



## Structure prediction and energy landscape exploration in the zinc oxide system

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### Abstract

*The rational planning of syntheses, i.e. the search for new crystalline compounds followed by their synthesis is a central topic of solid state chemistry. In order to gain new insights in the ZnO system, we have performed global explorations of the energy landscape using simulated annealing with an empirical potential, both at standard and elevated pressure (up to 100 GPa). Besides the well-known structure types (wurtzite, sphalerite and rock-salt), many new interesting modifications were found in different regions of the energy landscape, e.g. the “5-5” type, the NiAs type, and the  $\beta$ -BeO type. Furthermore, we observed many distorted variations of these main types, in particular new structures built-up from various combinations of structure elements of these types, exhibiting a variety of stacking orders.*

**Keywords:** structure prediction, zinc oxide

### I. Introduction

In materials science, ZnO is known as a II-VI semiconductor with a band gap of 3.3 eV at room temperature, showing a number of desirable properties: good transparency, high electron mobility, wide bandgap, strong room-temperature luminescence, etc. Due to these properties, ZnO is already used in emerging applications for transparent electrodes in liquid crystal displays, as well as in energy-saving or heat-protecting windows. Furthermore, ZnO powder is widely used as an additive to numerous materials and products including plastics, ceramics, glass, cement, rubber, oil lubricants, paints, adhesives, sealants, pigments, foods, batteries, electronics, etc. [1,2].

The physical properties of porous semiconducting zinc oxide depend on the amount and nature of chemisorbed oxygen [3]. The excitonic photoluminescence of ZnO is very sensitive to the quality of the crystal and to the presence of defects. However, there is as yet no clear understanding of defect-related luminescence phenomena in ZnO [4]. Similarly, there are strong effects of impurities and dopants on the physical properties of ZnO [1,5,6].

The special topics of this study are the ideal crystalline modifications of ZnO that might find application in e.g. ceramics technology. There are numerous methods of fabricating ZnO-based materials; e.g. for industrial use, primary zinc oxide is produced by three main processes: indirect (French) process, direct (American) process, and wet chemical process [1,7]. A significant number of production methods exist for producing zinc oxide for scientific studies and electronic applications. These methods can be distinguished by the form (bulk, thin film, nanowire), temperature (“low” ( $T \sim 273$  K) or “high” ( $T \sim 1273$  K)), process type (vapour deposition or growth from solution), etc. Large single crystals ( $\sim \text{cm}^3$ ) are usually grown by gas transport (vapour-phase deposition), melt growth [8], or hydrothermal synthesis [9,10], where the latter is most frequently used [8]. Thin films can be produced by chemical vapour deposition, metalorganic vapour phase epitaxy, electrodeposition, pulsed laser deposition, sputtering, sol-gel synthesis, atomic layer deposition, spray pyrolysis, etc. [11–15].

Ceramics sintered from mixtures of various oxides which include ZnO, have applications as varistors [16], and microwave devices [17]. Many properties of zinc oxide are dependent upon the wurtzite hexagonal, close packed arrangement of the Zn and O atoms [1]. Thus,

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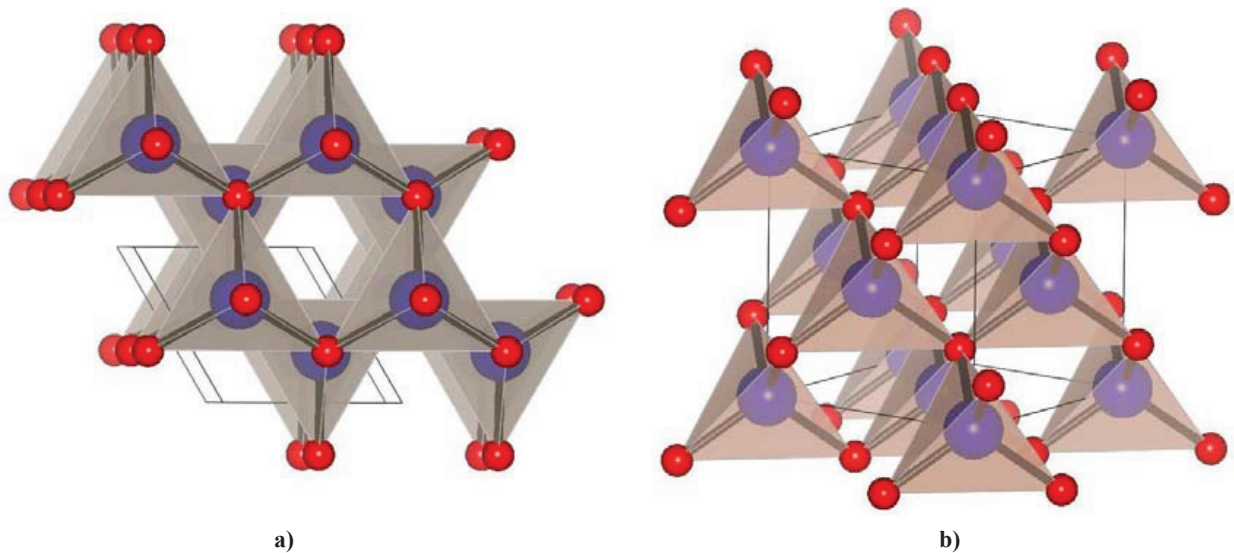


Figure 1. Visualization of the experimentally observed structure types (using VESTA [22] in ZnO system):  
a) Wurtzite type and b) Sphalerite type

it would be of great interest to know which possible (metastable) modifications could be present in the ZnO system, since this would also affect the properties and perhaps lead to some new applications.

In nature ZnO appears as mineral zincite with impurities of Fe and Mn, and ideal bulk zinc oxide adopts hexagonal wurtzite type of structure at ambient conditions (see Fig. 1a) [18,19]. There is a transition to the rocksalt modification under pressure and the coexistence of the two phases has been investigated (Fig. 2a) [18,20]. The sphalerite modification (Fig. 1b) can be stabilized by growing ZnO on substrates with cubic lattice structure resulting in ZnO thin films [11–13].

Since there are only three experimentally known modifications of ZnO, finding possible new polymorphs and understanding transitions among them would be very important. Thus, in this study, we explore the ener-

gy landscape of ZnO, determine new modifications, investigate the relations between them, and study the influence of pressure and temperature in the system.

## II. Theoretical methods

Our general approach to the determination of structure candidates has been given in detail elsewhere [23–25]; 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 on the enthalpy landscape of the chemical system of interest. At low temperatures, these regions are basins around local minima of the potential energy, while at elevated temperatures locally ergodic regions can encompass many (often structurally related) local minima [26]. These minima are identified using simulated annealing

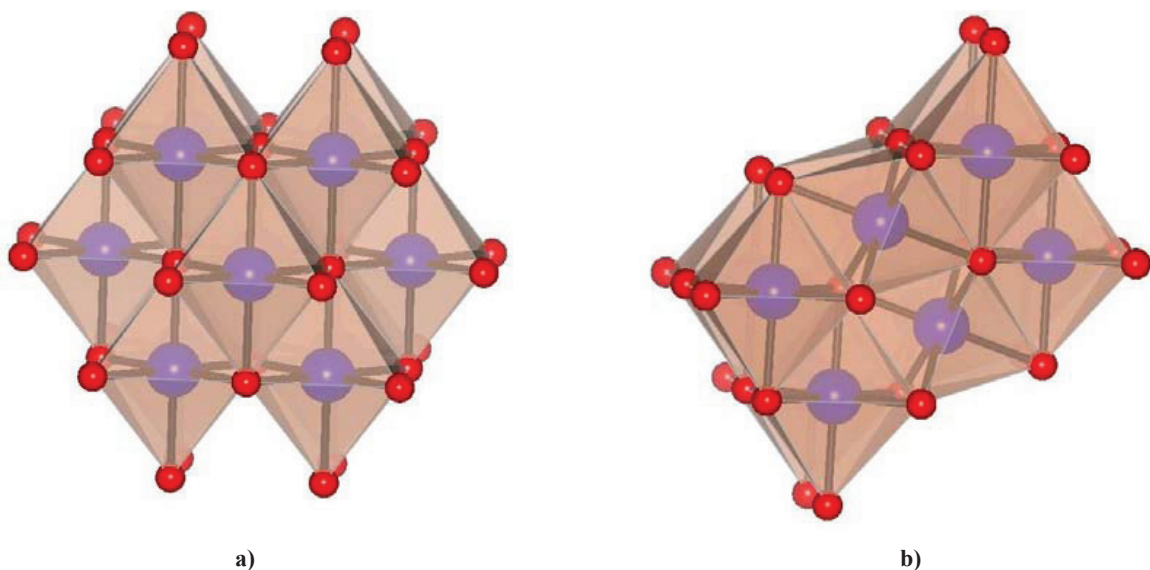


Figure 2. Visualization of the experimentally observed NaCl structure type (a) and calculated NiAs structure type (b) in ZnO system

[27], usually with up to 4 formula units/simulation cell, where both atom positions and cell parameters can be freely varied without any symmetry constraints. Energy barriers are determined using the threshold algorithm [28], where the landscape accessible from a local minimum below a sequence of energy barriers (thresholds) is systematically explored for all important local minima. In particular, we can measure the transition probability among the minima as a function of the threshold value.

In addition to the threshold runs, one can also perform prescribed path studies [29] when analyzing the barriers of the landscape. This algorithm is related to the nudged elastic band method [30], and is employed for finding saddle regions and minimum energy paths between various locally ergodic regions. The method works by optimizing the atom arrangement at a number of intermediate steps along a “reaction path”.

After the global optimizations and after the subsequent local minimizations, the symmetries and the space group of the structures found are determined using the algorithms SFND [31] and RGS [32], respectively, and duplicate structures are removed using the CMPZ-algorithm [33]. All three algorithms are implemented in the program KPLOT [34]. Since there are usually a very large number of structure candidates, both the local optimizations and the symmetry analysis are often automatically performed with a heuristic algorithm [35].

In this study, we have globally explored the zinc oxide system with an empirical potential (Coulomb+Lennard-Jones potential) employing simulated annealing, both at standard and elevated pressure (up to 100 GPa) using up to 6 formula units. The local optimization was performed using Hartree-Fock and various density functionals (LDA and B3LYP). After the global and local optimizations were finished, a full analysis of the energy landscape of the system was performed with the threshold algorithm, for different numbers of formula

units per simulation cell. However, since the particular focus of this study is the prediction of new modifications, we refer the reader to ref. [29] and [36] for the results of the threshold and prescribed path investigations of the barrier structure of ZnO.

### III. Results and discussion

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 [18–20] and previous calculations [21,37–40]. The wurtzite type together with the sphalerite type (see Fig. 1) is the stable modifications at ambient conditions. Both are known in the zinc/iron sulfides with the analogous formula, (Zn, Fe)S. Wurtzite (B4) exhibits space group  $P6_3mc$  and its structure is composed of  $ZnS_4$  tetrahedra that are stacked in a hexagonal sequence AB AB AB ... (HCP-packing). Sphalerite (B3) exhibits space group  $F-43m$ , and its structure can be visualized as an ABC ABC ABC ... cubic sequence of  $ZnS_4$  tetrahedra (FCC-packing) [41].

Our searches result in many interesting candidates which exhibit different stacking order similar to the ZnS system, while varying the numbers of formula units per simulation cell. There have been many examples in various systems where different stacking order, based on mixing the HCP and the FCC stacking, produce different polytypes [42,43]. We could relate our polytype structures to the ZnS system, due to some resemblance to the matraite structure in trigonal ( $R3m$ ) symmetry [44], or to the structures in the SiC system [45], where different polytypes have also been observed [46]. The appearance of such a stacking polytype in the global search could be an indication of many other similar structures in the ZnO system, and this is discussed in greater detail in ref. [36].

At high pressures (above 10 GPa) we observe the rock-salt modification (see Fig. 2a) in the ZnO system

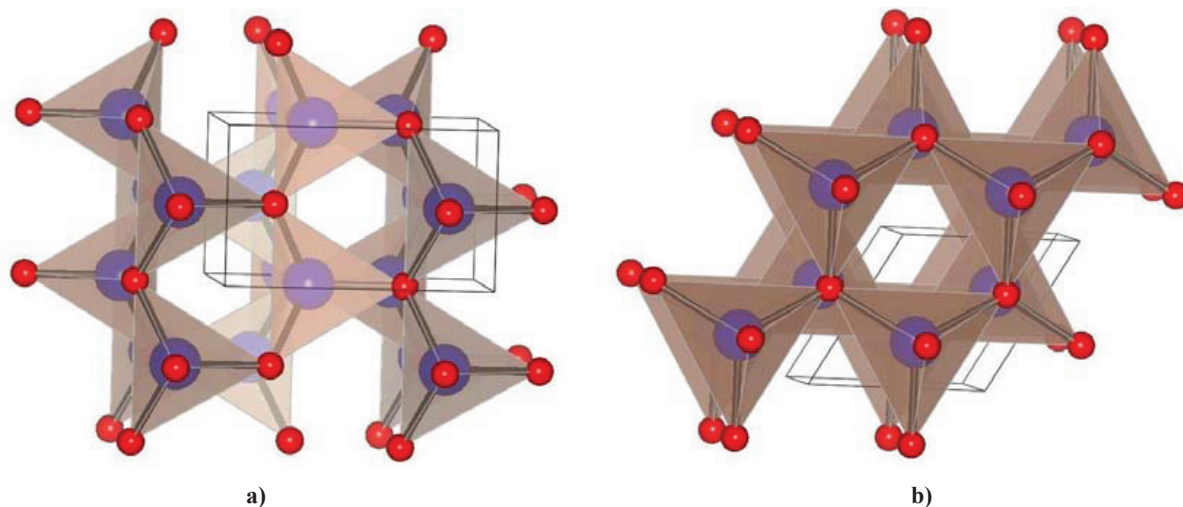


Figure 3. Visualization of the calculated (predicted) structure types in ZnO system: a)  $\beta$ -BeO-type and b) “5-5” type

as the most stable form, as well as several distorted variants of the NaCl (B1) type. In addition, we have found several new hypothetical modifications in the ZnO system. One of them is the NiAs (B8<sub>1</sub>) structure type that appeared as a meta-stable modification at standard conditions (see Fig. 2b). According to our calculations, this modification is meta-stable even with an increase of temperature and/or pressure; thus it would be very hard to synthesize, although its coordination number suggests that it might be a metastable phase at high pressures in the ZnO system.

At slightly negative pressures, we observe the  $\beta$ -BeO-type (see Fig. 3a) in the ZnO system. In the beryllium oxide (BeO) system, two known modifications occur:  $\alpha$ -BeO, which adopts the hexagonal wurtzite structure form [47] and  $\beta$ -BeO, a high temperature form which shows tetragonal symmetry [48]. The  $\beta$ -BeO-type exhibits space group  $P4_1/mnm$  and is hexagonal close packed (HCP). Be-atoms are located in tetrahedral interstices resulting in pairs of edge connected tetrahedral. The  $\beta$ -BeO-type of structure is closely related to the wurtzite type, with 4-fold coordination of the Be-atoms by O-atoms [48]. Analogously, one can expect a similar relation in the ZnO system, which would mean that with an increase of temperature one might be able to synthesize the  $\beta$ -BeO-type modification as a metastable phase in the ZnO system.

One further interesting structure candidate, which we found as a metastable phase along the route of the wurtzite(sphalerite) - NaCl transition is the so-called “5-5”-type (see Fig. 3b). This structure type has been found on the energy landscapes of many AB compounds [49–51], and furthermore its existence in the ZnO system has been proposed in some recent experiments [13,14]. We can describe this structure type as a fivefold coordination of Zn by O in a hexagonal lattice ( $P6_3/mmc$ ) with ABAB stacking. The O- and Zn- atoms form trigonal bipyramids around Zn and O, respectively. The 5-5 structure can be derived from the BN-structure by requiring that the bond length in the c-direction must be (nearly) identical to the one within the planar hexagons. The ZnO system appears to be a very good candidate to synthesize this new type of modification as a bulk phase.

#### IV. Conclusions

In order to gain new insights in the ZnO system, we have performed global explorations of the energy landscape using simulated annealing with an empirical potential, both at standard and elevated pressure (up to 100 GPa), in order to identify possible new ZnO modifications. We have found the observed structure types (wurtzite, sphalerite and rock-salt), in agreement with experiment. In addition, many new interesting modifications were calculated in different regions of the energy landscape. We have found the nickel-arsenide

(NiAs) type (B8<sub>1</sub>) as a meta-stable modification at standard conditions, and at slightly negative pressures we observe the  $\beta$ -BeO-type. With increase of pressure we also find the so called “5-5”-type, which it should be possible to synthesize as a metastable phase. Finally, we observe stacking variants of the wurtzite and the sphalerite modifications, which also should be accessible to the experiment.

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#### References

1. H.E. Brown, *Zinc oxide, Properties and Applications*, Int. Lead Zinc Org., New York, 1976.
2. A. Hernandez-Battez, R. González, J.L. Viesca, J.E. Fernández, J.M. Díaz Fernández, A. Machado, R. Chou, J. Riba, “CuO, ZrO<sub>2</sub> and ZnO nanoparticles as antiwear additive in oil lubricants”, *Wear*, **265** (2008) 422–428.
3. H. Sawada, R. Wang, A.W. Sleight, “An electron density residual study of zinc oxide”, *J. Solid State Chem.*, **122** (1996) 148–150.
4. T.-B. Hur, G.S. Jeon, Y.-H. Hwang, H.-K. Kim, “Photoluminescence of polycrystalline ZnO under different annealing conditions”, *J. Appl. Phys.*, **94** (2003) 5787–5791.
5. Z. Zhou, K. Kato, T. Komaki, M. Yoshino, H. Yukawa, M. Morinaga, K. Morita, “Effects of dopants and hydrogen on the electrical conductivity of ZnO”, *J. Eur. Ceram. Soc.*, **24** (2004) 139–146.
6. I.V. Markevich, V.I. Kushnirenkoa, “Photoluminescence of ZnO ceramics sintered with a flux”, *Solid State Commun.*, **149** (2009) 866–868.
7. F. Porter, *Zinc Handbook: Properties, Processing, and Use in Design*, CRC Press, 1991.
8. K. Takahashi, A. Yoshikawa, A. Sandhu, *Wide band-gap semiconductors: fundamental properties and modern photonic and electronic devices*, Springer, 2007.
9. S. Baruah, J. Dutta, “Hydrothermal growth of ZnO nanostructures”, *Sci. Technol. Adv. Mater.*, **10** [013001] (2009) 1–18.
10. D. Schulz, S. Ganschow, D. Klimm, K. Struve, “Inductively heated Bridgman method for the growth of zinc oxide single crystals”, *J. Cryst. Growth*, **310** (2008) 1832–1835.
11. W. Bragg, “The structure of thin films of certain metallic oxides”, *Trans. Farad. Soc.*, **28** (1932) 522–522.
12. O.E. Radczewski, R.F. Schicht, “Bestimmung der Gitterkonstante von kubischem Zinkmonoxyd“, *Naturwissenschaften*, **56** (1969) 514–514.
13. A.B.M.A. Ashrafi, A. Ueta, A. Avramescu, H. Kumano, I. Suemune, Y. Ok, T. Seong, “Growth and characterization of hypothetical zinc-blende ZnO films on GaAs (001) substrates with ZnS buffer layers”, *Appl. Phys. Lett.*, **76** (2000) 550–552.

14. C. Tusche, H.L. Meyerheim, J. Kirschner, “Observation of depolarized ZnO (0001) monolayers: Formation of unreconstructed planar sheets”, *Phys. Rev. Lett.*, **99** (2007) 026102–026106.
15. C.L. Pueyo, S. Siroky, S. Landsmann, M.W.E. van den Berg, M.R. Wagner, J.S. Reparaz, A. Hoffmann, S. Polarz, “Molecular precursor route to a metastable form of zinc oxide”, *Chem. Mater.*, **22** (2010) 4263–4270.
16. J.F. Cordaro, Y. Shim, J.E. May, “Defect clusters in zinc oxide”, *J. Appl. Phys.*, **60** (1986) 4186–4190.
17. E. Guan, W. Chen, L. Luo, “Low firing and microwave dielectric properties of BaTi<sub>4</sub>O<sub>9</sub> with B<sub>2</sub>O<sub>3</sub>-ZnO-La<sub>2</sub>O<sub>3</sub> glass addition”, *Ceram. Int.*, **33** (2007) 1145–1148.
18. Collaboration: Authors and editors of the volumes III/17B-22A-41B: *Zinc oxide (ZnO) Debye temperature, heat capacity, density, melting point, vapor pressure, hardness*. Ed. by O. Madelung, U. Rössler, M. Schulz, Springer Materials - The Landolt-Börnstein Database, DOI: 10.1007/10681719\_312
19. (<http://www.springermaterials.com>).
20. H. Sowa, H. Ahsbahs, “High-pressure X-ray investigation of zincite ZnO single crystals using diamond anvils with an improved shape”, *J. Appl. Cryst.*, **39** (2006) 169–175.
21. Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, H. Morkoç, “A comprehensive review of ZnO materials and devices”, *J. Appl. Phys.*, **98** [041301] (2005) 1–103.
22. H. Karzel, W. Potzel, M. Köfferlein, W. Schiessl, M. Steiner, U. Hiler, G.M. Kalvius, D.W. Mitchell, T.P. Das, P. Blaha, K. Schwarz, M.P. Pasternak, “Lattice dynamics and hyperfine interactions in ZnO and ZnSe at high external pressures”, *Phys. Rev. B*, **53** (1996) 11425–11438.
23. K. Momma, F. Izumi, “VESTA: a three-dimensional visualization system for electronic and structural analysis”, *J. Appl. Crystallogr.*, **41** (2008) 653–658.
24. J.C. Schön, M. Jansen, “First step towards planning of syntheses in solid-state chemistry: Determination of promising structure candidates by global optimization”, *Angew. Chem., Int. Ed Eng.*, **35** (1996) 1286–1304.
25. J.C. Schön, M. Jansen, “Prediction, determination and validation of phase diagrams via the global study of energy landscapes”, *Int. J. Mat. Res.*, **2** (2009) 135–152.
26. J.C. Schön, K. Doll, M. Jansen, “Predicting solid compounds via global exploration of the energy landscape of solids on the ab initio level without recourse to experimental information”, *Phys. Status Solidi b*, **247** (2010) 23–39.
27. J.C. Schön, M. Jansen, “From configuration space to thermodynamic space: Predicting new inorganic solids via global exploration of their energy landscapes”, *Mater. Res. Soc. Symp. Proc.*, **848** [FF7.1] (2005) 1–12.
28. S. Kirkpatrick, C.D. Gelatt, M.P. Vecchi, “Optimization by simulated annealing”, *Science*, **220** (1983) 671–680.
29. J.C. Schön, H. Putz, M. Jansen, “Studying the energy hypersurface of continuous systems - the threshold algorithm”, *J. Phys. Cond. Mat.*, **8** (1996) 143–156.
30. D. Zagorac, J.C. Schön, K. Doll, M. Jansen, “Structure prediction for PbS and ZnO at different pressures and visualization of the Energy Landscapes”, *Acta Phys. Pol. A*, (2011) in press.
31. D. Sheppard, R. Terrell, G. Henkelman, “Optimization methods for finding minimum energy paths”, *J. Chem. Phys.*, **128** [134106] (2008) 1–10.
32. R. Hundt, J.C. Schön, A. Hannemann, M. Jansen, “Determination of symmetries and idealized cell parameters for simulated structures”, *J. Appl. Crystallogr.*, **32** (1999) 413–416.
33. A. Hannemann, R. Hundt, J.C. Schön, M. Jansen, “A new algorithm for space-group determination”, *J. Appl. Crystallogr.*, **31** (1998) 922–928.
34. R. Hundt, J.C. Schön, M. Jansen, “CMPZ - an algorithm for the efficient comparison of periodic structures”, *J. Appl. Crystallogr.*, **39** (2006) 6–16.
35. R. Hundt, *KPLOT-program*, University of Bonn, Germany 1979, Version 9, 2007. ([www.crystalimpact.com/download/kplot.htm](http://www.crystalimpact.com/download/kplot.htm)).
36. J.C. Schön, Z.P. Cancarevic, M. Jansen, “Structure prediction of high-pressure phases for alkali metal sulfides”, *J. Chem. Phys.*, **121** (2004) 2289–2304.
37. D. Zagorac, J.C. Schön, M. Jansen, “Structure Prediction and electronic properties in zinc oxide at different pressures”, (2011) in preparation.
38. B. Amrani, I. Chiboub, S. Hiadsi, T. Benmessabih, N. Hamdadou, “Structural and electronic properties of ZnO under high pressures”, *Solid State Commun.*, **137** (2006) 395–399.
39. H.Y. Wu, X.L. Cheng, C.H. Hu, P. Zhou, “The structure and thermodynamic properties of zinc oxide with wurtzite and rocksalt structure under high pressures”, *Physica B*, **405** (2010) 606–612.
40. X.W. Sun, Z.J. Liu, Q.F. Chen, H.W. Lu, T. Song, C.W. Wang, “Heat capacity of ZnO with cubic structure at high temperatures”, *Solid State Commun.*, **140** (2006) 219–224.
41. S. Cui, W. Feng, H. Hu, Z. Feng, Y. Wang, “Structural and electronic properties of ZnO under high pressure”, *J. Alloy Compd.*, **476** (2009) 306–310.
42. U. Muller, *Inorganic Structural Chemistry*, Philipps-Universität Marburg, Germany, 2007.
43. S. Mardix, “Polytypism: A controlled thermodynamic phenomenon”, *Phys. Rev. B*, **33** (1986) 8677–8684.
44. G.Y. Chao, R. A. Gault, “The occurrence of two rare polytypes of wurtzite, 4H and 8H, at Mont Saint-Hilaire, Quebec”, *Canad. Mineralog.*, **36** (1998) 775–778.
45. S. Koch, “The associated occurrences of the three ZnS modifications in the Gyongyosoroszi”, *Acta Mineralogy. Petrog. Univ. Szegediensis*, **11** (1958) 11–22.
46. H. Schulz, K.H. Thiemann, “Structure parameters and polarity of the wurtzite type compounds SiC-2H and ZnO”, *Solid State Commun.*, **32** (1979) 783–785.

47. J-S. Lee, S-C. Yu, S-F. Tung, W-Ji Bai, J-S. Yang, Q-S Fang, Z. Zhang, “The crystal structure of natural 33R moissanite from Tibet”, *Zeit. Kristallog.*, **221** (2006) 213–217.
48. N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements* 2<sup>nd</sup> ed., Oxford: Butterworth-Heinemann, 1997.
49. D.K. Smith, C.F. Cline, S.B. Austerman, “The crystal structure of  $\beta$ -beryllia”, *Acta Cryst.*, **18** (1965) 393–397.
50. J.C. Schön, M. Jansen, “Determination of candidate structures for simple ionic compounds through cell optimisation”, *Comp. Mater. Sci.*, **4** (1995) 43–58.
51. J.C. Schön, “Enthalpy Landscapes of the Earth Alkaline Metal Oxides”, *Z. Anorg. Allg. Chem.*, **630**, (2004) 2354–2366.
52. Z. Cancarevic, J. C. Schön, M. Jansen, “Stability of alkali metal halide polymorphs as a function of pressure”, *Chem. Asian J.*, **3** (2008) 561–572.