



A high-pressure X-ray diffraction study of the crystalline phases in calcium aluminate cement paste

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ABSTRACT

Calcium aluminate cement (CAC) has wide application in civil engineering and castable refractory materials. The main binding phases of hardened CAC paste, $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ (CAH_{10}), inevitably converts to $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$ (C_2AH_8), $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ (C_3AH_6) and $\text{Al}(\text{OH})_3$ (AH_3), leading to a significant change in the mechanical properties of the CAC matrix. This work investigates the mechanical properties of the main crystalline components in hydrated and/or converted CAC systems, using synchrotron-radiation-based high-pressure X-ray diffraction. The anisotropic deformations of CaAl_2O_4 (CA), CAH_{10} and C_3AH_6 along each crystallographic direction are investigated, along with their bulk moduli. The density-driven stiffening hypothesis is validated for the studied phases and other cement-based minerals. An atom-scale topological analysis is proposed to explain the unusually high stiffness of CAH_{10} . The results provide fundamental information to understand the mechanical properties of single cement-based phases at molecular level, and enable predicting the changing mechanical properties of converted CAC matrix using homogenization models.

1. Introduction

Calcium aluminate cement (CAC) is an important member of the hydraulic cement family. In contact with water, its main component CA (cement chemistry notation, $\text{C}=\text{CaO}$ and $\text{A}=\text{Al}_2\text{O}_3$) hydrates rapidly, accompanied by a quick heat-release and a fast strength-development. Such cementing performance leads to the wide application of CAC in civil engineering practices [1,2]. However since the 1970s the concrete community suggested to limit the use of CAC in structural application, due to increasing numbers of failure reports of CAC concrete over the long-term service life [1–4]. In recent years, standards have been proposed to guide the proper use of CAC concrete in civil engineering [2,5]. Nonetheless, CAC continues to be applied in infrastructures that face severe chemical and abrasive load [4]. It is also widely used in producing castable refractory linings [6].

The hydration path of CA is strongly temperature-dependent. It hydrates to form CAH_{10} ($\text{H}=\text{H}_2\text{O}$) when the curing temperature is below 15–20 °C, whereas $\text{C}_2\text{AH}_8 + \text{AH}_3$ is the product when the temperature is between 20 and 30 °C. In ordinary service condition, these

phases account for the rapid early age strength development. However, CAH_{10} and C_2AH_8 inevitably convert to $\text{C}_3\text{AH}_6 + \text{AH}_3$, as the latter phases are thermodynamically more favorable. This conversion reaction significantly accelerates when temperature is higher than 30 °C [7–10]. A recent micro-spectroscopic study reported that CAH_{10} easily converts to C_2AH_8 via a solid-state-reaction path where the ion redistribution happens in a very short range inside the CAH_{10} crystals, resulting in a nanometer scale C_2AH_8 sheet structure [10,11]. The formation of C_3AH_6 is, on the contrary, more likely through solution. Since C_3AH_6 and AH_3 have higher densities than CAH_{10} and C_2AH_8 , the conversion reaction significantly increases the porosity of the hardened matrix, and is therefore the major cause of the strength-loss of CAC concrete.

Homogenization modeling schemes have been proved successful in predicting the mechanical properties, such as elastic modulus, of hardened Portland cement (PC) matrix [12–14]. Such schemes require two types of input: 1) the microstructural information of each phase, i.e. the volume fraction, shape and size of the a single phase domain; 2) the mechanical property of each single phase. Experimental investigations

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of the mechanical property of CAC-based concrete [15,16] and refractory linings [17,18] have been reported, however a homogenization modeling based on the structural evolution has yet to be proposed. To enable such modeling, the modulus of individual phases in the CAC matrix is needed, yet such information has not been systematically reported by the cement and concrete research community. It is also of mineralogical and materials science interest to understand the molecular-scale mechanism of how these minerals deform under mechanical loading.

Synchrotron-radiation-based high-pressure X-ray diffraction (HP-XRD) is reported to be a reliable method to probe the mechanical property of (nano)crystalline cement-based phases. Compared with nano-indentation which measures the average information of solid and porosity at the microscale, HP-XRD has the advantage of measuring the intrinsic mechanical property of crystalline solids that contains no contribution from inter-particle pores. It also provides atomistic scale mechanism of the deformation of crystals [20–24]. The earlier HP-XRD study [25] and molecular calculation [26] of C_3AH_6 reported bulk modulus of 66 ± 4 GPa and 56.3 GPa, respectively. Both did not observe any pressure-induced phase transition. A high-pressure single crystal X-ray diffraction study reported the phase transition from $Ia3d$ to $I-43d$ symmetry at 5 GPa, [27] which is later confirmed by high-pressure neutron powder diffraction and infrared spectroscopic study [28]. The reported high-pressure diffraction work on CA mainly focuses on the chemical environment evolving with pressure and temperature increase, yet the lattice deformation is rarely reported [32,33]. There is no existing report on the HP-XRD work of CAH_{10} .

In the present work, we aim to investigate the mechanical properties of the three major components in hardened CAC matrix, i.e. CA, CAH_{10} and C_3AH_6 , using Synchrotron-radiation-based HP-XRD. The significance of the present study is twofold: 1) to provide the mechanical properties of the single phase as input for homogenization modeling of the macro-scale mechanical behavior of CAC-based matrix, which dynamically evolves via hydration and the conversion reaction; 2) to add to the basic understanding of the molecular-scale mechanism of the deformation of cement-based minerals.

2. Materials and methods

2.1. Materials

The CA and C_3AH_6 were provided by *Mineral Research Processing Cie.* Pure CAH_{10} crystals were prepared as described in the published work [9,10]. In brief, CA was mixed with deionized water with a water-to-solid ratio of 10, which was then cured at 8 ± 2 °C for seven days, followed by vacuum-filtering in a N_2 -protected glove box. The CAH_{10} solids were then stored at 5 ± 1 °C until the X-ray diffraction measurement. These phases were verified by a *PANalytical X'Pert Pro^{TR}* diffractometer using a Co anode.

The crystal structure of CAH_{10} is hexagonal, with space group $P6_3/m$, and lattice parameter $a = b \sim 16.3$ Å, $c \sim 8.3$ Å [29,30]. Under ambient condition, C_3AH_6 is commonly known and described as the garnet-mineral katoite, i.e. the OH-analogue of grossular. It has cubic symmetry with space group $Ia-3d$ and lattice parameter $a = b = c \sim 12.6$ Å [31]. There is no other polymorph of CAH_{10} or C_3AH_6 reported under ambient conditions. CA has at least three reported polymorphs as a function of temperature and pressure, and they may be retained in ambient condition after a quenching process [32–35]. From a lab XRD data, the CA used in this study best-fits the structure reported by Ref. [34], i.e. monoclinic space group $P 2_1/n$, with $a \sim 8.7$ Å, $b \sim 8.1$ Å, $c \sim 15.2$ Å, and $\beta \sim 90.2^\circ$.

2.2. Methods

The HP-XRD experiment was conducted at beamline 12.2.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National

Laboratory (LBNL), [36] using a BX90 diamond anvil cell [37]. A 250 μm steel gasket was pre-indenting to 80 μm thickness, and a 150 μm diameter hole was drilled into the pre-indentation using a laser mill. Sample powders, together with one ruby sphere (diameter 3–5 μm), were placed into the whole to fill about half the empty space, followed by a complete fill with a drop of liquid pressure medium (methanol: ethanol = 4:1 by volume). With tunable external loading values, all the solid phases in the chamber are subjected to hydrostatic pressure in the order of several GPa, which is precisely measured via the fluorescence signal of the ruby particle [38]. For each sample, 6–9 diffraction patterns were collected from ambient pressure up to 9–12 GPa, using synchrotron X-ray (wavelength ~ 0.49755 Å) as the incident beam.

The 2D diffraction pattern were integrated to diffractograms using *Dioplas* software [39]. For each sample, the positions of the strong and isolated diffraction peaks were tracked as functions of applied pressure, using the *XFIT* code [40]. The peak positions were then used to refine the lattice parameters under each pressure value, using the *CELREF* code [41]. This approach is applicable in the present study since the samples yield strong diffraction [22]. The pressure induced volumetric change is related to the bulk modulus by the second-order Birch-Murnaghan equation of state (BM-EoS) [42]:

$$P = \frac{3}{2}K_0 \left[\left(\frac{V}{V_0} \right)^{\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{\frac{5}{3}} \right] \quad (1)$$

where V_0 is the initial unit cell volume at ambient pressure; V is the unit cell volume at pressure P ; K_0 is the bulk modulus at ambient pressure. With the volumetric strain defined as $\varepsilon_V = 1 - V/V_0$, Eq. (1) is written as:

$$P = \frac{3}{2}K_0 \left[(1 - \varepsilon_V)^{-\frac{7}{3}} - (1 - \varepsilon_V)^{-\frac{5}{3}} \right] \quad (2)$$

Due to the limited experiment time available at synchrotron facilities, the first probed pressure value needs to be noticeable via ruby calibration, which is slightly higher than ambient condition. We use the diffractograms under this pressure value (~ 0.2 GPa) to refine the ambient lattice parameters of CAH_{10} and C_3AH_6 . Under the second-order BM-EoS, this leads to a deviation below 1 GPa in bulk modulus, which is smaller than the estimated uncertainty (~ 2 GPa), and is therefore considered acceptable. It will be later shown that the refined volumes under ~ 0.2 GPa are different from the reported ambient values by a negligible amount (smaller than refinement uncertainty). The first probed pressure for CA (3.5 GPa) is much higher than the ambient condition, therefore its ambient lattice parameters are refined from lab-XRD data.

3. Results

3.1. Diffractogram as a function of the applied hydrostatic pressure

The powder diffractograms of CA under increasing hydrostatic pressure are shown in Fig. 1. Note that the ambient pressure (0 GPa) data was not collected using HP-XRD and the lab XRD data is used instead. At ambient pressure, the strongest diffraction of CA is at $1/d \sim 0.337$ Å⁻¹, corresponding to the merged diffraction of the (123) and (220) peaks. These two peaks maintain the strongest diffraction along with the increased pressure. To the right-hand-side of the strongest diffraction, there exists a group of diffractions with $1/d$ ranging from 0.39 to 0.42 Å⁻¹; and to the left-hand-side there are several isolated peaks corresponding to the diffraction of individual Miller indices, as labeled by the red dashed lines in Fig. 1.

There is a clear peak position drifting as the pressure increases, since the lattice structure is compressed from all directions. The shortening of the interplanar distance thus shifts the diffraction peaks to the direction of increasing $1/d$. As the hydrostatic pressure increases, all diffraction peaks tend to decrease in their absolute intensities, accompanied by a significant broadening of the half peak width. This

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