Tuning ferroelectrics to antiferroelectrics in multiferroic La$_x$Sr$_{1-x}$Fe$_{12}$O$_{19}$ ceramics

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Received: 19 February 2022; accepted: 18 April 2022; published online: 6 May 2022

The combination of antiferroelectricity and ferromagnetism in one structure would create new types of multiferroic candidates. Here, we propose a novel type of multiferroic candidate La$_x$Sr$_{1-x}$Fe$_{12}$O$_{19}$, whose room temperature state could be tuned from ferroelectrics (FEs) to antiferroelectrics (AFEs) by changing $x$ from 0 to 0.5. The AFE state in La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ remains as a stable phase between −163 and 233 °C and demonstrates double $P$–$E$ hysteresis loops which are fully separated by a straight line with zero polarization. La$_{0.2}$Sr$_{0.7}$Fe$_{12}$O$_{19}$, however, exhibits a hybrid FE/AFE state. Both compounds exhibit strong ferrimagnetism. In addition, the La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramic demonstrates strong magnetoelectric coupling and giant magnetoresistance effect. A 1.1 T magnetic field generates electronic polarization of 0.95 μC/cm$^2$, reduces the resistance by 117%, enhances dielectric constants by 540% and right shifts the maximum dielectric loss peak by 208 kHz. The combined functional responses provide an opportunity to develop novel multiferroic memories and energy storage devices.

Introduction

Multiferroic materials can be used to produce new generation of multifunctional devices: such as new magnetoelectric (ME) sensing devices, spintronic devices, high performance information storage devices [1]. For multiferroic material with ME coupling, a voltage rather than a current is used to regulate the magnetization direction and minimizes Joule heat dissipation. Their use can fundamentally solve the problem of high energy consumption in big data storage as well as develop new generation of memories with ultra-low power consumption and high processing speed. In addition, it is important to understand the interaction law of new generation of multiferroic candidate that combines antiferroelectrics (AFEs) and ferromagnetism (FM) together in single phase, since this may allow us to observe new quantum phenomena [2]. Furthermore, the control of new AFE parameters in these novel multiferroic materials would help us to develop new energy storage devices, which may be charged either electrically or magnetically, or even both [3, 4]. The ME coupling in multiferroic materials can induce electric polarization under a magnetic field. The B induced polarization $P(H)$ then generates a spin current or ME voltage, which can input additional charge into the energy storage devices upon the electrically charged energies. The second dimensional freedom of magnetically charged energies would improve the energy storage efficiency. However, the multiferroic candidates that combine AFE and FM orders together are rare [4, 5].

The first AFE state in the multiferroic family was reported to appear in the (Bi$_{1-x}$Re$_x$)$_2$FeO$_3$ (Re = La, Sm) thin film system, which exhibits a hybrid state of ferroelectrics (FEs) and AFE [6], whereas full multiferroic AFE feature was achieved in the Dy$_{0.75}$Gd$_{0.25}$FeO$_3$ system, which demonstrates pure double $P$–$E$ loops at 1.85 K [7]. These rare earth orthoferrites of RFeO$_3$ exhibit a combination of AFE and antiferromagnetism (AFM), but the AFE state appears only at very low temperature (1.85 K) with very low saturated polarization of 0.15 μC/cm$^2$ [7]. The discovery of a new type of multiferroic candidate combining both AFE and FM orders at room temperature (RT) would be scientifically significant, because it may not only be useful to build multiferroic memories, which could in principle enable data to be written electrically and read magnetically, but can also extend its application to the field of energy storage devices that could store both electric and magnetic energies.

Conventional AFE capacitors are used to store electric energy, they play a key role in mobile electronic devices, stationary power systems, and hybrid electric vehicles [8, 9]. These AFE materials include mainly non-magnetic perovskite compounds,
LaxSr$_{1-x}$Fe$_{12}$O$_{19}$ is gradually transformed from FEs to AFE with strong FM orders together. We will present how the state of increase the concentration of La ions replacing Sr$^2+$ ions in temperature with La concentration motivates us to further FE/AFE state [19]. The downward shift of FE/AFE switching in Fig. 1. The red lines show the standard diffraction spectrum of SrFe$_{12}$O$_{19}$ (PDF #33-1340). The diffraction peaks of La$_x$Sr$_{1-x}$Fe$_{12}$O$_{19}$ are in good agreement overall with those of the standard spectrum, suggesting that the replacement of 50% Sr with equal La in SrFe$_{12}$O$_{19}$ did not change its crystal structure, instead, a pure solid solution of La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ was successfully obtained.

Figure 2(a) displays XPS La 3d spectrum of La$_{0.3}$Sr$_{0.7}$Fe$_{12}$O$_{19}$, while that of LaFeO$_3$ is shown in Fig. 2(b) for comparison. The La 3d$_{3/2}$ and 3d$_{5/2}$ lines of La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ appear at 833.3 and 849.7 eV, whereas those of LaFeO$_3$ appear at 834.6 and 850.8 eV respectively. La 3d bands reportedly shifted to higher binding energy side when its valence charge gradually increased during exposing metallic La to air for longer time in XPS measurement [20, 21]. The longer is the exposure time of metallic La to air, the higher is the valence charge of La ions, leading to larger binding energy of La 3d lines [20]. The La 3d lines of La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ were chemically shifted to lower binding energy side by approximately 1.1–1.3 eV in comparison with those of LaFeO$_3$, indicating that the valence charge of La ions in La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ is lower than that in LaFeO$_3$ with 3 valence charge (La$^{3+}$). Therefore, the La ions in La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ are bivalent (La$^{2+}$), whereas those in LaFeO$_3$ are trivalent (La$^{3+}$).

It is worth to mention that when the La element is introduced into this compound, not only the peak position of the La 3d lines has shifted, but also the intensity has been lifted up quite a lot, as shown in Fig. 2(a). The larger intensity of La 3d spectrum in La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ (L5) results from the different chemical environment of La atoms in L5 unit cell over that in LaFeO$_3$. In L5 lattice, the substituting La atoms occupy Sr sites which locate in a big void space of its unit cell. These La atoms are loosely bound to four surrounding oxygen atoms which
are far away from the original Sr sites. This binding force is much weaker than that of La–O bonds in LaFeO₃. La atoms locate at B sites in the unit cell of ABO₃ perovskite structure in LaFeO₃, those B-positioned La atoms are tightly bound with six surrounding oxygen atoms. Therefore the electrons at La 3d levels in La₀.₅Sr₀.₅Fe₁₂O₁₉ are much easier to be excited by X-ray photons than that in LaFeO₃, thus the intensity of La 3d lines in La₀.₅Sr₀.₅Fe₁₂O₁₉ is raised a lot.

The Raman bands (Fig. S1 in the Supplementary Materials) of La₀.₅Sr₀.₅Fe₁₂O₁₉ are in good agreement with those of pure SrFe₁₂O₁₉ too, there appear no additional bands indexing to other oxide impurities. Both XPS and Raman spectra suggest that we have successfully replaced 50% Sr with equal La in SrFe₁₂O₁₉ and obtained a solid solution of La₀.₅Sr₀.₅Fe₁₂O₁₉. According to this formula, La ions would be bivalent (La²⁺) instead of trivalent, being in good agreement with the XPS valence spectrum (Fig. S2 in Supplementary Materials) and La 3d lines. Consequently, the valence charges of 0.5La + 0.5Sr would be + 2, whereas 12 Fe³⁺ ions provide + 36 positive charges; the total positive charges are then counted to be + 38, which may balance the total negative charges of − 38 from 19 O²⁻ ions in La₀.₅Sr₀.₅Fe₁₂O₁₉. The charge balance in this formula would leave no vacancies in the lattice.

The presence of oxygen vacancies was evaluated by electron spin resonance (ESR) spectroscopy. Figure 2(c) and (d) show the ESR spectra of La₀.₅Sr₀.₅Fe₁₂O₁₉ ceramics annealed in oxygen and annealed in vacuum, respectively. The ESR spectrum in Fig. 2(c) indicates that there are no oxygen vacancies in the La₀.₅Sr₀.₅Fe₁₂O₁₉ ceramic annealed in O₂, most of the oxygen vacancies were removed during O₂ annealing process. However, heat treatment of the ceramic in vacuum resulted in a high concentration of oxygen vacancies, as being indexed by a strong resonance peak at 3461 G in Fig. 2(d). This peak results from the oscillation of unpaired electrons at the energy level of oxygen vacancies. The spectrum of the same specimen annealed in O₂ atmosphere does not show this resonance peak, suggesting that the oxygen vacancies disappeared after the specimen was annealed in O₂. The XPS O 1s bands of the La₀.₅Sr₀.₅Fe₁₂O₁₉ specimen (Fig. S3, Supplementary Materials) also confirmed that there were no oxygen vacancies after annealing in O₂ atmosphere.

The chemical composition of the sintered La₀.₅Sr₀.₅Fe₁₂O₁₉ ceramic specimen has been checked by the energy-dispersive spectrum (EDS), which was detected in the Bruker scanning electron microscopy (SEM). The EDS spectrum is displayed in Fig. 3, it can be seen that all the elemental lines appear in the spectrum. Sr and La peaks have almost the same intensity, indicating that the atomic ratio of La over Sr approaches to the initial setting composition of 0.5:0.5. Obviously, Fe and O elemental peaks are much stronger than La and Sr elemental peaks in this EDS spectrum. Thus, the chemical composition detected by EDS is consistent with the designed molecular formula. The SEM image is displayed in Fig. S4 in Supplementary Materials.

**Figure 2:** (A) XPS La 3d lines of La₀.₅Sr₀.₅Fe₁₂O₁₉ (a) and LaFeO₃ (b) systems, and (B) electron spin resonance (ERS) spectrum of La₀.₅Sr₀.₅Fe₁₂O₁₉ ceramics, (c) being annealed in oxygen atmosphere and (d) annealed in vacuum.

Tuning La₁₋ₓSrₓFe₁₂O₁₉ from ferroelectricity to antiferroelectricity

SrFe₁₂O₁₉ (L₀ for x = 0) is FE [18], whereas La₀.₂₅Sr₀.₇₅Fe₁₂O₁₉ (L₂ for x = 0.25) exhibits a mixture state of FE and AFE [19]. By increasing the La concentration to x = 0.5, we obtained a pure AFE state in La₀.₅Sr₀.₅Fe₁₂O₁₉ (L₅ for x = 0.5). The transition from FE to AFE with changes in La concentration (x) in La₁₋ₓSrₓFe₁₂O₁₉ system is revealed by the evolution of the shape of P–E hysteresis loops, being illustrated in Fig. 4.

The pure FE state in L₀ phase (x = 0) is verified by a standard electric polarization (P–E) hysteresis loop with full saturation in Fig. 4(A) [18], whereas L₂ phase (x = 0.25) displays double P–E hysteresis loops mixing with a middle void loop in Fig. 4(B), indicating that La₀.₂₅Sr₀.₇₅Fe₁₂O₁₉ (L₂) presents in a hybrid FE/AFE state. Finally, the pure AFE state in L₅ phase (x = 0.5) is
Figure 3: The energy dispersive spectrum (EDS) of La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramic specimen.

Figure 4: (A) Standard FE $P$–$E$ hysteresis loops of SrFe$_{12}$O$_{19}$ ceramics (L0 phase) in full saturation, loops (1) and (2) were measured in the same specimen under different electric fields. (B) $P$–$E$ hysteresis loops of La$_{0.25}$Sr$_{0.75}$Fe$_{12}$O$_{19}$ ceramics, the combination of double $P$–$E$ loops with an intermediate void loop suggests a hybrid FE/AFE state in L2 phase. (C) Standard double $P$–$E$ hysteresis loops of La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramics separated by a linear AFE component with zero polarization. (D) Schematic diagram of double $P$–$E$ hysteresis loops of AFE. L0 (x = 0), L2 (x = 0.25) and L5 (x = 0.5) represent SrFe$_{12}$O$_{19}$, La$_{0.25}$Sr$_{0.75}$Fe$_{12}$O$_{19}$ and La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$, respectively. All the $P$–$E$ hysteresis loops were measured at RT.
verified by the standard double $P-E$ hysteresis loops in Fig. 4(C), where the two loops are fully separated by a linear AFE component with zero polarization. The mechanism of the transformation from FE status to the AFE status for $\text{La}_{0.5}\text{Sr}_{1-x}\text{Fe}_{12}\text{O}_{19}$ with varying $x$ ratio is proposed to be that the substituting La atoms at Sr sites break the displacement symmetry of the periodically aligned Sr atoms in the lattice, which is then divided into different pieces of periodic blocks. The more Sr atoms are replaced, the smaller will be the split blocks. These divided lattice parts would then become individual domains. The dipoles in adjacent domains align antiparallelly in opposite directions, thus triggering AFE status. If the initial complete lattice behaves in FE status, the broken lattice by the substituting La atoms would then evolve into AFE status. In case of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$, half of the Sr atoms are replaced by La atoms, the lattice is divided into small equal domains with antiparallelly ordered dipoles. Therefore, L5 ceramics demonstrate perfect AFE performance with fully separated double $P-E$ hysteresis loops.

A schematic diagram of the AFE polarization switching with reversal electric fields is displayed in Fig. 4(D). Two $P-E$ hysteresis loops represent FE polarization ($P$) component on opposite sides near the forward switching electric fields ($E_F$). The double loops are separated by a linear AFE component. In the AFE region ($-E_F < E < +E_F$), the initial positive dipoles ($P$) have the same magnitude as the adjacent negative ones but are aligned parallelly in opposite directions. These antiparallelly aligned dipoles thus counteract each other; the macroscopic $P$ vanishes to net zero and exhibits a linear relationship with $E$ [19]. Better linearity of the AFE component represents purer AFE state. Under weak electric fields, $E$ may not be able to switch the direction of those dipoles, they can still cancel each other. The cancellation of antiparallelly aligned dipoles in the AFE phase results in almost zero polarization in the macroscopic scale. Therefore, the net polarization approaches to zero within the AFE region, whereas its $P-E$ loop becomes a linear component. These initially antiparallel dipoles, however, can be forced to become parallel along the direction of a sufficiently strong external electric field to reach a FE state through an electric field-induced AFE–FE phase transition. This FE state behaves in one upward $P-E$ loop at positive electric field side of sufficient strength. Then, once the external electric field is removed, the induced FE phase can revert back to the initial AFE state. Upon switching the direction of electric field, there will appear a downward $P-E$ loop and a reversal AFE linear component at negative electric field side, thereby generating so-called double $P-E$ hysteresis loops.

The linear AFE component, which separates the double $P-E$ loops in Fig. 4(C), almost overlaps the $x$-axis. The net polarization of the AFE part approaches to zero through the cancellation of oppositely aligned polarization vectors in the full AFE phase of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$ system. The overall dipoles start to align along with the direction of the electric field ($E$) when $E$ exceeds the forward switching field ($+E_F$); where AFE transforms to FE and polarization increases sharply. On the reversal course of reducing electric field, the polarization decreases sharply when $E$ traverses over the backward switching field ($E_F$), where FE transitions back to AFE and the neighboring dipoles restore to align antiparallelly again. Therefore, the double $P-E$ hysteresis loops appears only within the range of $E_F - E_F$. The forward switching (AFE-to-FE) field $E_F$ is $\pm 145$ kV/cm, and the backward switching (FE-to-AFE) field $E_F$ is approximately $\pm 115$ kV/cm, the switching hysteresis $\Delta E$ is approximately $\pm 30$ kV/cm. The steep lines in the double $P-E$ loops are almost perpendicular to the $x$ axis, implying that the reversely aligned dipoles switch their directions instantly at $\pm E_F$ or $\pm E_F$. The maximum polarization in this double $P-E$ loops is approximately 24.7 µC/cm$^2$ at $E = 159$ kV/cm, and the net remnant polarization is almost zero, as shown in Fig. 4(C). Within the AFE linear component, the polarization decreases only from 0.5 to $-0.6$ µC/cm$^2$ when the electric field changes from 50 to $-66$ kV/cm. The AFE polarizations are ignorable in comparison with the FE ones. The two switching fields ($E_F$ and $E_F$) of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$ ceramics are comparable to those of classical AFE perovskites, such as Pb(Zr,Ti)$\text{O}_4$ [4, 15, 22] and AgNbO$_3$ [23], whose $E_F$ values range from 40 to 170 kV/cm and $E_F$ values cover from 100 to 230 kV/cm. Therefore, by changing the substitution concentration of La ions ($x$) from 0.0 to 0.5 in $\text{La}_{x}\text{Sr}_{1-x}\text{Fe}_{12}\text{O}_{19}$ system, we are able to tune its state from FE to AFE while maintaining the middle composition as a hybrid FE/AFE phase.

**Dielectric relaxation in $\text{La}_{x}\text{Sr}_{1-x}\text{Fe}_{12}\text{O}_{19}$ ceramics**

The tuning state of the $\text{La}_{0.5}\text{Sr}_{1-x}\text{Fe}_{12}\text{O}_{19}$ system at RT can be testified by changes in the phase configuration with the composition on the temperature-dependent dielectric diffusion spectrum. The real and imaginary parts of the dielectric constant usually exhibit abnormal change at the vicinity of phase transition temperature, across which the state switches from FE to AFE or to paraelectrics (PE). Figure 5 presents the temperature-dependent dielectric loss spectrum of $\text{La}_{0.5}\text{Sr}_{1-x}\text{Fe}_{12}\text{O}_{19}$ ceramics, which reveals the variation of phase configuration with $x$. The FE state switches to AFE state near RT as the phase transition peaks shift to lower temperature with $x$. At vicinity of RT, the L0 ($x = 0$) ceramic is FE [Fig. 5(A)], whereas the L5 ceramic ($x = 0.5$) is AFE [Fig. 5(C)]. The middle L2 ceramic ($x = 0.25$) is in a hybrid FE/AFE state [Fig. 5(B)].

The FE-to-AFE phase transition peak ($T_{F-A}$) appears at 235 °C (200 kHz) for L0 ceramic, this $T_{F-A}$ peak downward shifts to 18 °C when $x$ changes from 0 to 0.25 (L2). It further moves down to $-163$ °C as $x$ changes from 0.25 to 0.5 (L5). The FE-to-AFE transition in L5 occurs at $-163$ °C ($T_{F-A}$), below which it is FE while above this point it becomes AFE. In case of L2, the
FE-to-AFE phase transition happens at 18 °C (T_{F-A}), which is close to RT [Fig. 5(B)]. Therefore, it’s not surprising that the L2 ceramic takes a hybrid FE/AFE state at RT. The critical temperature (T_{A-P}) for the second phase transition from AFE to PE appears at 441 °C (200 kHz) for L0, 306 °C for L2 and 233 °C for L5. The variation in T_{F-A} and T_{A-P} with x is shown in Fig. 5(A)–(C).

Below 233 °C (T_{A-P}), L5 is AFE; while above 233 °C, L5 switches to PE [Fig. 5(A)]. Within the temperature range of −163 to +233 °C (T_{F-A} to T_{A-P}), La_{0.25}Sr_{0.75}Fe_{12}O_{19} ceramic (L5) takes an AFE state as a thermodynamically stable phase, as shown in Fig. 5(A) (see also Table S3 in the Supplementary Materials). RT falls just in the middle of this temperature scope (T_{F-A} to T_{A-P}), therefore L5 behaves in pure AFE state at RT. The clear region below the critical temperature of 235 °C (T_{F-A}) in L0 [Fig. 5(C)] suggests that SrFe_{12}O_{19} ceramic is FEs at RT, which is consistent with the experimental evidence in Fig. 4(A) and that in the literature [18].

It may be noted that the T_{F-A} peak in SrFe_{12}O_{19} [Fig. 5(C)] is impacted more apparently by frequency as compared to that of La_{0.5}Sr_{0.5}Fe_{12}O_{19} [Fig. 5(A)]. The reason is that the second one (L5) is AFE, while the first one (L0) is relaxor FE. Relaxors usually show broad and rounded peaks at the transition temperature (T_c), while FE or AFE have sharp transition peaks. In the normal FE, the real part of dielectric constants obeys the Curie–Weiss law at T_c. The relaxors, however, show divergence and strong dependence on frequencies at peak positions.

The temperature-dependent phase configuration of the La_{1-x}Sr_xFe_{12}O_{19} system is then deduced from the dielectric loss datasets at 200 kHz in Fig. 5. The configuration is shown in Fig. 6. The space for hosting FE or AFE phase down shifts to lower temperature region as the La concentration x increases. The phase transformation temperatures of T_{F-A} and T_{A-P} also move downwards to lower temperature side with increasing x value. The temperature space for hosting the AFE phase becomes wider when L0 changes to L5. The RT state changes from FE for L0 to hybrid FE/AFE for L2, and finally transforms to pure AFE for L5. The highest temperature for remaining hybrid FE/AFE state shifts from 235 °C for L0 down to 18 °C for L2 and then further down shifts to −163 °C for L5. Above this temperature will appear AFE status. Therefore, the RT state of La_{1-x}Sr_xFe_{12}O_{19} system can be tuned from FE to AFE by changing x from 0 to 0.5, as shown in Fig. 6.

The spectrum of the real part of the dielectric constant reveals similar changes in phase configuration varying with the La content in La_{1-x}Sr_xFe_{12}O_{19} system. The temperature-dependent dielectric (ɛ_r') spectrum is displayed in Fig. 7. The transition peak of T_{A-P} for L0 locates at 411 °C (200 kHz), this peak down shifts to 308 °C for L2 and decreases further to 232 °C for L5. On the other hand, T_{F-A} shifts from 211 °C for L0 down to 36 °C for L2 and then reduce to −145 °C for L5. The critical temperature of T_{F-A} in La_{1-x}Sr_xFe_{12}O_{19} system can be easily shifted by changing the value of x. This peak moves to a very low temperature far below RT when x is varied from 0 to 0.5, leaving a wide window of −145 to 232 °C to host the AFE state for L5. Consequently, the
RT state was tuned from the FE phase to the full AFE phase as x changes from 0 to 0.5. The temperature-dependent spectrum of dielectric constants reveals similar results to the dielectric loss spectrum. However, there is a little retardation between the two types of spectra, the real part lags the imaginary one for about 18 °C due to the phase difference. Accordingly, the transition temperatures \( T_{F-A} \) and \( T_{A-P} \) in spectrum of the real part \( \varepsilon' \) are lower than those in the dielectric loss spectrum. The transition temperatures of \( T_{F-A} \) and \( T_{A-P} \) in La\(_{0.5}\)Sr\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) system are summarized in Table S2, and the temperature ranges in which the FE, AFE and PE states can stably exist are listed in Table S3 in the Supplementary Materials.

In both dielectric spectra of real part \( \varepsilon' \) and imaginary part \( \tan\delta \), the phase transition peaks exhibit strong dispersion feature. \( T_{F-A} \) and \( T_{A-P} \) peaks are highly sensitive to the temperatures. In the dielectric loss spectrum of the La\(_{0.3}\)Sr\(_{0.7}\)Fe\(_{12}\)O\(_{19}\) ceramics [Fig. 5(A)], the critical temperature of \( T_{F-A} \) diffuses from −141 to −163 °C as the frequency changes from 50 kHz to 200 kHz, while \( T_{A-P} \) decreases from 250 to 233 °C. Similar variation of \( T_{F-A} \) and \( T_{A-P} \) with frequencies is also observed in the dielectric loss spectrum of the La\(_{0.25}\)Sr\(_{0.75}\)Fe\(_{12}\)O\(_{19}\) and SrFe\(_{12}\)O\(_{19}\) ceramics, as being shown in Fig. 5(B) and (C). The dispersion of the phase transition temperature upon frequencies suggests that these La\(_{0.5}\)Sr\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) ceramics undergoes diffuse transformation process. Note that the diffusion performance in the dielectric loss spectrum in Fig. 5 resembles Debye relaxation rather than Maxwell–Wagner (MW) relaxation. These dielectric loss peaks are very sharp and show a much narrower relaxation temperature range than that of MW relaxation. The later one origins from the charging at the heterogeneous interfaces between two types of materials with different dielectric constants, therefore it shows broad shoulder-like peaks which can span to a much wider range larger than 450 °C [24]. In addition, the FE related phase transition usually accompanies abrupt change in dielectric constants at the critical temperatures, MW relaxation, however, demonstrates gradual increment in \( \varepsilon' \) or \( \tan\delta \). Therefore, MW presents a wide smooth round-shaped peak, which differs greatly from phase transition peaks.

### Magnetic semiconducting performance of La\(_{0.5}\)Sr\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) compound

By definition, FM must present with AFE or FE order in multiferroic materials of single phase. SrFe\(_{12}\)O\(_{19}\) is a conventional magnetic compound, its magnetism should not change much when 50% Sr\(^{2+}\) ions were replaced with 0.5 La\(^{3+}\) ones because the content of Fe\(^{3+}\) ions, which provide unpaired electron spins for magnetism, was unchanged. The M–H hysteresis loops in Fig. 8(A) reveal the magnetic performance of the La\(_{0.5}\)Sr\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) ceramics. A lower annealing temperature results in stronger magnetism with higher remnant magnetization because the grains are smaller. The specimen being heat treated at 1350 °C holds a remnant moment of 20.3 emu/g and coercive force of 4195 Oe. These values change to 29.5 emu/g and 3995 Oe, respectively, when the annealing temperature is reduced to 1000 °C. These magnetic parameters are comparable to those of pure SrFe\(_{12}\)O\(_{19}\). The replacement of 50% Sr with equivalent La in SrFe\(_{12}\)O\(_{19}\) didn’t change the magnetism significantly, but it produces a novel type of multiferroic candidate that combines strong FM and full AFE in one single phase at RT.

The coexistence of AFE and FM in the La\(_{0.5}\)Sr\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) system is further evidenced by the well-separated double \( P-E \) hysteresis loops with a linear component in Fig. 8(C), which gives a recoverable energy density of approximately 12 J/cm\(^3\). Higher recoverable energy density in the La\(_{0.5}\)Sr\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) ceramics is evaluated to be around 14.3 J/cm\(^3\) at 320 kV/cm from the hysteresis \( P-E \) loop in the inset of Fig. 8(D). These AFE double \( P-E \) loops were measured from different La\(_{0.5}\)Sr\(_{0.5}\)Fe\(_{12}\)O\(_{19}\) ceramic specimens, indicating the reliability and repeatability of the experimental results. The energy density of 14.3 J/cm\(^3\) is twice that of lead lanthanum zircon titanate (PLZT) perovskite ceramics (6.7 J/cm\(^3\)) and is the largest value among those of the bulk AFE ceramics [25]. Similar energy densities have been obtained only in a 700 nm La-doped PbZrO\(_3\) thin film system under a high field of 600 kV/cm [26] and in a 500-nm Sr-doped PbZrO\(_3\) thin film under an even higher field of 900 kV/cm [14]. Further increase in energy density of buffered thin film
systems would require a much larger actuation electric field (> 1500 kV/cm) [25, 27]. The field dependent energy density of the \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19} \) ceramics is displayed in Fig. 8(D), where the energy density shows a nonlinear increase with increasing electric field. The advantage of the AFE state appearing in multiferroic materials is that it may provide one more degree of freedom to store magnetic energy through ME coupling, which could superimpose additional ME energy into the conventional electrically charged energy. This additional magnetically induced energy would then improve the energy storage density of multiferroic capacitors as in comparison with that of nonmagnetic perovskite ones, which may store electric energy only.

The double \( P–E \) hysteresis loops in Fig. 8(C) look more reasonable for AFE order than that in Fig. 4(C). The linear AFE part in Fig. 8(C) almost overlaps with \( X \) axis and extends to a wider range with net zero polarization. The two double-loops were measured from different ceramic specimens. The later one, which produced double \( P–E \) loops in Fig. 8(C), may be well annealed by \( \text{O}_2 \). It contains less oxygen vacancies than the first specimen. Lower concentration of oxygen vacancies may induce much less current leakage upon FE measurement. Thus, we may applied larger electric field on the second specimen to achieve well-separated double \( P–E \) loops in better shape than the first one. The difference of the shape comes from some minor change in preparation process, such as variation of oxygen pressure and concentration of organic solvents, etc. But the overall shape is similar, both specimens all present standard double \( P–E \) hysteresis loops which reflect AFE features. These similar results demonstrate the repeatability and reliability of this work.

In addition to the multiferroic functionality, \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19} \) is also a magnetic semiconductor. The semiconducting performance is revealed by the UV–Vis–near infrared optical spectrum in Fig. 8(B), which was measured using an HP Lambda 750 UV–Vis–near infrared spectrophotometer with an integrating sphere attachment. This spectrum displays a typical feature of direct-bandgap semiconductors, a cutoff edge appears within the wavelength range of 660–760 nm, where the absorption coefficient increases abruptly due to the interband transition of photon-excited valence electrons across the band gap. An Urbach tail at 760–960 nm is attributed to absorption by defects in the crystal. The inset of Fig. 8(B) shows the Tauc plot of \( \alpha^2E^2 \) as a function of photon energy \( E \). The direct band gap energy was determined to be 1.74 eV by a linear fit in the region of 660–760 nm to a plot of \( \alpha^2E^2 \) using a direct gap model, where \( \alpha \)
is the absorption coefficient in cm$^{-1}$ and $E$ is energy in eV. This band gap energy is comparable in magnitude to that of silicon but is slightly smaller than that of BiFeO$_3$.

**Magnetoelectric coupling and GMR effect in La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramics**

ME coupling is necessary for multiferroics to realize the magnetically read-out and electrically write-in operation in multiple state memories. For this purpose, we setup a ME device system to measure the variation in spin current and dielectric constants under different magnetic fields. The surfaces of the ceramic specimens were coated with silver electrodes. The specimen was clamped between two copper plates, which were fixed in a plastic box. The box was then placed in a space between two electric magnets, and the electrodes were wired to a Keithley 2450 Sourcemeter or a LCR meter for ME measurement. We switched on the electric magnets and increased the magnetic field $B$ continuously from 8 mT to 1.2 T, maintained the $B$ field at 1.2 T for 20–50 s, and then decreased the $B$ field from 1.2 T back to 8 mT. This operation was repeated several times. The changes in physical parameters (current and resistance) with magnetic field were continuously from 8 mT to 1.2 T, maintained the $B$ field at 1.2 T for 20–50 s, and then decreased the $B$ field from 1.2 T back to 8 mT. This operation was repeated several times. The changes in physical parameters (current and resistance) with magnetic field were continuously from 8 mT to 1.2 T, maintained the $B$ field at 1.2 T for 20–50 s, and then decreased the $B$ field from 1.2 T back to 8 mT. This operation was repeated several times. The changes in physical parameters (current and resistance) with magnetic field were continuously from 8 mT to 1.2 T, maintained the $B$ field at 1.2 T for 20–50 s, and then decreased the $B$ field from 1.2 T back to 8 mT. This operation was repeated several times.

The magnetically induced electric polarization $[P(H)]$ was calculated by integrating the spin current $(I)$ over time $(t)$. Figure S5 in the Supplementary Materials shows plots of the ME spin current versus time for different $B$ values. Figure 9(B) exhibits the polarization $[P(H)]$ varying with $B$. The magnetic field induced electric polarization $[P(H)]$ decreases with $B$ for $B < 200$ mT, above which $P(H)$ starts to increase with increasing $B$. The maximum $P(H)$ value of 0.95 μC/cm$^2$ was achieved at $B = 1.1$ T. The magnetic-field-induced electric polarization is reported to be around 0.4 × 10$^{-4}$ μC/cm$^2$ at 1 T and 2 K in the Ni$_2$V$_2$O$_7$ system [28] as well as 0.08 μC/cm$^2$ at 6.3 T and 15 K in the Eu$_{0.75}$Y$_{0.25}$MnO$_3$ system [29]. Therefore, the $P(H)$ value of the La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramics has a much higher magnitude (more than 1 order higher) than those of other multiferroic systems and is comparable to the electric-field-induced electric polarization $[P(E)]$ in PbTiO$_3$ ceramics.

The magnetically induced electric polarization $[P(H)]$ was generated through the interaction of two neighboring cycloid conic spins [30], $P(H) = A \sum_{ij} c_{ij} \times (S_i \times S_j)$ in the La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramics, where $c_{ij}$ denotes the unit vector connecting the spins $S_i$ and $S_j$. $A$ is a constant which depends mainly on the exchange interaction and the spin–orbit interaction. The interaction of two neighboring conic spins gives rise to electric polarization $P(H)$ through ME coupling effect, while $P(H)$ generates spin current as $i = dP/dt$. At low $B$ field, the directions of the conical axes in the cycloid spins within different grains are randomly distributed, some of the magnetically induced spin currents cancel each other because of the random orientations. As the strength of $B$ field increases, an increasing number of conical spin axes are aligned along with the same direction of the magnetic field, producing a larger parallel spin current or electric polarization $[P(H)]$. Therefore a stronger magnetic field induces a larger $P(H)$.

Figure 9(C) shows the $B$-dependent complex impedance as a function of frequency, which was measured using a Microtest 6630 LCR meter. The impedance ($Z$) spectrum shows a large decrease in magnitude with increasing $B$ field at low frequencies ($f < 1$ kHz). The module of the impedance ($|Z|$ or $R$) is 6.3 kΩ at 10 Hz when $B = 0$ mT, this value decreases gradually to 2.9 kΩ as $B$ is increased to 1.1 T. The maximum change ratio in
$Z$ with $B$ ($\Delta Z = \left[ Z(B) - Z(0) \right]/Z(0)$) is $-117.2\%$, which is comparable to the magnitude of the GMR of a Fe/Cr/Fe trilayers film system [31, 32] and of Cu/Co multilayers [33]. At high frequencies, however, this change ratio becomes much smaller. The real part ($Z'$) and imaginary part ($Z''$) of the complex impedance decreases simultaneously with increasing $B$, causing the radius of the Core–Core circle to decrease with increasing $B$, as shown in Fig. 9(D). The real part decreases from 6.2 kΩ down to 3 kΩ and the imaginary part decreases from 3.2 to 1.6 kΩ as the applied magnetic field $B$ increases from 0 to 1.1 T. The real and imaginary parts change by approximately $-100\%$ upon a $B$ field of 1.1 T. This change ratio of magnetoresistance is also comparable to the size of the GMR in magnetic/non magnetic metal film systems [31, 32].

The performance of the magnetoresistance effect of other material candidates from existing peer-review papers has been

Figure 9: Magnetoelectric (ME) coupling of the La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramics under various magnetic $B$ fields. (A) Variation in spin current ($I$) and resistance ($R$) with magnetic field (GMR). (B) Magnetic field induced electric polarization ($P(H)$) under different magnetic fields. (C) Change in impedance (or resistance) as a function of frequency under different $B$ fields. (D) Change in real and imaginary parts of impedance as a function of frequency upon varying $B$ field. (E) Change ratio in real part of dielectric constant ($\varepsilon'$) with $B$ field as a function of frequency. (F) Variation of dielectric loss ($\tan\delta$) with $B$ field as a function of frequency. The inset shows a magnified view of the maximum dielectric loss peak ($\tan\delta$) upon $B$ field diffusing with frequencies.
listed in Table 1. Note that high GMR ratio typically appears in multiple layers film system [34, 37, 41]. It can be seen from Table 1 that bulk ceramic systems usually have relative low MR ratio [31, 32]. The uniform orientation of spins in different grains in the ceramics may be described as follows. The spins in different grains in the ceramics are randomly aligned, and these randomly oriented spins decrease the mobility of the charge carriers (electrons and holes) through electron scattering, as they do in the Fe/Cr/Fe trilayers [32, 41], the spin-up and spin-down currents cancel each other somehow, thus the resistance remains high when $B = 0$. When a magnetic field was applied, these spins start to align themselves parallel to the same direction of the $B$ field. As the magnetic field becomes stronger, more spins are aligned parallel to the direction of $B$ field. In the parallel magnetic configuration, the electrons with the same spin direction can easily pass through all the magnetic grains, and the short circuit through this channel decreases the resistance. When the spins are randomly oriented, the electrons in each channel are slowed down in every other magnetic grains, and the resistance is high [31, 32]. The uniform orientation of spins in different grains would then increase the mobility of electrons and thus reduce the resistance with increasing $B$.

The dielectric response to a magnetic field is highly consistent with the observed change in $P(H)$ values [Fig. 9(B)], the $B$-dependent dielectric constants as a function of frequency are shown in Fig. 9(E). The higher $B$ field induces larger increment of real part of dielectric constant ($\varepsilon'_r$) while right shifts the phase or the whole spectrum of imaginary part ($\tan \delta$) to higher frequencies. The change in $\varepsilon'_r$ with $B$ is much larger at low frequencies than that at high frequencies. The maximum change ratio in $\varepsilon'_r$ upon $B$ [$\Delta \varepsilon'_r(B) = ([\varepsilon'_r(B) - \varepsilon'_r(0)]/\varepsilon'_r(0)) \times 100\%$] is approximately 540% at $B = 1.1$ T in a frequency range of 10–100 Hz. The change in $\varepsilon'_r$ increases with increasing $B$, $\Delta \varepsilon'_r(B)$ decreases rapidly at frequencies above 1 kHz, at higher frequencies, the change decreases to less than 100%. The dielectric loss spectrum in Fig. 9(F) shows the decrease in $\tan \delta$ with frequency, where $\tan \delta$ is maximum at 97 kHz for $B = 0$ mT. Both the real and imaginary parts of the dielectric constants decrease exponentially with frequency within the range from 500 Hz to 5 kHz, this behavior is consistent the Debye relaxation model, where $\varepsilon'$ and $\varepsilon'' \sim 1/(1 + \omega^2 \tau^2)$. The entire spectrum of real part was lift up, and the maximum loss peak right shifts from 97 to 305 kHz as the magnetic field was increased from 0 to 1.1 T. The strong magnetodielectric (MD) response is similar to that of BaFe$_{12}$Sc$_{18}$O$_{39}$ system [42]. The increase in $\varepsilon'_r$ with $B$ originates from ME coupling, which induces a spin current and generates magnetic-field-induced electric polarization $P(H)$. The total macroscopic polarization $P(E, H)$ would be enhanced by this additional $P(H)$ upon the electric field induced polarization $P(E)$, as such the capacitance or dielectric constant would be improved following the formula[43]:

$$
\varepsilon_r(E, H) = \frac{0.036\pi t \times P(E, H)}{U} \cdot \frac{1}{1 + \omega^2 \tau^2}
= \frac{0.036\pi t \times [P(E) + P(H)]}{U} \cdot \frac{1}{1 + \omega^2 \tau^2}
= \varepsilon_r(E) + \varepsilon_r(H),
$$

(1)

where $t$ is the thickness, $\omega$ is the frequency, $\tau$ is relaxation time, $U$ is the voltage, $P(E)$ is the polarization induced by the electric field, and $P(H)$ is the polarization driven by the magnetic field. For $B = 0 \Rightarrow \varepsilon_r(E, H) = \varepsilon_r(E)$. The spin current increases with increasing $B$, so does $P(H)$, since $P(H) = \int_{-\infty}^{\infty} dt$. Stronger $B$ field generates larger $P(H)$, which would induce higher dielectric constant ($\varepsilon'_r$) according to Eq. 1. Under a magnetic field, an additional term in the expression of $\varepsilon'_r(H)$ as a function of $P(H)$ originating from ME coupling is added to the $\varepsilon'_r(E)$ or $P(E)$ term, increasing the total dielectric constant to $\varepsilon'_r(E, H) = \varepsilon'_r(E) + \varepsilon'_r(H)$, as shown in Eq. 1. Higher $B$ induces larger $P(H)$ (Fig. 9(B)), which produces higher $\varepsilon'_r(E, H)$. Therefore $\Delta \varepsilon'_r(B)$ increases with increasing $B$. Because of the Debye relaxation term of $1/(1 + \omega^2 \tau^2)$ in Eq. 1, the increase in $\varepsilon'_r(E, H)$

| Materials candidate | Type       | GMR ratio (%) | Temperature (°C) | References |
|---------------------|------------|---------------|------------------|------------|
| La$_{0.5}$Dy$_{0.1}$Sr$_{0.3}$MnO$_3$ | Ceramics   | 2.2           | 21               | [34]       |
| La$_{0.5}$Dy$_{0.1}$Sr$_{0.3}$MnO$_3$/Ag$_{0.3}$ | Ceramics   | 16.3          | 21               | [34]       |
| BiFeO$_3$/Si        | Thin film  | −1.19         | 25               | [35]       |
| BiFeO$_3$           | Thin film  | 1.0           | 27               | [36]       |
| La$_3$CoMnO$_6$     | Ceramics   | −19           | 27               | [37]       |
| Pr$_{0.775}$Sr$_{0.225}$MnO$_3$ | Ceramics   | −50           | −73              | [38]       |
| La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ | Ceramics  | −117.2        | 25               | This work |

Note that high GMR ratio typically appears in multiple layers film system [34, 37, 41]. It can be seen from Table 1 that bulk ceramic systems usually have relative low MR ratio at RT [34, 37]. The merit of the La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ compound is that its GMR ratio is the highest among those reported ceramic materials, and is even higher than most of the superlattice structures and heterogeneous metallic thin films, as being shown in Table 1.

The performance of the magnetoresistance effect of reported material candidates at the vicinity of RT.
is much larger at low frequencies than at high frequencies. Consequently, the frequency for the maximum loss peak $\omega_m(H)$, which could be expressed as $\omega_m(H) = \sqrt{\varepsilon_\infty(H)/\varepsilon_\infty(H)}$, right shifts to higher frequency side because the magnitude of the increase in $\varepsilon_\infty(H)$ ($\omega \to 0$) is much larger than that of the increase in $\varepsilon_\infty(H)$ ($\omega \to \infty$).

**Conclusion**

By replacing $(1 - x)$ Sr$^{2+}$ ions in SrFe$_2$O$_3$ with $x$ La$^{3+}$ ions La$_{0.5}$Sr$_{1.5}$Fe$_2$O$_3$, we changed the FE state ($x = 0$) to AFE state ($x = 0.5$). The FE-to-AFE transition temperature decreased from 235 °C for SrFe$_2$O$_3$ to 163 °C for La$_{0.5}$Sr$_{1.5}$Fe$_2$O$_3$, while AFE-to-FE transition temperature moved from 441 °C down to 233 °C accordingly. Consequently, there appears a wide window of –163 °C to +233 °C to host AFE state of La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ as a thermodynamically stable phase, whereas RT falls in middle of this scope. Thus La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ system exhibits pure AFE nature at RT, while La$_{0.2}$Sr$_{0.7}$Fe$_{12}$O$_{19}$ takes a hybrid FE + P → E hysteresis loops. The linear AFE component separating the double P-E loops demonstrates zero net polarization, indicating that the polarization vectors ($P_{\uparrow} + P_{\downarrow}$) in the AFE region are antiparallelly aligned and thus cancel each other. The recoverable storage energy density of the La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ system was found to be 14.3 J/cm$^3$, which exceeds that of conventional perovskite ceramics. Meanwhile, La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ compound also exhibits magnetic semiconducting behavior; the measured direct band gap energy is 1.74 eV; the remnant moment and magnetic coercive force were estimated to be 29.5 emu/g and 3995 Oe, respectively. In addition, this compound exhibited strong ME coupling and GMR effects. A magnetic field of 1.1 T induced an electric polarization of 0.95 μC/cm$^2$. The change in complex impedance ($R$) at $B = 1.1$ T field was as high as ~117.2%, which is comparable to the magnitude of the GMR in an Fe/Cr/Fe trilayers film system. This magnetic field lifts up the entire dielectric constant spectrum by 540% and right shifts the maximum dielectric loss peak to higher frequency by 208 kHz. In summary, the La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ system is a novel multiferroic ceramic that combines FM and pure AFE orders, with magnetic semiconducting performance, strong ME coupling and high GMR effects.

**Methods**

Upon the idea of moving the FE-AFE switching temperature down to low temperature region and tuning rare earth doped M-type strontium hexaferrite (La$_{0.5}$Sr$_{1.5}$Fe$_2$O$_3$) from FEs to full AFE, we changed the percent $x$ of La$^{3+}$ ions in SrFe$_2$O$_3$ from 0 to 0.5. The synthesis method is similar to that of SrFe$_2$O$_3$ multiferroic ceramics [18]. Here, we describe the fabrication procedure of La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ ceramics. First, lanthanum acetate [La(CH$_3$COO)$_2$·3H$_2$O, 99.9%, Aladdin], strontium acetate [Sr(CH$_3$COO)$_2$·3H$_2$O, 99.9%, Aladdin], and ferric acetylacetonate (C$_{15}$H$_{21}$FeO$_6$, 99.9%, Alfa Aesar) were used as lanthanum, strontium, and iron sources. First of all, 6.0325 g of iron acetylacetone was dissolved in a mixture solvent of 50 mL ethanol with 70 mL acetone in a 250 mL three-flask inside a glove box. The mixture solution was heated and stirred on a mantle at 70 °C for 6 h. On the other hand, lanthanum acetate and strontium acetate were dissolved in 20 mL glycerin in a 50 mL flask outside the glove box. The molar ratio of (La + Sr) ions over Fe ones was set to be 1:10, whereas the Sr/La atomic ratio was fixed to be 0.5:0.5. The dispersion solution in the flask was distilled at 120 °C for 2 h in a rotary evaporator until the lanthanum and strontium acetates were fully dissolved. The lanthanum and strontium precursors were then transferred into the glove box, where the iron precursor and La + Sr precursor were mixed together and maintained on the mantle at 70 °C for another 8 h. Next, 60 mL of an ammonia solution was added into the mixture solution, which was further heated on the mantle at 70 °C for more than 48 h to precipitate the La + Sr and Fe ions completely. Finally, the particles suspended in the solution were separated from the solvent by centrifugation and then calcined into powders at 450 °C for 1 h. After grinding for 30 min, the powders were calcined a second time at 800 °C for 1 h to remove organic impurities. Pure La$_{0.5}$Sr$_{0.5}$Fe$_{12}$O$_{19}$ nanopowders were thus obtained. 0.06 g powders were poured into a cylinder mold and pressed into a pellet with a diameter of 6.2 mm and a thickness of ~0.55 mm. The pellet was sintered into ceramic at 1350 °C for 2 h. The ceramic specimen was subsequently annealed in a tube furnace with oxygen atmosphere at 800 °C for three times. Each O$_2$ annealing process lasted for 3 h with the upper surface being oriented upward and then downward alternatively. Afterwards, both surfaces of the ceramic specimen were coated with silver paste electrodes, which were solidified at 820 °C for 15 min. The structure of the specimens was determined by X-ray diffraction (XRD) measurement using Cu Ka radiation, and the magnetic properties were measured by a Quantum Device physical property measurement system (PPMS). The electric polarization hysteresis ($P-E$) loops were measured using a FE measurement system based on a Sawyer–Tower circuit. The temperature-dependent dielectric spectrum and impedance spectrum were measured using a Hioki IM 3533-01 LCR meter. The ME polarization performance and MD response were recorded using a Keithley 2450 source meter as well as a Microtest Precision 6630 LCR meter in a frequency range of 10 Hz to 10 MHz by applying a variable DC magnetic field.
Author contributions

DC did the experiments and made the measurements; TG conceives the concepts, analyzed the datasets and wrote the manuscript.

Funding

The authors acknowledge the financial support from the National Natural Science Foundation of China under Grant No. 11774276.

Data availability

Research data or code will be available to readers upon requested and will be deposited in the Springer Nature’s repositories.

Declarations

Conflict of interest There is no conflict of interests.

Supplementary Information

There is no conflict of interests.

The online version contains supplementary material available at https://doi.org/10.1557/s43578-022-00568-4.

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