

New insights into the zircon-reidite phase transition

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ABSTRACT

The structure, the elastic properties, and the Raman frequencies of the zircon and reidite polymorphs of ZrSiO_4 were calculated as a function of hydrostatic pressure up to 30 GPa using HF/DFT ab initio calculations at static equilibrium (0 K). The softening of a silent (B_{1u}) mode of zircon leads to a phase transition to a “high-pressure–low-symmetry” (HPLS) ZrSiO_4 polymorph with space group $I\bar{4}2d$ and cell parameters $a = 6.4512 \text{ \AA}$, $c = 5.9121 \text{ \AA}$, and $V = 246.05 \text{ \AA}^3$ (at 20 GPa). The primary coordination of SiO_4 and ZrO_8 groups in the structure of zircon is maintained in the high-pressure phase, and the new phase deviates from that of zircon by the rotation of SiO_4 tetrahedra and small distortions of the ZrO_8 dodecahedra. The new polymorph is stable with respect to zircon at 20 GPa and remains a dynamically stable structure up to at least 30 GPa. On pressure release, the new phase reverts back to the zircon structure and, therefore, cannot be quenched in experiments. In contrast, the transformation from zircon to reidite is reconstructive in nature and results in a first-order transition with a volume and density change of about 9%. The calculated energies from the DFT simulations yield an equilibrium transition pressure of 9.13(1) GPa at 0 K. Simulations of the Raman spectra of the three polymorphs at 20 GPa show how they can be distinguished. In particular, the peak due to the lowest-energy A_1 mode with a calculated wavenumber of 94 cm^{-1} is diagnostic of the HPLS phase because it does not overlap with any of the peaks of zircon or reidite.

Keywords: Zircon, reidite, phase transition, Raman spectroscopy, high pressure