

First-principles study of the wurtzite-to-rocksalt homogeneous transformation in ZnO: A case of a low-transformation barrier

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A homogeneous wurtzite-to-rocksalt phase transformation in ZnO is studied using a first-principles pseudo-potential method. The calculated transformation enthalpy barrier at the phase equilibrium transition pressure is much lower than the barriers previously studied in SiC and GaN. SiC, GaN, and AlN are found experimentally to transform at a pressure significantly higher than their respective phase equilibrium transition pressures. Interestingly we note that the experimentally observed transition pressure in SiC, GaN, and AlN occur for roughly the same value of the enthalpy barrier. In contrast, ZnO readily transforms at the phase equilibrium transition pressure consistent with the fact that its enthalpy barrier at that pressure is well below this critical barrier value.

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Pressure-dependent crystal structures of group-IV, -III-V, and -II-VI materials have been a long-standing topic of interests from both experimentalists and theorists. It is known that, under ambient pressure, the highly covalent materials favor the fourfold coordination structures [zinc blende and/or wurtzite (WZ)], whereas the highly ionic materials favor the sixfold [rocksalt (RS)] and higher coordination structures (for, e.g., CsCl structure). As pressure increased, covalent materials transform into the higher coordination structures. The degree of ionicity is an important factor that determines the transformation pressure. For example, the highly covalent material SiC starts to transform into RS at a pressure of ~ 100 GPa,¹ whereas the less covalent material GaN starts to transform at a much lower pressure of ~ 50 GPa.² The higher ionic materials such as MgO and CdO even favor rocksalt phase already at zero pressure (our prior study³ has shown that if the density of MgO is approximately 17% lower — corresponding to a negative pressure of 16.2 GPa — the hexagonal phase would have been stable). ZnO is a WZ material with a moderate degree of ionicity (increasing the tendency to form in RS structure). Because the cohesive energy of both phases are so close, the WZ-RS transformation pressure in ZnO is rather low [9.1 GPa (Ref. 4)], suitable for performing experiments. On the theory side, phase equilibrium transition pressure can be calculated. Most of the time, this has been done by calculating the energy-volume curves of the two phases and finding the common tangent. In the past, the calculated equilibrium transition pressure is frequently used to compare directly with the observed transformation pressure. It is now realized that there may be large kinetic barriers that impede the transition at the equilibrium pressure, leading to a hysteresis between the forward and backward transformations.⁵ The large hysteresis has indeed been observed in the transformations of SiC (Ref. 6) and GaN.⁷ This means, in order for the actual transformation process to take place, not only the enthalpy of the ending phase (in this case RS) has to be lower than or equal to the starting phase (in this case WZ) but also the enthalpy barrier of the transformation between the two phases has to be sufficiently low. To meet the later requirement, the observed transformation pres-

sure can be several GPa higher than the equilibrium transition pressure. For examples, GaN and SiC have high observed transformation pressures of ~ 50 and ~ 100 GPa in comparison to the calculated equilibrium transition pressures of 31 GPa (Ref. 8) and 60 GPa,⁹ respectively. Interestingly, for ZnO, the observed transformation pressure of 9.1 GPa (Ref. 4) essentially falls in the narrow range of the calculated equilibrium transition pressures, varied between 6.6 GPa (Ref. 10) and 10.45 GPa,¹¹ indicating that ZnO has a very small transformation barrier.

Since the barrier of transformation has an influence on the transformation pressure, it is challenging to use it to improve the prediction of transformation pressures. We propose that, by monitoring the decrease of enthalpy barrier with pressure and looking for the pressure that gives the threshold barrier (the barrier that is low enough for the transformation to take place), we can obtain a transformation pressure in the cases where the barrier dominates the transformation. A simple homogeneous transformation path between WZ and RS GaN has recently been proposed based on first principles calculations.⁸ This path was also shown to be a special case of a more general transformation path between arbitrary tetrahedrally coordinated polytypes of SiC and RS.⁹ Furthermore, essentially the same path was actually proposed as early as 1998 in CdS based on shock-wave experimental studies.^{12,13} This path has additional experimental confirmation in the studies of phase transitions in nanoparticles of CdSe.¹⁴ While the large volume change in the transition complicates the process of transformation, it is clear that the homogeneous transformation considered here provides a useful description of the nucleation process of the transition and thus its barrier should be a good indicator for when the actual transition can take place.

Our prior homogeneous WZ-RS phase transformation study in GaN (Ref. 3 and 8) and the work of Lambrecht group in SiC (Ref. 9) predict a rather high transformation enthalpy barriers (at the phase equilibrium transition pressure) in these two materials that qualitatively explain the high observed transformation pressures. In this report, using the barriers from those works combining with the additional