

Article

The Influence of Boron Doping on the Structures and Composition of Dicalcium Silicate: A Research Study

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Abstract: This paper investigates the structural transformation of dicalcium silicate (C₂S) crystals brought about through boron doping. Both qualitative and quantitative analyses were conducted to explore the correspondence between boron content and the structure of dicalcium silicate. The results show that boron doping can stabilize β-C₂S and the high-temperature phase α'_H-C₂S, and the structural transformation does not involve the modulation of α'_L-C₂S. There is a corresponding relationship between the unit cells of β-C₂S and α'_H-C₂S, which can be transformed using a transformation matrix. The relationship between boron content and the content of different C₂S structures, as well as the structural expressions for β-C₂S and α'_H-C₂S, is determined using linear fitting and multivariable linear regression analysis.

Keywords: dicalcium silicate; structure modulation; boron; quantitative analysis; regression analysis



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1. Introduction

Ordinary Portland cement (OPC) is extensively used in construction worldwide. In 2020, China accounted for 57% of global cement production with a production volume of about 2.37 billion tonnes [1,2]. The CO₂ emissions per tonne of cement and clinker were approximately 616.6 kg and 865.8 kg, respectively [3,4]. Given the global focus on carbon reduction, the cement industry, being one of the significant contributors to carbon emissions, faces immense pressure to achieve carbon peak and carbon neutrality goals.

Current research on low-carbon clinker production focuses mainly on low-calcium cement clinker [4–7] and alite structure modulation [8,9]. In recent years, some scholars have begun researching the coexistence of high-temperature phase (alite) and low-temperature phase (calcium sulfoaluminate) by introducing mineralizers to lower the formation temperature. The development of alite-belite-ye'elimite cement [4,5,10], as well as alite-ye'elimite cement [11–13], has been achieved. As the challenge of coexistence between alite and ye'elimite has been resolved, the research conducted by these scholars provides us with a new perspective: under the ordinary Portland cement system, lowering the C₃S content appropriately, increasing the C₂S content, and introducing a small amount of ye'elimite. Lowering the C₃S content implies a significant decrease in early strength, necessitating the inclusion of other mineral phases or the activation of existing mineral phases to supplement the strength. A small amount of ye'elimite can supplement early strength and scholars have previously demonstrated that ionic regulation can promote the early hydration of alite [8,9,14]. The key to maintaining the strength of this system compared to

ordinary Portland cement is to activate belite, promote its early hydration, and improve early strength.

Belite is a solid solution of dicalcium silicate and is one of the main mineral phases in ordinary Portland cement. It primarily contributes to the development of strength in the later stages. Dicalcium silicate, also known as calcium orthosilicate, possesses an island-like structure, wherein the basic structural units of $[\text{SiO}_4]$ tetrahedra are connected by $[\text{CaO}_x]$ polyhedra, forming a three-dimensional spatial structure. Dicalcium silicate exists in five crystal forms: α , α'_H , α'_L , β , and γ , as illustrated in Figure 1 [15]. The α form has the highest temperature presence, while the γ form has the lowest. Occasionally, the α'_H and α'_L forms are collectively referred to as α' type.

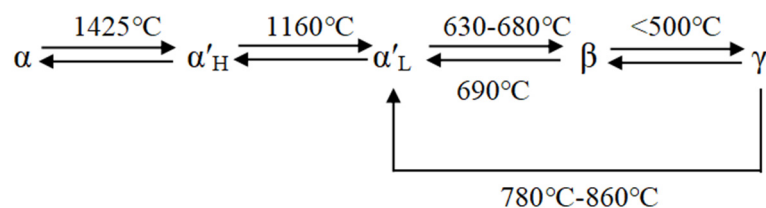


Figure 1. Phase transitions according to belite.

Pure dicalcium silicate exists in the γ phase at room temperature and exhibits a typical olivine structure [16]. In this structure, the $[\text{SiO}_4]$ tetrahedra are connected by $[\text{CaO}_6]$ octahedra with a calcium ion coordination number of 6. The high-temperature forms of dicalcium silicate also involve the connection of $[\text{SiO}_4]$ tetrahedra through calcium–oxygen polyhedra, but the coordination number of Ca^{2+} is not fixed as it is in the γ phase. In the β phase, the coordination numbers are 6 and 8, while in the α'_L phase, they are 9 and 10 [17,18]. According to Regound et al. [17], the transformation from β to γ and from β to α'_L can be attributed to irreversible reconstructive phase transitions. In the transformation from β to γ , the orientation of the $[\text{SiO}_4]$ tetrahedra and the coordination number of the Ca^{2+} change lead to a significant change in volume. The β to γ transition results in an approximately 13% increase in volume, which is responsible for the powdering of cement clinker [19]. The transformations from α'_H to α'_L and from α'_L to β belong to displacement-type phase transitions [17]. The crystal structures of the two types are very similar, with small changes occurring during the transition, to the extent that the transition between them was not initially recognized and was considered as a single phase (α' phase). The transition from α'_L to β is a first-order phase transition that involves changes in the coordination number of Ca^{2+} . The transition between α and α'_H is a semi-reconstructive phase transition in which half of the $[\text{SiO}_4]$ tetrahedra undergo rotation [17].

It is generally believed that the γ type dicalcium silicate with olivine structure does not react with water and does not exhibit hydraulic activity. However, there are studies suggesting that it has a lower level of hydration activity and can undergo hydration reactions to some extent over a long period of time [20]. The hydration activity of high-temperature forms of dicalcium silicate varies. The hydration activity of dicalcium silicate is influenced by factors such as crystal type and solid solution impurities. It is generally believed that the higher the temperature form of dicalcium silicate, the higher the activity, that is, the hydration activity follows the order $\alpha > \alpha' > \beta > \gamma$ [21]. The above regularity holds well for different crystal forms of dicalcium silicate with stable ion configuration. The hydration activity of α'_H is superior to the commonly found β type in clinker, therefore, one significant research topic in developing low-calcium cement systems is the controlled stabilization of α'_H , which exhibits higher hydration activity.

In addition to temperature, the presence of foreign ions can also lead to different crystal forms of dicalcium silicate. The incorporation of foreign ions into the dicalcium silicate crystal can impede the transformation from a high-temperature phase to a low-temperature phase during the cooling process, thereby stabilizing the β , α' , and even α forms of dicalcium silicate at room temperature. Numerous studies have been conducted by researchers on the stabilization of dicalcium silicate crystal forms brought about through the

introduction of foreign ions. In order to achieve crystallochemical stabilization of various polymorphs of C_2S , research has been conducted on doping C_2S with specific elements. These elements include Na^+ , K^+ , As^{2+} , Sr^{2+} , Ba^{2+} , B^{3+} , Fe^{3+} , P^{5+} , V^{5+} , and Cr^{6+} [22,23]. The elements K^+ [24], Ba^{2+} [25,26], B^{3+} [27–31], P^{5+} [32], and V^{5+} [33] can stabilize both the β -type and α' -type belite.

As the investigation of low-carbon clinker progresses, the study on the modulation of the crystal structure of dicalcium silicate using boron doping has regained scholarly attention. Cuesta et al. have found that in single boron doping, silicon is replaced by boron in the form of BO_4^{5-} , while in boron–sodium composite doping, boron exists as the triangular planar anion BO_3^{3-} . The authors have proposed that the composite doping of Na/B leads to the formation of a new structure, $\alpha'_H\text{-Ca}_{1.85}\text{Na}_{0.15}(\text{SiO}_4)_{0.85}(\text{BO}_3)_{0.15}$, which is suitable for the production of active belite cement samples with the addition of borax [27]. Duvallet et al. have effectively stabilized $\alpha'_H\text{-C}_2\text{S}$ and significantly reduced the presence of $\gamma\text{-C}_2\text{S}$ and $\beta\text{-C}_2\text{S}$ by adding 2.8 wt% borax [28]. Aranda et al. have found that the doping of B_2O_3 and Na_2O can effectively stabilize $\alpha'_H\text{-C}_2\text{S}$ in belite-sulfoaluminate clinkers and results in a faster hydration rate compared to $\beta\text{-C}_2\text{S}$. Among the dopant compositions which have been tested, the $\alpha'_H\text{-C}_2\text{S}$ content was highest for the group with 2.0 wt% B_2O_3 and 0.9 wt% Na_2O doping [29]. Li et al. have found that the hydration degree of $\alpha'_H\text{-C}_2\text{S}$ prepared by single and composite doping methods (using B/Na and B/Ba) is higher than that of undoped $\beta\text{-C}_2\text{S}$. Specifically, the hydration degree was higher with composite doping compared to single doping [30]. Moreover, Saidani et al. have investigated the effect of dopants (B, P, and S) on the stability of $\beta\text{-Ca}_2\text{SiO}_4$ and the results show that dopants can induce lattice distortion in Ca_2SiO_4 and lower the formation temperature of the α and α'_H phases [31]. Despite the extensive research on B doping for the control of C_2S crystal phases, the mechanisms and the relationship between the amount of B doping and the content of the target crystal phase have not been systematically studied.

In this study, the authors conducted a systematic investigation into the impact of boron doping on the structure of C_2S (dicalcium silicate), taking advantage of boron's ability to modulate structure. By introducing varying amounts of B_2O_3 (boron trioxide) into the raw materials, a correlation between boron content, C_2S crystal structure, and different structural proportions of C_2S was established. The characterization and analysis of the C_2S structure were performed using a range of techniques including XRD, high-temperature XRD, ICP-OES, FT-IR, and Raman spectroscopy. This paper successfully determines the positions of boron substitution in the C_2S structure as well as the mechanism behind structural modulation. These findings contribute to the theoretical foundation for the development of low-carbon clinker.

2. Materials and Methods

2.1. Sample Preparation

In the experiment, the materials used were CaCO_3 (99.95–100.05%, Sigma-Aldrich, Saint Louis, MO, USA), SiO_2 (99.9%, Sigma-Aldrich, Saint Louis, MO, USA), and B_2O_3 (99.9%, Supelco, Darmstadt, Germany). The raw materials used for the synthesis of C_2S were CaCO_3 and SiO_2 , in a molar ratio of $n(\text{CaCO}_3):n(\text{SiO}_2) = 2:1$. The amount of B_2O_3 added to the raw materials was determined by the desired mass of C_2S varying from 0.5% to 6.5% of the C_2S weight. A total of 13 experimental groups were established and labeled as blank, 1#, 2#, 3#, 4#, 5#, 6#, 7#, 8#, 9#, 10#, 11#, 12#, and 13#. The composition of each experimental group is provided in Table 1.

After weighing the samples according to the prescribed ratio, they were mixed with an equal mass of zirconia balls in a mixing bottle. The bottle was then placed on a mixing machine and mixed for 24 h. Once the samples were thoroughly mixed, they were sieved and compressed into circular discs with a diameter (R) of 30 mm and an approximate mass of 25 g per disc. The discs were then placed in covered crucibles to minimize the volatilization of B_2O_3 . The crucibles were subsequently placed in a box furnace for sample firing. The temperature of the furnace rose steadily, increasing in steps of 10 °C per minute,

starting from 25 °C and going up to 900 °C, then being held at that temperature for 0.5 h to ensure complete decomposition of calcium carbonate in the samples. Following this step, the temperature was further increased to 1300 °C and maintained for 4 h to facilitate sintering. Once the sintering process was completed, the samples were removed from the furnace and rapidly cooled down to room temperature using a fan.

Table 1. The raw meal loadings (wt%).

Sample	CaCO ₃	SiO ₂	B ₂ O ₃
Blank	76.91	23.09	0
1#	76.66	23.01	0.33
2#	76.41	22.93	0.66
3#	76.16	22.86	0.98
4#	75.91	22.78	1.31
5#	75.66	22.71	1.63
6#	75.42	22.64	1.95
7#	75.17	22.56	2.26
8#	74.93	22.49	2.58
9#	74.69	22.42	2.89
10#	74.45	22.35	3.20
11#	74.21	22.28	3.51
12#	73.98	22.20	3.82
13#	73.74	22.13	4.12

2.2. Characterization

2.2.1. Determination of Boron Content (ICP-OES)

ICP-OES was chosen for the determination of boron content. The instrument used was Agilent 5110 (Agilent Technologies, Santa Clara, CA, USA) from the United States. The instrument's working parameters were set as listed in Table 2.

Table 2. The working parameters of ICP-OES.

Pump Speed	Plasma Working Gas Flow Rate	Nebulizer Flow Rate	Stabilization Time	Auxiliary Gas Flow Rate	Reading Time	Sample Rinsing Time	RF Power
100 r/min	12.0 L/min	0.70 L/min	20 s	1.0 L/min	5 s	20 s	1150 W

2.2.2. Qualitative Test of the Samples at Room Temperature (RT-XRD)

The fired samples were ground to a fine powder using an agate mortar. The powdered samples were then sieved through a 400-mesh sieve (38 µm). A suitable quantity of the resulting powder was used for qualitative phase analysis employing a room-temperature X-ray diffraction (XRD) setup. The RT-XRD analysis parameters were set as listed in Table 3. The standard reference cards used for qualitative phase analysis were α' -C₂S (ICSD No. 81,097) [34], β -C₂S (ICSD No. 81,096) [34], γ -C₂S (ICSD No. 81,095) [34], and C₃S₂ (ICSD No. 34,338) [35].

2.2.3. Temperature-Dependent Testing of the Samples (HT-XRD)

High-temperature XRD analysis was conducted using the same device as for RT-XRD, while the test parameters are given in Table 3. The heating process was controlled at a rate of 10 °C per minute. Data collection commenced when the temperature reached 100 °C and data points were recorded every 100 °C, while maintaining a constant temperature. The standard reference cards used for qualitative phase analysis were α -C₂S (ICSD No. 82,998) [36], α' -C₂S (ICSD No. 82,997) [36], α'_L -C₂S (ICSD No. 82,996) [36], and β -C₂S (ICSD No. 81,096) [34].

Table 3. The working parameters of XRD.

Test Name	Device	Radiation Source	Accelerating Voltage/Current	Step Size	Scanning Range	Speed
RT-XRD	Rigaku SmartLab TM 9 kW diffractometer (Rigaku Co., Tokyo, Japan)	Cu K α , $\lambda = 0.15406$ nm without K α 2	45 kV/200 mA	0.01°	10°–70°	10°/min
Quantitative analysis	Rigaku SmartLab TM 9 kW diffractometer (Rigaku Co., Tokyo, Japan)	Cu K α , $\lambda = 0.15406$ nm	45 kV/200 mA	0.01°	10°–70°	1°/min
HT-XRD	Rigaku SmartLab TM 9 kW diffractometer (Rigaku Co., Tokyo, Japan)	Cu K α , $\lambda = 0.15406$ nm without K α 2	45 kV/200 mA	0.01°	10°–70°	10°/min

2.2.4. Fourier-Transform Infrared Spectroscopy (FT-IR)

The samples were scanned using an FT-IR spectrometer (Thermo Scientific Nicolet iS20, Thermo Fisher Scientific Inc., Waltham, MA, USA) in the range of 4000–400 cm^{−1} with a resolution of 4 cm^{−1}. Potassium bromide (KBr) was employed as the powdered sample carrier.

2.2.5. Raman Spectroscopy

Raman spectroscopy measurements were conducted using the LabRAM HR Evolution laser microscopic confocal Raman spectrometer (Horiba, Kyoto, Japan). This instrument model features a spectral resolution of ≤ 0.65 cm^{−1} and a spectral repeatability of $\leq \pm 0.2$ cm^{−1}. For the measurements, a laser with a wavelength of 532 nm and a power of 50 mW was employed. The wavenumber range chosen for testing was 50–4000 cm^{−1}.

2.2.6. Quantitative Analysis

The Rietveld method was utilized for the quantitative analysis of the phase composition in the sample. The XRD data of the sample was analyzed using the GSAS software (Version 1.0) with the EXPGUI package. The quantitative calculation procedures were carried out in accordance with the references [8,9]. The α' -C₂S (ICSD No. 81,097) [34], β -C₂S (ICSD No. 81,096) [34], γ -C₂S (ICSD No. 81,095) [34], and C₃S₂ (ICSD No. 34,338) [35] standard cards were employed for the quantitative calculations.

3. Results and Discussion

3.1. Boron Content in Samples

The determination of boron content in the samples is characterized using ICP-OES (Agilent 5110, Agilent Technologies, Santa Clara, CA, USA). The results for the levels of boron content in the raw materials and fired samples are shown in Table 4. When the boron content is low, there is a higher level of boron volatilization. As the boron content increases, the volatilization gradually decreases and stabilizes at around 40%, and then decreases to around 30%.

Qian et al. [37] stated that the volatilization of boron is related to the vapor pressure of boron in the system. When the vapor pressure of boron in the system is not saturated, it will continue to volatilize into the system. Due to the relatively low boron content in samples #1 and #2, most of the boron volatilizes into the system, resulting in less boron being retained in the samples and a higher volatilization rate.

As the boron content increases, the mineralization effect of boron oxide decreases the solid-phase reaction temperature and enhances the reaction degree. The amount of boron solid solution in the sample gradually increases, leading to a decrease in volatilization.

Table 4. Boron content in raw materials and samples.

Sample	Raw Materials/wt. %		Samples/wt. %			Boron Volatilization Rate
	B ₂ O ₃	Boron	B ₂ O ₃	Boron	STDEV	
1#	0.5	0.155	0.019	0.006	6.56×10^{-6}	96.14%
2#	1.0	0.311	0.274	0.085	1.09×10^{-5}	72.63%
3#	1.5	0.466	0.996	0.309	4.76×10^{-5}	33.69%
4#	2.0	0.621	1.481	0.460	7.69×10^{-5}	25.94%
5#	2.5	0.776	1.655	0.514	2.61×10^{-5}	33.79%
6#	3.0	0.932	1.877	0.583	5.05×10^{-5}	37.42%
7#	3.5	1.087	2.141	0.665	1.55×10^{-5}	38.82%
8#	4.0	1.242	2.328	0.723	4.25×10^{-6}	41.80%
9#	4.5	1.397	2.541	0.789	5.33×10^{-6}	43.54%
10#	5.0	1.553	2.824	0.877	2.02×10^{-5}	43.52%
11#	5.5	1.708	3.758	1.167	5.48×10^{-5}	31.67%
12#	6.0	1.863	4.344	1.349	4.41×10^{-5}	27.60%
13#	6.5	2.019	4.672	1.451	5.07×10^{-5}	28.12%

As the boron doping concentration in the sample increases further, equilibrium is reached between the boron concentration involved in the solid-phase reaction and the boron oxide vapor content in the crucible (observed in samples 6#–10#). The increase in the solubility of boron in the sample promotes the transformation of dicalcium silicate from the β phase to the α' phase, and at this point the level of boron volatilization remains stable at around 40%.

As the boron doping concentration continues to increase, a greater amount of boron remains in the sample, participating in the solid-phase reaction and dissolving into the crystal lattice of dicalcium silicate. This results in a significant increase in the content of the α' phase. At this stage, the level of boron volatilization stabilizes at around 30%.

3.2. C₂S Polymorphs

3.2.1. Room-Temperature XRD

The room-temperature XRD test results of samples blank to 13# are shown in Figure 2. The blank sample mainly consists of γ -C₂S, with a small amount of β -C₂S. From the stacked waterfall plot, it can be observed that boron doping can stabilize the β and α'_H type C₂S. At lower boron doping levels, sample 1# contains a small amount of γ -C₂S and the intermediate phase 3CaO·2SiO₂ (C₃S₂, Rankinite). This is because the presence of boron in the solid-phase reaction contributes to the stabilization of the C₂S. However, due to the partial volatilization of boron, the ratio of n (CaO) to n (SiO₂) fails to reach 2:1, resulting in a small amount of C₃S₂ formation. Interestingly, with the significant volatilization of boron, β -C₂S is also stabilized within the system. Similarly, in sample 2#, despite the absence of the intermediate phase C₃S₂, the boron dissolved in the system remains inadequate to fully stabilize β -C₂S. When the solid solubility of boron reaches 0.309 wt.% (seen in sample 3#), the C₂S undergoes a complete transformation into the β phase. Furthermore, as the solid solubility of boron increases, the crystal structure of C₂S transitions from the β phase to the α'_H phase.

In order to provide a clearer representation of the changes in the crystal structure of β -C₂S and α'_H -C₂S as the boron solid solubility varies, Figure 3a,b illustrate the comparison between samples 1# and 13# and the standard cards of β -C₂S and α'_H -C₂S. By comparing the main diffraction peaks, it is evident that sample 3# exhibits a perfect match with β -C₂S without any additional substitution peaks. This finding indicates that sample 3# has undergone a complete transformation into β -C₂S. As the level of boron doping increases, a gradual transition of the crystal structure from β -C₂S to α'_H -C₂S is observed, starting from sample 4#. This observation is consistent with the earlier discussion on the substantial change in boron evaporation between samples 3# and 4#, thereby mutually confirming the observed transformation. During the transformation from β -C₂S to α'_H -C₂S, characteristic

diffraction peaks exhibit noticeable changes. The range of 31.7° – 33° corresponds to the primary characteristic diffraction peaks of C_2S , and a significant transformation is observed within this range from sample 3# to 13#. The diffraction peaks at 34.2° , 35.3° , 36° – 38° , and 45.5° are distinctive features that differentiate β - C_2S from α' - C_2S . As the boron doping level increases, the intensity of these peaks gradually decreases until they eventually vanish. On the other hand, the diffraction peaks at 33.3° , 38° , 40.4° , 46.8° , and 52.2° characterize α' - C_2S , and their intensity becomes more prominent with higher concentrations of boron solid solution.

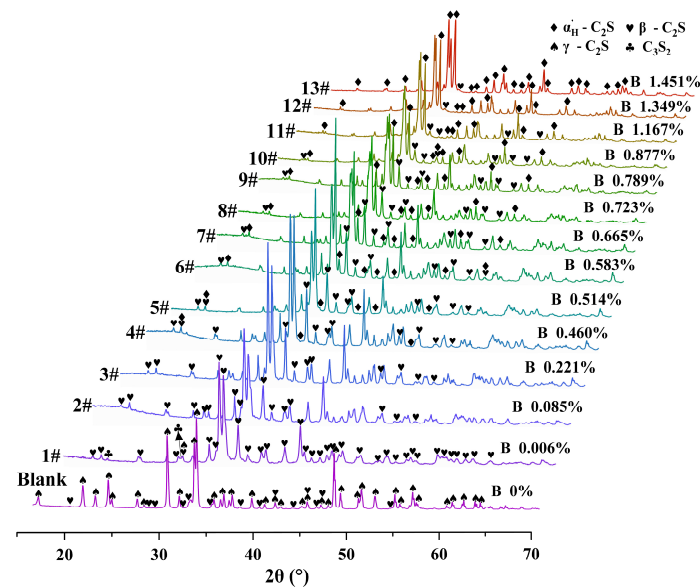


Figure 2. X-ray diffraction waterfall plot of C_2S doped with different boron contents.

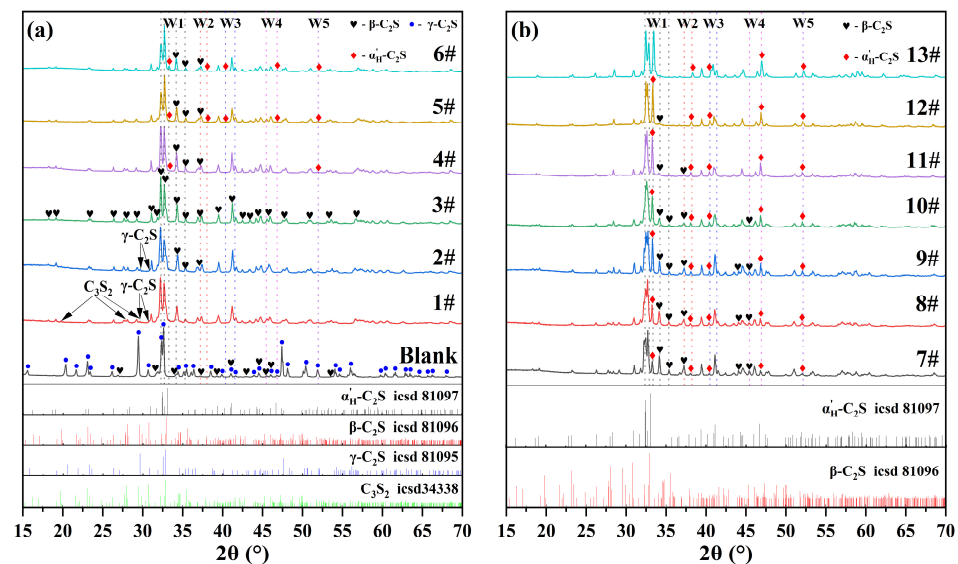


Figure 3. X-ray diffraction of C_2S doped with different content levels of boron. (a) Samples blank–6# and (b) samples 7#–13#.

The characteristic diffraction peaks of β - C_2S and α' - C_2S can be divided into five window regions, denoted as W1–W5, which are displayed in Figure 3. These window regions include the following angles: 30.5° – 35.7° , 36.5° – 39° , 40° – 42.2° , 45° – 48.5° , and 51.5° – 55° . Detailed comparisons are conducted by extracting the diffraction peaks within these regions, as illustrated in Figure 4. From an overall perspective, the diffraction peaks of samples 3#–5# exhibit the characteristics of β - C_2S primarily due to the relatively small

amount of α'_H -C₂S formed, which is not prominently reflected in the XRD pattern. In samples 6#–10#, with an increase in the boron solid solution content, the formation of α'_H -C₂S gradually increases, accompanied by more pronounced diffraction peaks, especially in the 32°–33° characteristic diffraction region. In samples 11#–13#, the XRD diffraction peaks are mainly attributed to α'_H -C₂S, with 13# showing almost no diffraction peaks of β -C₂S. This indicates that at this stage, C₂S has transitioned almost completely from the β phase to the α'_H phase.

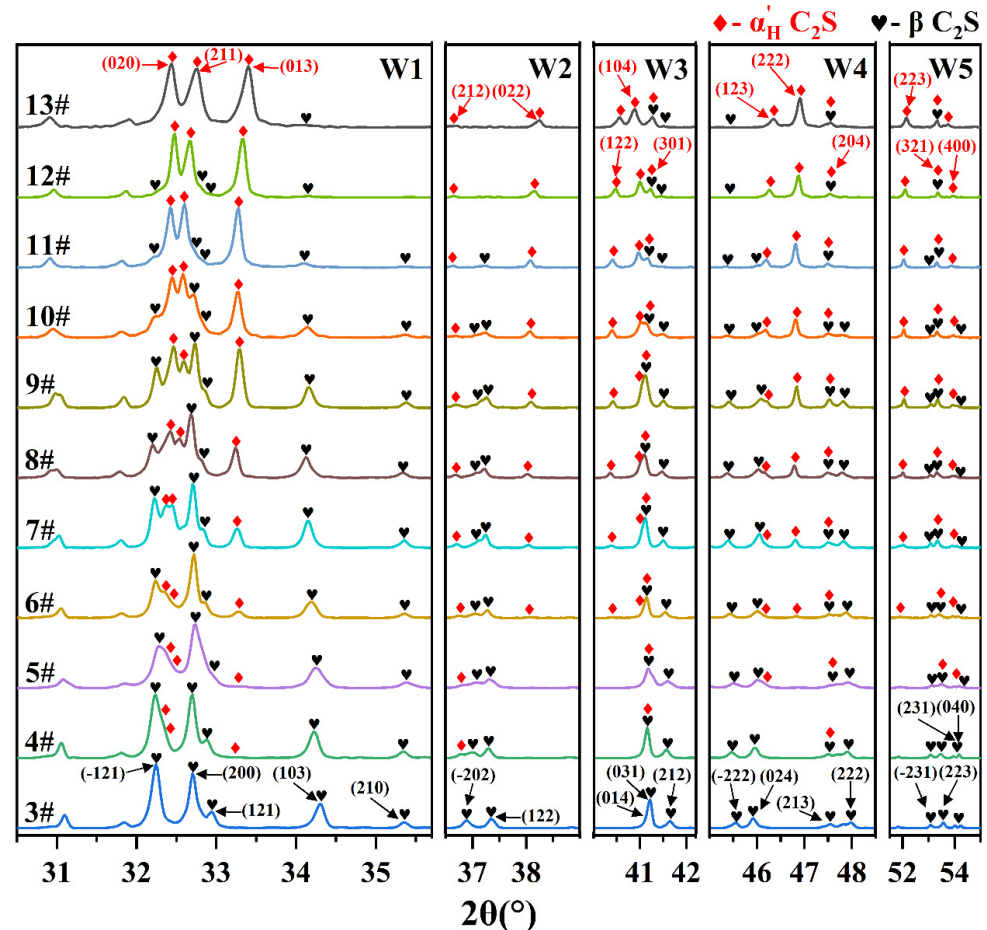


Figure 4. Comparison of characteristic diffraction windows for boron-doped samples.

The characteristic diffraction peaks in the five window regions were calibrated based on the ICSD standard cards for β -C₂S (ICSD No. 81,096) [34] and α'_H -C₂S (ICSD No. 81,097) [34]. In the W1 window, particularly in the 32°–33° region, the characteristic diffraction peaks of β -C₂S are primarily attributed to the crystal planes $(\bar{1}21)_\beta$, $(200)_\beta$, and $(121)_\beta$. As the transition to α'_H -C₂S occurs, the characteristic diffraction peaks are then generated by the crystal planes $(020)_{\alpha'_H}$ and $(211)_{\alpha'_H}$. The characteristic peaks of β -C₂S at around 34.3° and 35.3° are attributed to the crystal plane $(103)_\beta$ and $(210)_\beta$. These peaks gradually weaken and disappear as the boron solubility increases. Simultaneously, the characteristic peak of α'_H -C₂S at around 33.2° gradually emerges and strengthens, which is generated by the crystal plane $(013)_{\alpha'_H}$. The pattern of characteristic diffraction peaks in the W2–W5 windows is similar to that in the W1 window. We have compared the disappearance and formation of diffraction peaks in each window, as presented in Table 5.

Table 5. Comparison of characteristic peaks of β and α'_H -C₂S in five windows.

Characteristic Area	β -C ₂ S	α'_H -C ₂ S
W1, 32°–33°	$(\bar{1}21)_\beta$	$(211)_{\alpha'_H}$
	$(121)_\beta$	
	$(200)_\beta$	$(020)_{\alpha'_H}$
W1, 33°–34.5°	$(103)_\beta$	$(013)_{\alpha'_H}$
W1, 35.3°	$(210)_\beta$	-
W2, 36.5°–39°	$(\bar{2}02)_\beta$	$(022)_{\alpha'_H}$
	$(122)_\beta$	$(212)_{\alpha'_H}$
W3, 40°–42.2°	$(014)_\beta$	$(104)_{\alpha'_H}$
	$(031)_\beta$	$(301)_{\alpha'_H}$
	$(212)_\beta$	$(122)_{\alpha'_H}$
	$(\bar{2}22)_\beta$	$(222)_{\alpha'_H}$
W4, 45°–48.5°	$(222)_\beta$	
	$(024)_\beta$	$(204)_{\alpha'_H}$
	$(213)_\beta$	$(123)_{\alpha'_H}$
W5, 51.5°–55°	$(\bar{2}31)_\beta$	$(321)_{\alpha'_H}$
	$(231)_\beta$	
	$(223)_\beta$	$(223)_{\alpha'_H}$
	$(040)_\beta$	$(400)_{\alpha'_H}$

β -C₂S is classified as belonging to the monoclinic crystal system, while α'_H -C₂S is classified as belonging to the orthorhombic crystal system. During the process of structural transformation, the symmetry of the crystal increases, resulting in the equivalence of originally inequivalent crystal planes. For instance, the crystal planes $(\bar{1}21)_\beta$ and $(121)_\beta$, $(\bar{2}22)_\beta$ and $(222)_\beta$, as well as $(\bar{2}31)_\beta$ and $(231)_\beta$, become equivalent in the transition to the orthorhombic system. These equivalent crystal planes in the orthorhombic system are denoted as $(211)_{\alpha'_H}$, $(222)_{\alpha'_H}$, and $(321)_{\alpha'_H}$ in α'_H -C₂S by combining the corresponding relationships in Table 5. Upon examining the corresponding relationships in Table 5, a correlation between the crystal planes that cause the characteristic diffraction peaks of β -C₂S and α'_H -C₂S becomes apparent. In particular, $(h, k, l)_\beta \xrightarrow{\text{Transfer}} (k, h, l)_{\alpha'_H}$ or $(k, h, \bar{l})_{\alpha'_H}$ (equivalent crystal planes are taken into account). Furthermore, the β -C₂S has a unit cell with parameters $a = 5.5121 \text{ \AA}$, $b = 6.7575 \text{ \AA}$, $c = 9.3138 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 94.581^\circ$, and $\gamma = 90^\circ$ [34] while the α'_H -C₂S has a unit cell with parameters $a = 6.7673 \text{ \AA}$, $b = 5.5191 \text{ \AA}$, $c = 9.3031 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$ [34]. It can be deduced that during the transformation from β -C₂S to α'_H -C₂S, the β angle changes from 94.581° to 90° , while the a-axis and b-axis undergo an exchange simultaneously. After examining the unit cells of β -C₂S and α'_H -C₂S, it is evident that the β -C₂S crystal structure undergoes a

structural transformation using a transformation matrix $P = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$, then converts

the symmetry of transformed cells into an orthorhombic system with a space group of Pnma. As a result, the final transformed structure closely resembles that of α'_H -C₂S. The transformation process was simulated using VESTA software (Version 3.5.8) [38], as illustrated in Figure 5a–d. Figure 5a depicts the β -C₂S unit cell observed along the b-axis. Figure 5b exhibits the β -C₂S unit cell after undergoing a structural transformation

using the transformation matrix $P = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$, observed from the b-axis. Figure 5c represents the unit cell observed along the b-axis after modifying the symmetry to that of an orthorhombic system (with a space group Pnma) and setting the occupancies of Ca and O as 0.5. Figure 5d illustrates the α'_H -C₂S unit cell observed along the b-axis. Indeed, it is evident that the structure obtained from the transformation of the β -C₂S unit cell, as shown in Figure 5c, closely resembles the α'_H -C₂S unit cell.

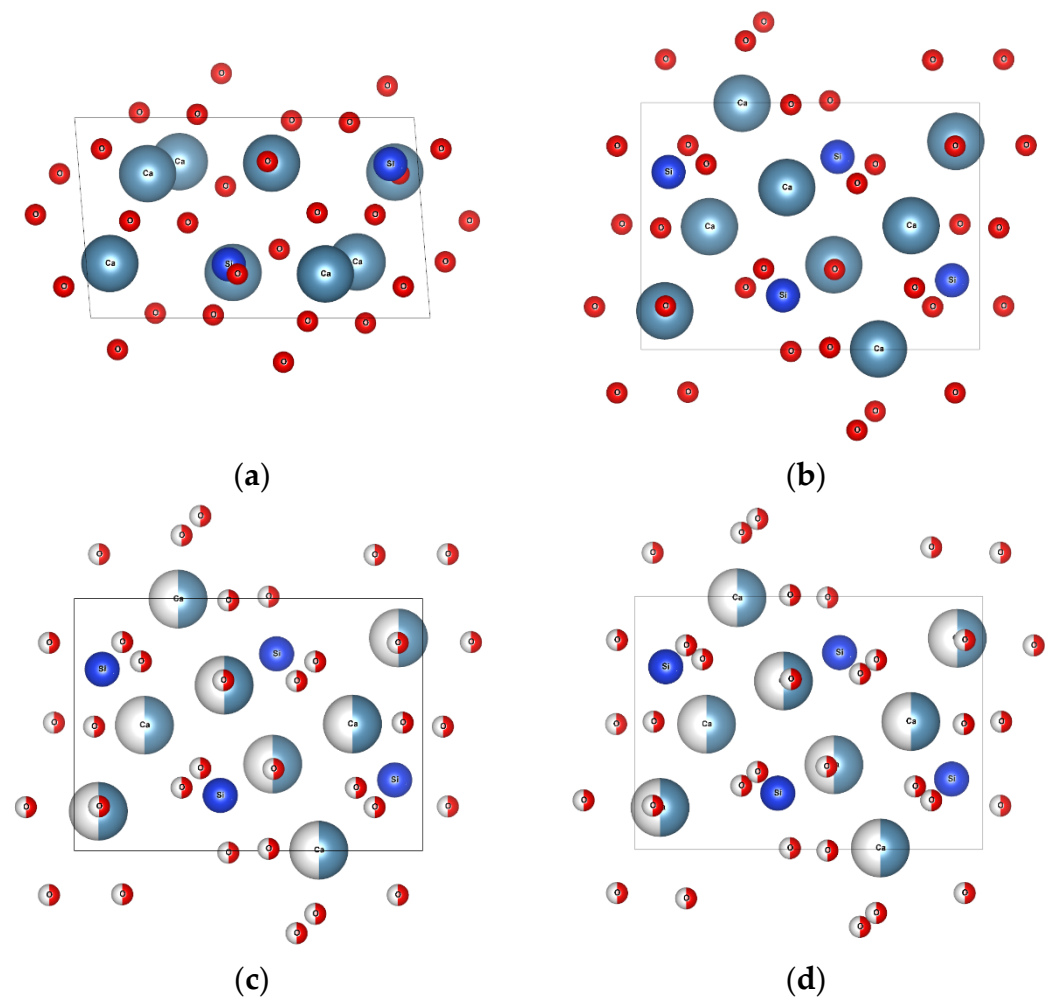


Figure 5. Simulation of the transformation process from β -C₂S unit cell to α'_H -C₂S unit cell using VESTA software. (a) β -C₂S unit cell observed along the b-axis; (b) β -C₂S unit cell after transformation using the transformation matrix P, observed along the b-axis; (c) modified unit cell after transformation, with adjusted symmetry (space group Pnma) and Ca/O occupancies set to 0.5, observed along the b-axis; and (d) α'_H -C₂S unit cell observed along the b-axis. (The red or partially red and white spheres represent oxygen atoms. The deep blue spheres represent silicon atoms. The light blue or partially light blue and white spheres represent calcium atoms).

As the two-unit cell has a transformation matrix, the planes also have the same corresponding relationships. Taking the plane $(\bar{1}21)_\beta$ as an example, let us see how the plane transforms during the phase transition. The process is given below.

$$(\bar{1} \ 2 \ 1)_\beta \Rightarrow (\bar{1} \ 2 \ 1) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \Rightarrow (2 \ \bar{1} \ \bar{1})_{\alpha'_H} \text{ equivalent } \Rightarrow (2 \ 1 \ 1)_{\alpha'_H}$$

The diffraction peak at around 35.3° in the β -C₂S phase is generated by the $(210)_\beta$ crystal plane, however, there is no corresponding diffraction peak in the α'_H -C₂S phase. The $(210)_\beta$ crystal plane theoretically corresponds to the $(120)_{\alpha'_H}$ crystal plane in α'_H -C₂S, but the structure of α'_H -C₂S is orthorhombic. Due to the symmetry of the space group, the $(120)_{\alpha'_H}$ crystal plane exhibits forbidden diffraction, leading to the absence of diffraction peaks generated by the $(120)_{\alpha'_H}$ crystal plane in α'_H -C₂S. As shown in Figure 6, a comparison is made between the zone axis $[1\bar{2}0]_\beta$ and $[\bar{2}10]_{\alpha'_H}$. It can be observed that the $(120)_{\alpha'_H}$ crystal plane belongs to the space group absence, therefore, no diffraction spots are observed.

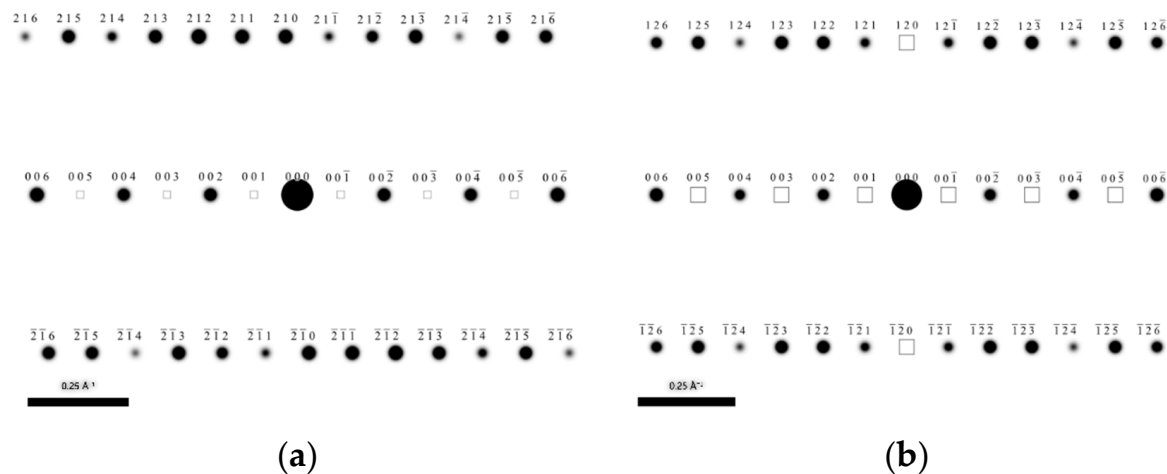


Figure 6. Simulated diffraction patterns for the zone axis $[1\bar{2}0]_\beta$ and $[\bar{2}10]_{\alpha'_H}$. (a) $[1\bar{2}0]_\beta$ and (b) $[\bar{2}10]_{\alpha'_H}$. (The circles represent diffraction spots while the squares represent forbidden diffraction).

3.2.2. In-Situ High-Temperature XRD

The analysis using room-temperature XRD confirmed that sample 3# is pure β -C₂S. In-situ high-temperature XRD testing was conducted on this sample by collecting data at regular intervals during the temperature ramp from 100°C to 1300°C , with data collected every 100°C . The temperature was maintained at a constant during the data acquisition process. The waterfall plot of the test data is shown in Figure 7. In general, as the temperature increases, the C₂S crystal structure undergoes a transformation from β to α'_L phase, and then to α'_H phase. Below 300°C , the crystal structure of C₂S is β phase. At 300°C , the appearance of the α'_L diffraction peak indicates the onset of phase transition. By 600°C , the characteristic diffraction peak of β -C₂S disappears completely, indicating a complete transformation to the α'_L phase. The transition temperature of β to α'_L is slightly lower than the temperature shown in Figure 1 (690°C), which can be primarily attributed to the decrease in transition temperature resulting from the presence of boron as a dopant. When the temperature reaches 1200°C , α'_L -C₂S transforms into α'_H -C₂S, which is consistent with the reported transition temperature of 1160°C for the α'_L to α'_H transformation. At 1300°C , no signs of α'_H -C₂S transforming into α -C₂S were observed. This may be due to the rapid transformation from α'_H -C₂S to α -C₂S, where the temperature range for the transformation is small, and the experimental temperature did not reach the phase transition temperature (1425°C). The α -Al₂O₃ diffraction peaks observed in Figure 7 are a result of the sample holder.

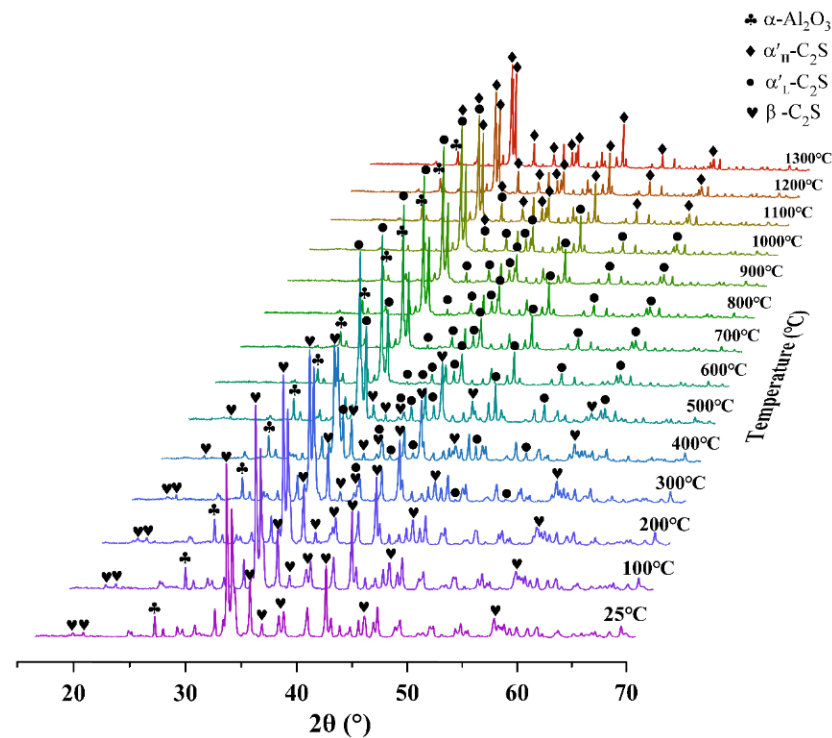


Figure 7. In-situ high-temperature XRD waterfall plot of sample 3# (25–1300 °C).

In order to facilitate the comparison of X-ray diffraction (XRD) results obtained at high temperatures and room temperatures, three specific windows were chosen to display the high-temperature XRD data. These windows cover the angles of 27°–30.5°, 31.5°–35°, and 35°–49°, respectively, as depicted in Figures 8 and 9. Figure 8 provides a visual representation of the transition process from β -C₂S to α'_L -C₂S that occurs within a moderate temperature range of 25 °C to 600 °C. When comparing the changes in the characteristic diffraction peak at 32°–33° between Figures 4 and 8, it becomes apparent that the phase transition process induced by boron ion doping does not align with the temperature-induced phase transition. Figure 8 showcases the temperature-induced phase transition, where only one high-intensity diffraction plane (002) α'_L emerges between the crystallographic planes ($\bar{1}21$) $_{\beta}$ and (200) $_{\beta}$ of β -C₂S, resulting from the transformation of the (200) $_{\beta}$ plane. Conversely, in the boron ion doping-induced phase transition, two high-intensity diffraction planes, (020) α'_H and (211) α'_H , appear between the planes ($\bar{1}21$) $_{\beta}$ and (200) $_{\beta}$. This indicates that boron ion doping mediates the structural modulation of β -C₂S, bypassing the α'_L -C₂S phase and directly transforming it into α'_H -C₂S. Notably, there is no existing literature [27–31] reporting the modulation of the C₂S crystal structure to achieve α'_L -C₂S through the process of boron doping. Figure 9 illustrates the transition process from α'_L -C₂S to α'_H -C₂S at medium to high temperatures (700–1300 °C). With the temperature ranging from 600 °C to 900 °C, C₂S remains in the α'_L phase, with slight variations in diffraction peaks (such as peaks at around 41°), which can be attributed to the thermal expansion of the α'_L phase. Throughout the transition from α'_L -C₂S to α'_H -C₂S, the characteristic diffraction peaks exhibit minimal changes, with the exception of the range of 32°–33°. Furthermore, even at a temperature of 1100 °C, the C₂S crystal structure predominantly maintains the α'_L -type, transitioning completely to α'_H -type at 1200 °C. These observations indicate a close resemblance between the α'_L and α'_H phases of C₂S, with a narrow temperature range for the transition, suggesting a rapid phase transformation.

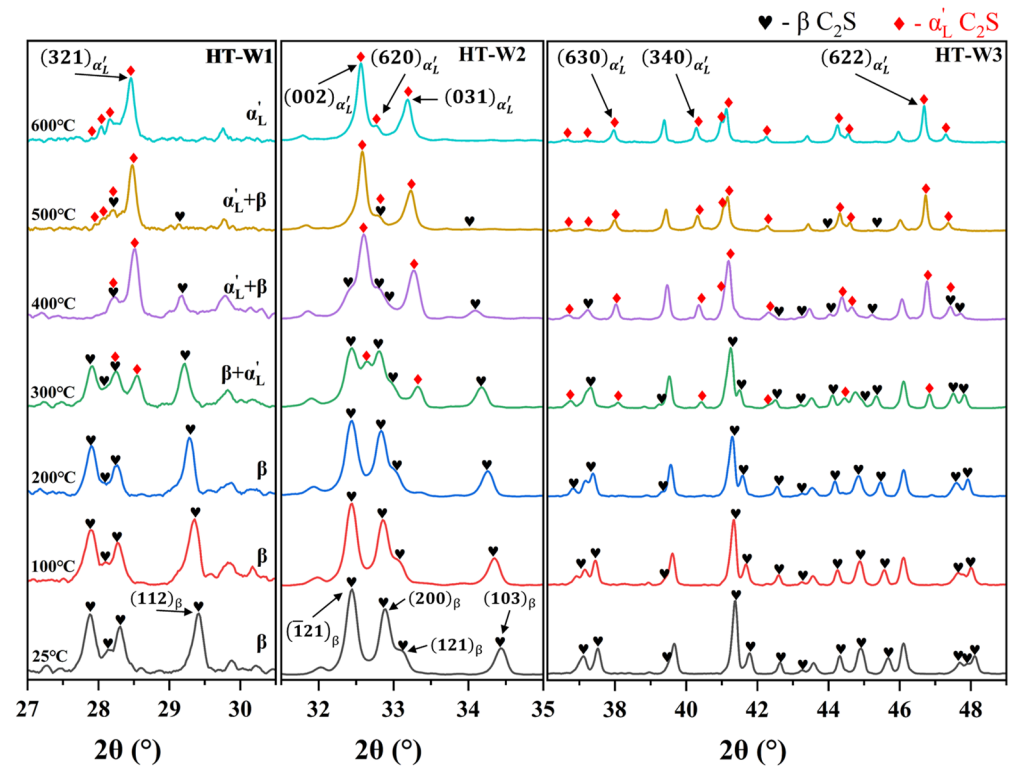


Figure 8. Comparative analysis of high-temperature XRD for sample 3# (25–600 °C).

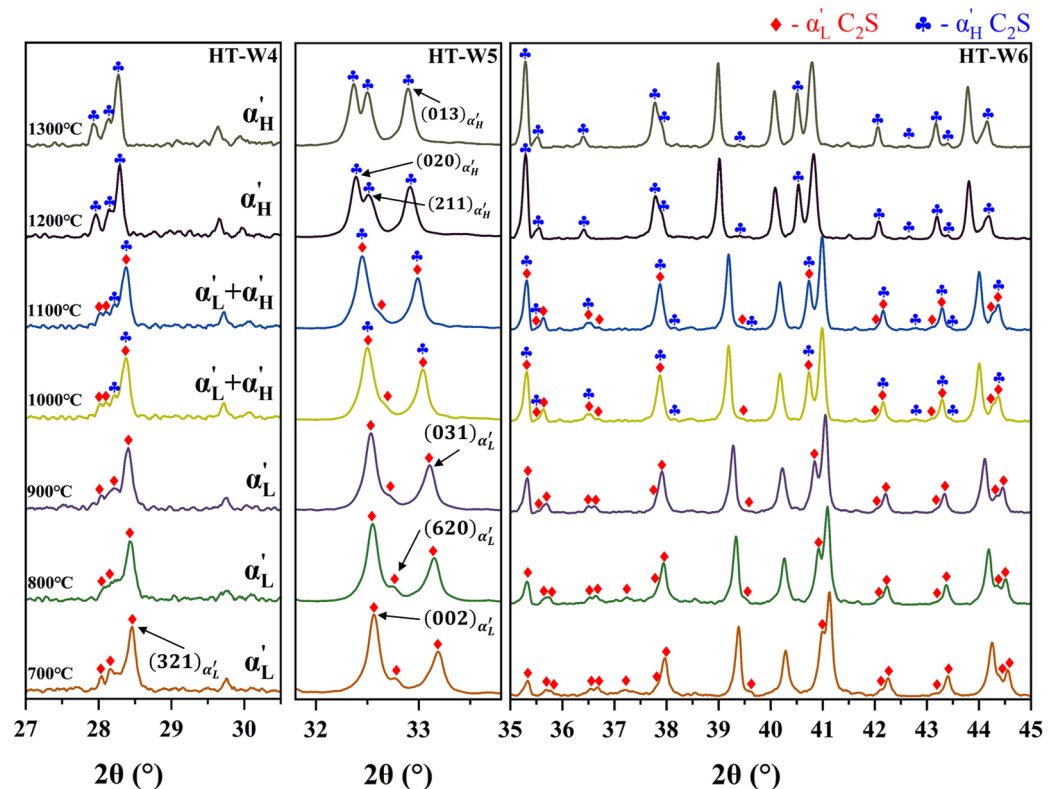


Figure 9. Comparative analysis of high-temperature XRD for sample 3# (700–1300 °C).

3.3. Fourier-Transform Infrared Spectroscopy (FT-IR)

Based on the XRD results obtained at room temperature and high temperature, it is evident that the incorporation of boron can effectively transform β -C₂S into the α'_H phase. However, further investigation is needed to determine the specific occupancy and

substitution behavior of boron within the C_2S structure. From the samples 3# to 13#, a total of 9 samples were selected for FT-IR testing based on the variation in boron content. The results are presented in Figure 10. Figure 10a indicates the absorption peak signals of the major functional groups. The absorption peaks observed at around 1250 cm^{-1} , 1200 cm^{-1} , and 660 cm^{-1} are attributed to the stretching vibrations of $[BO_3]^{3-}$ ions. The asymmetric stretching vibration absorption peaks of $[BO_4]^{5-}$ ions are observed in the range of 1080 cm^{-1} to 950 cm^{-1} [30]. The asymmetric stretching vibration absorption peaks of $V_3 [SiO_4]^{4-}$ ions are observed in the range of 996 cm^{-1} to 846 cm^{-1} , while the asymmetric bending vibration absorption peak of $V_4 [SiO_4]^{4-}$ ions is observed at around 518 cm^{-1} [28–31].

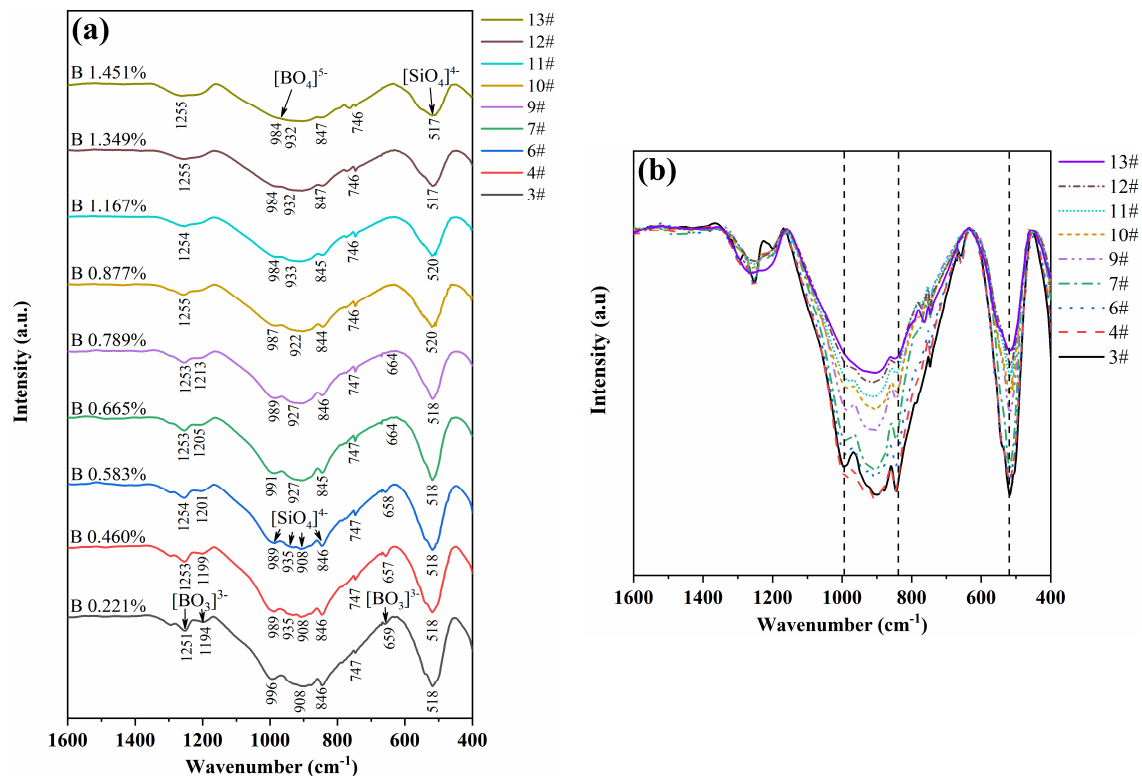


Figure 10. The FT-IR infrared spectra for C_2S doped with different content levels of boron. (a) stacked plot of the samples; (b) the samples plotted with the same baseline.

Combining Figure 10a,b, it can be observed that the absorption peaks of the stretching vibrations of $[BO_3]^{3-}$ ions are more pronounced in samples with a higher content of β - C_2S . After sample 10#, the vibration absorption peak at around 660 cm^{-1} disappears, while the signals at 1250 cm^{-1} and 1200 cm^{-1} gradually weaken and eventually disappear. At this point, the main crystal structure of C_2S in the sample is α'_H -type, indicating the absence of $[BO_3]^{3-}$ groups in the crystal structure of α'_H -type C_2S . The absorption peak signal of the asymmetric bending vibration of $V_4 [SiO_4]^{4-}$ ions at around 518 cm^{-1} gradually weakens with an increase in boron solubility. This indicates a gradual reduction in the $[SiO_4]^{4-}$ groups in the system, which can be attributed to the substitution of B^{3+} for Si^{4+} or the formation of Si^{4+} vacancies due to B^{3+} filling the interstitial sites. By observing the absorption peak signals in the range of 1000 cm^{-1} to 846 cm^{-1} , it can be seen that the absorption peaks at 996 cm^{-1} and 846 cm^{-1} correspond to the asymmetric stretching vibrations of $V_3 [SiO_4]^{4-}$ ions. With an increase in boron doping, the intensity gradually decreases, which is consistent with the variation trend of the absorption peak at around 518 cm^{-1} for $V_4 [SiO_4]^{4-}$. The absorption peak signals in the range of 950 cm^{-1} to 900 cm^{-1} mainly occur at around 935 cm^{-1} and 908 cm^{-1} . Specifically, in sample 3#, the main absorption peak signal is near 908 cm^{-1} , while samples 4# and 6# exhibit absorption

peaks near 935 cm^{-1} and 908 cm^{-1} . Starting from sample 7#, the main absorption peak signal occurs near 935 cm^{-1} , with a slight shift. By considering the boron solubility and the changes in the crystal structure of C_2S , it can be analyzed that sample 3# corresponds to $\beta\text{-C}_2\text{S}$, with its absorption peak signal in the range of 950 cm^{-1} to 900 cm^{-1} primarily occurring near 908 cm^{-1} . With an increase in boron doping, an absorption peak signal near 935 cm^{-1} becomes evident. In the samples with higher boron content, the intensity at this position gradually weakens. This can be attributed to the overlapping effects of the asymmetric stretching vibration absorption peaks of $\text{V}_3 [\text{SiO}_4]^{4-}$ and $[\text{BO}_4]^{5-}$ ions. In other words, boron-doped $\beta\text{-C}_2\text{S}$ exhibits a characteristic absorption peak near 908 cm^{-1} , while $\alpha'_\text{H}\text{-C}_2\text{S}$ exhibits a characteristic absorption peak near 935 cm^{-1} . Additionally, the absorption peak at around 747 cm^{-1} is speculated to be a result of the formation of free SiO_2 , further confirming the role of boron in altering $[\text{SiO}_4]^{4-}$.

Furthermore, the radius of B^{3+} ions is closer to that of Si^{4+} ions, and boron has an electronegativity of 2.0, silicon has an electronegativity of 1.9, while calcium has an electronegativity of 1.0. Comparatively, boron shares more similarities with silicon in terms of properties. Therefore, boron ions have a greater influence on silicon ions in the C_2S structure. Combining the FT-IR vibration peak variations, it can be speculated that in boron-doped C_2S , the stabilization of the $\beta\text{-C}_2\text{S}$ structure is primarily due to the influence of boron ions in the form of $[\text{BO}_3]^{3-}$ groups on the $[\text{SiO}_4]^{4-}$ groups. On the other hand, in boron-doped $\alpha'_\text{H}\text{-C}_2\text{S}$, the stabilization is due to the substitution of boron ions in the form of $[\text{BO}_4]^{5-}$ groups for the $[\text{SiO}_4]^{4-}$ groups. Therefore, when the boron content is low, the $\beta\text{-C}_2\text{S}$ structure can be inferred as $\text{Ca}_2(\text{SiO}_4)_{1-x}(\text{BO}_3)_x\text{O}_{\frac{x}{2}}$. However, when the boron content is high, $[\text{BO}_3]^{3-}$ binds with free oxygen to form $[\text{BO}_4]^{5-}$, which replaces $[\text{SiO}_4]^{4-}$. At the same time, excess B^{3+} partially substitutes for Ca^{2+} , following a similar mechanism to the substitution of Al^{3+} in olivine by Mg^{2+} [29]. This forms a structure of $\text{Ca}_{2-x}\text{B}_x(\text{SiO}_4)_{1-x}(\text{BO}_4)_x$, consistent with the proposed structure for single boron doping into the C_2S structure by Cuesta et al. [33]. The difference is that they represent $[\text{BO}_3]^{3-}$, which is derived from the triangular structure formed after B^{3+} replaces Ca^{2+} . However, in this experiment, it was observed that as the boron content increases, the relative content of $[\text{BO}_3]^{3-}$ gradually decreases, which does not correspond to $\text{Ca}_{2-x}\text{B}_x(\text{SiO}_4)_{1-x}(\text{BO}_4)_x$. Therefore, $\text{Ca}_2(\text{SiO}_4)_{1-x}(\text{BO}_3)_x\text{O}_{\frac{x}{2}}$ is more suitable to represent the $\beta\text{-C}_2\text{S}$ structure.

3.4. Raman Spectroscopy

Nine samples ranging from 3# to 13# were selected for Raman spectroscopy analysis, which was the same as for the Fourier-transform infrared (FT-IR) spectroscopy. The resulting data is presented in Figure 11. Within the frequency range of $300\text{--}50\text{ cm}^{-1}$, the vibrations arise from the lattice's internal components and are primarily attributed to the presence of Ca-O bonds [39]. There is a progressive attenuation in the vibrations of Ca-O observed at 165 cm^{-1} , 236 cm^{-1} , and 303 cm^{-1} as the boron content increases. This suggests that during the conversion process from $\beta\text{-C}_2\text{S}$ to $\alpha'_\text{H}\text{-C}_2\text{S}$, B^{3+} replaces Ca^{2+} ions. This observation corroborates the indications from the FT-IR spectroscopy analysis regarding the $\alpha'_\text{H}\text{-C}_2\text{S}$ structure. The symmetric bending vibrations of $\text{V}_2 [\text{SiO}_4]^{4-}$ are observed at 371 cm^{-1} and 424 cm^{-1} [39–41]. As the boron content increases, $[\text{BO}_4]^{5-}$ gradually replaces $[\text{SiO}_4]^{4-}$, resulting in an interaction between the two which produces an overlapping vibration peak at 390 cm^{-1} and 405 cm^{-1} . Similarly, the overlapping vibration peaks at 846 cm^{-1} and 880 cm^{-1} are attributed to $[\text{BO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ [42]. It is evident that starting from sample 10#, the peak at 846 cm^{-1} significantly broadens, indicating an enhanced role of $[\text{BO}_4]^{5-}$ in the structure. This observation is consistent with the significant weakening of the characteristic absorption peak of $[\text{BO}_3]^{3-}$ in the FT-IR spectroscopy results from sample 10#. The symmetric stretching vibrations of $[\text{BO}_4]^{5-}$ are observed in the range of 962 cm^{-1} to 900 cm^{-1} , and, starting from sample 10#, there is a noticeable enhancement in these vibrations, indicating a gradual increase in the content of $[\text{BO}_4]^{5-}$. The attenuation of the vibration peak at around 977 cm^{-1} of $[\text{SiO}_4]^{4-}$ further confirms the substitution of $[\text{BO}_4]^{5-}$ for $[\text{SiO}_4]^{4-}$.

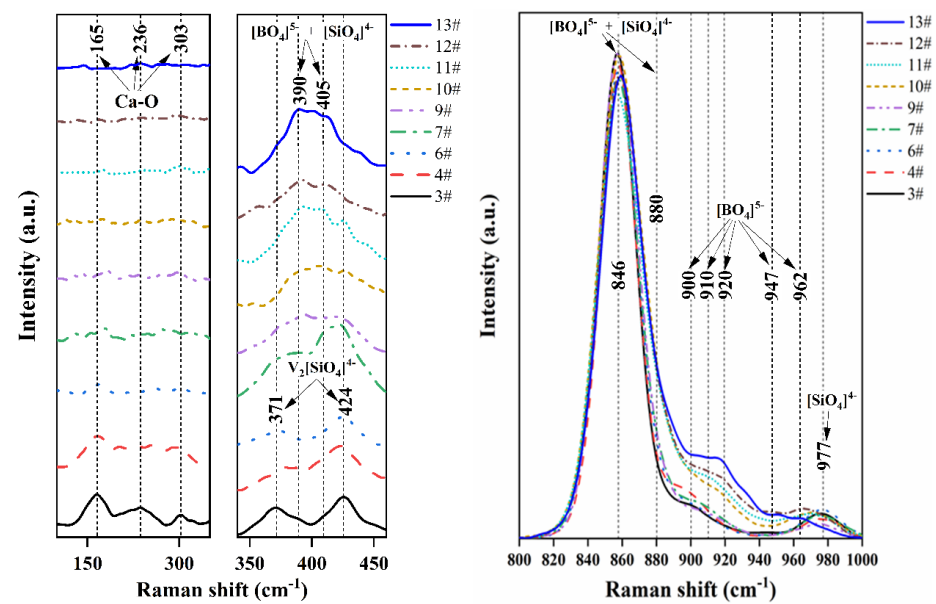


Figure 11. The Raman spectroscopy for C_2S doped with different content levels of boron.

3.5. Quantitative Analysis

The results of the chemical composition analysis of the samples are shown in Table 6. The samples were analyzed using the Rietveld method to quantify the content of different structures of C_2S in samples blank to 13#. Rankinite ($3CaO \cdot 2SiO_2$, short for C_3S_2), γ -, β -, and α'_H - C_2S as well as boron content and the calculated fitting error Rwp are presented in Table 7. The fitting errors for samples 1# to 13# ranged from 0.04 to 0.05 (4–5%), which is significantly lower than the acceptable fitting error of 0.1 (10%). This indicates that the quantitative calculation steps and initial structure selection were correct, and the actual mineral phase structures in the samples are consistent with the initially selected structures.

Table 6. The chemical composition of the samples (wt.%).

Sample	CaO	SiO ₂	B ₂ O ₃	LOI
Blank	64.99	34.83	0.00	0.18
1#	64.96	34.80	0.02	0.21
2#	64.76	34.69	0.27	0.27
3#	64.32	34.46	0.99	0.23
4#	64.03	34.30	1.48	0.20
5#	63.93	34.25	1.65	0.16
6#	63.73	34.14	1.87	0.26
7#	63.60	34.07	2.14	0.19
8#	63.46	34.00	2.32	0.21
9#	63.32	33.92	2.54	0.23
10#	63.12	33.82	2.82	0.24
11#	62.51	33.49	3.75	0.26
12#	62.14	33.29	4.33	0.24
13#	61.91	33.17	4.66	0.26

Sample 1# contains 2.10 wt% of the intermediate phase, Rankinite. This is attributed to the relatively low boron content in the system, which, under the specified firing temperature and holding time conditions, prevents the $3CaO \cdot 2SiO_2$ from combining with the free CaO to form C_2S . In sample 2#, the presence of the intermediate phase Rankinite is no longer observed. However, the boron content in the system is not enough to fully convert C_2S into the β -type. Complete transformation to the β - C_2S is only achieved when the boron content reaches 0.309 wt%, as observed in sample 3#. These findings are consistent with the qualitative analysis of XRD phase identification. The content of β - C_2S gradually decreases

with increasing boron solid solution, while the content of $\alpha'_H\text{-C}_2\text{S}$ increases. At a boron content level of 1.451 wt%, the C_2S in the system is predominantly $\alpha'_H\text{-C}_2\text{S}$ (95.40 wt%). The quantitative fitting analysis plots for samples 3#, 6#, 11#, and 13# are shown in Figure 12.

Table 7. Rietveld quantitative phase analysis (wt.%) of the samples.

Sample	$\beta\text{-C}_2\text{S}$	$\alpha'_H\text{-C}_2\text{S}$	$\gamma\text{-C}_2\text{S}$	C_3S_2	f-CaO	B *	R_{wp}
Blank	10.92	0.00	89.08	0.00	0.00	0	0.0442
1#	86.07	0.00	9.67	2.10	2.16	0.006	0.0432
2#	96.86	0.00	3.14	0.00	0.00	0.085	0.0451
3#	100	0.00	0.00	0.00	0.00	0.309	0.0483
4#	88.38	11.62	0.00	0.00	0.00	0.460	0.0534
5#	84.88	15.12	0.00	0.00	0.00	0.514	0.0445
6#	78.43	21.57	0.00	0.00	0.00	0.583	0.0518
7#	70.99	29.01	0.00	0.00	0.00	0.665	0.0442
8#	62.85	37.15	0.00	0.00	0.00	0.723	0.0443
9#	55.81	44.19	0.00	0.00	0.00	0.789	0.0455
10#	48.01	51.99	0.00	0.00	0.00	0.877	0.0438
11#	25.68	74.32	0.00	0.00	0.00	1.167	0.0429
12#	12.18	87.82	0.00	0.00	0.00	1.349	0.0520
13#	4.60	95.40	0.00	0.00	0.00	1.451	0.0516

* Note: The boron content was determined using ICP-OES testing, as previously presented in Table 4.

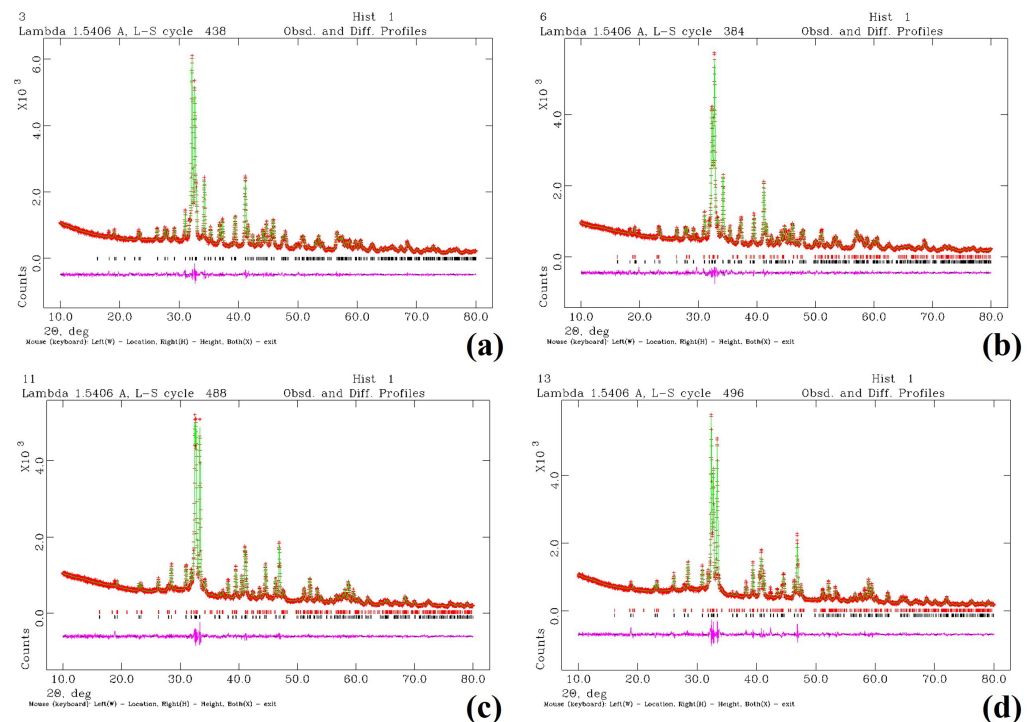


Figure 12. Fitting graph for quantitative calculation of the sample. (a) 3#; (b) 6#; (c) 11#; and (d) 13# (The black stripes represent $\beta\text{-C}_2\text{S}$, while the red stripes represent $\alpha'_H\text{-C}_2\text{S}$).

Analysis of the data presented in Table 7 reveals a linear correlation between the content of $\beta\text{-C}_2\text{S}$, $\alpha'_H\text{-C}_2\text{S}$, and boron solid solution. Linear fitting was conducted on the data and the results are illustrated in Figure 13. The obtained R^2 value of 0.9916 signifies a strong linear relationship between the boron solid solution content and the C_2S structure.

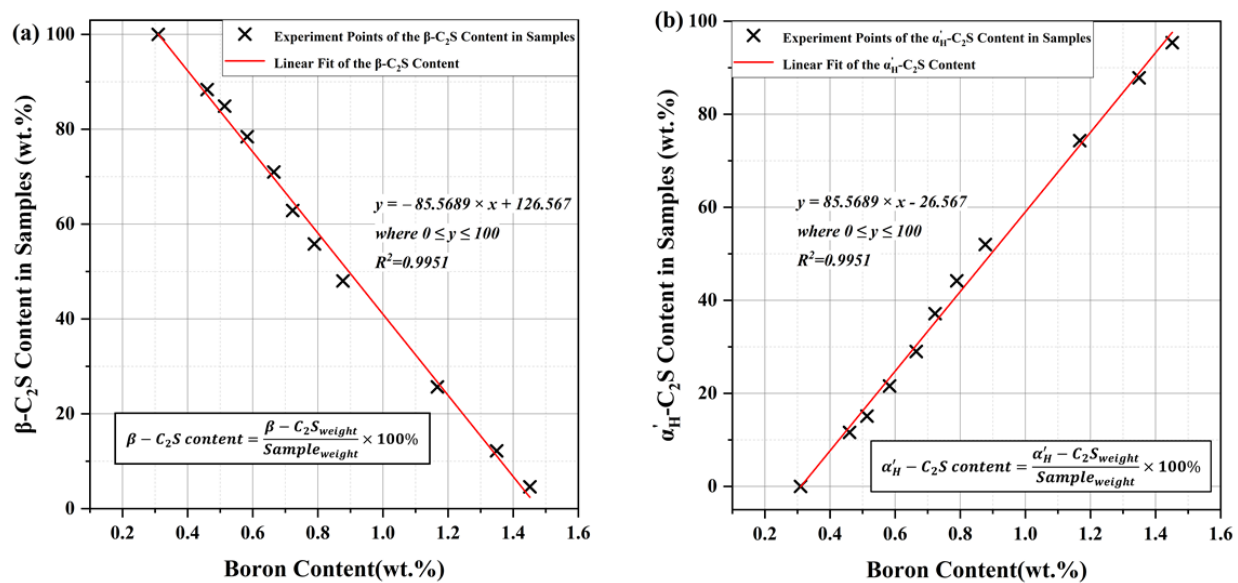


Figure 13. The linear fitting of the boron and C₂S content. (a) Boron vs. β -C₂S and (b) boron vs. α'_H -C₂S.

According to the linear relationship between the content of boron solid solution and the content of β -C₂S and α'_H -C₂S, the variable x in β -Ca₂(SiO₄)_{1-x}(BO₃)_xO₂ and α'_H -Ca_{2-x}B_x(SiO₄)_{1-x}(BO₄)_x has a specific value. A function relationship is constructed with the β -C₂S content (β -C₂S_{content}) and α'_H -C₂S content (α'_H -C₂S_{content}) as independent variables, and the boron solid solution content (C_{Boron}) as the dependent variable: $c_\beta \times \beta\text{-C}_2\text{S}_{\text{content}} + c_{\alpha'_H} \times \alpha'_H\text{-C}_2\text{S}_{\text{content}} = C_{\text{Boron}}$. For the calculation data of samples 3# to 13# in Table 7, a multiple linear regression analysis was conducted. The constant of the regression equation was set to 0, and the confidence level was set at 95%. The results of the regression analysis are shown in Table 8. The constructed function relationship is given by the equation $0.3142 \times \beta\text{-C}_2\text{S}_{\text{content}} + 1.4753 \times \alpha'_H\text{-C}_2\text{S}_{\text{content}} = C_{\text{Boron}}$. In this equation, $c_\beta = 0.3142$ represents the boron content in the β -Ca₂(SiO₄)_{1-x}(BO₃)_xO₂ structure, and the calculated value of x is found to be 0.05. This calculation indicates that the β -C₂S structure is composed of Ca₂(SiO₄)_{0.95}(BO₃)_{0.05}O_{0.025}. Similarly, $c_{\alpha'_H} = 1.4753$ represents the boron content in the α'_H -Ca_{2-x}B_x(SiO₄)_{1-x}(BO₄)_x structure, and the calculated value of x is found to be 0.11. This finding suggests that the α'_H -C₂S structure is composed of Ca_{1.89}B_{0.11}(SiO₄)_{0.89}(BO₄)_{0.11}.

Table 8. The results of multiple linear regression analysis.

Regression Analysis				Coefficients			
R ²	Standard Error	c_β	Standard Error	p-Value	$c_{\alpha'_H}$	Standard Error	p-Value
0.9993	0.02752	0.3142	0.01674	0.000	1.4753	0.01843	0.000

4. Conclusions

This study investigates the evolution patterns of the crystal structure of boron-doped C₂S using various characterization techniques. Structural models for β -C₂S and α'_H -C₂S are constructed, and the correlation between boron doping levels and different levels of C₂S content is determined using regression analysis. Additionally, the structural formulas for boron-doped C₂S are derived. The main findings of this study can be summarized as follows:

1. Boron doping can stabilize both the β -C₂S and high-temperature phase α' _H-C₂S. As the boron solubility increases, the crystal structure of C₂S transitions directly from the β -phase to the α' _H-phase, without the intermediate structure of α' _L-C₂S, which is in contrast to the high-temperature XRD behavior.
2. The β -C₂S and α' _H-C₂S structures exhibit a corresponding relationship in terms of their characteristic diffraction peaks. This relationship can be represented by a transformation matrix P, where $P = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$.
3. When the boron content is 0.309 wt%, the C₂S structure completely transforms into the β -phase. When the boron content is 1.451 wt%, the C₂S structure is predominantly in the α' _H-phase. Furthermore, the boron content shows a linear relationship with the concentrations of β -C₂S and α' _H-C₂S, respectively.
4. The structural models for β -C₂S and α' _H-C₂S were determined using structural analysis. It was found that β -C₂S has a structural formula of Ca₂(SiO₄)_{1-x}(BO₃)_xO₂^{x/2}, while α' _H-C₂S has a structural formula of Ca_{2-x}B_x(SiO₄)_{1-x}(BO₄)_x. Regression analysis was performed using the quantitative calculation results and boron content data, which yielded the following structural formulas: β -C₂S is Ca₂(SiO₄)_{0.95}(BO₃)_{0.05}O_{0.025}, and α' _H-C₂S is Ca_{1.89}B_{0.11}(SiO₄)_{0.89}(BO₄)_{0.11}.

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