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Dynamic magnetoelectric coupling in "electronic ferroelectric" LuFe$_2$O$_4$

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Magnetoelectric (ME) coupling characteristics of LuFe$_2$O$_4$ were examined by monitoring the electrical voltage induced by an oscillating magnetic field under a static bias field (H_0). Interestingly, the room-temperature dynamic ME output exhibited a constant plateau behavior up to a certain static-field strength but showed a sudden drop above this critical value. In addition, two evidences of the intrinsic ME coupling were obtained by monitoring the pyroelectric response near the ferrimagnetic ordering temperature ($\sim$250 K) and by examining the temperature-dependent magnetization near the ferroelectric transition point ($\sim$345 K) between the two-dimensional charge-density-wave (CDW) state and the three-dimensional CDW state. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2798597]

The term multiferroics is used to indicate materials which simultaneously possess at least two among ferroelectric, ferromagnetic (or antiferromagnetic), and ferroelastic order parameters.[1] During the past few years, they have been extensively studied because of their potential applications including multiple-state memory elements, magnetic-field sensors, and electric-field-controlled ferromagnetic resonance devices with magnetically modulated piezoelectricity.[2,3]

LuFe$_2$O$_4$, an emerging candidate for room-temperature multiferroics, has been comprehensively investigated for its anomalous dielectric and charge-ordering behavior.[4–6] The charge ordering is associated with successive phase transitions following the sequence of "three dimensional charge-density-wave (3D-CDW) state $\rightarrow$ two-dimensional (2D)-CDW state $\rightarrow$ disorder" with increasing temperature. The charge frustration in the process of charge ordering is known to be closely related to observed large dielectric permittivities with a remarkable Debye-type relaxation effect.[5] The average valence of Fe ions in LuFe$_2$O$_4$ (LFO hereafter) is +2.5, and the centers of Fe^{2+} ions and Fe^{3+} ions do not coincide in the triangular lattice. The discord of these two centers then leads to ferroelectricity[7] even without a pairing of anion and cation which is the case of usual off-centering ferroelectrics.[8] Thus, LFO belongs to "electronic ferroelectrics" that originate from electron correlations[7] rather than from the covalency between anions and cations. Magnetic properties of LFO stemming from 2D ferrimagnetic ordering have also been investigated using neutron diffractions, magnetization, and Mössbauer measurements.[9]

Though magnetoelectric effects of antiferromagnetic ErFe$_2$O$_{4-\delta}$ (in the same RFe$_2$O$_4$ family) were briefly discussed by Ikeda *et al.*,[10] LFO has not been focused as a multiferroic material until recently.[7,10] Subramanian *et al.*[11] reported pronounced magnetodielectric effects in the vicinity of room temperature. Although the observed large change in the dielectric permittivity can be correlated with a nonzero value of the magnetoelectric (ME) susceptibility, it is an indirect indication of the ME coupling under a static magnetic-field condition. Thus, it is highly important to directly estimate the ME coupling susceptibility using dynamic ME outputs. The sinusoidally varying electrical voltage [$\delta E(t)$] induced by an oscillating magnetic field ($\delta H e^{-i\omega t}$) under a static bias field (H_0) is represented by two ME coefficients, i.e., complex linear ($\alpha_E = \alpha_E' - i\alpha_E''$) and nonlinear ($\beta_E = \beta_E' - i\beta_E''$) ME coefficients. It can be shown that[12]

$$\delta E(t) = \delta E e^{-i(\omega t - \delta)} = \{\alpha_E + \beta_E H_0\}\delta H e^{-i\omega t}, \qquad (1)$$

where δE denotes the amplitude of the magnetically induced voltage and δ is the phase lag between the voltage response and the oscillating magnetic field. Using Eq. (1), one can establish the following relation of the dynamic ME voltage susceptibility (χ_E) in terms of the linear and nonlinear ME coefficients:

$$\chi_E \equiv \frac{\delta E}{\delta H} = \{(\alpha_E' + \beta_E' H_0)^2 + (\alpha_E'' + \beta_E'' H_0)^2\}^{1/2}$$
$$\approx \alpha_E' + \beta_E' H_0. \qquad (2)$$

The last expression is strictly valid for sufficiently low frequencies under which the imaginary dissipation parts (α_E'', β_E'') are relatively negligible.

In this letter, the authors report the room-temperature dynamic ME coupling characteristics of polycrystalline LFO. In addition to these, the authors present two interesting evidences of the intrinsic ME coupling by examining the pyroelectric response near 250 K and the temperature-dependent magnetization, $M(T)$ near 345 K. For these purposes, polycrystalline LFO pellets were prepared by thoroughly mixing high-purity Lu$_2$O$_3$ (Aldrich, 99.9%), Fe$_2$O$_3$ (Alfa, 99.99%), and Fe metal powder in a stoichiometric ratio. The pelletized samples were sintered in an evacuated quartz tube at 1100 °C for 48 h for the stoichiometric composition of oxygen.[11] Reactive sintering was employed to obtain densely sintered pellets with a thin disk shape. The LFO samples for dielectric and pyroelectric measurements were prepared by applying silver electrodes on both sides of the polished surface.

θ-2θ x-ray diffraction (θ-2θ XRD) and x-ray photoelectron spectroscopy (XPS) experiments were carried out to examine the phase purity and the mixed valent state of Fe ions

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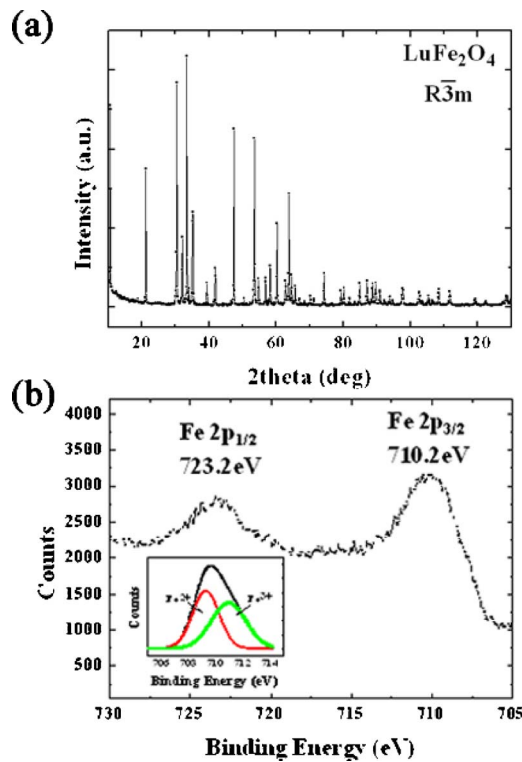
FIG. 1. (Color online) X-ray diffraction and spectroscopic data of $LuFe_2O_4$ (LFO) used in the present study. (a) High-resolution θ-2θ XRD pattern obtained using synchrotron radiation with the calibrated wavelength (λ) of 1.549 60 Å. (b) X-ray photoelectron spectrum of the Fe $2p$ lines for the binding energy between 705 and 730 eV.

(Fe^{2+}/Fe^{3+}). The synchrotron radiation from the 8C2 high-resolution powder diffraction (HRPD) beamline at the Pohang Light Source was used for θ-2θ XRD experiments. As presented in Fig. 1(a), the HRPD pattern indicates that the LFO sample is exclusively characterized by the rhombo-hedral phase [space group $R\bar{3}m$ (Ref. 13)] with the absence of any impurity phase. The estimated a- and c-lattice param-eters are 3.431 and 25.27 Å, respectively.[9]

A representative XPS scan of the Fe $2p$ lines is presented in Fig. 1(b). The Fe $2p_{3/2}$ peak is known to occur at 709.5 eV for Fe^{2+} and at 711.0 eV for Fe^{3+}.[14] As can be noticed from the XPS spectrum, the $2p_{3/2}$ peaks for Fe^{2+} and Fe^{3+} are not separated from each other but are positioned between these two values as a mixed peak. Therefore, the mixed peak was separated into two distinctive peaks, corresponding to Fe^{2+} and Fe^{3+} states [the inset of Fig. 1(b)].[15] The estimated ratio of Fe^{2+}:Fe^{3+} is 52:48. From this peak-fitting result, the au-thors conclude that the LFO sample is nearly characterized by an ideal mixed valent state, i.e., Fe^{2+}:Fe^{3+}=1:1. This estimate further indicates that the oxygen nonstoichiometry (i.e., δ value in $LuFe_2O_{4-\delta}$) is ~0.02.

Figure 2(a) presents relative dielectric permittivity data at six different ac frequencies. The frequency-dependent di-electric response (dielectric dispersion) observed for tem-peratures below ~330 K can be correlated with the ferro-electric transition from the 2D-CDW state to the lower-temperature 3D-CDW state.[6,7] This dielectric dispersion was interpreted in terms of the motion of the ferroelectric domain boundary.[7,16] The observed monotonous increase in the rela-tive permittivity in the 2D-CDW state (for $T \gtrsim \sim 330$ K) seems to be closely related to the increase in the electrical conductivity.[17]
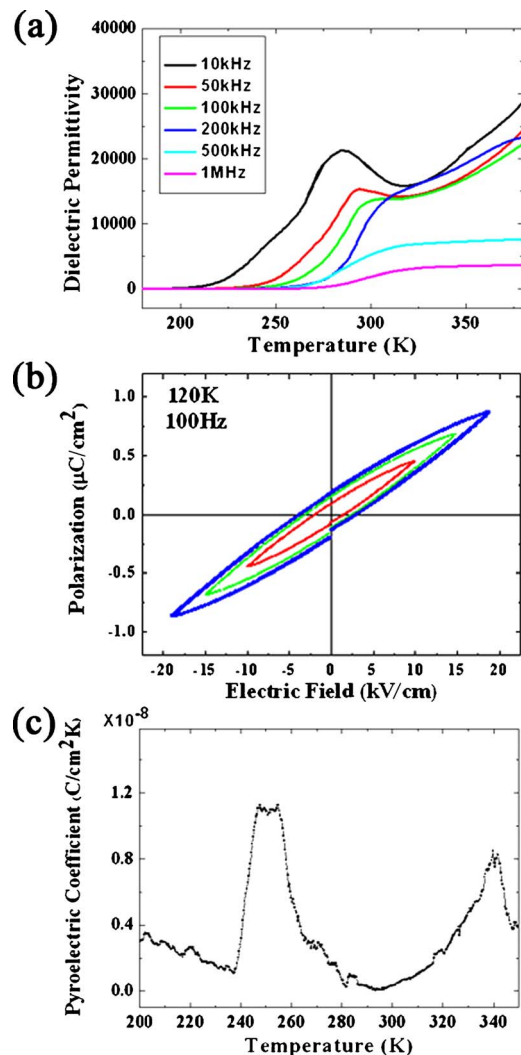

FIG. 2. (Color online) Summary of dielectric, ferroelectric, and pyroelectric responses of the rhombohedral LFO. (a) Temperature-dependent relative dielectric permittivity at six measuring ac frequencies. (b) Polarization-electric field (P-E) hysteresis loops at 120 K, measured using an ac fre-quency of 100 Hz. (c) Pyroelectric coefficient plotted as a function of tem-perature. For the measurement, a bias electric field of 10 kV/cm (at low temperatures) was applied during the cooling down to 200 K. The pyroelec-tric current was recorded during the heating (3 K/min) using a picoammeter.

Figure 2(b) presents a first-of-its-kind polarization-electric field (P-E) response of the sintered polycrystalline LFO pellet. The P-E curve at 120 K thus reflects the polar-ization response in the 3D charge-ordered state. Because of the dynamic fluctuation in the local polarization caused by the electron hopping between Fe^{2+} and Fe^{3+} sites, we ob-served very high dielectric responses but could not obtain a stable P-E curve at room temperature. Even at a temperature as low as 120 K, the P-E curve does not exhibit an ideal square-type response and is characterized by relatively large values of the nonswitching polarization.

As presented in Fig. 2(c), the pyroelectric responses are largely characterized by two pronounced peaks at 250 and 340 K. The latter can be attributed to a rapid increase in the spontaneous polarization by the ferroelectric transition at $T_{c(2D-3D)}$. On the other hand, a strong peak at 250 K which corresponds to the ferrimagnetic ordering[7] at T_N (Néel tem-perature) indicates an anomalous change in the spontaneous polarization at the magnetic transition temperature. This sug-
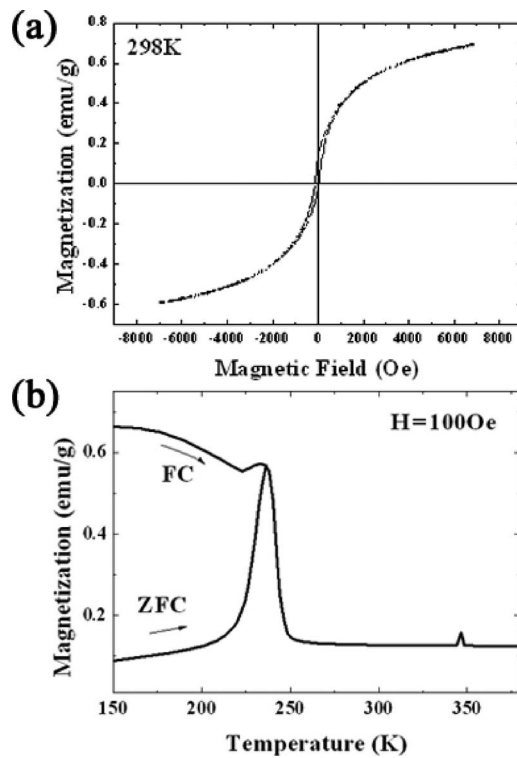
FIG. 3. Magnetic data of the rhombohedral LFO. (a) A magnetization-field (*M-H*) curve at room temperature. (b) Two low-field *M(T)* curves measured after ZFC and FC.
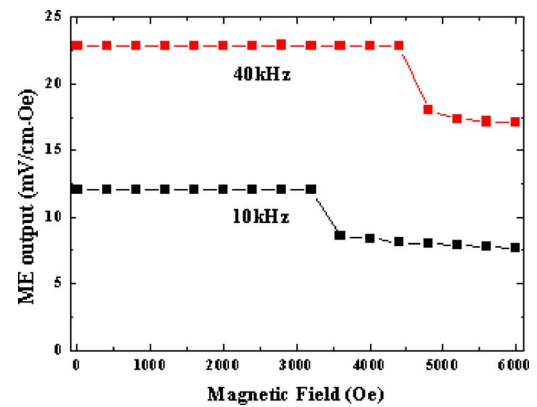

FIG. 4. (Color online) Longitudinal ME voltage coefficient plotted as a function of the static magnetic field (H_0) at two different oscillating magnetic-field frequencies (ω), 10 and 40 kHz. The polycrystalline LFO pellet was electrically poled at 10 kV/cm before ME measurements.

gests the presence of a strong intrinsic ME coupling between electric polarization (*P*) and magnetization (*M*), which reduces the free energy by the following term: $\Delta F = -\gamma P^2 M^2$, where γ denotes the intrinsic ME coupling constant.

Figure 3(a) presents a magnetization-field (*M-H*) curve of the polycrystalline LFO pellet measured at 298 K. Interestingly, the *M-H* curve apparently shows a weak ferromagnetic behavior at a temperature substantially above T_N, ~250 K. The temperature-dependent magnetization *M(T)* curve in Fig. 3(b) also shows that a small residual moment (~0.12 emu/g) persists up to 400 K and thus supports the room-temperature *M-H* curve. The synchrotron HRPD pattern (Fig. 1) indicates that the residual moment observed for temperatures above T_N is not caused by any magnetic impurity. *M(T)* data further show a discrepancy between zero-field cooling (ZFC) and field cooling (FC) curves, suggesting the existence of short-ranged magnetic clusters. According to the detailed study of Iida *et al.*,[9] a spin glasslike 2D-magnetic ordering occurs below about 220 K. Based on all these observations we tentatively conclude that the 2D-ferrimagnetic order does not decay immediately above T_N but a short-range magnetic order persists up to 400 K, at least. Another prominent feature of the *M(T)* curve in Fig. 3(b) is the appearance of a small peak at about 345 K, which coincides with the ferroelectric transition from the 2D-CDW state to the 3D-CDW state [Fig. 2(c)]. This indicates that the residual magnetic moment is perturbed by the change in the polarization vector at $T_{c(2D-3D)}$, demonstrating the existence of an intrinsic ME coupling in LFO.

Figure 4 shows the longitudinal ME output (χ_E) plotted as a function of the static magnetic field (H_0) at two different magnetic ac-field frequencies, 10 and 40 kHz. We used a home-built setup including a lock-in-amplifier (SRS Inc.,

SR830, USA) to determine dynamic ME responses.[12] The amplitude of an oscillating magnetic field (δH) is 10 Oe. Both the static bias field (H_0) and the oscillating field (δH) are applied parallel to the direction of the magnetically induced voltage or polarization (i.e., longitudinal mode). As shown in the figure, the ME output (χ_E) exhibits a plateau behavior up to a certain magnetic-field strength: 3300 Oe for 10 kHz and 4500 Oe for 40 kHz. This indicates that the nonlinear susceptibility (β_E) is negligibly small and, thus, $\chi_E \approx \alpha'_E$ [Eq. (2)]. There is a sudden drop in the ME output above this critical value of H_0. This suggests some changes in the direction of the residual magnetic moment presumably caused by the reorientation of short-ranged glasslike spin clusters[9] being parallel to the static-field direction above a certain critical value of H_0.

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