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Ab-initio Studies of Point Defects in TiO_2: A Density Functional Approach

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Titanium dioxide has been intensively studied as a wide band gap transition metal oxide due to its n-type semi-conducting property which makes it to have many applications in industry. Some of the observed conductivity arises from its intrinsic point defects. The structural properties and electronic band structures of TiO2 (rutile and anatase) phases, have been investigated using *ab-initio* methods. The structural properties were obtained using generalized gradient approximation (GGA) employing pseudopotentials and plane wave basis sets. For the two phases of TiO2, the calculated equilibrium lattice constants, bulk moduli and bond lengths were found to be in good agreement with other recent theoretical calculations and also with experimental data. After introduction of various defects to the perfect super cell, the Ti-O bond lengths were altered greatly. The apical bond lengths changed from a constant 1.959 Å to a range of values (1.718 - 1.861) Å, and the equatorial bond lengths changed from a constant 2.006 Å to a range of values (2.072 - 2.231) Å for rutile TiO2. The apical bond lengths changed from a constant 1.956 Å to a range of values (1.782 - 1.830) Å, and the equatorial bond lengths changed from a constant 2.050 Å to a range of values (2.112 - 2.214) Å, for anatase TiO2. Also altered were Ti-O-Ti angles, from the two constants (99.93, 131.04)° to a range of values (88.86 - 95.69 and 132.01 - 143.49)° for rutile TiO2. For anatase TiO2, Ti- O-Ti angles changed from the two constants (103.81, 152.39)° to a range of values (93.59 - 149.91 and 156.74 - 176.05)°. Electronic properties were investigated too. Perfect rutile and anatase super cells gave band gaps of 2.24 eV and 2.44 eV, respectively, underground-state conditions. Valence bandwidths (VB) and conduction bandwidths (CB) were also obtained for both phases. VB of 5.6 eV and CB of 1.654 eV were observed for rutile TiO2, while VB of 4.76 eV and CB of 2.35 eV were observed for anatase TiO2; all in good agreement with experimental values. This study also investigated the defect formation enthalpies of Frenkel and Schottky defects in both rutile and anatase phases of TiO2. This study also considered point defect stability in rutile and anatase phases of TiO2. The formation energies for oxygen and titanium atoms, defects were found to be in agreement with the experimental values, especially the case of rutile oxygen atom vacancy. Both Frenkel and Schottky defects were found to induce new energy states in titanium dioxide. Normally band gaps are reduced in defective TiO2 crystals, and in this study, reduced energy band gaps were reported for all the defective super cells. In rutile, the metal oxide gaps were found to almost vanish due to the presence of oxygen atom vacancy, oxygen atom Frenkel and titanium Frenkel defects. These gave direct energy band gaps: 0.35 eV, 0.207 eV and 0.327 eV, respectively. Defects in anatase phase showed a similar trend, with the least energy band gap being reported for the case titanium interstitial (0.041 eV, which is indirect). With such infinitesimal gaps, these otherwise insulating oxides can with ease become conducting metal oxides, by either increasing the temperatures or pressure since these calculations were done at 0 K and 0 pressure. It can thus be said that intrinsic point defects in titanium dioxide do contribute to the improvement of the electrical conductivity of this oxide.

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