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Aluminum solubility in TiO_2 rutile at high pressure and experimental evidence for a $CaCl_2$-structured polymorph

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Abstract

Aluminum incorporation into TiO_2 has been studied in the TiO_2-Al_2O_3 system as a function of pressure at temperatures of 900 and 1300 °C using commercial Al_2TiO_5 nanopowder as starting material. A new orthorhombic TiO_2 polymorph with the $CaCl_2$ structure has been observed in the recovered samples synthesized from 4.5 to 7 GPa and 900 °C and from 2.5 to 7 GPa at 1300 °C. The phase transition to the α-PbO_2 type TiO_2 phase takes place between 7 and 10 GPa at both temperatures. Two mechanisms of Al incorporation in TiO_2 rutile have been observed in the recovered samples. The substitution of Ti^{4+} by Al^{3+} on normal octahedral sites is dominant at lower pressures. High pressure induces the incorporation of Al^{3+} into octahedral interstices of the rutile structure, which is responsible for an orthorhombic distortion of the TiO_2 rutile structure and gives rise to a (110) twinned $CaCl_2$ type structure. This phase is probably a result of temperature quench at high pressure. Aluminum solubility in TiO_2 increases with increasing pressure. TiO_2 is able to accommodate up to 9.8 wt% Al_2O_3 at 7 GPa and 1300 °C. Temperature has a large effect on the aluminum incorporation in TiO_2, especially at higher pressures. High pressure has a strong effect on both the chemistry and the microstructure of Al-doped TiO_2. Enhanced aluminum concentration in TiO_2 rutile as well as TiO_2 grains with a microstructure consisting of twins are a clear indication of high-pressure conditions.

Keywords: Rutile, alumina, $CaCl_2$ type structure, multi-anvil experiments, phase transition, twinning, transmission electron microscopy