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Phonon dispersion relations and phase stability of ZnO polymorphs

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Abstract

The phonon dispersion relations and the phonon density of states for ZnO polymorphs: wurtzite-, zinc-blende, rocksalt-structures, and yet experimentally undiscovered CsCl-structure were computed using the first principles calculations. The phonon modes for wurtzite structure were calculated with GGA and LDA approximation and compared with experimental data. All the phases were exposed to pressures ranging from 0 to 16 GPa. The pressure-temperature phase diagram of ZnO was constructed and compared to experimental data, where available.

Introduction

ZnO has attracted considerable interest in recent years [1] due to its technological importance in varius fields:

- spinotronics
- transparent conducting oxide (TCO)
- a good material for blue/UV lasers and optoelectronics
- blue LEDs and transparent TFTs
- electronic devices in corresponding environment as a radiation hard material

Experimentally ZnO is reported to occur in three structures: wurtzite (B4), zinc-blende (B3) and rock-salt (B1)[2]. The most stable at atmospheric pressure is the hexagonal wurtzite structure. In this structure ZnO is a II-VI semiconductor with a direct band gap of 3.4 eV and a relatively large exciton binding energy of about 60 meV [3].

Recently it was demonstrated theoretically [4-6] that the eightfoldcoordinated CsCl (B2) structure of ZnO may also exist, in analogy to the alkali halides and alkaline-earth oxides.

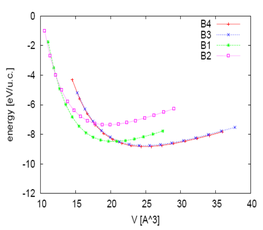

Fig. 1. Energy vs volume per single formula unit for ZnO in the B4, B3, B1 and B2 structures.

The B4 structure is definitely the most stable one, and the B3 is very close to it in energy. These results agree well with experimental results.

The B2 (CsCl) structure is the least stable one. However, its total energy is still negative. That's mean it may also exist.

Computational details

The calculations of ZnO were performed using two computer codes implemented in **MedeA** environment [7]. For structure optimization under specific pressure the **VASP** v. 4.6 package [8] was used. The calculations of the phonon properties were performed using **PHONON** software [9], which uses the Hellmann-Feymann forces calculated from the optimized supercell.

In the VASP calculations following parameters were chosen:

♦ *k*-spacing	0.4 1/ Å
♦ PW cutoff	500 eV
♦ Exchange correlation functional	GGA -PBE
♦ SCF conv.	1.00E-007 eV
♦ Smearing method	Gaussian

For phonon calculations the interaction range was set as 9.5 Å. The asymmetric atoms were displaced by +/-0.01 Å.

Results: Phonons

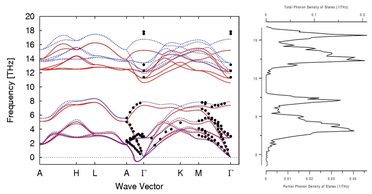

Fig. 2. Phonon dispersion relation and PDOS for ZnO (B4)

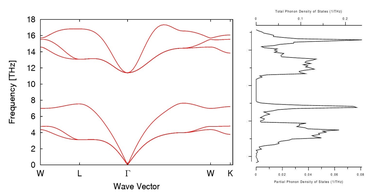

Fig. 3. Phonon dispersion relation and PDOS for ZnO (B3)

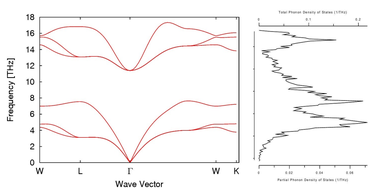

Fig. 4. Phonon dispersion relation and PDOS for ZnO (B1)

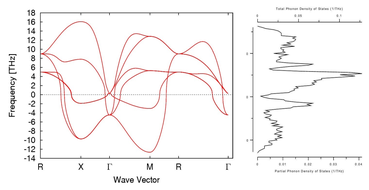

Fig. 5. Phonon dispersion relation and PDOS for ZnO (B2)

Phonon dispersion curves for ZnO in wurtzite structure (**Fig. 2**) were calculated with GGA method (red lines) and LDA method (blue dashed lines), and are compared with experimental data (black points) [13]. GGA approximation is known to overestimate lattice parameters, whereas LDA approach typically underestimate them. Therefore, phonon frequencies calculated with GGA approach should be usually lower then experimental data and LDA approximation should overestimate them. Significant part of the calculated phonon dispersion structure agrees well with this prediction.

ZnO in the wurtzite (B4) structure has four atoms in the primitive unit cell therefore there are 12 phonon branches. The six optical modes are separated from the lower branches by a phonon gap (it can be easily seen on the PDOS plot).

ZnO in the zinc-blende (B3), rocksalt (B1) and CsCl (B2) structure has only two atoms in the primitive unit cell, and this gives 6 phonon branches. There is no phonon gap between optic modes and acoustic modes for ZnO in B1 and B2 phases.

In Fig. 5 there are noticed large negative values of the phonon frequencies, which are called *soft modes*. It means that the ZnO in the CsCl structure is ***unstable*** in the external pressure.

Structural properties – pressure dependence

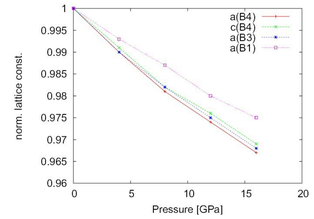

Fig. 6. Pressure dependence of the normalized lattice parameters

The figure 6 shows pressure dependence of the normalized lattice parameters. In the rocksalt structure ZnO has the lowest empty space volume in the unit cell so the pressure has the least influence on the lattice parameters.

P-T phase diagram

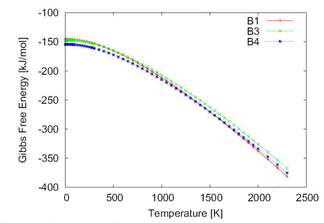

Fig. 7. Calculated Gibbs free energy vs temperature for ZnO in B1, B3 and B4 structure in pressure P = 8GPa. For temperature $T_c \approx$ 1500 K Gibbs free energy for B1 phase become lower then for B4 phase. This is the phase transition point

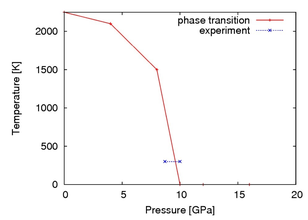

Fig. 8. Calculated *P-T* phase diagram for ZnO compared with experimental data of phase transition pressure (only minimum[10] and maximum[11] values)

The state with the lower Gibbs free energy at a given temperature T and pressure P represents the stable phase. Therefore, the crossing point of two curves representing the different structures denotes a first-order phase transition with coexistence temperature T_c and pressure P_c. This allowed us to construct the whole *P-T* phase diagram (Fig. 8). The calculated phase transition agrees well with the experimental data. The most stable at low pressures is the wurtzite structure, whereas at higher pressures and temperatures the rocksalt structure becomes the most stable one.

Conclusions and acknowledgments

The phonon dispersion relations and the phonon density of states for ZnO polymorphs: wurtzite, zinc-blende and rocksalt structures, and yet experimentally undiscovered CsCl-structure have been presented.

Detailed insight into the phase transition diagram of ZnO is crucial for the successful application of this material in many branches of the contemporary materials science.

The another interesting result of this research is that ZnO in B2 structure is unstable in the applied external pressure.

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