Polarization enhancement and ferroelectric switching enabled by interacting magnetic structures in DyMnO₃ thin films

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The mutual controls of ferroelectricity and magnetism are stepping towards practical applications proposed for quite a few promising devices in which multiferroic thin films are involved. Although ferroelectricity stemming from specific spiral spin ordering has been reported in highly distorted bulk perovskite manganites, the existence of magnetically induced ferroelectricity in the corresponding thin films remains an unresolved issue, which unfortunately halts this step. In this work, we report magnetically induced electric polarization and its remarkable response to magnetic field (an enhancement of ~800% upon a field of 2 Tesla at 2 K) in DyMnO₃ thin films grown on Nb-SrTiO₃ substrates. Accompanying with the large polarization enhancement, the ferroelectric coercivity corresponding to the magnetic chirality switching field is significantly increased. A picture based on coupled multicomponent magnetic structures is proposed to understand these features. Moreover, different magnetic anisotropy related to strain-suppressed GdFeO₃-type distortion and Jahn-Teller effect is identified in the films.

Multiferroics with coexisting and intimately coupled ferroelectric (FE) and magnetic orders, have attracted considerable attentions due to their vast application potentials and fundamental interest in the past decade¹–⁶. It has been confirmed that a series of magnetic configurations can break the spatial inversion symmetry and thus produce spontaneous polarization (P)⁷. One of the most frequently cited evidences is the spiral-spin-ordering (SSO) in orthorhombic manganites RMnO₃ (R = Tb and Dy), as highlighted by the first discovery of multiferroicity and giant magnetoelectric (ME) coupling in bulk TbMnO₃ (TMO) in 2003⁷. For these model multiferroics with SSO, successive phase transitions occur due to the proximate free energies of various phases in the low temperature (T) region. Upon cooling, the multiferroic RMnO₃ enters a collinear sinusoidal antiferromagnetic (AFM) state at TN (~40 K) from a paramagnetic (PM) one, and then the SSO develops with a locked period at TC (~20–30 K) and an improper FE polarization arises simultaneously via the inverse Dzyaloshinskii-Moriya (DM) interaction between adjacent spins. The as-generated P can be expressed as P = eₓ × (Sₓ × Sᵧ), where eₓ denotes the unit vector connecting the two spins Sₓ and Sᵧ. Upon further decreasing temperature to T < 10 K, the moment of rare-earth ions forms a long range ordering at TR and also modulates the ferroelectricity⁸–¹⁰.

To date, bulk SSO multiferroic manganites including single crystals have been intensively studied, and the associated physics has been progressively understood¹¹–¹⁵. However, research on the thin films is rare, and the insights are expected to play a core role in designing advanced multifunctional devices. From the fundamental viewpoint, fabrication of thin films will introduce additional degrees of freedom such as strain to mediate the multiferroicity besides the bulk-related routes, e.g., chemical doping. It is thus reasonable to expect intriguing properties in thin films since the delicate balance among different exchange interactions is sensitive to internal/external perturbations in multiferroic manganites. Indeed, a few recent papers reported emergent ferromagnetism related to the modified lattice distortion in TMO thin films, while no ferroelectricity associated with the SSO
was captured\textsuperscript{13–18}. This is quite different from the E-type AFM multiferroic manganite thin films, in which the magnetic ferroelectricity was reported in several materials\textsuperscript{19–21}.

According to the phase diagram of perovskite manganites, the SSO phase is rather sensitive to structure distortion, and can only exist within a very narrow region\textsuperscript{22}. Furthermore, the SSO in BiFeO\textsubscript{3} was revealed to be suppressed by strain\textsuperscript{22,23}. It thus seems reasonable to expect the suppression of SSO phase by strain in orthomanganite thin films. However, while the ground state of bulk \( \text{Y MnO}_3 \) is the E-type AFM\textsuperscript{20,21,25}, a strain-induced SSO phase accompanied by spontaneous polarization was reported in the corresponding thin films recently\textsuperscript{26}. In a recent ultrafast optical spectroscopy study, an anomaly around \( T = 30\,\text{K} \) (close to the FE Curie temperature \( T_{\text{C}} \approx 28\,\text{K} \) of TMO single crystal) was observed in TMO thin films, which hints the coexistence of SSO and ferroelectricity but no relevant data were reported\textsuperscript{27}. These works motivated us to explore the SSO induced ferroelectricity and the ME coupling in orthorhombic RMnO\textsubscript{3} thin films.

Along this line, we choose DyMnO\textsubscript{3} (DMO) thin films as the prototype to investigate the possible coexistence of multiple ferroic orders and the ME coupling among them. Besides TMO, DMO is one of the typical multiferroic manganites with SSO, and they possess quite similar physical properties. Particularly, in both materials, the SSO induces ferroelectricity through the inverse DM interaction, and magnetic field switches polarization from the \( c \) axis to the \( a \) axis (\( P \) flopping)\textsuperscript{8}. DMO lies far inside the SSO region in the magnetic phase diagram while TMO is somehow in the vicinity of the A-type AFM region, allowing more flexibility for spin order modulation in DMO than TMO\textsuperscript{22}. In addition, DMO single crystal exhibits much larger spontaneous polarization (\( P \approx 2100\,\mu\text{C/m}^2 \)) than that of TMO (\( P \approx 600\,\mu\text{C/m}^2 \)), which facilitates reliable measurements. More importantly, in bulk DMO, the Dy moments play a much more active role through the Dy-Mn interaction in generating FE polarization than the Tb moments in TMO, enabling fascinating physics unavailable in TMO\textsuperscript{28–33}.

In this work, we perform systematic experiments to investigate the structural, magnetic, dielectric, and ferroelectric properties of strained DMO thin films grown on Nd-SrTiO\textsubscript{3} (001) (NSTO). Magnetically induced ferroelectricity was clearly identified using the pyroelectric current method and the direct electric hysteresis loop measurement. Interestingly, both the polarization and ferroelectric coercivity can be significantly enhanced by magnetic field at \( T < T_{\text{C}} \), indicating the essential role of Dy moment on ferroelectricity. In addition, different magnetic anisotropy was observed. Notably, these multiferroic behaviors in DMO thin films are quantitatively different from but qualitatively similar to those for bulk DMO crystals, indicating that the strain may play a non-negligible role in modulating multiferroicity in such manganite thin films.

### Results

Fig. 1(a) presents the high resolution X-ray diffraction (HRXRD) pattern of one typical DMO/NSTO thin film, in which pure \( c \)-axis orientation can be seen for the film. The out-of-plane (OOP) lattice parameter of the film was found to be \( \approx 7.393\,\text{Å} \), which is larger than that of the bulk counterpart, indicating an in-plane compressive strain. Fig. 1(b) shows the rocking curve around the (002) reflection for the film, and the full width half maximum (FWHM) is \( \approx 0.72^\circ \). The NSTO substrate has a cubic crystalline structure with lattice parameter \( a = 3.905\,\text{Å} \), while the orthorhombic DMO has lattice parameters \( a = 5.278\,\text{Å}, b = 5.834\,\text{Å}, \) and \( c = 7.378\,\text{Å} \). Therefore, large lattice misfit is expected in the epitaxial growth. To get detailed information of the epitaxial growth, we perform asymmetric reciprocal space mapping (RSM) of the (103)\textsubscript{C} and (113)\textsubscript{C} reflections where the subscript ‘C’ refers to the pseudo-cubic lattice, and the data are shown in Fig. 1(c) and (d), respectively. Identical in-plane (IP) lattice parameters of the film with respect to the substrate can be

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**Figure 1** | (a) Symmetric X-ray \( \theta-2\theta \) scan of the DMO/NSTO thin film. The inset shows a schematic drawing of the epitaxial growth of DMO on (001) NSTO. (b) Rocking curve around the (002) reflection for the film. The FWHM is \( \approx 0.72^\circ \). (c) and (d) present the data of reciprocal space mapping around the (103)\textsubscript{C} and (113)\textsubscript{C} reflections of the substrates, respectively. (e) \( 2 \times 2\,\mu\text{m}^2 \) atomic force microscopy image of the film, in which islands dominate the surface morphology. The \( R_{\text{rms}} \) of film is estimated to be \( \approx 1.6\,\text{nm} \). The inset shows the topography with a smaller scanning size of \( 0.5 \times 0.5\,\mu\text{m}^2 \), in which the island size can be derived to range from 40 nm to 80 nm.
seen from the (103)_c reflection, indicating the coherent growth of the film on the substrate. However, two diffraction spots corresponding to (206)_a and (026)_c can be observed in Fig. 1(d), which suggests an orthorhombic twin crystalline structure of the film and thus consisting with the relative large FWHM of (002) reflection. The subscript ‘O’ refers to the orthorhombic lattice. Based on the RSM data, a sketch of the stacking model of DMO unit cells on NSTO substrate is shown in the inset of Fig. 1(a). A similar growth model was previously proposed for TMO thin films\(^{35}\). Moreover, the atomic force microscopy image (Fig. 1 (e)) shows an island surface for the film. The root-mean-square roughness (R\(_{\text{rms}}\)) of the film is estimated to be 1.6 nm, and the island size ranges from 40 nm to 80 nm. In addition, lattice parameters (and the corresponding variation ratio) of the orthorhombic DMO thin films can be estimated from the RSM data as, \(a = 5.288 \, \text{Å} (0.2\%)\), \(b = 5.770 \, \text{Å} (\sim 1.1\%)\), and \(c = 7.395 \, \text{Å} (0.2\%)\). Considering the relatively large uniaxial compressive strain along the \(b\) axis, we expect certain anisotropy in the physical properties of the film.

The \(T\)-dependences of magnetization (\(M\)) in the \(ab\) plane and along the \(c\) axis are measured under both field cooling (FC) and zero field cooling (ZFC) conditions, and the data are shown in Fig. 2(a). For both cases, the magnetization evolves smoothly with \(T\) until \(T_\text{R} \approx 9\, \text{K}\), at which distinct anomalies in the \((M)\) curves are observed and can be associated with the long range ordering of Dy moment. Usually, the large paramagnetic contribution of Dy moment will dominate the magnetic signal, and make the detection of AFM (or SSO) phase transition difficult, as reported for bulk DMO single crystal\(^{35}\). Although identical \(T_\text{R}\) is evidenced from the data in the \(ab\) plane and along the \(c\) axis, the clear difference in shapes of the \((M)\) curves implies the possible magnetic anisotropy within the films. In Fig. 2 (b) and (c), the \((M)\) curves measured under various temperatures are plotted. We calculate the demagnetization factor to be \(\sim 10^{-1}\) in the \(ab\) plane and \(\sim 1\) along the \(c\) axis for our sample (area: 3 mm \(\times\) 3 mm, thickness: 300 nm), which gives rise to the demagnetization field of \(\sim 1\) Oe in the \(ab\) plane and \(\sim 560\) Oe along the \(c\) axis at \(H = 7\,\text{T}\). Therefore, the demagnetization field only has very weak contribution to our magnetic measurements. Evidently, the magnetization of \(ab\) plane is much larger than that of \(c\) axis, which confirms the magnetic anisotropy in the films. A close examination of the \((M)\) curves reveals that the maximum magnetization (\(H = 7\, \text{T}\) and \(T < T_\text{R}\)) are \(M_{\text{ab}} = 10.3\, \mu_\text{B}/\text{f.u.}\) for \(ab\) plane and \(M_{\text{c}} = 1.08\, \mu_\text{B}/\text{f.u.}\) for \(c\) axis, which gives the magnetic anisotropy as large as \(M_{\text{ab}}/M_{\text{c}} \approx 10\). For DMO bulk single crystal, the magnetization at \(H = 7\, \text{T}\) and \(T < T_\text{R}\) was reported to be \(\sim 7.5\, \mu_\text{B}/\text{f.u.}\) for \(ab\) axis, \(\sim 4.1\, \mu_\text{B}/\text{f.u.}\) for \(a\) axis, and \(\sim 2.5\, \mu_\text{B}/\text{f.u.}\) for \(c\) axis which is obtained by an extrapolation considering the linear \((M)\) curve\(^{34}\), giving rise to the magnetic anisotropy to be \(M_{\text{ab}}/M_{\text{c}} \approx 1.7\) and \(M_{\text{ab}}/M_{\text{c}} \approx 3.4\). In Ref. 36, the \(M_{\text{b}}\) of bulk DMO was reported to be \(\sim 8.6\, \mu_\text{B}/\text{f.u.}\), leading to a slightly larger magnetic anisotropy \(M_{\text{b}}/M_{\text{c}} \approx 3.4\). Clearly, the magnetic anisotropy of bulk DMO is smaller than that of the thin films. Interestingly, a clear metamagnetic transition occurs around \(H = 1.5\, \text{T}\) below \(T_\text{R}\), marked by an arrow in Fig. 2(b), which was typically observed in bulk SSO multiferroic manganites and associated with the rare-earth moments\(^{30\sim 33}\). It is worthy of noting that such metamagnetic phase transition is always dependent on the SSO via the DM interaction, similar to the bulk counterparts\(^{34\sim 41}\). The SSO induced ferroelectric state is further attested by the well-shaped polarization-electric field (\(P-E\)) hysteresis loop, as shown in Fig. 3(c). Generally, in SSO multiferroics, the reversal of polarization from \(+ P_{\text{c}}\) to \(- P_{\text{c}}\) corresponds to the reversal of spin chirality (\(Q = S_x \times S_y\)) from clockwise \(Q_{-}\) (bc-) to counterclockwise \(Q_{+}\) (bc+) (or vice versa), marking the close link between magnetic and ferroelectric orders\(^{42}\).

Further cooling the film down to \(T \approx 12\, \text{K}\), both \(\varepsilon_c(T)\) and \(P_n(T)\) (red circles in Fig. 3(b)) abruptly decrease, indicating a possible transition between different magnetic configurations. Actually, similar features were also observed in bulk DMO, and a SSO to commensurate (CM) AFM phase transition of Dy moment was considered as the origin\(^{30\sim 35}\). In details, Dy moments form a SSO phase with the same propagation vector as the Mn magnetic lattice (\(Q = 2/3\) \(= 3\pi/6\,\text{rad}\)) at \(15\, \text{K} (\approx T_\text{c} \approx 18\, \text{K})\), due to the Dy-Mn spin interaction, and then make an additional contribution to \(P_n\). Further cooling causes a suppression of the Mn-promoted SSO of the Dy moment,
and a CM/AFM configuration with $t^{37\gamma} = 0.5b$ arises because of the dominance of the Dy-Dy interaction over the Dy-Mn spin coupling at $T < T_K^{31,33}$. As a consequence, abrupt decrease in $P_c$ and $e_c$ occurs, as observed in the $P_c(T)$ and $e_c(T)$ data of the film (Fig. 3(a) and (b)). Moreover, microscopic evidences revealed significant thermal hysteresis for the first order SSO-CM/AFM phase transition of Dy$_3$, which suggests a strong thermal history dependence of the microscopic process related to the emergence of FE polarization. To confirm this point, we polied the films using the same electric field down to 8 K (close to $T_K$), and then the polarization was collected by integrating the pyroelectric current. Remarkably different $P_c$ data evolving with $T$ for the two measuring processes were indeed obtained as shown in Fig. 3(b), indicating the important role of Dy moment to the improper ferroelectricity in the films.

To further explore the coupling between magnetic and ferroelectric orders, which in turn would be helpful for us to comprehensively understand the physics of multiferroicity in DMO thin films, we measure the $T$-dependent $e_c$ and $P_c$ under various magnetic fields. As displayed in Fig. 4, rather different magnetic responses of $e_c(T)$ and $P_c(T)$ can be identified when $H$ is applied along the $c$-axis or in the $ab$-plane. For $H//c$ axis, no substantial $H$ dependence in $P_c$ is seen although $T_C$ is slightly suppressed with increasing $H$. For $H//ab$ plane, remarkable enhancement in $P_c$ is observed, and a maximum value of $P_c(2T)/P_c(0T) \approx 9$ is estimated at $T = 2$ K. Correspondingly, the abrupt decrease in $e_c$ below 12 K, induced by the long range ordering of Dy moment, is significantly suppressed by $H//ab$ plane, indicating the essential role of Dy moment in mediating the FE polarization in the films. At $H > 5$ T, the FE phase transition in $e_c(T)$ becomes dispersive, and as a consequence $P_c$ is largely suppressed even in the temperature region $T > T_C$. It implies possible $P$-flopping due to the rotation of the $bc$-spiral to the $ab$-spiral caused by $H//ab$ plane.

In Fig. 5, the $H$ dependence of pyroelectric current $I$, $P_c$ and $e_c(H)/e_c(0)$ at $T = 2$ K are displayed. Distinct current peaks and valleys in
Fig. 5. Another striking feature is the dramatic increase in $I(H)$ signal the change (for example flopping or onset) in $P_c$ related to the variation of spin configuration induced by the magnetic field. Accordingly, we can roughly partition the data into three regions, namely, phase I ($H < 1.5$ T), phase II ($1.5$ T $< H < 4.5$ T), and phase III ($H > 4.5$ T). In phase I, the CM-AFM phase of Dy moment coexists with the SSO phase of Mn, and $P_c$ totally originates from the spirally ordered Mn sublattice, following the DM mechanism. Around $H \sim 1.5$ T, coinciding with the metamagnetic phase transition of Dy in $M(H)$ (Fig. 2(b)), the integrated FE polarization $P_c$ (in Fig. 5(b)) exhibits an abrupt increase, which is accompanied by anomaly in $e_c(H)$ (in Fig. 5(c)). It suggests the direct effect of the $H$ induced new magnetic orders of Dy on the ferroelectricity, while microscopic evidence is needed to determine whether it is the spiral spin order similar to the case in bulk DMO. In phase II, multicomponent magnetic structures coexist with each other, and $P_c$ reaches a plateau. As $H > 4.5$ T in phase III, $P_c$ is gradually suppressed and hysteresis anomaly can be observed in $e_c(H)$, likely indicating the magnetic field induced rotation of the $bc$-spiral ($P_c$) to the $ab$-spiral ($P_a$).

A key feature in Fig. 5 is the emergence of the new spin ordering phase of Dy around 1.5 T, which is accompanied by distinct enhancement in $P_c$. This feature implies dramatic change in the multiferroic domain structure, and thus leading us to expect a different ferroelectric switching behavior along with the phase transition of Dy. Fig. 6(a) shows the $P$-$E$ loops measured under $T = 5$ K and various magnetic fields, in which clear difference in the FE coercive field ($E_c$) can be observed besides the different polarizations upon increasing $H//ab$ plane. In Fig. 6(b), the $P_c$ and $E_c$ is plotted as a function of $H$. As expected, the $P_c$ shows a sudden increase around $H = 1.5$ T (corresponds to the metamagnetic phase transition of Dy moment), which is well consistent with the pyroelectric current data shown in Fig. 5. Another striking feature is the dramatic increase in $E_c$ around $H = 1.5$ T, which implies a higher energy cost in the ferroelectric switching (or chirality $Q$ switching). A sketch of energy diagram on the FE switching process is plotted in Fig. 6(c). It is clear that the reversal of chirality $Q$ from $Q_{a}(Q_{-a})$ to $Q_{-c}(Q_{c})$ should overcome the barrier coming from the energy difference $\Delta E$ between $Q_{a-c}$ ($bc$ spiral) and $Q_{-a-c}$ ($ab$ spiral)43. Therefore, the larger $E_c$ suggests a higher energy barrier between the $ab$ and $bc$ spirals (indicated by red dot line in Fig. 6(c)) caused by the emergence of Dy spin order.

**Discussion**

To this stage, we have demonstrated the magnetic ferroelectricity and ME coupling in DMO thin films. In qualitative sense, the DMO films do show similar physical properties to the bulk counterpart, including the anisotropic magnetism, the SSO phase induced ferroelectricity, and the magnetic field induced polarization enhancement$^{12-15}$. These similarities imply the similar physics of multiferroicity for both thin film and bulk DMO. The present work marks a successful copy of the bulk properties to the thin films for SSO multiferroic rare-earth manganites. In fact, contrast to the case of DMO thin films shown here, so far no ferroelectric polarization has been reported in earth manganites. In fact, contrast to the case of DMO thin films shown here, so far no ferroelectric polarization has been reported in earth manganites. Therefore, the SSO phase in TMO thin films can be sensitively influenced by perturbations...
such as strain, while the SSO phase in DMO thin films shows relatively high stability against the strain.

Even though the substantial similarity in those multiferroic behaviors between the DMO bulk and thin film, one still can identify several qualitative differences in these behaviors between them. First, for DMO thin films, the in-plane and out-of-plane magnetizations are different from those of the bulk as aforementioned, giving rise to a larger magnetic anisotropy

\[ M_{an} = M_{an} \sim 10 \] 

in the thin films. Based on the phase diagram and crystalline structure of perovskite manganites, we note that the $a/b$ ratio exhibits the same trend of evolution with the GdFeO$_3$-type distortion and the Jahn-Teller (JT) effect as the A-site rare-earth element is changed from La to Er, which means the larger $a/b$ value the smaller GdFeO$_3$-type distortion and JT effect$^{31-44}$. Therefore, the larger $a/b \sim 0.916$ in the DMO thin films implies the partial suppression of the JT and GdFeO$_3$-type distortion by the IP compressive strain, as compared with the bulk DMO in which the $a/b$ ratio is $0.905^{44}$. Consistently, the larger $a/b$ ratio accompanied by the suppression of the JT distortion was also reported for bulk DMO by synchrotron XRD experiments carried out under static pressure$^{45}$, which is analogous to the compressive strain in our thin films. Moreover, it is well known that the large JT and GdFeO$_3$-type distortion are responsible for the SSO phase in multiferroic manganites$^{9-12}$. Thus, the compressive strain suppressed JT and GdFeO$_3$-type distortion will weaken the spin-spirals (also the DM interaction) and give rise to a reduced $P_c$ ($\sim 31 \mu$C/cm$^2$ at 2 K and $H = 0$) in the thin films. From another perspective, according to the model of Mochizuki et al.$^{46-48}$, which can theoretically reproduce the phase diagram of orthorhombic multiferroic manganites, the DM interaction coexists and competes with the single-ion anisotropy in a way that the $bc$-spiral is favored by the former while the $ab$-spiral is stabilized by the latter. Because of the weakening of DM interaction by strain in the films, more pronounced magnetic anisotropy is thus anticipated, in comparison with the bulk counterpart. Indeed, the magnetism of both bulk and thin film manganites was revealed to well scale with the $a/b$ value$^{45}$, which further confirms our explanation on the strain mediated magnetic anisotropy in the DMO thin films.

Besides the magnetic anisotropy, an enhancement in $P_c$, ($P_c(2T)/P_c(0T) \sim 9$ at $T = 2$ K) is observed in the DMO thin films, as shown in Fig. 4(d), which is larger than that ($P_c(2T)/P_c(0T) \sim 3$ at $T = 2$ K) in the bulk counterpart$^{25}$. On one hand, because of the large magnetic anisotropy in the DMO thin films, the possible Dy-spiral phase indeed deserves further microscopic characterization. On the other hand, the above outlined experimental results reveal direct effect of Dy moment on the ferroelectric polarization, which signals the Dy-Mn spin interaction and thus leads us to argue a coherence of spin configurations for Dy and Mn. In fact, the coherence of R and Mn was extensively identified in multiferroic RMnO$_3$ (R = Tb, Dy, Ho) due to the R-Mn spin interaction$^{31,35,37-48}$. Such magnetic structure meets well the configuration of symmetric magnetostriiction effect$^{39-45}$, that is, each Dy spin chain is sandwiched by two antiferromagnetically coupled Mn spiral spin chains with the same propagation vector. The stacking of the magnetic orders is along the $c$ axis, and the Dy orders would displace cooperatively toward (away) the Mn orders with antiparallel (parallel) spins via the symmetric magnetostriiction effect and, as a consequence, polarization along the $c$ axis would be generated, as sketched in Fig. 7(a). Actually, the symmetric magnetostriiction effect was proposed as the origin of the polarization enhancement in bulk DMO before the Dy-spiral phase was demonstrated experimentally$^{25}$. Moreover, the symmetric magnetostriiction effect between coherent Dy and Mn magnetic orders would also be expected in bulk DMO which has Dy-spiral phase exhibiting the same propagation vector with Mn SSO, as shown in Fig. 7(b). However, the different magnetic anisotropies for thin film and bulk DMO would induce different magnetostriiction effects on the polarization, which is the possible origin of the $H$-induced enhancement in $P_c$ shown in the present work.

Figure 7 | Sketch of the coherence of magnetic configurations for Dy and Mn spins. (a) the magnetic order of Dy just has the same propagation vector as Mn-spiral phase. (b) Dy has a spiral spin ordering as Mn spins. The both configurations meet the magnetic structure of symmetric magnetostriiction effect, and thus possibly leading polarization ($P_c$) along $c$ axis due to the uniform displacement of Dy.

In summary, multiferroic DyMnO$_3$ thin films are epitaxially grown on Nb-SrTiO$_3$ (001) substrates, and intensively characterized. Our results reveal intriguing multiferroicity in DMO thin film, including i) large magnetic anisotropy

\[ M_{an} = M_{an} \sim 10 \] 

below $T_S$, which is induced by the compressive strain suppressed GdFeO$_3$-type distortion and Jahn-Teller effect in the thin films; ii) large enhancement in $P_c$ ($\sim 800\%$ at $T = 2$ K) and FE coercive field $E_c$, which was proposed to be understood by interacting magnetic structures. Our work shows a successful copy of the spiral spin ordering induced multiferroicity from the bulk to thin films, which opens the possibility to integrate such materials into functional devices.

**Methods**

Pure phase DMO thin films with thickness $t = 300$ nm were epitaxially deposited on (001) Nd-SrTiO$_3$ (NSTO) substrates using pulsed laser deposition (PLD) at 800°C in 0.2 mbar oxygen. KrF excimer laser ($l = 248$ nm) was used with an energy density of $\sim 1 \text{J/cm}^2$. After the growth, the samples were cooled to room temperature in 400 mbar oxygen ambient at a rate of 5°C/minute. Conducting NSTO substrates were used as both growth templates and bottom electrodes. Detailed crystalline structure investigations, including the normal $\theta$-2$\theta$ scan, rocking curve, and the asymmetric reciprocal space mapping, were carried out using a high resolution X-ray diffraction system (Panalytical X-pert Pro). The surface morphology of the film was probed using tapping mode atomic force microscope (Digital Instrument).

Magnetization as a function of $T$ and magnetic field ($H$) was measured using a Magnetic Properties Measurement System (MPMS, Quantum Design). The cooling and measuring field during the $M(T)$ measurements was fixed at 0.1 T. To obtain the FE polarization along the $c$ axis, $P_c$ of the films, square Au top electrodes of 300 $\mu$m in diameter were prepared on the film surface, and the pyroelectric current method was used to probe the polarization. For each measurement, the sample was first cooled from 60 to 2 K under a poling electric field of 100 kV/cm. Then, the poling electric field was turned off and the sample was short-circuited for a sufficient period of time to release the charges accumulated on the sample. The pyroelectric current was measured using a Keithley 6514A electrometer during the heating process with a constant ramping rate (2 K/min to 5 K/min). For the pyroelectric current measurements under a magnetic field, $H$ was applied during the poling and the subsequent measuring processes. The ferroelectric hysteresis loops were measured using the positive-up-negative-down (PUND) method (TF Analyzer 2000 from AixACCT Co), and the frequency was set as 100 Hz. The dielectric susceptibility $\varepsilon_r$ of the sample with the same device structure was measured using a HP4294A impedance analyzer. The
crysogenic environment and the magnetic field during the pyroelectric current and dielectric susceptibility measurements were provided by a Physical Properties Measurement System (PPMS, Quantum Design).

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Author contributions
C.L.L. and T.W. conceived and designed the experiments. C.L.L. and Z.B.Y. carried out the experiments. C.L.L., S.D., T.W. and J.M.L. wrote the paper. Z.C.X., H.L., H.W.W., Z.M.T. and S.L.Y. reviewed and commented on the paper. All the authors discussed the results and commented on the manuscript.

Additional information
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