Electronic supplementary information (ESI)

Title: Artificially induced normal ferroelectric behaviour in aerosol deposited relaxor 65PMN-35PT thick films by interface engineering

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[#]Author Contributions: A. Thakre and A. Kumar contributed equally to this work.

Sc1: Calculations of the dielectric parameters ΔT_m, T_{cw}, and γ with equations.

Sc2: Calculations of the electric field distribution across each capacitor.

Supplementary figures:

Fig. S1: Atomic force microscopy images (5 μm x 5 μm) of the (a) bare 65PMN-35PT/Pt/Si thick films and with an Al_2O_3 dielectric layer thickness of (b) 20 nm (c) 50 nm and (d) 100 nm.

Fig. S2: Frequency-dependent impedance spectra for Pt/Al_2O_3/65PMN-35PT/Pt/Si heterostructure with varying the thickness of the dielectric Al_2O_3 layer.

Fig. S3: Temperature-dependent dielectric response of the (a) bare 65PMN-35PT/Pt/Si thick films and with an Al_2O_3 dielectric layer thickness of (b) 20 nm (c) 50 nm and (d) 100 nm, measured at different frequencies. Arrow direction in the figures (a) and (d) shows the frequency-dependent (RFE) and frequency-independent (FE) dielectric maxima temperature.

Fig. S4: Reciprocal of the dielectric constant w.r.t. temperature for the (a) bare 65PMN-35PT/Pt/Si thick films and with an Al_2O_3 dielectric layer thickness of (b) 20 nm (c) 50 nm and (d) 100 nm.

Fig. S5: Al_2O_3 thickness-dependent remnant polarisation and the coercive electric field of AD thick films of 65PMN-35PT material measured at 900 kV/cm.

Sc1: Calculations of the dielectric parameters ΔT_m, T_{cw}, and γ with equations

The degree of deviation from the Curie-Weiss law (ΔT_m) can be calculated from the Eq. 1,

$$\Delta T_m = T_{cw} - T_m \tag{1}$$

where T_{cw} denotes the temperature in the reciprocal of dielectric constant *vs*. temperature graphs (Fig. S4) from which permittivity starts to deviate from the Curie-Weiss law and T_m is the dielectric maxima temperature.

The degree of diffuseness (γ) in the dielectric peak can be calculated by a modified empirical expression (Eq. 2)

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{max}} = \frac{(T - T_{\varepsilon max})^{\gamma}}{C_1} \tag{2}$$

where ε and ε_{max} are the dielectric constants at temperature T ($T > T_m$) and T_m, respectively. C_1 is a Curie like constant. The parameter γ was calculated from the linear curve fit, $ln(1/\varepsilon - 1/\varepsilon_{max})$ vs. $ln(T - T_m)$ where γ represents the slope of the curve (Fig 4(c)). For $\gamma = 1$, normal Curie-Weiss behavior (sharp peak in ε *vs*. T curve), $\gamma = 2$ complete relaxor type phase transition (broad peak in ε *vs*. T curve).

Sc2: Calculations of the electric field distribution across each capacitor.

The effective capacitance (C_{eff}) of the heterostructure is the series combination of the capacitances from Al_2O_3 layer and PMN-PT film. Since the current flowing through each individual capacitance is same, the amount of stored charge will be the same in each capacitor irrespective of the value of each capacitance. However, the electric field across each capacitor will be different according to their value of capacitance.

As the electric field across each capacitor can be expressed as;

$$E_{C_{Al2O3}} = E_S \cdot \frac{C_{eff}}{C_{Al2O3}} \tag{3}$$

$$E_{C_{PMN-PT}} = E_S \cdot \frac{C_{eff}}{C_{PMN-PT}} \tag{4}$$

where, E_{CAl2O3} and $E_{CPMN-PT}$ are the electric fields across the capacitances *i.e.* C_{Al2O3} and C_{PMN-PT} due to Al_2O_3 and PMN-PT layers respectively, and E_s (Electric field ≈ 900 kV/cm) is the voltage across the heterostructure.

The measured capacitance of the PMN-PT (C_{PMN-PT}) was 67 pF and the measured effective capacitances of the heterostructures were 49 pF, 35 pF and 19 pF for the Al_2O_3 layer thickness 20 nm, 50 nm, and 100 nm; respectively. The calculated capacitances of the Al_2O_3 layer with varied thickness are 186 pF, 74 pF, and 26 pF for 20 nm, 50 nm and 100 nm; respectively. From the Eq. 3 and Eq. 4, the calculated electric field across Al_2O_3 and PMN-PT layers in the heterostructure are as below.

S.N.	**Al_2O_3 thickness**	C_{eff} (pF)	C_{PMN-PT} (pF)	C_{Al2O3} (pF)	E_{CAl2O3} (kV/cm)	$E_{CPMN-PT}$ (kV/cm)
1.	0	67	67	-	-	900
2.	20	49	67	186	236	659
3.	50	35	67	74	425	470
4.	100	19	67	26	644	250

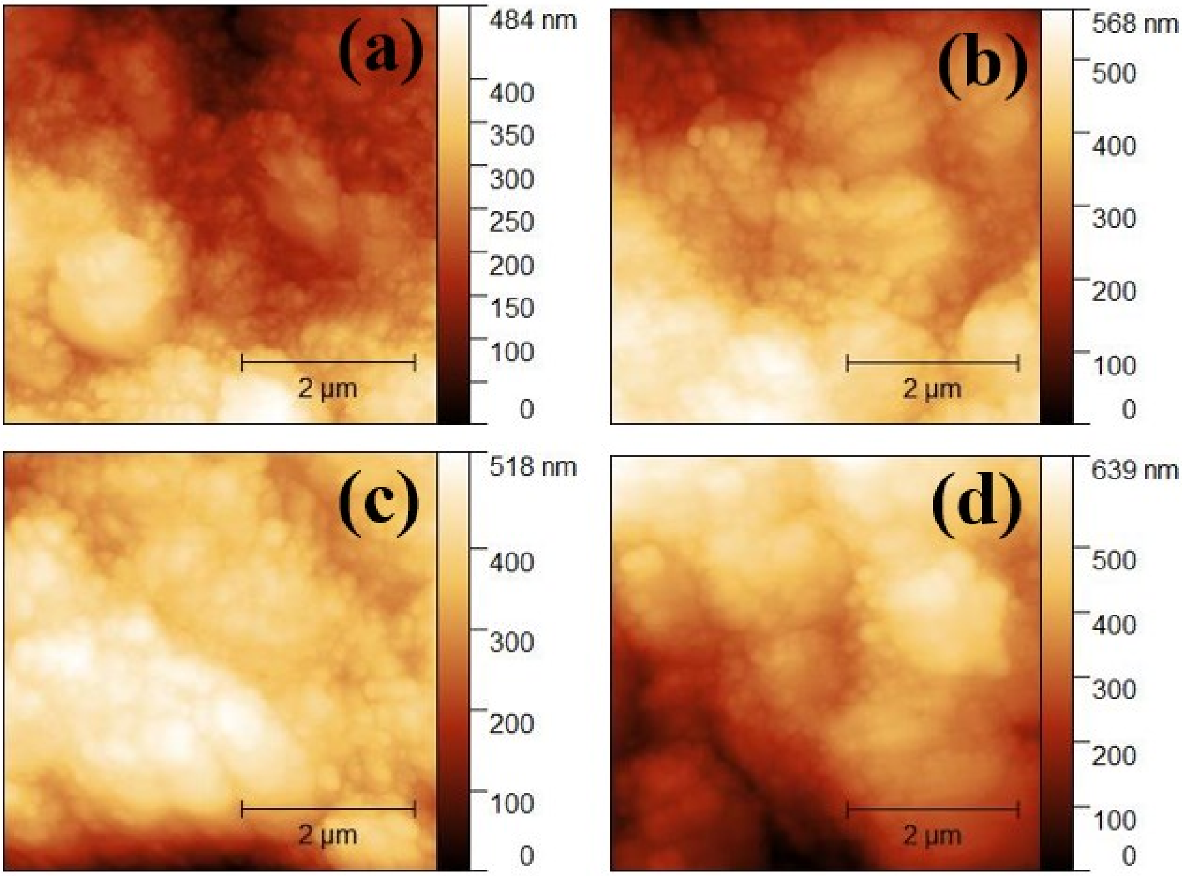


Fig. S1: Atomic force microscopy images (5 µm x 5 µm) of the (a) bare 65PMN-35PT/Pt/Si thick films and with an ALD Al_2O_3 dielectric layer thickness of (b) 20 nm (c) 50 nm and (d) 100 nm.

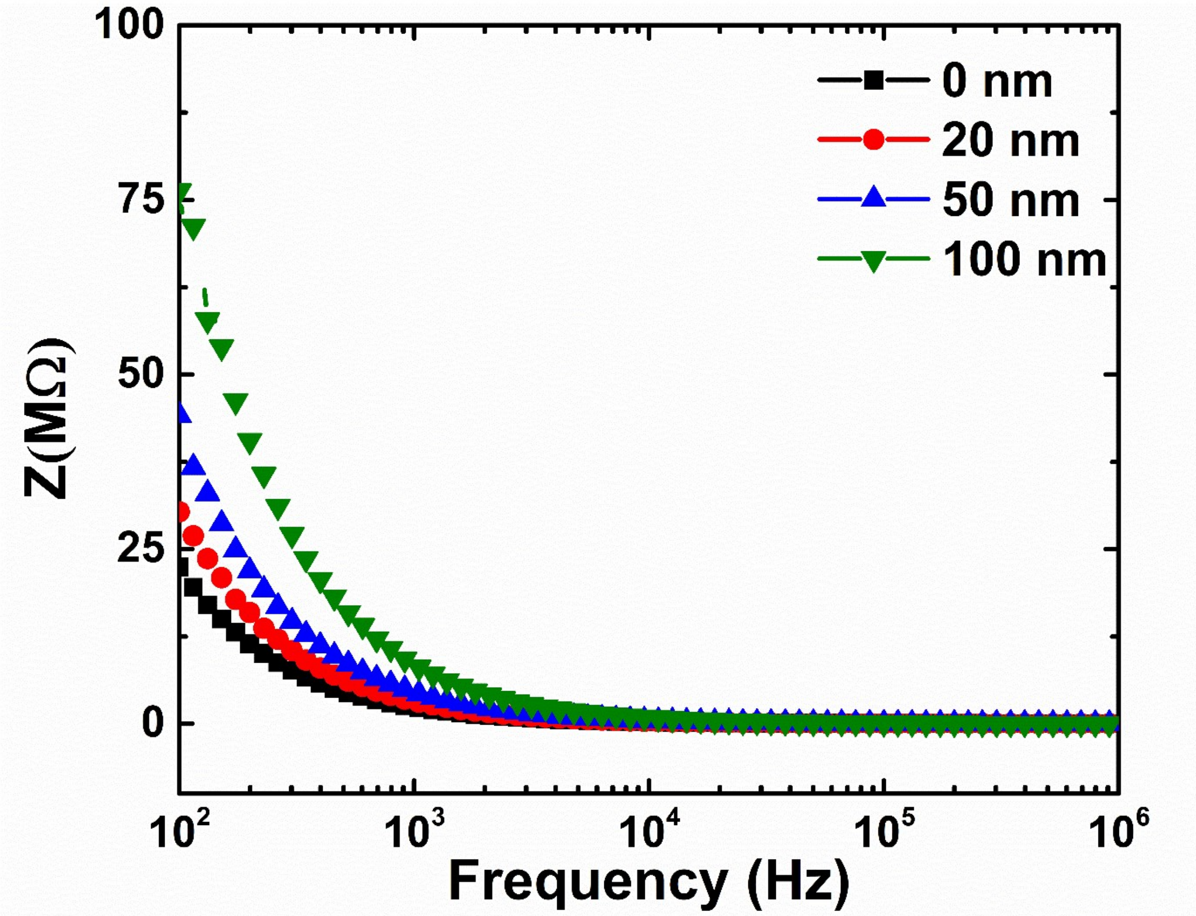


Fig. S2: Frequency-dependent impedance spectra for Pt/Al_2O_3/65PMN-35PT/Pt/Si heterostructure with varying the thickness of the dielectric Al_2O_3 layer.

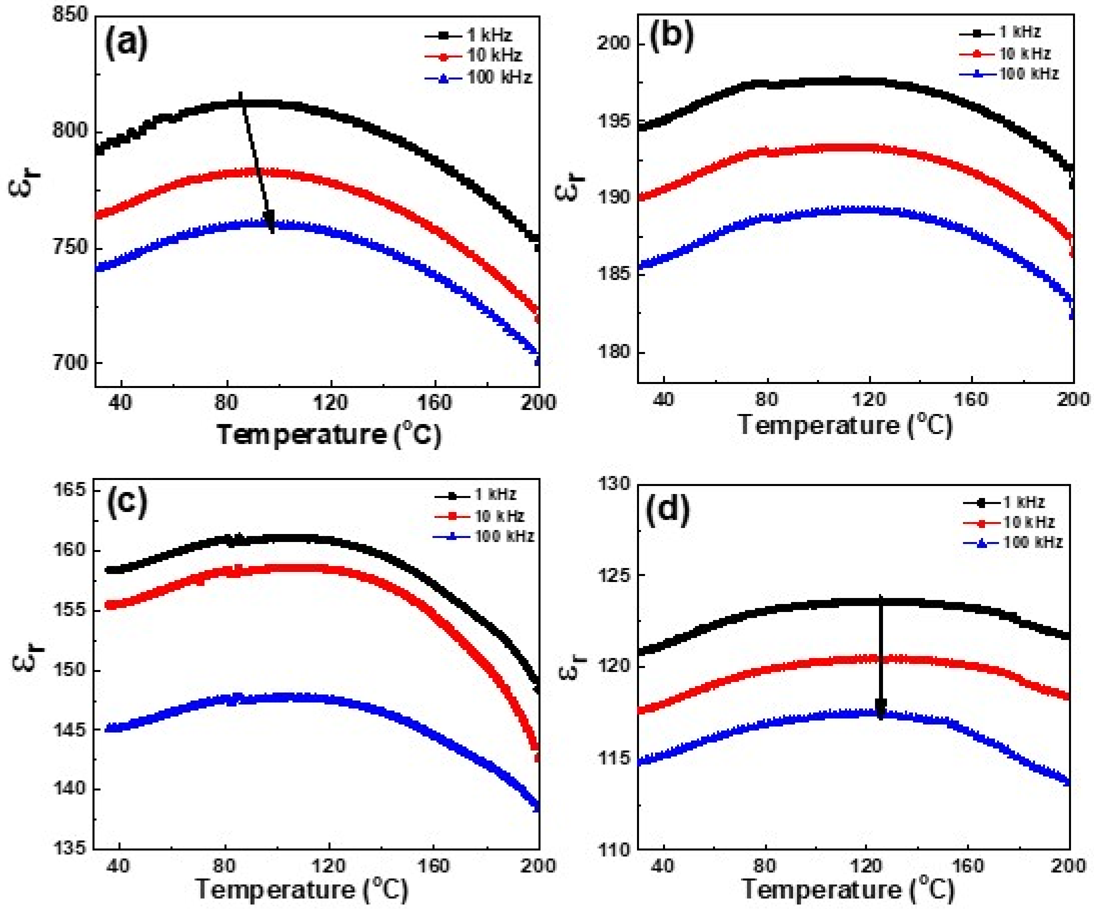


Fig. S3: Temperature-dependent dielectric response of the (a) bare 65PMN-35PT/Pt/Si thick films and with an Al_2O_3 dielectric layer thickness of (b) 20 nm (c) 50 nm and (d) 100 nm, measured at different frequencies. Arrow direction in the figures (a) and (d) shows the frequency-dependent (RFE) and frequency-independent (FE) dielectric maxima temperature.

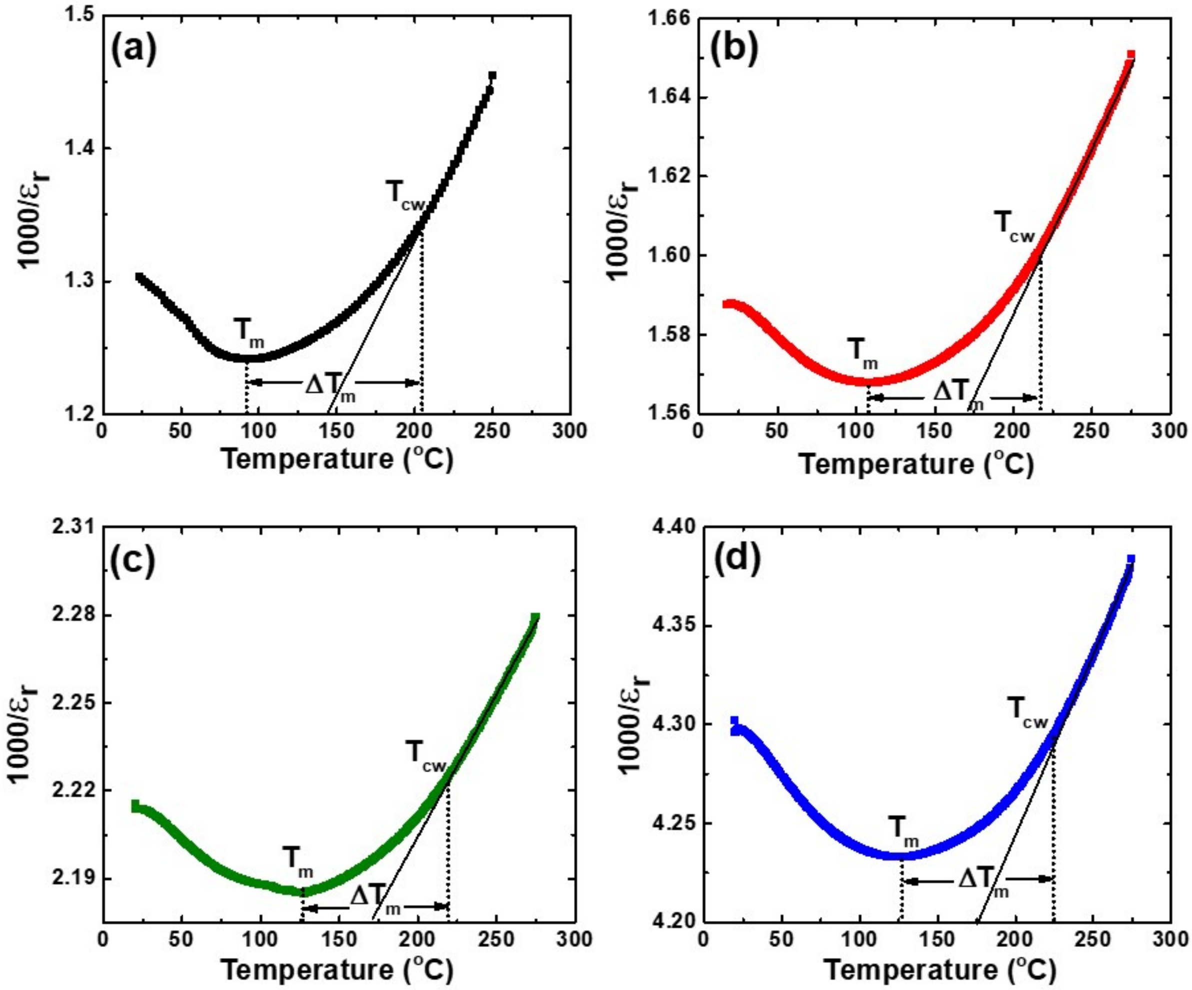
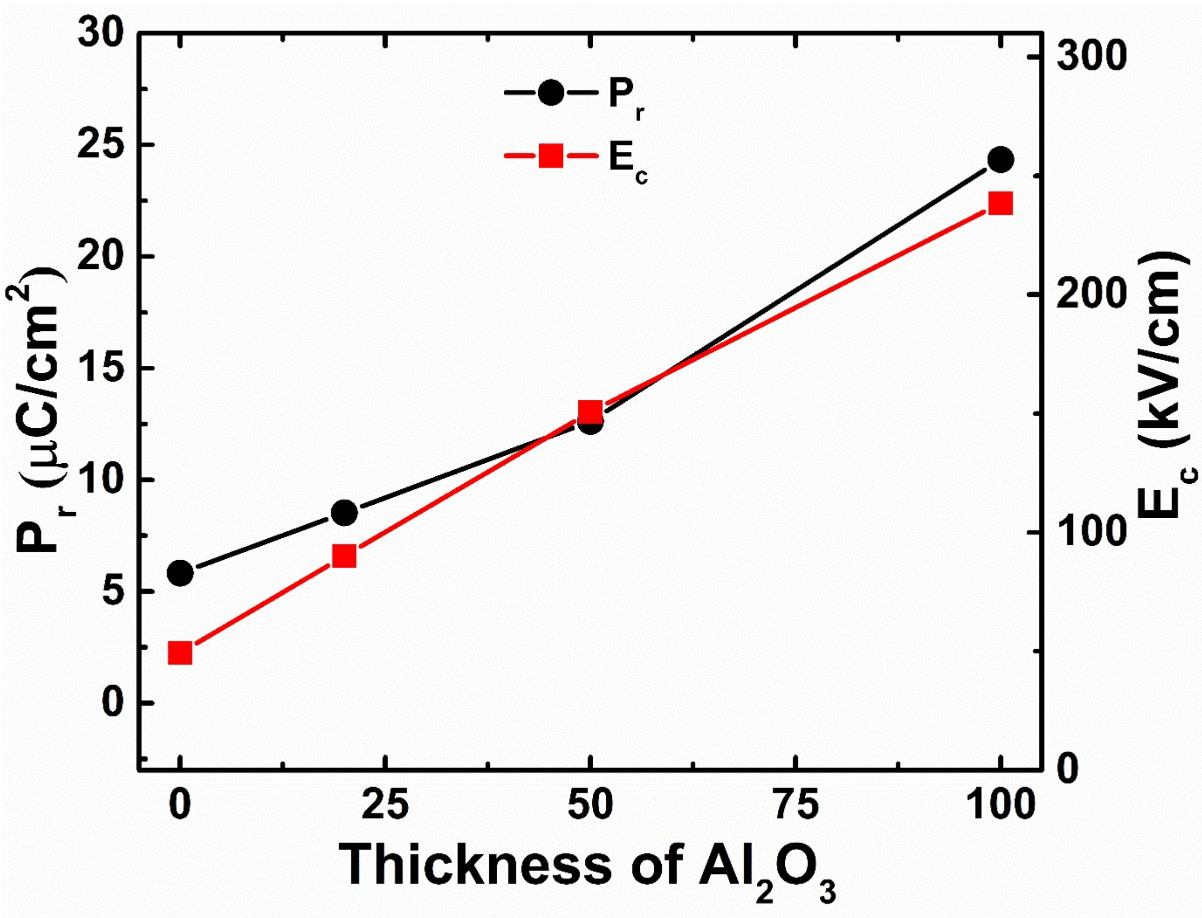


Fig. S4: Reciprocal of the dielectric constant w.r.t. temperature for the (a) bare 65PMN-35PT/Pt/Si thick films and with an Al_2O_3 dielectric layer thickness of (b) 20 nm (c) 50 nm and (d) 100 nm.



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