Emergent ferroelectricity in disordered tri-color multilayer structure comprised of ferromagnetic manganites*

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Multiferroic materials, showing the coexistence and coupling of ferroelectric and magnetic orders, are of great technological and fundamental importance. However, the limitation of single phase multiferroics with robust magnetization and polarization hinders the magnetoelectric effect from being applied practically. Magnetic frustration, which can induce ferroelectricity, gives rise to multiferroic behavior. In this paper, we attempt to construct an artificial magnetically frustrated structure comprised of manganites to induce ferroelectricity. A disordered stacking of manganites is expected to result in frustration at interfaces. We report here that a tri-color multilayer structure comprised of non-ferroelectric $La_{0.9}Ca_{0.1}MnO_3$(A)/$Pr_{0.85}Ca_{0.15}MnO_3$(B)/$Pr_{0.85}Sr_{0.15}MnO_3$(C) layers with the disordered arrangement of ABC–ACB–CAB–CBA–BAC–BCA is prepared to form magnetoelectric multiferroics. The multilayer film exhibits evidence of ferroelectricity at room temperature, thus presenting a candidate for multiferroics.

Keywords: multiferroic materials, disordered stacking, ferroelectricity

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1. Introduction

The conventional mechanism for multiferroics is that the ferromagnetism requires transition metal ions with partially filled d shells; while in ferroelectric, empty d shells are essentially required.[1–3] The mutual exclusion of the two mechanisms is considered to be the top difficulty in finding and preparing single phase multiferroic materials.[4–8] Otherwise, as the ferroelectric and magnetic orders in these materials are associated with different ions, the coupling between them is weak.[4–8] A number of routes to new multiferroics have been pursued,[9–11] such as atomic-level layering to design specific magnetic ordering through super-exchange interactions, and the use of compositional ordering that breaks space inversion symmetry to enhance polarization.[2,3] Symmetry broken theory in understanding the coexistence of magnetic and electrical ordering has generated a flurry of research activities on magnetoelectric multiferroics.[2] Artificially layered structure with the novel magnetic frustration mechanism could give rise to simultaneous ferromagnetism and ferroelectricity.[3] This type of magnetic frustration mechanism is expected to produce remarkably large magnetoelectric coupling, owing to the fact that ferromagnetism and ferroelectricity originate from an identical source in artificial-stacking nano-multilayer films. This overcomes the typical drawback of ordinary composite materials. Moreover, epitaxial strain and interface effects in artificial stacking structure are favorable for ferroelectricity and magnetoelectric coupling.[3,12,13] On the basis of the above theory, tri-color superlattice with an A–B–C–A–B–C$\cdots$ arrangement,[14] breaking the space inversion symmetry, was proposed which exhibits enhanced polarization[15] and large non-linear optical response.[16] However, ferroelectricity constituents are essential for so-called tri-color superlattice studied so far.[16,17] Recently, Rogdakis *et al.* reported the discovery of ferroelectricity in artificial tri-color superlattices consisting of non-ferroelectricity antiferromagnets manganite. However, the ferroelectricity was observed below 40 K, making its technological applications difficult.[18]

In the present paper, we select three perovskites: $La_{0.9}Ca_{0.1}MnO_3$ (LCMO), $Pr_{0.85}Ca_{0.15}MnO_3$ (PCMO), and $Pr_{0.85}Sr_{0.15}MnO_3$ (PSMO) as parent compounds of the tri-color multilayer structure. Our choice is based on the following ideas. First, all of them are ferromagnetic, essential for multiferroics, and insulators, necessary for ferroelectricity.[16,17] Second, none of the parent compounds are ferroelectric, providing a way to check the influence of asymmetrical artificial stacking as a cause for ferroelectricity. An ABC–ACB–CAB–CBA–BAC–BCA arrangement with enhanced broken space inversion symmetry is employed to constitute disordered multilayer structure here. We demonstrate that the disordered stacking structure composed of non-ferroelectric ferromagnetic manganite generates emergent room temperature ferroelectricity and magnetoelectric coupling.

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2. Preparation and construction

$La_{0.9}Ca_{0.1}MnO_3$, $Pr_{0.85}Ca_{0.15}MnO_3$, $Pr_{0.85}Sr_{0.15}MnO_3$, and $La_{0.33}Sr_{0.67}MnO_3$ (LSMO) targets were prepared by the standard solid-state reaction technique through using high-purity La_2O_3, $CaCO_3$, MnO_2, Pr_6O_{11}, and $SrCO_3$. Tri-color asymmetrical multilayer structure (sample 1) was grown on a (001)-oriented $LaAlO_3$ single crystal substrate at 973 K under an oxygen pressure of 0.3 Pa by using a multi-target laser molecular beam epitaxy (laser-MBE) technique. The multilayer structure was grown on the substrate of $SrTiO_3$ in an ABC–ACB–CAB–CBA–BAC–BCA arrangement as shown in Fig. 1(a). The laser ablation was executed at a laser fluence of 1.6 J/cm^2 with a repetition rate of 1 Hz by using a KrF excimer laser with a wavelength of 248 nm. The growth was monitored *in situ* by reflection high-energy electron diffraction (RHEED) allowing the precise control of the thickness on a unit cell (u.c.) scale. After the deposition was completed, the thin film was annealed in an oxygen atmosphere of 4 Pa at 1023 K for 1 h, then cooled down to room temperature at a rate of 5 K/min. To perform electrical measurements, another sample (sample 2) with a structure of Pt/multilayer/LSMO was also prepared to form a capacitor. The bottom electrode LSMO of $\sim$ 100 nm was deposited at 973 K at an oxygen pressure of 4 Pa using laser-MBE. Platinum electrodes with 160 μm×160 μm dimensions were sputtered through a shadow mask by plasma sputtering.

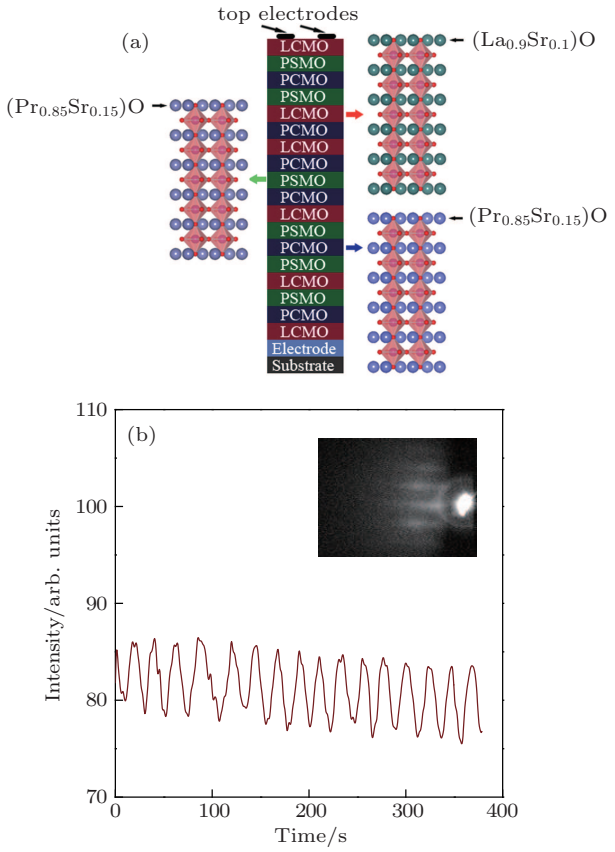


Fig. 1. (color online) Details about the sample structure and RHEED pattern. (a) Schematic view of the multilayer structure. (b) RHEED patten and intensity oscillations during deposition.

3. Results and discussion

The RHEED image and intensity oscillation during the growth of the multilayer structure are shown in Fig. 1(b). The observed intensity oscillation indicates that the multilayer structure is grown in a layer-by-layer growth mode. Combined with the results of thickness tests, the growth rates of LSMO, LCMO, PCMO, and PSMO films are confirmed, showing that one period of RHEED oscillations corresponds to 24 s for 1-u.c. thick film. The thickness of each monolayer of the multilayer structure is 5 u.c.

Figure 2 shows the evidence of the existence of ferroelectricity in the multilayer structure. The surface piezoelectric responses are investigated by using an atomic force microscopy (AFM) (MFP-3D-SA, Asylum Research). A Pt-coated conducting tip (AC240TM, Olympus) is used for PFM, and the same setup is augmented to carry out the advanced switching spectroscopy PFM (SS-PFM). The polarization–electric field (P–E) hysteresis loops are measured at room temperature by using the modified Sawyer–Tower circuit (Precision LC, Radiant). Magnetization measurements are performed by using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. Figure 2(a) shows the out-of-plane piezoresponse phase image of the surface of the sample, the scan size is 1 μm×1 μm. Violet and yellow contrasts are the signatures of the possible polarization vectors of ferroelectric domains, and the variation range of phase value is $\sim$ 185°, implying that the multilayer structure could be ferroelectric. Figure 2(b) shows the PFM phase image (4 μm×4 μm) of the multilayer structure after direct-current-(DC) based switching (tip bias: +6 V for dark area, −6 V for light area and 0 V for the other area). The PFM measurement was performed 20 min after the poling showing different polarizations on the surface. The contrast of polarization in different areas is a strong indication that ferroelectricity exists in the multilayer structure and can be switched upon applying an external voltage. Local PFM spectroscopic measurements of the multilayer structure are shown in Fig. 2(c). A typical well-shaped butterfly loop is obtained, and the variation range of phase is about 145°, corresponding to a nearly complete polarization switching behavior in the as-grown multilayer film, which provides further proof of the existence of ferroelectricity. Figure 2(d) shows macroscopic polarization as a function of electric field in the multilayer film measured at room temperature at a frequency of 1 kHz. A signature of saturation occurs above $\sim$ 43.9 kV/cm as expected for ferroelectrics. The opening of the P–E loop is observed, similar to what was reported in the literature,[21] indicating the existence of defects in the as-grown film. The coercive field (E_C) is $\sim$ 30 kV/cm and remanent polarization reaches up to 31.7 μC/cm^2. It should be noted that the value of Pr appears to be too large, and a high leakage due to the oxygen vacancy, surface roughness and electrode could give rise to the mobile

charges that are responsible for the abnormal remanent polarization. However, it cannot be regarded as the basic reason for the mechanism of polarization. The polarization mainly originates from the broken space inversion symmetry due to the cationic asymmetry and the existence of Mn^{3+}/Mn^{4+} mixed valency that leads to the polar discontinuity of interfaces. It should be pointed out that this kind of mechanism can induce the enhanced polarization and magnetoelectricity. A large Pr of 2.7 μC/cm^2 has been reported in previous literature,[18] which has significantly exceeded the normal value of improper polarization. Actually, the components in this paper, LCMO, PSMO, and PCMO, exhibit the mixed valency of Mn^{3+}/Mn^{4+} in their bulk phases. It indicates that the polar discontinuity exists not only in the multilayer interfaces, but also in the lattice of each monolayer. This could give rise to larger polarization than that in the reported tri-color structure comprised of $NdMnO_3/SrMnO_3/LaMnO_3$ layers.[18] Furthermore, the disordered stacking of components will also contribute to the enhanced polar discontinuity of interfaces due to the frustrated magnetic ordering. We also prepare a multilayer structure comprised of the ordering arrangement of ABC–ABC–⋯–ABC layers, which can hardly exhibit the ferroelectricity. That is to say, the polar discontinuity of interfaces from the disordered spin induced broken space inversion symmetry is the true reason for the polarization mechanism. In the present work, we mainly prepare a tri-color multilayer structure in which the effect of leakage cannot be ignored. If the tri-color artificial structure can be built as a well-prepared superlattice structure to avoid the leakage, we believe that the measurement of polarization will be more intrinsic and the value of Pr will be larger than the previously reported value of 2.7 μC/cm^2. This is our main work in the future.

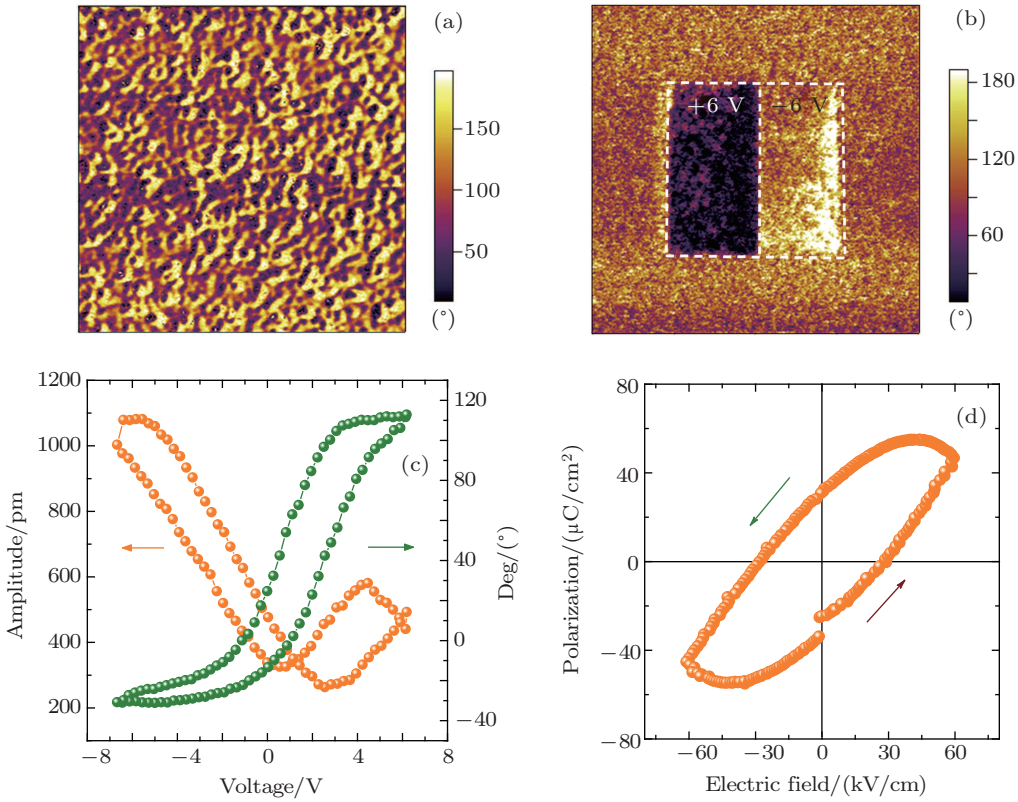


Fig. 2. (color online) Local and macroscopic evidence of the existence of ferroelectricity in the multilayer structure. The measurements are carried out on sample 2. (a) Out of plane piezoresponse phase image showing distinct grains. The scan size of the image is 1 μm×1 μm. (b) PFM phase image (4 μm×4 μm) after poling by +6 V and −6 V dc bias, demonstrating the switching of the ferroelectric. The dotted boxes are a schematic of the applied bias (tip bias: +6 V for dark area, −6 V for light area and 0 V for the other area). (c) Single-point PFM phase-voltage hysteresis loop and amplitude-voltage butterfly loop. (d) Polarization as a function of electric field in the multilayer film measured at room temperature at the frequency of 1 kHz.

Further studies focus on the relationship between magnetic and dielectric properties. Figure 3(a) displays the field-cooled (FC) magnetization as a function of temperature for the multilayer structure under a magnetic field of 100 Oe (1 Oe = 79.5775 A·m^{-1}). The temperature (T_m) ∼ 103 K corresponds to the transition between the canted ferromagnetic phase and the ferromagnetic metal phase. At the low temperature (lower than 103 K), the canted spin allows the ferromagnetic insulator to occur, thus the magnetization remarkably decreases by the increased temperature. When temperature is large (103 K–230 K), the ferromagnetic mechanism is gradually dominated by the competition between canted spin ordering and the JT distortion induced double exchange effect, and the metal state arises in the insulated phase. Phase mixture between insulator and metal states contributes to the apparent semiconductor behavior of the artificial structure. When

temperature continually increases, the film undergoes another transition from ferromagnetic phase to paramagnetic phase, with the transition temperature T_c of 230 K, which is similar to the Curie temperature of LCMO, PCMO, and PSMO, respectively, according to the literature.[20–22] Figure 3(b) shows a magnetic hysteresis loop of the multilayer structure at 50 K after magnetic-field cooling with 100 Oe from 300 K. The observed hysteresis indicates the existence of an ordered magnetic phase. We obtain a remanent magnetization (M_r) of ~ 188 emu/cm^3 and a coercivity field (H_c) of ~ 230 Oe.

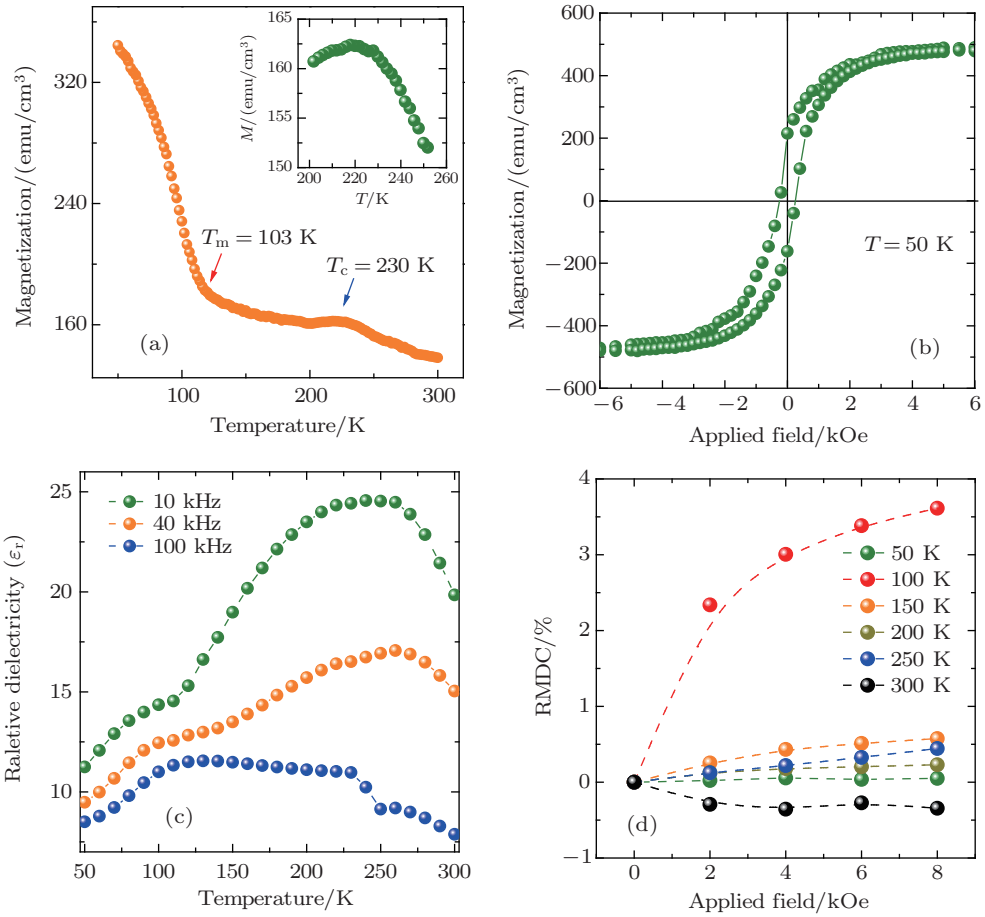


Fig. 3. (color online) Magnetic, dielectric and magnetoelectric measurements. (a) Field-cooled temperature dependence of magnetization for sample 1. Magnetic field of 100 Oe is applied parallel to the film surface. (b) Field dependence of magnetization of the multilayer structure at 50 K for sample 1. (c) Temperature dispersion of the dielectric constant (ε) at different frequencies for sample 2. (d) Magnetic field induced variations of the dielectric constant at different temperatures and a frequency of 10 kHz for sample 2.

The variations of dielectric constant (ε) with temperature ranging from 50 K to 300 K at frequencies of 10 kHz, 40 kHz, and 100 kHz are illustrated in Fig. 3(c), respectively. Remarkable features in the ε–T curves are anomalous around 100 K and 230 K, corresponding to T_m and T_c respectively, which is consistent with the above discussion about the magnetization. It suggests the coupling between the ferromagnetic and dielectric properties. To further clarify the character of the magnetocapacitance effect, we display in Fig. 3(d) the variations of dielectric constant with applied magnetic field at a frequency of 10 kHz under various temperatures, where the relative magnetic dielectric coefficient (RMDC) is defined as $(\varepsilon(H) - \varepsilon(0))/\varepsilon(0)$. It is shown that the variation of the magnetic dielectric constant is considerably dependent on temperature. A notable magnetocapacitance in the vicinity of the ferromagnetic transition temperature T_m is observed, which is the characteristic of electric polarization in frustrated magnets, the dielectric constant increases dramatically with applied magnetic field, and the value of RMDC reaches a maximum of 3.6% at 0.8 T, which is remarkably large compared with that of the ordinary multiferroics.

Results presented so far show that an emergent ferroelectricity in the disordered multilayer structure and robust coupling between magnetic and dielectric properties can result from spatial frustration ferroelectricity. Because of the disordered stacking of ferromagnetic manganite, magnetic ordering is inhomogeneous, resulting in engineer magnetic frustration. From the viewpoint of symmetry arguments, magnetic ordering breaks space inversion symmetry in the as-grown multilayer structure. For this kind of magnetic ordering set, the magnetocapacitance effect can be phenomenologically explained in terms of Lifshiz–Landau theory for the second-order phase transition of ferroelectromagnets,[23] the electric polarization $\boldsymbol{P}$ induced by magnetization $\boldsymbol{M}$ can be written

as[2,23]

$$\boldsymbol{P} \propto [(\boldsymbol{M}\cdot\partial)\boldsymbol{M} - \boldsymbol{M}(\partial\cdot\boldsymbol{M})]. \quad (1)$$

This shows the role of frustration, which induces spatial variations of magnetizations and then causes electric polarization $\boldsymbol{P}$. So we ascribe the frustration as the key factor to the existence of ferroelectricity and the coupling between magnetic and dielectric properties.

4. Conclusions

Our present work is to construct an artificial magnetic frustrated structure for creating the magnetic frustration mechanism to produce ferroelectricity. In particular, a disordered stacking of a multilayer comprised of tri-color perovskite manganites is grown on the substrate of STO with the layer-by-layer growth mode. PFM measurement shows the ferroelectric domains with the reversal range of 185°. Different polarization zones can be switched by applying an external voltage. Local PFM measurement shows the well-shaped d_{33} loop and butterfly loop. Ferroelectric analysis measures the opening of the *P*–*E* loop, with a coercive field of 30 kV/cm and remanent polarization of 31.7 μC/cm^2. The magnetic hysteresis shows a remanent magnetization of $\sim$ 188 emu/cm^3 and coercivity field of $\sim$ 230 Oe and the relative magnetic dielectric coefficient (RMDC) exhibits a maximum value of 3.6% at 0.8 T. It well supports the emergent ferroelectricity and the obvious existence of the magnetoelectric coupling due to the magnetic frustration mechanism.

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