

Machine-learning-guided exploration of domain walls in the hybrid improper ferroelectric $\text{Ca}_3\text{Ti}_2\text{O}_7$

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Ruddlesden-Popper phases are highly tunable and naturally layered structures, in which polarization can arise via a hybrid improper ferroelectric mechanism. This enables a complex domain wall (DW) structure where multiple order parameters, like octahedral rotations, polar distortions and strain, interact. In this work, we explore the rich set of DW structures in prototypical $\text{Ca}_3\text{Ti}_2\text{O}_7$, mapping out the DWs in the $\{100\}$, $\{110\}$ and $\{001\}$ pseudo-tetragonal planes using group theory and machine-learned interatomic potentials (MLIPs). The trained potential reproduces the density functional theory (DFT) order parameter and polarization profiles for all wall types and orientations considered. A charge-aware training framework combined with reference Born effective charges reduces the prediction errors for the DW formation energies by 70 %, revealing the importance of including long-range electrostatics to model symmetry-broken interfaces. Finally, the MLIP is used to identify minimum energy pathways at the atomic scale with nearly the precision of DFT calculations, revealing a low-energy antipolar configuration for polarization switching.

Ferroelectric materials, with their spontaneous and switchable polarization, are a crucial component in current and emerging device technologies. With advances in the spatial resolution of imaging and characterization techniques, these applications now extend beyond bulk polarization switching and include nanoscale device architectures that functionalize the domain boundaries themselves [1]. These domain walls (DWs) are two-dimensional topological defects where the symmetry-breaking and confined structural distortion enable compelling emergent phenomena [2–4]. They are also naturally occurring interfaces that can be dynamically controlled by an external field, as opposed to fixed heterostructures. Device concepts cover atmospheric sensing, diodes, memory, and circuitry in unconventional computing schemes [5–10].

At the heart of controlling ferroelectric switching, regardless of the particular device design, is understanding the microscopic properties of the domain structure and DW configuration. This is because polarization switching and hysteretic behavior are fundamentally driven by DW motion. Modeling the dynamic behavior of complex domain structures requires finite temperature simulations on the atomistic or mesoscale level. Large-scale atomistic simulations in this field, commonly based on molecular dynamics (MD), have been mostly confined to the prototypical proper ferroelectrics, like PbTiO_3 , BiFeO_3 , and BaTiO_3 [11–17]. In these materials the primary order parameter of the ferroelectric phase transition is a single polar lattice distortion, originating from covalent mechanisms such as lone-pair or second-order Jahn-Teller effects [18].

In improper ferroelectrics, on the other hand, the ordering transition is driven by a non-polar lattice distortion that couples indirectly to a secondary polar mode arising, for instance, from geometric constraints [19]. Since the polarization is not the primary order parameter but is locked to a robust structural distortion [20], it is less readily suppressed by the depolarization fields that degrade device performance in thin films [21]. A promising class of such materials emerged with the discovery of hybrid improper ferroelectricity [22, 23], characterized by two non-polar lattice distortions coupled to a polar mode through a trilinear coupling mechanism. In the Ruddlesden-Popper (RP) phases, which have a quasi-two-dimensional layered perovskite structure, this connection is established by two octahedral rotational distortions breaking inversion symmetry through the activation of a zone-center mode.

In $\text{Ca}_3\text{Ti}_2\text{O}_7$ and its Sr-doped counterpart $(\text{Ca},\text{Sr})_3\text{Ti}_2\text{O}_7$, the composite form of the order parameter results in a complex domain structure of intertwined ferroelastic and ferroelectric DWs with varying charge states [24–26]. For bulk and epitaxial thin films of $\text{Ca}_3\text{Ti}_2\text{O}_7$, a switchable polarization of $8\mu\text{C}/\text{cm}^2$ was experimentally verified [27, 28]. Several other isostructural RP phases of different chemical compositions have also been found to exhibit ferroelectricity, such as $(\text{Ca},\text{Sr})_3\text{Sn}_2\text{O}_7$ and $\text{Sr}_3\text{Zr}_2\text{O}_7$ [20]. Due to the improper nature of the ferroic order, these materials also introduce an avenue for robust magnetoelectric coupling, where the magnetic order and polarization are determined by the same distortion [21, 29, 30]. The RP crystal structure is highly tunable through A-site substitution or by controlling the perovskite slab thickness, resulting in a rich phase diagram [31, 32]. Straining has been shown to promote superconductivity [33, 34] while the reduced dimensionality gives favorable band gaps for

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optoelectronic applications in chalcogenides and halides [35–37].

Theoretical studies have made important progress toward understanding how these properties relate to the crystal structure and provide insight into the atomistic mechanisms that underpin ferroelectric switching. These include thermal and strain evolution of distortion modes during phase transitions [38, 39], and group-theoretical identification of possible low-energy pathways [40, 41]. These calculations are performed using bulk structures and cannot capture the confined geometry, electrostatics, or other gradient-dependent properties of DWs. There are currently only a few first-principles studies explicitly investigating DWs for the RP phase [40, 42], while large-scale MD simulations are lacking. This is likely due to the complexity of the domain structure and large supercells required to resolve the order-parameter switching at the wall. Such supercells are far beyond what is tractable with density functional theory (DFT), but are in principle accessible with machine-learned interatomic potentials (MLIPs). Whether a conventional MLIP suffices is not obvious, since DWs involve a discontinuous polarization and long-range electrostatic contributions that lie outside a local description of the energy [43].

Here, we address this gap with a comprehensive study of the static and dynamic properties of ferroelastic and ferroelectric DWs in the prototypical RP $\text{Ca}_3\text{Ti}_2\text{O}_7$. Group-theoretical analysis is used to map out the symmetry-allowed wall configurations in the $\{100\}_{\text{pt}}$, $\{110\}_{\text{pt}}$ and $\{001\}_{\text{pt}}$ planes, and formation energetics, order parameter, and polarization profiles are characterized using DFT and neuroevolution potential (NEP)-based MLIPs. Notably, charge-aware NEP (qNEP) models trained with target Born effective charges (BECs) lower the root-mean-square error (RMSE) by 70 % compared to a conventional NEP training scheme, and all local DW geometries and polarization profiles are accurately reproduced. Minimum energy pathways of the $\{100\}_{\text{pt}}$ walls confirm that the ferroelectric and ferroelastic walls in $\text{Ca}_3\text{Ti}_2\text{O}_7$ switch through a polar state, while the purely ferroelectric walls split into an antipolar $Pnma$ 90° configuration that lowers the electrostatic energy. These findings clarify the switching mechanisms in $Cmc2_1$ RP phases and can explain the anomalously low coercive field reported for $\text{Ca}_3\text{Ti}_2\text{O}_7$ [28]. Overall, this work demonstrates that NEP models can accurately and efficiently simulate the structural and electrostatic properties of complex domain structures.

RESULTS

The RP structure comprises a series of compounds with general formula $A_{n+1}B_nX_{3n+1}$, where n denotes the number of octahedral layers in the quasi two-dimensional $(\text{ABX}_3)_n$ perovskite slabs, each separated by an AX rock-salt layer. The aristotype has space group $I4/mmm$, where the octahedral layers are displaced relative to each

other by half the face diagonal of the unit cell (Fig. 1a). On cooling from this ideal phase, in-phase or out-of-phase octahedral rotations appear, distinguished by whether successive octahedra along a given axis rotate in the same or in opposite directions.

The ground state has $Cmc2_1$ symmetry with a $\phi\phi\psi_z\phi\phi\psi_z$ tilting pattern in Aleksandrov notation [44]. ϕ denotes out-of-phase rotations and ψ indicates in-phase rotations, and ψ_z is the tilting around the ‘out-of-plane’ direction perpendicular to the octahedral layers. In the more commonly encountered Glazer notation, this corresponds to an $a^-a^-c^+$ pattern in each slab [45]. The latter notation does not account for the two perovskite slabs being symmetrically distinct, which allows for inequivalent tilting patterns in each layer and the possibility of a relative phase difference in the case that they are identical. There is for instance a distinction between the polar $Cmc2_1$ and non-polar $Pnma$ ($\phi\phi\psi_z\phi\phi\bar{\psi}_z$) phases, although they are energetically very close. The unit cell is $\sqrt{2}a_t \times \sqrt{2}a_t \times c$, a_t being the in-plane lattice parameter of the tetragonal phase. From here on all referenced directions will be given in a coordinate basis coinciding with the pseudo-tetragonal lattice vectors and the tilt axes, where z is the out-of-plane direction.

The phonon dispersion of the $I4/mmm$ phase exhibits a range of unstable imaginary modes at multiple high-symmetry points (Fig. 1b). This is indicative of the flexibility of the RP phase for engineering tailored structural or functional properties, and reflects the large number of competing low-energy structures. At the X -point, the first and third lowest phonon modes correspond to the in-phase and out-of-phase rotations found in the $Cmc2_1$ structure, with irreps X_2^+ and X_3^- , respectively. These are the primary order parameters in the antiferrodistortive transition (Fig. 1c–d). The second band at the X -point is the X_1^- mode responsible for out-of-phase rotations in the z -direction. The polar distortion in the ground state is a stable and doubly degenerate Γ_5^- mode. It consists of an alternating in-plane displacement of the Ca atoms, and the off-centering of Ti from the center of the TiO_6 octahedra (Fig. 1e). The remainder of the imaginary modes correspond to unconventional tilting or cation displacements not found through mode decomposition of the ground state.

Since the polar mode is stable, applying it to the high-symmetry structure gives a single-well potential with no further energy-lowering, as opposed to the double well potentials of the rotational modes, see Fig. 1f. However, the rotational modes are non-polar distortions and cannot break inversion symmetry on their own. Hybrid improper ferroelectricity therefore originates as a secondary effect, through the trilinear coupling mechanism between these rotational modes and the zone-center polar mode. This manifests itself as a free energy term,

$$F = \alpha Q_{X_3^-} Q_{X_2^+} Q_{\Gamma_5^-}, \quad (1)$$

where Q is the mode amplitude and α is the coupling coefficient. As a result, the polar mode becomes energetically

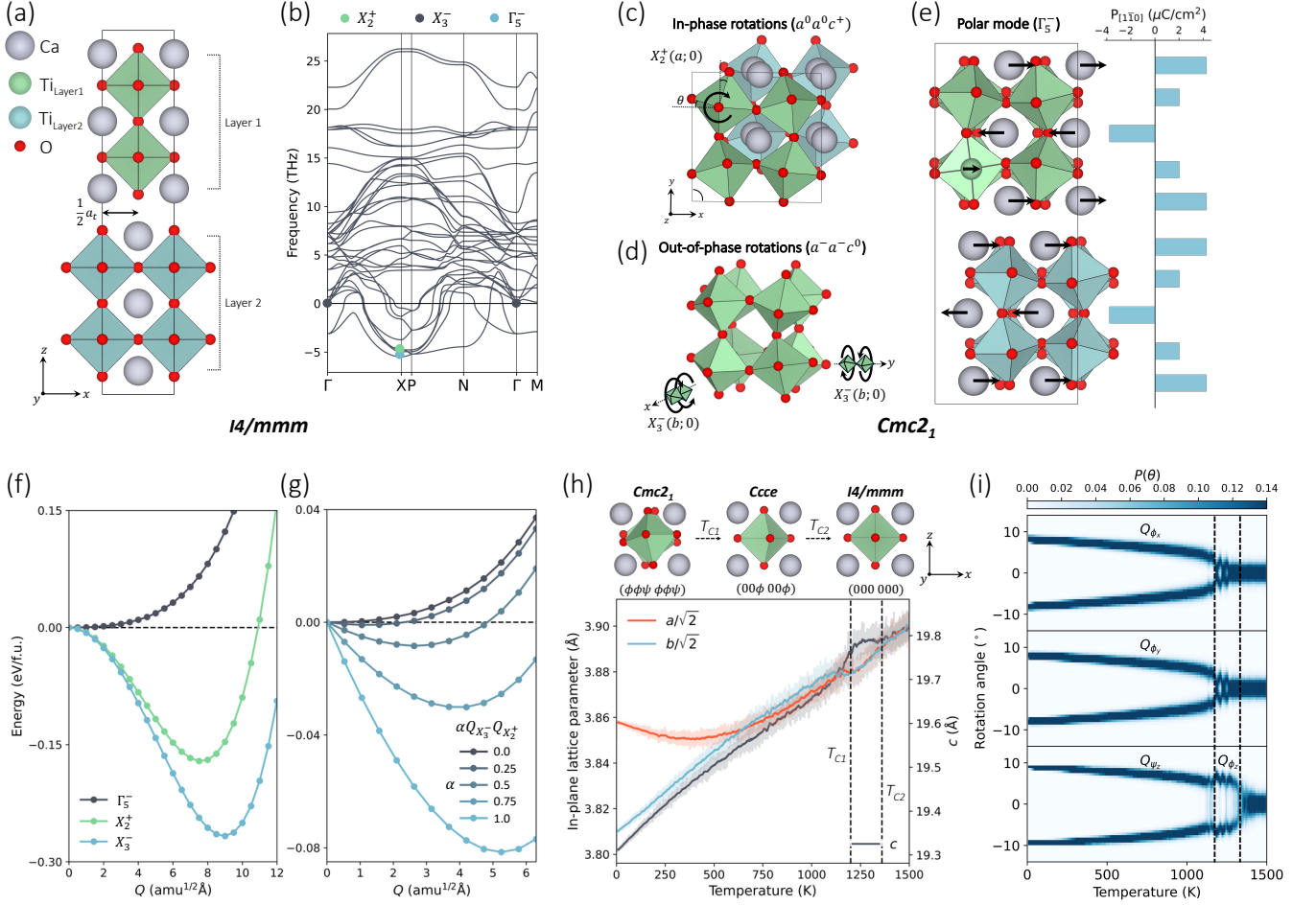


FIG. 1. (a) The aristotype tetragonal structure of the RP phase and the high-temperature phase of $\text{Ca}_3\text{Ti}_2\text{O}_7$. Each perovskite slab contains two layers of TiO_6 octahedra, displaced by half of the face diagonal of the ab -plane. (b) The phonon dispersion of the $I4/mmm$ phase, with markers for distortion modes present in the ground state. (c-d) Rotational distortion modes that make up the orthorhombic $Cmc2_1$ phase. The X_2^+ irrep represents in-phase rotations around the out-of-plane axis, while X_3^- are out-of-phase rotations around the x and y axes. The twin angle (γ) is indicated by the arc in the lower left corner, $90^\circ + \gamma$. (e) The polar mode consists of alternating in-plane displacements (black arrows) of the Ca atoms, resulting in a single layer of uncompensated Ca atoms for all even n . There is an off-centering of Ti from the octahedron center of mass contributing to the total polarization. Note that the unit cell used is an extended cell with respect to the primitive cell. To the right is the calculated polarization (in the $[1\bar{1}0]$ direction) for each atomic layer. (f) Energy as a function of mode amplitude (Q), when applying the Γ_5^- , X_2^+ and X_3^- modes to the $I4/mmm$ structure. (g) Energy as a function of the polar mode amplitude, $Q(\Gamma_5^-)$, at fixed amplitudes of the rotational modes. $\alpha = 1$ corresponds to the equilibrium displacements from (f). (h) Pseudo-tetragonal lattice parameters and (i) tilt angle evolution when heating to 1500 K. Black dashed lines show the transition temperatures, T_{C1} and T_{C2} , separating the $Cmc2_1$, $Ccce$ and $I4/mmm$ phases.

ically favorable only once the rotational distortions are already active, as shown in Fig. 1g [20, 46]. This free energy term is analogous to the $R_4^+ \oplus M_3^+ \oplus X_5^+$ coupling between octahedral rotational modes and antipolar A-site distortion in the perovskite structure [47, 48]. However, because of the termination at each layer in the RP structure, there is a net displacement producing an in-plane polarization for each layer (when n is even).

The calculated total polarization of the ground state is $17.5 \mu\text{C}/\text{cm}^2$, close to the structural polarization of $20 \mu\text{C}/\text{cm}^2$ obtained by Rietveld refinement [49]. It exceeds the largest switchable polarization reported for

bulk single crystals, $8 \mu\text{C}/\text{cm}^2$ [50], which is expected since the calculation describes a monodomain system at 0 K and therefore excludes both thermal and disorder contributions. The layer-resolved contributions to the total polarization for successive CaO and TiO_2 atomic layers also show that there is a slightly higher polarization associated with the edge CaO layers as opposed to the internal CaO layer (Fig. 1e).

The sequence of phase transitions in $\text{Ca}_3\text{Ti}_2\text{O}_7$ was investigated with MD simulations using the final qNEP potential (see Methods). It is known that $\text{Ca}_3\text{Ti}_2\text{O}_7$ transitions from the ideal tetragonal $I4/mmm$ structure into

an intermediate non-polar phase, before reaching its ferroelectric and ferroelastic $Cmc2_1$ ground state. However, the symmetry of the intermediate phase has been a subject of discussion, with several different space groups proposed [26, 51, 52]. In simulations of the lattice parameter evolution on heating from 1 K to 1500 K (Fig. 1h), the polar ground state transitions into a non-polar orthorhombic phase at 1200 K and into the tetragonal high-symmetry phase at around 1360 K.

Tracking the octahedral rotation angles (Fig. 1i), the structure maintains the $\phi\phi\psi_z$ tilt pattern up to T_{C1} , where the tilts around the x and y axes vanish and the rotations around the z -axis flip from in-phase (ψ_z) to out-of-phase (ϕ_z), yielding the $Ccce$ phase. The remaining ϕ_z rotations disappear at T_{C2} , completing the $Cmc2_1 \rightarrow Ccce \rightarrow I4/mmm$ sequence. This is consistent with a more recent high-temperature diffraction study [38], and is analogous to the tilt pattern of the three phases in CaTiO_3 [53]. We also note that there is a crossover between the a and b lattice parameters close to 600 K, even though the octahedral tilting stays rigid. This could be explained by a competition between tilt modes and internal Ti–O–Ti angle distortion, as observed in three-dimensional perovskites like CaMnO_3 and LaFeO_3 [54–56]. The qNEP potential was also used to successfully reproduce the phase transitions in CaTiO_3 . For more details on the analysis of these simulations, see the Supplementary Information [57].

Domain wall geometry

The antiferrodistortive rotations generate a spontaneous strain in $\text{Ca}_3\text{Ti}_2\text{O}_7$ that is switchable under shear stress. It is therefore a ferroelastic as well as ferroelectric material. The strained state manifests itself as a twin angle of 0.6° in the extended orthorhombic unit cell (Fig. 1c). The ferroelectric distortion is locked to this strain state through the trilinear coupling, most notably through the off-centering of A-site cations to accommodate the octahedral rotations. The resulting polarization points in the $\langle 110 \rangle$ directions. Enumeration of the possible configurations for the irreps X_3^- and X_2^+ in the $Cmc2_1$ space group yields eight different symmetry equivalent domains. Each of these can be uniquely categorized in terms of the strain state, tilts and rotations of a single octahedron and the polarization direction (Fig. 2a).

Since a ferroelastic DW is defined in terms of a change in strain state, it is accompanied by a 90° rotation of the polarization. Following the structure of Fig. 2a, combining any domain state on each side of the red dashed line yields a 90° wall which is both ferroelastic and ferroelectric. Purely ferroelectric DWs are associated with a 180° rotation of the polarization, resulting from combining domains within each row on either side of the purple dashed line. The various walls will therefore be referred to here as either 180° or 90° walls to distinguish between them

TABLE I. All symmetry-distinct DWs associated with any wall plane. Every wall is named according to which tilt phases change sign at the boundary in each respective layer, and whether they are 180° (ferroelectric) or 90° (ferroelectric and ferroelastic). The paired columns refer to the two layers.

Wall type	Q_{ϕ_x}		Q_{ϕ_y}		Q_{ψ_z}		broken tilt phases	
180° DW								
$\phi_x\phi_y$	-1	-1	-1	-1	1	1	2	2
ψ_z	1	1	1	1	-1	-1	1	1
90° DW								
$\phi_x\psi_z - \phi_y$	-1	1	1	-1	-1	1	2	1
$\phi_y\psi_z - \phi_x$	-1	1	1	-1	1	-1	1	2

being purely ferroelectric or also ferroelastic. Walls separating domains of equivalent polarization direction but different rotational states (within each quadrant) produce structural antiphase boundaries not considered in this work.

Although there are multiple ways of combining these domains to form a ferroic wall, there is a small number of symmetry-distinct DWs, which can be systematically mapped out by symmetry analysis. Following Refs. 24, 27, the trilinear coupling term of Eq. (1) can be decomposed in terms of the tilting around each axis as

$$F_{\text{Layer}} = \alpha_1 Q_{\phi_x} Q_{\psi_z} P_x + \alpha_2 Q_{\phi_y} Q_{\psi_z} P_y. \quad (2)$$

F_{Layer} applies separately to each of the two layers, giving one such equation per layer, and the tilt amplitudes in the two equations are coupled through space group symmetry. ϕ_x and ϕ_y are the out-of-phase rotations around the x and y axes, while ψ_z is the in-phase rotation which is always in the out-of-plane direction. A 180° wall is then associated with switching both P_x and P_y , achieved by reversing either ϕ_x and ϕ_y or ψ_z in both layers independently. On the other hand, a 90° wall is produced by switching either P_x or P_y , which is done by reversing the tilts of ϕ_x and ψ_z in one layer and ϕ_y in the other, and vice versa. Thus, there is a layer-dependent wall asymmetry for twin walls, and each type is distinguished by what ϕ -component is perpendicular to the wall plane. Choosing that the x -direction is normal to the DW plane for the $(100)_{\text{pt}}$ walls, the $\phi_y\psi_z - \phi_x$ wall (reversing ϕ_y and ψ_z in one layer and ϕ_x in the other) leads to a mirror symmetry across the boundary, while a $\phi_x\psi_z - \phi_y$ wall exhibits a 90° rotation. This excludes the $(001)_{\text{pt}}$ plane where ϕ_x and ϕ_y are indistinguishable. Overall, this establishes the existence of four possible DWs which should be representative for the entire configurational space (Table I).

Domain wall energetics and profiles

For this study, the DWs listed in Table I were created with four $(100)_{\text{pt}}$, four $(110)_{\text{pt}}$ and three distinct

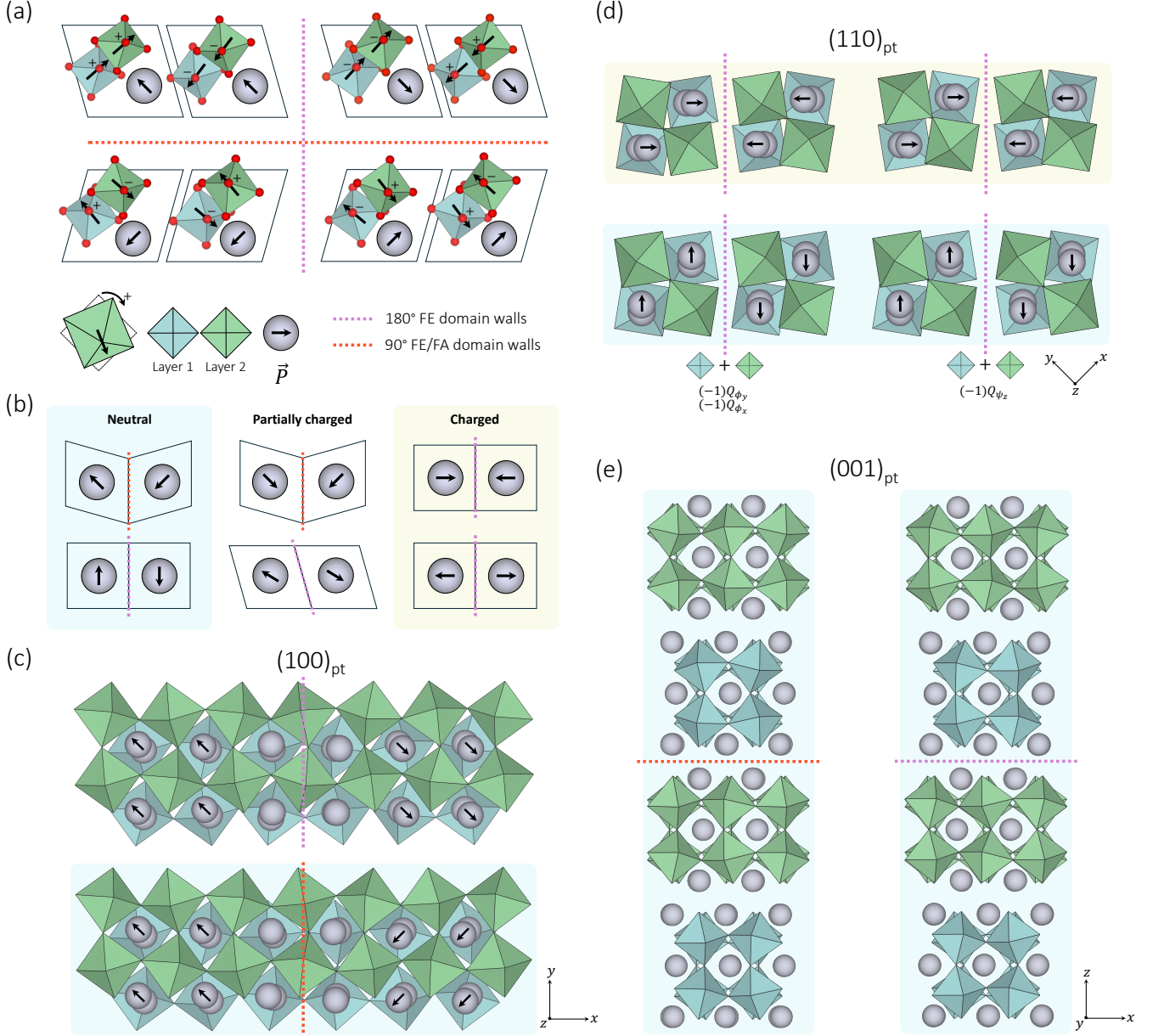


FIG. 2. (a) Each of the eight domain states for $\text{Ca}_3\text{Ti}_2\text{O}_7$ in the $Cmc2_1$ phase as seen from the z -direction, characterized in terms of the tilting of a specific octahedron, the strain state and the polarization ($\vec{P}$) direction. For the octahedra, the + and - signs represent the clockwise or counterclockwise rotation of ψ_z , while the arrow shows the combined tilting state of ϕ_x and ϕ_y . The strain is represented by the cell shape with an exaggerated twin angle (γ). Any combination of domains separated by the purple dashed line creates a 180° ferroelectric (FE) DW, while the red line separates a 90° ferroelectric and ferroelastic (FA) DW. (b) The different charge states used to characterize the walls along with examples in the $(100)_{\text{pt}}$ and $(110)_{\text{pt}}$ planes. (c) Examples of relaxed $\phi_x\psi_z - \phi_y$ and $\phi_x\phi_y$ $(100)_{\text{pt}}$ DWs. (d-e) Examples of charged and neutral DWs in the $(110)_{\text{pt}}$ plane, and 90° and 180° DWs in the $(001)_{\text{pt}}$ plane.

$(001)_{\text{pt}}$ planes, amounting to a total of 11 different DWs (in the $(001)_{\text{pt}}$ planes, the 90° DWs become symmetrically equivalent). Depending on the geometry of the wall, there is a bound surface charge density at the interface, $\sigma_b = (P_2 - P_1) \cdot \vec{n}_{\perp\text{DW}}$, if there exists a discontinuous polarization component normal to the DW plane. This is usually described as the walls having a head-to-

head (H-H) or tail-to-tail (T-T) configuration [58]. In $\text{Ca}_3\text{Ti}_2\text{O}_7$, three categories can be used to describe the various charge states, illustrated in Fig. 2b. If the polarization is parallel to the DW, there is no bound charge and the wall is electrostatically neutral. Meanwhile, the charged walls can be distinguished by whether the polarization is at a 45° or 90° to the wall plane. These two

cases will therefore be referred to as partially charged and charged to distinguish them relative to one another. Charged DWs of any kind are highly unstable due to unfavorable electrostatic fields and are therefore rare except in improper ferroelectrics where DW formation is geometrically driven, such as the hexagonal manganites [59, 60] or RP phases.

The domain structure in undoped $\text{Ca}_3\text{Ti}_2\text{O}_7$ has been experimentally observed to consist of parallel 90° DWs, interspersed with 180° DWs inside each domain. The planar distribution shows that they predominantly exist within the $\{100\}_{\text{pt}}$ planes, while A-site doping with Sr stabilizes additional walls in the $\{110\}_{\text{pt}}$ plane [27, 61]. These only exist as 180° ferroelectric DWs due to the lattice mismatch in the orthorhombic structure, and are either charged or neutral. DWs in the $(001)_{\text{pt}}$ planes, parallel to the perovskite layers, have also been observed in several RP systems like $(\text{Ca}, \text{Sr})_3\text{Ti}_2\text{O}_7$ and $\text{Ca}_3\text{Ru}_2\text{O}_7$ [46, 62]. Examples of DW structures for each plane are shown in Fig. 2c–e.

Three MLIPs were created based on a training set with DFT evaluated structures, as described in the Methods section. One was trained only on structural information through angular and radial descriptors, while the other two use the qNEP framework, incorporating electrostatic contributions to the total energy [63, 64]. The two qNEP models differ by the inclusion of an additional DFT dataset with target BECs. All three models were used to relax each of the structures and evaluate formation energies, following the exact same procedure as the DFT calculations. Although there are only four symmetry-distinct DW configurations, any gradient-dependent properties, such as the local strain gradient, order parameter, or polarization profiles depend on the orientation of the wall. All the structures are therefore different both in terms of electrostatics and local wall geometry.

In general, the formation energies (Table II) show an increase in cost with the number of broken tilt phases and the larger structural distortion this entails, as well as with the wall having an H–H or T–T component of the polarization. The ferroelectric $\phi_x\phi_y$ wall, which switches the phase of both ϕ_x and ϕ_y in both layers, consistently has the largest formation energy within each plane. Meanwhile, for the completely neutral $(001)_{\text{pt}}$ plane, the ψ_z DW has an almost negligible energy cost compared to the other walls. The formation energies mostly range from about 100 to 200 mJ/m^2 , which is a typical magnitude for many ferroic systems, such as the 180° DWs in PbTiO_3 (120–160 mJ/m^2) [66, 67] or structural antiphase boundaries in PbZrO_3 (190 mJ/m^2) [68]. For the $(100)_{\text{pt}}$ ferroelastic DWs, the formation energy is close to the average of perovskite CaMnO_3 , isostructural to CaTiO_3 , where DWs with one or two broken tilt phases have calculated formation energies of 67 mJ/m^2 and around 163 mJ/m^2 [48], respectively.

The comparison between target and predicted formation energies for all three models is presented in Fig. 3.

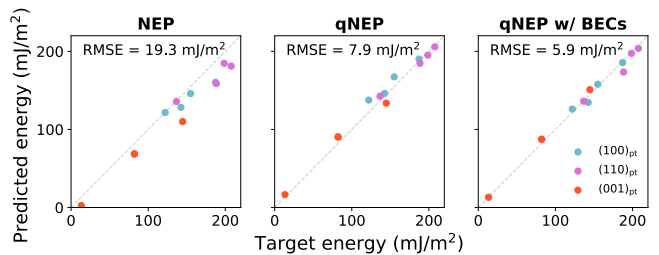


FIG. 3. Parity plots comparing the predicted formation energies of DW structures to target energies from DFT. The calculated root-mean-square error (RMSE) is lowered from 19.3 mJ/m^2 to 5.9 mJ/m^2 , amounting to a 70 % decrease when training using the qNEP framework with a dataset including target Born effective charges (BECs).

With the conventional NEP, the formation energies are systematically underestimated even though the relaxed walls are structurally almost identical to those obtained with DFT. The closest agreement is for the $\phi_x\psi_z - \phi_y$ wall in the $(100)_{\text{pt}}$ plane, which is the only wall in the set with a continuous normal component of the polarization (H–T) and which NEP reproduces exactly. This is because the total energy is only calculated as a sum of local site energies. When using qNEP, there is a considerable improvement in the formation energies relative to DFT values. Using the same dataset, trained with the qNEP architecture, the RMSE is lowered from 19.3 mJ/m^2 to 7.9 mJ/m^2 . An extended dataset with target BECs lowers the RMSE further to 5.9 mJ/m^2 , a 70 % reduction relative to the conventional NEP model. Meanwhile, the overall RMSE in target vs. predicted energies for the entire dataset is not lowered for any of the qNEP potentials compared to regular NEP (for the full parity plots of each model see Figs. S3–S5 in the Supplementary Information [57]). This demonstrates the benefit of a charge-aware treatment for the interfaces considered here, particularly when long-range electrostatics are important.

The DW structures relaxed with DFT and the final qNEP model were analyzed by calculating the order parameter and polarization profiles. The order parameter profile shows the evolution of the X_2^+ and X_3^- irreps, and is calculated as the rotation angle around each of the axes. Fig. 4a–c shows the profiles for one neutral DW structure in each plane, while the corresponding polarization profiles are displayed in Fig. 4d–f. Depending on whether the tilting changes phase or not, the order parameter follows a tanh or sech profile across the wall, consistent with Landau theory [69]. The $(001)_{\text{pt}}$ walls have significantly less distortion and are notably narrower than those in the other planes, reflecting the weaker interaction between perovskite layers. Across all six panels of Fig. 4 the qNEP and DFT order parameter profiles are very close, reproducing the wall position, the wall width and the approach to the bulk plateau; the only visible deviation is a slight broadening of Q_{ϕ_x} at the $(110)_{\text{pt}}$ wall. The polarization profiles likewise agree in shape and wall

TABLE II. Formation energies of the 11 different DWs considered in this work, calculated with DFT and the three MLIPs. The best agreement with DFT is found for the qNEP model trained with target BECs. $P_{\perp DW}$ indicates whether the normal components of the polarization vectors meeting at the wall point toward or away from each other (H-H/T-T) or are continuous (H-T). The wall width (w_{DW}) is determined from order parameter profiles. See Table I for how each wall type is categorized in terms of tilt phases.

Plane	Wall type	E_{DW}^f (mJ/m ²)*				$P_{\perp DW}$	w_{DW} (Å)	Cell length [†] (u.c.)
		DFT	NEP	qNEP	qNEP with BECs			
(100) _{pt}	180° DW: $\phi_x\phi_y$	187	160	190	186	H-H/T-T	18	6
	ψ_z	155	146	167	158	H-H/T-T	19	6
	90° DW: $\phi_x\psi_z - \phi_y$	122	122	138	126	H-T	15	6
	$\phi_y\psi_z - \phi_x$	142	128	146	135	H-H/T-T	20	6
(110) _{pt}	180° DW: $\phi_x\phi_y$	208	181	206	204	H-H/T-T	20	8
	ψ_z	188	159	185	174	H-H/T-T	20	8
	$\phi_x\phi_y$	199	185	195	197	(neutral)	19	8
	ψ_z	137	136	143	136	(neutral)	14	8
(001) _{pt}	180° DW: $\phi_x\phi_y$	145	110	134	151	(neutral)	13.5	4
	ψ_z	13	2.5	16	13	(neutral)	6	4
	90° DW: $\phi\psi_z - \phi$	82	69	90	87	(neutral)	13.5	4

* For each wall all methods use the same supercell, so the comparison between DFT and the MLIPs is consistent. Note that the absolute formation energies of the charged and partially charged DWs are inherently cell-size-dependent [65].

† Supercell length in terms of the number of unit cells normal to the DW plane. A 48-atom unit cell was used for the (110)_{pt} DWs, and a 96-atom cell was used for (100)_{pt} and (001)_{pt} DWs.

width, and differ only by a nearly uniform offset of about 1 $\mu\text{C}/\text{cm}^2$ in magnitude, corresponding to roughly 10 % of the bulk value. This offset originates in the predicted BECs of the reference $I4/mmm$ structure, which are systematically lower than those from DFT (Fig. S6), rather than in the wall structure itself. Recomputing the polarization with the actual BECs of the relaxed supercells from qNEP gives the same profiles, with the magnitude reduced by about 8 %.

We remark that for the charged and partially charged DWs, the H-H and T-T components of the polarization induce a highly unfavorable internal electric field. As a result there is an attractive force between the walls, and the formation energy does not converge with cell size. This is also found in other computational studies of charged DWs, where the gradient of the electrostatic potential is independent of DW distance [65]. With a conventional NEP this dependence is absent altogether once the walls are separated by more than the descriptor cutoff, which is in itself a signature of the long-range character of the interaction. For the H-H/T-T walls in this study, the electrostatic potential was lowered by the Ti atoms reversing their off-centering from the TiO_6 center of mass, even if parts of the mid-domain were frozen during relaxation with both DFT and qNEP. It is therefore expected that the true formation energies for these walls are even higher.

Atomistic switching mechanisms

Because of the hybrid improper mechanism for switching in $\text{Ca}_3\text{Ti}_2\text{O}_7$, both 90° and 180° DW movement requires entire octahedra to change their rotational patterns, and is thus associated with high coercive fields for switching. Despite this, a range of field strengths have been reported, mostly above 100 kV/cm, though also as low as 5 kV/cm [28, 50]. There are many factors influencing the field magnitude, but most fundamental is the atomistic switching pathway with which the DW moves. Knowing this intrinsic mechanism is also essential to design effective approaches to lowering coercive fields, while retaining a stable polarization.

Several studies have enumerated these minimum switching pathways and calculated the associated energy barriers from bulk structures [40, 41, 70]. However, this process requires prior knowledge of the full order parameter space and it is difficult to predict how these switching mechanisms unfold in an actual DW. The trained qNEP potential is a convenient alternative to determine these minimum energy pathways because any DW propagation transpires through the lowest-energy configuration, with nearly the precision of DFT. One can then also investigate the dynamics of wall motion, such as in- or out-of-plane correlation or nucleation events.

To determine exactly how each of the four DWs preferentially moves, MD simulations were conducted on long supercells with 48 CaTiO_3 units in the x -direction, perpendicular to the (100)_{pt} wall plane. Wall motion can then be ascertained from thermal fluctuations around the positional average. The DW is topologically protected

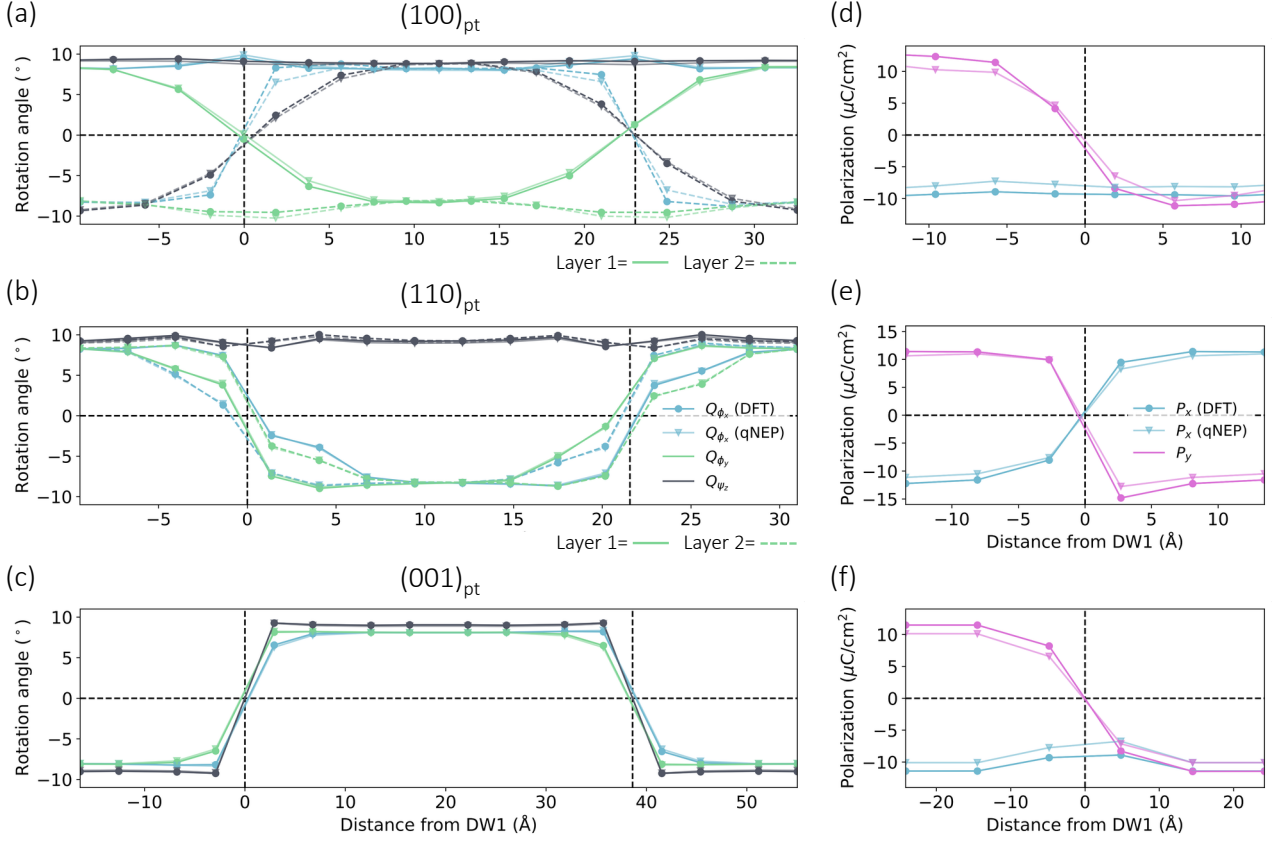


FIG. 4. Order parameter profiles for the (a) $\phi_x\psi_z - \phi_y$ DW, (b) the $\phi_x\phi_y$ neutral wall and (c) the $\phi\psi_z - \phi$ wall. The mode amplitude (Q) is calculated as the rotation angle around the x , y and z axes, except for the $(110)_{\text{pt}}$ wall where the tilt axis is at 45° with the lattice axes. (d–f) Polarization profiles corresponding to the first DW (DW1) in the supercells used for order parameter plots. Note that for the $(001)_{\text{pt}}$ wall it is not possible to meaningfully assign a phase to the tilts due to the asymmetry between the perovskite layers. The positions of DWs are indicated with vertical dashed lines. Throughout, DFT results are shown in the darker and qNEP results in the lighter shade of each color.

against spontaneously vanishing, and can only annihilate in the case that it meets the wall on the opposite side of the cell. While the mobility depends on temperature and system size, the switching pathway does not as it remains the same at every temperature and cell size examined. The mobility decreases as the supercell is enlarged in the wall plane, approaching a small value in the large-cell limit (Fig. S18). This reflects the fact that the walls are not rigid: they roughen within their own plane, so that, depending on the wall type, different segments fluctuate largely independently and the displacement of the wall as a whole is an average that is increasingly suppressed as the wall grows. In the presence of an applied field the mobility will instead be dominated by the field-driven motion. Wall trajectories from these simulations, including a case in which two walls annihilate, are shown in Fig. S19.

90° DWs. For the two different 90° walls, $\phi_x\psi_z - \phi_y$ and $\phi_y\psi_z - \phi_x$, the switching was observed to proceed through a one-step mechanism where individual octahedra reverse their tilting. Due to the asymmetry in these DWs (see Table I), this involves reversing two tilt-

ing phases in one layer, and a single phase in the other. Despite this, the displacement remains coherent across the stacking direction, even with 20 layers stacked along z . The simulation of a $\phi_x\psi_z - \phi_y$ wall displacing a single step at 300 K can be seen in Fig. 5a, with the evolution in tilting angles plotted in Fig. 5b. The intermediate configuration throughout the process is $\phi_x 0 \psi_z 0 \phi_y 0$, which in bulk would be consistent with a polar $Amm2$ symmetry, as illustrated in Fig. 5c. For the $\phi_y\psi_z - \phi_x$ DW this switching procedure looks exactly the same, only with ϕ_x and ϕ_y in opposite layers.

It is important to note that although the instantaneous wall symmetry can be characterized in terms of a three-dimensional space group, a DW is a quasi-two-dimensional object and therefore inherently symmetry-broken. The energy difference between the bulk ($Cmc2_1$) and wall symmetry therefore does not necessarily relate to the energy cost of moving a pre-existing wall. The energy cost for switching was estimated using the NEB method with the qNEP potential (Fig. 5d), resulting in a barrier of 4.9 mJ/m² for the $\phi_x\psi_z - \phi_y$ wall and 5.9 mJ/m² for the $\phi_y\psi_z - \phi_x$ wall, which is considerably

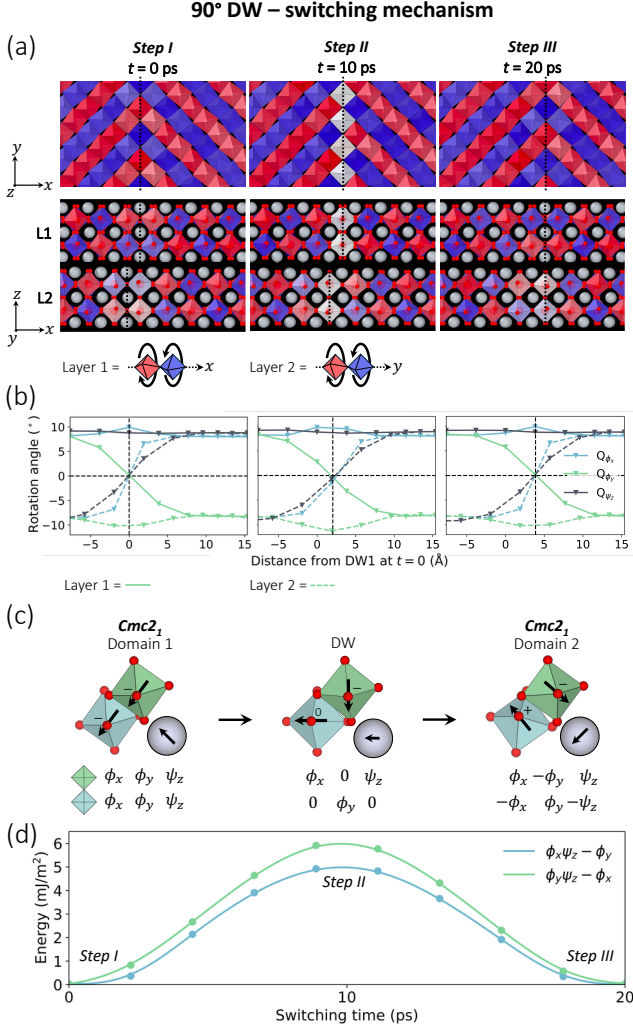


FIG. 5. (a) MD simulations of the displacement of a $\phi_x\psi_z - \phi_y$ wall at 300 K. In the top panels, every octahedron is color-coded with respect to the ϕ_x rotation, clearly showing the rotation by 90° at the wall. For the bottom panels, layer 1 (L1) and layer 2 (L2) use the rotations around x and y to accentuate the position of the wall. (b) The order parameter profiles corresponding to step I, II and III in (a), with the solid lines representing layer 1 and dashed lines representing layer 2. (c) Symmetries of each domain state and the instantaneous wall symmetry, illustrated with the change in tilting and polarization across the boundary. (d) NEB calculations of the energy barrier for switching each of the two 90° wall types.

lower than the formation energies. This minimum energy switching mechanism is qualitatively consistent with the orthorhombic twin switching in Ref. 40, but it is not possible to directly compare the barrier energies.

180° DWs. On heating from their 0 K relaxed structures, the $\phi_x\phi_y$ and ψ_z ferroelectric DWs turn out to be trapped in metastable local minima when the analysis starts from a sharp wall configuration. The true ground state for the $\phi_x\phi_y$ DW is a configuration where

the 180° wall is split up into two low-energy ferroelastic-type boundaries connected by symmetry. This means that at each split boundary, only a single out-of-phase rotational mode reverses in each layer, producing an antipolar mid-domain and effectively lowering the electrostatic energy. The size of this splitting was found to increase with temperature, growing from about $25 \text{ \AA}$ at 0 K to about $30 \text{ \AA}$ at 150 K. The simulated splitting process is depicted in Fig. 6a, with the energies of the relaxed split and non-split structures calculated with DFT and qNEP. $8 \times 1 \times 1$ supercells were used to accommodate the widening of the DWs, which explains the discrepancy between these formation energies and those of Table II.

When a 180° DW splits in this way, it creates two interfaces that can move somewhat independently both of each other and between layers. The total switching barrier can then be lowered by sequentially moving one element of the wall at a time, as opposed to moving the whole wall coherently. This could explain the low coercive field observed for ferroelectric switching. Unfortunately, it was not feasible to determine a definitive splitting barrier using NEB because there are multiple moving boundaries in a supercell with two split DW configurations. However, the qualitative transition from one local minimum to a global minimum is plotted in Fig. 6b. This does not show the energy cost from DW movement, but instead demonstrates the inherent limitations that come with manually creating and relaxing these structures with DFT. We note that this splitting was present also for the regular NEP model without charges. The calculated evolution of the order parameters is presented in Fig. 6c.

The atomistic switching mechanism is a transition from $Cmc2_1$ to an antipolar $Pnma$ domain where the polarization points in opposite directions in adjacent perovskite slabs, and where the instantaneous symmetry of the 90° boundaries corresponds to $Pmn2_1$ in bulk, see Fig. 6d. The size of the splitting is essentially a competition between the cost of the boundaries and the volume of the $Pnma$ domain. This is analogous to extended dislocations in face-centered cubic metals, where two partial dislocations surrounding a stacking fault reach an equilibrium distance, balancing repulsive and attractive forces [71]. Within ferroelectrics, such splitting is an instance of the domain wall decomposition reactions recently proposed as a general feature of multiple-order-parameter systems [72].

The ψ_z ferroelectric DW exhibits the same kind of splitting, where the points of reversal of in-phase rotations in each layer move away from each other. This creates a 180° switching of the polarization in one perovskite slab at a time, resulting again in a $Pnma$ mid-domain. These boundaries are not associated with any strain as for the previous $\phi_x\phi_y$ DW. The instantaneous DW symmetry is $Pmc2_1$. When $(100)_{pt}$ ψ_z DWs inside consecutive layers move away from one another, this creates a $(001)_{pt}$ ψ_z DW in the rocksalt layer between them. Since these have a very low formation energy (see Ta-

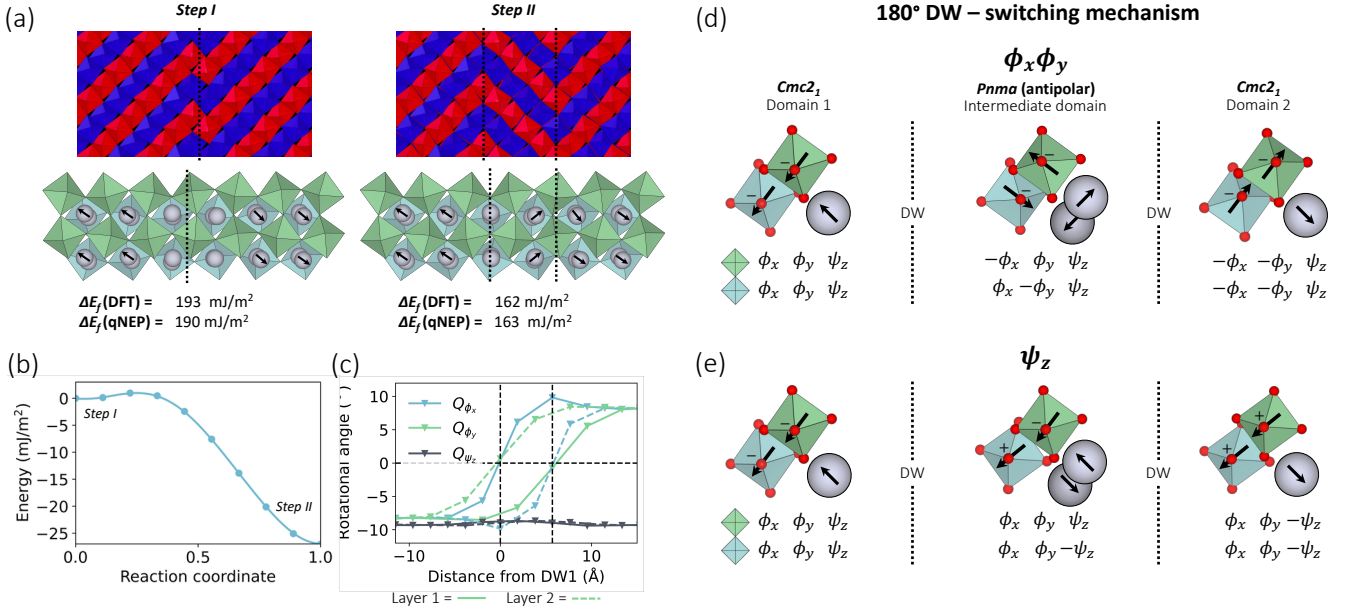


FIG. 6. (a) The $\phi_x \phi_y$ DW before (step I) and after (step II) the splitting process, along with the formation energies for each configuration calculated with DFT and qNEP. (b) NEB calculations of an approximate energy barrier that separates a metastable non-split (step I) and a stable split configuration (step II). This is not an energy barrier resulting from switching or DW motion. (c) The order parameter profile depicting the asymmetry between each layer, producing an antipolar $Pnma$ symmetry in between the two coupled ferroelectric walls. The atomistic switching mechanism for the (d) $\phi_x \phi_y$ and (e) ψ_z ferroelectric walls. They both switch through a two-step process, but for ψ_z the polarization flips by 180° in one perovskite layer at a time. Two arrows are used when there is a difference in polarization direction between the top (lighter gray sphere) and bottom layers (darker gray sphere).

ble II), these walls exhibit a much higher mobility and have less inter-layer coherence than $\phi_x \phi_y$ walls. Order parameter profiles for the non-split $\phi_x \phi_y$ configuration and the two 180° (001)_{pt} DWs can be found in Figs. S14 and S15 in the Supplementary Information [57].

The identified atomistic switching mechanisms are consistent with the lowest energy switching pathways found in Ref. 40, and offer a two-step pathway through an antipolar phase as a mechanism for the unexpectedly low coercive fields reported for $\text{Ca}_3\text{Ti}_2\text{O}_7$. Other switching pathways through alternative rotation patterns have been proposed that are not observed here [41, 70]. MD simulations of charged and neutral ferroelectric walls in the (110)_{pt} planes at finite temperature show the exact same splitting (Fig. S17), although a full analysis of these walls was not considered in the current work. Antipolar intermediate domains have also been experimentally observed to screen head-to-head and tail-to-tail DWs in $(\text{Ca}, \text{Sr})_3\text{Ti}_2\text{O}_7$ [73].

DISCUSSION

We have demonstrated that MLIPs based on the NEP framework can accurately reproduce the local geometry and electrostatics of DWs in $\text{Ca}_3\text{Ti}_2\text{O}_7$. The charge-aware qNEP models also systematically lower the error in

the DW formation energies. The order parameter profiles are almost identical to those from DFT, and the polarization profiles are reproduced up to a small offset in magnitude. MD simulations establish the switching mechanisms of the four symmetry-distinct (100)_{pt} DWs in $\text{Ca}_3\text{Ti}_2\text{O}_7$, revealing low-energy pathways for both inter-layer and intra-layer DW movement. The 90° DWs display a polar intermediate structure, while the 180° DWs split into two boundaries enclosing an antipolar domain and switch through a two-step mechanism. These atomistic simulations thereby establish a microscopic mechanism of domain wall motion.

Beyond accuracy, qNEP offers a computational advantage for exploring DWs in layered perovskite systems with large unit cells, at a fraction of the computational cost of DFT. Even the smaller supercells of the RP phase are at the limit of what is feasible with DFT, while qNEP can obtain optimized wall geometries for significantly bigger cells within minutes. This is ideal for systematically exploring stabilization mechanisms of charged DWs in $(\text{Ca}, \text{Sr})_3\text{Ti}_2\text{O}_7$ or other compositionally tuned RP phases. The fast optimization could also be utilized for additional phenomena such as magnetoelectric coupling, for example by using isolated DW structures as input for further analysis with DFT. Furthermore, the efficiency of the NEP method paves the way for field-driven large-scale simulations of nucleation, growth and

switching dynamics.

METHODS

Density functional theory

DFT calculations were used both to evaluate the training data and to determine the formation energies and local geometries of the various DWs. They were performed using the VASP [74, 75] code and the PBEsol functional (Perdew–Burke–Ernzerhof revised for solids), within the generalized gradient approximation [76]. The electronic wave functions are represented using the projector augmented wave approximation [77], where $\text{Ca}(3s^2, 3p^6, 4s^2)$, $\text{Ti}(3p^6, 3d^3, 4s^1)$ and $\text{O}(2s^2, 2p^4)$ were treated as valence electrons. The plane-wave cutoff energy was set to 550 eV.

A Γ -centered $9 \times 9 \times 9$ k -point mesh was used for the primitive cubic cell of CaTiO_3 , with an equivalent k -point density for all other cell sizes. For bulk structures, atomic positions were relaxed until the residual forces on all atoms were below 1 meV/Å. For the DW structures, which contain between 192 and 768 atoms depending on the wall type, the residual forces were relaxed below 20 meV/Å. The same threshold was applied in the corresponding MLIP relaxations, so that the comparison between methods is not affected by the choice of tolerance. The supercells were relaxed with fixed lattice parameters such that they remain equal to the bulk RP phase.

DW formation energies were calculated following

$$E_{\text{DW}}^f = \frac{1}{2A}(E_{\text{DW}} - E_{\text{bulk}}), \quad (3)$$

where E_{DW} is the total energy of a supercell with two DWs, and E_{bulk} is the total energy of a corresponding monodomain supercell. A is the cross-sectional area of the wall. BECs were calculated using density functional perturbation theory.

For the creation and analysis of the DW structures, the exact same procedure was also used with the MLIPs. Polarization profiles were calculated using BECs from the high-symmetry $I4/mmm$ structure, with a mid-layer Ca atom as the unit cell origin. Phonon modes were analyzed with the finite difference method implemented in PHONOPY [78, 79]. Mode decomposition of the ground state structure was calculated with ISODISTORT [80, 81]. All crystal structures are visualized using VESTA [82]. Optimized supercell structures can be retrieved on Zenodo [83].

Neuroevolution potential model

An MLIP was constructed using the NEP scheme [63] implemented in GPUMD [84, 85], following the procedure outlined in Ref. 86. The model was trained iteratively,

starting with a selection of ideal, strained, and rattled perovskite and RP structures with one to four octahedral layers per perovskite slab, adding snapshots from MD runs in the second iteration. For the rattled structures, atoms were randomly displaced using a Monte Carlo procedure supplied by the HIPHIVE package [87]. In addition, ferroelastic DW structures in CaTiO_3 and a subset of DWs in $\text{Ca}_3\text{Ti}_2\text{O}_7$ were included. Every structure was evaluated in terms of energies, forces, and stresses with DFT.

Three different models were trained, one using the regular NEP framework based on radial and angular descriptors, and two qNEP models using a charge-aware approach treating partial charges as latent and learnable model features [64]. The difference between the latter two models is the inclusion of an additional dataset with evaluated BECs, bringing the training set of the final potential to 760 structures. The ASE [88] and CALORINE [89] packages were used to prepare the training data and for post-processing. Energy barriers for switching pathways were calculated using the NEB method [90] as implemented in ASE [91]. Ten images were relaxed at fixed volume using the final qNEP model and the BFGS optimizer. To avoid any additional contributions from wall–wall interactions to the energy profile, a stiff spring constant of $10 \text{ eV}/\text{\AA}^2$ was employed, ensuring that both walls moved coherently. In all cases, the lowest-energy path that still corresponded to the isolated movement of a single wall was used. For additional information on the models, the training set and validation, see the Supplementary Information [57, 92–99].

Molecular dynamics

MD simulations were carried out with the GPUMD code. The NPT ensemble was consistently used in all simulations, with temperature and pressure controlled through the velocity-rescaling and stochastic cell-rescaling methods [100, 101]. To evaluate the phase transitions in $\text{Ca}_3\text{Ti}_2\text{O}_7$ and the performance of the NEP and qNEP potentials, heating simulations were conducted for each of the three trained models. Supercells containing approximately 30 000 atoms were heated from 1 K to 1500 K, with a heating rate set to 0.4 K/ps. For further details on these simulations, as well as the results concerning the two initial models, see the Supplementary Information [57]. This also includes equivalent heating simulations and analysis for CaTiO_3 .

The qNEP model including target BECs was also used when modeling dynamic DW motion, with the particle-particle-mesh (PPPM) method employed for computational speed. Compared with regular Ewald summation, PPPM consistently overestimates the DW formation energies, but the difference is only 1.7% on average (Fig. S7). The time step was set to 1 fs, sampling the trajectory every 5 ps. All DW supercells were optimized prior to the MD runs, although an equilibrium

configuration was consistently found even with unrelaxed cells. All trajectories were visualized with OVITO [102].

DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.22801877> [83].

CODE AVAILABILITY

The NEP and qNEP models generated in this study, as well as the domain wall structures evaluated, are openly available in Zenodo at <https://doi.org/10.5281/zenodo.22801877> [83], in a format suitable for the GPUMD package [84, 85]. All other software used in this work is publicly available, as described in the Methods section.

ACKNOWLEDGMENTS

We gratefully acknowledge financial support from the Research Council of Norway (No. 302506), the Swedish Research Council (Nos. 2020-04935 and 2025-03999), and the Knut and Alice Wallenberg Foundation (No. 2024.0042). Computational resources were provided by

UNINETT Sigma2 (Project No. NN9264K), as well as the National Academic Infrastructure for Supercomputing in Sweden (NAISS) at C3SE, partially funded by the Swedish Research Council through grant agreement No. 2022-06725, and the Berzelius resource provided by the Knut and Alice Wallenberg Foundation at NSC.

AUTHOR CONTRIBUTIONS

I.C.S. performed the majority of the analysis and wrote the original draft. E.F. contributed to the analysis, methodology, and supervised the technical work. L.Ö.W. contributed to the development of the training dataset. B.A.D.W. and S.M.S. supervised the work. N.C.B. contributed to overall interpretation and technical discussions. P.E. led and supervised the project. I.C.S., S.M.S., and P.E. conceived and designed the study. All authors reviewed the manuscript and approved the final version.

FUNDING

Open access funding provided by Chalmers University of Technology.

COMPETING INTERESTS

The authors declare no competing interests.

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- [1] G. F. Nataf, M. Guennou, J. M. Gregg, D. Meier, J. Hlinka, E. K. H. Salje, and J. Kreisel, *Nat. Rev. Phys.* **2**, 634 (2020).
 - [2] D. Meier, *J. Phys.: Condens. Matter* **27**, 463003 (2015).
 - [3] D. Meier and S. M. Selbach, *Nat. Rev. Mater.* **7**, 157 (2022).
 - [4] J. Seidel, L. W. Martin, Q. He, Q. Zhan, Y. H. Chu, A. Rother, M. E. Hawkrige, P. Maksymovych, P. Yu, M. Gajek, *et al.*, *Nat. Mater.* **8**, 229 (2009).
 - [5] J. A. Mundy, J. Schaab, Y. Kumagai, A. Cano, M. Stengel, I. P. Krug, D. M. Gottlob, H. Doğanay, M. E. Holtz, R. Held, *et al.*, *Nat. Mater.* **16**, 622 (2017).
 - [6] J. R. Whyte and J. M. Gregg, *Nat. Commun.* **6**, 7361 (2015).
 - [7] L. Richarz, I. C. Skogvoll, E. Y. Tökle, K. A. Hønnestad, U. Ludacka, J. He, E. Bourret, Z. Yan, A. T. J. van Helvoort, J. Schultheiß, *et al.*, *ACS Appl. Mater. Interfaces* **17**, 47576 (2025).
 - [8] G. Sanchez-Santolino, J. Tornos, D. Hernandez-Martin, J. I. Beltran, C. Munuera, M. Cabero, A. Perez-Muñoz, J. Ricote, F. Mompean, M. Garcia-Hernandez, *et al.*, *Nat. Nanotechnol.* **12**, 655 (2017).
 - [9] P. Maksymovych, J. Seidel, Y. H. Chu, P. Wu, A. P. Baddorf, L.-Q. Chen, S. V. Kalinin, and R. Ramesh, *Nano Lett.* **11**, 1906 (2011).
 - [10] J. Sun, Y. Li, Y. Ou, Q. Huang, X. Liao, Z. Chen, X. Chai, X. Zhuang, W. Zhang, C. Wang, *et al.*, *Adv. Funct. Mater.* **32**, 2207418 (2022).
 - [11] Y.-H. Shin, I. Grinberg, I.-W. Chen, and A. M. Rappe, *Nature* **449**, 881 (2007).
 - [12] S. Liu, I. Grinberg, and A. M. Rappe, *Appl. Phys. Lett.* **103**, 232907 (2013).
 - [13] S. Liu, I. Grinberg, and A. M. Rappe, *Nature* **534**, 360 (2016).
 - [14] J. Očenášek, J. Minár, and J. Alcalá, *npj Comput. Mater.* **9**, 118 (2023).
 - [15] F. Gómez-Ortiz, H. Aramberri, J. M. López, P. García-Fernández, J. Íñiguez, and J. Junquera, *Phys. Rev. B* **107**, 174102 (2023).
 - [16] R. Khachatryan, Y. Yang, S.-H. Teng, B. Udofia, M. Stricker, and A. Grünebohm, *Phys. Rev. Mater.* **8**, 024403 (2024).
 - [17] A. Sehrawat, K. Albe, and J. Rohrer, *J. Phys.: Condens. Matter* **38**, 015402 (2026).
 - [18] P. S. Halasyamani and K. R. Poeppelmeier, *Chem. Mater.* **10**, 2753 (1998).
 - [19] A. P. Levanyuk and D. G. Sannikov, *Sov. Phys. Usp.* **17**, 199 (1974).
 - [20] N. A. Benedek and M. A. Hayward, *Annu. Rev. Mater. Res.* **52**, 331 (2022).
 - [21] X.-Z. Lu, H.-M. Zhang, Y. Zhou, T. Zhu, H. Xiang, S. Dong, H. Kageyama, and J. M. Rondinelli, *Sci. Adv.* **9**, eadi0138 (2023).

- [22] E. Bousquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J.-M. Triscone, and P. Ghosez, *Nature* **452**, 732 (2008).
- [23] N. A. Benedek and C. J. Fennie, *Phys. Rev. Lett.* **106**, 107204 (2011).
- [24] F.-T. Huang, F. Xue, B. Gao, L. H. Wang, X. Luo, W. Cai, X.-Z. Lu, J. M. Rondinelli, L. Q. Chen, and S.-W. Cheong, *Nat. Commun.* **7**, 11602 (2016).
- [25] K. A. Smith, E. A. Nowadnick, S. Fan, O. Khatib, S. J. Lim, B. Gao, N. C. Harms, S. N. Neal, J. K. Kirkland, M. C. Martin, *et al.*, *Nat. Commun.* **10**, 5235 (2019).
- [26] B. Gao, F.-T. Huang, Y. Wang, J.-W. Kim, L. Wang, S.-J. Lim, and S.-W. Cheong, *Appl. Phys. Lett.* **110**, 222906 (2017).
- [27] Y. S. Oh, X. Luo, F.-T. Huang, Y. Wang, and S.-W. Cheong, *Nat. Mater.* **14**, 407 (2015).
- [28] X. Li, L. Yang, C. F. Li, M. F. Liu, Z. Fan, Y. L. Xie, C. L. Lu, L. Lin, Z. B. Yan, Z. Zhang, *et al.*, *Appl. Phys. Lett.* **110**, 042901 (2017).
- [29] T. Zhu, X.-Z. Lu, T. Aoyama, K. Fujita, Y. Nambu, T. Saito, H. Takatsu, T. Kawasaki, T. Terauchi, S. Kurosawa, *et al.*, *Nat. Mater.* **23**, 182 (2024).
- [30] I. Marković, M. D. Watson, O. J. Clark, F. Mazzola, E. Abarca Morales, C. A. Hooley, H. Rosner, C. M. Polley, T. Balasubramanian, S. Mukherjee, *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **117**, 15524 (2020).
- [31] Q.-X. Chen and J.-Z. Zhao, *J. Phys. Chem. C* **129**, 5221 (2025).
- [32] P. Kayastha, E. Fransson, P. Erhart, and L. Whalley, *Phys. Rev. Lett.* **136**, 086101 (2026).
- [33] F. Jerzembeck, H. S. Røising, A. Steppke, H. Rosner, D. A. Sokolov, N. Kikugawa, T. Scaffidi, S. H. Simon, A. P. Mackenzie, and C. W. Hicks, *Nat. Commun.* **13**, 4596 (2022).
- [34] H. Sakakibara, M. Ochi, H. Nagata, Y. Ueki, H. Sakurai, R. Matsumoto, K. Terashima, K. Hirose, H. Ohta, M. Kato, Y. Takano, and K. Kuroki, *Phys. Rev. B* **109**, 144511 (2024).
- [35] R. Zhang, M. S. Senn, and M. A. Hayward, *Chem. Mater.* **28**, 8399 (2016).
- [36] Y. Zhang, T. Shimada, T. Kitamura, and J. Wang, *J. Phys. Chem. Lett.* **8**, 5834 (2017).
- [37] W. Li, S. Niu, B. Zhao, R. Haiges, Z. Zhang, J. Ravichandran, and A. Janotti, *Phys. Rev. Mater.* **3**, 101601 (2019).
- [38] F. Pomiro, C. Ablitt, N. C. Bristowe, A. A. Mostofi, C. Won, S.-W. Cheong, and M. S. Senn, *Phys. Rev. B* **102**, 014101 (2020).
- [39] G. Clarke, D. Daisenberger, X. Luo, S. W. Cheong, N. C. Bristowe, and M. S. Senn, *Phys. Rev. B* **109**, 094107 (2024).
- [40] E. A. Nowadnick and C. J. Fennie, *Phys. Rev. B* **94**, 104105 (2016).
- [41] S. Li and T. Birol, *npj Comput. Mater.* **6**, 168 (2020).
- [42] G. Stone, D. Puggioni, S. Lei, M. Gu, K. Wang, Y. Wang, J. Ge, X.-Z. Lu, Z. Mao, J. M. Rondinelli, and V. Gopalan, *Phys. Rev. B* **99**, 014105 (2019).
- [43] P. Zhong, D. Kim, D. S. King, and B. Cheng, *npj Comput. Mater.* **11**, 384 (2025).
- [44] K. S. Aleksandrov and J. Bartolomé, *Phase Transit.* **74**, 255 (2001).
- [45] H. T. Stokes, E. H. Kisi, D. M. Hatch, and C. J. Howard, *Acta Crystallogr. Sect. B* **58**, 934 (2002).
- [46] S. Lei, M. Gu, D. Puggioni, G. Stone, J. Peng, J. Ge, Y. Wang, B. Wang, Y. Yuan, K. Wang, *et al.*, *Nano Lett.* **18**, 3088 (2018).
- [47] A. T. Mulder, N. A. Benedek, J. M. Rondinelli, and C. J. Fennie, *Adv. Funct. Mater.* **23**, 4810 (2013).
- [48] I. C. Skogvoll, B. A. D. Williamson, and S. M. Selbach, *Phys. Rev. B* **113**, 224102 (2026).
- [49] M. S. Senn, A. Bombardi, C. A. Murray, C. Vecchini, A. Scherillo, X. Luo, and S. W. Cheong, *Phys. Rev. Lett.* **114**, 035701 (2015).
- [50] B. H. Zhang, X. Q. Liu, and X. M. Chen, *J. Phys. D: Appl. Phys.* **55**, 113001 (2021).
- [51] X. Q. Liu, J. W. Wu, X. X. Shi, H. J. Zhao, H. Y. Zhou, R. H. Qiu, W. Q. Zhang, and X. M. Chen, *Appl. Phys. Lett.* **106**, 202903 (2015).
- [52] H. Wu, W. Cai, C. Zhou, Q. Zhang, R. Gao, G. Chen, X. Deng, Z. Wang, and C. Fu, *Mater. Lett.* **278**, 128447 (2020).
- [53] M. Yashima and R. Ali, *Solid State Ion.* **180**, 120 (2009).
- [54] S. M. Selbach, J. R. Tolchard, A. Fossdal, and T. Grande, *J. Solid State Chem.* **196**, 249 (2012).
- [55] Q. Zhou and B. J. Kennedy, *J. Phys. Chem. Solids* **67**, 1595 (2006).
- [56] C. A. Dixon, C. M. Kavanagh, K. S. Knight, W. Kockelmann, F. D. Morrison, and P. Lightfoot, *J. Solid State Chem.* **230**, 337 (2015).
- [57] See Supplementary Information at [URL will be inserted by publisher] for more details on the training and validation of the NEP models, phase transition simulations of $\text{Ca}_3\text{Ti}_2\text{O}_7$ and CaTiO_3 , and domain wall motion analysis. This includes Table S1-S5, Fig. S1-S19 and Refs. [92–99].
- [58] P. S. Bednyakov, B. I. Sturman, T. Sluka, A. K. Tagantsev, and P. V. Yudin, *npj Comput. Mater.* **4**, 65 (2018).
- [59] D. M. Evans, V. Garcia, D. Meier, and M. Bibes, *Phys. Sci. Rev.* **5**, 20190067 (2020).
- [60] J. Schaab, I. P. Krug, F. Nickel, D. M. Gottlob, H. Doğanay, A. Cano, M. Hentschel, Z. Yan, E. Bourret, C. M. Schneider, *et al.*, *Appl. Phys. Lett.* **104**, 232904 (2014).
- [61] H. Nakajima, K. Shigematsu, Y. Horibe, S. Mori, and Y. Murakami, *Mater. Trans.* **60**, 2103 (2019).
- [62] H. Nakajima, K. Kurushima, S. Mine, H. Tsukasaki, M. Matsuoka, B. Gao, S.-W. Cheong, and S. Mori, *Commun. Mater.* **2**, 109 (2021).
- [63] K. Song, R. Zhao, J. Liu, Y. Wang, E. Lindgren, Y. Wang, S. Chen, K. Xu, T. Liang, P. Ying, *et al.*, *Nat. Commun.* **15**, 10208 (2024).
- [64] Z. Fan, B. Tang, E. Berger, E. Berger, E. Fransson, K. Xu, Z. Yan, Z. Liu, Z. Song, H. Dong, S. Chen, L. Li, Z. Wang, Y. Zhu, J. Wiktor, and P. Erhart, *J. Chem. Theory Comput.* **22**, 4787 (2026).
- [65] D. R. Småbråten, Q. N. Meier, S. H. Skjærvø, K. Inzani, D. Meier, and S. M. Selbach, *Phys. Rev. Mater.* **2**, 114405 (2018).
- [66] A. Chandrasekaran, D. Damjanovic, N. Setter, and N. Marzari, *Phys. Rev. B* **88**, 214116 (2013).
- [67] X. Zhang, B. Wang, Y. Ji, F. Xue, Y. Wang, L.-Q. Chen, and C.-W. Nan, *Acta Mater.* **242**, 118351 (2023).
- [68] X.-K. Wei, A. K. Tagantsev, A. Kvasov, K. Roleder, C.-L. Jia, and N. Setter, *Nat. Commun.* **5**, 3031 (2014).
- [69] E. Salje, *Phase transitions in ferroelastic and co-elastic crystals* (Cambridge University Press, 1990).

- [70] J. M. Munro, H. Akamatsu, H. Padmanabhan, V. S. Liu, Y. Shi, L.-Q. Chen, B. K. VanLeeuwen, I. Dabo, and V. Gopalan, *Phys. Rev. B* **98**, 085107 (2018).
- [71] D. Hull and D. J. Bacon, *Introduction to dislocations*, 5th ed. (Elsevier, 2011).
- [72] S. Zhou, S. Qin, and A. M. Rappe, *Phys. Rev. Lett.* **134**, 136802 (2025).
- [73] M. H. Lee, C.-P. Chang, F.-T. Huang, G. Y. Guo, B. Gao, C. H. Chen, S.-W. Cheong, and M.-W. Chu, *Phys. Rev. Lett.* **119**, 157601 (2017).
- [74] G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- [75] G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [76] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [77] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- [78] A. Togo, *J. Phys. Soc. Jpn.* **92**, 012001 (2023).
- [79] A. Togo, L. Chaput, T. Tadano, and I. Tanaka, *J. Phys.: Condens. Matter* **35**, 353001 (2023).
- [80] H. T. Stokes, D. M. Hatch, and B. J. Campbell, *Isotropy software suite, iso.byu.edu*.
- [81] B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, *J. Appl. Crystallogr.* **39**, 607 (2006).
- [82] K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- [83] I. C. Skogvoll, E. Fransson, L. Ö. Westin, B. A. D. Williamson, N. C. Bristowe, S. M. Selbach, and P. Erhart, Data for "Machine-learning guided exploration of domain walls in the hybrid improper ferroelectric $\text{Ca}_3\text{Ti}_2\text{O}_7$ ", Zenodo (2026), <https://doi.org/10.5281/zenodo.22801877>.
- [84] Z. Fan, Y. Wang, P. Ying, K. Song, J. Wang, Y. Wang, Z. Zeng, K. Xu, E. Lindgren, J. M. Rahm, *et al.*, *J. Chem. Phys.* **157**, 114801 (2022).
- [85] K. Xu, H. Bu, S. Pan, E. Lindgren, Y. Wu, Y. Wang, J. Liu, K. Song, B. Xu, Y. Li, T. Hainer, L. Svensson, J. Wiktor, R. Zhao, H. Huang, C. Qian, S. Zhang, Z. Zeng, B. Zhang, B. Tang, Y. Xiao, Z. Yan, J. Shi, Z. Liang, J. Wang, T. Liang, S. Cao, Y. Wang, P. Ying, N. Xu, C. Chen, Y. Zhang, Z. Chen, X. Wu, W. Jiang, E. Berger, Y. Li, S. Chen, A. J. Gabourie, H. Dong, S. Xiong, N. Wei, Y. Chen, J. Xu, F. Ding, Z. Sun, T. Ala-Nissila, A. Harju, J. Zheng, P. Guan, P. Erhart, J. Sun, W. Ouyang, Y. Su, and Z. Fan, *Mater. Genome Eng. Adv.* **3**, e70028 (2025).
- [86] E. Fransson, J. Wiktor, and P. Erhart, *J. Phys. Chem. C* **127**, 13773 (2023).
- [87] F. Eriksson, E. Fransson, and P. Erhart, *Adv. Theory Simul.* **2**, 1800184 (2019).
- [88] A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dułak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, *et al.*, *J. Phys.: Condens. Matter* **29**, 273002 (2017).
- [89] E. Lindgren, M. Rahm, E. Fransson, F. Eriksson, N. Österbacka, Z. Fan, and P. Erhart, *J. Open Source Softw.* **9**, 6264 (2024).
- [90] G. Henkelman, B. P. Uberuaga, and H. Jónsson, *J. Chem. Phys.* **113**, 9901 (2000).
- [91] E. L. Kolsbjerg, M. N. Groves, and B. Hammer, *J. Chem. Phys.* **145**, 094107 (2016).
- [92] E. Bitzek, P. Koskinen, F. Gähler, M. Moseler, and P. Gumbsch, *Phys. Rev. Lett.* **97**, 170201 (2006).
- [93] J. Guénolé, W. G. Nöhring, A. Vaid, F. Houllé, Z. Xie, A. Prakash, and E. Bitzek, *Comput. Mater. Sci.* **175**, 109584 (2020).
- [94] R. Ali and M. Yashima, *J. Solid State Chem.* **178**, 2867 (2005).
- [95] M. A. Carpenter, *Am. Mineral.* **92**, 309 (2007).
- [96] Y. Gu, K. Rabe, E. Bousquet, V. Gopalan, and L.-Q. Chen, *Phys. Rev. B* **85**, 064117 (2012).
- [97] H. Zhang, M. M. Schmitt, L. Bastogne, X. He, and P. Ghosez, *Phys. Rev. B* **112**, 224103 (2025).
- [98] S. Yoshida, H. Akamatsu, R. Tsuji, O. Hernandez, H. Padmanabhan, A. Sen Gupta, A. S. Gibbs, K. Mibu, S. Murai, J. M. Rondinelli, *et al.*, *J. Am. Chem. Soc.* **140**, 15690 (2018).
- [99] E. Gradauskaite, *Small Sci.* **6**, e202500488 (2026).
- [100] G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).
- [101] M. Bernetti and G. Bussi, *J. Chem. Phys.* **153**, 114107 (2020).
- [102] A. Stukowski, *Modell. Simul. Mater. Sci. Eng.* **18**, 015012 (2010).

Supplementary Information:

Machine-learning-guided exploration of domain walls in the hybrid improper ferroelectric $\text{Ca}_3\text{Ti}_2\text{O}_7$

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Contents

Neuroevolution potentials	S2
Training set	S2
Validation	S3
Particle-particle particle-mesh evaluation	S5
Phase transitions	S9
CaTiO_3	S9
$\text{Ca}_3\text{Ti}_2\text{O}_7$	S9
Domain walls	S15
Order parameter analysis	S15
Domain wall dynamics	S16
Supplementary References	S19

Neuroevolution potentials

The neuroevolution potential (NEP) framework is a machine-learned interatomic potential method based on a feed-forward neural network (NN) architecture with a single hidden layer and an evolutionary training algorithm. It provides accurate atomistic simulations at computational speeds and size scales far exceeding what is feasible with density functional theory (DFT). It is implemented in the software GPUMD¹, which provides a regular NEP framework and a charge-aware NEP (qNEP). The NEP architecture uses a local environment descriptor based on short-range radial and angular information, where forces and energies are calculated as a sum of site energies (U^{NEP}). With qNEP, charges are predicted using the same single-NN architecture as NEP, treating the total energy as a sum of the site energies and electrostatic contributions (U^{ES}). Reference partial charges are therefore not needed in the training data, but target Born effective charges (BECs) may be included for training².

In the present work three models were trained, one regular NEP model, one qNEP model using the same training set and lastly a qNEP model including an additional set of structures with BECs as reference values. The two latter models were trained with charge mode 1, where both real-space and reciprocal space components of the electrostatics are evaluated. The schematic in Fig. S1 illustrates the difference between the NEP and qNEP frameworks, and summarizes the three different models.

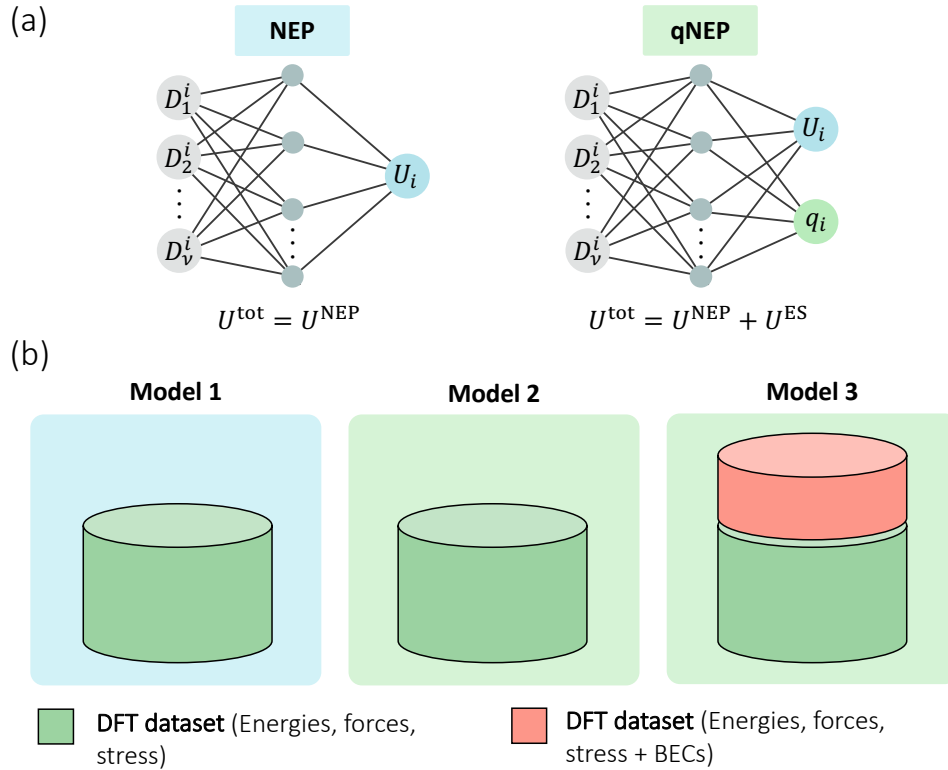


Figure S1: (a) The single-NN architecture of the NEP and qNEP methods. The input for both is the local environment descriptor (D_ν^i). The total energy is calculated as a sum of site energies with the NEP approach, while the qNEP approach additionally predicts charges and electrostatic contributions to the energy. (b) Each model described in terms of the dataset used and the method employed for training (blue and green squares representing NEP and qNEP, respectively). Model 3 differs from the former models by the inclusion of an additional dataset with target BECs. Adapted from Ref. 2.

Training set

The NEP training dataset was constructed in two iterations and in each generation every structure was evaluated using DFT to extract the formation energy, forces and stress tensors. The training set comprises

symmetry-constrained relaxed structures for polar and non-polar structures in the CaTiO_3 perovskite family, and various crystal structures in the $\text{Ca}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden-Popper (RP)-series with n ranging from 1 to 4. Strained or rattled structures, as well as molecular dynamics (MD) snapshots, are evaluated using single-point calculations. The number of structures evaluated within each category was determined to strike a balance between the number of atoms and the associated computational cost.

Altogether, the training set for models 1 and 2 totals 459 structures, where the sizes range from 5 atoms to 576 atoms and cover both ground states and highly distorted structures. For model 3, 301 additional MD snapshots with 20 to 28 atoms and DFT calculated BECs were added. The number of structures in each category, along with their space group and tilting pattern, is listed in Tables S1, S2, and S3. The domain wall (DW) structures used in the training set are consistent with a subset of the ones detailed in the main manuscript.

The ASE³ and CALORINE⁴ packages were employed to generate the training structures, configure the MD simulations and post-process the resulting data. Random displacements were created using the HIPHIVE package⁵.

Table S1: The type and number of perovskite structures used in the first training set created for models 1 and 2. An empty cell indicates that no structures were evaluated. We note that although there is a distinction between the generation 1 and generation 2 structures, all structures listed were used for the generation 2 training set. The tilt patterns are given in the modified Glazer notation introduced in Ref. 6, where the superscripts denote the octahedral tilt pattern while the subscripts denote the direction of B-site displacements along each respective axis. Calculated energies are listed as relative energies with respect to the ground state, which is $Pnma$. While structures that share the same tilt pattern but differ in polarity have very similar energies, they remain symmetry-distinct.

SG	Tilt pattern	Energy (eV/f.u.)			Generation 1		Generation 2
		DFT	NEP	#Ideal	#Strained	#Rattled	#MD snapshots
$Pm\bar{3}m$	$a_0^0 a_0^0 a_0^0$	0.3526	0.3531	1	7	4	20
$Pnma$	$a_0^+ b_0^- b_0^-$	0	0	1	7	4	8
$Cmcm$	$a_0^0 b_0^+ c_0^-$	0.0638	0.0605	1		4	10
$P4/mbm$	$a_0^0 a_0^0 c_0^+$	0.1302	0.1313	1		4	
$I4/mmm$	$a_0^0 b_0^+ b_0^+$	0.1235	0.1174	1		4	
$I4/mcm$	$a_0^0 a_0^0 c_0^-$	0.0931	0.0933	1		4	8
$Imma$	$a_0^0 b_0^- b_0^-$	0.0597	0.0662	1		4	
$P4mm$	$a_0^0 a_0^0 c_0^+$	0.2863	0.2936	1		4	
$R3m$	$a_+^0 a_+^0 a_+^0$	0.3132	0.3283	1		4	
$Amm2$	$a_0^+ b_0^0 c_0^+$	0.1206	0.1269	1		4	
$R3c$	$a_-^0 a_-^0 a_+^0$	0.0532	0.0559	1		- ^a	
$P4bm$	$a_0^0 a_0^0 c_+^+$	0.1302	0.1313	1		4	
$Fmm2$	$a_0^- b_0^0 c_0^+$	0.0931	0.0933	1		4	
$Ama2$	$a_0^- b_0^+ c_0^+$	0.0632	0.0605	1		4	
$P\bar{1}$	$a_0^- b_0^- c_0^-$	-	-	- ^b			

^a Convergence issue

^b Relaxed to a different structure

Validation

All models were trained using the same radial and angular cutoff parameters, $r_C^R = 8 \text{ \AA}$ and $r_C^A = 4 \text{ \AA}$. For validation, loss and root-mean-square error (RMSE) as well as parity plots were calculated for the full model (trained on the entire dataset) and for each of the 10 cross-validation splits (each trained on 90% of the training set). The loss curves for the full models can be found in Fig. S2. Parity plots with the calculated RMSE, using the fully trained model and cross-validation splits for testing, can be found in Figs. S3, S4, and S5. In addition, parity plots with BECs for each species are presented in Fig. S6. The train and test RMSEs are similar and low, showing no signs of overfitting. As discussed in the main text, however, low aggregate

Table S2: The type and number of RP phases used in the training set created for models 1 and 2. The tilt pattern uses the Aleksandrov notation, as explained in Ref. 7. Symbols ψ and ϕ denote in- and out-of-phase rotations, respectively. Calculated energies using DFT and the NEP model are listed relative to the lowest-energy structure for each n .

SG	Tilt pattern	Energy (eV/f.u.)		#Ideal	Generation 1		Generation 2
		DFT	NEP		#Strained	#Rattled	#MD snapshots
<i>n</i>=1							
<i>I4/mmm</i>	000 000	0	0	1	7	4	19
<i>C2/c</i>	$\phi\phi\psi\ \phi\phi\psi$	- ^a					15
<i>Pccn</i>	$\phi\phi\psi\ \phi\phi\bar{\psi}$	- ^a					15
<i>n</i>=2							
<i>I4/mmm</i>	000 000	0.4765	0.4485	1	7	4	14
<i>Cmce</i>	$00\psi_z\ 00\psi_z$	0.1862	0.1769	1		4	17
<i>P4₂/mcm</i>	$\phi00\ 0\bar{\phi}0$	0.2497	0.2397	1		4	15
<i>Cmc2₁</i>	$\phi\phi\psi\ \phi\phi\psi$	0	0	1	7	4	20
<i>Pnma</i>	$\phi\phi\psi\ \phi\phi\bar{\psi}$	0.0146	0.0006	1		4	13
<i>n</i>=3							
<i>I4/mmm</i>	000 000	0.6880	0.6837	1	7	4	14
<i>C2/c</i>	$\phi\phi\psi\ \phi\phi\psi$	0.0118	0.0064	1	7	4	16
<i>Pccn</i>	$\phi\phi\psi\ \phi\phi\bar{\psi}$	0	0	1		4	15
<i>n</i>=4							
<i>Cmc2₁</i>	$\phi\phi\psi\ \phi\phi\psi$						11
<i>Pnma</i>	$\phi\phi\psi\ \phi\phi\bar{\psi}$						13

^a Relaxed to a different structure

Table S3: The number of 90° (ferroelastic and ferroelectric) and 180° (ferroelectric) DW structures for the RP phase and ferroelastic DWs for the perovskite phase. The number of ideal structures includes both relaxed and unrelaxed DW cells. Only (100)_{pt} DW structures were used in training.

Wall type	#Ideal	#Rattled	#MD snapshots
RP			
90° DW	6	6	8
180° DW	6	6	8
Perovskite			
90°	2	6	8

errors do not by themselves guarantee accurate DW formation energies.”

Relative energies, lattice parameters and twin angles were also calculated for each of the phases in CaTiO₃ and Ca₃Ti₂O₇, presented in Tables S4 and S5. The correct ground state is reproduced both for CaTiO₃ and Ca₃Ti₂O₇. For the prediction of the intermediate phases, see the following section on phase transitions. All models show good agreement with DFT values. The largest discrepancy in energy was found for the *Ccce* phase which was not in the training set. Notably, all models give a higher twin angle for the *Pnma* and *Cmc2₁* phases, meaning 90° DWs exhibit a higher strain gradient with the NEPs.

Table S4: Relative energies, lattice parameters and twin angles (γ) calculated for each of the phases predicted for CaTiO_3 , using DFT and the trained potentials in models 1, 2, and 3.

CaTiO_3	DFT	Model 1	Model 2	Model 3
Orthorhombic, $Pnma$ ($a^+b^-b^-$)				
a (Å)	5.446	5.451	5.457	5.451
b	5.344	5.338	5.331	5.341
c	7.604	7.598	7.610	7.605
γ (degrees)	1.079	1.203	1.338	1.171
Tetragonal, $I4/mcm$ ($a^0a^0c^-$)				
ΔE (eV/f.u.)	0.0931	0.0933	0.0873	0.0847
a_t	5.346	5.348	5.342	5.345
c	7.770	7.787	7.793	7.776
Cubic, $Pm\bar{3}m$ ($a^0a^0a^0$)				
ΔE	0.3526	0.3531	0.3416	0.3404
a_c	3.847	3.849	3.849	3.846

Table S5: Relative energies, lattice parameters and twin angles calculated for each of the phases predicted for $\text{Ca}_3\text{Ti}_2\text{O}_7$, using DFT and the trained potentials in models 1, 2, and 3.

$\text{Ca}_3\text{Ti}_2\text{O}_7$	DFT	Model 1	Model 2	Model 3
Orthorhombic, $Cmc2_1$ ($\phi\phi\psi\phi\phi\psi$)				
a (Å)	5.447	5.446	5.459	5.456
b	5.389	5.376	5.374	5.388
c	19.311	19.368	19.345	19.307
γ (degrees)	0.602	0.731	0.897	0.724
Orthorhombic, $Ccce$ ($00\phi00\phi$)				
ΔE (eV/f.u.)	0.2125	0.1434	0.1491	0.1447
a	5.329	5.337	5.335	5.330
b	5.330	5.338	5.335	5.330
c	19.891	19.877	19.858	19.885
Tetragonal, $I4/mmm$ (000000)				
ΔE	0.4765	0.4485	0.4595	0.4478
a_t	3.838	3.840	3.841	3.842
c	19.409	19.406	19.425	19.403

Particle-particle particle-mesh evaluation

The calculation of the reciprocal space contribution to the electrostatic energy can be accelerated using fast Fourier transform (FFT) methods, such as the particle-particle particle-mesh (PPPM) algorithm. This results in an $\mathcal{O}(N \log N)$ scaling, compared with $\mathcal{O}(N^{3/2})$ for optimally tuned Ewald summation. The simulation time is then only slightly increased using a qNEP model, compared to a NEP model². To ensure that this did not impact the accuracy of the simulations, DW formation energies were evaluated with regular Ewald summation and with PPPM. For PPPM, the fast inertial relaxation engine was used for optimization^{8,9}. It was found that PPPM evaluation consistently overestimates the formation energies, with an average increase of 1.7%. For a comparison, see Fig. S7.

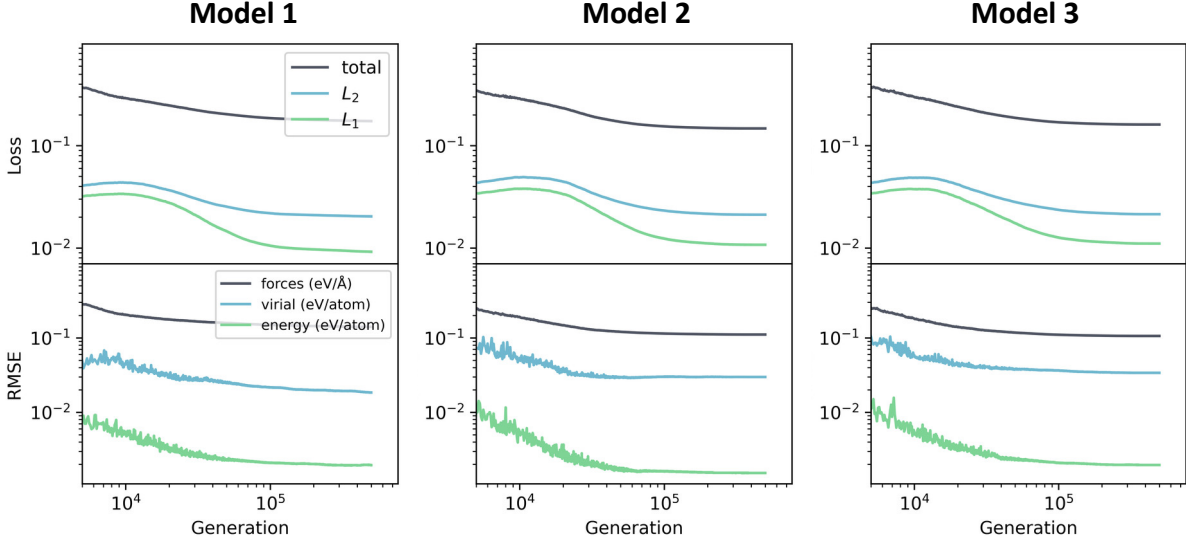


Figure S2: Evolution of the loss curves and RMSEs for the energies, forces and virial stresses during training of the full models. L_1 and L_2 represent the regularization penalties used to avoid overfitting the potential.

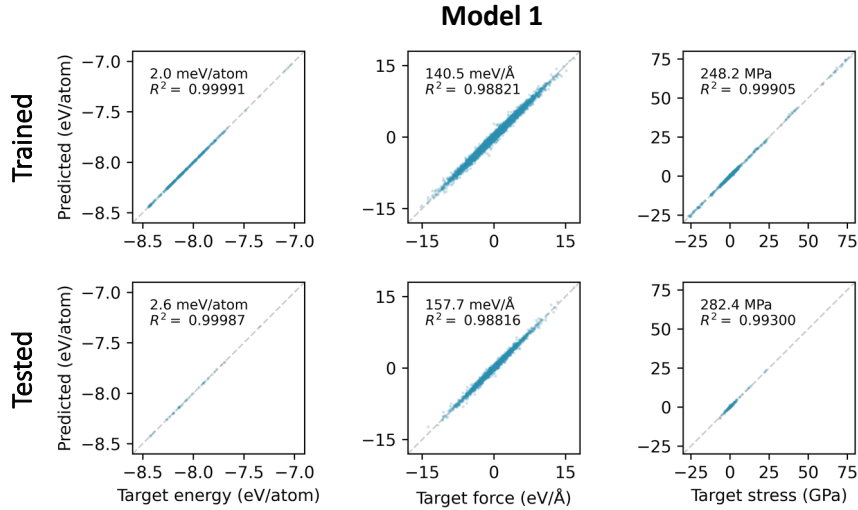


Figure S3: Parity plots for model 1 with trained and tested structures, which show the predicted and target values for energy, force, virial stress and stress tensors calculated for the training data.

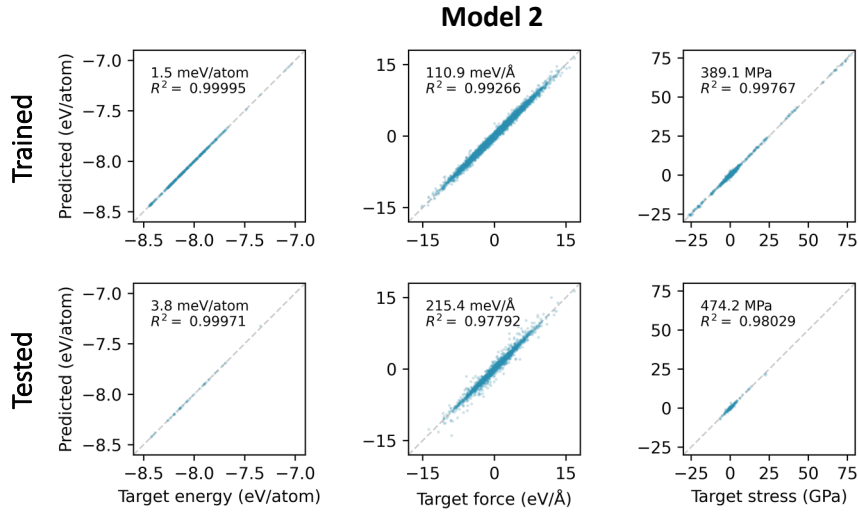


Figure S4: Parity plots for model 2 with trained and tested structures, which show the predicted and target values for energy, force, virial stress and stress tensors calculated for the training data.

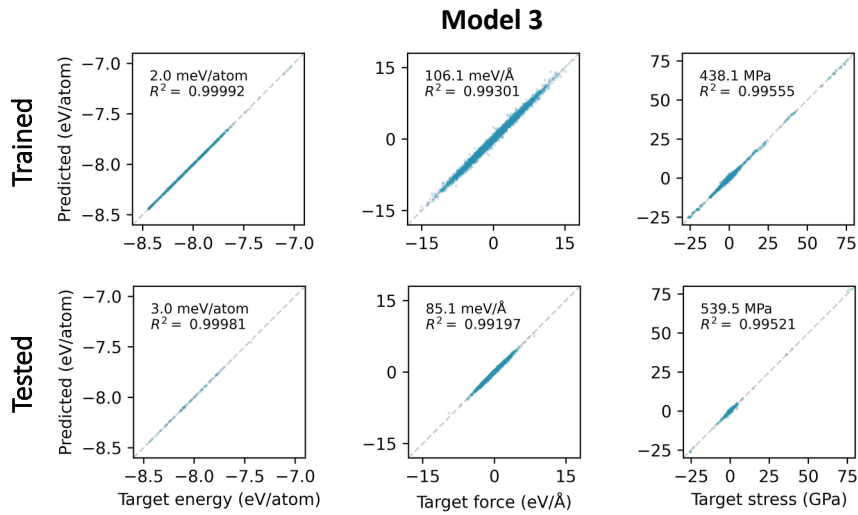


Figure S5: Parity plots for model 3 with trained and tested structures, which show the predicted and target values for energy, force, virial stress and stress tensors calculated for the training data.

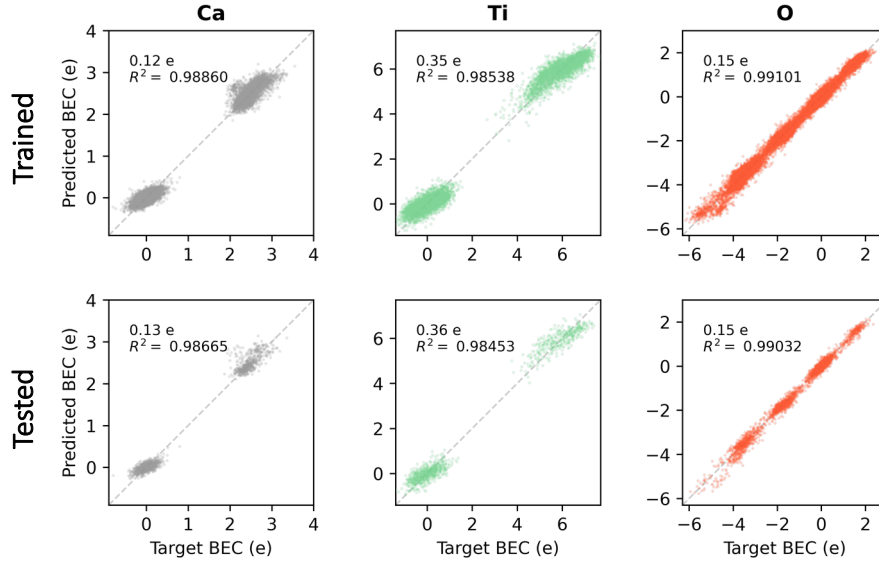


Figure S6: Parity plots with the RMSE of predicted and target BECs for Ca, Ti and O, using trained and tested structures evaluated with model 3.

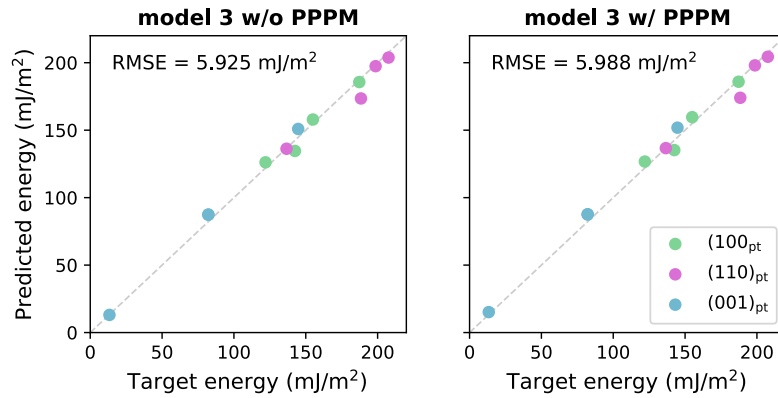


Figure S7: Parity plots for the DW formation energies of walls in the $(100)_{\text{pt}}$, $(110)_{\text{pt}}$ and $(001)_{\text{pt}}$ planes. Formation energies were calculated using regular Ewald summation (without PPPM) and with PPPM.

Phase transitions

Capturing the physics involved in critical behavior hinges on the accurate estimation of the free energy landscape, discerning the potentially subtle structural and energetic differences separating competing phases. Computationally reproducing experimentally observed phase transitions is therefore a useful measure of validation, showing that the training data effectively samples phase space. The remaining deviation from experiment combines the error of the model with respect to the underlying DFT functional and the error of the functional itself, whose transition temperatures are not known independently. All three models were therefore tested both for CaTiO_3 and $\text{Ca}_3\text{Ti}_2\text{O}_7$, which undergo a series of phase transitions from the orthorhombic ground state to a high-symmetry phase with no octahedral rotations. Details on these results are provided in the subsections below.

CaTiO_3

The phase transitions of CaTiO_3 in the perovskite phase have been extensively studied over the past decades. Although there is consensus on the ground state being $Pnma$, the existence of and number of intermediate phases is still debated. Rietveld analysis of neutron and x-ray diffraction data by Yashima and Ali suggests that CaTiO_3 sequentially transitions from $Pnma$ to $I4/mcm$ ($a^0a^0c^-$) and $Pm\bar{3}m$ ($a^0a^0a^0$) at around 1500 K and 1635 K, while previous works propose that there is an additional $Cmcm$ ($a^0b^+c^-$) phase before the $I4/mcm$ stage^{10,11}. Several theoretical works have attempted to clarify this apparent disparity in the literature. According to Landau theory there has to be an intermediate state between $Pnma$ and $I4/mcm$ for the transition to be continuous¹². Previous theoretical simulations based on phenomenological thermodynamic and second-principles interatomic potentials find that there is an intermediate state, but report this to be either $Cmcm$ or $C2/m$ ($a^0b^-c^-$)^{13,14}.

Here, we heat CaTiO_3 from 1 K to 2000 K with a heating rate of 0.4 K/ps. A $9 \times 9 \times 9$ supercell (29 160 atoms) was used to simulate the evolution in rotation and twin angle, while a $12 \times 12 \times 12$ supercell (34 560 atoms) was used to monitor lattice parameters. The latter cell is based on the primitive unit cell of the $Pnma$ phase (20 atoms), while the former is spanned by the pseudo-cubic axes (40 atoms). Plotting the rotation angles of the octahedra as a function of temperature, all models exhibit the same sequence of phases, $Pnma \rightarrow I4/mcm \rightarrow Pm\bar{3}m$, see Fig. S8. Snapshots of the simulation cells in each phase can be found in Fig. S9.

The first antiferrodistortive transition is accompanied by an abrupt jump in the order parameter consistent with a first-order phase transition, which does not require that the phases are in a group-subgroup relationship. We also observe that the lattice parameters change to $a = b$ and c (Fig. S12a), fitting well with a tetragonal cell with octahedral rotations around a single axis. The first-order nature of the phase transition is also clearly visible in the sudden vanishing of the twin angle (Fig. S13a). There are no signs of an additional intermediate phase separating $Pnma$ and $I4/mcm$. At T_{C2} the structure transforms smoothly into the cubic high-symmetry structure through a second-order type transition. The transition temperatures differ between models but all fall close to the experimentally measured values (Fig. S8).

$\text{Ca}_3\text{Ti}_2\text{O}_7$

$\text{Ca}_3\text{Ti}_2\text{O}_7$ has one of the higher Curie temperatures of the various $\text{A}_3\text{B}_2\text{O}_7$ structures. This is in line with the negative linear relationship between T_C and the Goldschmidt tolerance factor for the RP structures, resulting from the geometric origin of the polarization^{15,16}. It initially transitions from the polar orthorhombic $Cmc2_1$ phase to a non-polar orthorhombic phase, losing its hybrid improper ferroelectricity. This Curie temperature, T_{C1} , is reported in multiple experimental works to be around 1050 K to 1100 K, although the reported symmetry of this intermediate phase varies^{17–19}. However, crystallographic analysis of variable temperature synchrotron x-ray diffraction data establishes that $\text{Ca}_3\text{Ti}_2\text{O}_7$ exhibits a first-order phase transition to a non-polar $Ccce$ ($00\phi 00\phi$) phase at 1100 K²⁰. This structure has a single axis of out-of-phase rotations which is locked to the direction perpendicular to the octahedral layers. There are however no reports of the second transition temperature, T_{C2} , into the aristotype $I4/mmm$ structure.

Heating simulations of $\text{Ca}_3\text{Ti}_2\text{O}_7$ were conducted from 1 K to 1500 K with a heating rate of 0.4 K/ps. A $8 \times 8 \times 5$ supercell (30 720 atoms) was used for the tilt pattern evolution, while a $9 \times 9 \times 9$ cell (34 992 atoms) was used for lattice parameters. The tilt angle distributions and simulation snapshots of the different phases can be found in Figs. S10 and S11. Both qNEP models show a $Cmc2_1 \rightarrow Ccce \rightarrow I4/mmm$ sequence,

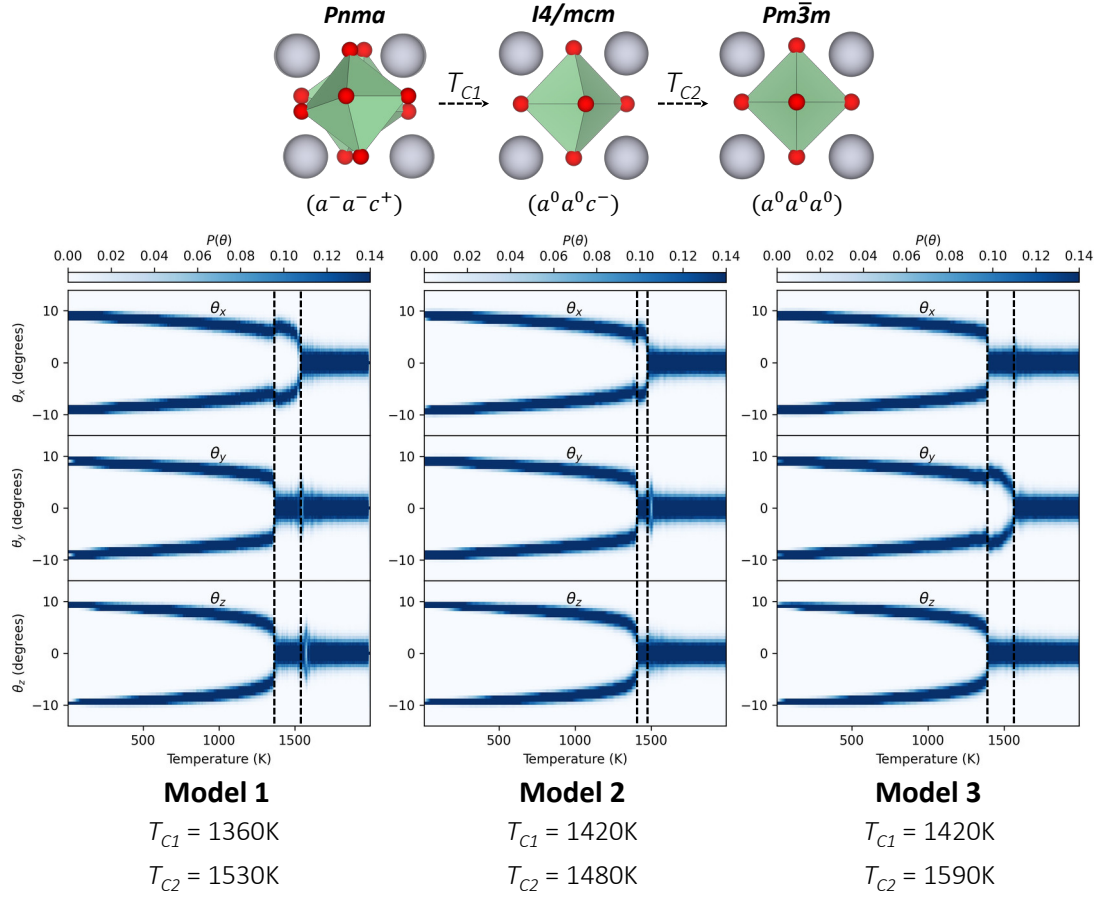


Figure S8: Maps of tilting angle distributions in CaTiO_3 as a function of temperature, for each of the three models. The angle θ is calculated as the Euler angle around each of the pseudo-cubic axes x , y and z . Black dashed lines mark the phase transitions. The transition sequence and structure of each phase is indicated above, illustrated by the consecutive changes of a single octahedron.

in agreement with experimental observations and analogous to CaTiO_3 in terms of tilt pattern. Model 1 behaves differently. The in-phase tilting around the z axis begins to fluctuate as the temperature approaches the ferroelectric and ferroelastic transition at T_{C1} , which makes both the order of the transition and the resulting phase impossible to identify. The same behavior is observed in repeated simulations. The model therefore fails to reproduce the switch from in-phase to out-of-phase tilting that is expected in the $Ccce$ phase. That only the qNEP models capture this transition underlines the importance of including electrostatics in the total energy, which for ferroic materials contributes significantly to the overall energetics.

With model 2, T_{C1} and T_{C2} are found to be about 1110 K and 1350 K. The transition from $Cmc2_1$ to $Ccce$ is smoother than for CaTiO_3 , implying a more second-order character. Although there are no reports of T_{C2} , T_{C1} is close to the experimentally reported range (Fig. S10).

Model 3 exhibits the same sequence of phases, with T_{C1} at 1200 K and T_{C2} at 1360 K. The first transition is not as prominent as for model 2 because there is some flipping of the octahedra between equivalent domain states. A larger simulation cell would be expected to suppress this, since it raises the energy barrier for simultaneous rotation reversal of all octahedra. Model 3 is used throughout this work, since it reproduces the DW formation energies considerably more accurately than the other two models, which is the property of primary interest here.

Model 3 also shows a crossover between the a and b parameters (Fig. S12b), meaning the cell is temporarily tetragonal with no strain and a twin angle at 0° (Fig. S13b). A similar change in strain state has been observed for orthorhombic perovskites LaFeO_3 and CaMnO_3 ^{21–23}. The evolution of the c lattice parameter shows close

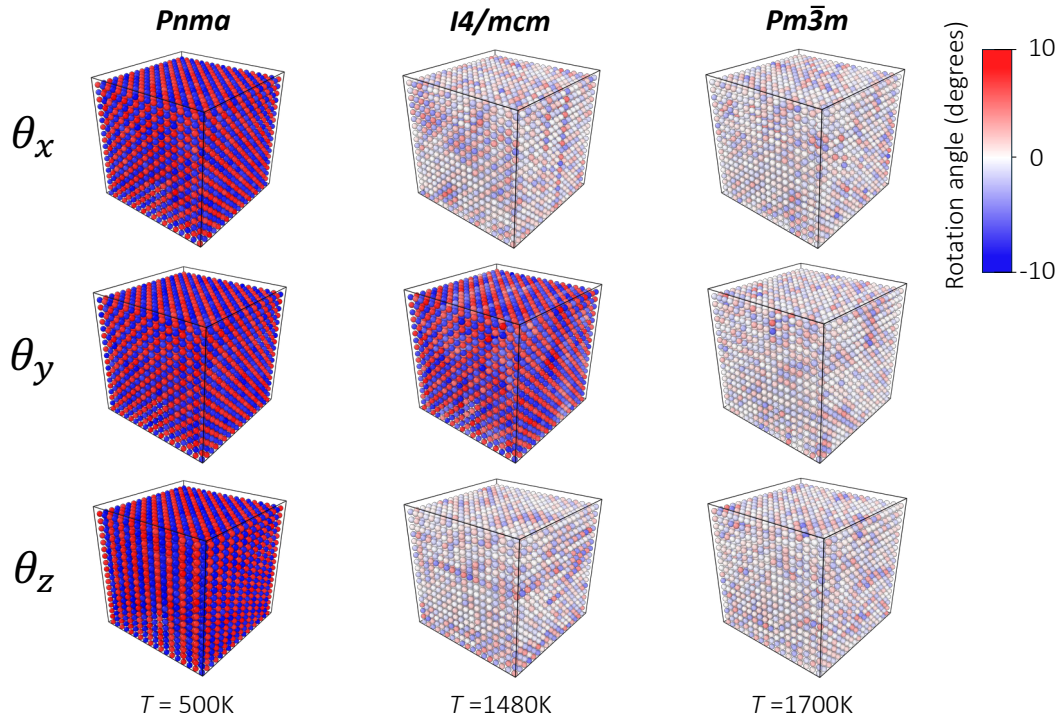


Figure S9: Snapshots from the heating simulation of CaTiO_3 using the potential in model 3. Each TiO_6 octahedron in the simulation cell is represented by a sphere, color-coded according to the tilting angle θ around each of the pseudo-cubic axes.

agreement with that of Pomiro et al.²⁰.

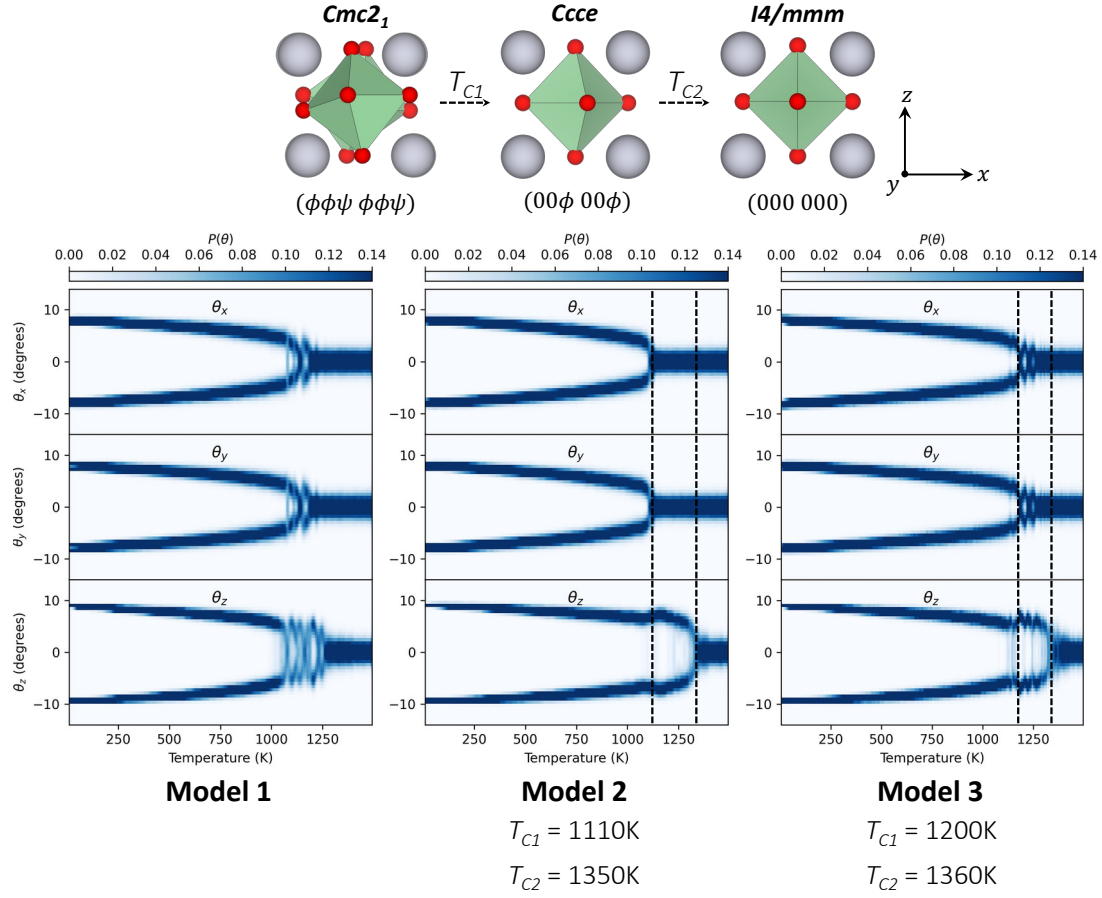


Figure S10: Maps of tilting angle distributions in $\text{Ca}_3\text{Ti}_2\text{O}_7$ as a function of temperature, for each of the three models. The angle θ is calculated as the Euler angle around each of the pseudo-tetragonal axes, x , y and z . Black dashed lines mark the phase transitions. The transition sequence and structure of each phase is indicated above, showing only a single octahedron seen from the y direction.

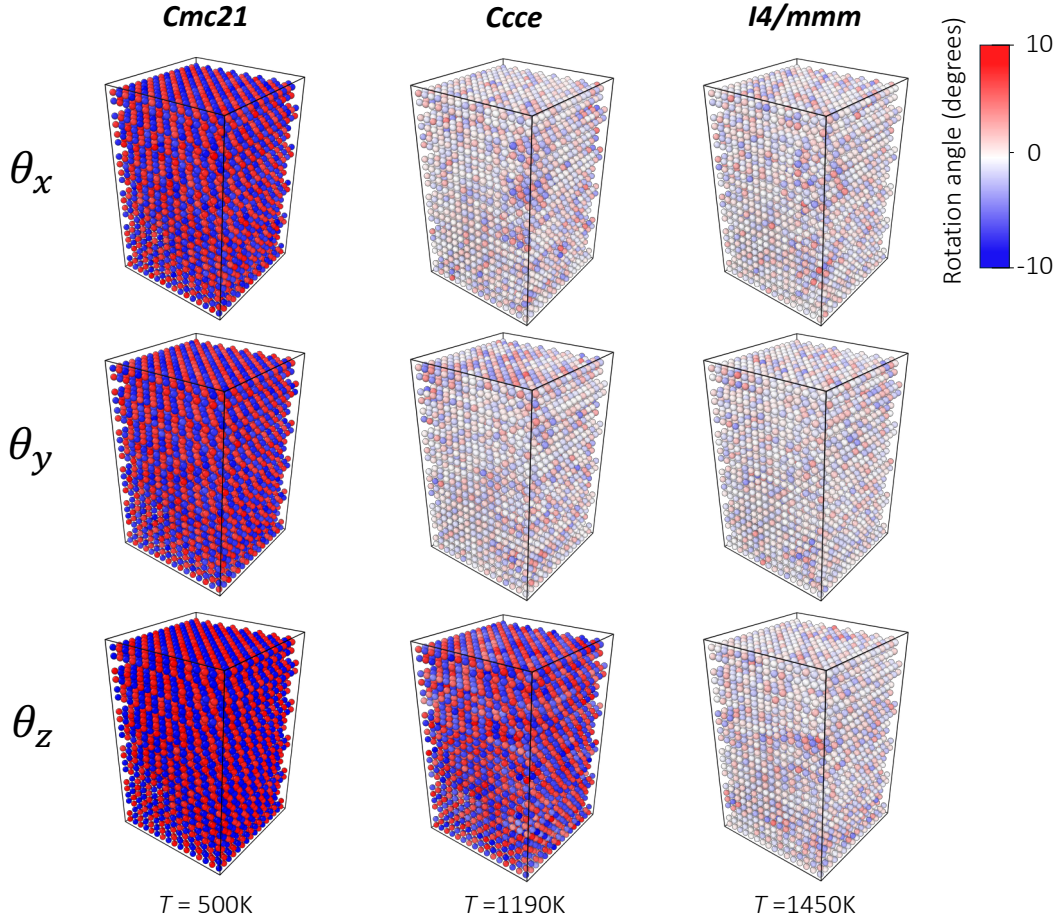


Figure S11: Snapshots from the heating simulation of $\text{Ca}_3\text{Ti}_2\text{O}_7$. Each TiO_6 octahedron in the simulation cell is represented by a sphere, color-coded according to the tilting angle θ around each of the x , y and z axes, corresponding to a , b and c .

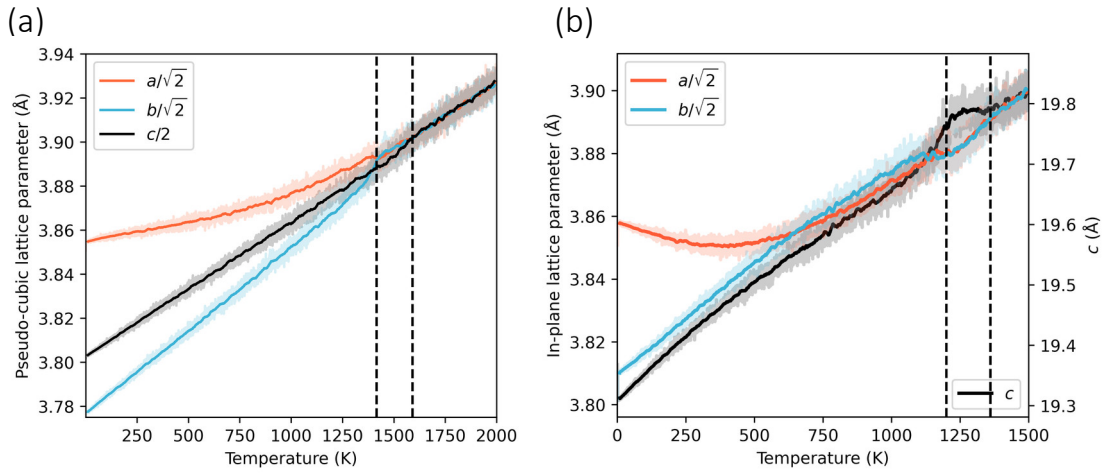


Figure S12: Lattice parameters as a function of temperature for (a) CaTiO_3 and (b) $\text{Ca}_3\text{Ti}_2\text{O}_7$ using model 3. The phase transition temperatures are indicated with black dashed lines.

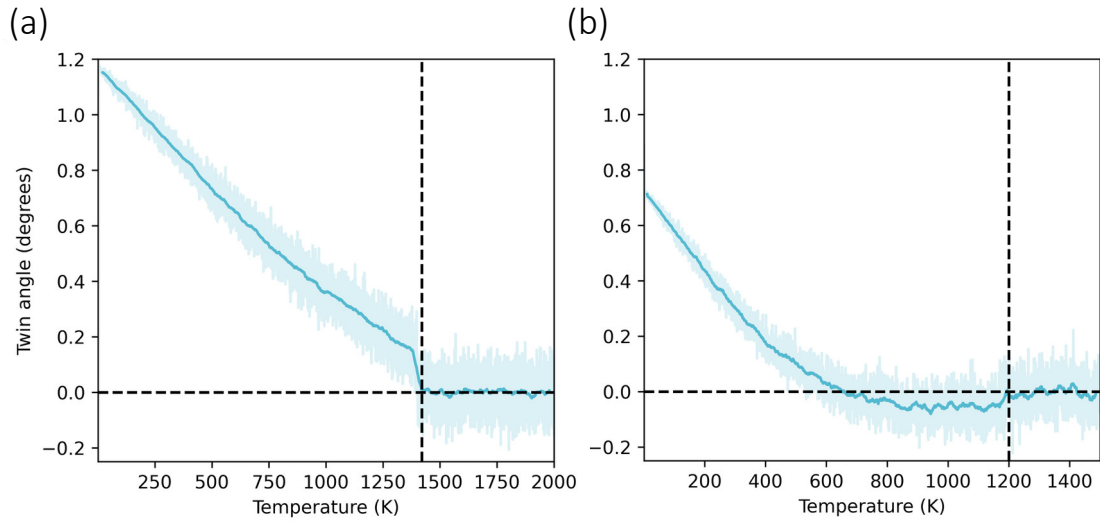


Figure S13: Evolution of the twin angle, calculated as the deviation of the angle between the a and b lattice directions from 90° , for (a) CaTiO_3 and (b) $\text{Ca}_3\text{Ti}_2\text{O}_7$ with model 3. The solid line shows a rolling average of the actual calculated twin angle, plotted in the same color at a higher transparency.

Domain walls

Order parameter analysis

The domain wall geometry can be analyzed by calculating the evolution of the X_2^+ and X_3^- irreducible representations. This was done by determining mode amplitudes Q_{ϕ_x} , Q_{ϕ_y} and Q_{ψ_z} , defined as the rotation angle of each of the octahedra around the pseudo-tetragonal axes, x , y and z . Fig. S14 shows the order parameter evolution of the $(100)_{\text{pt}}$ $\phi_x\phi_y$ DW relaxed from the sharp configuration. At finite temperature the 180° DWs split into two separate boundaries separated by an antipolar domain, as shown in Fig. 6 of the main manuscript. Fig. S15 presents the difference between the $\phi_x\phi_y$ and ψ_z DWs in the $(001)_{\text{pt}}$ plane. Their formation energies differ substantially, 145 mJ/m^2 against 13 mJ/m^2 with DFT, which can be attributed to the larger distortion of the octahedra in the former DW. The ψ_z DW is almost sharp, with no deviation from bulk values. All the 11 relaxed domain wall structures are openly available in Zenodo at <https://doi.org/10.5281/zenodo.22801877>²⁴.

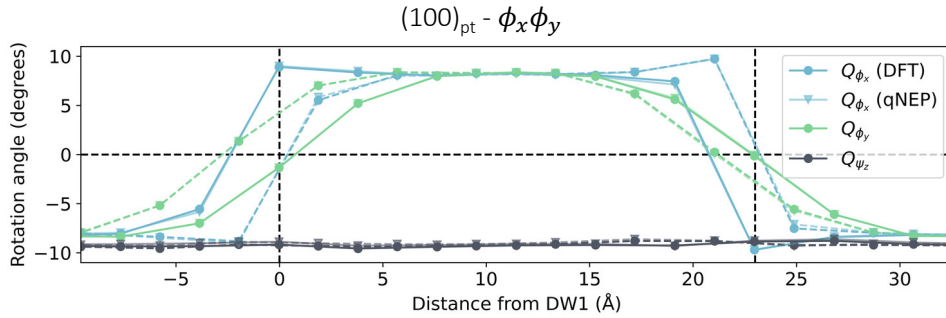


Figure S14: Order parameter profiles of the $\phi_x\phi_y$ DW in the $(100)_{\text{pt}}$ plane. Solid and dashed lines show one perovskite layer each in the RP structure.

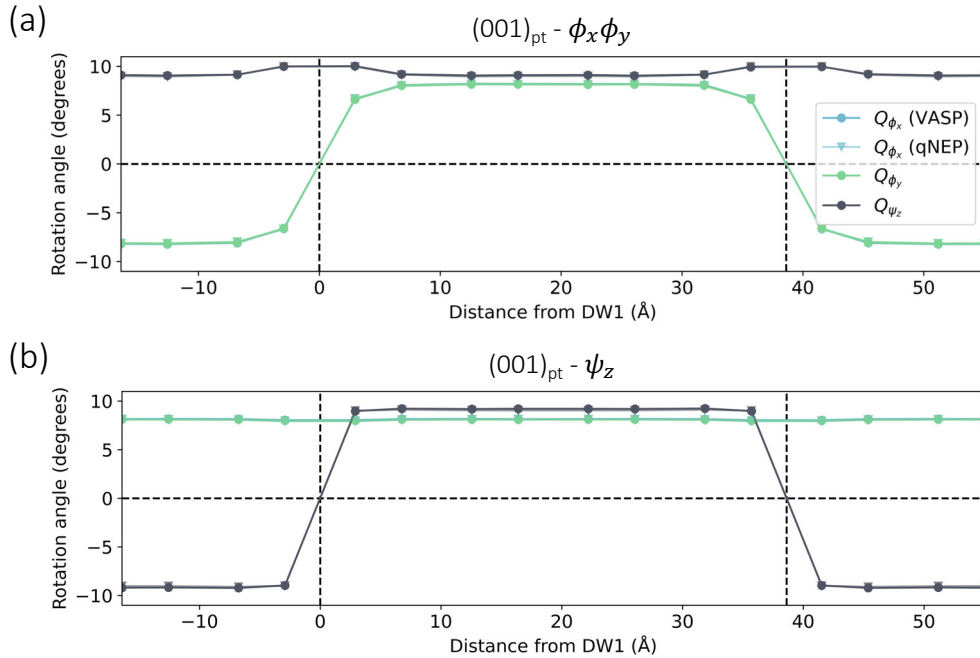


Figure S15: Order parameter profiles of the (a) $\phi_x\phi_y$ DW and (b) ψ_z DW, in the $(001)_{\text{pt}}$ plane. The blue and green lines perfectly align.

Domain wall dynamics

The behavior of the four different 90° and 180° DWs at finite temperatures was investigated with MD simulations. From the thermal fluctuations of each wall it was possible to determine the atomistic switching mechanism of each wall type, as outlined in the main paper. Examples displaying the splitting process of the $\phi_x\phi_y$ and ψ_z 180° DWs are given in Fig. S16. This kind of splitting was also observed for the charged and neutral $(110)_{\text{pt}}$ DWs, with the same kind of antipolar mid-domain (Fig. S17).

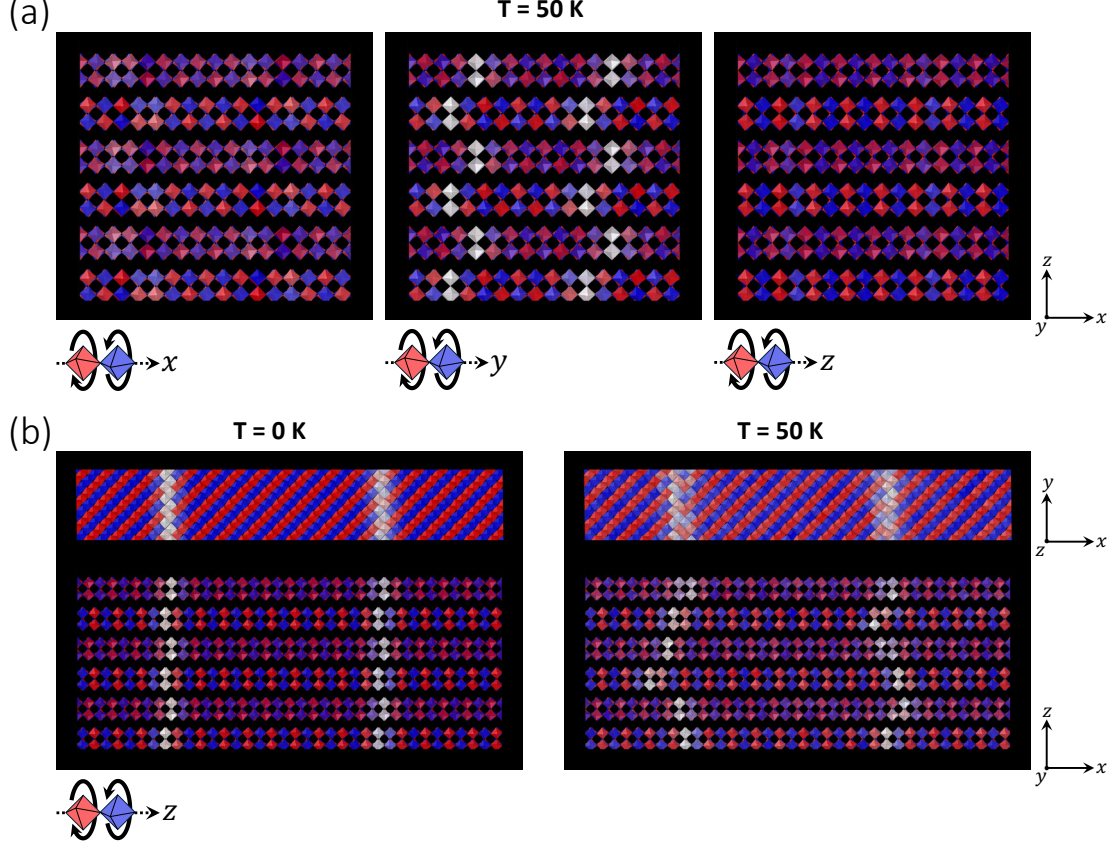


Figure S16: (a) An example of the stabilized splitting of a $\phi_x\phi_y$ DW at 50 K. The three figures show the TiO₆ octahedra color-coded according to the rotation around x , y and z . The position of a wall can be seen either by the phase breaking from e.g. red-blue to red-red, or from a white octahedron with no tilting. (b) Top and side views of a supercell with ψ_z DWs. At 50 K, the walls start moving away from each other and are almost uncorrelated between layers.

The DW mobility was investigated with respect to size and temperature. The mobility simulations were conducted with supercell sizes ranging from $24 \times 8 \times 4$ to $24 \times 20 \times 10$, containing 73 728 to 460 800 atoms. Temperatures of 350 K and 450 K were used for the 90° $\phi_x\psi_z - \phi_y$ DW, and 450 K and 550 K for the 180° $\phi_x\phi_y$ DW, which requires higher temperatures to move on the accessible time scale. Trajectories were written to file every 5 ps. Since the formation energies and switching barriers are DW dependent, it is expected that some walls will move more easily and be more susceptible to fluctuations. The interlayer correlations also depend on the formation energies of the $(001)_{\text{pt}}$ walls, since such a wall is created between perovskite layers whose DWs move apart. Generally, the mobility increases with temperature, while it decreases with supercell size (in the directions parallel to the DW). At lower mobilities, the DW propagation can be seen as “jumps” from one stable position to another, see Fig. S18. The position $x(t)$ of each of the two walls within one supercell was tracked by calculating the normalized layer-projected order parameter and determining the point where it passes through zero. An example of this, where two walls annihilate during the simulation, is presented in Fig. S19.

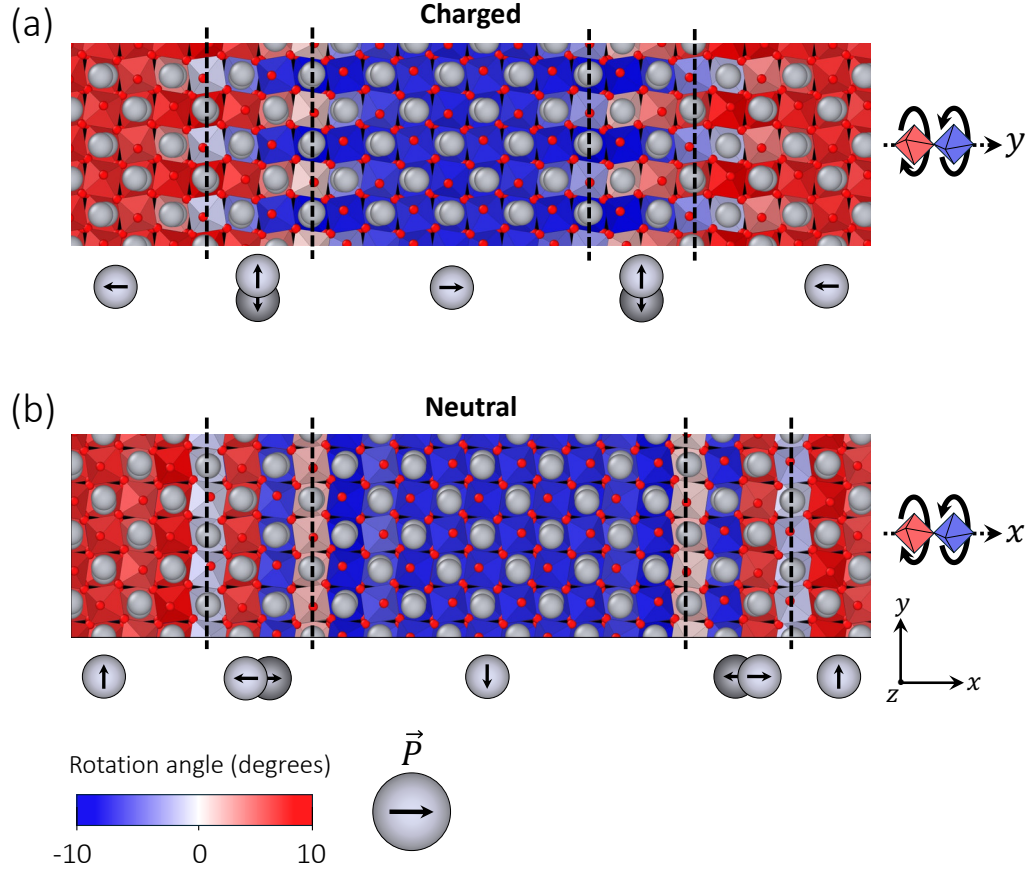


Figure S17: An example of the splitting configurations observed in (a) charged and (b) neutral $(110)_{\text{Pt}}$ DWs at finite temperature. The polarization direction in each domain is displayed by the grey spheres, with two spheres representing each layer for the antipolar mid-domains. The rotation axis for color-coding is chosen to best visualize the position of the walls (along with the black dashed lines).

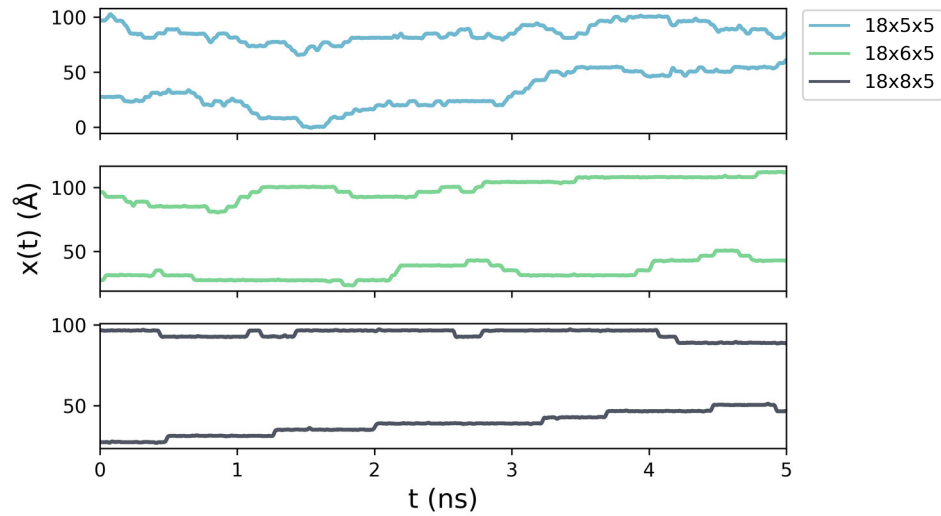


Figure S18: The position $x(t)$ of each of the two $90^\circ \phi_x \psi_z - \phi_y$ DWs in a supercell at cell sizes ranging from $18 \times 5 \times 5$ to $18 \times 8 \times 5$. These cell sizes were used here for the purpose of illustration. The production runs were carried out using larger cells as described in the text.

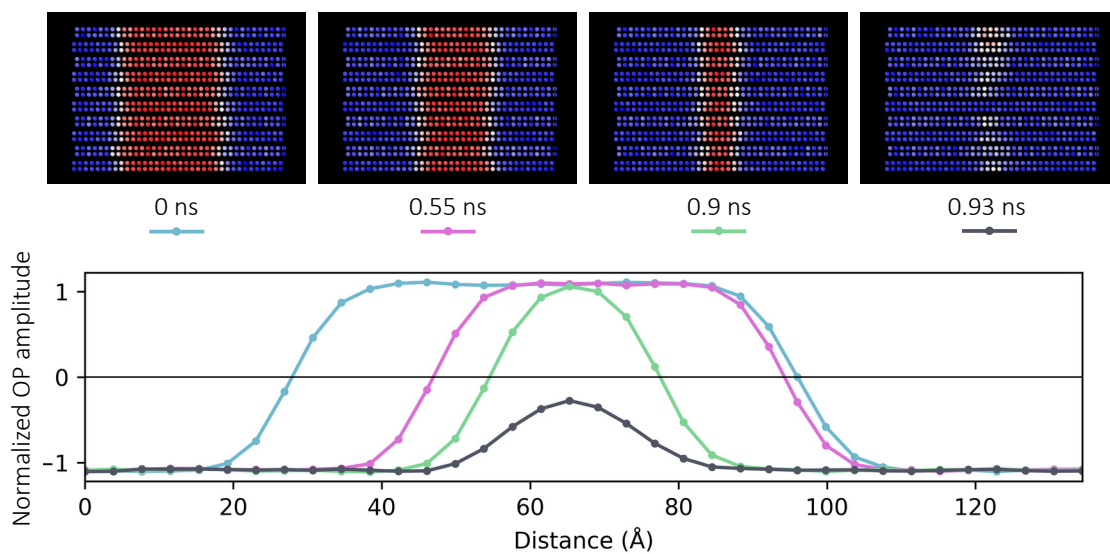


Figure S19: Order parameter (OP) profiles at different times during a mobility simulation. The two domain walls annihilate at 0.93 ns, creating a monodomain cell.

Supplementary References

- [1] Z. Fan, Y. Wang, P. Ying, K. Song, J. Wang, Y. Wang, Z. Zeng, K. Xu, E. Lindgren, J. M. Rahm, *et al.*, J. Chem. Phys. **157**, 114801 (2022).
- [2] Z. Fan, B. Tang, E. Berger, E. Berger, E. Fransson, K. Xu, Z. Yan, Z. Liu, Z. Song, H. Dong, S. Chen, L. Li, Z. Wang, Y. Zhu, J. Wiktor, and P. Erhart, J. Chem. Theory Comput. **22**, 4787 (2026).
- [3] A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dulak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, *et al.*, J. Phys.: Condens. Matter **29**, 273002 (2017).
- [4] E. Lindgren, M. Rahm, E. Fransson, F. Eriksson, N. Österbacka, Z. Fan, and P. Erhart, J. Open Source Softw. **9**, 6264 (2024).
- [5] F. Eriksson, E. Fransson, and P. Erhart, Adv. Theory Simul. **2**, 1800184 (2019).
- [6] H. T. Stokes, E. H. Kisi, D. M. Hatch, and C. J. Howard, Acta Crystallogr. Sect. B **58**, 934 (2002).
- [7] K. S. Aleksandrov and J. Bartolomé, Phase Transit. **74**, 255 (2001).
- [8] E. Bitzek, P. Koskinen, F. Gähler, M. Moseler, and P. Gumbsch, Phys. Rev. Lett. **97**, 170201 (2006).
- [9] J. Guénolé, W. G. Nöhring, A. Vaid, F. Houllé, Z. Xie, A. Prakash, and E. Bitzek, Comput. Mater. Sci. **175**, 109584 (2020).
- [10] R. Ali and M. Yashima, J. Solid State Chem. **178**, 2867 (2005).
- [11] M. Yashima and R. Ali, Solid State Ion. **180**, 120 (2009).
- [12] M. A. Carpenter, Am. Mineral. **92**, 309 (2007).
- [13] Y. Gu, K. Rabe, E. Bousquet, V. Gopalan, and L.-Q. Chen, Phys. Rev. B **85**, 064117 (2012).
- [14] H. Zhang, M. M. Schmitt, L. Bastogne, X. He, and P. Ghosez, Phys. Rev. B **112**, 224103 (2025).
- [15] S. Yoshida, H. Akamatsu, R. Tsuji, O. Hernandez, H. Padmanabhan, A. Sen Gupta, A. S. Gibbs, K. Mibu, S. Murai, J. M. Rondinelli, *et al.*, J. Am. Chem. Soc. **140**, 15690 (2018).
- [16] E. Gradauskaite, Small Sci. **6**, e202500488 (2026).
- [17] X. Q. Liu, J. W. Wu, X. X. Shi, H. J. Zhao, H. Y. Zhou, R. H. Qiu, W. Q. Zhang, and X. M. Chen, Appl. Phys. Lett. **106**, 202903 (2015).
- [18] B. Gao, F.-T. Huang, Y. Wang, J.-W. Kim, L. Wang, S.-J. Lim, and S.-W. Cheong, Appl. Phys. Lett. **110**, 222906 (2017).
- [19] H. Wu, W. Cai, C. Zhou, Q. Zhang, R. Gao, G. Chen, X. Deng, Z. Wang, and C. Fu, Mater. Lett. **278**, 128447 (2020).
- [20] F. Pomiro, C. Ablitt, N. C. Bristowe, A. A. Mostofi, C. Won, S.-W. Cheong, and M. S. Senn, Phys. Rev. B **102**, 014101 (2020).
- [21] S. M. Selbach, J. R. Tolchard, A. Fossdal, and T. Grande, J. Solid State Chem. **196**, 249 (2012).
- [22] Q. Zhou and B. J. Kennedy, J. Phys. Chem. Solids **67**, 1595 (2006).
- [23] C. A. Dixon, C. M. Kavanagh, K. S. Knight, W. Kockelmann, F. D. Morrison, and P. Lightfoot, J. Solid State Chem. **230**, 337 (2015).
- [24] I. C. Skogvoll, E. Fransson, L. Ö. Westin, B. A. D. Williamson, N. C. Bristowe, S. M. Selbach, and P. Erhart, Data for "Machine-learning guided exploration of domain walls in the hybrid improper ferroelectric $\text{Ca}_3\text{Ti}_2\text{O}_7$ ", Zenodo (2026), <https://doi.org/10.5281/zenodo.22801877>.