Research Article

Lin Chi, Ailian Zhang, Zedong Qiu, Linchun Zhang, Zheng Wang, Shuang Lu*, and Dezhi Zhao

Hydration activity, crystal structural, and electronic properties studies of Ba-doped dicalcium silicate

https://doi.org/10.1515/ntrev-2020-0082
received September 14, 2020; accepted September 30, 2020

Abstract: High belite cement has a wide application potential due to its low energy consumption, low CO2 emission, and excellent durability performance. Due to the low hydration rate and strength development at an early age, the activation of beta-dicalcium silicate (β-C2S) crystallographic structure is essential to improve the early strength of high belite cement. In this study, the β-C2S phase is activated by dissolving Ba2+ ions into the crystal lattice to improve the hydration rate. Unlike the traditional analysis methods of thermodynamics and dynamics theory, the first principle and density functional theory were applied to study the effect of Ba2+ ions on the activation of β-C2S, especially on the crystallographic structure, lattice parameters, and electronic structure change. The crystallographic structure of β-C2S can be activated by doping Ba atom and the crystal formation energy increases and the bandgap between VBM and CBM become narrow in the activated β-C2S crystallographic structure. Comparing the Ca2+ substitution in [CaO6] or [CaO8], the lattice deformation and hydraulic reactivity is more significant in Ba2+-C2S and Ba2+2-C2S. The first principle and density functional theory explains the change of the electronic structure of the activated crystallographic structure and provides a theoretical basis for the purposeful design of material structures.

Keywords: crystallographic structural, electronic properties, dicalcium silicate

Highlights

1. The electron structure variation is related to the variation of charge exchange and atomic hybridization orbital in Ba-doped β-C2S.
2. The lattice deformation and hydraulic reactivity are more significant in Ba-doped β-C2S with Ba → Ca/[CaO6].
3. The crystal formation energy increases and the bandgap between VBM and CBM become narrow in Ba-doped β-C2S.

1 Introduction

The traditional cement manufacture has been lasting for less than 200 years. Due to the consumption of high-grade limestones, the high-grade limestone resource in our country is not enough for the next 40 years [1,2]. Therefore, low-grade ore should be used in cement manufacture in point of view of sustainable development. High belite cement has a wide application potential due to its low energy consumption, low CO2 emission, and excellent durability performance [3–8]. Compared with Ordinary Portland cement, high belite cement consists of more than 40% dicalcium silicate (C2S) [9,10]. Due to its low CaO consumption, the cement calcining process becomes more energy-saving and a large sum of low-grade ore can be recycled [11–13].

β-C2S belongs to an island structure, due to the lack of coplanar structure in the [CaO6]2x−2 polyhedron, the length of the Ca2+ ion migration path is quite long, thus inhibits the hydraulic reaction of β-C2S during the hydration process [14,15]. Due to the low hydration rate and strength development in an early age, the application of high-belite cement is limited. The activation of the C2S
crystallographic structure is essential to improve the early strength of high belite cement. By calcining at high temperature, dopant ions are incorporated in the crystal lattice of $\beta$-C$_2$S in the form of the lattice vacancy or site substitution [16,17]. With the reduction of the crystal symmetry and the formation of crystal lattice distortion, the microstress in the lattice increases and the lattice activation of $\beta$-C$_2$S is achieved. Activators such as As$_2$O$_5$, V$_2$O$_5$, CrO$_3$, MgO, BaO, CrO, P$_2$O$_5$, R$_2$O, etc. are commonly used in cement industry production [18,19]. At the same time, the addition of activators can effectively reduce the formation energy in chemical reaction thermodynamics [3].

Many researches have studied the activation mechanism of doped ions on the crystal structure transformation of $\beta$-C$_2$S [16,20–23]. Cuesta et al. [24] studied the activation mechanism of doped B$^{3+}$ ions on belite cement and found that Ca$^{2+}$ ions and Si$^{4+}$ ions in the [SiO$_4$] tetrahedron have been replaced, which contributes to the hydraulic reaction during cement hydration. Wang et al. [25] studied the activation effect of BaSO$_4$ on $\beta$-C$_2$S in belite cement clinker during calcination, and the results showed that BaSO$_4$ could dissolve into the crystal structure of $\beta$-C$_2$S and improve the early compressive strength.

The first principle and density functional theory can explain the change of the electronic structure of the activated crystal structure and also provide a theoretical basis for the purposeful design of the material structure [26–28]. Based on the traditional thermodynamics and kinetics theory, first-principles quantum mechanics calculations have been applied to study the relationship between electronic structure and reaction activity of C$_2$S polymorphs [29,30]. In this study, the $\beta$-C$_2$S phase is activated by dissolving ions into the crystal lattice to improve the hydration rate. The first principle and density functional theory were applied to study the effect of different ions on the activation of C$_2$S, especially on the crystallographic structure and lattice parameters and electronic structure change.

## 2 Materials and methods

### 2.1 Synthesis of Ba-doped C$_2$S

Analytical reagents and deionized water are applied during the solution preparation. $\beta$-C$_2$S is synthesized according to ref. [16]. Analytical SiO$_2$ and CaO with a stoichiometric proportion of Ca:Si = 2:1, 4% BaSO$_4$ with total mass were mixed and ground uniformly by a small ball mill for 20 min until the sieve residue is less than 5%. After mixing anhydrous ethanol, the samples were made into a pill with a diameter of 15 mm and dried in a vacuum drying oven at 105℃. The samples were calcined in the furnace with the calcination temperature 1250℃, the heating rate 10℃/min, and heat preservation for 3 h. The samples were rapid cooling in the case of crystal transformation. The clinker was crushed and ground into a fine powder, and the chemical composition of $\beta$-C$_2$S was analyzed by X-ray fluorescence spectrometry (ThermoFisher, ESCALAB 250Xi).

### 2.2 Characterization method

The structural variation of $\beta$-C$_2$S doping Ba$^{2+}$ ions was further analyzed by Nuclear Magnetic Resonance ($^{29}$Si MAS-NMR) and Fourier transform infrared (FT-IR) spectroscopy. $^{29}$Si MAS-NMR was measured by a Bruker Avance II 400 MHz spectrometer with a field strength of 9.4 T, operating at 99.2 MHz. The chemical shifts were referenced to tetramethylsilane (TMS). FT-IR patterns were obtained by a Fourier transform infrared spectrometer (Nicolet is5003) with a wave length range from 250 to 4,000 cm$^{-1}$.

### 2.3 Molecular dynamics simulation

In this paper, the first principle calculation is based on the density functional theory (DFT) and the plane-wave pseudopotential method (PWP) [31], and the CASTEP module of molecular structure and mechanics simulation software Materials Studio@ (Accelrys 6.2) is employed to calculate the electronic structure and cohesive energy $\beta$-C$_2$S with/without doping Ba ions.

The state of the electronic structure is described by density functional and the generalized gradient approximation (GGA) [32]. The exchange–correlation functionals were calculated using Generalized Gradient Approximation (GGA) with the Perdew–Burke–Ernzerhof functional (PBE functional) [33]. The Brillouin zone was sampled with $4 \times 4 \times 4$ $k$-points in the primitive cell. The values of kinetic energy cutoff $E_c$ and the $k$-points number are increased until the calculated energy converges within the required tolerance, where $E_c$ determines the number of plane waves and $k$ points does the sampling of the irreducible wedge of the Brillouin zone [34]. The cutoff energy of plane-wave (PW) was 380 eV,
the energy tolerance was $5 \times 10^{-7}$ eV/atom, the force tolerance was 0.03 eV/Å, the stress tolerance was 0.05 GPa, and the displacement tolerance was 0.001 Å.

# 3 Results and analysis

## 3.1 Activation of Ba-doped $\beta$-C$_2$S

The chemical composition of the calcined Ba-doped C$_2$S is shown in Table 1, which shows that 2.55% Ba$^{2+}$ is stabilized in the system. The NMR spectrum can reflect the atomic coordination and adjacent atomic effect. The crystallographic structure variation of C$_2$S reported can be described by the shift of $^{29}$Si NMR spectrum [35,36]. Figure 1 shows $^{29}$Si spectrum peak shifts and the appearance of the secondary peak right beside the main peak in the NMR spectrum. It infers to the atom subordination change and secondary peak right beside the main peak in the NMR spectrum. It infers to the atom subordination change and octahedral transformation in the Ba-doped C$_2$S.

FT-IR analysis was further carried out to verify the lattice variation in Ba-doped C$_2$S. FT-IR patterns of hydration activity, crystal structural, and electronic properties Ba$doped C_2S$ hydration at different curing age are shown in Figure 2. New peaks at 900 and 845 cm$^{-1}$ in Ba-doped $\beta$-C$_2$S are ascribed to the asymmetric stretching vibration of the [SiO$_4$] tetrahedron, which confirmed that Ba$^{2+}$ enters the crystal lattice after calcination and is consistent with the observation in NMR analysis [37]. The [SiO$_4$] tetrahedral stretching vibration at 3,440, 1,420, and 1,020 cm$^{-1}$ can be attributed to the formation of C–S–H gel [38]. The appearance of a stronger absorption at 1420 cm$^{-1}$ is attributed to the faster $\beta$-C$_2$S hydration rate after the Ba doping. It can be concluded that Ba$^{2+}$ doping can significantly promote the $\beta$-C$_2$S hydration at an early age.

## 3.2 Crystal structure and lattice parameters

The lattice parameters of $\beta$-C$_2$S are $a = 5.502$ Å, $b = 6.745$ Å, $c = 9.297$ Å, $\alpha = \gamma = 90.00^\circ$, and $\beta = 94.59^\circ$, which belongs to the monoclinic system with the $P2_1/n_1$ space group [39]. There are 8Ca atoms, 4Si atoms, and 16O atoms in a single Ca$_2$SiO$_4$ lattice. According to the lattice model present in Figure 3 by Crystal Maker@ software, Ca atoms can combine with O atoms to form [CaO$_6$] octahedron and [CaO$_3$] hexahedron. With Ba substituted Ca in $\beta$-C$_2$S lattice, a new solid/solution Ca$_{1-x}$Ba$_x$SiO$_4$ (x corresponds to the weight percentage) is formed [15]. Two solid/solution ratios of doped Ba are investigated, Ca$_{1.969}$Ba$_{0.031}$SiO$_4$ with single Ba substitution and Ca$_{1.938}$Ba$_{0.062}$SiO$_4$ with double Ba substitution [40]. Therefore, Ba$_{(12)}$-C$_2$S and Ba$_{(12,22)}$-C$_2$S in Table 2 represent two substitution sites of Ca atoms, where Ba$_1$ and Ba$_2$ represent Ca atom in the [CaO$_6$] octahedron and the [CaO$_3$] hexahedron, respectively. According to the lattice parameters listed in Table 1, the calculated parameters ($a = 5.57$ Å, $b = 6.81$ Å, $c = 9.37$ Å, $\alpha = \gamma = 90.00^\circ$, $\beta = 94.66^\circ$) are basically the same as the theoretical parameters. The error is less than 2%, which confirms the accuracy of the model [41].

When compared with general $\beta$-C$_2$S, the addition of Ba leads to the lattice deformation and the reduction of formation energy in Ba-doped C$_2$S. The spacing of each crystal plane is increased, and the inner holes are enlarged accordingly. Higher degrees of Ba$^{2+}$ substitution leads to higher variants of crystalline structure. Comparing the Ca$^{2+}$ substitution in [CaO$_6$] or [CaO$_3$], the lattice deformation and hydraulic reactivity are more significant in Ba$_2$-$C_2$S and Ba$_{22}$-$C_2$S.

### Table 1: Chemical composition of Ba-doped C$_2$S (wt%)

<table>
<thead>
<tr>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>SO$_3$</th>
<th>BaO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.89</td>
<td>62.12</td>
<td>30.06</td>
<td>1.12</td>
<td>0.23</td>
<td>0.67</td>
<td>0.21</td>
<td>0.45</td>
<td>2.55</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Figure 2: FT-IR patterns of hydrated β-C₂S (left) and Ba-doped β-C₂S (right) at different curing age.

Figure 3: Crystalline structure of β-C₂S (Red balls represent O atoms; green balls represent Ca atoms; yellow balls represent Si atoms.) Ca1 and Ca2 atoms in β-C₂S can combine with O atom to form [CaO₆] octahedron and [CaO₈] hexahedron. Si atom in β-C₂S can combine with O atom to form [SiO₄] tetrahedron.

Table 2: Lattice parameters of β-C₂S and Ba-doped C₂S space group P2₁/n₁

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Formation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂Sₗ₀</td>
<td>5.50</td>
<td>6.75</td>
<td>9.30</td>
<td>90</td>
<td>94.59</td>
<td>90</td>
<td>-15480.52</td>
</tr>
<tr>
<td>C₂Sₗ₁</td>
<td>5.57</td>
<td>6.81</td>
<td>9.37</td>
<td>90</td>
<td>94.66</td>
<td>90</td>
<td>-15481.62</td>
</tr>
<tr>
<td>Ba₁₋C₂S</td>
<td>5.63</td>
<td>6.99</td>
<td>9.39</td>
<td>90.91</td>
<td>90</td>
<td>89.93</td>
<td>-15177.56</td>
</tr>
<tr>
<td>Ba₂₋C₂S</td>
<td>5.60</td>
<td>6.92</td>
<td>9.63</td>
<td>90.88</td>
<td>93.38</td>
<td>89.55</td>
<td>-15177.47</td>
</tr>
<tr>
<td>Ba₁₁₋C₂S</td>
<td>5.77</td>
<td>7.09</td>
<td>9.42</td>
<td>91.05</td>
<td>89.22</td>
<td>89.99</td>
<td>-14873.37</td>
</tr>
<tr>
<td>Ba₁₂₋C₂S</td>
<td>5.67</td>
<td>7.06</td>
<td>9.81</td>
<td>91.36</td>
<td>91.42</td>
<td>89.08</td>
<td>-14873.21</td>
</tr>
<tr>
<td>Ba₂₂₋C₂S</td>
<td>5.59</td>
<td>7.10</td>
<td>9.71</td>
<td>91.47</td>
<td>92.17</td>
<td>89.66</td>
<td>-14873.29</td>
</tr>
</tbody>
</table>
The low hydraulic reactivity of $\beta$-C$_2$S is ascribed to two aspects, one is the H$_2$O molecules cannot enter the cavity in the $\beta$-C$_2$S island structure, the other is that Ca attached to the tetrahedron [SiO$_4$] is not easily dissolved out [28,42]. Pritts et al. [43] have found that Ba, Fe, Al, and Pb doped in $\beta$-C$_2$S clinkers can reduce crystalline symmetry and increase the hydraulic reactivity [40–44]. Due to the limitations of microscopic characterization methods, the correlation between the mechanism of hydration kinetics and the crystallographic structure of Ba-doped C$_2$S remains to be further studied; therefore, the electronic structure Ba-doped C$_2$S is further studied in the following.

3.3 Electronic structure of Ba-doped C$_2$S

The total and partial density of states (TDOS and PDOS) for $\beta$-C$_2$S, Ba$_{122}$C$_2$S and Ba$_{6122}$C$_2$S calculated are shown in Figure 4. The main contribution to valence band in $\beta$-C$_2$S

![Graphs showing density of states](image-url)
arises from the O-2p located from −4 to 0 eV below the Fermi energy, the main contribution to the conduction band in β-C2S arises from the Ca-3d located from 5 to 7 eV above the Fermi energy. The band gap between VBM and CBM is 4.887 eV. In the case of Ba1 above the Fermi energy, the conduction band in Ba22−C2S is greatly improved with the formation of BaC2S can be activated by doping Ba atom and the crystal formation energy increases and the band gap between VBM and CBM become narrow in the activated β-C2S crystallographic structure.

Acknowledgments: The authors would like to appreciate the financial sponsored by Shanghai Sailing Program No. 20YF1431800 and National Natural Science Foundation of China (No.51872064).

Author contributions: Investigation, writing – original draft preparation, visualization, software: L. C.; Investigation, formal analysis: A. Z., L. C., D. Z.; Writing – review & editing: S. L., Z. Q.; Supervision: Z. W.

Conflict of interest: The authors declare no conflict of interest regarding the publication of this paper.

References


Manohar CS, Kumar BS, Sadhu SPP, Srimadh SK, Varma KBR. Novel Lead-free biocompatible piezoelectric Hydroxyapatite (HA)-BCZT (Ba0.65Ca0.37Zr0.1Ti0.9O3) nanocrystalline composites for bone regeneration. Nanotechnol Rev. 2019;8(1):61–78.


