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$_{1g}$) mode of zircon leads to a phase transition to a “high-pressure–low-symmetry” (HPLS) ZrSiO$_4$ polymorph with space group $I4_2d$ and cell parameters $a = 6.4512$ Å, $c = 5.9121$ Å, and $V = 246.05$ Å$^3$ (at 20 GPa). The primary coordination of SiO$_4$ and ZrO$_6$ 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$_6$ 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

INTRODUCTION

Zircon (ZrSiO$_4$, space group $I4_1/amd$) is an extremely stiff material, and upon meteorite bombardment shock microstructures form within it at pressures of 20 GPa or more (Leroux et al. 1999). These microstructures remarkably survive subsequent metamorphism without being obliterated and, therefore, they can provide diagnostic criteria to identify impact structures (French 1998; French and Koeberl 2010; Wittmann et al. 2006). During shocks zircon may transform into the high-pressure scheelite-type polymorph reidite (space group $I4_1/a$). Naturally occurring reidite was first identified using X-ray diffraction (XRD) in zircon grains from Eocene ejecta associated with the ~90 km diameter, ca. 35.7 Ma Chesapeake Bay impact structure (Glass and Liu 2001; Glass et al. 2002) and subsequently in several other impact structures (Gucsik et al. 2004; Wittmann et al. 2006; Wittmann and Reimold 2009; Chen et al. 2013; Cavosie et al. 2015; Singleton et al. 2015; Reddy et al. 2015; Cavosie et al. 2018). Therefore, to study the origin of impact structures and to further constrain the impact conditions it is crucial to understand the stability relationships between zircon and its high-pressure polymorph reidite.

This phase transition from zircon to reidite has a volume decrease of about 9% (e.g., Reid and Ringwood 1969; Ono et al. 2004a), which suggests that it is thermodynamically first-order. Moreover, the topological differences in the atomic linkages indicate that the zircon-reidite phase transition is reconstructive, which is supported by ab initio calculations (e.g., Marqués et al. 2006; Dutta and Mandal 2012a). Because of the reconstructive nature of the zircon-reidite transformation, the equilibrium transition pressure is not well constrained. At elevated temperatures of 1000–1500 K the pressure-induced zircon-to-reidite phase transition occurs near 8 GPa (Reid and Ringwood 1969; Ono et al. 2004b). Several static loading experiments in diamond-anvil pressure cells at room temperature have shown the presence of reidite when the pressure is increased above 18–23 GPa (Knittle and Williams 1993; Van Westrenen et al. 2004; Morozova 2015). However, there seems to be a discrepancy between the detection of reidite by Raman spectroscopy in the samples compressed to ca. 20 GPa and higher pressures at room temperature, and the results of X-ray diffraction that show evidence only of zircon (van Westrenen et al. 2004). On the other hand, shock wave studies found this transformation to occur at much higher pressures (30–50 GPa) (Liu 1979; Kusaba et al. 1986; Gucsik et al. 2004) and very quickly, at microsecond timescales. The latter observation favors a martensitic transformation mechanism for impact-produced reidite, since other solid-state mechanisms seem unlikely to operate on the nanosecond to seconds timescale of shock events because diffusion rates are too slow (Langenhorst and Deutsch 2012).

Therefore, to elucidate the pressure-induced structural transformations of zircon we have performed ab initio simulations of zircon and reidite to determine their structures, elastic behavior,