Supporting Information

Thermal treatment effects on PMN-$_{0.4}$PT/Fe multiferroic heterostructures

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PMN-$_{0.4}$PT polarization switching

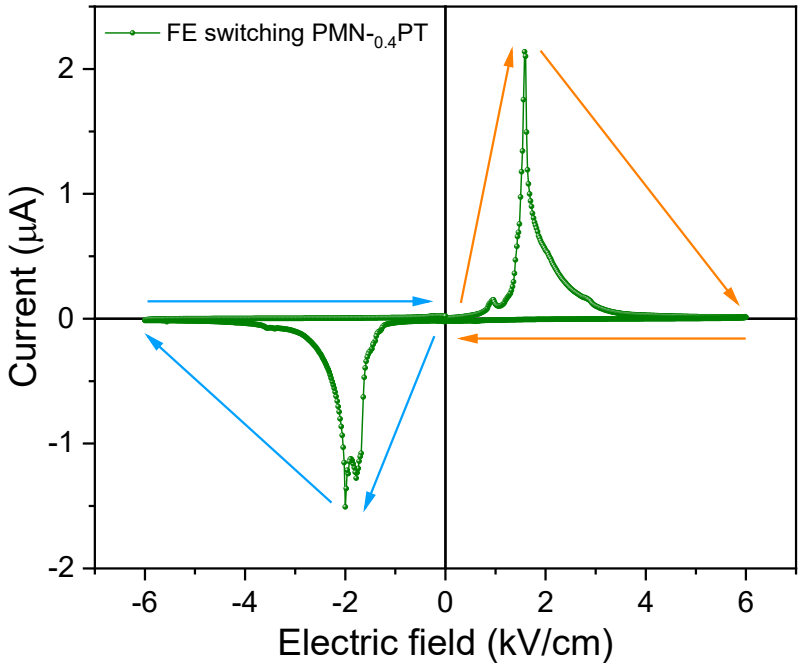

Figure S1: I(E) curve of PMN-$_{0.4}$PT (001) heterostructure, showing ferroelectric transitions around ±2 kV cm^{-1}.

To confirm the ferroelectric behavior of PMN-$_{0.4}$PT substrate, I(E) curves was recorded by applying an electric field up to ±6 kV cm^{-1} through the thickness of the substrate, sweeping the field along the [001] crystallographic direction from -6 to +6 kV cm^{-1} and then back to zero (**Figure S1**). Stable FE transitions were recorded around ±2 kV cm^{-1}, consistently with what previously reported by our group on similar substrates.[1,2]

XRD characterization

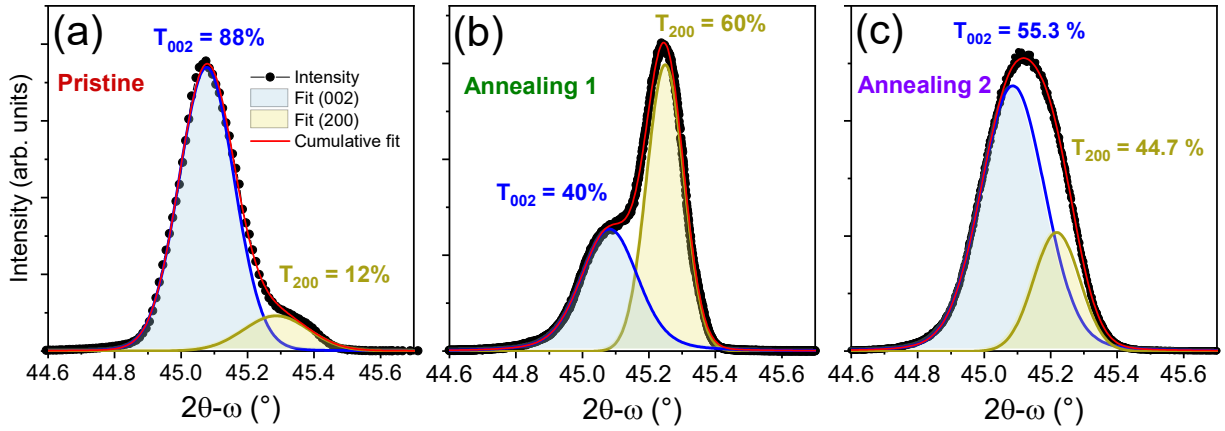

Figure S2: **(a-c)** XRD 2θ-ω scans for pristine and after the two thermal treatments of PMN-$_{0.4}$PT/Fe heterostructure, with relative fittings of the (002) and (200)/(020) contributions for the three cases.

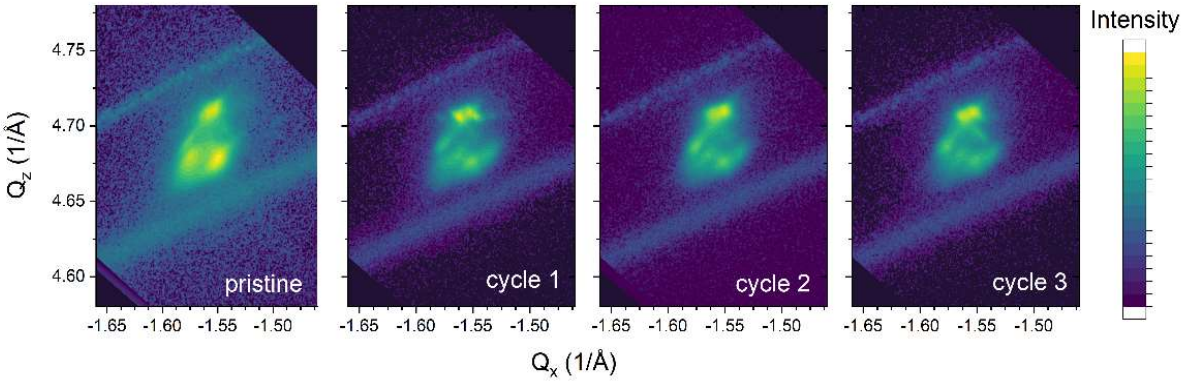

Figure S3: 2D RSMs of a PMN-$_{0.4}$PT crystal in pristine and after different thermal cycles in "annealing 1" condition.

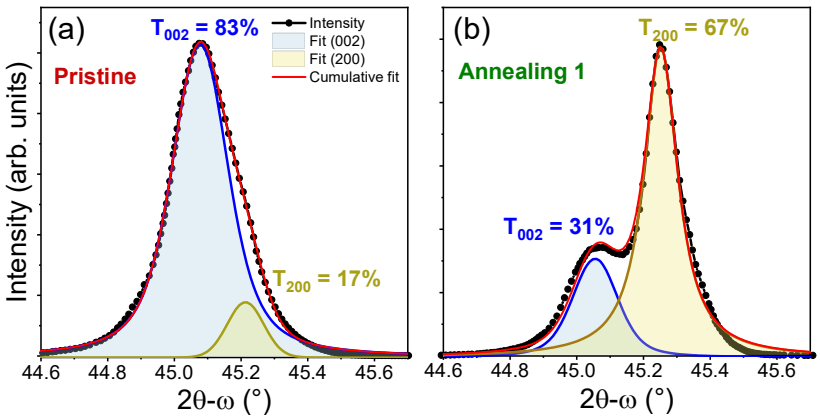

Figure S4: XRD 2θ-ω scans of pristine unannealed and after the first thermal treatment of PMN-$_{0.4}$PT/Fe heterostructure used for Raman characterizations.

XRD symmetric 2θ-ω scans were taken on PMN-$_{0.4}$PT/Fe heterostructure, as shown in **(Figure S2 and S4)**, on which the same phase analysis was repeated. A similar evolution of the ratios between the in-plane and out-of-plane domains was observed as a function of the thermal annealing treatments, proving both a good reproducibility of the process in terms of modification of the structural properties of PMN-$_{0.4}$PT substrate and a negligible role played by the interfacial layer.

micro-Raman characterization

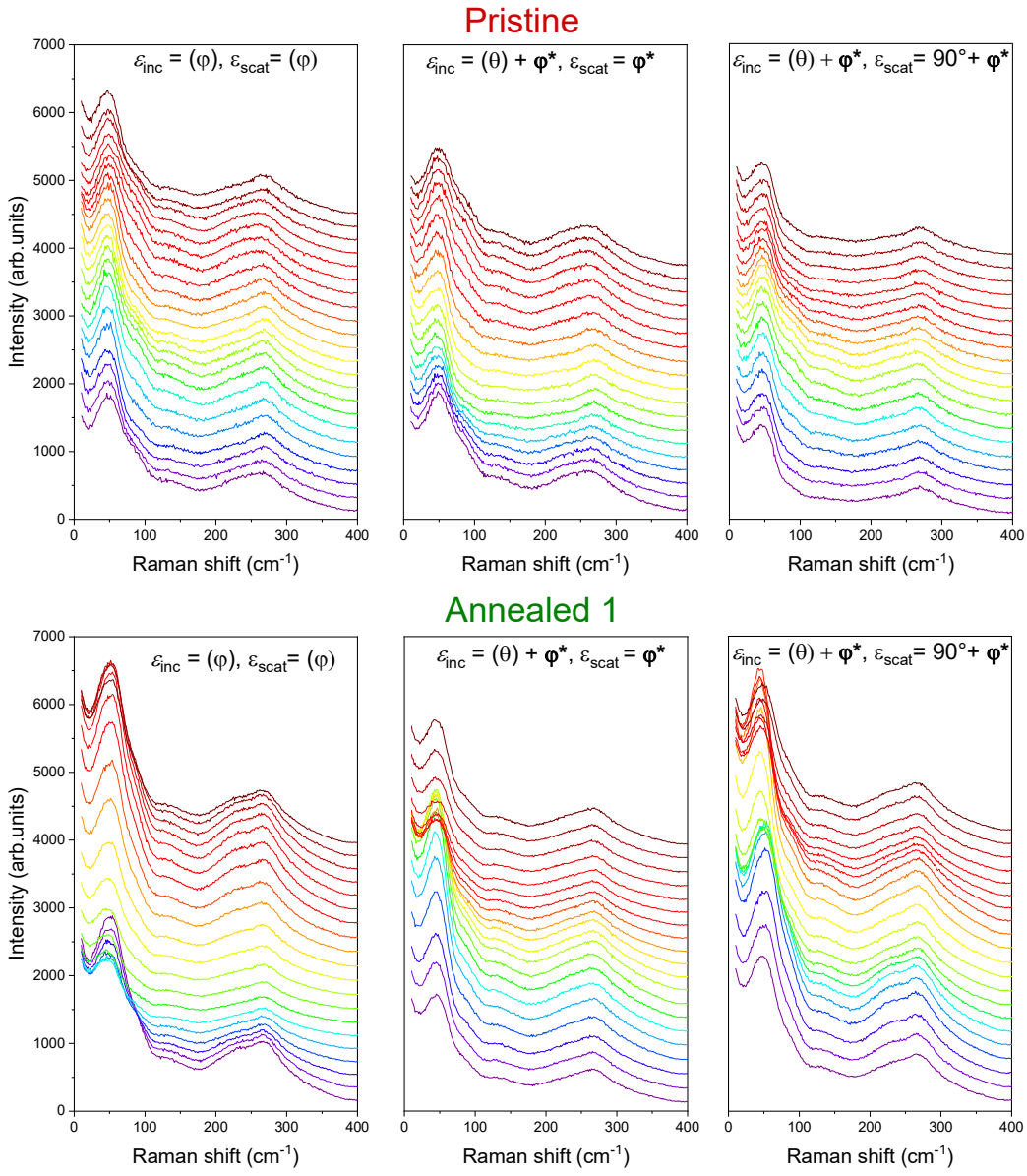

Figure S5: Polarization dependent Raman spectra of PMN-$_{0.4}$PT/Fe heterostructure in the three polarization configurations for pristine unannealed and annealed 1 case. Polarization notation as in Figure 4 of the main text.

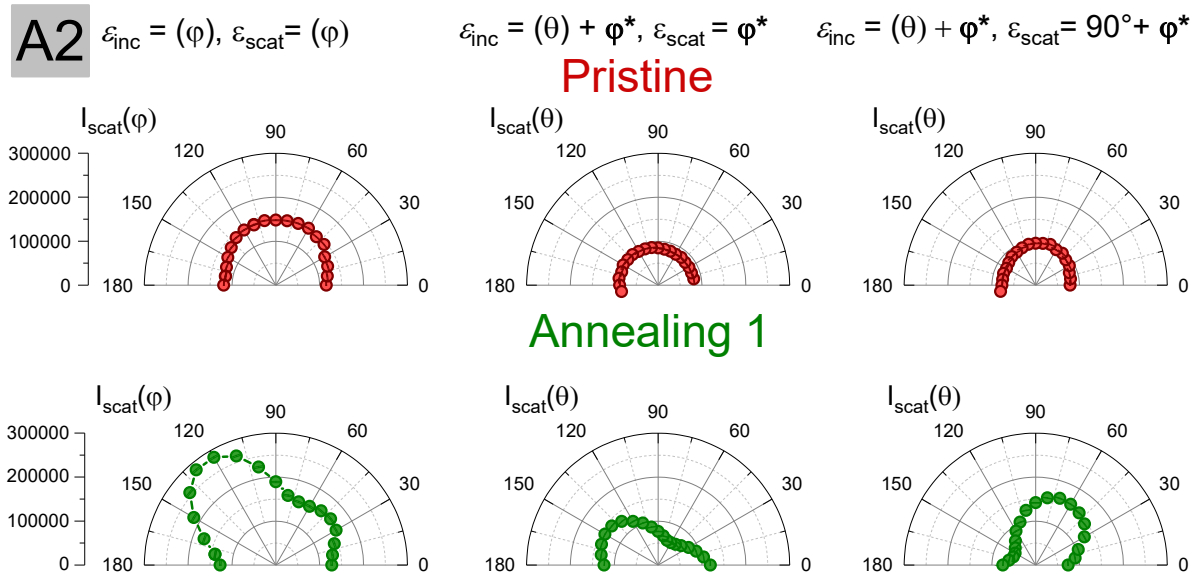

Figure S6: Polar plots of the **A2** Raman mode intensity acquired on PMN-$_{0.4}$PT/Fe (001) heterostructures (pristine and annealed 1) in the three polarization configurations indicated above.

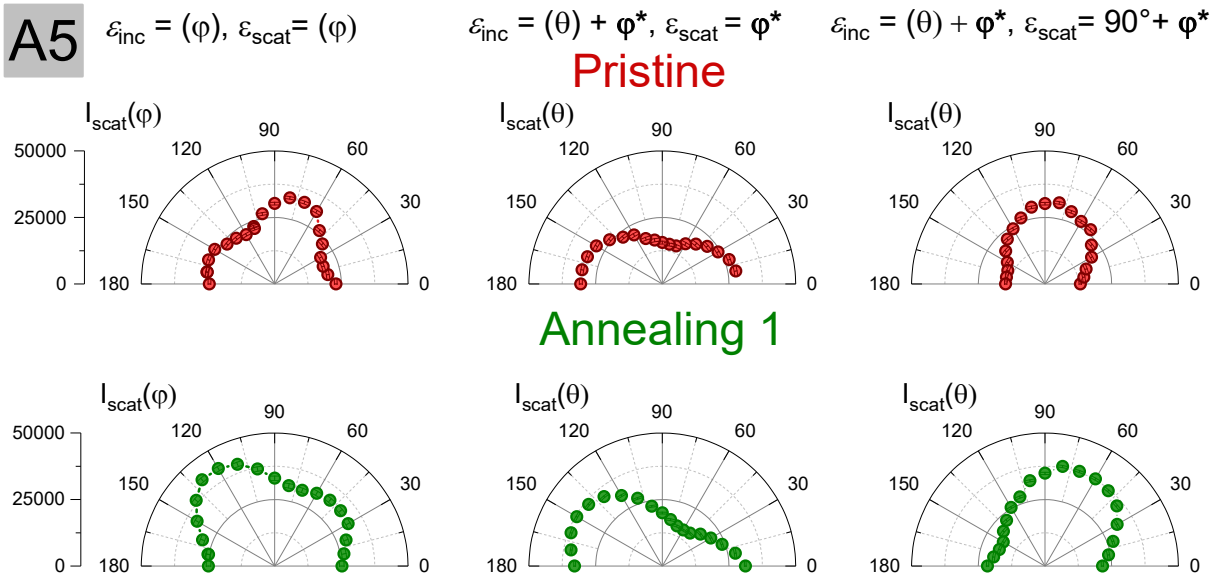

Figure S7: Polar plots of the **A5** Raman mode intensity acquired on PMN-$_{0.4}$PT/Fe (001) heterostructures (pristine and annealed 1) in the three polarization configurations indicated above.

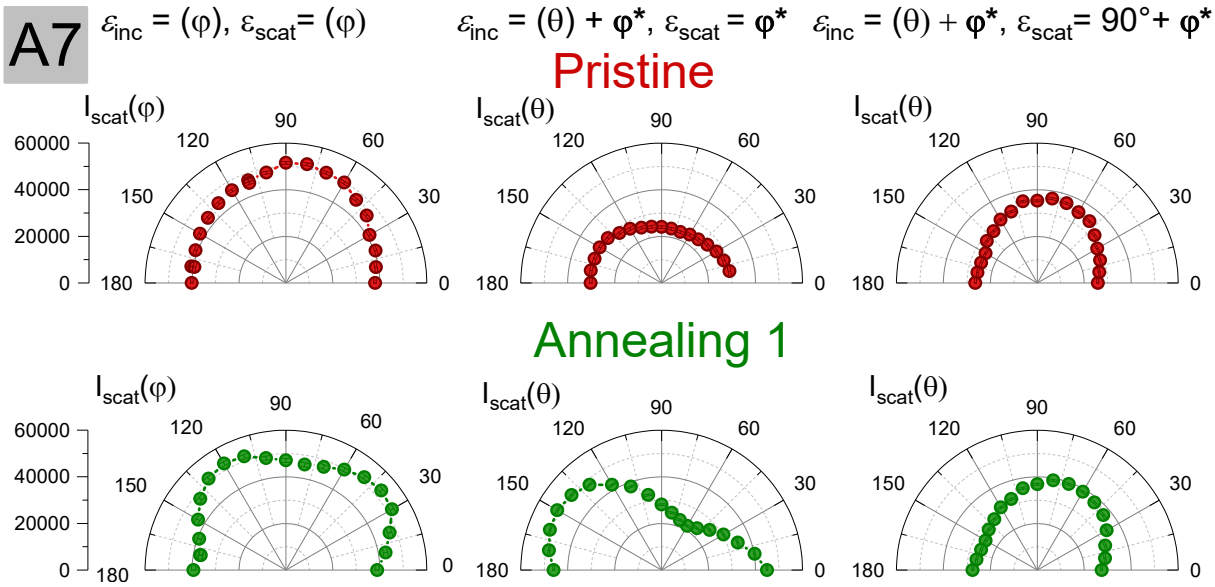

Figure S8: Polar plots of the **A7** Raman mode intensity acquired on PMN-$_{0.4}$PT/Fe (001) heterostructures (pristine and annealed 1) in the three polarization configurations indicated above.

MOKE characterization

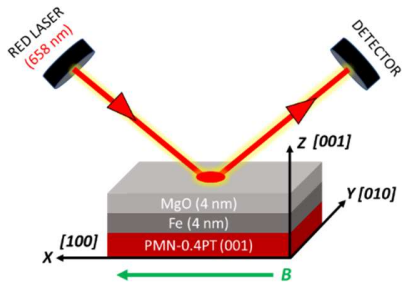

Figure S9: Schematic representation of the PMN-$_{0.4}$PT/Fe heterostructure and experimental setup of longitudinal MOKE. A He-Ne laser of 658 nm wavelength was used.

Figure S9 shows the sample stack of the PMN-$_{0.4}$PT/Fe heterostructure and the schematics of the setup used for longitudinal MOKE measurements. The magnetic hysteresis loops and polar plots were measured by applying an in-plane magnetic field with respect to the surface of the sample. The angle convention used for the polar plots assigns 0° for *B* along [010] PMN-PT direction and 90° along [100]. An example of polar plots and angle dependent MOKE measurement is shown in **Figure S10** for PMN-$_{0.4}$PT/Fe sample after annealing 1 procedure.

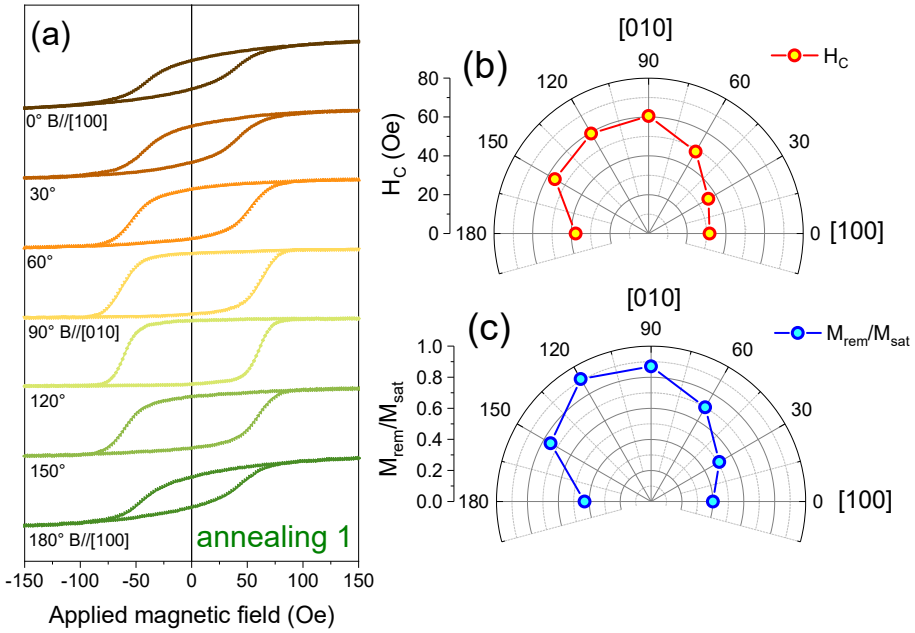

Figure S10: (a) angle dependent hysteresis loops of PMN-$_{0.4}$PT/Fe heterostructure after annealing 1, with the corresponding polar plots of **(b)** coercive field and **(c)** magnetic remanence.

References

(1) Vinai, G.; Motti, F.; Bonanni, V.; Petrov, A. Y.; Benedetti, S.; Rinaldi, C.; Stella, M.; Cassese, D.; Prato, S.; Cantoni, M.; Rossi, G.; Panaccione, G.; Torelli, P. Reversible Modification of Ferromagnetism through Electrically Controlled Morphology *Adv. Electron. Mater.* **2019**, *5* (7), 1900150.

(2) Motti, F.; Vinai, G.; Bonanni, V.; Polewczyk, V.; Mantegazza, P.; Forrest, T.; Maccherozzi, F.; Benedetti, S.; Rinaldi, C.; Cantoni, M.; Cassese, D.; Prato, S.; Dhesi, S. S.; Rossi, G.; Panaccione, G.; Torelli, P. Interplay between Morphology and Magnetoelectric Coupling in Fe/PMN-PT Multiferroic Heterostructures Studied by Microscopy Techniques *Phys. Rev. Mater.* **2020**, *4* (11), 114418.