



Zinc oxide: Connecting theory and experiment[#]

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Abstract

Zinc oxide (ZnO) is a material with a great variety of industrial applications including high heat capacity, thermal conductivity and temperature stability. Clearly, it would be of great importance to find new stable and/or metastable modifications of zinc oxide, and investigate the influence of pressure and/or temperature on these structures, and try to connect theoretical results to experimental observations. In order to reach this goal, we performed several research studies, using modern theoretical methods. We have predicted possible crystal structures for ZnO using simulated annealing (SA), followed by investigations of the barrier structure using the threshold algorithm (TA). Finally, 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. The results were in good agreement with previous theoretical and experimental observations, where available, and we have found several additional (meta)stable modifications at standard, elevated and negative pressures. Furthermore, we were able to gain new insight into synthesis conditions for the various ZnO modifications and to connect our results to the actual synthesis and transformation routes.

Keywords: structure prediction, zinc oxide, prescribed path, threshold algorithm

I. Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor ($E_{gap} = 3.3$ eV at room temperature), with a large number of desirable properties for industrial applications (e.g. transparency, luminescence, high electron mobility, etc.) [1]. Ideal bulk zinc oxide adopts the hexagonal wurtzite type of structure (B4) at ambient conditions [2,3], with an experimentally confirmed transition to the rocksalt type (B1) modification at a pressure of about 10 GPa [1,4,5]. In addition, a sphalerite type modification (B3) can be stabilized in nanocrystalline ZnO thin films [6–9], and recently, very thin films (< 15 atomic layers) of a ZnO modification exhibiting the 5-5-structure type have been synthesized [10–12].

The focus of this study is the ideal crystalline modifications of ZnO that might find application in e.g. ceramic

engineering. Many properties of zinc oxide are dependent upon the wurtzite hexagonal, close packed arrangement of the Zn and O atoms. Clearly, it would be of great interest to know which other possible (metastable) modifications could exist in the ZnO system, since these might exhibit different properties and perhaps lead to some new applications. An important part of such an investigation would consist of understanding the stability of, and transitions among, the existing and proposed polymorphs, with information about the influence of pressure and/or temperature, which would allow us to connect theoretical results to experimental observations.

II. Theoretical methods

Our general approach to the exploration of the energy landscape of chemical systems for the determination and analysis of structure candidates has been given in detail elsewhere [13,14]; here we will just outline the main steps of the method and provide information specific to this investigation. The (meta)stable phases capable of existence correspond to locally ergodic regions

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on the enthalpy landscape of the chemical system of interest, which, at low temperatures, are basins around local minima of the potential energy. These minima are identified using simulated annealing [15], where both atom positions and cell parameters can be freely varied without any symmetry constraints. After the optimizations, the symmetries and the space group of the structures found are determined using the algorithms SFND [16] and RGS [17], respectively, and duplicate structures are removed using the CMPZ-algorithm [18]. All three algorithms are implemented in the program KPLOT [19].

The barrier structure is explored using the threshold algorithm [20], where the landscape accessible from a local minimum below a sequence of energy barriers (thresholds) is systematically explored for all important local minima, and via the prescribed path algorithm [21,22], which works by optimizing the atom arrangement at a number of intermediate steps along a “reaction path” (c.f. Fig. 1a). This method allows us to explore transition routes and barriers between even distant minima, suggesting possible transition states and specific transition paths for more detailed analysis, as well as to gain more insights into the temperature dependence of the synthesis and transformation processes in the system.

In this study, we have employed an empirical potential (Coulomb + Lennard-Jones potential) for the global optimizations, threshold runs and prescribed path explorations, using up to 6 formula units. The local optimizations were performed on *ab initio* level using Hartree-Fock and various density functionals (LDA and B3LYP).

III. Results and discussion

3.1 Structure prediction using simulated annealing

Our calculations show that the experimentally observed polymorphs of zinc oxide are the energetically lowest and thermodynamically most stable ones, which is in agreement with experiment [1,2] and previous calculations [23,24]. The wurtzite (*B4*) type together with the sphalerite (*B3*) type are the stable modifications at ambient conditions. Both structures are based on corner-connected ZnO_4 tetrahedra; however, wurtzite exhibits a *hcp*-packing of the oxygen atoms, and sphalerite a cubic *fcc*-packing, respectively. Besides the *B4* and *B3* modifications, our searches resulted in several candidates which exhibit different stacking order [25]. These new polytype structures of ZnO are related to the analogous ones that have been observed in ZnS and SiC [26–28].

At high pressures (above 10 GPa) we observed the rock-salt modification in the ZnO system as the most stable form, while at slightly negative pressures, we found a β -BeO-type modification (space group $P4_2/mnm$), which is also based on a *hcp*-packing of O-atoms but

where we find pairs of edge connected ZnO_4 tetrahedra. In BeO, the wurtzite and the β -BeO-type are the low- and high-temperature polymorphs; one would expect a similar relation in the ZnO system, suggesting that with an increase of temperature one might be able to synthesize the β -BeO-type modification as a metastable phase in ZnO. In addition, we observe many interesting modifications from previous calculations, e.g. from the PbS [29,30] or the BN [31] system.

One further interesting structure candidate, which we found as a metastable phase, is the so-called “5-5”-type, which consists of corner-connected ZnO_5 trigonal bipyramids forming an ionic analogue to the *h*-BN-structure. This structure type has been found on the energy landscapes of many AB compounds [32–34], and its existence in ZnO has been proposed in some recent experiments [10–12], thus making the ZnO system a very good candidate to synthesize this new structure type as a bulk phase. For more details, we refer to references [35,36].

3.2 Energy landscape investigation of ZnO using the threshold algorithm

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. 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. Since the amount of data obtained is huge, we can only highlight some results for standard pressure; for more details we refer to references [35,37].

With $Z = 2$, we observe that the wurtzite and the sphalerite type are most likely to be reached, irrespective of the starting point. However, at higher energy lids, we also observe a distorted variant of the wurtzite structure, exhibiting the space group $I-4m2$ (no. 119). For $Z = 3$, we find, besides the sphalerite and the rock salt structure type, the new trigonal polytype $6H$ and $9R$ in space group $R3m$ (no. 160); recall that neither wurtzite, β -BeO, nor the 5-5-type can be described with a unit cell for $Z = 3$. For $Z = 4$, the most frequently found minima are again wurtzite and sphalerite, but also β -BeO and the “5-5” structure type are commonly reached. Finally, 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,

Table 1. Structural analysis of the energy landscape of ZnO with $Z = 6$ and the NaCl structure as the starting point of the threshold runs: Results for the first 5 lids (from -6.3 to -5.9 eV). Different unit cells for the same structure are characterized by the unit cell lengths a , b , and c .

Space group and modification	Times found [count (%)]	Cell parameters (a, b, c) [Å]	Times found [%]
<i>Fm-3m</i> (no. 225) NaCl	185 (11.45)	(9, 6, 3)	100
<i>F-43m</i> (no. 216) Sphalerite	633 (39.20)	(9.5, 6.4, 3.2)	54
		(13.5, 6.4, 3.2)	46
<i>I4mm</i> (no. 107) GeP	433 (26.81)	(9, 6.2, 3.1)	100
<i>P6₃mc</i> (no. 186) Wurtzite	60 (3.71)	(9.6, 7.6, 3.2)	100
		(13, 6.3, 3.2)	2.6
		(10.2, 6.3, 3.2)	1.3
<i>R3m</i> (no. 160) New polytype	77 (4.77)	(9.2, 6.4, 3.2)	96.1
		(9.5, 6.4, 3.2)	50
<i>Cm</i> (no. 8) Dist. β -BeO	6 (0.37)	(10.3, 6.2, 3.2)	50
		Badly strained cand.	-

Table 2. Structural analysis of the energy landscape of ZnO with $Z = 6$ for the NaCl structure as starting point of the threshold runs: Results of the 5 lids from -5.8 to -5.4 eV.

Space group and modification	Times found [count (%)]	Cell parameters (a, b, c) [Å]	Times found [%]
<i>Fm-3m</i> (no. 225) NaCl	10 (0.61)	(9, 6, 3)	100
		(8.5, 6.4, 3.2)	15.84
<i>F-43m</i> (no. 216) Sphalerite	423 (25.62)	(9.6, 7.5, 3.2)	60.75
		(10.1, 5.6, 3.2)	4.96
		(11.5, 6.4, 3.2)	13.24
		(12.4, 5.6, 3.2)	4.49
		(13.6, 6.4, 3.2)	0.7
<i>P6₃mc</i> (no. 186) Wurtzite	161 (9.75)	(8.3, 6.1, 3.2)	39.75
		(9.7, 6.1, 3.2)	47.82
		(11.7, 6.1, 3.2)	12.42
<i>R3m</i> (no. 160) New polytype	644 (39.01)	(8.6, 5.6, 3.2)	26.71
		(9.2, 5.6, 3.2)	51.7
		(10.3, 6.6, 3.2)	12.73
		(11.2, 5.6, 3.2)	5.59
		(12.2, 6.4, 3.2)	3.26
<i>Cm</i> (no. 8) Dist. β -BeO	80 (4.85)	(9.5, 5.9, 3.2)	45
		(10.3, 6.3, 3.1)	1.25
		(11.2, 5.3, 3.3)	21.25
		(12.3, 6.5, 3.2)	22.5
<i>PI</i> (no. 1) “Amorphous”	260 (15.75)	Badly strained cand.	4.5

conversely, this also suggests that a transformation from the polytypes to e.g. the wurtzite modification might happen relatively easily.

When analysing the results for $Z = 6$ in more detail, we observe that many of the structures are found with several different unit cells (see Tables 1 and 2 for an example). In particular, at higher lids, wurtzite, sphalerite and their polytype variants show very diverse sets of cell parameters. Among these, the $6H$ - and the $9R$ -type appear to be particularly easily accessible from many directions on the energy landscape, at least at these energies. From a fundamental point of view, this illustrates an important difference between the energy landscape of molecules and crystals: due to the translational symmetry, the landscape becomes topologically non-trivial, because the various minima representing the

same structure cannot be transformed into each other in a continuous fashion, in contrast to the landscape of a molecule, where the different rotational orientations and locations of the molecule inside the simulation cell are smoothly connected.

Finally, a typical observation for all starting minima and numbers of formula units is that with higher energy lids, most of the time we reach “amorphous” (PI) structures, independent of the starting point, indicating that the number of minima associated with distorted structures rapidly increases with energy.

3.3 Prescribed path investigations of transition routes

In the third part of our study, the focus is on the influence of the temperature on the transformations along the paths connecting the wurtzite-, the sphalerite-, and the rock salt-type modifications of ZnO. Figure 1b gives a

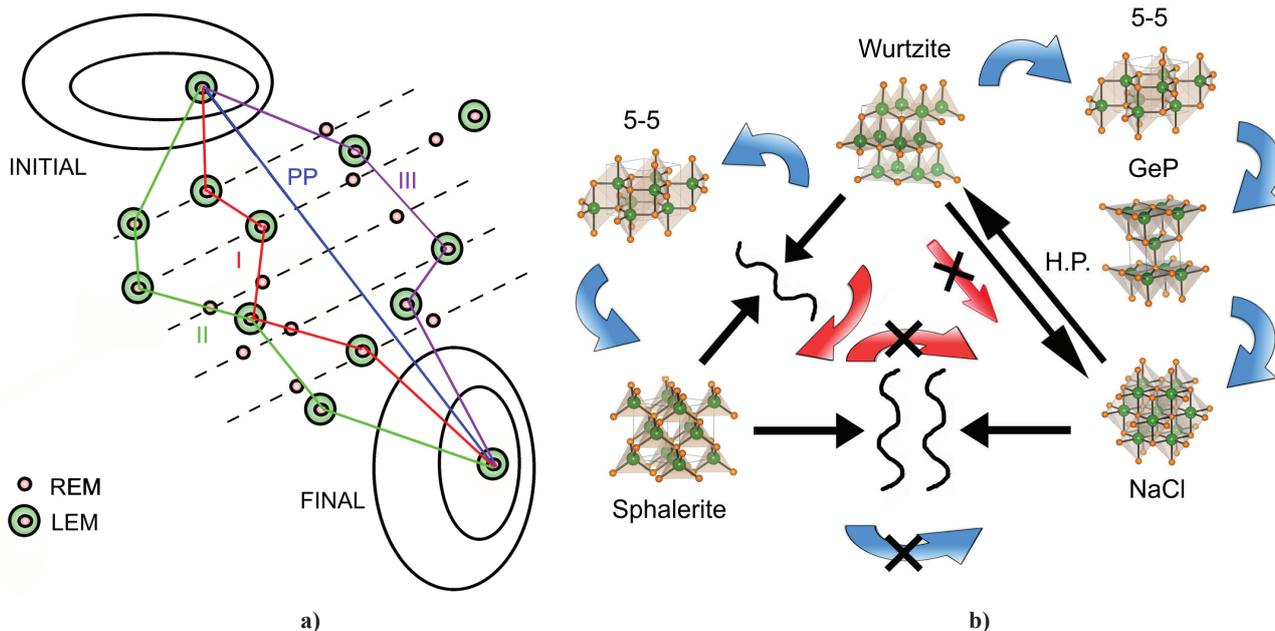


Figure 1. (a) A simplified model of the prescribed path algorithm: two separate minima, representing initial and final atom configuration, are connected in a high-dimensional space via a prescribed path, where they can relax to different transition routes. Along the transition route, one might encounter different restricted energy minima (REM), which would finally converge to local energy minima (LEM). (b) Overview of prescribed path investigations for 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. Reprinted with permission from [22]. Copyright 2013 American Chemical Society.

summary of the results of our prescribed path calculations.

Along the prescribed path between the wurtzite and the rocksalt (*B1*) structure, essentially no barriers are observed if high pressure is used ($p > 10$ GPa). With calculations performed at low temperatures ($T < 250$ K), small barriers are observed, which can possibly be bypassed via two intermediate structures of the “5-5” and the GeP type [36]. With a further increase of temperature, generalized barriers become very high and a synthesis/transformation becomes highly unlikely. Similarly, if the wurtzite (*B4*) and the sphalerite (*B3*) structure are connected, small barriers are observed at low temperatures with a possible transition via the “5-5” structure. However, between the sphalerite and the rock salt modification, we observe extremely high barriers, regardless of any temperature employed; so we conclude that a direct transformation in bulk from the sphalerite to the NaCl modification is rather unlikely [22].

The results of our calculations are in good agreement with the experimental data available, and we suggest several possible transition states such as the 5-5 and the GeP type along the *B4–B1* transition path in agreement with previous calculations. This approach of analyzing transition route bundles among (predicted) modifications can suggest possible pathways, along which eventually controlled synthesis of (meta)stable ZnO modifications and transformation of metastable nanocrystalline zinc oxide should be feasible.

IV. Conclusions

In order to gain new insights in the ZnO system, we have performed theoretical studies of the energy landscape of ZnO, using simulated annealing, the threshold algorithm and the prescribed path method. Besides the already known structure types, we predict new modifications for ZnO, in particular polytypes of the wurtzite structure, which should be accessible to the experiment, but might easily transform to the wurtzite or sphalerite structure at elevated temperatures. Furthermore, we analyzed the transition routes connecting the wurtzite, sphalerite and rocksalt modifications, suggesting how certain metastable polymorphs such as the 5-5-type might be accessible as intermediates along these transition routes.

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