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A First-Principles Computational Study of Structural and Elastic Properties of ZnO

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Introduction

The purpose of this study is to determine structural and mechanical properties of zinc oxide (ZnO) using first-principles computational methods. ZnO is a semiconductor widely used in many electronic and optical applications. ZnO is also economically and environmentally desirable – first, both the constituent elements are abundant on Earth and therefore inexpensive for large-scale applications; second, it is non-toxic. The most significant contribution of this study is the simulations of the high-pressure phases. These high-pressure simulations are important because the rock salt phase of ZnO obtained at high pressure can be recovered at ambient pressure, and this new structural phase possesses different properties that may be more useful for certain applications.

Method

The primary tool used in this paper is the Vienna Ab Initio Simulation Package (VASP), which is based on the density functional theory (DFT) to calculate the ground-state property of a substance. There are three known phases of ZnO, namely wurtzite (W), rock salt (RS), and zinc blende (ZB). The initial step is to determine the transition pressure for the structural transformation between the ZnO phases. This helps set a clear distinction between the high-pressure and ambient-pressure calculations.

The second step is to obtain the bulk modulus. To calculate the bulk modulus, each structure is placed under a series of uniform pressure values. The resulting energy data are then fitted against the Birch-Murnaghan Equation of States (EoS). The third step is to calculate the elastic constants. The W structure is a hexagonal closely packed lattice. The RS and ZB phases have cubic lattices. To calculate the elastic constants, distortions are applied to the lattice. By using the difference in energy between the distorted and undistorted structure, the elasticity of the structure can be calculated.

Literature Review

Several past studies have been referenced for the present work. The first such study calculated the elastic constants using the computer code CRYSTAL98 [Orlando R, Dovesi R, Ugliengo P, Roetti C, and Saunders VR, International Journal of Inorganic Materials, Vol. **1**, 147-155 (1999)]. The second study for comparison obtained the elastic constants using the DFT package ABINIT [Duan Y, Qin L, Tang G, and Shi L, The European Physical Journal B, Vol. **66**, 201-209 (2008)]. The third study for comparison obtained the elastic constants using the DFT package WIEN2k [Mohammadi AS, Baizaee SM, and Salehi H, World Applied Sciences Journal, Vol. **14**, 1530-1536 (2011)]. While the elastic constants are the main focus of this study, there is a multitude of publications on ZnO that address its potential uses in many other areas of science and technology. In the next box on the right, we list several other applications of ZnO.

ZnO has numerous uses in electronics. For example, ZnO has been studied as a candidate material for use in LEDs, n-p junctions, and Al/Au ohmic contacts. There has been recent interest in Al-doped ZnO for its thermoelectric properties. This is because this material possesses a high Seebeck coefficient, which measures the electrical potential generated by applying a thermal (temperature) gradient. The structural stability at temperatures above 1300 °C allows ZnO to be used as a high-temperature thermoelectric generator.

ZnO nano-particles have been studied for photocatalytic applications. A photo-catalyst is used as a catalyst for a chemical reaction under certain lighting conditions. ZnO thin films can be used to degrade chemicals such as methyl blue into less toxic chemicals.

ZnO thin films have been studied for use as a fiber-optic temperature sensor, and it can also be used as a NH_3 gas sensor. Au-ZnO thick films have been studied for use as an ethanol sensor. Various forms of ZnO with dopants or composites have been studied for use as a variety of bio-sensors. ZnO inverse opal electrodes have been studied for use as a glucose sensor. A ZnO based paste has been studied for use as a BPA sensor. A flower shaped ZnO nanostructure has been studied for detection of meningitis. ZnO has even been added to cellulose to study for increasing immune response.

More details of these works can be found in the project report.

Results & Discussion

Transition Pressure & Bulk Modulus

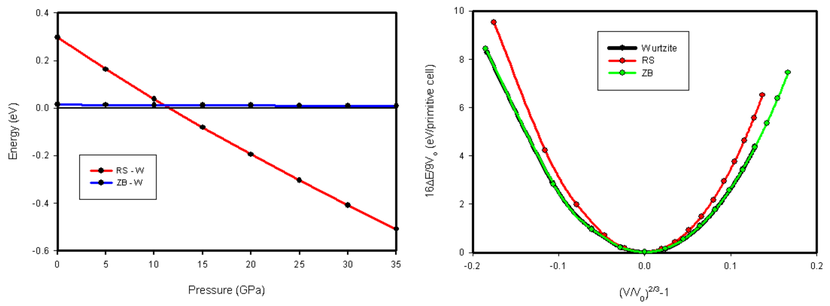

Figure 1. ***Left:*** The energy-pressure graph. The energies for the RS & ZB phases are plotted relative to the W phase energy. The crossover indicates a transition pressure of 11 GPa. At low pressures the W phase is more stable. At high pressure the RS phase is more stable. The high-pressure RS ZnO structure can be recovered at ambient pressure. ***Right:*** The fitting of calculated energies to the Birch-Murnaghan EoS. The resulting bulk moduli are 129, 166, and 129, GPa for the W, RS, and ZB phases, respectively.

The transition pressure from figure 1 gives a clear distinction between high and low pressure calculations. The high pressure calculations were done at 15 GPa. By using a direct derivative method, we calculated the bulk modulus for the high pressure ZnO structures. The resulting bulk moduli are 193, 229, and 192, GPa for the W, RS, and ZB phases, respectively.

Elastic Constants

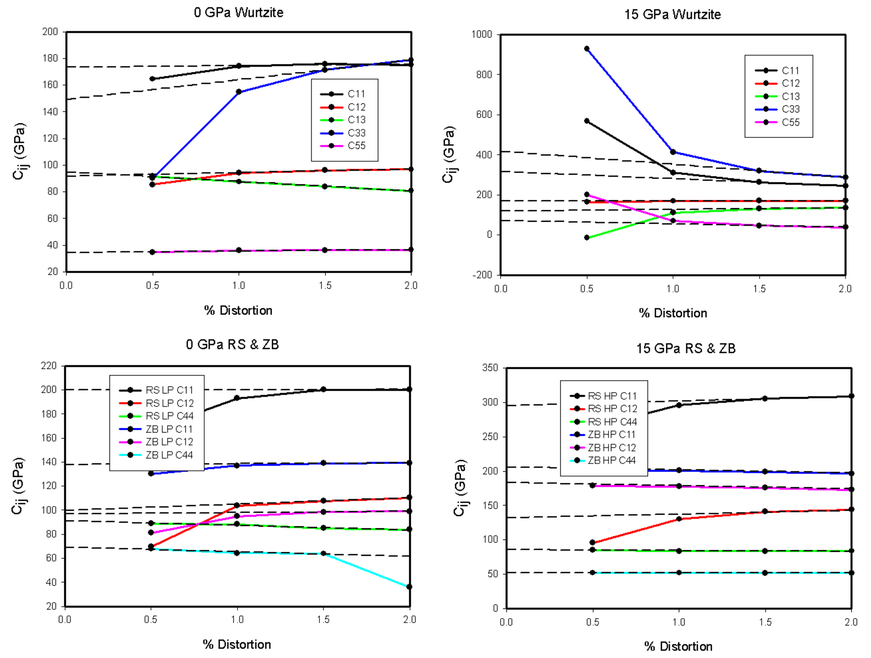

Figure 2. ***Top Left:*** The ambient-pressure elastic constants for the W ZnO phase. ***Top Right:*** The high-pressure elastic constants for the W ZnO phase. ***Bottom Left:*** The ambient-pressure elastic constants for the RS & ZB phases. ***Bottom Right:*** The high-pressure elastic constants for the RS & ZB phases. The distortions used were kept small to keep the change in volume small. The dashed lines are the results of linear fits. These linear fits are used to extrapolate the elastic constants for 0% distortion.

Conclusions & Further Study

The present work predicts a structural transition from the wurtzite to RS phase of ZnO at 11 GPa. We therefore performed high-pressure calculations at 15 GPa. The bulk moduli for the ambient-pressure structures are within 5% of previously reported results. Our calculations indicate that the high-pressure bulk moduli of ZnO phases increase between 38% and 50%. The RS and ZB phases of ZnO show increasing values of elastic constants C_{11} and C_{12} at higher pressure, while the value of C_{44} decreases at higher pressure. On the other hand, the wurtzite phase shows all increased elastic constants with increasing pressure. A comparison was made between the elastic constants of the ZnO phases and those of silicon. With the exception of C_{55} and C_{66} in the wurtzite phase, the three phases of ZnO exhibit higher values of elastic constants, indicating their higher strength under structural deformation. An important topic for future study of ZnO is to explore the electronic band structure and phonon dispersion, which will determine the properties crucial in many device applications. The structural results obtained in this work have laid a key foundation for continued research.