

Density Functional Study of Ti Antisites in SrTiO₃, BaTiO₃, and PbTiO₃

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In a recent decade, lots of peculiar physical properties found in SrTiO₃, e.g., electron-doping induced insulator-metal transition and superconductivity, blue-light luminescence, a two-dimensional electron-gas at the interfaces with other oxides, and ferroelectric states in cation-site doped and reduced samples, have triggered extensive investigations to elucidate their origins and mechanisms. From these investigations, the O vacancy has been proposed as a possible cause for some of these properties. Very recently, a density functional study [1] demonstrated that Ti antisites (Ti_{OC}), which are constructed by a Ti ion off-centered from the Sr site, are likely to form and even comparable in formation energy to the O vacancy under a Ti-rich condition. These defects were suggested to be the origins of the blue-light luminescence and ferroelectric state in reduced SrTiO₃.

In this study, we systematically investigated Ti_{OC} in SrTiO₃, BaTiO₃, and PbTiO₃. The results were discussed and compared in terms of energetics and electronic structure. For a comparative study, the cubic structures were taken into account for the three systems. Our calculations were carried out using the projector augmented wave method [2] and the Perdew-Burke-Ernzerhof generalized gradient approximation [3] as implemented in the VASP code [4-6]. In order to correct the spurious on-site Coulomb interaction of the Ti 3*d* orbitals, a rotationally invariant +*U* method [7] was applied.

Figure 1 shows the stable atomic configurations of Ti_{OC} in SrTiO₃. Similarly, Ti off-centering along the [100] (Ti_{OC:100}) or [110] (Ti_{OC:110}) crystal directions gains energies and stabilizes the antisitelike configurations in BaTiO₃ and PbTiO₃. Each Ti_{OC:100} and Ti_{OC:110} can be regarded as a defect pair, composed of a Ti interstitial and an A-site vacancy (A = Sr, Ba, and Pb). Their formation energies under a Ti-rich condition are shown in Fig. 2. Both Ti_{OC:100} and Ti_{OC:110} have low formation energies, indicating that they are likely to form in all systems. For the neutral charge state, the formation energies are ~1.3-2.3 eV, and Ti_{OC:100} is slightly more stable than Ti_{OC:110}. We predict that Ti_{OC} can strongly influence the ferroelectricity-related and/or optical properties in BaTiO₃ and PbTiO₃, similar to the case of SrTiO₃ [1].

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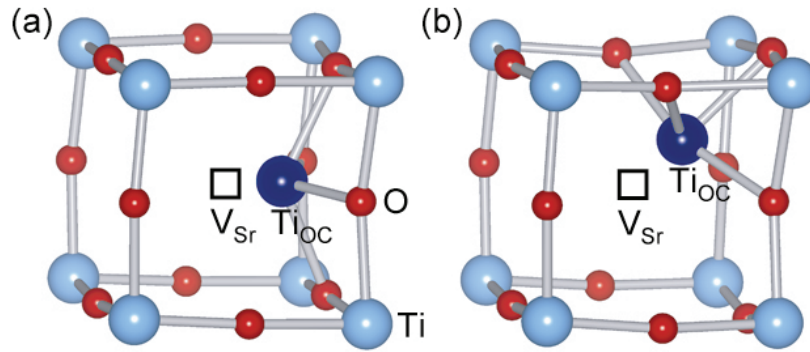


FIG. 1. Local atomic configurations of (a) $\text{Ti}_{\text{OC}:100}$ and (b) $\text{Ti}_{\text{OC}:110}$ in SrTiO_3 .

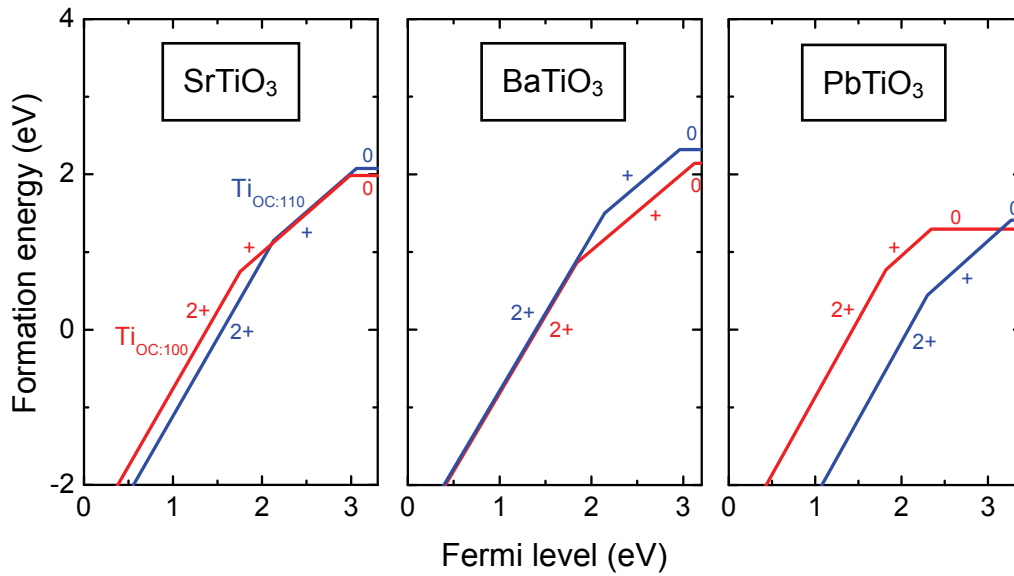


FIG. 2. Formation energies of Ti_{OC} in SrTiO_3 (left), BaTiO_3 (middle), and PbTiO_3 (right) under a Ti-rich condition. The slope corresponds to the charge state as indicated in the figure.