An Accurate Deep Learning Force Field for Dielectric and Ferroelectric $Hf_xZr_{1-x}O_2$ Solid Solutions

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1. Introduction

$Hf_xZr_{1-x}O_2$ (HZO) solid solutions exhibit ferroelectric, dielectric, and antiferroelectric properties over a wide compositional range due to their polymorphism, offering new pathways for low-power logic circuits and high-density memories. However, both experiments and classical simulations face challenges in accurately capturing the atomic-level phase behavior of HZO. Here, we develop a deep-learning interatomic force field trained on *ab initio* data to describe dielectric and ferroelectric behavior in HZO systems. The potential model accurately predicts the static structural properties of HZO, achieving accuracy comparable to density functional theory.

2. Methods

2.1 Training dataset

The training dataset for the interatomic potential model was generated from first-principles DFT calculations, as implemented in the Vienna *Ab initio* Simulation Package (VASP).

2.2 DP model construction

The deep learning interatomic potential model for HZO was trained using the DeepMD-kit package[1]. The training process aims to minimize the following loss function[2]:

$$L(p_\epsilon, p_f, p_\xi) = p_\epsilon \Delta\epsilon^2 + p_f \frac{\sum_i |\Delta f_i|}{3N} + p_\xi \frac{|\Delta\xi|^2}{9}. \quad (1)$$

2.3 MD simulations

MD simulations were carried out using the LAMMPS package [3] with periodic boundary conditions under ambient pressure to investigate the finite-temperature dynamical properties of HZO.

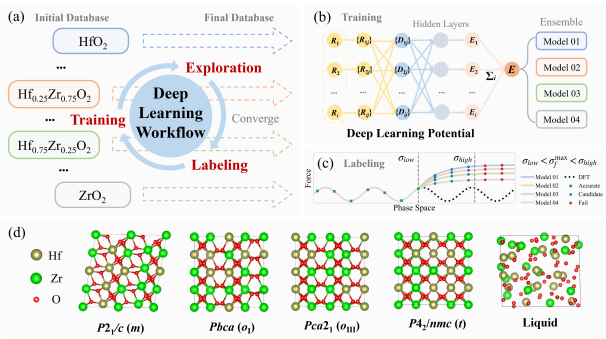

Fig. 1: Workflow for constructing DP models of $Hf_xZr_{1-x}O_2$ solid solutions, including training, exploration, and labeling.

3. Results and discussions

3.1 Accuracy of the DP model

Using 61 DP-GEN iterations, 29,354 configurations (0.31%) were labeled from 8.7 million samples. The resulting DP model reproduces DFT energies and forces for HZO across compositions with high accuracy ($R^2 > 0.98$), yielding MAEs of 2.82 meV/atom for energy and 0.16 eV/Å for forces (Fig. 2).

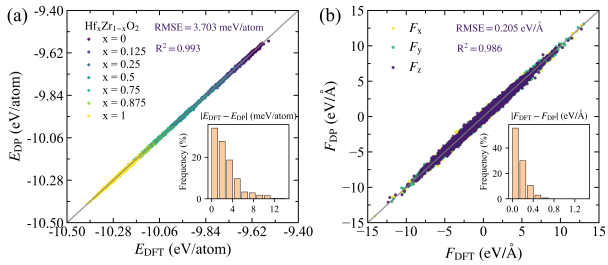

Fig. 2: Comparison of (a) energies E and (b) atomic forces F predicted by the DP model with DFT results for HZO solid solutions.

3.2 Predictions of static properties of HZO polymorphs

Equation-of-state (EOS) results results (Fig. 3) show that the DP model accurately reproduces DFT energy–volume relations and the relative phase stability.

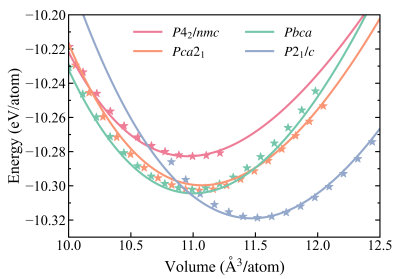

Fig. 3: EOS of $Hf_{0.5}Zr_{0.5}O_2$ polymorphs from DFT (lines) and DP (stars).

Phonon spectra provide a stringent benchmark for the DP model by probing the second derivatives of the potential energy, and the model accurately reproduces the HZO spectra (Fig. 4).

3.3 Phase stability and dielectric response

We investigated the finite-temperature phase stability of HZO using QHA-DFT and DPMD simulations. DFT predicts that the o_{III} phase is stable up to 1025 K, above which the t phase becomes thermodynamically favored (Fig. 5a). To capture strong anharmonic

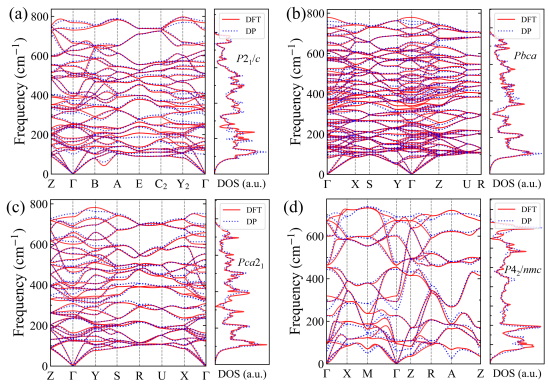

Fig. 4: Phonon dispersions of hafnia for the (a) m, (b) o_{I}, (c) o_{III}, and (d) t phases, computed using the PHONOPY package[4].

effects, MD simulations with an $8 \times 8 \times 8$ HZO supercell were performed. Two descriptors—local O-atom displacements and lattice symmetry—reveal a first-order o–t transition, with the transition temperature increasing from 1300 K in ZrO_2 to 1600 K in HfO_2 (Fig. 4b–d). Introducing 1.56% oxygen vacancies lowers the transition temperature substantially, e.g., to 500 K in ZrO_2, demonstrating strong tunability of phase transitions via defect engineering (Fig. 4e,f).

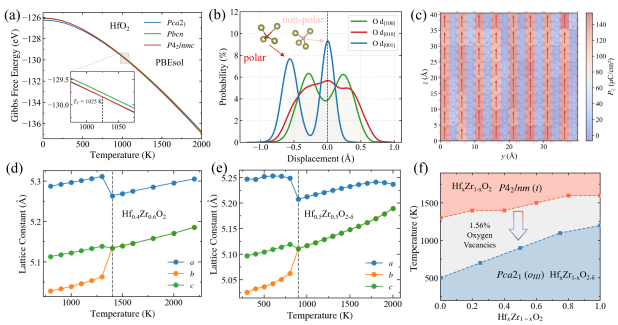

Fig. 5: Phase stability and structural properties of HZO: (a) Gibbs free energies of o_{III}, t, and $Pbcn$; (b) O-atom displacements; (c) polarization; (d,e) lattice constants of pristine and oxygen-deficient HZO; (f) effect of V_{O} on the o–t transition.

We computed the dielectric response of HZO under external fields. With increasing Zr content, all phases show enhanced dielectric performance, peaking at 70.55 for $Hf_{0.25}Zr_{0.75}O_2$ (8.5% increase over undoped, Fig. 6a). Analysis of the t phase reveals that polarization is dominated by O-atom displacements along [010], which have larger amplitude and higher symmetry than Hf/Zr, facilitating dipole reorientation and enhancing the dielectric response (Figs. 6b–d).

Conclusion

In summary, a transferable DPMD potential for $Hf_xZr_{1-x}O_2$ was developed and validated against DFT. Simulations show that the o_{III}–t transition temperature decreases with increasing Zr content and is strongly suppressed by oxygen vacancies, reaching ~500 K in ZrO_2. The high dielectric response arises from the large displacement freedom and high-symmetry ordering of O atoms in the t phase, highlighting compositional and defect engineering as effective routes to stabilize this phase.

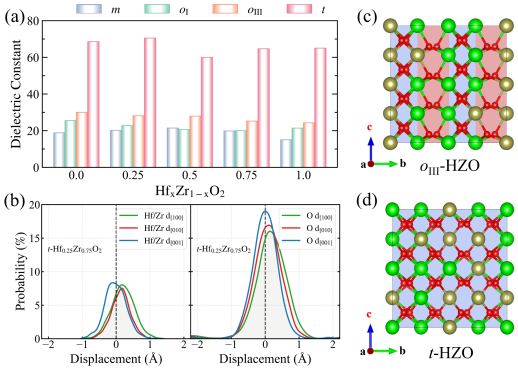

Fig. 6: Dielectric response of HZO: (a) average dielectric constant vs. Zr content from DPMD; (b) atomic displacements in t-$Hf_{0.25}Zr_{0.75}O_2$ under 0.004 eV/Å field; (c,d) schematics of o_{III} and t phases showing polar (red) and nonpolar (blue) regions.

Acknowledgments

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References

[1] Han Wang, Linfeng Zhang, Jiequn Han, et al. DeePMD-kit: A deep learning package for many-body potential energy representation and molecular dynamics. *Comput. Phys. Commun.*, 228:178–184, 2018.

[2] Linfeng Zhang, Jiequn Han, Han Wang, Roberto Car, and Weinan E. Deep potential molecular dynamics: a scalable model with the accuracy of quantum mechanics. *Phys. Rev. Lett.*, 120(14):143001, 2018.

[3] Aidan P Thompson, H Metin Aktulga, Richard Berger, Dan S Bolintineanu, W Michael Brown, Paul S Crozier, Pieter J In't Veld, Axel Kohlmeyer, Stan G Moore, Trung Dac Nguyen, et al. LAMMPS-a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comput. Phys. Commun.*, 271:108171, 2022.

[4] Atsushi Togo. First-principles phonon calculations with phonopy and phono3py. *J. Phys. Soc. Jpn.*, 92(1):012001, 2023.