5 presents the dynamic magneto-resistance in form of $\text{MR} = (R_H - R_{H=0})/R_{H=0}$. A negative MR effect is observed at 310 K as shown in Figure 5(a). The result

confirms our assumption. On the contrary, when the temperature is 285 K or 250 K, the material experiences a magnetic phase transition from WFM to AFM. The MDC may be contributed by the following possible factors: first, MR effect induced by spin polarized tunnelling between charge depleted grain boundaries;²⁰ second, the intrinsic magnetoelectric effect due to magnetostriction;²² third, the spin pair correlation, as explained in the phenomenal model.²³ In our case, the magnetostriction effect should be very small and negligible, as the sample is not a typical magnetostriction material. In addition, the spin pair correlation cannot induce such a giant MDC effect. Hence, the most likely factor is the contribution by MR effect induced by spin polarized

FIG. 5. Frequency dependence of dynamic MR at 310 K, 285 K, and 250 K, respectively.

tunnelling, despite the AFM property. This is proved by the positive MR effects are observed at 280 K and 250 K as shown in Figures 5(b) and 5(c), which could induce a negative MDC according to the Maxwell-Wagner model. In the light of this, the MDC at low frequency range below the cut-off frequency $1/RC$ is related to space charge effect, which can be further confirmed by the strong frequency dependence and MR effect. For the case at high frequency range above the cut-off frequency $1/RC$, the MDC effect becomes weaker, which should due to the absence of space charge effect. Different magnetic states will affect the strength and mode of spin-phonon interaction and dielectric constant is consequently modified.^{8,24} Similar effect is observed in Mn_3O_4 , in which opposite MDC effects happen above and below magnetic transition temperature.²⁵ Hence, spin-phonon interaction is supposed to be responsible for the MDC at high frequency range.

IV. CONCLUSIONS

In summary, we have studied the phase transitions and MDC effect in $DyMn_{0.33}Fe_{0.67}O_3$. Two magnetic phase transitions are found at 290 K and 450 K, corresponding to spin reorientation and the antiferromagnetism-paramagnetism transition, respectively. MDC show strong temperature and frequency dependence. Giant positive and negative MDC effects are observed in the vicinity of the spin reorientation temperature. Magnetoresistance based Maxwell-Wagner model is employed to explain the MDC at low frequency range below the cut-off frequency $1/RC$ and spin-phonon interaction is responsible for the MDC at high frequency range above the cut-off frequency $1/RC$. These effects make it promising to produce multifunctional devices based on such kinds of materials.

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