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# Zinc oxide phase transitions under non-ambient conditions

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## Introduction:

In order to investigate phase transitions under non-ambient conditions of zinc oxide, we have performed several sets of calculations using different approaches. First, we have performed crystal structure prediction for ZnO using simulated annealing (SA), with an empirical potential and local optimization on *ab initio* level. [1,2,3] We have found the experimentally observed structures wurtzite, sphalerite, and rock salt in agreement with previous ZnO research. In addition, full analysis of the energy landscape was performed and many new interesting non-equilibrium modifications were found in different regions of the energy landscape, at elevated pressures and/or temperatures.

Very important aspect beyond the identification of equilibrium ZnO structure (global minimum) is the analysis of the energy barriers and energy landscape surrounding the global minimum, and of the possible transition paths connecting the major locally ergodic regions. [4,5] Therefore, we have performed threshold algorithm (TA) calculations for various pressures and temperatures, and for different numbers of formula units of ZnO. Furthermore, we have performed calculations using the prescribed path algorithm (PP), where connections between experimental structures on the energy landscape, and in particular transition states, were investigated in detail.

## High pressures (HP); Crystal structure prediction (CSP):

Here, we show brief presentation of the CSP method [6,7]:

(1) Global optimization (GO) – two-body empirical potential (Coul+LJ):

$$\dot{V}_{ij}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + \varepsilon \cdot \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$

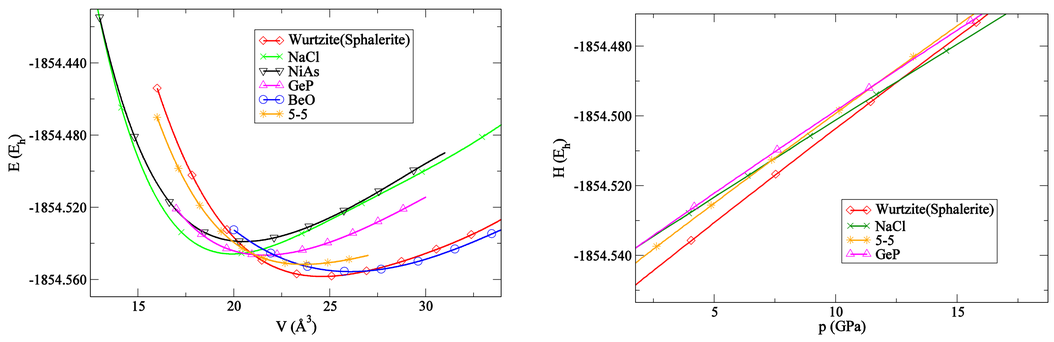
(2) Simulated annealing (SA) – Heating the system over melting point (↑↑E(s))

(3) Monte Carlo (MC) simulations – cooling the system (↓E(s)) and accepting only energetically lower atomic configurations (Metropolis criterion)

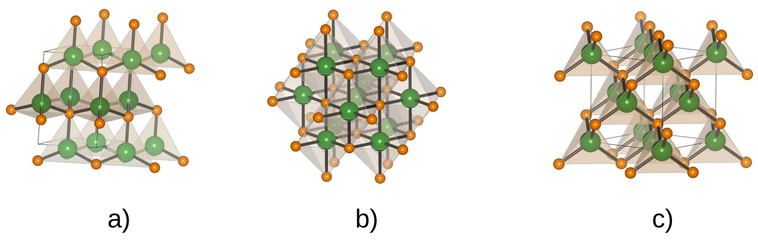
(4) Relaxed (GO, annealed or quenched) structure at 0K (usually leads to distorted structure)

(5) Local optimization (LO) on *ab initio* level using Hartree Fock (HF), DFT (LDA) and hybrid (B3LYP) approximation, (gives ideal bulk structure at 0K).

(6) The symmetries and the space group of the structures found are determined and duplicate structures are removed using the CMPZ-algorithm.

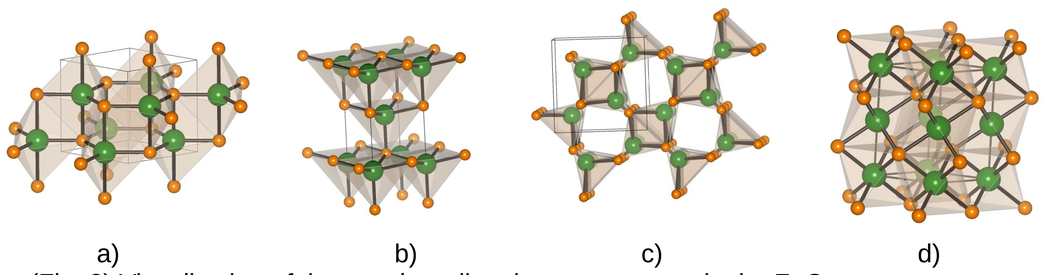



(Fig. 1) *E(V)* and *H(p)* curves of ZnO as function of pressure calculated using B3LYP functional



a) b) c)

(Fig. 2) Visualization of the experimentally observed structure types in the ZnO system: a) Wurtzite type [8]; b) NaCl type (high pressure) [9]; c) Sphalerite type [10].

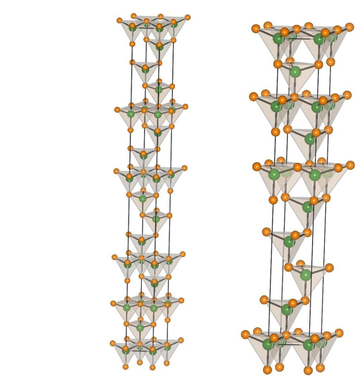


a) b) c) d)

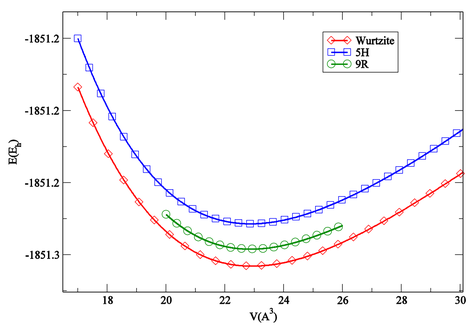
(Fig. 2) Visualization of the novel predicted structure types in the ZnO system at non-ambient conditions: a) 5-5 type (HP) [2,11]; b) GeP type (HP) [2,12]; c) β-BeO type (NP) [2,13]; d) NiAs type (HP+HT) [2]

## High temperatures (HT);Threshold algorithm (TA):

The barrier structure is explored using the threshold algorithm [15], where the landscape accessible from a local minimum below a sequence of energy barriers (thresholds) is systematically explored for all important local minima. The threshold calculations were performed for different numbers of formula units ($Z$ = 1–6), employing several different starting structures (rocksalt, wurtzite, sphalerite, 5-5, etc.). Each set of calculations consisted of 28 lids, ranging from –6.3 to –3.9 eV, with a step size of 0.1 eV.



(Fig. 1)




(Fig. 2)

In this way, we are able to investigate the energy landscape in more detail; we start from the low energy minimum, and increase the energy lid, until the next minimum is reached. The sum of the energy lids employed in this calculation gives us the actual size of the energy barrier dividing these two minima [4].

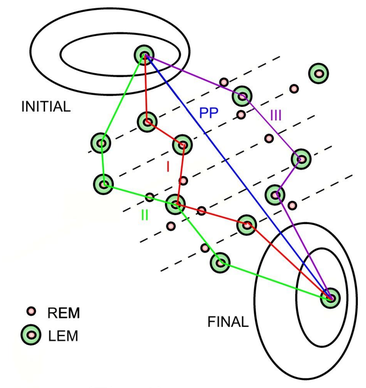
for $Z$ = 6, the energy landscape becomes more diverse, and it is dominated at mid-level energy lids by the new trigonal polytype *6H* and *9R*. This shows that for large system sizes the wurtzite and sphalerite basins shrink in relative terms, and that the polytypes are separated only by relatively small barriers from the most highly ordered wurtzite and sphalerite types. Thus the appearance of stacking faults is quite likely; however conversely, this also suggests that a transformation from the polytypes to e.g. the wurtzite modification might happen relatively easily [3,4].

Fig. 1 Visualization of the calculated HT polytypes on the *ab initio* level in the ZnO system [14]: a) 5H [3]; b) 9R [3];

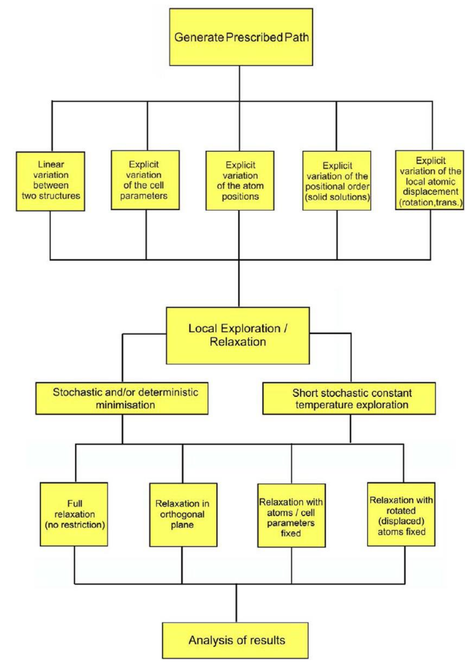
Fig. 2 Calculated *E(V)* curves of ZnO hierarcihal polytpe structures found at high temperatures (HT) computed using B3LYP functional [3].

## HP and HT; Prescribed path (PP):

The prescribed path (PP) method [5] works by optimizing the atom arrangement at a number of intermediate steps along a “reaction path” (Fig. 1). In particular, various MC simulations at finite temperatures yield several relaxed paths and allow us to cross small barriers in the direction orthogonal to the “reaction coordinate”.

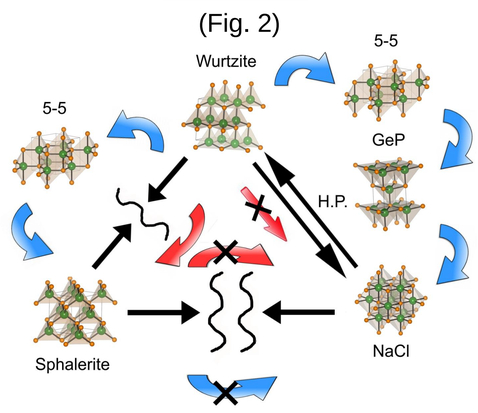



(Fig. 1)




(Fig. 2)

From the flowchart of the prescribed path (PP) algorithm (Fig. 2) we observe three main parts of the PP method [5]:
-Generate prescribed path: periodic boundary conditions; define: initial and final state (usually LO structures), moveclasses: atomic positions, unit cell, rotation of groups of atoms or atom exchange,
-Local Exploration and relaxation: define energy (cost) function and MC parameters
-Analysis of results: Thermal Stability Analysis (TSA), Crystallographic analysis




(Fig. 3) Overview of PP investigations in ZnO

-Black arrows represent prescribed paths between experimentally observed structures in the ZnO system: the wurtzite, the sphalerite, and the rock salt type. The wavy black lines indicate the size of the barrier along the prescribed path in comparison to other paths. The blue arrows represent low-temperature transition routes, and the red arrows represent high-temperature transition routes, respectively.

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