Hessisches Kompetenzzentrum
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Electron/Hole Small Polarons in PbTiO3, BaTiO3 and NaNbO3

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Clusters
Lichtenberg II Cluster Darmstadt

Software
VASP, Quantum ESPRESSO

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Introduction

In this project the stability of small and bound polarons as a possible charge-compensation mechanism in the perovskite oxides lead titanate, barium titanate, and sodium niobate has been investigated, focusing on their lowest-temperature crystal phases. These materials are widely used in electronic and electromechanical applications, and their performance can be strongly influenced by how excess charge created by defects or impurities is accommodated inside the crystal. One important possibility is formation of polaron, where an extra electron or a missing electron becomes trapped in a small region and causes local distortions of nearby atoms. To model this reliably with density functional theory, it is necessary to use sufficiently large simulation cells so that the localized charge does not artificially interact with its periodic images and the surrounding lattice can relax realistically. Large cells greatly increase computational cost and memory requirements, making these calculations impractical on a standard personal computer. Therefore, access to a high-performance computer is essential to run the large-scale simulations and obtain trustworthy conclusions about polaron stability in these perovskites.

Methods

All first-principles calculations are performed using the Vienna Ab initio Simulation Package (VASP), employing the plane-wave pseudopotential method. Electron-ion interactions are treated within the Projector Augmented-Wave (PAW) framework. The exchange-correlation energy is described using the PBEsol parametrization of the Generalized Gradient Approximation

(GGA). The initial structure is taken from the experimental CIF file. The primitive cell is fully relaxed with respect to both lattice parameters and internal coordinates; subsequent *3 x 3 x 3* supercell calculations relax only the ionic positions while assessing the stability of the polaronic state. Polaron formation requires two ingredients: (i) a local lattice distortion that lowers the symmetry and creates a potential well, and (ii) localization of the excess charge at a specified cation site using a Hubbard correction (DFT + U). To realize these conditions, we initialize the electronic state using occupation-matrix control (a constrained-DFT scheme) to place the extra charge on a chosen center. During the ensuing ionic relaxation, the lattice responds and the required bond distortions develop around that site. Once the distortion is established, the constraint is removed and the system is re-relaxed. Here, the key parameter is trapping energy. The polaron trapping energy is defined as the total-energy difference between the localized and delocalized charge configurations. Thermodynamic stability of the polaron requires that the localized state is energetically favored. To compare and check the dependence of the trapping energy of small polaron on the choice of DFT code, we perform a cross-check with Quantum ESPRESSO (QE) code using the PBEsol exchange–correlation functional and PBEsol-consistent PAW pseudopotentials.

Results

We find that a small electron polaron localized on Ti is energetically favorable, whereas a small hole polaron localized on O is not. Since tetragonal $PbTiO_3$ exhibits polarization along the tetragonal (c) axis, we constructed a neutral domain wall with a 180^o PbO-terminated wall plane separating up- and down-polarized domains. For this domain-wall configuration, the trapping energy of an electron polaron on a Ti site close to the domain wall does not change significantly compared to the trapping energy of an electron polaron on a Ti site far from the domain wall. In rhombohedral $NaNbO_3$, we find that a small hole polaron localized on O is energetically favorable, in contrast to an electron polaron localized on Nb. We compared these results with $LiNbO_3$ rhombohedral phase, which is known to host an electron polaron on Nb. The key difference appears to be the strength of electron-phonon coupling associated with the conduction-band states (primarily Nb-derived): this coupling is stronger in $LiNbO_3$, which stabilizes an electron polaron on Nb, whereas it is weaker in $NaNbO_3$. In rhombohedral $BaTiO_3$, we find that a small hole polaron is energetically favorable. Moreover, when the hole polaron is associated with Fe on the Ti site (Fe_{Ti} doping), the system favors a lower-energy Fe^{3+}-O^{-1} configuration.

Discussion

As an outlook, the current calculations highlight polaron formation as an important yet poorly explored charge-compensation mechanism in electroceramic perovskites. As a quantum-mechanical entity, a polaron can strongly influence both charge transport and optical response. Moreover, polaron stability sets practical upper and lower limits on the Fermi level: in particular, the tendency toward oxygen oxidation (hole-polaron formation on O) can define a lower Fermi-level limit. This connects directly to the concept of Fermi-level engineering, which is central to our FLAIR (DFG) proposal. Establishing how the Fermi level is constrained by O oxidation provides a pathway to better understand temperature-driven phase transitions in perovskites and may help rationalize why certain structural phase (e.g., hexagonal) is accessible for $BaTiO_3$, whereas it is not accessible in other systems such as $SrTiO_3$.

Publications

Amirabbasi M.; Rohrer J.; Albe K.: "Interaction between small electron-polaron and neutral domain wall in PbTiO3: A DFT+U study "; DPG-Frühjahrstagung (DPG Spring Meeting); December 16-21 (2025); Regensburg (Germany)

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