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Complete substitution of Si for Ti in titanite $Ca(Ti_{1-x}Si_x)^{VI}Si^{IV}O_5$

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ABSTRACT

Phase relations on the join $CaTiSiO_5$-$CaSi_2O_5$ were determined at 1350 °C over the pressure range 3.5–12 GPa by a combination of synthesis and reversal experiments in a piston cylinder and a multi-anvil press. Titanite-like phases were recovered from all experiments in this pressure range. At 3.5 GPa the maximum Si^{VI} content of titanite is 3.0 ± 0.6 mol%, whereas bulk compositions with higher Si content yield a mixture of titanite solid solution plus coesite and walstromite-structured $CaSiO_3$. The maximum Si^{VI} content of the titanite increases with pressure to 21 ± 2 mol% at 7 GPa and 46 ± 2 mol% at 7.5 GPa. At pressures of 8.5 to 12 GPa all intermediate compositions yield a single titanite phase. X-ray and TEM analysis show that these have the *A*2/*a* symmetry of the titanite aristotype. The variations of the room-pressure unit-cell parameters of the *A*2/*a* phases with composition can be described by the equations a [Å] = 7.040(9) − 0.492(15) $X(Si^{VI})$; b [Å] = 8.713(7) − 0.316(11) $X(Si^{VI})$; c [Å] = 6.564(4) − 0.220(7) $X(Si^{VI})$; β [°] = 113.721(6) − 0.537(12) $X^2(Si^{VI})$; V (cell) [Å^3] = 367.8(9) − 47.5(1.6) $X(Si^{VI})$. For the $CaSi_2O_5$ composition the recovered material has $I\bar{1}$ symmetry but is known to transform back to *A*2/*a* titanite structure at 0.2 GPa at room temperature. Similarly, with increasing pressure the $P2_1/a$ $CaTiSiO_5$ transforms to *A*2/*a* symmetry at 3.6 GPa at room temperature. The conclusion is that at 1350 °C and pressures in excess of 8.5 GPa there is complete solid solution between $CaTiSiO_5$ and $CaSi_2O_5$ based upon the isovalent exchange of Si for Ti in the octahedral site of the *A*2/*a* structure. Rietveld structure analysis of intermediate compositions reveals no evidence for ordering or intermediate phases. Preliminary experiments at pressures between 13.5 GPa and 16 GPa yielded mixtures of titanite solid solution plus perovskite and stishovite. From these data and information on the phase relations for the $CaSiO_3$-$CaTiO_3$ join the topology of the phase relations between ~3 and ~13 GPa in the central part of the CaO-TiO_2-SiO_2 ternary have been deduced.