Elasticity and phase transformation at high pressure in coesite from experiments and first-principles calculations

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ABSTRACT

The crystal structure and equation of state of coesite (space group C2/c) and its high-pressure polymorph coesite-II (space group P2₁/n) under pressure have been studied using X-ray powder diffraction in a diamond-anvil cell (DAC) up to 31 GPa at room-temperature and first-principles calculations at 0 K up to 45 GPa. New diffraction peaks appear above 20 GPa, indicating the formation of coesite-II structure. The calculated enthalpies provide theoretical support for the pressure-induced phase transformation from coesite to coesite-II at ~21.4 GPa. Compared with coesite, the coesite-II structure is characterized by a “doubled” b-axis and the breakdown of the linear Si1-O1-Si1 angle in coesite into two distinct angles—one is ~176°, close to linear, whereas the other decreases by 22 to 158°. Coesite is very anisotropic with the a-axis the shortest and twice more compressible than the b- and c-axis. By comparison, coesite-II is not so anisotropic with similar compressibilities in its a-, b-, and c-axis. As analyzed by a third-order Eulerian finite strain equation of state, the bulk modulus of coesite at 21.4 GPa is 182.3 GPa, and that of coesite-II is 140.8 GPa, indicating that coesite-II is much more compressible than coesite. The existence of coesite-II in the coldest subduction zone will change the elasticity and anisotropic properties of the subducting materials dramatically.

Keywords: Coesite, phase transition, diamond-anvil cell, first-principles calculation

INTRODUCTION

Coesite is a high-pressure polymorph of quartz with the monoclinic structure and space group C2/c. It is thermodynamically stable at pressures and temperatures above 2.5 GPa and 500 °C (Akaogi and Navrotsky 1984; Akaogi et al. 1995). Natural coesite has been discovered in meteorite craters and metamorphic rocks in subduction or collision zones and used as a pressure marker for these events (e.g., Sobolev et al. 2000). The mid-ocean ridge basalt (MORB) is believed to contain an appreciable amount of SiO₂ (Ricard et al. 2005; Irifune and Tsuchiya 2007; Stixrude and Lithgow-Bertelloni 2012), and it has been proposed as a main candidate to explain the seismic observed X-discontinuity in the depth range 250–350 km (Chen et al. 2015; Williams and Revenaugh 2005; Schmerr et al. 2013). Given the importance of these geological processes, it is particularly significant to understand the thermodynamics and elastic properties of coesite under pressure and/or temperature conditions.

Crystal structure studies show that coesite is a framework silicate with the Si atom coordinated with four O atoms (Fig. 1). The SiO₂ tetrahedra in coesite form four-membered rings by corner sharing, which then build up the “double-crankshaft” chain running parallel to the c-axis of the unit cell. There are eight distinct Si-O bonds and five distinct Si-O-Si angles in coesite structure with a linear Si1-O1-Si1 angle. Static compression studies showed that these bonds and angles decrease under pressure, with the smaller angles and shorter bonds undergoing more compression than larger or longer ones, and the Si1-O1-Si1 remains linear due to the requirement of the symmetry (Levien and Prewitt 1981). Coesite has 16 units of SiO₂ in a unit cell, with almost equal a- and c-axis, and β close to 120 °C at room conditions (Levien and Prewitt 1981), which resembles that of a hexagonal structure.

The behavior of SiO₂ under pressure has long been of interest to geoscience and material science due to its abundance in Earth crust and mantle, and its relative simple chemistry but rich polymorphism under elevated pressure and/or temperature conditions, which could help to understand the properties of silicate tetrahedra under pressure. It has been shown that under pressure, the a-axis of coesite is much more compressible than c-axis, whose compressibility is close to that of b-axis; and the β angle becomes larger with increasing pressure (Levien and Prewitt 1981; Angel et al. 2001), indicating strong anisotropic compression of its structure. The elastic properties of coesite have been found to be anomalous under pressure by several studies. For example, Angel et al. (2001) studied the compressional behavior of coesite up to 9.6 GPa using single-crystal X-ray diffraction and reported an unusual positive Kₐ, which they attributed to the unusual compression of the c-axis. Our recent study (Chen et al. 2015) showed that the shear wave velocity of coesite undergoes anomalous softening and decreases with increasing pressure within 0–12.6 GPa. The anomalous behavior of the shear wave velocity and shear modulus may be a precursor to the pressure-induced phase transition or amorphization.