

Silicon coordination in rutile and TiO₂-II at ambient and high pressures: Si-29 NMR

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ABSTRACT

The structural environment of silicon dissolved in rutile and α -PbO₂-structured TiO₂ (TiO₂-II) was probed using ²⁹Si MAS NMR on ²⁹Si-enriched samples. At 1 atm, about 0.01 wt% SiO₂ is incorporated into TiO₂ as ^{IV}Si, presumably in interstitial sites. Rutile recovered from 6 GPa, 1600 °C contains about 0.6 wt% SiO₂, incorporated both as ^{VI}Si (~90%) and ^{IV}Si (~10%). TiO₂-II, synthesized at 12 GPa, 1200 °C, contains only ^{VI}Si. The chemical shift for ^{VI}Si in TiO₂-II is slightly less negative than that for rutile, and the peak is split, suggesting either a more complex mechanism of substitution or a different response to quenching or decompression in the lower-symmetry structure. Future thermodynamic studies of the TiO₂-SiO₂ solid solution will have to take into account the mixed coordination environment of the Si in TiO₂, at low pressures.

Keywords: Crystal structure, rutile, TiO₂-II, high-pressure studies, NMR spectroscopy