Oxygen vacancy diffusion in bulk SrTiO3 from density functional theory

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The migration energy of oxygen vacancy diffusion in $SrTiO_3$ (STO) is one of the critical characteristic parameters that could potentially influence many aspects of its physical properties [1,2]. Thus it is imperative to obtain an accurate value of the energy barrier. However, the existing data [3-7] determined using either experimental or theoretical techniques varies significantly. In this study, the isolated neutral and charged oxygen vacancy diffusion energy barriers in n × n × n STO supercells (n increased from 2 to 5) have been obtained using density functional theory (DFT) in combination with nudged elastic band (NEB) method. The effects of several factors that can potentially influence the results have been examined. These factors include supercell sizes, spin, octahedral rotation induced by the oxygen vacancy, charge state of oxygen vacancy, the type of the chosen exchange and correlation functionals, e.g. PBE and PBEsol and the effects of +U. Surprisingly, the results show that oxygen octahedral rotation cooperating with boundary condition of STO supercell significantly affects the oxygen vacancy diffusion energy barrier. The effects of charge states of oxygen vacancy and exchange-correlation functionals on the energy barrier are found to be diminishing as the size of STO supercell increases. Moreover, within a sufficiently large supercell (5x5x5), DFT underestimates the migration energy barrier, regardless of which functionals or whether the DFT+U has been employed. This work offers a comprehensive picture of oxygen vacancy diffusion in bulk STO using DFT calculations and provides fundamental insights on how to accurately simulate defect transport in other perovskite oxide compounds.

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