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Direct observation of magnetodielectric effect in type-I multiferroic $PbFe_{0.5}Ti_{0.25}W_{0.25}O_3$

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ABSTRACT

In type-I multiferroics, where ferroelectricity and magnetism arise from different origins, the explicit measurement of magnetoelectric effect is commonly prohibited due to the weak magnetoelectric coupling. From our investigation of magnetic and dielectric properties in a perovskite $PbFe_{0.5}Ti_{0.25}W_{0.25}O_3$, we have directly demonstrated magnetic-field-driven change of dielectric constant in a highly non-linear fashion. Our result offers a potential utilization of magnetoelectric functionality in type-I multiferroics.

1. Introduction

Materials with various order parameters that are strongly correlated provide new opportunities for multiple functionalities. For instance, multiferroics in which ferroelectric and magnetic orders are simultaneously present allow advanced technological utilization such as data storage [1–3] and sensors [4], engineering their cross-coupling effects. Multiferroics are commonly classified into two types [5]. In type-II multiferroics, ferroelectricity originates from the lattice relaxation via exchange strictions in the specific spin order with broken spatial inversion symmetry [6], which naturally leads to strong controllability of ferroelectric properties by applying external magnetic fields [7–11]. However, in this type, the magnitude of ferroelectric polarization is very small compared to that in conventional ferroelectrics and multiferroicity appears at very low temperature inherent from frustrated spin nature [12–14]. In contrast, type-I multiferroics reveal separate origins for structural distortion and magnetic order. Therefore, they tend to have a huge difference in critical temperatures of ferroelectric and magnetic orders and also exhibit comparatively weak magnetoelectric effect. However, the ferroelectricity and magnetism in type-I multiferroics often arise at fairly high temperatures [15–18], suggesting a practical benefit for device application utilizing magnetoelectric effect.

One of the noticeable type-I multiferroics is $Pb(Fe_{2/3}W_{1/3})O_3$ (PFW) which exhibits the relaxor ferroelectricity at $T_{FE} \approx 180$ K with high dielectric permittivity and diffusive phase transition, and two consecutive magnetic transitions at $T_1 = 20$ K and $T_2 = 350$ K. The weak ferromagnetic order at T_1 originates from the superexchange interaction via Fe^{3+}-O^{2-}-W^{6+}-O^{2-}-Fe^{3+} pathway, and the antiferromagnetic order at T_2 does from the strong interaction via Fe^{3+}-O^{2-}-Fe^{3+} pathway [19]. The emergence of distinct long-range ferroelectric order can be anticipated in a mixed compound of a conventional perovskite ferroelectric $PbTiO_3$ (PT) ($T_{FE} \approx 760$ K) and PFW, i.e., $(1-x)$PFW-xPT ($0 < x < 1$) [20,21]. PFW exhibits the structural phase transition from cubic to rhombohedral phase at $T_{FE} \approx 180$ K, while PT displays the transition from cubic to tetragonal phase at $T_{FE} \approx 760$ K. In $0.25 \leq x \leq 0.35$, the phase transition between rhombohedral and tetragonal ferroelectric phases occurs regarding the morphotropic phase boundary. In $x = 0.25$, i.e., $PbFe_{0.5}Ti_{0.25}W_{0.25}O_3$ (PFTWO), the phase transition from cubic to tetragonal phase is observed at $T_{FE} \approx 290$ K, where the proper ferroelectricity below 760 K in PT transforms into the near-room-temperature diffusive ferroelectric state. Our powder X-ray diffraction data at room temperature shows the mixture of the major cubic (space group $Pm\bar{3}\ m$) and minor tetragonal (space group $P4mm$) phases, consistent with the previous result [22]. This suggests the introduction of the slight ferroelectric phase for the first order phase transition with certain temperature broadness. Additional structural transition is found to be at ~250 K, indicating the tetragonal to rhombohedral transition across the morphotropic

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phase boundary [20]. Note that this transition has been observed in differential scanning calorimetry and acoustic emission. The magnetic transitions in $T_1 = 60$ K and $T_2 = 125$ K are associated with the Fe^{3+}-O^{2-}-W^{6+}/Ti^{4+}-O^{2-}-Fe^{3+} and Fe^{3+}-O^{2-}-Fe^{3+} superexchange pathways, respectively. Thus, PFTWO becomes a type-I multiferroic below T_2 [22]. In usual type-I multiferroics, discrepancy of the origin and transition temperature between ferroelectricity and magnetism impedes the explicit measurement of the magnetoelectric couplings. Herein, we demonstrate the direct observation of the nonlinear magnetodielectric effect in type-I multiferroic of PFTWO.

2. Methods

PFTWO crystallizes in a perovskite structure, where B-sites ions are randomly distributed. The polycrystalline sample was prepared by the solid state reaction method. X-ray diffraction using Rigaku D/Max 2500 powder X-ray diffractometer confirms the formation of the major phase with a cubic structure (space group $Pm\bar{3}\ m$) and the other minor phase with a tetragonal (space group $P4mm$) structure at room temperature with a unit cell parameter $a \approx 4$ Å, agreeable with a previous study. Magnetizations were obtained using a SQUID magnetometer (Quantum Design MPMS). Dielectric measurements were performed in a Quantum Design PPMS (Physical Properties Measurement System) equipped with an LCR meter.

3. Results and discussion

Fig. 1(a) shows the temperature dependence of magnetic susceptibility, $\chi = M/H$, measured in $H = 1$ T, upon warming after zero-field-cooling (ZFC) and upon cooling in the same field (FC). As the temperature decreases, the χ increases smoothly with small anomalies exhibiting consecutive magnetic transitions, $T_1 = 60$ K and $T_2 = 125$ K. The magnetic transition temperatures are identified by the troughs in the temperature derivative of χ. The splitting of the ZFC and FC curves starts at ~35 K, indicating the onset of magnetic irreversibility. The similar magnetic anomalies of χ to the ones in PFW [19] suggest that T_1 and T_2 in PFTWO correspond to the weak ferromagnetic order resulting from the superexchange path of Fe^{3+}-O^{2-}-W^{6+}/Ti^{4+}-O^{2-}-Fe^{3+} and the antiferromagnetic order from the path of Fe^{3+}-O^{2-}-Fe^{3+} [22]. In comparison with PFW, the incorporation of Ti^{4+} ions lowers T_2 in PFTWO, resulting from the dilution of magnetic Fe^{3+} ions. The slight increase in T_1 also occurs due to the modification of long distance superexchange interaction via Fe^{3+}-O^{2-}-W^{6+}/Ti^{4+}-O^{2-}-Fe^{3+} pathway [23]. The weak ferromagnetic moment below T_1 is evidenced in the isothermal magnetization, $M(H)$, measured up to 7 T upon ramping up and down at $T = 5$ K (Fig. 1(b)). A small magnetic hysteresis was observed with the coercive field (H_c) of 0.22 T and the remnant magnetization (M_r) of 0.005 μ_B/f.u.

The temperature dependences of dielectric constant, $\varepsilon'(T)$, and tangential loss, $tan\ \delta(T)$, with the fixed frequency $f = 10$ kHz upon warming and cooling are presented in Fig. 2. Upon warming, ε' smoothly increases and suddenly escalates above 250 K. A distinct peak at ~300 K indicates the ferroelectric phase transition. The first order nature of this transition is manifested by the substantial thermal hysteresis. The inset of Fig. 2(a) displays the temperature dependent $\varepsilon'(T)$ at various frequencies, $f = 1$, 10, 100 kHz, and 1 MHz. Compared to the dielectric properties of PFW, the maximum of $\varepsilon'(T)$ in PFTWO becomes sharper with reduced frequency dependence. But the residual broadness of the maximum and slight temperature shift of $\varepsilon'(T)$ in different frequencies suggest that the relaxor ferroelectric behavior still remains in PFTWO. Fig. 2(b) exhibits sufficiently low magnitude of $tan\ \delta$. The occurrence of thermal hysteresis at ~300 K was also observed in consistent with the ferroelectric transition. In low temperature range, the two consecutive anomalies emerge at the similar temperatures with the two sequential magnetic transitions below 150 K which implies the

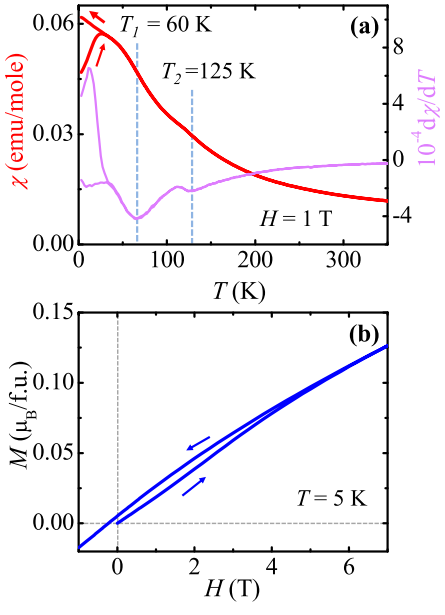

Fig. 1. (a) Magnetic susceptibility of polycrystalline $PbFe_{0.5}Ti_{0.25}W_{0.25}O_3$ as a function of temperature, $\chi = M/H$, measured in $H = 1$ T upon warming after zero-field-cooling (ZFC) and upon cooling in the same field (FC). Temperature derivative of magnetic susceptibility. Dotted lines indicate two consecutive magnetic anomalies at $T_1 = 60$ K and $T_2 = 125$ K. (b) Isothermal magnetization, $M(H)$, with both ramping and down measurements up to 7 T at 5 K.

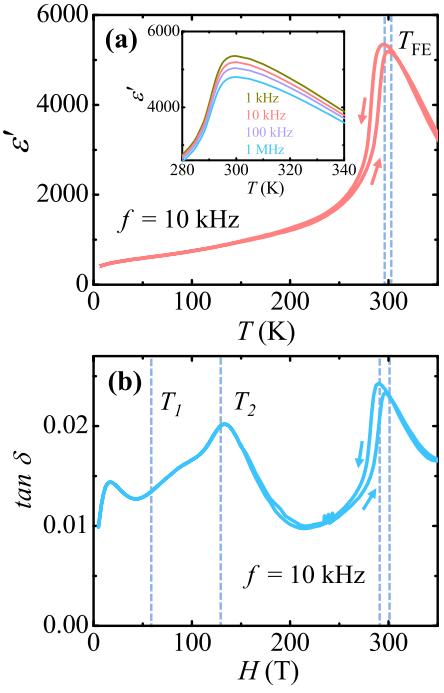

Fig. 2. (a) Temperature dependence of dielectric constant, $\varepsilon'(T)$, measured upon both cooling and warming at $f = 10$ kHz. Inset: Temperature dependence of dielectric constant, $\varepsilon'(T)$, at different frequencies, $f = 1$, 10, 100 kHz, and 1 MHz. (b) Temperature dependence of dielectric loss, $tan\ \delta(T)$, measured at $f = 10$ kHz.