ENGINEERING OF ADVANCED MATERIALS

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

Overview of modern computational methods in the research of advanced materials from bulk crystals to nanoscale structures

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Introduction:

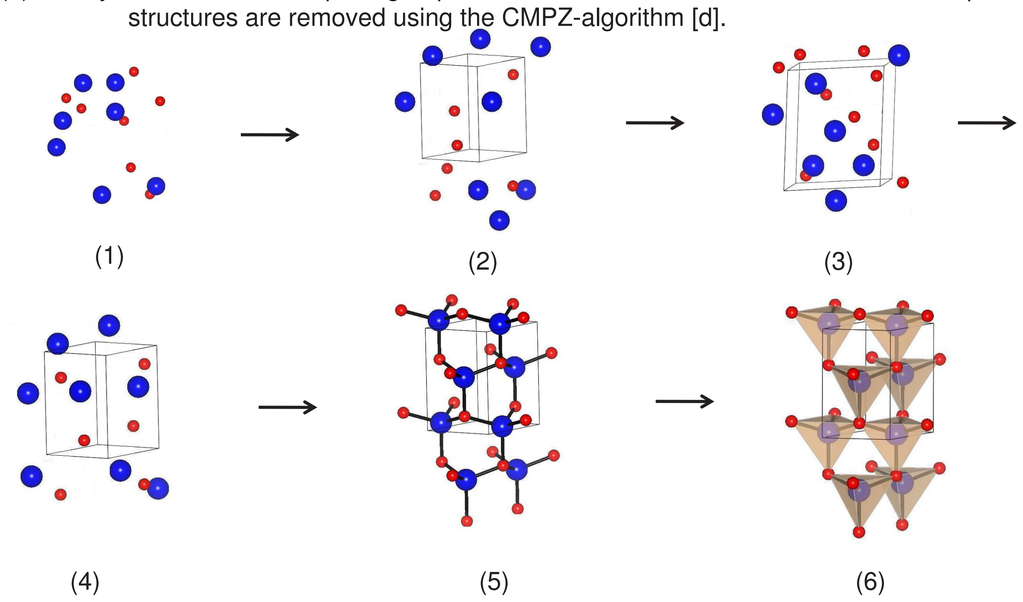
The search for new crystalline compounds is one of the major issues in inorganic chemistry and material sciences. Scientists have successfully synthesized many new materials and studied their properties, but the pure experimental approach is no longer the only route to discover new compounds. The theoretical prediction of new compounds and new (meta)-stable modifications of already existing solids followed by their synthesis is fast becoming an alternative.[1]

Here, we present some of the modern computational methods used in the reserch of advanced materials: crystal structure prediction, *ab initio* minimization data mining approach and prescribed path method.

Crystal structure prediction:

First, we show brief presentation of the crystal structure prediction method [1,6]:

(1) Global optimization (GO) – periodic boundary conditions; define: initial state (s) - choice of atom (type, no., charge), moveclasses: atomic positions, unit cell, charges, or/and numbers of atoms, energy (cost) function and SA parameters [b]
(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 (gives ideal bulk structure at 0K) [c]
(6) The symmetries and the space group of the structures found are determined and duplicate structures are removed using the CMPZ-algorithm [d].

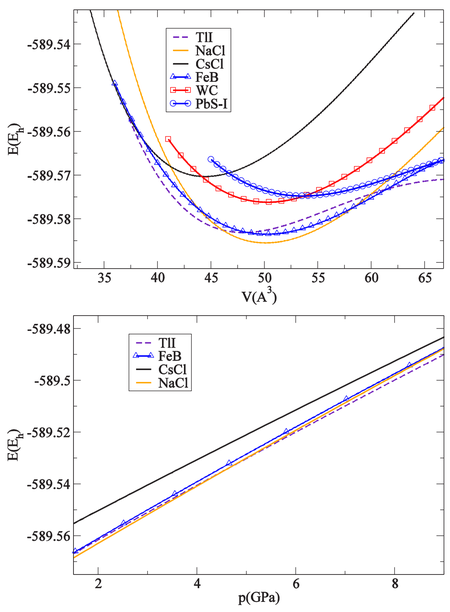


In the second part, we show the results of crystal structure prediction for PbS and ZnO.

PbS results [7]

-GO on *ab initio* level (Hartree-Fock (HF) approximation)
-LO on *ab initio* level (HF, B3LYP and LDA)

E(V) and *H(p)* curves of PbS calculated using LDA functional



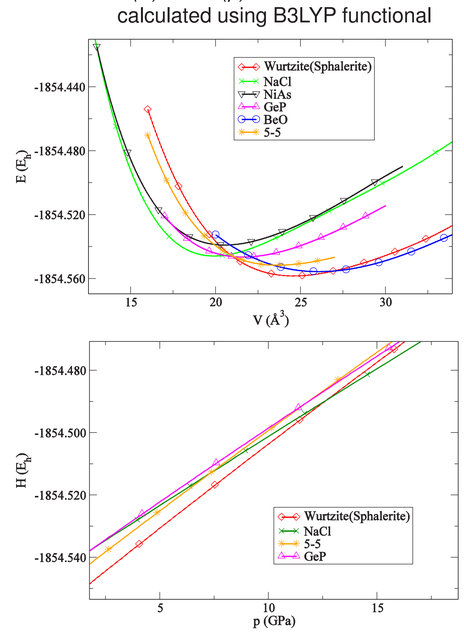
ZnO results [8]

- GO using two-body empirical potential (Coul+LJ):

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

- LO on *ab initio* level (HF, B3LYP and LDA)

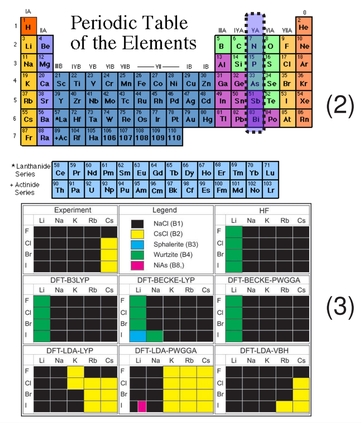
E(V) and *H(p)* curves of ZnO calculated using B3LYP functional



Ab initio minimization data mining approach:

Motivation:
A feasibility study of synthesizing the "5-5" structure (1) in different binary compounds combining data mining and quantum mechanical methods [2].

(1)



(2)

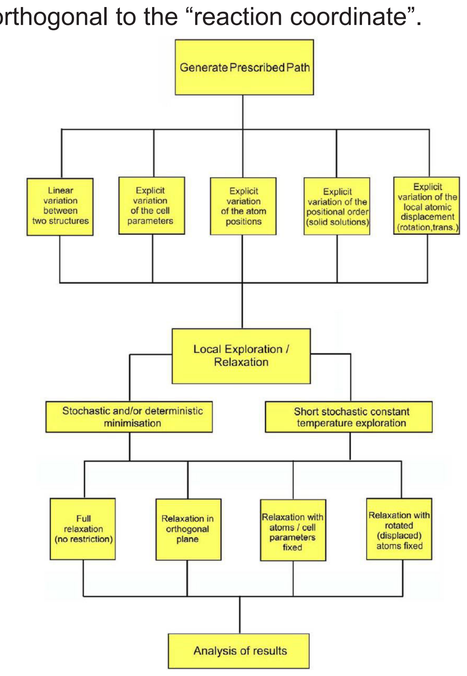
(3)

Method:
-Data mining [3,a] based explorations in group V, IV - VI, and III - VII binary compounds (2)
-Local optimizations on *ab initio* level [4,c] for the 5-5 structure and typical AB-structure types (3).

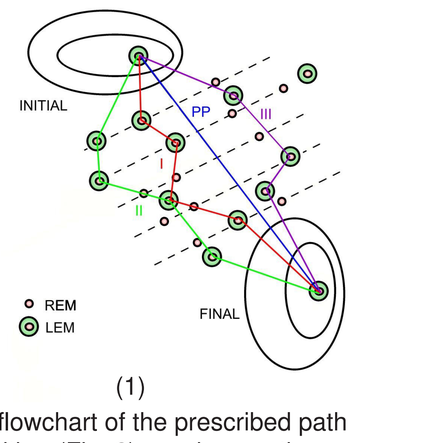
Results:
-TlF, SnO, SnS, SnSe, GeS, GeSe, PbO, PbS, ZnO and ZnS were chosen as candidate systems
-DFT-LDA was chosen for local optimization
-after the optimization, GeSe and ZnO are the most suitable for synthesizing the 5-5 structure type [5].

Prescribed path:

The prescribed path (PP) method [9] 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".



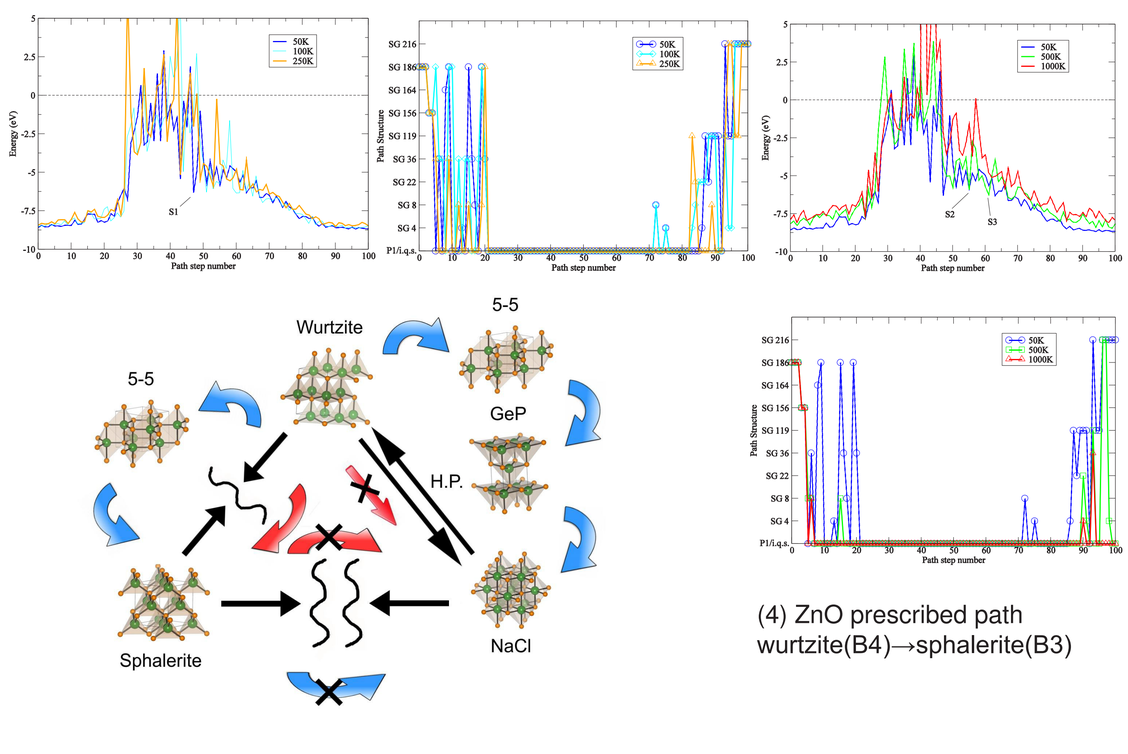
(2)



(1)

From the flowchart of the prescribed path (PP) algorithm (Fig. 2) we observe three main parts of the PP method [9]:
-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, [b]
-Local Exploration and relaxation: define energy (cost) function and MC parameters [b,c]
-Analysis of results: Thermal Stability Analysis (TSA), Crystallographic analysis [d]

ZnO results [9]



(3) Overview of PP investigations in ZnO

(4) ZnO prescribed path wurtzite(B4)→sphalerite(B3)

References:

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Software and databases:

[a] Crystal structure databases: Inorganic crystal structure database (ICSD), Pearson's Crystal Data (PCD), American Mineralogist Crystal Structure Database (AMCSD), Crystallography Open Database (COD).
[b] GO software: G-42, SPuDS.
[c] LO software: CRYSTAL09 (new release CRYSTAL14), VASP, GULP.
[d] Crystallographic analysis and visualization software: KPLOT, VESTA, XCRYSDEN, CRGRA, LOAD, FILTER, Bilbao Crystallographic Server (KVEC,SUBGROUPGRAPH).

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