



## Experimental and theoretical high pressure study of calcium hydroxyaluminate phases



A. Cuesta<sup>a</sup>, P. Rejmak<sup>b</sup>, A. Ayuela<sup>c</sup>, A.G. De la Torre<sup>d</sup>, I. Santacruz<sup>d</sup>, L.F. Carrasco<sup>e</sup>,  
C. Popescu<sup>a</sup>, M.A.G. Aranda<sup>a,d,\*</sup>

<sup>a</sup> ALBA synchrotron, Carrer de la Llum, 2-26, E-08290 Cerdanyola del Vallés, Barcelona, Spain

<sup>b</sup> Institute of Physics PAS, 02-668 Warszawa, Poland

<sup>c</sup> Centro de Física de Materiales CFM-MPC CSIC-UPV/EHU, Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco UPV-EHU, 20018 Donostia-San Sebastián, Spain

<sup>d</sup> Departamento de Química Inorgánica, Universidad de Málaga, Campus Teatinos S/N. 29071 Málaga, Spain

<sup>e</sup> Departament d'Enginyeria Civil i Ambiental, Universitat Politècnica Catalunya. BarcelonaTECH, 08028 Barcelona, Spain

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### ABSTRACT

Five calcium hydroxyaluminate phases have been investigated by synchrotron powder diffraction at high-pressure: two hydrogarnets, kuzelite, stratlingite and ettringite. The obtained bulk modulus,  $K_0$ , for kuzelite, stratlingite and ettringite were 23(1), 27(1) and 30(3) GPa, respectively. Kuzelite and stratlingite underwent transformations above 1 GPa likely releasing interlayer water. Kuzelite becoming markedly amorphous and stratlingite remained crystalline,  $K_0 = 58(6)$  GPa in the 1.5–5.5 GPa pressure range. The structural behavior for hydrogarnet samples is prone to the use of pressure transmitting media.  $K_0$  for  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  was 81(2) and 76(2) GPa for silicone oil and alcohol mixture, respectively. A similar study for  $\text{Ca}_3\text{Al}_{1.7}\text{Fe}_{0.3}(\text{OH})_{12}$  yielded 73(1) and 58(1) GPa for silicone oil and alcohol mixture, respectively. Atomistic calculations using periodic Density Functional Theory showed that the softening in iron-doped katoite, when compared to stoichiometric katoite, can be assigned primarily to greater compressibility of Ca—O dodecahedra, which overcompensates strengthening of hydrogen bonding between Al/Fe hydroxide groups.

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### 1. Introduction

The reaction between Portland cement phases and water yield amorphous and crystalline hydration products [1]. The most important hydration product is calcium silicate hydrate (C–S–H), which is poorly crystallized and it constitutes over half of the volume of the paste. The most common crystalline hydration products are portlandite,  $\text{Ca}(\text{OH})_2$  and calcium hydroxyaluminate phases: AFm and Aft. AFm stands for the abbreviation ‘alumina, ferric oxide, mono-sulfate’ or ‘ $\text{Al}_2\text{O}_3$ – $\text{Fe}_2\text{O}_3$ –mono’ and it refers to a family of hydrated calcium hydroxyaluminates based on the hydrocalumite structure,  $\text{Ca}_4\text{Al}_2(\text{OH})_{12} \cdot [\text{Cl}(\text{OH}) \cdot 6\text{H}_2\text{O}]$ . The archetype AFm phase is  $\text{Ca}_4\text{Al}_2(\text{OH})_{12} \cdot [\text{SO}_4 \cdot 6\text{H}_2\text{O}]$  known as kuzelite, but Al can be partly replaced by Fe and  $\text{SO}_4^{2-}$  can be partly or fully replaced by  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SiO}_4^{4-}$  and other anions [2,3]. The different hydration stages within the layers strongly influence the X-ray powder diffraction patterns [4,5]. Similarly, Aft stands for ‘alumina, ferric oxide, tri-sulfate’ or ‘ $\text{Al}_2\text{O}_3$ – $\text{Fe}_2\text{O}_3$ –tri’. The most common Aft phase is ettringite which has the following stoichiometry

$\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ . Additionally, there are other calcium hydroxyaluminate phases like hydrogarnet. This family of phases, based on  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , forms from the hydration of the calcium aluminate and ferrite phases in specific conditions and so there are present in small amounts in some OPC pastes.

During the hydration of calcium aluminate cements,  $\text{CaAl}_2\text{O}_4$  being the main phase, and depending on temperature and pore solution composition, hydrogarnet phases precipitate. Initial phases can be metastable and finally convert to the stable cubic hydrate, hydrogarnet,  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , also known as silicon-free katoite [6–8]. At temperatures higher than 30 °C,  $\text{CaAl}_2\text{O}_4$  hydrates according to reaction (1).

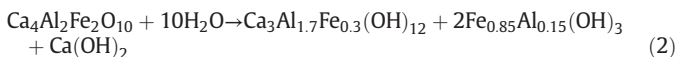


$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$  is present in ordinary Portland cements, calcium aluminate cements and in calcium sulfobelite cements [9–11]. The hydration of this phase is similar to the hydration of calcium aluminate phases although the hydration products partially incorporate iron [12–14]. In a previous work, the stoichiometry of the iron-hydrogarnet formed in the hydration reaction of  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$  was determined by synchrotron X-ray powder diffraction and Rietveld analysis, according to reaction (2) [15], where this iron-containing katoite,

\* Corresponding author at: ALBA synchrotron, Carrer de la Llum, 2-26, E-08290 Cerdanyola del Vallés, Barcelona, Spain.

E-mail address: [migarcia@cells.es](mailto:migarcia@cells.es) (M.A.G. Aranda).

$\text{Ca}_3\text{Al}_{1.7}\text{Fe}_{0.3}(\text{OH})_{12}$ , was the only observed crystalline phase:



Silicon-free katoite is reported to be the only thermodynamically stable calcium hydroxyaluminate hydrate in cement pastes [16]. The crystal structure of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , belonging to space group  $Ia\bar{3}d$ , is well known [17]. Moreover, it has been recently reported that  $\text{Al}^{3+}$  can be partially replaced by  $\text{Fe}^{3+}$  in silicon-free katoite [15] as well as in silicon-containing katoites [18].

On the other hand, the bulk modulus is one of the key mechanical properties of structural materials including cement hydration products. This parameter can be determined from several approaches including X-ray powder diffraction with samples loaded in diamond anvil cells (DAC). In this context, it must be noted that the use of synchrotron radiation to characterize cement hydrated phases under pressure has been recently reviewed [19] and that computational methods are important for validating, and a better understanding of, the experimental results [20]. Powder diffraction using DAC approach has been used to study the behavior of C–S–H and related compounds [21–24]. Several AFm type-phases have also been studied, hemicarboaluminate with  $K_0 = 15$  GPa [25], monocarboaluminate with  $K_0 = 54$  GPa [26] and stratlingite with  $K_0 = 23$  GPa [25]. The mechanical properties of monocarboaluminate have also been investigated by first-principle calculations [27]. We note that to the best of our knowledge, kuzelite has not been studied at high pressures. AFt has been studied by powder diffraction up to 6 GPa. The two main outputs of this study were the isothermal bulk modulus of ettringite, 27 GPa, and its transformation to an amorphous phase at pressures above 3 GPa [28]. The mechanical properties of ettringite have also been studied by single crystal methods [29] and by theoretical calculations [30].

The high-pressure behavior and bulk modulus of silicon-free katoite have been thoroughly studied experimentally, by using single crystal and powder diffraction, as well as by using computational methods. In an initial work [31], a bulk modulus of 66(4) GPa for  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  was determined from energy-dispersive X-ray diffraction being much smaller than that of grossular,  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ , 168(25) GPa, as expected. A subsequent neutron powder diffraction work [32] gave a bulk modulus of 52(1) GPa. Part of these authors extended this research by using single crystal X-ray diffraction with 4:1 methanol:ethanol mixture in a DAC [33]. An unconstrained third-order Birch-Murnaghan fit for  $Ia\bar{3}d$  symmetry gave  $V_0 = 1987.6(1) \text{ \AA}^3$ ,  $K_0 = 58(1)$  GPa and  $K_0' = 4.0(7)$ . Furthermore, above  $\sim 5$  GPa a phase transition was reported to a structure in space group  $I\bar{4}3d$ . The last experimental study was carried out in a sample containing also hemicarboaluminate using both silicone oil and methanol/ethanol as pressure transmitting medium (PTM) [25]. Second-order Birch-Murnaghan fits ( $K_0'$  fixed to 4.0) gave  $K_0$  values of 69(4) and 72(4) GPa and  $V_0$  values of 1987.1 and 1984.5  $\text{ \AA}^3$  for the alcohol mixture and silicone oil datasets, respectively.

Computational methods also give a wide range of bulk modulus values for silicon-free katoite. In the first study [34], an *ab initio* investigation gave  $V_0 = 2021.8 \text{ \AA}^3$ ,  $K_0 = 56(1)$  GPa and  $K_0' = 3.6(1)$ . Subsequently, a periodic *ab initio* quantum mechanical study with the CRYSTAL program was undertaken by using a Gaussian type basis set and both Hartree-Fock (HF) and hybrid B3-LYP methods [35]. The obtained bulk moduli were very similar, 67 and 68 GPa for HF and B3-LYP studies, respectively. However, the  $V_0$  values showed a significant spread, 2051.8 and 2024.2  $\text{ \AA}^3$ , for HF and B3-LYP studies, respectively. Finally,  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  has been very recently reinvestigated with an *ab initio* simulation performed at the B3-LYP level of theory, by using all-electron basis sets with the CRYSTAL periodic program [36]. In this work, a deep study of the evolution of the crystal structure under pressure, up to 60 GPa, was undertaken mainly focused on the interatomic distances involving hydrogen atoms. The calculations for  $P = 2$  GPa gave 74 and 75 GPa for the bulk modulus, derived from selected elastic

constants of katoite and from the Birch-Murnaghan EoS, respectively. Furthermore, the existence of a phase transition at high pressures to a lower symmetry phase, space group  $I\bar{4}3d$ , was validated but interestingly, the  $Ia\bar{3}d$  phase becomes the lowest energy phase at very high pressures.

The main aim of this work is to study the behavior under pressure of calcium hydroxyaluminate phases. Stoichiometric katoite,  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , stratlingite,  $\text{Ca}_4\text{Al}_2(\text{OH})_{12}[\text{Al}_2\text{Si}_2\text{O}_4(\text{OH})_8 \cdot 6\text{H}_2\text{O}]$ , and ettringite,  $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ , have been investigated as reference materials. Chiefly, we report new data for silicon-free iron-containing katoite,  $\text{Ca}_3\text{Al}_{1.7}\text{Fe}_{0.3}(\text{OH})_{12}$  and kuzelite,  $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{SO}_4) \cdot 6\text{H}_2\text{O}$ . Furthermore, selected experiments were carried out using two different PTM: silicone oil which serves as a quasi-hydrostatic PTM, and methanol-ethanol as hydrostatic PTM. The selection of the PTM is important as it should not induce any structural modification to the studied phase and it must allow the widest possible pressure range. For the theoretical study of katoites, atomistic calculations using periodic Density Functional Theory have been carried out.

## 2. Experimental section

### 2.1. Sample preparation

Stoichiometric katoite,  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ , was prepared following two different methodologies:

A first sample was synthesized by hydrating  $\text{Ca}_3\text{Al}_2\text{O}_6$  at a water-to-solid mass ratio of 1 during one week at room temperature (RT). The resulting powder was finally dried at 50 °C.  $\text{Ca}_3\text{Al}_2\text{O}_6$  was synthesized by using suitable amounts of  $\text{CaCO}_3$  (99.95%, Alfa-Aesar) and  $\text{Al}_2\text{O}_3$  (99.997%, Alfa-Aesar). The mixture was preheated at 1000 °C for 6 h and ground for 15 min in an agate mortar. The resulting powder was die-pressed and heated at 1450 °C for 6 h. This sample resulted in a single phase crystalline  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  powder according to reaction (3):



It is important to clarify that initially  $\text{Ca}_3\text{Al}_2\text{O}_6$  reacts quickly with water to form metastable platelets of calcium aluminate hydrates (Eq. (4)) and finally the conversion to  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  takes place.



A second katoite sample was prepared by hydrating  $\text{CaAl}_2\text{O}_4$  at a water-to-solid mass ratio of 1 for eight days at 50 °C. The sample was filtrated in a Whatman system (90 mm diameter Whatman filter with a pore size of 2.5  $\mu\text{m}$  on a Teflon® support) and washed twice with acetone and finally with ether [37]. In this case, a mixture of crystalline  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  and poorly-crystalline gibbsite,  $\text{Al}(\text{OH})_3$ , was obtained as evidenced by X-ray powder diffraction according to reaction (1).  $\text{CaAl}_2\text{O}_4$  was prepared by using suitable amounts of  $\text{CaCO}_3$  (99.95%, Alfa-Aesar) and  $\text{Al}_2\text{O}_3$  (99.997%, Alfa-Aesar). The mixture was ground in a Fritsch planetary mill (model Pulverisette 7, with a 45  $\text{cm}^3$  agate vessel containing 7 agate balls with a diameter of 15 mm) during 30 min. The resulting powder was heated at 1250 °C for 1 h and finally heated twice at 1300 °C during 2 h.

Iron-containing katoite,  $\text{Ca}_3\text{Al}_{1.7}\text{Fe}_{0.3}(\text{OH})_{12}$ , was obtained by hydrating ferrite,  $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ , see reaction (2), as previously reported [15]. In that work, high-resolution SXRPD was employed to study the crystal structure of crystalline  $\text{C}_3(\text{A},\text{F})\text{H}_6$  obtained by direct hydration of  $\text{C}_4\text{AF}$ . The structural description reported by Lager et al. [17] was used as a starting model. The final Rietveld refinement of this dataset converged to an Fe/Al ratio of 0.18.

The sample containing kuzelite and ettringite phases was prepared as follows: 2 g of ye'elimite, prepared as reported in [38], were weighted and the exact amount of water was added to obtain a weight water-to-solid ratio of 2.5. The paste was mixed by hand for 2 min and then it was

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