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RESEARCH

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Fundamental Discrepancy of Chemical Reactivity of Tricalcium Oxy Silicate (alite), Dicalcium Silicate (Belite), and Their Polymorphs: A Density Functional Theory Study

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Abstract

Tricalcium oxy silicate (C_3S) and dicalcium silicate (C_2S) are the major constituents of cement. In this study, the reactivity of polymorphs of calcium silicates is quantitatively investigated using Density Functional Theory. The result of combining the DFT calculation and the Bader charge analysis elucidates that the main difference in reactivity between C_3S and C_2S is the presence of oxy ions in C_3S which has smaller partial charge compared to that of other oxygen in the crystals. For the C_3S, the reactivity of among different C_3S polymorphs is decisively affected by the Bader charge of oxy ions. In contrast, total internal energy of C_2S determines the quantitative chemical reactivity of C_2S polymorphs. This result suggests that oxy ion has more dominant impact on the thermodynamic stability of calcium silicates. Furthermore, total energy can be used to estimate the chemical reactivity of calcium silicates, where there is no oxy ion exists.

Keywords: cement, alite, belite, reactivity, density functional theory

1 Introduction

Two major constituents in ordinary Portland cement (OPC) are tricalcium oxy silicate ($Ca_3O(SiO_4)$, Alite) and dicalcium silicate ($Ca_2(SiO_4)$, Belite). In cement chemistry notation ($C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $Fe=Fe_2O_3$), alite and belite are C_3S and C_2S, respectively (Taylor, 1997). It is well known that these constituents undergo hydration with water, turning them into phase formation of C–S–H gel and portlandite which determines the most of engineering properties of cement-based materials (Barnes & Bensted, 2002). These minerals have different polymorphs depending on conditions, such as sintering temperature and ion substitution (Balonis & Glasser, 2009). For example, it has been reported that there are seven (M1-, M2-, M3-, T1-, T2-, T3-, R-C_3S) and five (α-, α'_H-, β-, α'_L-, γ-C_2S) polymorphs existing for alite and belite, respectively (Courtial et al., 2003; Cuberos et al., 2009; Taylor, 1997; Torre et al., 2008). These polymorphs have identical chemical formula but some of them have different crystal structures. For example, M, T, and R in alite polymorphs refers to monoclinc, triclinic, and rhombohedral crystal structure, respectively. Recently, Plank revisited the key difference between the alite and belite is the existence of interspersed oxide anions, O^{2-} between Ca^{2+} and $SiO_4{}^{4-}$ tetrahedra in alite, while belite only contains ortho silicate $SiO_4{}^{4-}$ units and Ca^{2+} cations. This makes significant differences between these two calcium silicate minerals including higher required calcination temperature, higher reactivity, and more formation of portlandite in alite crystal (Plank, 2020). Therefore, he concluded that the correct nomenclature of alite should be tricalcium oxy silicate ($Ca_3O(SiO_4)$) not

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the conventionally used tricalcium silicate ($3CaO.SiO_2$). Following the suggestion, the corrected nomenclature has been used in this study.

Given the mineralogical similarities among those minerals, quantitative research on the reactivity of alite, belite, and polymorphs is very challenging and has not been fully investigated experimentally and computationally. For example, clear relationship of chemical reactivity among different calcium silicates has not been completely elucidated although it has been using over hundred years. Several experimental methods have been applied to build the relationship between the reactivity differences between polymorphs of each alite and belite crystals. For the five polymorphs of belite, the experimental results showed that the reactivity order is $\alpha\text{-}C_2S > \alpha'_H\text{-}C_2S > \beta\text{-}C_2S > \alpha'_L\text{-}C_2S > \gamma\text{-}C_2S$ (Bensted, 1978; Cuberos et al., 2009; Fukuda & Taguchi, 1999; Wang et al., 2014). In the case of alite, only three polymorphs have been studied as the order of reactivity is known as $R\text{-}C_3S > T1\text{-}C_3S > M3\text{-}C_3S$ (Harada et al., 1978). Although these experimental results are valuable in terms of producing optimized cement phases and developing more sustainable cements, more fundamental-level analysis is required for better understanding the origin of different reactivities between alite and belite as well as among different polymorphs, especially in a quantitative manner. Due to the fact that those crystals have high similarities and uncertainty of having other factors determining the crystal structure, such as ion substitution (Bensted, 1978; Cuberos et al., 2009; Fukuda & Taguchi, 1999), experimental investigation on the reactivity of those crystals is quite challenging.

To investigate the fundamental discrepancy of the reactivity of calcium silicates, it is appropriate to compare the reactivity of pure polymorphs without the potential effect from ion substitution. Given the complexity of synthesizing pure phases without ion substitutions, Density Functional Theory (DFT) method can be advantageous because of the high accuracy of calculation relying on quantum mechanics. The study of the reactivity of calcium silicates using DFT calculation has been continuously conducted by identifying the energy gap and the density of states (DOS) of the cement-based minerals for studying reactivities, surface energies, and water dissociation (Durgun et al., 2014; Huang et al., 2014; Wang et al., 2014; Wang et al., 2014). The relation between reactivity and electronic structure of $\alpha'_L\text{-}C_2S$, $\beta\text{-}C_2S$ and $\gamma\text{-}C_2S$ is explained by PDOS analysis (Wang et al., 2014). The research on water adsorption in $\beta\text{-}C_2S$ has been conducted with additional DFT calculation and PDOS analysis (Wang et al., 2018). The polymorphism of belite is also been reveled (Rejmak et al., 2019). The explanation on reactivity of doped cement clinkers were done through calculation of local charge densities and partial density of states (Tao et al., 2019). The previous research using other analysis including DOS analysis was meaningful in studying reactivity from a point of view on energy of crystals, but there has been no clear quantitative order of investigation among all reported polymorphs of calcium silicates.

In this study, the relationship between energy and reactivity of calcium silicates was quantitatively investigated through DFT calculation. In addition, attempts were made to elucidate the reactivity of each polymorph of calcium silicates in terms of atoms with the data of Bader charge analysis, which has been first reported herein.

2 Crystal Structures and Computational Methods

2.1 Crystal Structure Selection for Computation

Fig. 1 shows the phase change processes according to the temperature between polymorphs of belite and alite in the published order of each reactivities (Bensted, 1978; Cuberos et al., 2009; Fukuda & Taguchi, 1999; Wang et al., 2014). Belite exists in the state of $\alpha\text{-}C_2S$ having a hexagonal crystal structure above 1425 °C. It changes to the polymorphic states of $\alpha'_H\text{-}C_2S$, $\alpha'_L\text{-}C_2S$, and $\beta\text{-}C_2S$ as the temperature decreases, and to $\gamma\text{-}C_2S$, a polymorph that rarely reacts with water at lower temperature. All of these belong to the same space group of orthorhombic crystal structure except for $\beta\text{-}C_2S$ having a monoclinic crystal structure. Alite belongs to three space groups of rhombohedral, monoclinic, and triclinic crystal structure depending on the sintering temperature. Monoclinic and triclinic crystal structures have three polymorphs each, so they are numbered in the order of low temperature to distinguish them. Although alite has a triclinic crystal

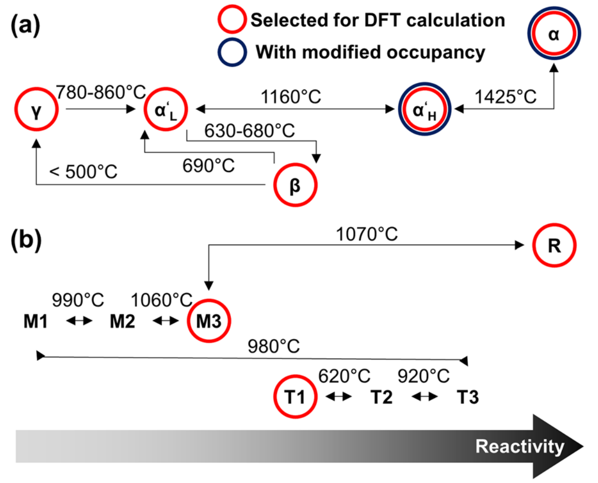

Fig. 1 High-temperature phase transition among **a** belite and **b** alite polymorphs.

structure at room temperature, it changes to monoclinic and rhombohedral crystal structure as the temperature rises. Unlike belite, where all polymorph structures (including atomic positions) are known, only three crystal structures have been revealed for alite polymorphs. Therefore, DFT calculations were performed on the 8 crystal structures marked with red circles whose crystal structures have been identified to date. In the case of α-C_2S and α'$_H$-C_2S, partial occupancy exists in the original crystal structures, which was artificially modified to satisfy their chemical formula.

2.2 Computational Details

Quantum Espresso DFT package was used for modelling calcium silicates (Giannozzi et al., 2009). The initial models of the C_2S and C_3S were taken from the known lattice parameters (Additional file 1: Table S1) (Balonis & Glasser, 2009). In α-C_2S and α'$_H$-C_2S, since the early model had atoms with partial occupancy, the atoms were properly removed considering their chemical formula. In all of the cases, relaxation with and without lattice parameter optimization were separately performed to represent a potential state of crystal structure including the relative positions of individual atoms at 0 K and room temperature, respectively. The DFT calculations were performed using Perdew–Burke–Ernzerhof (PBE)–Generalized-Gradient-Approximation (GGA) exchange–correlation functionals, because previous DFT study on the PBE–GGA shows higher accuracy for cement crystals than Local-Density-Approximation (LDA) functionals (Moon et al., 2015). The energy convergence threshold and force convergence threshold were set to 10^{-3} Ry and 10^{-4} Ry/au, respectively. The pseudopotentials were made by ultrasoft-postprocessing. The plane-wave basis set was converged with the energy cutoff of 800 Ry. The structural models of all crystals were relaxed with the Broyden–Fletcher–Goldfarb–Shanno algorithm. Gamma-point sampling was used due to the large size of the unit cell.

Fig. 2 shows the obtained energy-unit cell volume curves of calcium silicates. Circled dots indicate the volume and energy values of crystal structures according to the applied pressure from -3 GPa to 3 GPa. For normalization purpose, each value was calculated by dividing by the Z value corresponding to the multiple of the formula present in each unit cell. The filled circles indicate the vc-relax points that have been optimized by releasing both the lattice parameter and atomic positions. These vc-relax points show the state at 0 K, which is the stable state owing to the lowest energy of corresponding crystal structure. Relax points marked with an X represent crystal structures that release only the atomic positions without optimizing the lattice parameters. Therefore, atomic positions of each atom were determined with the lowest internal energy under the given lattice parameters.

Bader charge analysis was separately performed using the DFT simulation results of lattice parameters and atomic positions of the crystal structure. The Bader

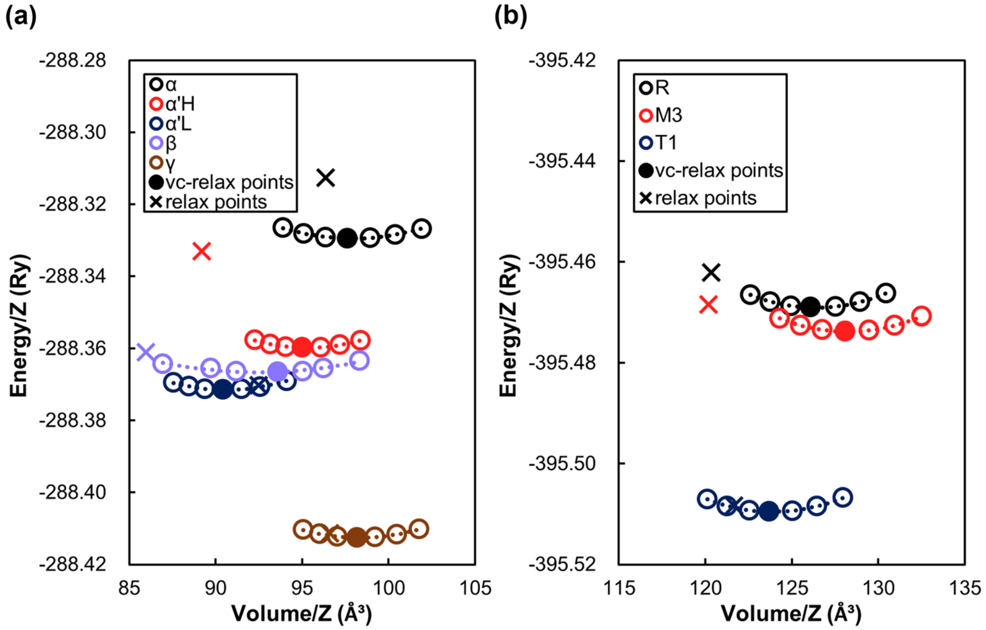

Fig. 2 Energy variation of polymorphs of **a** belite and **b** alite crystals.

charges of each atoms were calculated based on the number of electrons reduced or increased when a stable crystal structure was obtained compared to the number of valence electrons originally possessed by a neutral atom (Arnaldsson & Jonsson, 2006; Bader, 1990; Sanville et al., 2007; Tang & Sanville, 2009; Yu & Trinkle, 2011).

3 Computational Results

3.1 Optimization of Atomic Positions

Fig. 3 shows the final unit cells of crystal structures with optimized atomic positions of belite and alite. Additional file 1: Table S1 summarizes the changes in lattice parameters and energy/Z value before and after the optimization. In all polymorphs of belite, there was no significant change in angles of cell structure. On the other hand, the change in length was relatively prominent. α-C_2S showed the largest change, where length of *a* increased by 9.25% and length of *c* decreased by 4.76%. The overall change of length of *a*, *b*, and *c* showed a tendency to change less as it approached the more stable polymorph γ-C_2S. This can be interpreted as the higher the reactivity, the higher the temperature that can be stabilized, and the difference from the optimized crystal structure at 0 K is significant. The polymorphs of alite showed less change in lattice parameters than those of belite. There was no significant change in angles of cell structure as observed in the change of belite.

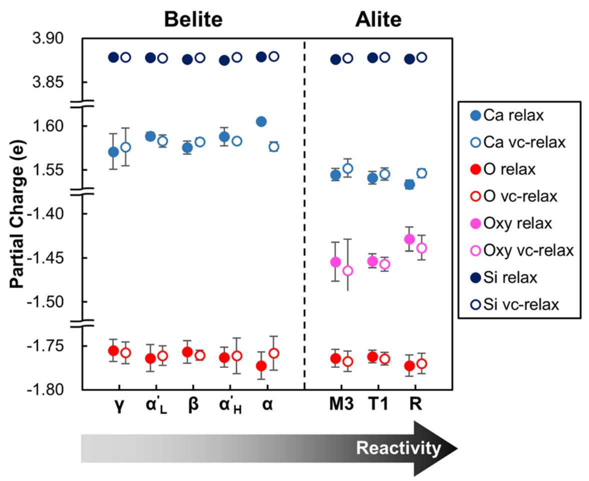

Fig. 4 Partial charge of atoms of belite and alite polymorphs.

3.2 Bader Charge Analysis

Fig. 4 shows the average value and the standard deviation of the partial charge of all atoms in belite and alite. In all belite polymorphs, the partial charge difference before and after optimization was negligible. Almost no difference within 0.01 e was shown after the optimization. In calcium and oxygen atoms, the difference before and after optimization in α-C_2S, which is the most reactive polymorph, was large. This can suggest

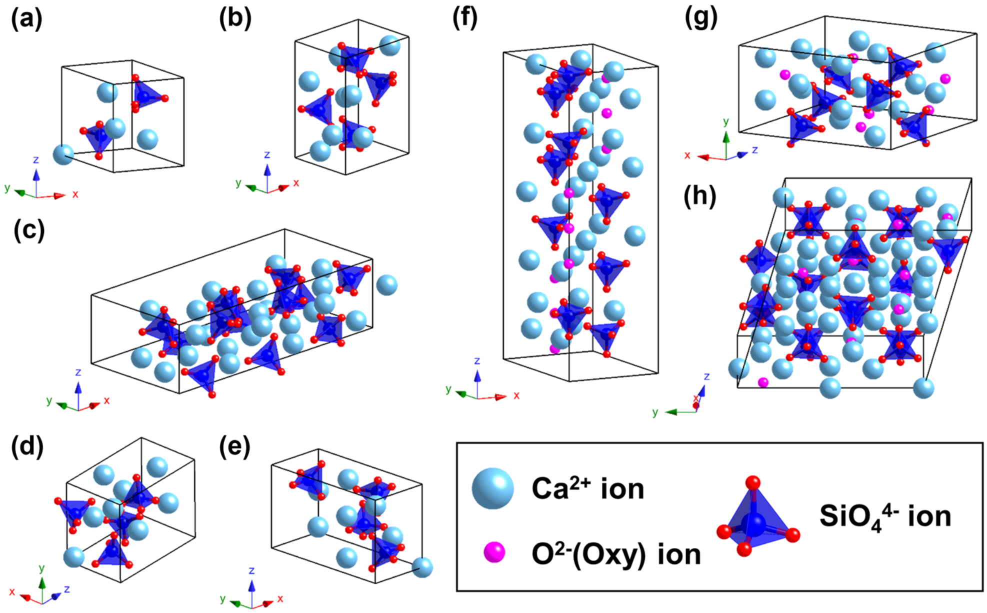

Fig. 3 Unit cells of crystal structures with optimized atomic positions of **a** α-C_2S, **b** α'$_H$-C_2S, **c** α'$_L$-C_2S, **d** β-C_2S, **e** γ-C_2S, **f** R-C_3S, **g** M3-C_3S and **h** T1-C_3S.

that α-C_2S might be difficult to exist at room temperature without ion substitution.

In all polymorphs of alite, the difference before and after optimization was found to be within 0.012 e. In addition, there was no significant difference between the polymorphs in both cases. A significant difference about 0.3 e in partial charge value between oxy ions and O atoms in SiO_4 tetrahedra has been found. Furthermore, the variation of oxy ions was large, and the charge of Ca ions was 0.03 e lower than that of belite. Since this is not an error within the standard deviation, it can be interpreted that it is due to oxy ions not present in belite.

4 Discussion on Dominant Reactivity Factor

4.1 Dicalcium Silicate

The total internal energy was calculated differently according to the crystal structure, and the difference in reactivity was quantitatively well explained, as shown in Fig. 5. This tendency was confirmed in the comparison before and after optimization. Regardless of the cell relaxation, it can be directly confirmed that there is a proportional relationship between the chemical reactivity and total internal energy of dicalcium silicate. The partial charge of the oxygen atom did not show a significant relationship with the difference in reactivity between polymorphs, as shown in Fig. 4. Likewise, partial charges of calcium and silicon ions also showed little variation.

4.2 Tricalcium Oxy Silicate

Total internal energy was calculated differently according to the crystal structure, and unlike belite, there was no correlation between reactivity and total internal energy among polymorphs. However, the charge of oxy ions well explained the difference in reactivity. This tendency appeared well before and after optimization. Due to the presence of these oxy ions, the change in partial charge of calcium ions also occurred. The partial charge of calcium ions in alite was about 0.03 e lower when compared to belite. This refers to the low electrical attraction of calcium ions and oxy ions, and it explains relatively high reactivity and solubility than belite. In particular, this tendency was consistent with the known order of reactivity of alite.

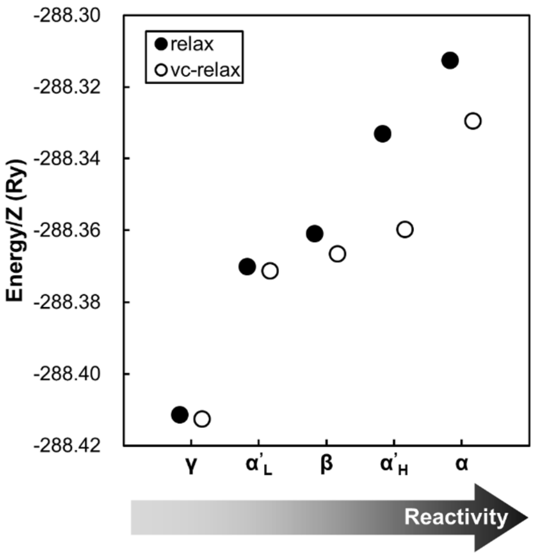

Fig. 5 Total energy/Z vs reactivity of belite.

4.3 Distortion of SiO_4 Tetrahedra

Fig. 6 shows the degree of distortion of SiO_4 tetrahedra of belite and alite. In both cases, there was no significant difference in Si–O distance, O–Si–O angle and volume of SiO_4 tetrahedra between polymorphs. These results suggest that SiO_4 tetrahedra has strong covalent bonds on its own, so it is not easily broken upon reaction. This eventually explains that orthosilicate ions do not significantly affect the difference in reactivity between polymorphs, rather than calcium or oxy ions.

5 Conclusions

The study revealed the origin of discrepancy of chemical reactivity among the polymorphs of belite and alite. First, it was suggested that the reactivity difference between belite and alite would be related to the presence or absence of oxy ions by comparing the partial charge of O atoms in SiO_4 tetrahedron in oxy ions. This finding consists with the conclusion drawn from similar DFT calculation on calcium silicates (Durgun et al., 2014; Saritas et al., 2015). In addition, the difference in reactivity between polymorphs in belite is closely related to the difference in energy per molecule in crystalline structures that causes instability in the crystal structure. Aside from the difference in energy, alite in which oxy ions exist is thought to increase reactivity as the partial charge of oxy ions decreases as the oxy ions become lower. As a result of comparing between before and after optimization, the polymorphs were more stable when optimization was performed. It has also been found that the degree of distortion of SiO_4 does not significantly differ depending on the polymorph, and thus has less influence on the reactivity of belite and alite.

The methodology to evaluate the chemical reactivity of crystals proposed herein, can be further applicable to investigate thermodynamic stability or reactivity of other C_3S-like minerals (e.g., $M_3O[TO_4]$) containing oxy ion. Additional studies can be also performed on other important cement clinker materials, such as tricalcium aluminate (C_3A) and tetracalcium

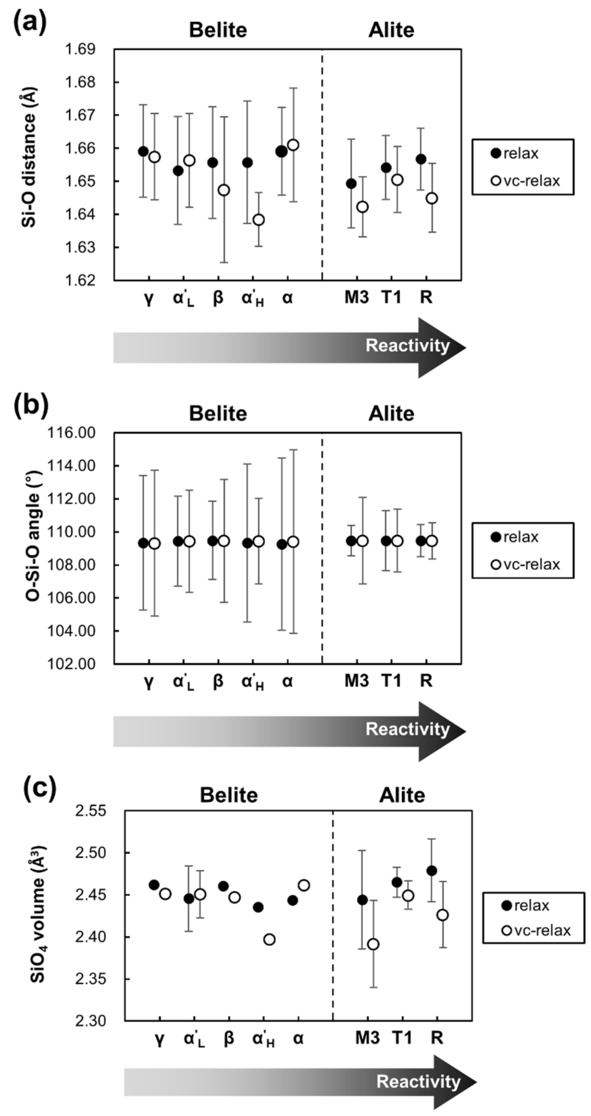

Fig. 6 **a** Si–O distance, **b** O–Si–O angle and (**c**) volume of SiO_4 tetrahedra in calcium silicates.

aluminoferrite (C_4AF), following the research on solubility of C_3A and C_4AF (Myers et al., 2017; Plank, 2020; Wang et al., 2014).

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40069-022-00539-3.

Additional file 1: Table S1. Cell parameters and total energy of unit cells of belite and alite. **Table S2.** Partial charge value of atoms in belite and alite. **Table S3.** Si-O distance, O-Si-O angle, total volume of SiO_4^{4-} tetrahedra of belite and alite.

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Author contributions

SK: investigation, data curation, formal analysis, visualization, and writing—original draft. YL: investigation. JP: conceptualization, writing—reviewing, and editing. JM: methodology, writing—reviewing and editing, and supervision. All authors read and approved the final manuscript.

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Availability of data and materials

All the data sets associated with this study are available from the corresponding author upon request.

Declarations

Ethics approval and consent to participate

All authors of the manuscript confirm the ethics approval and consent to participate following the Journal's policies.

Consent for publication

All authors of the manuscript agree on the publication of this work in the International Journal of Concrete Structures and Materials.

Competing interests

The authors declare no conflict of interest.

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