

Finite-temperature ferroelectric phase transitions from machine-learned force fields

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Simulating finite-temperature phase transitions from first principles is computationally challenging. Recently, molecular-dynamics (MD) simulations using machine-learned force fields (MLFFs) have opened a new avenue for finite-temperature calculations with near-first-principles accuracy. Here we use MLFFs, generated using on-the-fly training, to investigate structural phase transitions in four of the most well-studied ferroelectric oxides: BaTiO₃, PbTiO₃, LiNbO₃, and BiFeO₃. Only using the 0 K ground-state structure as input for the training, the resulting MLFFs can qualitatively predict all the main structural phases and phase transitions, while the quantitative results are sensitive to the choice of exchange-correlation functional with PBEsol found to be more robust than LDA and r^2 SCAN. MD simulations also reproduce the experimentally observed order-disorder character of Ti displacements in BaTiO₃, the abrupt first-order transitions of BiFeO₃ and PbTiO₃, and the mixed order-disorder and displacive character of the ferroelectric transition in LiNbO₃. Finally, we discuss the potential and limitations of using MLFFs for simulating ferroelectric phase transitions.

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I. INTRODUCTION

Ferroelectric oxides, particularly perovskites, are of great technological and scientific interest and find applications in, e.g., sensors, actuators, transducers, and nonvolatile memory technologies [1–3]. The mechanisms of their ferroelectric phase transitions are imperative in order to understand the microscopic origins of spontaneous polarization, and is thus enabling knowledge for designing new and improved ferroelectrics. Although first-principles computational approaches have been tremendously successful in elucidating fundamental properties and mechanisms at 0 K [4–7], the corresponding finite-temperature calculations have been prohibitively expensive. *Ab initio* molecular dynamics has been feasible only for relatively small systems where long-range electrostatic interactions, such as those in ferroelectrics, are not well captured or described.

Machine-learned force fields (MLFFs), and in particular on-the-fly MLFFs [8,9], have recently opened a new avenue for finite-temperature calculations with near-first-principles accuracy. Potentials are trained using a combination of molecular dynamics (MD), density-functional theory (DFT), and machine learning to decide when to perform DFT steps and update force fields [10]. This approach can be utilized to train force fields for complex functional materials and allow for calculations of very large supercells that are not feasible using standard DFT. MLFFs have recently been used to predict phase transitions in a wide range of materials [11–20],

but ferroelectric materials and their phase transitions pose an additional challenge with their sensitivity to pressure and lattice parameters, and inherent balance between long- and short-range forces [21,22].

Ferroelectric materials show an electric field-switchable spontaneous electric polarization that emerges from a phase transition from a centrosymmetric high-temperature structure to a noncentrosymmetric low-temperature structure at the Curie temperature T_C . BaTiO₃, PbTiO₃, BiFeO₃, and LiNbO₃ are prototypical ferroelectric materials, with the first three belonging to the perovskite family, whereas LiNbO₃ adopts a closely related structure. These four ferroelectric oxides span I-V, II-IV and III-III distributions of formal oxidation states; they include two examples of d^0 -driven second-order Jahn-Teller mechanism of stabilizing polarization, and two examples of A-site $6s^2$ lone pair-driven polarization, the latter two of which we find one multiferroic with a non- d^0B -site (BiFeO₃) and one with a d^0B -site (PbTiO₃) cation. These four well-studied oxides thus constitute a robust testing ground for applying MLFFs to understand ferroelectric phase transitions and we briefly review the basics of their phase transitions below.

BaTiO₃ undergoes three phase transitions upon heating; $R3m \xrightarrow{\sim 193\text{ K}} Amm2 \xrightarrow{\sim 273\text{ K}} P4mm \xrightarrow{393\text{ K}} Pm\bar{3}m$ with the latter being the paraelectric aristotype phase [23]. All three phase transitions are first order and are associated with diverging dielectric constants and discontinuous volumes. While BaTiO₃ is a prototypical displacive (soft-mode driven) ferroelectric, recent studies support a microscopic order-disorder picture rather than coherent, uniform displacements of Ti⁴⁺ relative to the center of mass of the TiO₆ octahedra [24–29].

In contrast to BaTiO₃, PbTiO₃, LiNbO₃, and BiFeO₃, each exhibit only a single bulk ferroelectric phase. PbTiO₃ undergoes a first-order transition, $P4mm \xrightarrow{768\text{ K}} Pm\bar{3}m$ [30], which is accompanied by a large, discontinuous decrease in molar

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volume. LiNbO_3 keeps its trigonal symmetry across the polar to nonpolar ferroelectric transition, $R3c \xrightarrow{\sim 1480 \text{ K}} R\bar{3}c$ [31,32].

The ferroelectric phase transition of BiFeO_3 initially proved difficult to study experimentally [33,34] because of the high T_C , the volatility of Bi, and the chemical incompatibility towards common sample supporting materials like platinum, alumina (Al_2O_3), and silica (SiO_2) [35]. Arnold *et al.* conclusively established the nature of the ferroelectric transition of BiFeO_3 to be $R3c \xrightarrow{\sim 1100 \text{ K}} Pbnm$ [36]. The absence of a group-subgroup relationship between $Pbnm$ and $R3c$ implies that this transition must be first order, and this is corroborated by a large negative change in molar volume and discontinuous enthalpy and electrical resistivity across T_C [36,37]. An even more debated phase transition of BiFeO_3 is that from paraelectric $Pbnm$ (the β phase, $Pnma$ is the standard setting) to the elusive γ phase, occurring just ~ 10 K below the peritectic decomposition temperature of ~ 1200 K [34,35,38].

In this work, we generate and use machine-learned force fields (MLFFs) as interatomic potentials to accurately predict phase transitions in the well-known ferroelectric oxides BaTiO_3 , PbTiO_3 , LiNbO_3 , and BiFeO_3 . We use only their ground-state structure as input for training the force fields. Similar to 0 K first-principles calculations, we show that the quantitative results are strongly dependent on the choice of exchange-correlation functional. Finally, we discuss the potential and limitations of MLFFs for studying ferroelectrics.

II. METHODS

Density-functional theory (DFT) and molecular-dynamics (MD) calculations were performed using the VASP code [39–41]. Interactions between core and valence electrons [Ba: ($5s^2, 5p^6, 5d^{0.01}, 6s^{1.99}$), Ti: ($3s^2, 3p^6, 3d^3, 4s^1$), O: ($2s^2, 2p^4$), Pb: ($5d^{10}, 6s^2, 6p^2$), Li: ($1s^2, 2s^1$), Nb: ($4s^2, 4p^6, 4d^4, 5s^1$), Bi: ($5d^{10}, 6s^2, 6p^3$), Fe: ($3s^2, 3p^6, 3d^7, 4s^1$)] were described using the projector-augmented wave (PAW) method [42,43]. A large plane-wave energy cutoff of 700 eV was used for all DFT calculations to avoid Pulay stresses associated with the large volume changes during the training of the MLFFs. Three sets of MLFFs were generated using LDA [44], PBEsol [45], and $r^2\text{SCAN}$ [46] and used for MD simulations to assess the consequences of generating interatomic potentials using different functionals. MD simulations were performed within the NpT ensemble using the Parrinello-Rahman barostat [47,48] with a pressure of 1 atm and the Langevin thermostat [49]. Langevin-friction coefficients were set to 5 ps^{-1} for all atoms. A fictitious mass of 1000 amu and a friction coefficient of 5 ps^{-1} were used for the lattice degrees of freedom for all simulations. DFT calculations of BiFeO_3 were initialized with a G -type antiferromagnetism, and a Hubbard U of 4 eV on Fe d was used when generating MLFFs with LDA and PBEsol.

An initial equilibration was first performed of the DFT optimized ground-state structures using the on-the-fly scheme at temperatures of 50 K, 300 K, 500 K, and 500 K for BaTiO_3 , PbTiO_3 , LiNbO_3 , and BiFeO_3 , respectively. The equilibrations were performed using 50 000 time steps with a step length of 1 fs. Supercells of 120 atoms, similar to a $2 \times 2 \times 1$ expansion of the conventional $R3c$ unit cell of LiNbO_3 and BiFeO_3 , were used for the initial equilibrations and all

training. This supercell allows for antiphase tilting of O octahedra in all directions and maximizes the cell size without making the generation of interatomic potentials too computationally demanding. γ -centered k -point grids of $3 \times 3 \times 2$ were used for all DFT calculations. All interatomic potentials generated during the initial equilibrations were discarded.

Generation of MLFFs was done by heating (100 steps per K) the equilibrated structures from the initial temperatures to temperatures well above the respective ferroelectric phase transition (BaTiO_3 : 500 K, PbTiO_3 : 1000 K, LiNbO_3 : 1700 K and BiFeO_3 : 1300 K) using the on-the-fly scheme. A cutoff radius of 8 Å was used to limit the atomic environments described by MLFFs. Generated MLFFs are uploaded to Zenodo [50].

Thereafter, production runs were done with equilibrium MD simulations at specific temperatures using the generated potentials. Production runs were carried out in series, meaning that simulations were performed from low to high temperature, where the final structure of the previous calculation was used as the initial structure of the next calculation. The length of all production runs was 40 ps with a time step of 1 fs. For all calculations, the lattice parameters converged within 20 ps, and only the final 20 ps of each simulation were analyzed. For PbTiO_3 , LiNbO_3 , and BiFeO_3 a supercell containing 2000 atoms, similar to a $5 \times 5 \times 4$ expansion of the conventional $Pbnm$ unit cell of BiFeO_3 , was used for all production runs. Due to narrow temperature intervals of the different phases, simulations of BaTiO_3 were performed using a 4900 atom supercell ($7 \times 7 \times 5$ expansion) to reduce thermal fluctuations.

III. RESULTS

Lattice parameters as a function of temperature for BaTiO_3 , PbTiO_3 , LiNbO_3 , and BiFeO_3 are displayed in Figs. 1, 4, 5, and 7, respectively. The top panels show average lattice parameters from equilibrium MD simulations using MLFFs generated with the PBEsol functional, while the bottom panels show experimental lattice parameters from the literature [36,51–53]. In the Supplemental Material (SM) [54], Figs. S4, S7, S11, and S15 show the experimental and simulated lattice parameters are plotted together as a function normalized to the T_C . Results from simulations using MLFFs generated with LDA and $r^2\text{SCAN}$ are displayed in the SM [54] Figs. S6, S10, S14, and S18.

A. BaTiO_3

Equilibrium MD simulations, using MLFFs generated with PBEsol, qualitatively predict all the correct phases and transitions for BaTiO_3 upon heating. Estimated phase-transition temperatures are systematically about 70 K lower than experimentally observed transition temperatures [51]. The calculated lattice parameters are in general about 0.01 Å larger than the experimental values, which can be attributed to the subtle underbinding tendency of PBEsol [55]. Except for the underestimated transition temperatures, the main difference between the experimental and our calculated lattice parameters is the change in volume over the phase transitions. Kay *et al.* [51] reports a small increase in volume at the transition from $R3m$ to $Amm2$ and from $Amm2$ to $P4mm$.

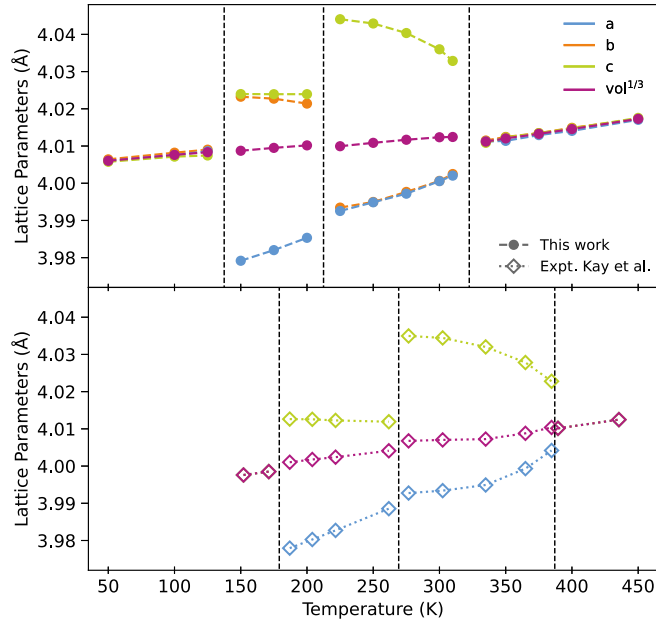


FIG. 1. Evolution of lattice parameters as a function of temperature for BaTiO₃. The top panel displays predicted lattice parameters from MD simulations performed using MLFFs generated with the PBEsol functional, while the bottom panel shows experimental results from Kay *et al.* [51]. The dashed and dotted vertical black lines indicate the phase-transition temperatures.

While our calculations predict a subtle decrease in volume at these transitions, the negative volume change across the ferroelectric transition is correctly reproduced by our simulations.

The LDA and r^2 SCAN functionals also predict the correct phases and transitions. However, LDA underestimates the lattice parameters (SM [54] Fig. S6), due to its well-known tendency to overbind [56], while r^2 SCAN overestimates the lattice parameters. Furthermore, this is reflected in the estimated phase-transition temperatures, where LDA predicts erroneously low transition temperatures, while transition temperatures from r^2 SCAN are closer to the experimental values than those predicted from PBEsol (Fig. 1).

The probability distributions of the absolute Ti displacements in BaTiO₃ at various temperatures, shown in Fig. 2, reveal a decrease in the Ti displacements upon heating up to the formation of the cubic phase. As the temperature increases further, the Ti displacements gradually increase. Each phase transition is marked by a steplike shift in the peak position, as indicated by the dashed vertical lines. Additionally, the probability distributions broaden with increasing temperature, reflecting enhanced thermal fluctuations.

The direction of the Ti displacements at 50 K, 150 K, 250 K, and 350 K are displayed using Mercator projections shown in Fig. 3. At 50 K, all Ti atoms are displayed in one of the $\langle 1, 1, 1 \rangle$ directions, consistent with the $R3m$ space group. At 150 K, Ti atoms are displaced in two different $\langle 1, 1, 1 \rangle$ directions, and the average orientation of the displacements gives rise to the direction of the macroscopic polarization observed in orthorhombic BaTiO₃. Moreover, at 250 K, Ti atoms are disordered in between four different $\langle 1, 1, 1 \rangle$ directions, where the average gives rise to tetragonal BaTiO₃. At

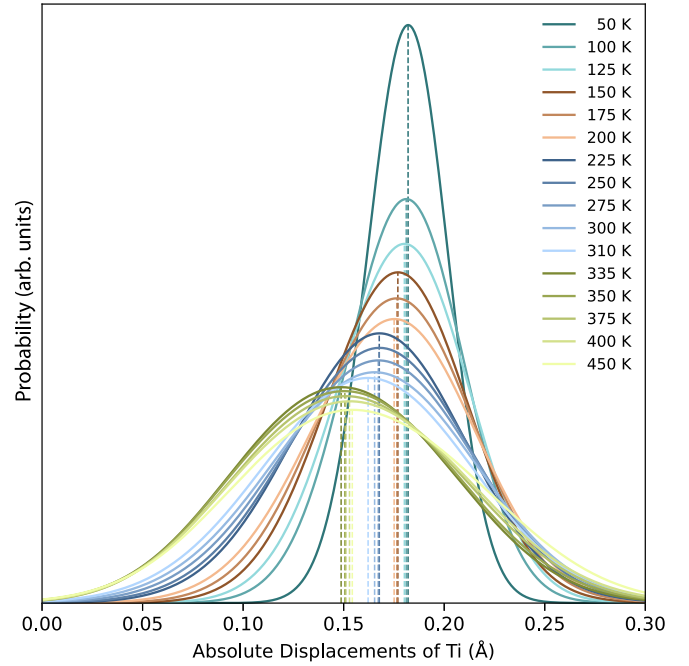


FIG. 2. Probability distribution of absolute displacements of Ti from the O octahedral centers in BaTiO₃ from equilibrium MD simulations using MLFFs generated with PBEsol. The colors indicate the average space groups (turquoise: $R3m$, orange: $Amm2$, blue: $P4mm$, green: $Pm\bar{3}m$) and the dashed vertical lines are guidelines for the peak positions.

350 K, the orientation of the Ti displacements is disordered between all $\langle 1, 1, 1 \rangle$ directions. A similar cation off centring has, for instance, been reported by K. Page *et al.* for Nb-substituted cubic BaTiO₃ [57]. Thermal energy gives broader distributions, making the disorder between $\langle 1, 1, 1 \rangle$ directions at higher temperatures less obvious.

The temperature-dependent evolution of Ti displacements, as visualized in the Mercator projections, clearly supports the order-disorder picture of phase transitions in BaTiO₃ [24–27,58,59]. Similar to work by Holma *et al.* [28], our calculations do not support the formation of static linear chains of correlated displacements proposed by Comes *et al.* [24,59], but are instead more consistent with the dynamic description by Hüller *et al.* and Harada *et al.* [29,60,61].

B. PbTiO₃

Simulations of PbTiO₃ using PBEsol, Fig. 4, show the same lattice-parameter evolution as reported from the seminal experiments by Shirane *et al.* [52], albeit a significantly lower transition temperature of about 230 K. Both simulations and experiments show a slowly decreasing cell volume with increasing temperature up until the phase transition followed by a significant reduction at the transition temperature. Thereafter, a slow increase in volume with increasing temperature is observed. Similar results are shown by LDA and r^2 SCAN and are displayed in SM [54] Fig. S10. LDA, again, severely underestimates the lattice parameters and the phase transition temperature, while r^2 SCAN overestimates the lattice parameters.

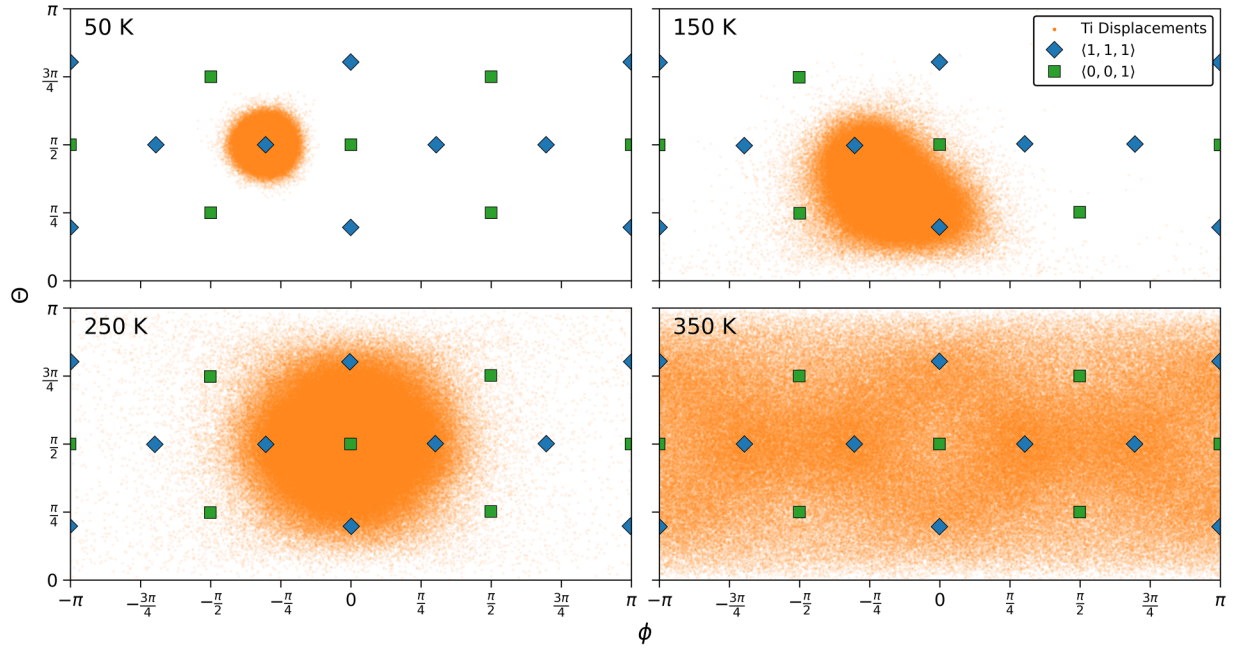


FIG. 3. Mercator projections showing the direction of the Ti displacements in BaTiO₃ at 50 K, 150 K, 250 K, and 350 K extracted from equilibrium MD simulations using MLFFs generated with the PBEsol functional. Small orange data points display the direction of the displacement of single Ti atoms from the center of the respective O octahedra relative to the $\langle 1, 0, 0 \rangle$ (green squares) and $\langle 1, 1, 1 \rangle$ (blue diamonds) directions. Mercator projections for the orientation of the Ba displacements are shown in SM Fig. S5.

Probability distributions of the displacements of Pb and Ti from the center of oxygen polyhedra, in SM [54] Fig. S1, show that both cations are significantly displaced at all

temperatures. These distributions show a clear change in trend and jump in peak position from 500 K to 550 K (see also plotted peak positions in SM [54] Fig. S2). Similar to the ferroelectric transition in BaTiO₃, at the T_C , the average atomic displacements from polyhedral centers revert from decreasing, go through a minimum, and start increasing upon further heating.

Contrary to BaTiO₃, in the $P4mm$ phase, cation displacements in PbTiO₃ are not disordered and only displaced along one $\langle 0, 0, 1 \rangle$ direction, as reported experimentally by Cheong *et al.* [26] and supported by the Mercator projections in SM [54] Fig. S8 and S9. Above the T_C , in the paraelectric phase, the displacements are fully disordered in all directions.

The average B -cation displacement was also fitted as a function of the temperature to the power law $A(T_C - T)^\beta$ (see SM [54] Fig. S3), giving a value of 0.27 for the critical exponent β . This is reasonably close to the theoretical prediction of 0.25 for a tricritical phase transition, as expected for PbTiO₃. For more details on the calculation of critical exponents, see SM [54] Sec. II.

C. LiNbO₃

Similar to lattice parameters from experiments by Lehnert *et al.* [53] and Sugii *et al.* [62], the calculated a -lattice parameter increases linearly up to and beyond the phase transition, while the c parameter starts decreasing when approaching the phase-transition temperature (Fig. 5). Due to the second-order nature of the phase transition in LiNbO₃, the Curie temperature is very difficult to estimate exclusively from the changes in lattice parameters alone. However, similar to the probability distributions for cation displacements in BaTiO₃, PbTiO₃, and BiFeO₃ (SM [54] Fig. S1), there is a clear abrupt change

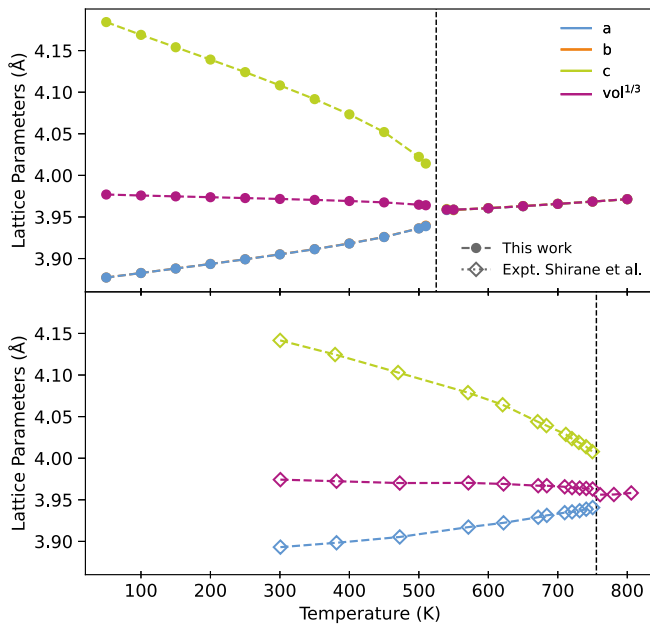


FIG. 4. Evolution of lattice parameters as a function of temperature for PbTiO₃. The top panel displays predicted lattice parameters from the MD simulations using MLFFs generated with the PBEsol functional, while the bottom panel shows experimental results from Shirane *et al.* [52]. The dashed and dotted vertical black lines indicate the phase-transition temperatures. In our data, the a and b lattice parameters overlap almost perfectly, making the b lattice parameter difficult to distinguish.

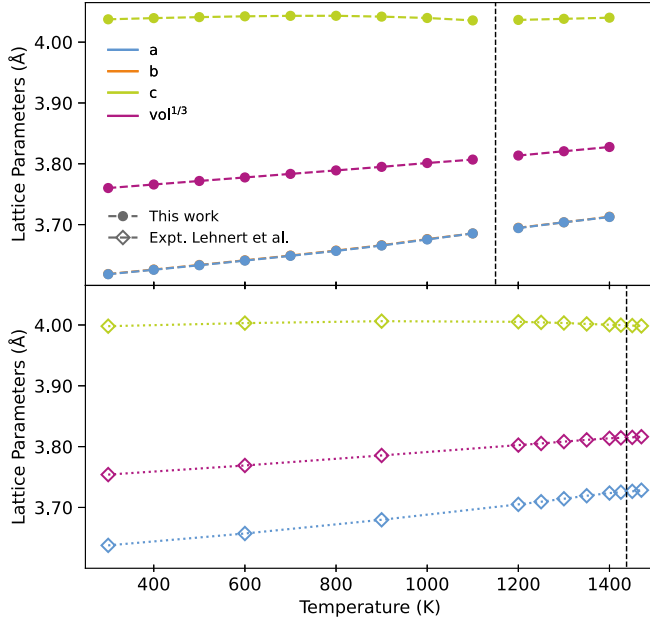


FIG. 5. Evolution of lattice parameters as a function of temperature for LiNbO_3 . Lattice parameters are converted from the hexagonal conventional unit cell to a pseudocubic cell by dividing a and c by $\sqrt{2}$ and $\sqrt{12}$, respectively. The top panel displays predicted lattice parameters from the MD simulations using MLFFs generated with the PBEsol functional, while the bottom panel shows experimental results from Lehnert *et al.* [53]. The dashed and dotted vertical black lines indicate the phase-transition temperatures. In our data, the a and b lattice parameters overlap almost perfectly, making the b lattice parameter difficult to distinguish.

in the evolution of the absolute displacements of Li and Nb from 1100 K to 1200 K, indicating the T_C to be in between these temperatures. Using MLFFs generated with PBEsol, the

predicted T_C is about 300 K lower than the experimentally observed T_C . With LDA and $r^2\text{SCAN}$, lattice parameters are again underestimated and overestimated, respectively, see SM [54] Fig. S14. Below the T_C , both Li and Nb are displaced along the same $\langle 1, 1, 1 \rangle$ direction. Displacements along this $[1,1,1]$ direction, displayed in Fig. 6, highlight the differences between Li and Nb when approaching the phase-transition temperature. Li, Fig. 6(a) clearly shows an order-disorder transition, while Nb shows a displacive transition. Similar distributions and results have been reported from *ab initio* MD by Sanna *et al.* [63]. The order-disorder and the displacive transitions are also clearly shown in the Mercator projections in SM [54] Figs. S12 and S13, respectively. The mixed character of the phase transition cannot be revealed by probability distributions showing absolute displacements from the O polyhedral centers, as displayed in SM [54] Fig. S1. Mixed displacive and order-disorder characteristics of a ferroelectric transition have also been observed for other uniaxial ferroelectrics like hexagonal manganites, h-RMnO_3 [64].

From 1100 K to 1200 K, at the estimated T_C , there is a jump in the evolution of the displacements of both Li and Nb. However, the distributions of Li and Nb indicate that the material is still weakly polar, which could be explained by insufficient thermal energy to reach full ergodicity within the limited simulation time analyzed.

A power-law fitting of the average B -cation displacement resulted in a β value of 0.34, in very good agreement with the expected value for a second-order ferroelectric phase transition, as well as the experimental value of $\beta = 0.355$ measured for isostructural LiTaO_3 [65].

D. BiFeO_3

Both the nonlinearity and the thermal stability of the ferroelectric $R3c$ phase of BiFeO_3 is fairly well described

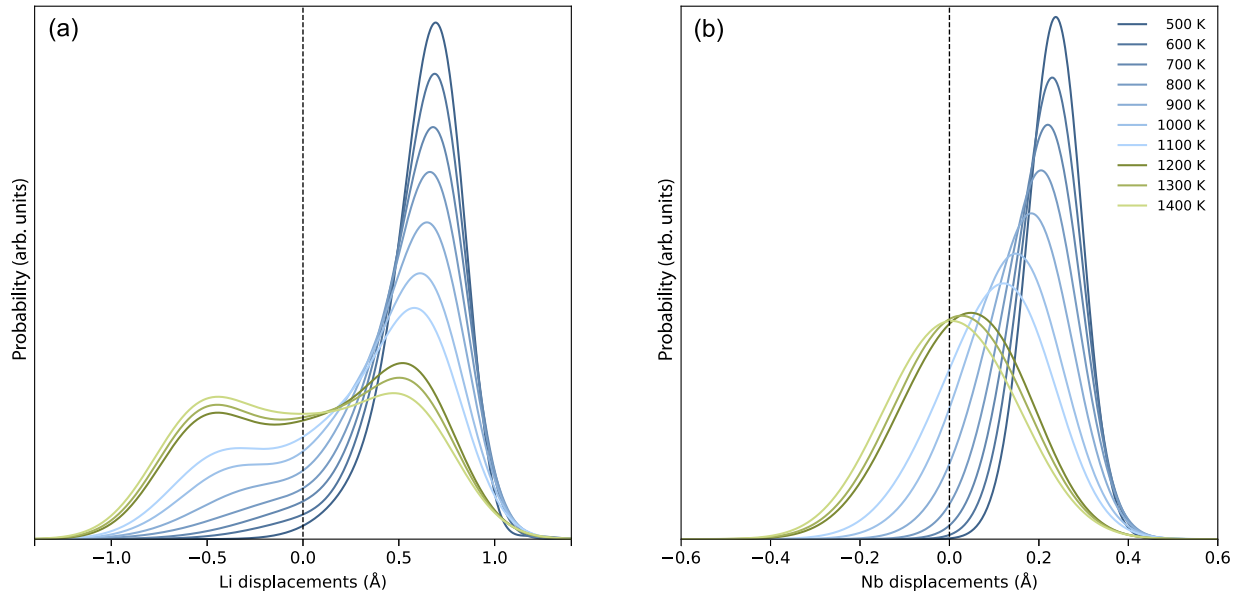


FIG. 6. Probability distributions, from equilibrium MD simulations using MLFFs generated with the PBEsol functional, of Li (a) and Nb (b) displacements from their respective centrosymmetric positions in the polar $[1,1,1]$ direction. The centrosymmetric positions used as a reference were determined from the position of the O planes. The colors indicate the space groups (blue: $R3c$, green: $R\bar{3}c$) and the gradient shows the temperature.

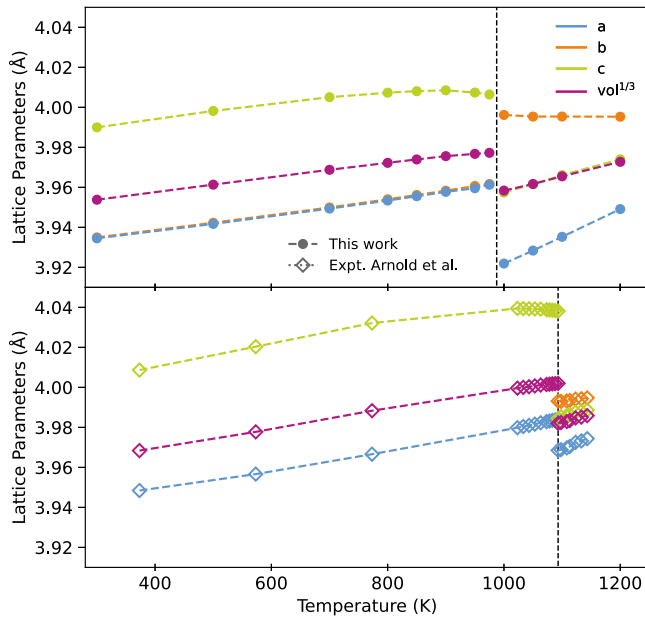


FIG. 7. Evolution of lattice parameters as a function of temperature for BiFeO_3 . Similar to LiNbO_3 , in the rhombohedral phase, lattice parameters are converted from the hexagonal conventional unit cell to a pseudocubic cell by dividing a and c by $\sqrt{2}$ and $\sqrt{12}$, respectively. Lattice parameters from the orthorhombic structure are converted by dividing a/b and c by $\sqrt{2}$ and 2, respectively. The top panel displays predicted lattice parameters from the MD simulations in this work, while the bottom panel shows experimental results from Arnold *et al.* [36]. The dashed and dotted vertical black lines indicate the phase-transition temperatures.

by the PBEsol-based simulations, including the premonitory phenomenon of the lattice parameter c , parallel to the spontaneous polarization (similar to LiNbO_3), starting to contract as T_C is approached [36]. The large negative and discontinuous volume change across the ferroelectric phase transition of BiFeO_3 is also reproduced, as shown in Fig. 7, in agreement with Arnold *et al.* [36].

At the T_C , MLFFs generated using LDA and PBEsol predict a transition from rhombohedral $R3c$ to orthorhombic $Pbnm$, with LDA again underestimating the lattice parameters. $r^2\text{SCAN}$, on the other hand, gives a qualitatively different result and shows a transition from $R3c$ directly to cubic $Pm\bar{3}m$. Using LDA and PBEsol, the difference between the calculated a , b , and c lattice parameters in the $Pbnm$ phase is substantially larger than experimentally reported. However, DFT-optimized lattice parameters at 0 K give similar values, see SM [54] Table S1.

The volume contraction of the unit cell is also reflected in the distributions of absolute cation displacements, shown in SM [54] Fig. S1, with drastic changes to the peak positions for both the Bi and Fe distributions. Except for the abnormal changes at the T_C , these peak positions show only a weak temperature dependence (SM [54] Fig. S2). These distributions show increased broadening as a function of increasing temperature for the displacements of both Bi and Fe.

The Mercator projections for Bi and Fe, in SM [54] Figs. S16 and S17, are relatively similar to the Mercator projections for LiNbO_3 , with the main differences being a

very abrupt phase transition in BiFeO_3 and the fact that the displacements of Bi are not disordered, but instead ordered in an alternating fashion in the high-temperature phase, in agreement with the structural degrees of freedom of the paraelectric $P6mm$ phase.

IV. DISCUSSIONS

The observed underestimation of phase-transition temperatures may be caused by several factors. Finite-size effects, due to the use of limited cell sizes and periodic boundary conditions during both generation of MLFFs and production runs, will prevent the system from behaving as it would have done at the thermodynamic limit. As ferroelectric phase transitions are governed by long-range collective displacements of atoms, local fluctuations of the positions of individual atoms may easily destabilize the ferroic order. Moreover, MLFFs in VASP only describe the environment around atoms closer than a specific cutoff radius (default 8 Å), and thus, long-range interactions are not directly described by the generated MLFFs. Furthermore, ferroelectric materials often experience decreasing and more diffuse T_C with decreasing particle sizes [66–73]. Strain from the surfaces hinders the collective displacements and suppresses the ferroelectric phase.

A larger cutoff radius as well as larger supercells for both production runs and training of the interatomic potentials may mitigate the present errors in transition temperatures. However, increasing the cell size significantly will be computationally expensive. Supporting this notion, it has been reported that, for LiNbO_3 , performing *ab initio* MD with an 80-atom supercell underestimates the T_C significantly [63], while a 640-atom supercell gives a T_C very close to the experimental value [74]. Additionally, generating MLFFs using different exchange-correlation functionals has proven to give vastly different transition temperatures [12,13] and, thus, finding the optimal functional for the system is crucial. As of now, there is no “safe” choice of a single functional for training MLFFs for predicting ferroelectric phase transitions.

In BaTiO_3 , the spontaneous polarization is solely due to second-order Jahn-Teller distortions caused by partial covalency between $\text{Ti } 3d$ and $\text{O } 2p$. This results in Ti being displaced towards one of the faces of the O octahedron, causing polarization in one of the $\langle 1, 1, 1 \rangle$ directions. The other directions of polarization observed experimentally are just combinations of polarization in multiple $\langle 1, 1, 1 \rangle$ directions, as visualized with the Mercator projections in Fig. 3. PbTiO_3 also has $\text{Ti } d^0$, but only shows polarization in the $\langle 0, 0, 1 \rangle$ directions, reflecting that the lone pair, caused by hybridization of $\text{Pb } 6s$ and $6p$ states, dictates the direction of the polarization and the strongly coupled unit-cell distortion. Furthermore, G. Laurita *et al.* showed that the introduction of lone pair cations, by Sn substitution in BaTiO_3 , drives local ordering and results in a behavior closely resembling that of PbTiO_3 [75].

Similar to BaTiO_3 , polarization in LiNbO_3 is only caused by d^0 second-order Jahn-Teller distortions. In spite of this, LiNbO_3 only show two different phases ($R3c$ and $R\bar{3}c$). The small size of Li atoms stabilizes antiferrodistortive rotations and thus also the $R3c$ and $R\bar{3}c$ phases. This also explains the order-disorder character of Li observed in Fig. 6(a) and in the Mercator projections in SM [54] Fig. S12. Li is too small to

be stable in the center of the O polyhedra even at temperatures above the T_C .

The simulated lattice parameters differ quantitatively from the experimental for the high-temperature $Pbnm$ phase of BiFeO_3 , with the simulated unit cell being more metrically distorted. This is one possible reason why a transition to the experimentally observed γ phase is not found in our simulations. Another obvious reason for the discrepancy is the possible evaporation of Bi and O at high temperatures, which would be very challenging to accurately predict and represent computationally. Our current simulations within the isothermal-isobaric NpT ensemble do not allow exchange of particles, and extending the MLFF approach to the grand canonical ensemble implies several challenges we will not discuss further here. Experiments where 30 molar % of Fe has been replaced by Mn to lower the structural phase-transition temperatures agree on the T_C and the symmetries of the ferroelectric and the paraelectric phases, but not on the γ phase [76,77], emphasizing the challenging nature of this particular phase transition and the need for further work to clarify, e.g., the possible role of nonstoichiometry.

In general, except for special situations, the choice of functional does not change the results qualitatively. Moreover, disregarding thermal expansion, the generated MLFFs closely follow lattice parameters from regular DFT calculations with the respective functional. LDA is known to underestimate lattice parameters [78], which is reflected in the MD simulations using MLFFs generated with LDA. This leads to further underestimation of phase-transition temperatures, which can make it difficult to separate and study phases that experimentally show narrow temperature windows such as BaTiO_3 . Similarly, $r^2\text{SCAN}$ has been shown to, on average, overestimate lattice parameters [46], and our MD simulations, performed using MLFFs generated with $r^2\text{SCAN}$, also tend to overestimate lattice parameters. Furthermore, these MLFFs fail to correctly describe both phase transitions in BiFeO_3 , which may partly be due to the overestimated lattice parameters. Our results suggest that functionals that agree well with experimental values at the DFT level also result in MLFFs that accurately describe lattice parameters at elevated temperatures. Therefore, PBEsol is, in most situations, a good choice in terms of both speed and accuracy.

A major advantage of using MD simulations is access to massive supercells. This can allow for calculations of larger phenomena such as surfaces, grain boundaries, superstructures, amorphous materials, nanoparticles, and domain walls and their interactions with defects. The flexibility of using on-the-fly machine-learned interatomic potentials makes it easy to apply the methodology shown in this work to phenomena such as those mentioned above, as well as to completely new and unknown systems. The balance between long-range and short-range electrostatic forces, and the dipole-stabilizing second-order Jahn-Teller effect (or improper ferroelectric mechanisms) is particularly challenging for MLFFs, necessarily leading to difficult tradeoffs between cost and accuracy. However, this also implies that ferroelectrics are ideal test beds for further method development of MLFF approaches to achieve near-first-principles accuracy at a fraction of the cost.

V. CONCLUSIONS

We have demonstrated that we can accurately predict lattice parameters and phase transitions of ferroelectric materials using MLFFs trained from first-principles calculations. Qualitatively, our calculations get all the correct phases and transitions, except for the β - γ transition in BiFeO_3 , although predicted phase-transition temperatures are in general significantly lower than what is observed experimentally. This method can be used to resolve and describe more subtle structural changes, such as the magnitude of the B -cation displacements and the orientation of these displacements.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [50].

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