Supporting Information Text

Polaron formation in Ferroelectric $PbTiO_3$: An Ab Initio Theoretical Study

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1. Computational Details of the Periodic Supercell Approach

To verify our results, we conducted spin-polarized DFT calculations using the VASP software package[1] [2]and compared the local conditions and formation energy changes of electron polarons with and without SOC considered. Firstly, the original unit cell of tetragonal $PbTiO_3$ was optimized using the exchange-correlation functional (PBE) in the generalized gradient approximation [3]. The plane-wave cutoff energy was set to 500 eV, and the convergence threshold for the self-consistent electronic calculation was set to 10^{-4} eV. The first-principles calculation method based on density functional theory + Hubbard U correction (DFT+U) was adopted to simulate the formation process of electron polarons. A 3×3×3 supercell system containing 135 atoms was selected as the calculation model. To effectively overcome the self-interaction error existing in the traditional DFT method, we referred to the parameterization scheme proposed by Gou[4] et al. and applied a correction parameter of U = 4.75 eV on the 3d orbitals of Ti. When using the supercell model for calculation, a 2×2×2 K-point was adopted. The formation energy of polaron is as shown in Formula 9.

$$E_p(f) = E_T^p - E_T^{np} \#（1）$$

E_T^p represents the energy when there are polarons in the structure, E_T^{np} represents the energy when there are no polarons in the structure, and $E_p(f)$ is the energy difference between E_T^p and E_T^{np}.

Reference

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3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
4. G. Gou, J. W. Bennett, H. Takenaka and A. M. Rappe, *Physical Review B—Condensed Matter and Materials Physics*, 2011, **83**, 205115.