

Abstract

We use first-principles calculations based on density functional theory to study the structural properties and pressure-induced solid-solid phase transitions of ZnO. Both the local-density approximation (LDA) and the PBE96 form of the generalized gradient approximation (GGA) are employed together with the projector augmented wave (PAW) method to mimic the electron-ion interaction. The electronic structure is investigated by the HSE hybrid functional and a partially self-consistent GW approximation. We consider the wurtzite (B4), rocksalt (B1), zinc blende (B3), CsCl (B2), PbO (B10), NaTl (B32), WC (B_h), BN (B_k), NiAs (B_{8_1}) and AsTi (B_i) modifications of ZnO. The calculated structural properties in the B4, B3, B1 and B2 phases compare acceptably well with those found in previous theoretical studies, as is the transition pressure between them. We find that the B4 phase is the most preferred low-pressure candidate in ZnO while the B2 phase is favorable at high pressures. Apart from the previously reported $B4 \rightarrow B1 \rightarrow B2$ phase transition, our study reveals other possible paths for a transition from B4 to B2 phase with the B_k , B_h , B10, and B_{8_1} structures as intermediate phases. It is found that the HSE and the GW approach offer a significant improvement to the prediction of band-gaps in ZnO. The band-gaps are found to increase with increasing pressure leading to the structural phase transitions.