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A quantitative analysis of dicalcium silicate synthesized via different sol-gel methods

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HIGHLIGTTS
- Hiding of CaO and SiO₂ in XRD-amorphous leads to a false impression of the purity.
- Calcium polymer network via the Pechini method yields pure β-dicalcium silicate.
- CaCO₃ formation leads to an increase in the calcination temperature.
- The big crystallite size (D cryst) lowers the yield of β-dicalcium silicate.
- The change in Ca/Si stoichiometry from 2.0 to 1.7 is not recommended.

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ABSTRACT
In this paper, the synthesis of dicalcium silicate (C₂S) via sol-gel (acid-catalyzed) process including aqueous route, non-aqueous route, and the Pechini method is reported. The composition of C₂S (α, β, and γ) polymorphs, by-products, and amorphous content is established by employing QXRD (quantitative X-ray diffraction) studies. The attention has been focused to comprehend assay-amorphous relationships of C₂S yield. The intermediate dried gels have been investigated via thermal analysis to monitor changes in the gel structures and precursors at low temperatures. The synthetic parameters including calcination time and temperature, Ca/Si molar ratio and mode of cooling have been optimized to get pure β-C₂S with low amorphous content. The dependency of β → γ C₂S polymorphic transformation on mean crystallite size (D cryst) is studied. Overall, the Pechini method exhibits the most promising results for the purity and tuning of β-C₂S polymorph. Moreover, the non-aqueous and aqueous routes require calcining the dried gel at a temperature higher than 1200 °C due to the presence of CaO precursors as CaCO₃. The theoretical calculations of amorphous content have revealed that the change in the stoichiometry from 2.0 to 1.7 Ca/Si ratio is not a viable solution to improve the C₂S product yield.

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1. Introduction
Dicalcium Silicate (C₂S) is an important natural mineral known as larnite or belite. It is a monoclinic (β) polymorph of C₂S and exhibits interesting properties for the non-toxic bioactivity, excellent stability under thermal and chemical conditions, high energy storage capacity as well as flame-resistant [1-3]. It is used in various applications such as white light-emitting diodes (LEDs), high-density energy storage and energy production, environmental remediation, and biomedical engineering [4-7].
C2S is also a minor component of Portland cement clinker (5–10 wt%) and is becoming more relevant due to the increasing use of alternative binders (belleite clinkers contain between 40 and 60 wt% belite mineralogically) [8,9]. It is currently investigated as a solution to reduce the CO2 emissions of the cement industry as well as supplementary cementitious materials that contain C2S such as converter steel slag [7,10-12,13]. Therefore, it is important to understand the formation and hydraulic properties of C2S which is complicated by the existence of five crystalline polymorphs (Fig. 1) [14,15]. The most common modification in the aforementioned materials is β-C2S and will be the focus of this investigation. The thermodynamically stable polymorph at room temperature is γ-C2S, which is highly undesirable in Portland cement due to the low hydraulic activity. The transition from α (orthorhombic) to β (monoclinic) is reversible while the transformation from β (monoclinic) to γ (orthorhombic) causes the irreversible disintegration of the beta phase due to microcracks because of a 14 % increase in lattice volume in a phenomenon known as dusting. The C2S reactivity, in general, depends on the polymorph, foreign ion substitution, and crystallite size. It is possible to stabilize polymorphs other than γ-C2S at room temperature by the incorporation of dopants such as Al3+, B3+, P5+, S6+, Fe3+, and K1+ [16]. The general order of reactivity of different polymorphs of C2S is as follows [17,18]:

Amorphous C2S > α-C2S > β-C2S > γ-C2S

C2S can be synthesized by various traditional (solid-state or fusion) processes and alternatives such as self-combustion or solution combustion synthesis, hydrothermal synthesis, aerosol flame synthesis, and heated at atmospheric temperature. The sol–gel methods have been added in the gelation of colloidal particles, hydrolysis, polycondensation of nitrates or alkoxides, and hypercritical drying of gel [27]. The resulting product is dried and heated at atmospheric temperature. The sol–gel methods have advantage of synthesizing β-C2S that has a high specific surface area (up to 26.5–27 m²/g) and is stable at room temperature without using any additional chemical stabilizers/dopants. The synthesis temperatures also tend to be lower compared to solid-state synthesis [28,22,29,30]. The stability of β-C2S synthesized via sol–gel method has been attributed to the small particle size (1–3 μm) that prevents a transformation into γ-C2S [30].

A qualitative X-ray powder diffraction (XRD) is the standard analytical tool for identifying C2S polymorphs [31]. However, the diffractograms are typically complex with an overlap of the diffraction peaks of α, β, and γ-C2S. If the reaction is incomplete other phases such as wollastonite, quartz or free lime can also be present, making analysis even more complex. So, it is often not possible to identify all impurities or C2S polymorphs, especially if their content is very low. Moreover, the method allows no insight into the amorphous content meaning it is frequently ignored [32]. However, the amorphous C2S tends to be the most reactive part of the sample, so its content should be known to reliably design materials for various applications.

Quantitative XRD (QXRD, Rietveld method) can solve these problems, especially if an internal standard is applied to determine the amorphous content. It can also be used to derive additional information about a sample, such a crystallite size, which is an important parameter that can determine the stability of C2S polymorphs. However, this method is rarely applied [16,23,27,28,33,34] and to the best of the author’s knowledge, not detailed QXRD including amorphous content determination exists of C2S synthesized via sol–gel (aqueous, non-aqueous, and the Pechini) methods [16,35-37].

Therefore, the aim of this paper is to study the content of C2S (α′, β, γ) polymorphs quantitatively including amorphous phase and minor phases via three different sol–gel (acid-catalyzed) using the Pechini method, non-aqueous route, and aqueous route. The three methods are compared to see which sol–gel route provides high β-C2S polymorph yield with low amorphous content [5,38,7]. The different calcination temperatures and durations are compared, as well as changing the Ca/Si stoichiometry [26,39]. The calcination temperatures and times have been chosen to get a clear insight into the relationship between amorphous content, secondary phases, and total C2S content [16,28,40,41].

The molar ratio, calcination temperature, and time, as well as reaction parameters, have been summarized in Table 1 and are based on previously reported synthesis [16,26].

2. Materials

Ca(NO3)2·4H2O (Sigma-Aldrich CAS: 13477–34-4, ≥99.0 %), colloidal SiO2 (30 wt% Ludox AM Sigma-Aldrich), colloidal SiO2 (40 wt% Ludox AM Sigma-Aldrich), CH3CO2H glacial (Sigma-Aldrich CAS: 64–19-7), SiOCl2·H2O (Sigma-Aldrich CAS:78–10-4, ≥99.0), CH3O-H2O (VWR, Analytical grade, CAS: 5949–29–1), HNO3 (Sigma-Aldrich, CAS:7697–37-2, ≥65 %) and CH3OH (Sigma-Aldrich CAS:64–17–5) were used as received. The reagents were added in the stoichiometric ratios corresponding to the synthesis of C2S unless indicated otherwise.

The molar ratio, calcination temperature, and time, as well as reaction parameters, have been summarized in Table 1 and are based on previously reported synthesis [16,26].

3. Methods

3.1. Pechini method

The Ca(NO3)2·4H2O and colloidal silica (40 wt% suspensions in water) were employed as a cation source of Ca and Si at a 2:1 M ratio. The citric acid monohydrate was chosen as a source of α-hydroxy acid to chelate with Ca2+, and ethylene glycol to construct a gel through esterification. The resin content (Rc) was fixed to 85 %, as it gives the best results according to the literature [16]. The Rc can be adjusted with Equation (1):

![Fig. 1. Different polymorphs of dicalcium silicate (C2S) and their transition temperatures [11,15].](image-url)
1.7901 Å and \( K_\alpha \) 1.7929 Å, Detector: LynxEye). Both instruments have a fixed divergence slit with an opening of 0.5° and 0.04 rad Soller slits. The 2 Theta range was 5° to 90° with a step size of 0.02. All samples for qualitative and quantitative analysis were prepared via back-reflection. The synthesized phases were identified with X’Pert Highscore Plus 2.2 employing the ICDD PDF-2 database.

For QXRD (Quantitative X-ray diffraction), an internal standard (Si: 10 wt% of the total sample) was mixed homogenously by using an XRD McCrone micronizing mill. TOPAS 4.2 Bruker software was employed for the quantification and determination of crystallite size using the fundamental peak fitting parameter approach. The crystal structures for quantification were obtained from the ICSD database as shown in Table 2. The error values given in the results are the errors as calculated by TOPAS.

The thermal analysis was done on dried gel samples using a Jupiter STA 49 F1 Netzsch instrument. The sample was heated from 40 °C to 1000 °C at the rate of 5 °C/min under air environment.
The IR spectra were measured with a Fourier-Transform-Infrared spectrometer (FT-IR) from Perkin Elmer Frontier FTIR. The spectrometer was equipped with diffuse reflectance device Gladi. ATR. Sixty scans were acquired with optical retardation of 0.25 cm and a resolution of 4 cm\(^{-1}\) from 400 to 4000 cm\(^{-1}\).

Scanning Electron Microscopy (SEM) was performed using a Phenom Pro-X scanning electron microscope. The sample was prepared by spreading the powder on conductive carbon adhesive tapes followed by coating with gold. Micrographs were recorded using a backscattered electron detector (BSE) at 15 kV with a spot of four.

4. Results and discussion

4.1. Results of C\(_2\)S synthesis via the Pechini method

The intermediate, amorphous gel produced with the Pechini method was charred at 250 °C and then TG/DSC was analyzed to determine the lowest calcination temperature C\(_2\)S synthesis (Fig. 3(a, b)). The decomposition of the dried gel can be broadly divided into three main steps. The first mass-loss step from 40 to 250 °C can be attributed to the loss of water physisorbed on the surface of the dried gel. The second exothermic step (250–600 °C) can be assigned to the resin breakdown and residual carbon combustion. The mass loss step around 251–350 °C can be attributed to the polymer fragmentation, formed by polyestersification of citric acid and ethylene glycol. The mass loss step around 405–445 °C may occur due to the decomposition of the carboxylic group, carbonates, and nitrates. The exothermic peak of polymer fragmentation may overlap with the endothermic process of decomposition of nitrates and carbonates in DTA analysis. The third slight exothermic step (600–700 °C) is attributed to the crystallization of C\(_2\)S. The TG signal becomes stable at around 650 to 700 °C. So, 700 °C was chosen as the lowest calcination temperature [31].

The C\(_2\)S synthesized via the Pechini method has been investigated after heating the precursor to temperatures in the range of 700–1400 °C and a calcination time of 1–3 h with cooling Method 1 unless stated otherwise. The XRD diffractograms without internal standard (Silicon) are shown in Fig. 4. And the results of QXRD are shown in Table 3.

At 700 °C, the a’-C\(_2\)S (22.5 wt%) polymorph and amorphous content (68.3 wt%) were the major phases with minor amounts of b-C\(_2\)S (9.2 wt%). The particles calcined at 700°C appeared spherical, porous, and highly agglomerated (Fig. 8(a)), which is align with the literature [42].

By increasing the calcination temperature to 800 °C, the dominant crystalline phase became b-C\(_2\)S (27.5 wt%) alongside a’-C\(_2\)S (19.4 wt%) and amorphous content (53.1 wt%). The high amorphous content at 700–800 °C points out that the C\(_2\)S (a’ and b) polymorphs matrix is poorly crystalline.

When the calcination temperature was raised to 900 °C, the a’-C\(_2\)S completely transformed to b-C\(_2\)S (83.0 wt%). The amount of amorphous content decreased from 53.1 to 16.8 wt% while only b-C\(_2\)S crystallized out of the amorphous matrix. A further increase in calcination temperature to 1000 °C led to only a small increase in b-C\(_2\)S (83.7 wt%). At 1100 °C, γ-C\(_2\)S (2.9 wt%) started to appear, which increased slightly (3.7 wt%) at 1200 °C. The γ-C\(_2\)S formation was observed at a calcination temperature of 1300 °C with natural furnace cooling (cooling Method 1) in the earlier studies [37]. Overall, b-C\(_2\)S was the dominant product in the range of 900–1200 °C. The sequence of phase development was consistent with previous studies [36]. Minor amounts of wollastonite, quartz, grossular, and CaNaAlO were observed during the synthesis. The quartz and wollastonite are likely due to incomplete conversion of reactants, while the impurity phases of grossular and CaNaAlO may form due to trace amounts of aluminum and sodium in the reagent or the corundum from the crucible [37].

At 1400 °C, the amount of γ-C\(_2\)S reached 23.4 wt% in the sample cooled via Method 1. The γ-C\(_2\)S is not formed at 1400°C, because it is a low-temperature modification. Instead, it is formed out of b-C\(_2\)S during cooling. The phenomenon of b → γ-C\(_2\)S transformation is dependent upon particle size [41]. With increasing the calcination temperature, the crystallite size of the C\(_2\)S increases due to sintering effects. The internal strain is generated inside the b-C\(_2\)S crystals during cooling. This strain becomes larger with increasing crystallite size and will result in the transformation of b-C\(_2\)S into γ-C\(_2\)S once a critical crystallite size is achieved. The β-destabilization can be restricted by increasing the cooling speed (physical stabilization) above the γ-stability field temperature or by incorporating impurities into the crystal structure (chemical stabilization) [39]. The calcined sample at 1400 °C cooled down via Method 2 decreased γ-C\(_2\)S from 23.4 wt% to 5.7 wt% with 92.0 wt% b-C\(_2\)S [41]. The metastable b-C\(_2\)S achieved at 1400 °C with cooling Method 2 was analyzed 8 weeks later and no conversion into γ-C\(_2\)S had taken place. The average crystallite size (Dcrystalline) growth at increasing calcination temperature and its correlation with C\(_2\)S polymorphic transformation is discussed in Section 4.4.

A few representative FTIR spectra have been taken to investigate bonding systems (Fig. 7(a)). In the case of the Pechini method, the strong and broad bands around 3696 cm\(^{-1}\) and 509 cm\(^{-1}\) are attributed to \(\alpha\)-\(\beta\)-C\(_2\)S (orthorhombic). The band at 997 cm\(^{-1}\) can be attributed to b-C\(_2\)S. At 900 °C and 1000 °C, the new bands 503 cm\(^{-1}\), 540 cm\(^{-1}\) in the SiO\(_2\)-bending region and 847 cm\(^{-1}\), 865 cm\(^{-1}\), 895 cm\(^{-1}\), 992 and 1016 cm\(^{-1}\) in the SiO\(_2\)-stretching region clearly indicates the presence of b-C\(_2\)S. As the calcination temperature is elevated higher than 1000 °C, a new band appears at 497 cm\(^{-1}\) in the SiO\(_2\)-bending region indicating the presence of γ-C\(_2\)S. The strong band regions at 519 cm\(^{-1}\), 541 cm\(^{-1}\), 841 cm\(^{-1}\), 893, and 991 cm\(^{-1}\) indicate the strong presence of b-C\(_2\)S. The FTIR studies of C\(_2\)S synthesized via the Pechini method exhibited complete agreement with previous studies [43,27,41].

4.2. Results of C\(_2\)S synthesis via the non-aqueous route

The thermal events of intermediate gel dried at 150 °C were analyzed via TG and DSC as shown in Fig. 3(c, d). The first endothermic mass loss step occurs due to the loss of physisorbed water on the dried gel sample. The second strong endothermic event is comprised of the three mass loss steps. The mass loss of around 440–535 °C occurs due to the removal of by-products (H\(_2\)O and C\(_2\)H\(_5\)OH) upon completion of TEOS hydrolysis and condensation. The mass loss around 536–584 °C is attributed to the resin breakdown and residual carbon combustion. The mass loss around 536–584 °C may form due to trace amounts of aluminum and sodium in the gel [39]. The calcined sample at 1400 °C reached 23.4 wt% in the sample. The mass loss of around 440–535 °C occurs due to the removal of by-products (H\(_2\)O and C\(_2\)H\(_5\)OH) upon completion of TEOS hydrolysis and condensation. The mass loss around 536–584 °C is attributed to the resin breakdown and residual carbon combustion. The mass loss around 536–584 °C may form due to trace amounts of aluminum and sodium in the gel [39]. The calcined sample at 1400 °C reached 23.4 wt% in the sample.
Fig. 3. Thermal analysis of intermediate dried gels from all sol–gel routes (a) TG and DTG (b) DTA analysis of the dried gel synthesized from the Pechini method pre-charred at 250 °C (c) TG and DTG (d) DTA analysis of the dried gel synthesized via non-aqueous route and pre-dried at 150 °C (e) TG and DTG (f) DTA analysis of the dried gel synthesized via aqueous route and pre-dried at 150 °C.
temperature for the complete conversion of reactants into a product. For the C$_2$S synthesis via the non-aqueous route, the precursors were calcined in the temperature range of 1000–1200°C and a calcination time from 5 to 8 h was chosen [30]. The XRD patterns without internal standards are shown in Fig. 5 and the results of QXRD are shown in Table 4.

When the intermediate dried-gel was fired at 1000°C for 8 h, the major phase was β-C$_2$S (73.4 wt%) with wollastonite (5.1 wt%), unreacted lime (7.6 wt%), and (12.3 wt%) XRD amorphous. The presence of free-lime and wollastonite indicates that the conversion of reactants was incomplete. Therefore, the calcination temperature was elevated to 1200°C for 5 h, and γ-C$_2$S (4.5 wt%) appeared alongside β-C$_2$S (81.3 wt%) with a clear decrease in wollastonite (1.7 wt%) and free-lime (4.9 wt%) as well as a decrease of the amorphous content to 5.7 wt%. A further increase of the calcination time from 5 to 8 h at 1200°C yielded more γ-C$_2$S (16.7 wt%) and a decrease in β-C$_2$S (from 81.3 to 75.1 wt%). The 3.8 wt% of amorphous content at 1200°C for 8 h calcination suggested that most of the C$_2$S matrix was crystalline. However, it was successful in further decreasing the lime (2.7 wt%) and wollastonite (0.6 wt%) content. A small amount of quartz and cristobalite was also visible, as the remaining, unreacted SiO$_2$ in the amorphous content.
started to crystallize. It seems clear that the content of these two phases is only reduced due to sintering reactions taking place at elevated temperatures as well as longer reaction times. Moreover, the wollastonite and lime crystallize directly out of the amorphous phase showing an incomplete reaction. It can be explained based on the thermal events of precursors’ transformation during calcination. Firstly, the presence of calcium carbonate during thermal events delays the reaction with the silica network (Fig. 3 (c, d)). Second, the formation of Si-O-Si bonds traditionally takes place at high temperatures while the condensation reaction between the –OH group begins at room temperature. However, many of Si-O-Si bonds are not stable even at a temperature higher than 1000 °C elevating the incomplete polycondensation reaction of Si-O-Si bondingly is completed via high-temperature calcination.

An interesting phenomenon was observed when the dried-gel intermediate was calcined in the form of loose powder at 1200 °C for 5 as opposed to the standard pellet. The QXRD showed higher β-C2S (6.6 wt%) than the pressed pellet results (XRD-amorphous = 3.8 wt%, CaO = 7.6 wt%). As the energy of the constrained particle is different from the isolated particle. That’s why, the pressing of the pellet likely contributes toward the matrix constraint for particle growth and stabilizes more β-C2S [39]. Considering the results, all the intermediate dried-gel samples synthesized via non-aqueous and aqueous routes are pressed into a pellet before calcination to obtain optimal results. The transmittance pattern at the 1459–1460 cm\(^{-1}\) and 3639 cm\(^{-1}\) can be attributed to the calcium carbonates and hydroxide synthesized via the non-aqueous route due to partial carbonation of free lime (Fig. 7 (b)). The bands in the region 992–998 cm\(^{-1}\), 896 cm\(^{-1}\), 840–870 cm\(^{-1}\) correspond to β-C2S, and the broadening of peaks can be attributed to the formation of γ-C2S at 1200 °C for 8 h calcined sample [30].

### 4.3. Results of C\(_2\)S synthesis via aqueous route

The synthesis of C\(_2\)S was also done using the aqueous route of the sol–gel method. The thermal events of intermediate gel dried at 150 °C via aqueous route exhibited the mass loss events such as removal of water of nitrates and physisorbed water followed by the decomposition of nitrates, dehydroxylation of silica network and calcium hydroxide as well as the removal of carbon dioxide from calcium carbonate respectively. (Fig. 3 (e, f)). The initial Ca/Si molar ratio was 2 and the sample was calcined at 1200°C for 5 h. The major phase was β-C2S (77.6 wt%) alongside γ-C2S (6.6 wt%) and a low amount of XRD-amorphous (3.7 wt%) phase (Table 5). The amount of CaO was rather higher as 9.1 wt% than non-aqueous route (4.9 wt%). Minor phases like quartz (0.1 wt%) and cristobalite (0.8 wt%) were also observed. The high CaO amount indicated an incomplete reaction between the calcium and silica precursors like the non-aqueous synthesis route. However, the lime content was much higher and the amorphous content lower, which seems the point to a problem with the stoichiometry instead (Table 5). To test this hypothesis as well as to avoid unreacted free lime, the Ca/Si ratio from 2.0 to 1.7 was adjusted as reported in a few studies [26,39]. The intermediate dried gel with a 1.7 Ca/Si starting molar ratio was fired at 1000 °C, 1140 °C, and 1200 °C respectively.

The XRD patterns with the internal standard are shown in Fig. 6 and the results of QXRD are shown in Table 5. At 1000 °C the sample was calcined for 8 h and the major phases were β-C2S (46.1 wt%) and XRD-amorphous phase (41.3 wt%) beside CaO (6.1 wt%) and wollastonite (3.1 wt%). As the temperature was elevated to 1140 °C (5 h calcination), the amount of wollastonite decreased to 0.7 wt% while the CaO content increased (7.8 wt%). A further increase of the calcination temperature to 1200 °C (5 h calcination) leads to a slight increase in CaO content (8.7 wt%). The comparison of both starting molar ratios (1.7 and 2.0) indicates that there was no significant decrease in the unreacted CaO (from 9.1 to 8.7 wt%) despite the lower CaO content.

The results clearly show that a reduction in the starting CaO content was not successful in reducing the free lime content after calcination. To make sure that the results are not due to an incorrect quantification, the theoretical composition of the amorphous content was calculated via subtracting all the mineral phases determined with QXRD from the bulk composition (Table 6). If the difference is positive that means the QXRD results are at least theoretically possible. This calculation was done for two samples, one with a Ca/Si ratio of 2 and the other with a Ca/Si ratio of 1.7, both calcined at 1200 °C for 5 h.

The theoretical composition of the amorphous content for the Ca/Si = 2 sample is CaO = 0.6 mol. % and SiO\(_2\) = 3.5 mol. %, showing that a lot of the SiO\(_2\) remains XRD-amorphous while the CaO tends to crystallize. In the Ca/Si = 1.7 sample, the theoretical composition of the amorphous content is CaO = -1 mol. %, SiO\(_2\) = 4.3 mol. %. The CaO content is negative that is not possible for a real phase. Considering the error of QXRD, it can be assumed that the real CaO content in the amorphous phase is around 0 mol. %, and thus it consists entirely of amorphous SiO\(_2\). Conclusively, the change in stoichiometry (2.0 to 1.7 Ca/Si molar ratio) is not a viable solution to convert more reactants into β-C2S.

The TG/DSC analysis of the pre-dried intermediate at 150 °C offers an explanation for this phenomenon (Fig. 3 (c,d,e,f)). It clearly shows that the formation of calcium carbonate and the incomplete Si-O-Si network are the inherent issues of the aqueous and non-aqueous routes of sol–gel synthesis. Conclusively, the part of the calcium tends to react with the amorphous silica during high-temperature sintering and long calcination time. This explains the gradual decrease of free lime and wollastonite when the

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<td>Calcination time (h)</td>
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<td>8 Pressed pellet</td>
<td>5 Powder</td>
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<tr>
<td>β-C(_2)S (wt. %)</td>
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<td>γ-C(_2)S (wt. %)</td>
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<td>Wollastonite-triclinic (wt. %)</td>
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<td>Wollastonite-2 M (wt. %)</td>
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<td>Lime (wt. %)</td>
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<td>Grossular (wt. %)</td>
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<td>Grossular (wt. %)</td>
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<td>XRD-amorphous (wt. %)</td>
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Table 5
QXRD of the product synthesized by aqueous route with error values.

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<td>Ca/Si molar ratio (mol)</td>
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<td>1.7</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>β-C2S (wt. %)</td>
<td>46.1 ± 0.3</td>
<td>74.3 ± 0.3</td>
<td>78.7 ± 0.3</td>
<td>77.6 ± 0.9</td>
</tr>
<tr>
<td>γ-C2S (wt. %)</td>
<td>2.8 ± 0.2</td>
<td>11.6 ± 0.2</td>
<td>7.8 ± 0.2</td>
<td>6.6 ± 0.3</td>
</tr>
<tr>
<td>Lime (wt. %)</td>
<td>6.1 ± 0.2</td>
<td>7.8 ± 0.1</td>
<td>8.7 ± 0.1</td>
<td>9.1 ± 0.2</td>
</tr>
<tr>
<td>Grossular (wt. %)</td>
<td>0.5 ± 0.2</td>
<td>1.0 ± 0.2</td>
<td>1.0 ± 0.2</td>
<td>2.0 ± 0.3</td>
</tr>
<tr>
<td>Quartz (wt. %)</td>
<td>0.04 ± 0.02</td>
<td>0.04 ± 0.02</td>
<td>0.1 ± 0.05</td>
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</tr>
<tr>
<td>Cristobalite (wt. %)</td>
<td></td>
<td></td>
<td></td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>Wollastonite-2M (wt. %)</td>
<td>0.7 ± 0.2</td>
<td>0.6 ± 0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wollastonite-1A (wt. %)</td>
<td>3.1 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XRD amorphous (wt. %)</td>
<td>41.3 ± 1.2</td>
<td>4.6 ± 1.2</td>
<td>3.2 ± 1.3</td>
<td>3.7 ± 2.3</td>
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</table>

Fig. 6. XRD pattern of C2S synthesized via an aqueous route of the sol–gel method. The crystalline phases are labeled as Si = as internal standard, β = β-C2S, W = wollastonite-2M, L = lime, G = grossular, γ = γ-C2S, WI = wollastonite-1A.

Fig. 7. a) FTIR spectra of C2S synthesized via Pechini method. b) FTIR spectra of C2S synthesized via non-aqueous and aqueous routes.
calcination temperature is raised from 1000 to 1200 °C (Table 4). Moreover, the alkoxide-assisted Si-O-Si network as in the case of the non-aqueous route tends to react with calcium precursors more efficiently than an aqueous route. (Table 4 and 5)

The FTIR studies of the aqueous route (1.7 Ca/Si molar ratio at 1140 °C), the broadening of vibration peaks indicated the change in the symmetry order from $b$ (monoclinic) to $c$ (orthorhombic) showing the presence of $c$-C$_2$S (Fig. 7 (b)). All this information exhibited a compromise with previously reported FTIR studies [41].

4.4. Effect of calcination temperature on C$_2$S mean crystallite size ($D_{\text{cryst}}$):

The idea of mean crystallite size ($D_{\text{cryst}}$) helps to understand the C$_2$S polymorphic transformation at varying calcination temperatures because it is the main factor for the stabilization of $b$-C$_2$S without any chemical stabilizer [41]. In the case of the Pechini method, the $D_{\text{cryst}}$ increases as the calcination temperature are raised from 700 °C to 1400 °C (Fig. 9).

The $D_{\text{cryst}}$ size can be determined for each C$_2$S polymorph as part of the QXRD and as such is taken directly from TOPAS. At 700–800 °C, a $D_{\text{cryst}}$ size $< 27$ nm was observed for the $\alpha$- C$_2$S polymorph and would be one of the reasons for the high-temperature polymorphic stabilization. From 700 to 1400 °C, the crystallite size of $b$-C$_2$S increases from 27 nm to as big 102 nm in the case of cooling Method 1. The $c$-C$_2$S started to appear with a $D_{\text{cryst}}$ of about 59 nm alongside $b$-C$_2$S 83 nm at 1100 °C. In the previous studies, the critical particle size 5–10 μm was reported for $b$-C$_2$S stabilization [39,41]. In the

<table>
<thead>
<tr>
<th>Ca/Si molar ratio</th>
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<tr>
<td></td>
<td>QXRD (wt. %)</td>
<td>CaO (mol. %)</td>
</tr>
<tr>
<td>Starting Composition</td>
<td>66.7</td>
<td>33.3</td>
</tr>
<tr>
<td>Total C$_2$S</td>
<td>84.2</td>
<td>56.2</td>
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<tr>
<td>Lime</td>
<td>9.1</td>
<td>9.1</td>
</tr>
<tr>
<td>Grossular</td>
<td>2</td>
<td>0.9</td>
</tr>
<tr>
<td>Quartz</td>
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<td>0.1</td>
</tr>
<tr>
<td>Cristobalite</td>
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<td>0.8</td>
</tr>
<tr>
<td>Wollastonite-2 M</td>
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<td></td>
</tr>
<tr>
<td>Total</td>
<td>66.2</td>
<td>29.8</td>
</tr>
<tr>
<td>Amorphous</td>
<td>3.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Fig. 8. SEM micrograph of C$_2$S synthesized via a) the Pechini method calcined at 700 °C (b) non-aqueous route at 1000 °C.

Fig. 9. Correlation between temperature (°C), mean crystallite size $D_{\text{cryst}}$ (nm) and polymorphic transition of C$_2$S ($\alpha$, $b$, $c$) synthesized by the Pechini method (**=the sample is cooled according to Method 1), (***=the sample is cooled down via Method 2).
present studies, the $D_{\text{crist}}$ is considered which is much smaller than the reported critical particle size. Therefore, the critical $D_{\text{crist}}$ for $\beta$-$\text{C}_2\text{S}$ stabilization at room temperature seems to be below 83 nm in the case of Pechini synthesis. At 1400 °C, the $D_{\text{crist}}$ for $\beta$-$\text{C}_2\text{S}$ can grow to a size of 102 nm approximately at which internal strain generated during cooling may induce $\gamma$-$\text{C}_2\text{S}$ formation (23.4 wt%) in a naturally cooled sample in a furnace (cooling Method 1). When the sample was cooled with Method 2 (Pechini method), the resultant $\beta$-$\text{C}_2\text{S}$ $D_{\text{crist}}$ becomes higher than 102 nm, the $D_{\text{crist}}$ of $\beta$-$\text{C}_2\text{S}$ cooled via Method 1. This observation points out that the facilitated cooling prevents the larger $\beta$-$\text{C}_2\text{S}$ crystal to transform into the $\gamma$-$\text{C}_2\text{S}$ and leads to an increase in the overall mean crystallite size [41].

In the case of the non-aqueous and aqueous route of the sol–gel method (Fig. 10 (a and b)), the calculated $D_{\text{crist}}$ of $\beta$ and $\gamma$-$\text{C}_2\text{S}$ polymorph lies in the range of 36–78 and 91–170 (min. to the max.) nm respectively. The $D_{\text{crist}}$ also increases with the calcination temperature and time. It can be concluded that the different route (aqueous, non-aqueous, and the Pechini method) of sol–gel synthesis exhibits their own critical mean crystallite size for the $\beta \rightarrow \gamma$ transformation which depends on synthetic route, starting precursors, calcination temperature, and time as well as cooling conditions and matrix composition (Ca to Si molar ratio). The critical $D_{\text{crist}}$ for the $\beta$-$\text{C}_2\text{S}$ stabilization can only be defined in consideration of the aforementioned parameters.

5. Summary and conclusion

The synthesis of $\text{C}_2\text{S}$ was investigated via the sol–gel (acid-catalyzed) method including the aqueous route, non-aqueous route, and the Pechini method. The $\text{C}_2\text{S}$ synthesized at 700 and 800°C via the Pechini method contain $\alpha_{\text{IR}}$-$\text{C}_2\text{S}$ (22.5–19.4 wt%) along with a high XRD-amorphous (53.1–68.3 wt%) content. The lowest possible temperature for pure $\beta$-$\text{C}_2\text{S}$ (83.0 wt%, 16.8 wt% amorphous content) synthesis in the present study was 900 °C. Moreover, a small amount of $\gamma$-$\text{C}_2\text{S}$ started to appear at 1100 °C, and a sudden increase happened at 1400 °C due to an increase in the mean crystallite size. However, the adjustment of cooling conditions such as air-quenching of the sample at 542 °C (cooling Method 2) reduced the $\gamma$-$\text{C}_2\text{S}$ amount from 23.4 wt% to 5.7 wt% at 1400 °C. The Pechini method was found to be the best method for pure $\text{C}_2\text{S}$ synthesis at low calcination temperature. This can easily be attributed to the efficient calcium polymer network as an intermediate, avoiding the formation of calcium hydroxide and calcium carbonate that only tends to react with the silica network at high temperatures. The non-aqueous route of the sol–gel method exhibited the second most promising results to synthesize a high amount of $\beta$-$\text{C}_2\text{S}$ (81.3 wt%) with low lime (2.7 wt%) and amorphous (3.8 wt%) content at 1200 °C calcined for 5 h. The product calcined at 1000 °C always contains wollastonite and unreac-ted lime. The insight about by-products such as quartz, cristobalite, wollastonite, and lime can easily be overlooked via standard XRD analysis due to high peak overlapping. The presence of these phases is due to the formation of calcium carbonate and amorphous silica during calcination leads to an inherent problem of the non-aqueous route. The only mitigation strategy is to calcine the samples at high temperatures for a long time. This strategy would negate the advantage of sol–gel synthesis to some extent and stabilize $\gamma$-$\text{C}_2\text{S}$ due to the large mean crystallite size. Moreover, the pressing of intermediate dried gel into pellet is recommended for high $\beta$-$\text{C}_2\text{S}$ yield and low amorphous content. Comparatively, the aqueous route of a sol–gel method was found to be the least promising method of sol–gel synthesis. The lack of alkoxide assisted Si-O-Si efficient network and formation of calcium carbonate promotes the high amount of unreacted CaO and silica phases. The calculation of QXRD and theoretical composition of amorphous content concluded that any change in the stoichiometry of Ca and Si precursors lower than 2 would lead to the unreacted silica and calcium oxide hiding as XRD amorphous content rather than facilitate $\beta$-$\text{C}_2\text{S}$ synthesis. That’s why the change in stoichiometry is not recommended. It has been observed that the $D_{\text{crist}}$ (mean crystallite size) for $\beta \rightarrow \gamma$ transformation depends on the thermal history (calcination temperature and time, mode of cooling), route of sol–gel (Pechini, non-aqueous and aqueous) synthesis, and matrix (calcium or silica-rich) composition. Considering...
all these parameters, the critical $D_{\text{cryst}}$ for $\beta$-C$_2$S stabilization was recorded below 83 nm approximately in the case of Pechini method synthesis.

In summary, the present work provides a detailed understanding of the advantages and disadvantages of the different sol–gel methods. This study shows the importance of considering the amorphous content, as it can mask impurities/secondary phases in the synthesized samples. This knowledge can be used for reliably designing and understanding the C$_2$S based materials for electronics, biomedical engineering, and building materials applications.

Data availability statement:

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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