

Temperature-Dependent Phase Transitions of ZrO₂

The temperature-induced phase transition from monoclinic to tetragonal ZrO₂ is predicted from first principles calculations using a quasi-harmonic approach for the vibrational enthalpy and entropy. The computed transition temperature is within 15% of the experimental value. Relative trends due to vacancies, alloying elements, and mechanical stress can be expected to have a higher accuracy. The present results show the importance of thermal expansion, which is here also obtained from first principles.

Keywords: zirconia, phase transition, computations, first-principles, phonon, vibrations, entropy, thermal expansion

Experimental Facts

At low temperatures, the most stable phase of ZrO₂ is a monoclinic form, which occurs naturally as the mineral Baddeleyite. At a temperature of 1478 K and ambient pressure, a

tetragonal structure becomes thermodynamically stable. At 2650 K the tetragonal structure changes into a cubic calcium fluoride structure. The mineral name zirconia is used for both the tetragonal and the cubic structures. ZrO₂ melts at 2983 K (*cf.* Fig. 1).

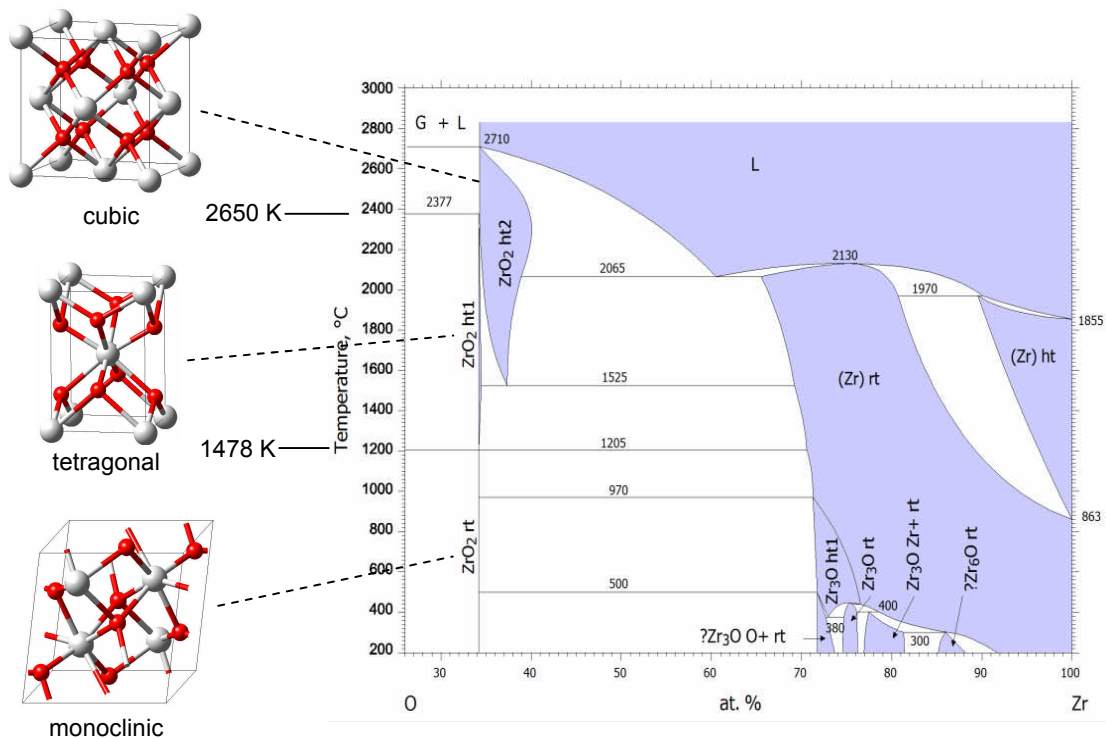


Figure 1. O-Zr phase diagram (after Ref. 1) and structures of ZrO₂ in the room temperature (rt) monoclinic phase, the high temperature (ht1) tetragonal phase and the high temperature (ht2) cubic phase. The phase transitions are observed at 1205 °C (1478 K) and 2377 °C (2650 K).

Computed Free Energy Difference between tetragonal and monoclinic ZrO_2

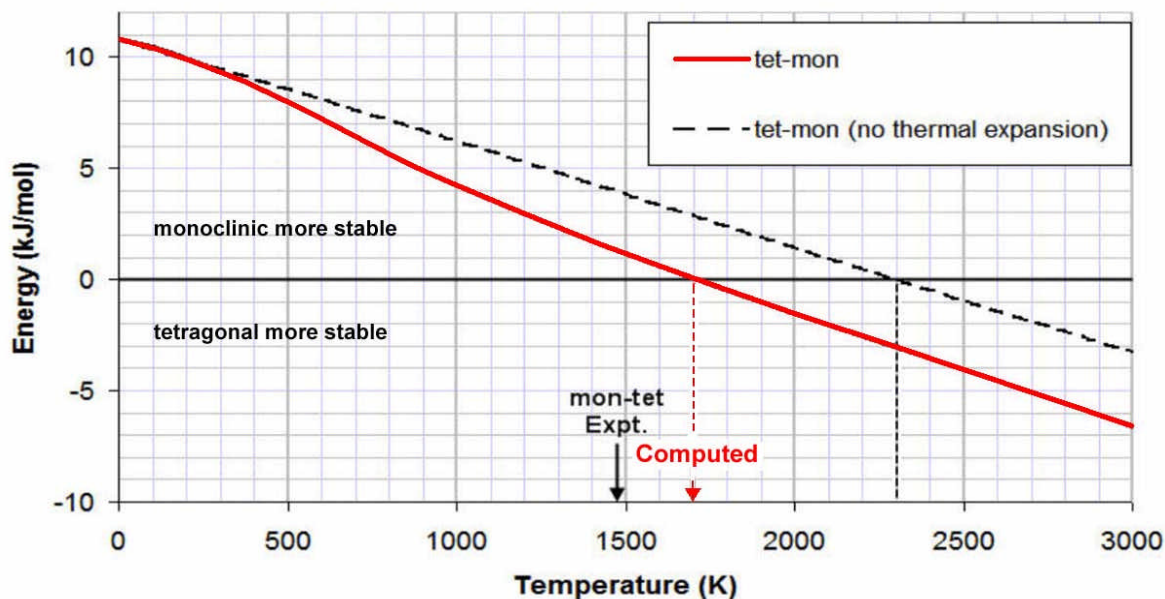


Figure 2. Difference in the free energy of the low-temperature monoclinic and the high-temperature tetragonal phases of zirconia. The solid red line includes effects of thermal expansion. The results shown as dashed line use the computed lattice parameters at $T=0$ K.

Computed results

The present first-principles calculations correctly predict the monoclinic phase of ZrO_2 to be more stable at low temperatures with the tetragonal phase becoming more favorable at high temperatures. The computed transition temperature is 1700 K compared with an experimental value of 1478 K. This deviation of 15% is a respectable result given the subtle nature of temperature-induced phase transitions.

Significance

The ability to predict temperature-dependent phase transitions with a first-principles method opens the door for systematic studies of the effect of vacancies, dopants, and external strains on the transition temperature providing useful materials property data as well as insight into the role and mechanism of vacancies, doping, and mechanical load. Relative trends such as stress-induced changes are likely to be more

accurately described than the absolute value of a transition temperature.

MedeA modules used for this application

The present calculations were performed with the MedeA platform using the following integrated modules of the MedeA software environment

- Standard MedeA framework including crystal structure builders and geometric analysis tools as well as JobServer and TaskServers
- InfoMaticA with structural databases (ICSD, Pearson, Pauling) – in this case each of these databases contains the various phases of ZrO_2
- VASP 4.6 and its graphical user interface as integrated in MedeA
- Phonon as integrated in MedeA

Comments

The phase transition of ZrO_2 from the monoclinic to the tetragonal structure is driven by vibrational entropy. For a given temperature the vibrational entropy of the tetragonal phase is larger than that of the monoclinic phase. The electronic energy of the monoclinic phase is lower than that of the tetragonal phase even if the lattice expands. Therefore, an accurate

calculation of the vibrational entropy is critical. This task is accomplished with the MedeA-Phonon module, which computes the full phonon dispersions of crystalline structures. Integration over all phonon branches gives a phonon density of states, which leads directly to the temperature-dependent terms of the enthalpy, the zero-point energy, and the vibrational entropy as a function of temperature. These results are shown in Fig. 3.

Computed Phonon Dispersions and Density of States for ZrO_2

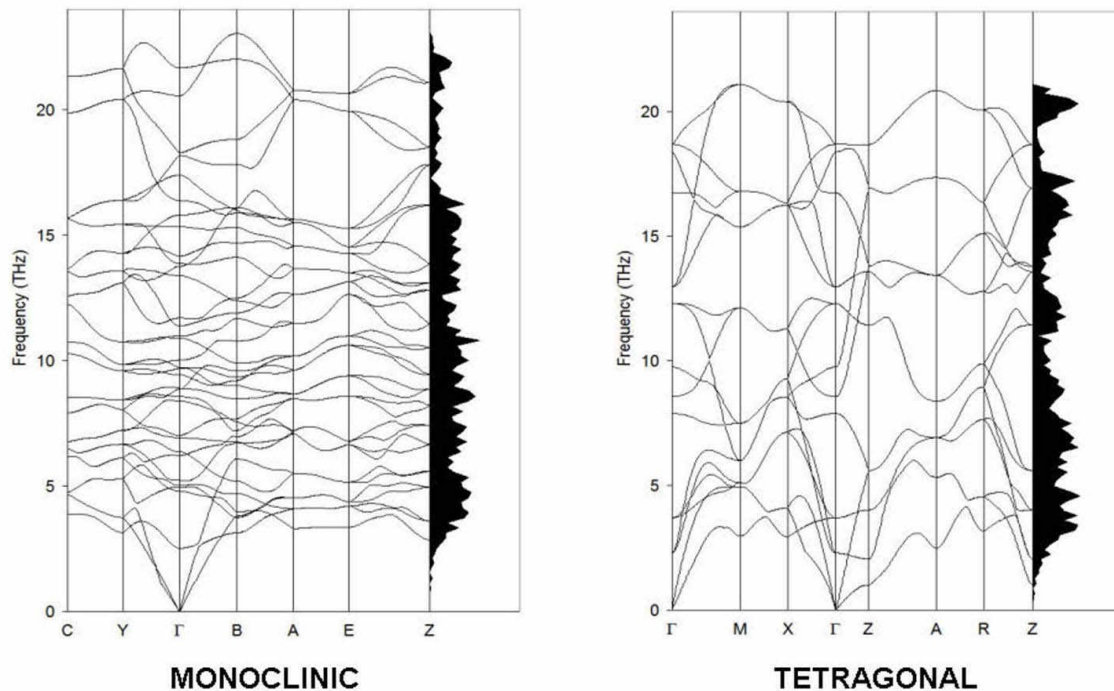


Figure 2. Phonon dispersions and phonon densities of states for monoclinic and tetragonal ZrO_2 computed from first-principles using MedeA with VASP and Phonon. Note that the monoclinic phase shows higher frequencies than the tetragonal phase.

The coefficient of thermal expansion for the two phases of zirconia are obtained from a series of electronic structure and phonon calculations for different lattice parameters. Minimization of the free energy for each temperature gives an equilibrium lattice parameter for that temperature. The computed temperature-

dependent functions of the enthalpy and entropy are then used to include the effects of thermal expansion.

The high-temperature cubic phase is dynamically stabilized by cooperative displacements of chains of oxygen atoms oscillating in a double-well potential. The

prediction of this second phase transition is more complicated and requires a theoretical approach beyond the quasi-harmonic approximation used in the present work.

The approach outlined in this application note has recently been used by the group of Prof. Isao Tanaka at Kyoto University as described in Ref. [2].

References

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