Mechanical properties of jennite: A theoretical and experimental study

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ABSTRACT

The objective of this study is to determine the mechanical properties of jennite. To date, several hypotheses have been proposed to predict the structural properties of jennite. For the first time as reported herein, the isothermal bulk modulus of jennite was measured experimentally. Synchrotron-based high-pressure x-ray diffraction experiments were performed to observe the variation of lattice parameters under pressure. First-principles calculations were applied to compare with the experimental results and predict additional structural properties. Accurately measured isothermal bulk modulus herein ($K_0 = 64(2)$ GPa) and the statistical assessment on experimental and theoretical results suggest reliable mechanical properties of shear and Young's modulus, Poisson's ratio, and elastic tensor coefficients. Determination of these fundamental structural properties is the first step toward greater understanding of calcium–silicate–hydrate, as well as provides a sound foundation for forthcoming atomic level simulations.

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1. Introduction

Cement paste is a porous and hierarchical material consisting of various levels of structures across different length scales [1]. Each scale has a different characteristic size and accordingly different structural properties, which make concrete a highly complex material. The main components of cement paste are poorly crystalline calcium–silicate–hydrate (C–S–H gel) and crystalline phases of portlandite, ettringite, and Al_2O_3–Fe_2O_3-mono (AFm) phases, such as monosulfate and monocarboaluminate.

Among the different cement hydration products, the C–S–H gel is the most important component in concrete. Not only because it constitutes a large volume of cement paste, but it is responsible for numerous important properties of concrete, including setting, hardening, shrinkage, and creep [1]. The disordered nature and compositional variance make research on C–S–H gel challenging [2–4]. It has been proposed that C–S–H(I) and C–S–H(II) are semi-crystalline versions of crystalline calcium silicate hydrate minerals, tobermorite 14 Å, and jennite, respectively [5–7]. Other researchers have postulated that C–S–H gel can be treated as a mixture of tobermorite- and jennite-like structures. The jennite-like structure is proposed as a dominant phase with age [2–4,8,9].

Jennite, $Ca_9(Si_6O_{18})(OH)_6 \cdot 8H_2O$, is a rare natural mineral, usually found in contact with tobermorite 14 Å [10]. It can be synthesized in suspensions of $Ca(OH)_2$ and hydrous silica at 60–100 °C [11]. An ideal Ca/Si ratio is 1.5, which is higher than that of tobermorite 14 Å (Ca/Si ratio of 1) [12,13]. The crystal structure of jennite has been determined by x-ray diffraction refinement [14]. The structure of jennite is composed of (1) the tilleyite ribbons of edge-sharing calcium octahedral; (2) the Si–O dreierketten chains running along [010]; and (3) the additional calcium octahedral sitting between the chains [14]. Upon dehydration at 70–90 °C, water molecules are lost, which alters the atomic environment of interlayer Ca. To be a stable configuration, the structure shrinks in the c direction, leading to metajennite, $Ca_9[Si_6O_{16}(OH)_2](OH)_8.2H_2O$. Above 350 °C, the Ca–OH groups of metajennite are eliminated, forming an amorphous phase, which finally transforms to wollastonite and larnite (β-Ca_2SiO_4) above 800 °C [15].

With increasing interests in mineral analogs of C–S–H, fundamental structural properties are undoubtedly an important part for the understanding of mechanical characteristics of C–S–H. Using first-principles calculation [16,17] and molecular dynamics simulation [18], several studies have been made to predict mechanical properties of tobermorite and jennite. Along with simulation studies, the bulk moduli of tobermorite crystals have been experimentally measured [19,20]. For the very first time, the study reported herein measures experimentally the isothermal bulk modulus of jennite. The results report a synchrotron-based x-ray diffraction experiment that gives reliable pressure–volume data for jennite crystal. As a benchmark to the experimental data, first-principles calculations using different exchange–correlation functionals are performed to support the experimental results. Lastly, statistical assessment on the experimental and theoretical results is discussed.

The remainder of the present study is organized as follows. Experimental procedure and results are given in Section 2. Section 3 focuses on the application of first-principles calculations. The combination of

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experiment and simulation allows systematic comparison with previous simulation data, and a comprehensive understanding of the structural mechanism is discussed in Section 4. Section 5 summarizes the major conclusions achieved in this study.

2. High pressure x-ray experiments

Jennite crystals (see Fig. 1) from Zeilberg, Bavaria, Germany were obtained for the experiments. Ambient-condition identification was confirmed by laboratory scale x-ray diffraction, and high pressure x-ray diffraction experiments (HPXRD) were carried out at beamline 12.2.2 of the Advanced Light Source [21], using a synchrotron monochromatic x-ray source. Experimental details can be found in previous publications [22–24]. The pressure-transmitting medium consisted of a 4:1 mixture of methanol:ethanol (ME) used in the first run and silicone oil (SO) for the second run. For the alcohol mixture, an x-ray wavelength of $\lambda = 0.6199$ Å and sample-to-detector distance of 221.4 mm were selected. For the silicone oil, different setting of $\lambda = 0.4959$ Å and 387.5 mm was chosen. Ambient and high-pressure x-ray diffraction patterns of jennite are shown in Figs. 2 and 3, measured in the alcohol mixture and silicone oil, respectively. The position and relative intensities of ambient x-ray reflections agree well with the data obtained in Ref. [22]. Unindexed peaks of 4.7° and 9.4° in Fig. 2 and the observed hump in Fig. 3 might have resulted from the diamond anvil cell or impurities in the pressure transmitting media. Almost identical results from different media indicate that these did not affect hydrostatic state on the jennite crystals.

Accurate peak positions were determined by a pseudo-Voight function implemented in XFit software [25]. The peak positions are summarized in Tables 1 and 2. Due to its low symmetry, it is quite challenging to refine lattice parameters of jennite. The mathematical relation between d-spacing and Miller indices in triclinic symmetry is,

$$\frac{1}{d^2} = \frac{1}{V^2}\left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl\right) \quad (1)$$

where $S_{11} = b^2c^2 \sin^2\alpha$, $S_{22} = a^2c^2 \sin^2\beta$, $S_{33} = a^2b^2 \sin^2\gamma$, $S_{12} = abc^2(\cos\alpha \cos\beta - \cos\gamma)$, $S_{23} = a^2bc(\cos\beta \cos\gamma - \cos\alpha)$, and $S_{13} = ab^2c(\cos\gamma \cos\alpha - \cos\beta)$.

Nonlinear regression using the Newton–Raphson method and normal distribution (also known as Gaussian function) [26] was used to refine the lattice parameters of jennite. X-ray diffraction peaks given in Tables 1 and 2 were selected for the nonlinear regression method. Given the d-spacing and hkl information, lattice parameters of a, b, c, α, β, and γ were successfully refined by iteratively solving Eq. (1). Pressure above 2.9 GPa resulted in x-ray diffraction peaks that were

broader and overlapped considerably; therefore, refinement of unit cell was not successful, regardless of the type of pressure-transmitting media. The refined lattice parameters using the alcohol mixture versus silicone oil are summarized in Table 3. Note that standard deviations in the unit cell are dependent on the number and selection of peaks used for the refinement. Refinement in the case of ambient pressure and silicone oil yielded larger deviations compared to the refinement in the case of the alcohol mixture.

The refined ambient lattice parameters agree well with the results of Bonaccorsi et al. [14], with less than 1% error range (Table 3). Nevertheless, the existence of disorder in the jennite crystal structure [14,27,28] and the anomalous hump from an external source made it difficult to apply the Rietveld refinement method to the experimental data. Application of the nonlinear regression method, however, gave an acceptable error range in lattice parameters considering the complexity of crystal structure of jennite. The variation of lattice parameters under pressure is shown in Figs. 4 and 5. As stated early in this section, it shows almost identical results in both media.

The pressure normalized volume data were fitted by a second- and third-order finite strain equation of state (i.e., the Murnaghan and Birch–Murnaghan equation of state) [29]. Below is the Birch–Murnaghan equation of state (BM EoS).
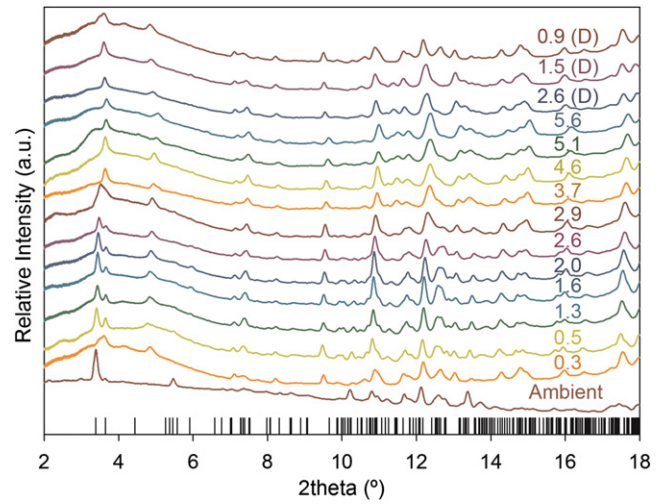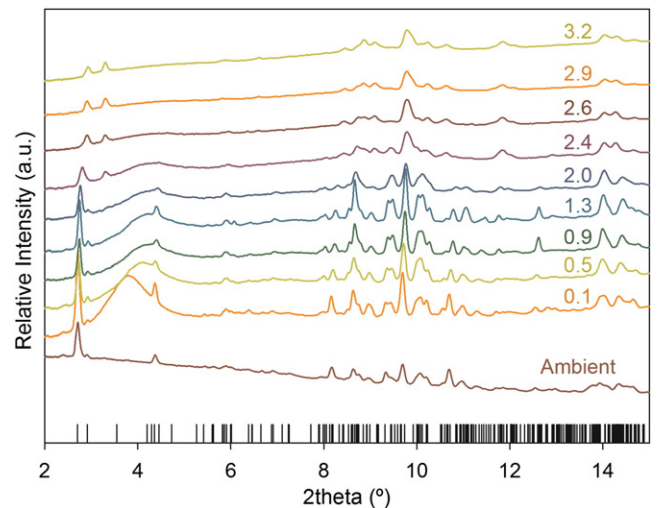
Fig. 2. X-ray diffraction patterns of jennite ($\lambda = 0.6199$ Å) with alcohol mixture (Methanol:Ethanol = 4:1). Bottom peaks indicate reference peak positions from [14].

Fig. 1. Jennite crystal collected from Zeilberg, Bavaria, Germany.

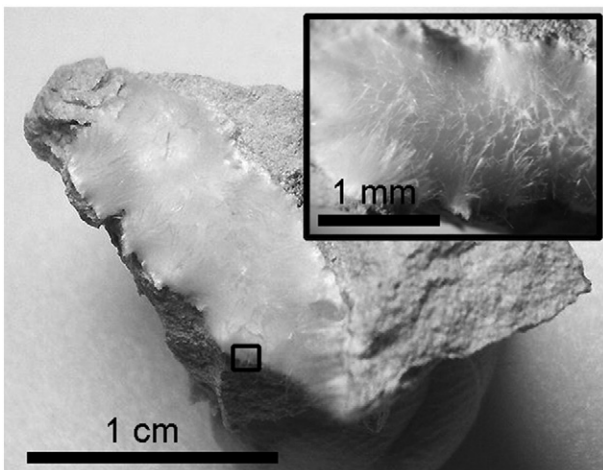Fig. 3. X-ray diffraction patterns of jennite ($\lambda = 0.4959$ Å) with silicone oil. Bottom peaks indicate reference peak positions from [14].