Electronic Supplementary Information

Electric field control of magnetism through modulating phase separation in (011) - $Nd_{0.5}Sr_{0.5}MnO_3$/PMN-PT heterostructures

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S1. The bright field image of NSMO/PMN-PT

Fig. S1 shows the bright field image of NSMO/PMN-PT obtained from [100] zone axis. The area for obtaining the selected area electronic diffraction (SAED) patterns is illustrated by the red circle. The film thickness obtained is 65 nm.

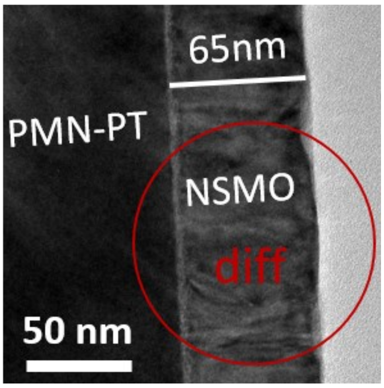

Fig. S1 Bright field TEM images of NSMO/PMN-PT from the [100] zone axis, the circles present the areas where the SAED patterns in Fig. 1(c) was taken.

S2. The *M-T* curves measured with −6 kV cm^{-1} electric field (*E*) applied along the [100] direction

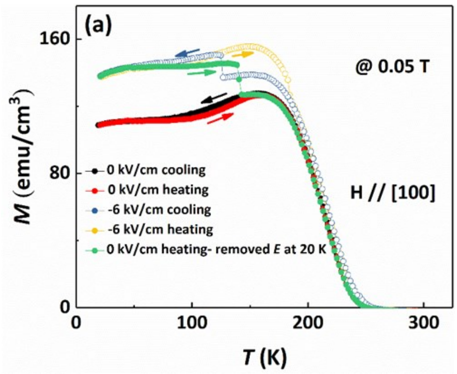

Fig. S2 *M-T* curves measured along in-plane [100] directions with 0 kV cm^{-1} and – 6 kV cm^{-1} *E* applied, as well as field heating runs at 0 kV cm^{-1} after withdrawing *E* at the lowest measuring temperature of 20 K.

The sample was first poled with *E* of −6 kV cm^{-1} at room temperature, then with −6 kV cm^{-1} *E* applied, the field cooling and field heating runs along [100] direction were measured in 0.05 T magnetic field. As shown in Fig. S2, compared to 0 kV cm^{-1} curves, the magnetizations increase from T_C, and shows a sudden increase around 120 K. Besides, when removing −6 kV cm^{-1} at 20 K, the magnetization does not recover to 0 kV cm^{-1} plot, demonstrating non-volatile memory effect. The magnetization curves under −6 kV cm^{-1} *E* show similar behaviors with that obtained under +6 kV cm^{-1} E, which is consistent with the room temperature strain curves in which the bipolar $\pm$ 6 kV cm^{-1} electric fields cause symmetric strain states.

S3. The *M-H* curves along [01$\bar{1}$] direction measured after the sample was cooled with +6 kV cm^{-1} *E* applied from room temperatures

The sample was firstly cooled to the target temperatures with 0 kV cm^{-1} (black plot) and +6 kV cm^{-1} (red plot) applied from room temperature respectively, then the *M-H* curves along [01$\bar{1}$] direction were measured with the respective 0 kV cm^{-1} and +6 kV cm^{-1} E applied. Besides, after finishing measurement of *M-H* curve with +6 kV cm^{-1}, the +6 kV cm^{-1} E was in-situ removed and another *M-H* curve at 0 kV cm^{-1} (yellow plot) was subsequently measured. The curves at different temperatures are shown in Fig. S3, it is seen the pre-applied +6 kV E increases the magnetizations, and there exists memory effect below 70 K, meaning the magnetization along the [01$\bar{1}$] direction exhibits similar response with that along [100] direction to the pre-applied electric field. These facts further demonstrate that the E control of magnetization was mainly realized through manipulating phase separation in NSMO film.

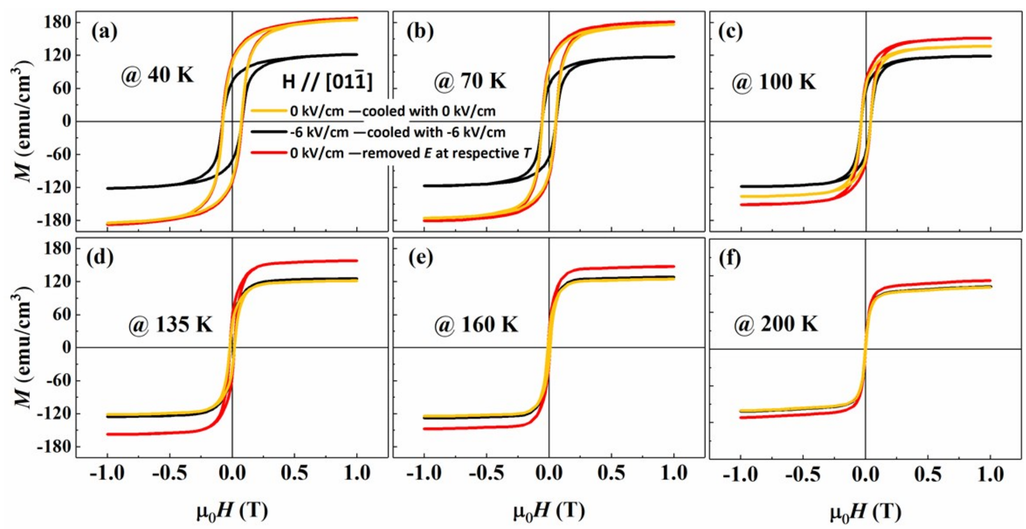

Fig. S3 The *M-H* curves at 0 kV cm^{-1} after cooling with 0 kV cm^{-1} (black curves), at +6 kV cm^{-1} after cooling with +6 kV cm^{-1} from 300 K (red curves), as well as the one measured at 0 kV cm^{-1} after removing +6 kV cm^{-1} E (yellow curves) at respective temperatures of 40 K (a), 70 K (b), 100 K (c), 135 K (d), 160 K (e), and 200 K (f).

S4. (022)-XRD peaks of PMN-PT with cycling E from +6 kV cm^{-1} to −6 kV cm^{-1}.

Figure S4 (a) shows the original (022)-XRD peaks of PMN-PT measured with cycling E from +6 kV cm^{-1} to −6 kV cm^{-1}, the profiles were fitted and the Cu Kα_1 and Cu Kα_2 components were distinguished. Fig. S4(b) illustrates the fitting details of three typical profiles measured with +6 kV cm^{-1}, +2 kV cm^{-1} and 0 kV cm^{-1} E applied. In which, the black curves are the original profiles, the red curves are the fitted ones, the solid lines correspond to peaks from Cu Kα_1 X-ray, and the dashed lines correspond to the peaks from Cu Kα_2 components. In order to give an intuitive presentation of the structural evolution of PMN-PT with cycling electric field,

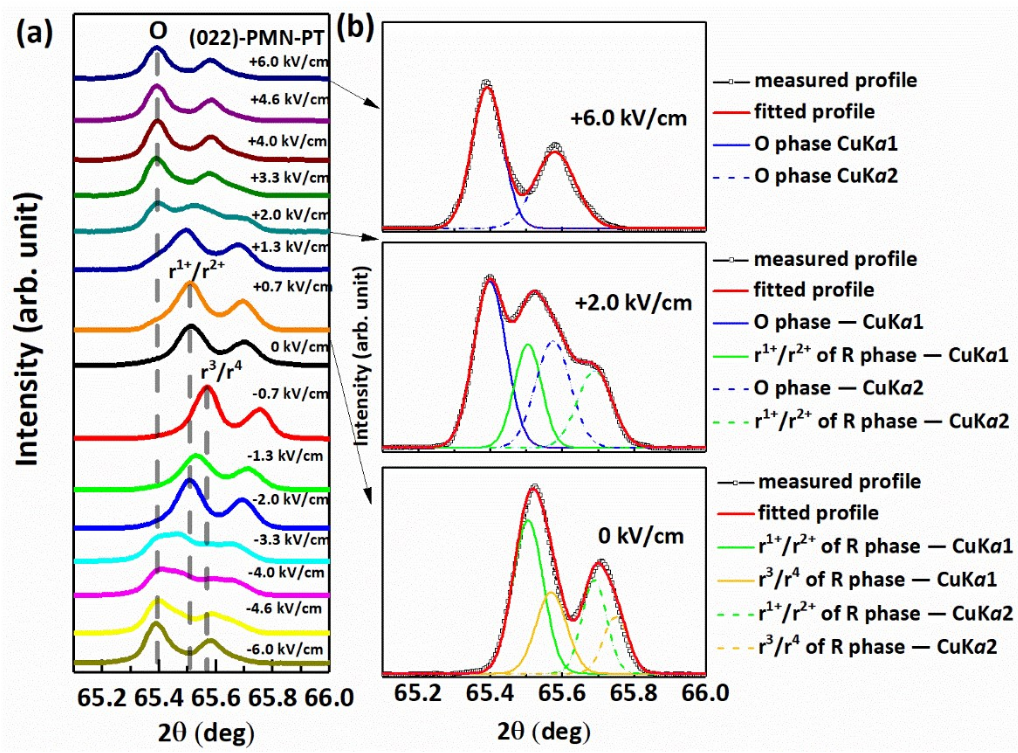

Fig. 5(b) in the main article only illustrates the Cu Kα_1 components.

Fig. S4 The measured (022) – XRD peaks of PMN-PT with cycling electric fields (a) and the detailed fitting process of the profiles measured at +6 kV cm^{-1}, +2 kV cm^{-1} and 0 kV cm^{-1} E (b). The solid lines in (b) are the diffractions from Cu Kα_1 X-ray, and the dashed lines are the diffractions from Cu Kα_2 X-ray. The black lines are the measured data, the red lines are the fitted curves, the blue lines belong to orthorhombic (O) phase, the green and yellow ones belong to the and r^{1+}/r^{2+}, r^3/r^4 polarizations of rhombohedral (R) phase respectively in PMN-PT.

S5. The (011)-XRD peaks evolution with cycling *E* for NSMO/PMN-PT

Fig. S5 demonstrates the evolution of (011)-XRD peaks of both NSMO film and PMN-PT substrate (Cu Ka_1 and Cu Ka_1 components) with cycling electric fields, obviously NSMO film peak shows similar evolution with that of PMN-PT substrate under electric fields, which means that the strain induced in PMN-PT can dynamically transfer to NSMO film.

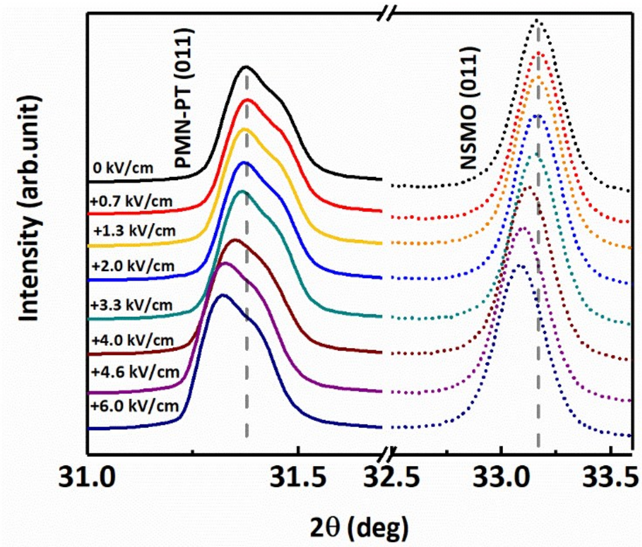

Fig. S5 The measured (011)-XRD peaks with cycling electric fields for PMN-PT (solid lines) and NSMO film (dashed lines), where the gray vertical lines give guidance to the peak position of 0 kV cm^{-1}.

S6. The *M-H* curves measured with different *E* after cooling firstly without electric field

To further study the *E* control of magnetization in NSMO/PMN-PT, the *M-H* curves were measured in another mode: the sample was firstly cooled to the target temperatures from room temperature without *E*, and the *M-H* curves were measured under 0 kV cm^{-1} (black curve), following which, +6 kV cm^{-1} (red) was applied and the *M-H* curves were measured, subsequently, the +6 kV cm^{-1} *E* was removed and *M-H* curves were measured at 0 kV cm^{-1} (yellow), finally the −6 kV cm^{-1} *E* was applied and the *M-H* curves were measured (blue). The measured curves at 150 K, 100 K, 70 K and 40 K along both [100] and [01$\bar{1}$] directions are displayed in Fig. S6. It can be identified that, for both the [100] and [01$\bar{1}$] directions, the magnetization decreases for +6 kV cm^{-1} and increase for −6 kV cm^{-1}. This behavior indicates that under this case, the *E* can also modulate phase separation in NSMO/PMN-PT films. Moreover, the magnetization responses to *E* are quite different from the measurement procedure where the *M-H* curves were measured with *E* pre-applied from room temperature during the cooling process: 1) the magnetization decreases under +6 kV cm^{-1} and increases under –6 kV cm^{-1}; 2) the E induced change of magnetization maximizes at 100 K, and then reduces with further decreasing temperature, and finally reaches almost 0 disappears at 40 K.

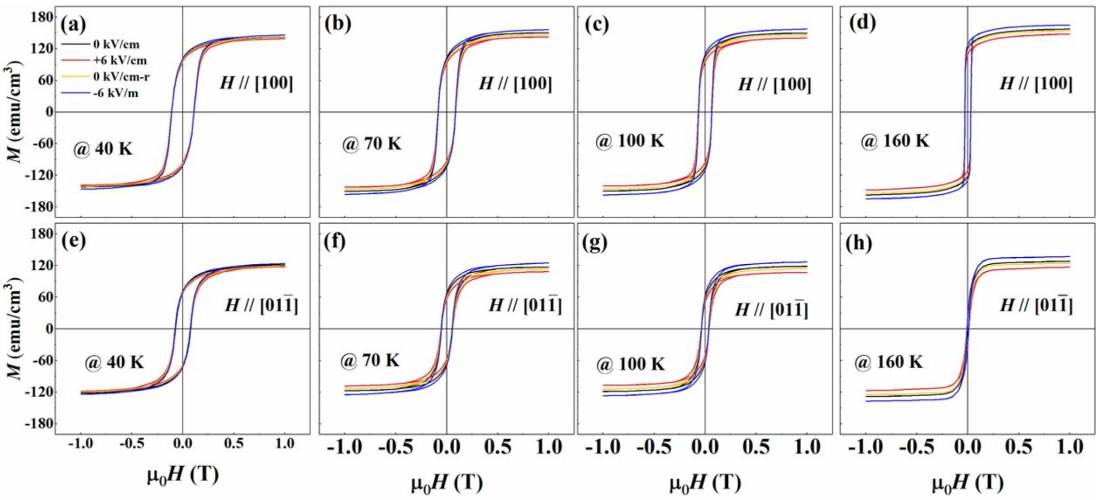

Fig. S6 *M-H* curves measured along [100] direction after cooling the sample without E to target temperature of 40 K (a), 70 K (b), 100 K (c) and 160 K (d), and along [01$\bar{1}$] direction after cooling the sample without E to target temperature to 40 K (a), 70 K (b), 100 K (c) and 160 K (d). Where black loops were measured at 0 kV cm^{-1}, red loops were measured at +6 kV cm^{-1} following the measurement at 0 kV cm^{-1}, yellow loops named 0 kV cm^{-1}-r were measured at 0 kV cm^{-1} after removing +6 kV cm^{-1} E and the blue loops were measured at −6 kV cm^{-1} following 0 kV cm^{-1}-r curves.

In order to clarify this different behavior, the strain versus E curves at different temperatures after cooling the sample to the target temperature without E were further measured (as shown in Fig. S7). The strain curves at 280 K shown in Fig. S7(a) and (e) denote that the coercive E increases compared to the one at 300 K. At 250 K [Fig. S7(b) and (f)], the strain curves along in-plane [100] and [01$\bar{1}$] directions show butterfly shape, which is consistent with the ones obtained from the poling process of the R phase at room temperature [S1], denoting that ± 6 kV cm^{-1} E cannot intrigue the R-O phase transition in PMN-PT. This strain-E behavior is consistent with the previous reports [S2] that lowering temperature causes the reduction of thermal agitation and the increase of the coercive field for the phase transition and domain switching of PMN-PT [S2]. Further lowering the temperature without E, at 200 K and 150 K, the driving E of ± 6 kV cm^{-1} can only rotate a portion of ferroelectric domains of R phase, which results to the loop like strain curve, with the +6 kV cm^{-1} E induces tensile strain while the −6 kV cm^{-1} E induces compressive tensile strain along the [100] direction, and the strain reduces largely compared to the ones at room temperature. Though the strain curves at temperatures lower than 150 K were not accessible due to the limitation from the strain gauge, it can be reasonably assumed that the strain will further decrease with lowering temperatures.

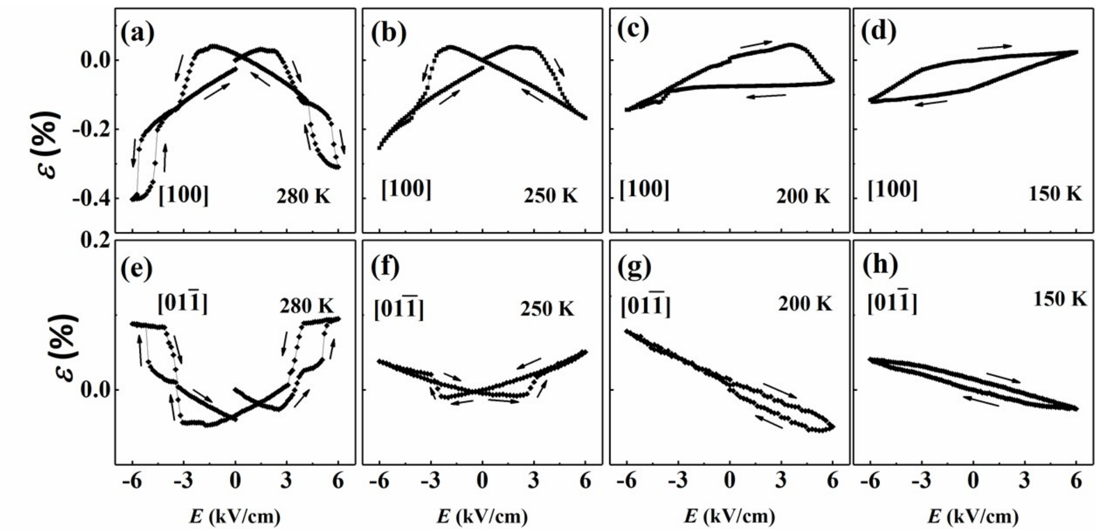

Fig. S7 Strain versus E curves measured along [100] direction after cooling the sample without E to target temperature to 280 K (a), 250 K (b), 200 K (c) and 150 K (d), and along [01$\bar{1}$] direction after cooling the sample without E to target temperature to 280 K (e), 250 K (f), 200 K (g) and 150 K (h).

The mechanism of E control of magnetization under this measuring mode can then be understood combining the strain behavior of PMN-PT substrate. Taking the 150 K case as an example, after cooling without E, the film has partially gets into the COO AFM states, at this state, the applied +6 kV cm^{-1} E will introduce tensile strain along [100] direction, which will exaggerate the anisotropic strain of NSMO film, and favor the COO AFM state, thus reducing magnetization along both [100] and [01$\bar{1}$] directions; on the contrary, the –6 kV cm^{-1} E introduce compressive strain along [100] direction, and causes the enhancement of magnetization. At lower temperatures, the E hardly induces strain in PMN-PT, and the controlling effect of magnetization becomes weak; when the temperature was lowered to 40 K, the electric manipulation of magnetization almost disappears. These results demonstrate that the E control of magnetization under this mode can also be ascribed to the strain mediated phase separation of NSMO film.

Reference:

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[S2] H. Wang, T. Matsunaga, H. T. Lin, A. M. Mottern, Smart Mater. Struct., 2012, 21, 025009.