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Enhanced magneto-electric effect in manganite tricolor superlattice with artificially broken symmetry*

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The magneto-electric effect in magnetic materials has been widely investigated, but obtaining an enhanced magneto-electric effect is challenging. In this study, tricolor superlattices composed of manganese oxides—$Pr_{0.9}Ca_{0.1}MnO_3$, $La_{0.9}Sr_{0.1}MnO_3$, and $La_{0.9}Sb_{0.1}MnO_3$—on (001)-oriented Nb:$SrTiO_3$ substrates with broken space-inversion and time-reversal symmetries are designed. Regarding the electric polarization in the hysteresis loops of the superlattices at different external magnetic fields, both coercive electric field E_c and remnant polarization intensity P_r clearly show strong magnetic-field dependences. At low temperatures (< 120 K), a considerable magneto-electric effect in the well-defined tricolor superlattice is observed that is absent in the single compounds. Both maxima of the magneto-electric coupling coefficients ΔE_c and ΔP_r appear at 30 K. The magnetic dependence of the dielectric constant further supports the magneto-electric effect. Moreover, a dependence of the magneto-electric effect on the periodicity of the superlattices with various structures is observed, which indicates the importance of interfaces. Our experimental results verify previous theoretical results regarding magneto-electric interactions, thereby paving the way for the design and development of novel magneto-electric devices based on manganite ferromagnets.

Keywords: multiferroic, magneto-electric effect, superlattice

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1. Introduction

Since the magneto-electric (ME) effect—induction of magnetization by an external electric field or induction of electric polarization by an external magnetic field—was theoretically confirmed in 1959–1960 by Astrov,[1–3] it has been the hottest topic in the field of condensed matter physics for a long period. During the last half of the 20th century, ME effects have been observed in many single-phase materials and composites.[4–7] For example, Wang *et al.* reported the electric and magnetic properties and the ME effect in $Ba_{0.8}Sr_{0.2}TiO_3/CoFe_2O_4$ heterostructure films.[8] Unfortunately, the magnitude of the observed ME effect is too low to meet the application requirements of practical devices.

Two or all three ferroic orders (ferroelectrics, ferromagnetics, and ferroelastics) can coexist in multiferroic materials.[9–12] Currently, the research of new materials with gigantic ME coupling is attracting a great deal of attention. Two main reasons exist for the focus on multiferroic materials. First, multiferroics with simultaneously coupled magnetic and electronic degrees of freedom offer an additional degree of freedom for the design of many advanced functional devices, e.g., sensors, drivers, or storage devices.[13–15] Second, owing to the coupling between ferromagnetic and ferroelectric states, certain novel features absent in the single states can be expected.[16] Unfortunately, such materials are rare in nature because the ferroelectricity and magnetism need different broken inversion symmetries in micro-electronic states. Although new multiferroics have been reported, their ME coupling is limited or the properties cannot appear at room temperatures.[17] Therefore, obtaining strongly coupled electrical polarization and magnetization at room temperatures is still a great challenge, and more research on multiferroic materials should be conducted to improve the ME effect. Owing to the rapid development of the thin-film deposition technology, it is possible to grow atomic-scaled flat films. This development encourages theoretical investigations and leads to the emergence of numerous artificial materials.[18–20] Controlling the growth progress of dissimilar materials at an atomic scale is expected to obtain fascinating enhanced and novel properties. At present, many different approaches are used to increase the ME coupling, e.g., chemical doping, highly oriented epitaxial films, or heterojunction composite films composed of ferroelectric and ferromagnetic layers.[21–24] Among these approaches, superlattices (SLs) can be viable candidates. They are composed of thin layers of two or more different compositions that are stacked in a specific sequence. This system can produce striking properties that do not exist in its constituent compounds. Norton *et al.* (1994) reported the superconductivity in SLs composed of non-superconducting $SrCuO_2$ and $BaCuO_2$.[25] Kida *et al.* (2007) reported an enhanced optical ME effect in a patterned artificial tricolor SL.[26] Furthermore,

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Tokura predicted that non-ferroelectrics can give rise to a ferroelectric state in a magnetically ordered state in a fabricated tricolor SL with artificially broken symmetry.[27] This hypothesis was confirmed in our early studies on frustration-induced ferroelectricity in manganite tricolor SLs.[28] Moreover, perovskite manganese oxide exhibits a strong correlation and coupling system regarding the degrees of freedom of orbit, spin, and lattice, which can lead to the emergence of certain electric and magnetic states and physical properties.[29,30]

In our previous study, we have investigated a tricolor SL composed of non-ferroelectric $La_{0.9}Sr_{0.1}MnO_3$ (LSMO, A), $Pa_{0.9}Ca_{0.1}MnO_3$ (PCMO, B), and $La_{0.9}Sb_{0.1}MnO_3$ (LSbMO, C), which exhibits a multiferroic state below 30 K.[23] The ferroelectricity of SLs on periodicity has shown that interfaces play a key role for ferroelectricity and that the ferroelectric properties of SLs vary with the number of interfaces.

In the present study, we concentrate on the role of a magnetic field on the ferroelectric polarization of tricolor SLs. Therefore, a series of SLs $[(LSMO)_n/(PCMO)_n/(LSbMO)_n]_m$ were fabricated by conducting laser molecular-beam epitaxy (L-MBE) deposition, where n is the thickness of each sublayer and m is the periodicity of the alternating cycle. The SL structure is ABCABC-stacked and labeled by (n,m).

2. Experiment

The SL film growth was carried out at 1053 K with 0.5 Pa of flowing oxygen targeting the (001)-oriented Nb:$SrTiO_3$ (NSTO) single-crystal substrate. The total sample thickness was fixed to 51.25 nm and controlled with a transmission electron microscope (TEM) (JEM-2100 F, JEOL). The electric polarization $\boldsymbol{P}$ versus the electric field $\boldsymbol{E}$ (P–E), i.e., the hysteresis loops of the SL films, are measured with a modified Sawyer–Tower circuit (Precision LC, Radiant Technologies) and by placing the samples into a closed-circuit cryostat (C300, Janis Research Company). The dielectric properties of the SL films are calculated from the capacitance values measured with an LCR meter (E4980 A, Keysight Technologies). More details on the sample preparation and structural characterization of SLs can be found in Ref. [28] .

3. Results and discussion

To measure the electrical properties of the SL films, aurum electrodes are fabricated on their surfaces using a shadow mask to obtain ohmic contacts. The size of each aurum electrode is 1×1 mm^2. The measuring current is perpendicular to the in-plane direction. Figure 1(a) presents the configuration diagram of the film and electrodes. Based on previous studies,[23] the magnetic-field dependences of the P–E loops of the SL with $(n,m) = (3,15)$ are measured at temperature $T = 30$ K and frequency $f = 2$ kHz, as shown in Fig. 1(b).

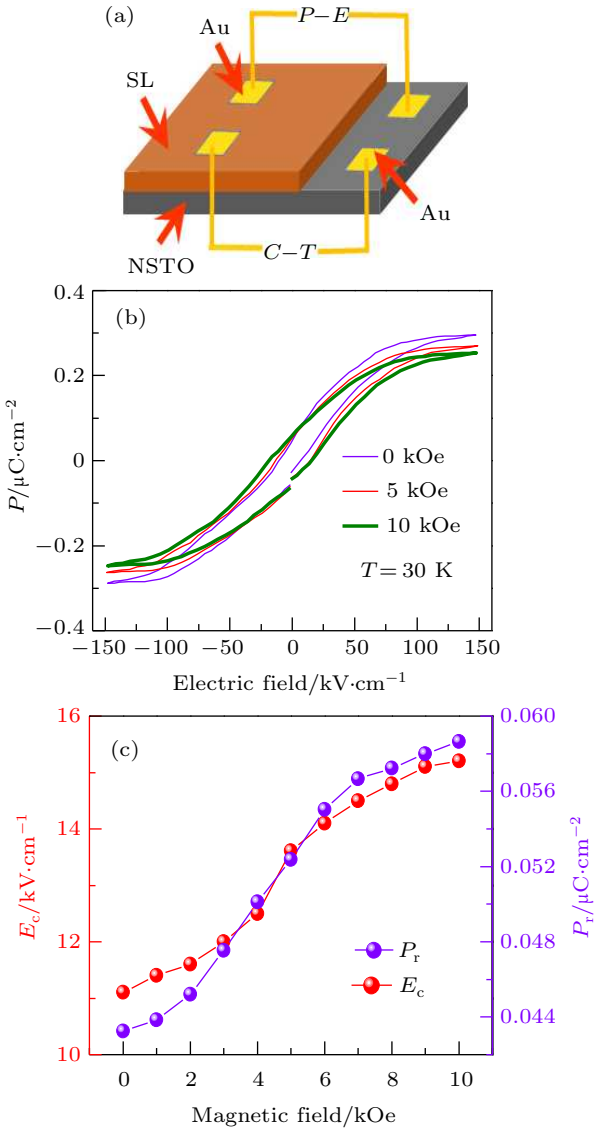


Fig. 1. (color online) Measurements of ME effect. (a) Schematic view of four electrodes fabricated on SL. (b) Polarization as a function of electric field (P–E) in SL film measured at $T = 30$ K under $H = 0$ kOe, 5 kOe, and 10 kOe. The frequency is 2 kHz. (c) Dependences of E_c and P_r on magnetic field.

Evidently, $\boldsymbol{P}$ increases and reaches a saturation value P_s with increasing electric field. When a small electric field is applied, some parts of the electric dipole moments are still chaotic instead of pointing in an equal direction. With a continuously increasing electric field, the orientations of the electric dipole moments gradually converge and $\boldsymbol{P}$ reaches its maximum. The P–E loop without an applied magnetic field exhibits a typical S shape, which corresponds to the ferroelectric behavior of the SL. When external magnetic fields of $H = 5$ kOe and 10 kOe are applied in-plane to the SL, the P–E loops are also S-shaped. However, the coercive electric field E_c and remnant polarization intensity P_r increase monotonously, as shown in Fig. 1(c). Additionally, the P–E loops with out-of-plane magnetic field are measured. However, no differences from the in-plane case appear. Thus, the P–E loops are independent of the magnetic-field direction. To quantify the effect of the mag-

netic field on the ferroelectric performance of SLs, the relative change rates ΔE_c and ΔP_r are statistically analyzed. They are defined as

$$\Delta E_C = \frac{E_C(H) - E_C(0)}{E_C(0)} \times 100\%, \quad (1)$$

$$\Delta P_r = \frac{P_r(H) - P_r(0)}{P_r(0)} \times 100\%, \quad (2)$$

where $E_c(H)$ and $E_c(0)$ are the coercive electric field with and without an external magnetic field, respectively; $P_r(H)$ and $P_r(0)$ are the remnant polarization intensity with and without an external magnetic field, respectively.

Figure 2 presents E_c, P_r, ΔE_c, and ΔP_r as functions of the temperature. All measurements are carried out in heating processes. According to Fig. 2(a), E_c without an applied magnetic field increases monotonously with increasing temperature, whereas P_r without an applied magnetic field decreases monotonously. The trends of E_c and P_r with $H = 5$ kOe and 10 kOe are in accordance with those without an applied magnetic field. The values exhibit positive change rates induced by the external magnetic field at low temperatures. However, ΔE_c does not behave monotonously with increasing temperature, as seen in the upper panel of Fig. 2(b). From 10 K to 30 K, ΔE_c increases slowly to its maximum. Then, ΔE_c rapidly drops to a low value until 120 K. The maxima of ΔE_c at $H = 5$ kOe and 10 kOe are 22.61% and 36.94%, respectively. According to the lower panel of Fig. 2(b), ΔP_r behaves similarly to ΔE_c: ΔP_r reaches its maximum also at 30 K. At $T > 30$ K, owing to strong thermal motion, the magnetic and charge orders are perturbed, resulting in a decrease in magnetization or polarization.[31] However, the distances between adjacent atoms increase with increasing temperature, leading to a decreasing exchange interaction and magnetization. Thus, the ME coupling decreases inevitably with increasing temperature. Below 30 K, ME coupling increases with increasing temperature. Please note that the magnetization of tricolor SLs as a function of temperature has been measured in our previous work.[20] The change trend of the ME coupling is very similar to the case of tricolor-SL magnetization. Thus, we believe that the decreasing ME coupling below 30 K is related to the decreasing magnetization. However, several mechanisms influence the magnetization at low temperatures, e.g., the spin glass state, and competition between spin, orbit, and charge order.[32,33] More research is necessary to control such mechanisms. The situation in tricolor SLs is even more complicated. Nevertheless, at low temperatures (< 120 K), the change trends of ΔE_c and ΔP_r indicate that the ferroelectric property of the tricolor SL has an obvious dependence on the magnetic field, thereby suggesting strong ME coupling.

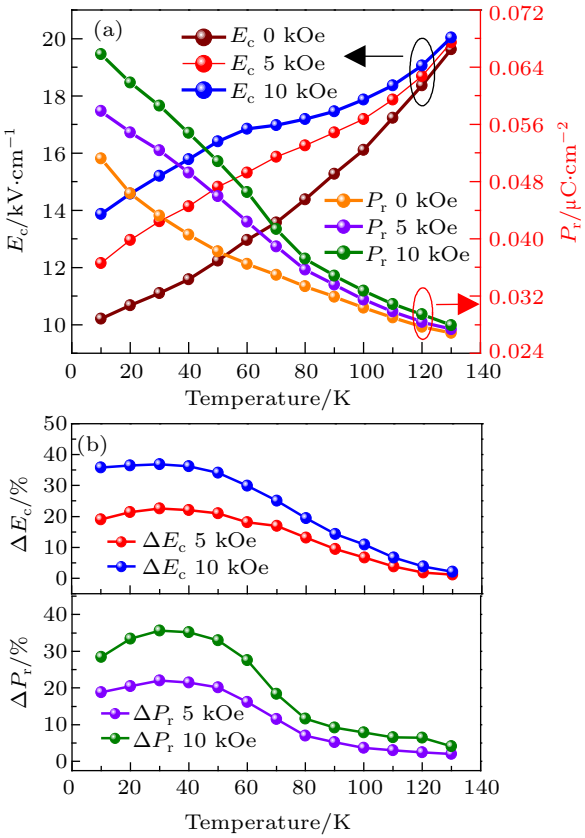


Fig. 2. (color online) Temperature dependence of ME effect. (a) E_c and P_r as functions of temperature in (3, 15) SL under external magnetic fields of 0 kOe, 5 kOe, and 10 kOe and 2 kHz. (b) Temperature dependences of ΔE_c and ΔP_r at different magnetic fields. Their maxima appear at 30 K.

In a multiferroic, the dielectric constant, like the polarization, is coupled to the magnetic order. Since the magnetic field affects the magnetic order, the field also indirectly alters the dielectric constant of ME multiferroics.[34,35] Therefore, the magneto-capacitance effect can reflect the ME effect to a certain extent. As shown in Fig. 3(a), the changes in the dielectric constant and loss for an SL with $(n,m) = (3,15)$ are recorded in a frequency range of 1 kHz–1000 kHz at $T = 30$ K under external magnetic fields of 0 kOe, 5 kOe, and 10 kOe. Two important features can be seen. First, the dielectric constant of the sample decreases with increasing frequency and remains at small values for high frequencies. In general, four polarizations exist, i.e., space charge polarization, dipole orientation polarization, electronic polarization, and ionic polarization.[36,37] Owing to the long building time, space charge polarization should be considered only at low frequencies. Dipole polarization can appear at frequencies up to 10^{10} Hz, along with a maxima in the dielectric loss. By contrast, electronic and ionic polarization can exist below 10^{13} Hz. Since the dielectric loss increases monotonously in our sample, only electronic and ionic polarizations contribute to the dielectric constant. Second, the dielectric constant decreases with increasing magnetic field in the tested frequency range, suggesting a negative magneto-dielectric (MD) effect. The di-

electric loss at $H = 0$ kOe, 5 kOe, and 10 kOe in Fig. 3(a) indicates that the film has a low dielectric loss in the frequency range of 1 kHz–1000 kHz. Thus, the sample exhibits a good insulation performance. In some cases, the magneto-resistance (MR) effect contributes to the MD effect. However, whether a magnetic field is applied or not, the resistance of the SL films exceeds the limit of 10^{12} Ω of the measuring instrument, suggesting that the MR effect in our sample is limited.

To gain more knowledge on the observed MD effect, the dielectric constant and loss versus temperature are measured at 2 kHz under 0 kOe, 5 kOe, and 10 kOe, as shown in Fig. 3(b). The dielectric constant decreases monotonously with increasing temperature, whether an external magnetic field is applied or not. A reason might also be the strong thermal motion.

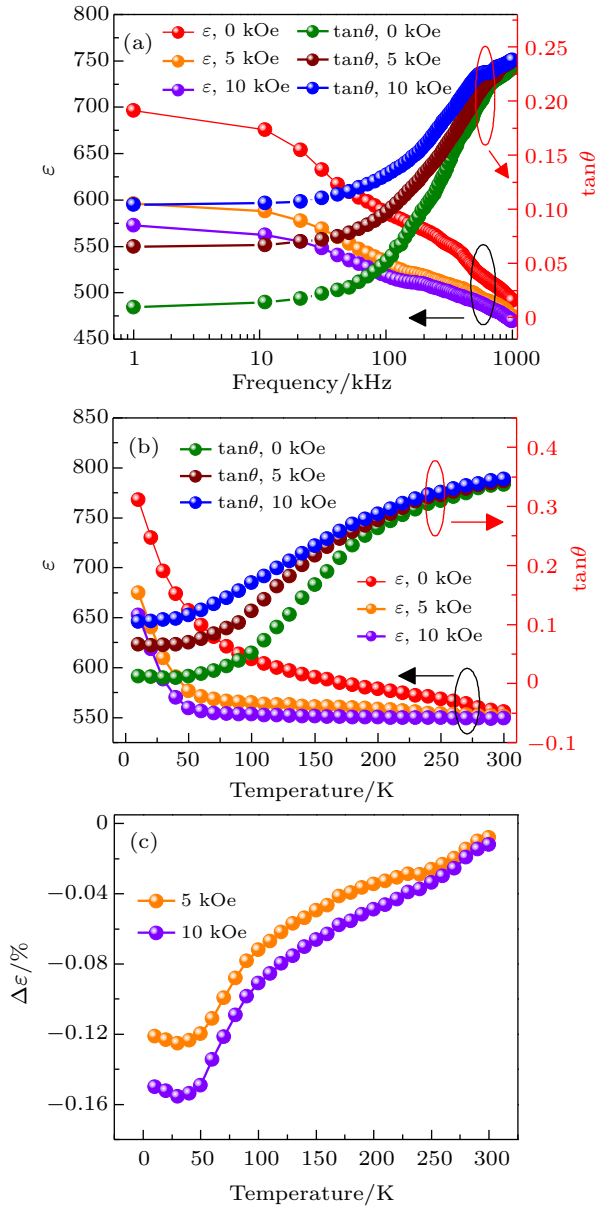


Fig. 3. (color online) Measurements of the MD effect. (a) Dielectric constant and loss as functions of frequency for (3, 15) SL under external magnetic fields of 0 kOe, 5 kOe, and 10 kOe at $T = 30$ K. (b) Dielectric constant and loss as functions of temperature at different magnetic fields. (c) Temperature dependence of the MD effect. A maximum appears at 30 K.

When an external magnetic field is applied in-plane, the dielectric constants decrease with increasing magnetic field. This corresponds to the presence of an MD effect. It can be defined as $\Delta\varepsilon = 100\% \times [\varepsilon(H) - \varepsilon(0)]/\varepsilon(0)$, where $\varepsilon(H)$ represents the dielectric constant with an external magnetic field. The MD effect is negative compared to ΔE_c and ΔP_r. It increases with decreasing temperature and reaches its maximum of 15.54% at 30 K. The trend is similar to the behavior of ΔE_c and ΔP_r, which indirectly supports the ME effect.

In order to understand the true nature of the ME effect, P–E hysteresis loops of a series of tricolor SLs with various (n, m) are measured. Figure 4 depicts the change trends of ΔE_c and ΔP_r of SLs with $(n, m) = (3, 15)$, (5, 9), (7, 6), and (15, 3) as functions of the periodicity m. It is obvious that ΔE_c and ΔP_r strongly depend on m. This clearly suggests that interfaces play a key role in strong ME and MD effects. Owing to spin-polarized carriers in manganite SLs, the local magnetic moments of Mn^{3+} and Mn^{4+} ions tend to be parallel when an external magnetic field is applied, which leads to an orbital reconstruction. Finally, it can affect the polarization state in the SL via the interface effect. Unlike in bicolor SLs, the interface polarization can be accumulated in tricolor SLs. In other words, the more interfaces exist, the larger $\boldsymbol{P}$ values are inevitably accumulated. Accordingly, the ME effect increases with increasing m. It can further rule out the influence of the MR effect on the observed results owing to a fixed sample thickness.

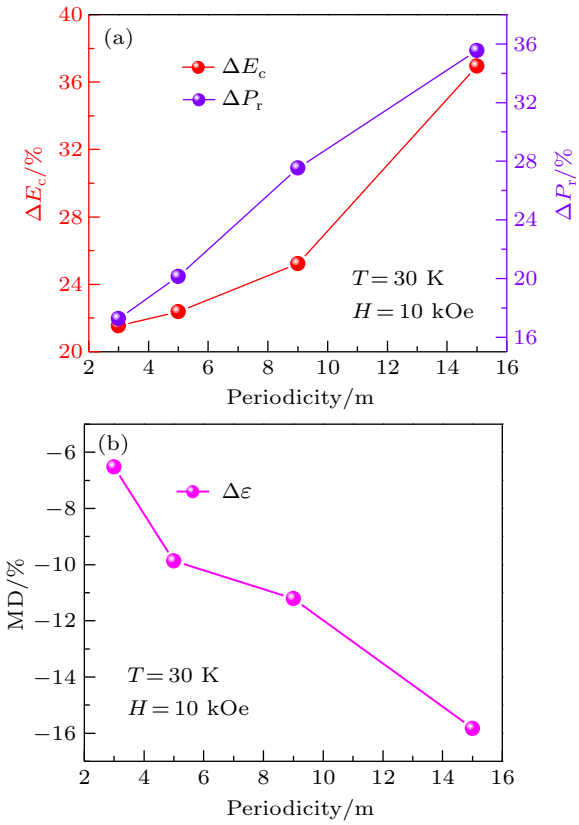


Fig. 4. (color online) (a) Periodicity dependence of E_c and P_r under an external magnetic field of 10 kOe at $T = 30$ K. (b) MD effect as a function of periodicity at $H = 10$ kOe and $T = 30$ K.

4. Conclusions

We successfully fabricated $[(LSMO)_n/(PCMO)_n/(LSbMO)_n]_m$ tricolor SL films on (001)-oriented Nb:$SrTiO_3$ single-crystal substrates with (L-MBE) at 1053 K to investigate the ME and MD effects of SL films. According to the electric-polarization hysteresis loops at different external magnetic fields, both coercive electric field and remnant polarization intensity of the SLs show strong dependences on the magnetic field, suggesting a strong positive ME effect that does not appear in the single-phase compounds. Further, a negative MD effect is observed at low temperatures, which indirectly supports the ME effect. Both ME and MD effects depend on (n,m). Consequently, the interfaces contribute to an increased ME effect. The maximum ME coupling coefficient in the SL is obtained with $(n,m) = (3,15)$ at 30 K. Our results confirm that the ME effect can be increased by employing asymmetric tricolor SLs—even though the SL components are non-multiferroic materials. These results pave the way for the design of novel ME devices.

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