

Al³⁺ and H⁺ substitutions in TiO₂ polymorphs: Structural and vibrational investigations

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ABSTRACT

Rutile is the most common TiO₂ mineral on Earth's surface and transforms to CaCl₂- and α -PbO₂-type structures at elevated pressures in subducted basaltic crusts. In this study, we synthesized hydrous CaCl₂- and α -PbO₂-type TiO₂ crystals with various Al³⁺ concentrations using a multi-anvil press. Al³⁺ is incorporated into the CaCl₂- and rutile-type phases mainly in the form of $3\text{Ti}^{4+} = 4\text{Al}^{3+}$, while the coupled substitution of $\text{Ti}^{4+} = \text{Al}^{3+} + \text{H}^{+}$ is dominant in the α -PbO₂-type structure, forming Ti_{1-x}(AlH)_xO₂ solid solutions. Consequently, the water solubility in Al-bearing α -PbO₂-type TiO₂ is at least one order of magnitude greater than those in rutile- and CaCl₂-type TiO₂ phases, making TiO₂ a significant water carrier at the pressure-temperature (*P-T*) conditions in the mantle transition zone (410 to 660 km depth in deep Earth's interior), when coexisting with Al³⁺ and Fe³⁺. High-*P* and high-*T* Raman spectra were collected for these synthetic samples. The CaCl₂- and α -PbO₂-type phases irreversibly transform to a rutile-type structure at 950 K and ambient pressure. A reversible α -PbO₂ \rightarrow baddeleyite phase transition in TiO₂ is detected at approximately *P* = 10 GPa and *T* = 300 K, and incorporating smaller amounts of Al³⁺ cations increases the phase transition pressure. The lattice vibrational modes typically shift to lower frequencies at elevated temperature and higher frequencies with increasing pressure due to variations in Ti(Al)-O bond length with temperature or pressure. Fourier transform infrared (FTIR) spectroscopic measurements were conducted on the samples under high-*T* or high-*P* conditions. Both *T*- and *P*-dependences are negative for the OH stretching vibrations in these TiO₂ polymorphs, except that the OH bands in the α -PbO₂-type samples exhibit a blueshift at elevated temperature. A negative linear correlation can be drawn between the measured OH stretching frequencies and the incorporated $M^{3+}\text{O}_6$ quadratic elongation, which were computed based on first-principles calculations. The local octahedral distortion can provide useful insights for understanding the M^{3+} and H⁺ incorporation mechanisms in TiO₂ and SiO₂ structures.

Keywords: TiO₂ polymorphs, Al-H coupled substitution, structure refinement, OH stretching vibration, octahedral distortion