Crystal structure of CaSiO$_3$ perovskite at 28–62 GPa and 300 K under quasi-hydrostatic stress conditions

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ABSTRACT

To find the thermodynamically stable crystal structure of CaSiO$_3$ perovskite (CaPv) at high pressure and 300 K, we have conducted synchrotron X-ray diffraction (XRD) on thermally stress-annealed samples in a Ne pressure medium in the diamond-anvil cell at 28–62 GPa. Rietveld refinements of the diffraction patterns are significantly improved in fitting the positions and intensities of the split lines of CaPv if the starting model is a tetragonal perovskite-type structure with the SiO$_6$ octahedral rotation around the tetragonal c-axis. The result is in contrast with other previous experiments, but is consistent with first-principles calculations, reconciling the discrepancy between computations and experiments on the crystal structure of CaPv. We attribute the observed difference to the formation of the thermodynamically more stable phase under improved stress conditions in our experiments. Our fitting shows that the bulk modulus of CaPv is 223 ± 6 GPa when its pressure derivative fixed to 4, which is also consistent with first-principles calculations. The previous observations of the diffraction patterns of CaPv inconsistent with the first-principles studies could be due to the formation of a metastable crystal structure of CaPv under elevated deviatoric stresses.

Keywords: CaSiO$_3$ perovskite, crystal structure, hydrostatic stress, X-ray diffraction, equation of state

INTRODUCTION

Perovskite-structured CaSiO$_3$ (hereafter CaPv) is the third most abundant mineral (5–7 wt%) in the pyrolitic model composition of the Earth’s mantle (Kesson et al. 1998; Murakami et al. 2005; Ricouleau et al. 2009). CaPv is stable over a wide depth range from the transition zone to the lowermost mantle (Shim et al. 2000; Ohta et al. 2008). In mid-oceanic ridge basalt (MORB) in subducting slabs at lower-mantle pressures, CaPv represents 23 wt% of the mineralogy, comparable to the amount of bridgmanite, that is 35 wt% (Hirose et al. 2005; Ricolleau et al. 2009). CaPv is stable over a wide depth range from the transition zone to the lowermost mantle (Kesson et al. 1998; Murakami et al. 2005; Ricouleau et al. 2009). CaPv represents 23 wt% of the mineralogy, comparable to the amount of bridgmanite, that is 35 wt% (Hirose et al. 2005; Ricouleau et al. 2010; Grocholski et al. 2012).

Existing studies are in agreement in that CaPv has a phase transition from a non-cubic to a cubic perovskite-type structure with heating ($T > 500$ K) (Komabayashi et al. 2007; Noguchi et al. 2013; Sun et al. 2016) at pressures ($P$) expected for the lower mantle. However, there remain significant discrepancies between computations and experiments on the crystal structure of the lower-temperature form of CaPv and its compressibility. In the 1980s, it was believed that CaPv adopts the cubic perovskite structure ($Pm\bar{3}m$) at 300 K and lower mantle pressures from energy-dispersive X-ray diffraction (Liu and Ringwood 1975; Mao et al. 1989; Tamai and Yagi 1989; Wang et al. 1996). Ab initio calculations first predicted a lower symmetry structure for CaPv. Stixrude et al. (1996) found the instability of the cubic structure with a SiO$_6$ octahedral rotation of 7° toward the tetragonal $I4/mcm$ subgroup. Caracas et al. (2005) performed a more exhaustive search for the ground state of CaPv and tetragonal $I4/mcm$ was regarded as one of the most energetically competitive structures at low temperature and high pressure.

Using high-resolution angle-dispersive diffraction technique, Shim et al. (2002) found a non-cubic unit cell for CaPv at 20–46 GPa and 300 K. However, they found that the positions and intensities of the split peaks (in particular the 200 peak splitting) were consistent with a longer $a$-axis than $c$-axis ($c_p/a_p < 1$). The ratio is opposite to what is expected for the crystal structures predicted by computations, which predicted the octahedral rotation ($c_p/a_p > 1$) as an origin of the non-cubic structure. Instead, the experimental observation is more straightforward to understand if one of the three axes of the SiO$_6$ octahedra is shorter than the other two (therefore, direct distortion of the octahedra). Later XRD studies have shown a similar pattern of the 200 peak splitting as Shim et al. (2002) in CaSiO$_3$ (Komabayashi et al. 2007; Sun et al. 2016), peridotite (Ono et al. 2004), and MORB (Hirose et al. 2005) compositions at room (ambient) $T$ and high $P$. A multi-anvil press experiment identified an orthorhombic CaPv...