Enhanced magnetism-generated ferroelectricity in highly frustrated Fe-doped Ho$_2$Ti$_2$O$_7$

L. Lin,$^{1,2}$ Y. L. Xie,$^{2}$ Z. Y. Zhao,$^{2}$ J. J. Wen,$^3$ Z. B. Yan,$^{2}$ S. Dong,$^{1,a}$ and J.-M. Liu$^{2,b}$

$^1$Department of Physics, Southeast University, Nanjing 211189, China
$^2$Laboratory of Solid State Microstructures and Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China
$^3$Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21218, USA

(Submitted 7 November 2014; received 1 September 2014; accepted 12 December 2014; published online 14 April 2015)

We present careful experiments on the ferroelectric (FE), dielectric, and magnetic behaviors of Ho$_{2-x}$Fe$_x$Ti$_2$O$_7$ with Fe$^{3+}$ substitution for Ho$^{3+}$. A remarkable enhancement of polarization up to 235 µC/m$^2$ is obtained at a low level $x = 0.08$, accompanied with the FE transition up to $\sim$80 K. The ac susceptibility under magnetic fields shows an expected saturated maximum in the real part $\chi'$, along with an unexpected frequency-dependent peak in the imaginary part $\chi''$, indicating unusual slow spin relaxation. The coupled correlated spin domains through dipolar interaction are argued to give rise to nonzero electric-dipole via Dzyaloshinskii-Moriya interaction.

I. INTRODUCTION

In the past decade, multiferroics have been receiving continuous attention because of their fascinating physical phenomena and promising prospect for multi-functional devices based on the mutual modulation of magnetic order and electric-dipole order.$^{1-4}$ The pioneering work on rare-earth manganite TbMnO$_3$ led to a unique branch of multiferroics (the so-called the type-II multiferroics), in which the ferroelectricity was directly generated and thus intrinsically controlled by spin orders.$^{3,4}$ In some of these type-II multiferroics, the spontaneous polarization ($P$) is driven by the spiral spin order, via the inverse Dzyaloshinskii-Moriya (DM) interaction.$^{5-7}$ To pursuit the utilization of the intrinsic mutual control between the magnetic and ferroelectric (FE) orders, more research efforts on the type-II multiferroics remain needed, e.g., to explore new materials with better performance.

Interestingly, almost all type-II multiferroics can be categorized into the spin-frustrated systems, in which the energies of competing interactions cannot be entirely minimized.$^{8-10}$ Even though, as far as we know, only very few works have touched the multiferroicity of pyrochlore magnet Re$_2$B$_2$O$_7$ (Re = rare-earth ion and B = Ti, Sn, Mo, and Ru) in which the rich noncollinear spin structures may hide plenty opportunities for novel multiferroics.$^{11-14}$ In fact, the so-called spin ice discovered in some of these frustrated magnets has received particular attention, in which the spins of rare earth ions at low temperatures ($T$) precisely mimic the protons’ behavior in water ice, giving nonzero entropy even down to the absolute zero-$T$ limit.$^{15,16}$

As a typical spin ice, Ho$_2$Ti$_2$O$_7$ (HTO) is composed of corner-shared TiO$_6$ octahedron and HoO$_4$ tetrahedron (Fig. 1(a)), in which the four Ho$^{3+}$ spins staying on the corners of each tetrahedron satisfy the “two-in-two-out” ice rule with macroscopic degeneracy.$^{11}$ Along the (111) axis, every spin

$^a$Electronic mail: sdong@seu.edu.cn.
$^b$Electronic mail: liujm@nju.edu.cn.
chain shows noncollinear spin configuration, and thus, the inverse DM interaction may take effect for these Ho⁺⁺ -O²⁻ - Ho⁺⁺ pairs, generating local electric dipoles, as shown in Fig. 1(b). However, it should be noted that any of the ground states following the “ice rule” would not allow macroscopic polarization, since neighboring electric dipoles would cancel each other. Even though, the latest theoretical work predicted that the elementary excitation in spin ice materials (the so-called magnetic monopole) not only carries magnetic charge but also electric-dipole, which manifests another type of intrinsic coupling between magnetic and electric properties. If a long-range order can be established for these electric-dipoles, a macroscopic electric polarization may be expected.

Indeed, the ferroelectricity has already been evidenced in both the single crystal and polycrystalline H₀₂T₁₂O₇ samples, while the measured polarization is very small. Along this line, to pursue better multiferroic performance, any modulation of the magnetic monopole excitation is meaningful. For example, it may be possible to tune the magnetic monopole excitation and thus, its multiferroicity by substitution of other magnetic species with large disparity in moment and ionic radius, e.g., Fe³⁺. Fig. 1(c) presents the schematic diagram of the spin configuration with Fe-substitution to the spin ice state, which may allow particular modulation in magnetic interactions and dynamics of magnetic monopoles, as well as the polarization.

II. EXPERIMENTAL DETAILS

A series of Ho₂₋ₓFeₓT₁₂O₇ (HFTO) was prepared by standard solid-state reaction method. In detail, the stoichiometric starting material Ho₂O₃, Fe₂O₃, and TiO₂ were first thoroughly ground and sintered at 1200 °C–1400 °C with several intermittent heating and grinding steps until high quality single phase was obtained. The measured XRD pattern for a series of HFTO samples are shown in Fig. 1(d). It can be seen that all the samples are well crystallized and indexed by single phase cubic pyrochlore structure, without any detectable impurity phase. The ac magnetic susceptibility (χ' and χ'') was measured with the corresponding powder sample using the physical properties measurement system (PPMS) (Quantum Design, Inc.) with the ACMS option (frequency f = 10 Hz–10 kHz). The T-dependence of the dielectric constant (ε) was measured using the HP4294A impedance analyzer integrated with PPMS. The measurement of specific heat (C_p) was carried out using the PPMS in the standard procedure. To probe the polarization, pyroelectric current method was used, and other extrinsic contributions, such as the de-trapped charges, were carefully excluded. The T-dependent P under magnetic field (H) was collected at a warming rate of 4 K/min with a fixed magnetic field during the whole process. The poling field (E) before the pyroelectric measurement is 7.69 kV/cm.

III. RESULTS AND DISCUSSION

First, the ferroelectric and dielectric properties of the Fe-substituted Ho₂T₁₂O₇ (HFTO) samples are presented. For example, let us take the substitution concentration x = 0.1. Fig. 2(a) shows the T-dependence of the pyroelectric current (I_p) under different ramping rates of 2, 4, and 6 K/min. It can be seen that two clear peaks show up. No obvious deviation of these peaks is observed with different warming scan rates, implying that the measured pyroelectric current is intrinsic. Also, it should be noted that there is a dim anomaly around 40 K, which is not well understood yet due to the limited knowledge of magnetic structure. To simplify the discussion below, we only focus on the main features, leaving this open question to future studies. In addition, we also measured the I_p-T curve after a negative poling electric field with 6 K/min warming rate, as shown in Fig. 2(b). The two curves of ±7.69 kV/cm poling fields are almost antisymmetric, which implies that the polarity can be fully reversed by external electric field, further confirming the existence of ferroelectricity.

Fig. 2(c) shows the T-dependent P over the whole T-range from 2 K to 100 K, in which two FE phase transitions at T_c ≈ 80 K and T_p ≈ 30 K, are observed. The inset of Fig. 2(c) shows the enlarged P-T curve of x = 0.1, in which the FE transition T_c can be clearly clarified. For comparison, the measured P(T) curve of pure polycrystalline Ho₂T₁₂O₇ is also presented in Fig. 2(c). Two striking changes in our Fe-substituted samples are detected. First, a remarkable enhancement of polarization up to 135 μC/m² was obtained at the low substitution level x = 0.1, accompanied with the FE phase transition (T_c) up to ~80 K, while the low-T P and T_c in HTO is only ~0.6 μC/m², and ~60 K, respectively. Second, the value of P in pure HTO almost reaches saturation below 50 K, whereas in the Fe-substituted sample continues to increase with decreasing T, until the saturated value at ~15 K. These two significant differences indicate that Fe-substitution can substantially tune the...
the multiferroicity of HTO. In addition, there is a kink around 50 K for the sample $x = 0.10$, which might be the feature of pure HTO. The dielectric constant ($\varepsilon$) also show changes upon Fe-substitution, which first increases with decreasing $T$, reaching a broad bump roughly at $T_c$ as shown in Fig. 2(d). Besides, the frequency ($f$) dispersion behavior is also observed for the dielectric constant. Both the broad bump and $f$-dispersion reflect the characteristic behavior of a ferroelectric relaxor.26

The enhancement of ferroelectricity upon Fe’s partial substitution is not limited to the $x = 0.10$ sample. The corresponding $P$-$T$ data of a series of HFTO samples with various $x$ are presented in Fig. 2(e). It can be seen that all samples show clear ferroelectricity, with two ferroelectric transition points, although the values of $P$ and $T_c$ depend on $x$. The detailed $x$-dependence of $P$ at $T = 2$ K is shown in the inset of Fig. 2(e). The value of $P$ at 2 K first increases with the Fe-substitution level $x$, reaching the maximum $\sim 235 \mu C/m^2$ at $x = 0.08$, while further substitution leads to suppression. Meanwhile, the critical point $T_c$ also shows similar behavior, which increases first but decreases rapidly at $x > 0.08$, e.g., $T_c = 40$ K for $x = 0.15$.

To uncover the intrinsic correlation between magnetic and ferroelectric properties, the magnetoelectric (ME) responses of HFTO samples are investigated under selected magnetic fields. Still taking the $x = 0.10$ sample, for example, Fig. 2(f) shows that the external magnetic field suppresses $P$ in the whole FE phase region, implying the significant response of $P$ to $H$. The reduced value of $P$ under $H = 9$ T can reach up to $\sim 20 \mu C/m^2$ at low $T$, confirming the intrinsic type-II multiferroicity.

To shed light on the mechanism of multiferroicity, we turn to investigate the magnetism and specific heat of HFTO sample. Aforementioned HFTO samples show similar $P$-$T$ behavior and ME response, suggesting a common mechanism for various $x$. In the following, the substitution concentration $x = 0.04$ is shown as an example. Fig. 3(a) shows that the real part of the ac susceptibility ($\chi'$) at $f = 1$ kHz monotonically rises with decreasing $T$ under zero magnetic field, closely following the canonical paramagnetic behavior.27 However, as shown in Figs. 3(a) and 3(b), the corresponding real part $\chi'$ and imaginary part ($\chi''$) of $ac$ susceptibility taken at $H = 3$ T demonstrate an expected freezing temperature $T_f \sim 28$ K for

the $\chi'$, together with an unexpected $f$-dependent peak for the imaginary part $\chi''$. In particular, the magnitude of the peak of $\chi''(T)$ gradually grows with decreasing frequency at lower $f$ range ($f < 1$ kHz), and the application of magnetic field can enhance the value of $T_f$. This abnormal freezing phenomenon reminds us that an unusual slow spin relaxation occurs in the highly spin polarized state, similar to that of Tb$_2$Ti$_2$O$_7$.28 Besides, it should be noted that the prominent $f$-dependence of $\chi''(T)$ behave more like spin ice.29-31 In other words, a low level substitution dramatically changes the dynamic of spin relaxation process, with the coexistence of spin-ice freezing and Tb$_2$Ti$_2$O$_7$-like relaxation. Such a relaxation process in this highly polarized cooperative paramagnetic system is argued to be originated with the development of correlated regions of spins coupled through dipolar interactions.28

To uncover more information of the magnetism of HFTO, both the specific heat data of HFTO ($x = 0.04$) ($C_{HFTO}$) and Y$_2$Ti$_2$O$_7$ (YTO) ($C_{YTO}$) were obtained. As YTO is structurally analogous to HTO but without magnetism, the lattice vibration contribution term ($C_{lat}$) of specific heat of HTO can be approximated by measuring the nonmagnetic YTO. Consequently, the magnetic term ($C_{mag}$) of specific heat can be evaluated by deducting the lattice vibration contribution: $C_{HFTO} - C_{YTO}$. As shown in Fig. 3(e), $C_{mag}$ gradually rises with decreasing $T$, and subsequently turns into a broad platform below 60 K, which indicates that there are still spin fluctuations within the system. In this context, the timescale of the dynamic response is long enough to allow the system to respond to the varying magnetic field. Hence, the correlated $T$-dependent $C_{mag}$, $\chi$ and $P$ imply close relationship between magnetism and ferroelectricity.

Finally, the possible origin of enhanced ferroelectricity in HFTO is discussed. As mentioned in the Introduction, Khomskii’s theory based on the magnetic monopole of spin ice proposes the new possibility to mutual control of magnetic monopoles and electric dipoles.21 Of course, convincing experimental evidences are still scarce, as far as we know, due to the complexity of magnetism in these spin ice systems. Thus, here our discussion is only for qualitative and preliminary reference.

First, let us start with the discussion of FE mechanism of pure HTO. A schematic diagram of Ho$^{3+}$ spin configurations at $T_{d} < T < T_{c}$, and $T < T_{d}$ for HTO is presented in Figs. 4(a) and 4(b), respectively. It is known that HTO shows paramagnetic (PM) behavior at $T_{d} < T < T_{c}$, and thus, the FE $P$ cannot be driven by specific spin order. The measured polarization shown in Fig. 2(c) is likely to be caused by the ion-displacement associated with the Ti-O octahedral distortion.22 When the system enters into the low temperature $(T < T_{d})$ region, a number of magnetic monopoles as labeled by the dashed rectangles are activated, which thus give rise to the electric dipoles. However, the macroscopic polarization driven by magnetic monopoles should be very limited,21 since the electric dipole alignment driven by electric field can be more complicated. The electric field driven dipole flip is actually realized by the motion of the associated monopoles, e.g., the local creation and annihilation of magnetic monopoles by the manipulation field.

However, the above explanation appears not plausible for the Fe-doped HTO, since the change of magnetic

FIG. 3. (a) and (b) Measured $ac$ susceptibility of the sample $x = 0.04$ versus temperature for several frequencies at $H = 3$ T. (a) Real part $\chi'$. (b) Imaginary part $\chi''$. The $\chi'(T)$ without magnetic field at $f = 1$ kHz is also presented in Fig. 3(a) (right axis). (c) The $T$-dependence of magnetic contribution term $C_{mag}$ of specific heat for sample $x = 0.04$. 17D915-3 Lin et al. J. Appl. Phys. 117, 17D915 (2015)
monopoles should not be so dramatic upon such tiny substitutions.\textsuperscript{21} As demonstrated by the $ac$ susceptibility, the original dynamics of typical spin ice is significantly weakened; instead, highly correlated cooperative paramagnetic (CCPM) behavior is dominated in the Fe-substituted samples. In this context, all spins should be immensely correlated, where ordered noncollinear spin pattern is highly possible to be formed, e.g., propagating along $\langle 001 \rangle$ direction as illustrated in Figs. 4(c) and 4(d). It is believed that there is a strong competition between spin fluctuations and dipolar interaction. Hence, with the coupled correlated regions through dipolar interactions, a macroscopic $P$ is gradually established. However, excess Fe-substitution will weaken the dipolar interactions between $\text{Ho}^{3+}$-$\text{Ho}^{4+}$ pairs, leading to the decreasing $P$ and $T_c$, as shown in Fig. 2(e). In addition, the observation of the $ac$ susceptibility shown in Fig. 3(a) can be explained as the formation of correlated magnetic domains, in most of which the spins are polarized along the field and in a few of which the spins are polarized antiparallel to the field.\textsuperscript{20} Switching these oppositely polarized domains needs a large energy barrier, making the spin relaxation becoming much slow. Therefore, accompanied by the switching of domains, the long-range spiral spin order may be partially broken, leading to the suppressed $P$ by the application of magnetic field. Of course, an unambiguous clarification of the underlying microscopic mechanism, as well as the dynamics of creation and annihilation of magnetic monopoles by electric field, desires further experimental and theoretical investigations.

IV. CONCLUSION

In conclusion, we have demonstrated a remarkable enhancement of polarization in Fe-doped $\text{Ho}_2\text{Ti}_2\text{O}_7$. The $ac$ susceptibility indicates that the original typical spin ice behavior changes into unusual slow spin relaxation. We argue that the competition between correlated spins and dipolar interactions gives rise to the finite electric dipoles via the inverse DM interaction. Our experimental measurements indicate a magnetic multiferroic behavior in such a pyrochlo red oxide, which extends the scope and deepens the understanding of exotically magnetically induced ferroelectricity in frustrated magnets.

ACKNOWLEDGMENTS

This work was supported by the 973 Projects of China (Grant No. 2011CB922101), the Natural Science Foundation of China (Grant Nos. 11234005, 11374147, 51332006, and 51322206), and the Priority Academic Program Development of Jiangsu Higher Education Institutions, China.

\textsuperscript{1}S.-W. Cheong and M. Mostovoy, Nat. Mater. 6, 13 (2007).