Equations of state and phase boundary for stishovite and CaCl$_2$-type SiO$_2$

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ABSTRACT

Silica is thought to be present in the Earth’s lower mantle in subducting plates, in addition to being a prototypical solid whose physical properties are of broad interest. It is known to undergo a phase transition from stishovite to the CaCl$_2$-type structure at $\sim$50–80 GPa, but the exact location and slope of the phase boundary in pressure-temperature space is unresolved. There have been many previous studies on the equation of state of stishovite, but they span a limited range of pressures and temperatures, and there has been no thermal equation of state of CaCl$_2$-type SiO$_2$ measured under static conditions. We have investigated the phase diagram and equations of state of silica at 21–89 GPa and up to $\sim$3300 K using synchrotron X-ray diffraction in a laser-heated diamond-anvil cell. The phase boundary between stishovite and CaCl$_2$-type SiO$_2$ can be approximately described as $T = 64.6(49) \cdot P - 2830(350)$, with temperature $T$ in Kelvin and pressure $P$ in GPa. The stishovite data imply $K''_0 = 5.24(9)$ and a quasi-anharmonic $T^2$ dependence of $-6.0(4) \times 10^{-6}$ GPa cm$^3$/mol K$^2$ for a fixed $q = 1$, $\gamma_0 = 1.71$, and $K'_0 = 302$ GPa, while for the CaCl$_2$-type phase $K'_0 = 341(4)$ GPa, $K''_0 = 3.20(16)$, and $\gamma_0 = 2.14(4)$ with other parameters equal to their values for stishovite. The behaviors of the $a$ and $c$ axes of stishovite with pressure and temperature were also fit, indicating a much more compressible $c$ axis with a lower thermal expansion as compared to the $a$ axis. The phase transition between stishovite and CaCl$_2$-type silica should occur at pressures of 68–78 GPa in the Earth, depending on the temperature in subducting slabs. Silica is denser than surrounding mantle material up to pressures of 58–68 GPa, with uncertainty due to temperature effects; at higher pressures than this, SiO$_2$ becomes gravitationally buoyant in the lower mantle.

Keywords: Silica, SiO$_2$, stishovite, phase diagram, equation of state, phase transition, X-ray diffraction

INTRODUCTION

Silica (SiO$_2$) is expected to be present in subducted mid-ocean ridge basalt in the Earth’s lower mantle (e.g., Hirose et al. 2005). It may also occur in the $D^*$ layer as a result of Si and O becoming less soluble in liquid iron as the core cools (Hirose et al. 2017), since the metal–silicate partitioning of O and especially Si are strongly temperature dependent (e.g., Fischer et al. 2015; Tsuno et al. 2013). Despite its importance in geophysics, as well as physics and materials science, there remains disagreement surrounding the phase diagram of silica at high pressures ($P$) and temperatures ($T$). Additionally, only limited research has been done on the thermal equation of state for the CaCl$_2$-type phase of silica, stable under lower mantle conditions. In this study, we focus on elucidating the location and slope of the stishovite/CaCl$_2$-type phase boundary, as well as providing better constraints on the thermal equations of state of these important phases.

Coesite (monoclinic SiO$_2$ with space group $C2/c$) transforms to stishovite (rutile-type SiO$_2$ with space group $P4_2/mnm$) at $\sim$7–13 GPa and high temperatures (e.g., Zhang et al. 1996), marking a transition in Si coordination from tetrahedral to octahedral. At lower mantle pressures, stishovite undergoes a second-order, reversible phase transition to the CaCl$_2$-type structure (space group $Pnmn$) of SiO$_2$, in which the tetragonal unit cell of stishovite distorts into an orthorhombic unit cell (Tsuchida and Yagi 1989). Reports of the location and slope of this phase