Supporting Information

Unlocking the Key Mechanism Behind Field-Induced Ferroelectric Phase Transition in Sodium Niobate for Energy Storage Systems

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S1. OPTIMIZED LATTICE PARAMETERS

TABLE S1. Optimized lattice parameters (a_0, b_0, and c_0 in Å, and calculated relative energies (ΔE in meV/f.u.) with respect to the cubic $Pm\bar{3}m$ of bulk $NaNbO_3$ P and Q phases. Our theoretical values are calculated using the PBEsol functional. The percentage value inside the parenthesis shows the error with respect to experimental lattice parameters provided from Reference 1.

xc	Phase	a_0 (Å)	b_0 (Å)	c_0 (Å)	ΔE (meV/f.u.)
PBEsol	P	5.492 (0.23 %)	5.555 (0.26 %)	15.474 (0.28 %)	−125.728
	Q	7.746 (0.31 %)	5.500 (0.26 %)	5.556 (0.08 %)	−125.696
Experiment	P	5.505	5.569	15.518	–
	Q	7.746	5.500	5.556	–

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S2. STRUCTURAL ANALYSIS

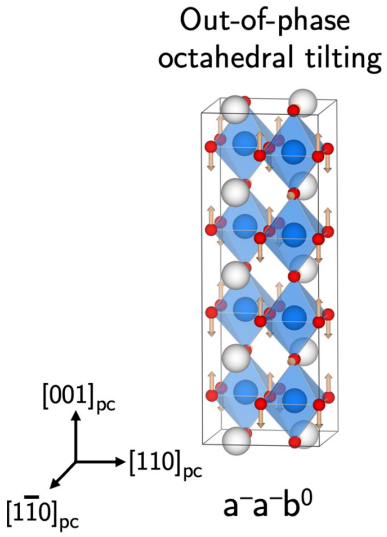

FIGURE S1. Schematic representation of the out-of-plane octahedral tilting mode with the axis of the pseudo-cubic [110] direction, $[001]_{pc}$, (i.e., $a^-a^-b^0$ in Glazer's notation).

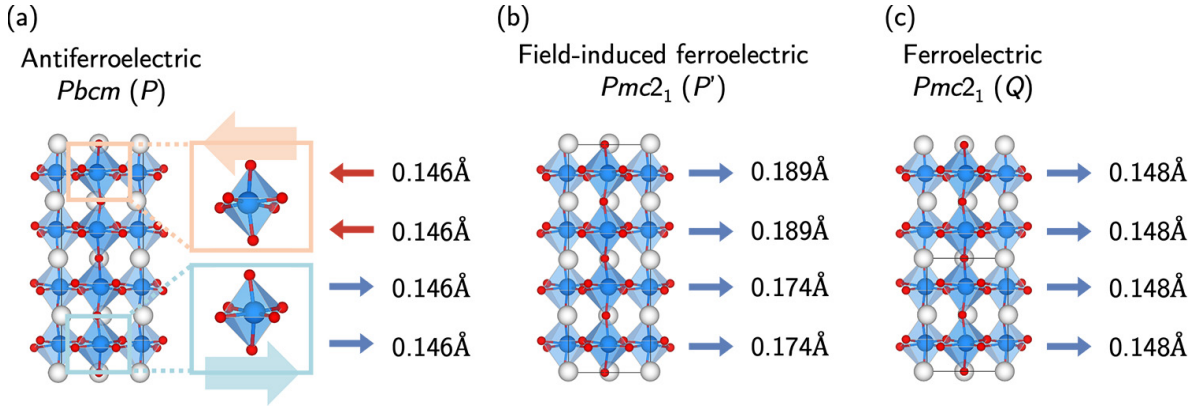

FIGURE S2. Atomic crystal structures of the (a) antiferroelectric *Pbcm* (*P*), (b) field-induced ferroelectric $Pmc2_1$ (*P*′), and (c) ferroelectric $Pmc2_1$ (*Q*) phases of $NaNbO_3$. Schematic representations of ferroelectric distortion are illustrated with straight arrows, where the straight arrow depicts the layer-by-layer Nb displacement within an octahedron. The specific values represent the Nb displacement, measured in units of Å, indicating the magnitude of the distortion as the Nb atoms deviate from the centroid of the octahedron.

S3. MINIMUM PHASE TRANSITION PATHWAY AND LANDAU-DEVONSHIRE MODEL

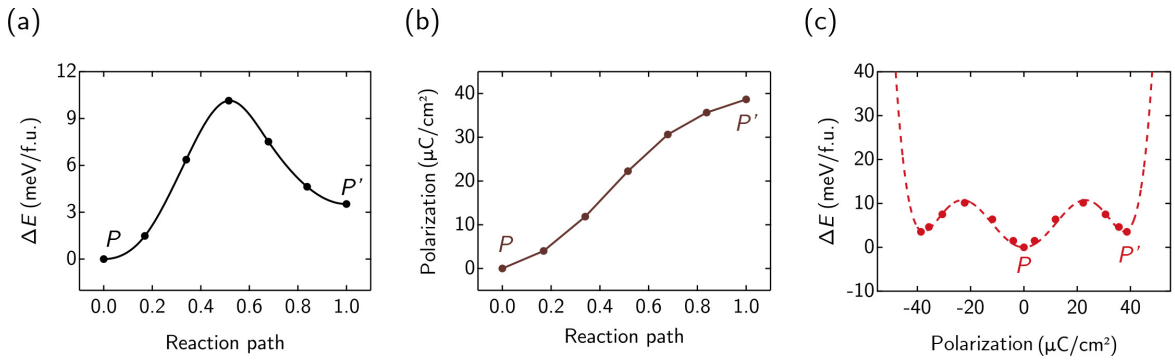

FIGURE S3. (a) Relative energies (in meV per formula-unit, taken with respect to the staring phase) for the DFT-PBEsol the generalized solid-state (climbing-image) nudged elastic band (SSNEB)-determined phase transition pathway from P to P'. (b) Polarization values (in unit of μC/cm^2), corresponding to the reaction paths of P to P'. (c) Energy (ΔE)–polarization curve for the polarization switching path from $-P'$ to P' via P using the phenomenological Landau–Devonshire model. This curve is obtained by a 6th-order polynomial least-squares regression (represented by the red dashed line), with actual computed DFT data points indicated in red markers.

S4. ENERGY POTENTIAL UNDER APPLIED EXTERNAL FIELD

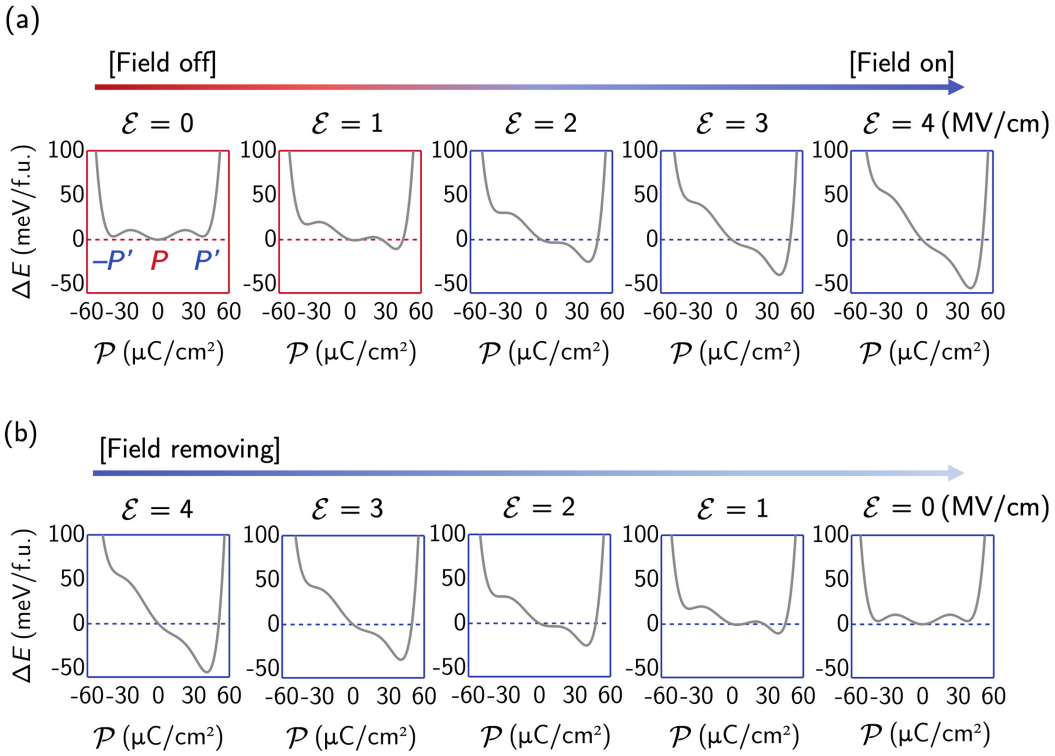

FIGURE S4. (a) Energy-polarization (ΔE-$\mathcal{P}$) curve for an electric field, $\mathcal{E}$ ranging from 0 to 4 MV/cm. (b) ΔE-$\mathcal{P}$ curve for the range $\mathcal{E}$ from 4 to 0 MV/cm.

[1] G. Gouget, M. Duttine, E. Durand, A. Villesuzanne, V. Rodriguez, F. Adamietz, T. L. Mercier, M.-D. Braida, A. Demourgues. Isolating the Two Room-Temperature Polymorphs of $NaNbO_3$: Structural Features, Optical Band Gap, and Reactivity. *ACS Appl. Electron. Mater.* **2019**, *1*, 513–522.