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Role of dopants (B, P and S) on the stabilization of β -Ca₂SiO₄

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Abstract

The interest in belite (Ca₂SiO₄ + impurities or dopants) phase increases significantly since new types of clinkers based essentially on this phase become promising alternatives to Portland clinker for reducing CO₂ emission. Belite is also of interest as a biomedical cement. For the cement industry, stabilization of the β -polymorph is essential since the γ -polymorph has no hydraulic activity. In order to understand the mechanism of β -polymorph stabilization, this paper explores the addition of three dopants, namely P, B and S. It turns out that these dopants can modify the lattice parameters of Ca₂SiO₄ and induce specific twinning morphologies and surface relief, as well as grain boundaries deformations. A link between the addition of dopant leading to significant microstructural changes and the stabilization of β -polymorph has been established.

1 Introduction

Dicalcium silicate is used for different applications, such as bioceramics and cement. In the cement field, belite (Ca₂SiO₄, with impurities or dopants) clinker appears as one of the most promising route to reduce CO₂ emission in the cement industry [1,2]. Di-calcium silicate faces different issues: nature of the stable form as a function of sintering temperature and quenching, reactivity with water [3]. It presents five polymorphs as a function of decreasing temperature, namely α , α'_H , α'_L , β and γ [4]. Unfortunately, γ polymorph, which is stable at room temperature, does not react with water [5]. The stabilization of water reactive polymorphs of Ca₂SiO₄ (α , α'_H , α'_L and β), is essential in order to ensure reactivity with water for cement application [6]. β -polymorph is the well-known polymorph in the cement field [7]. Recently, β -Ca₂SiO₄ gets more importance in biomedical field since it revealed a good biocompatibility and bioactivity [8,9]. The stability of this phase as well as its mechanical properties became increasingly interesting [10,11]. This phase was reported as heavily

twinned, which might be due to the $\alpha'_L \rightarrow \beta$ transformation [12]. This property is specific to the β -structure [13]. Further, Shahsavari et al. [14] suggest the presence of dislocations in β - Ca_2SiO_4 which makes the phase the most brittle polymorph.

The stabilization during cooling of high temperature polymorphs of Ca_2SiO_4 depends on three parameters: particle size [15], thermal treatment [16] and the presence of impurities [17]. The increase of particle size leads to the destabilization of β polymorph and stimulates the formation of γ polymorph during cooling [15]. β -polymorph is favored by quenching the clinker [6]. Researchers studied the incorporation of foreign ions inside Ca_2SiO_4 structure [17,18,19,20]. The mechanism of stabilization was also investigated and different theories were established [21]. Pritts and Daugherty [22] developed a β polymorph stabilization model involving the charge and the radius of the foreign ions to explain the mechanism of stabilization. Xiuji and Shizong [23] proposed that the ability of ion polarization might be an important factor to estimate the effect of element on the stability of β - Ca_2SiO_4 . Lai et al. [17] studied the stability of β - Ca_2SiO_4 doped with ions (Li^+ , K^+ , Na^+ , Sr^{2+} , Mn^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} , Ti^{4+} , Mn^{4+} , P^{5+} and S^{6+}) and deduced that the relation between cation radius and β stabilization was complicated.

Twin domains can contribute to surface energy of particles and thus the stability of specific crystallographic structure [24]. Twins domains of β polymorph were studied by different researchers [13,12,25,26]. During the $\alpha'_L \rightarrow \beta$ transformation, twin domains are formed thus consuming the strain energy provided during the transition [25,6]. Kim et al. [25] claimed the presence of two types of twins: $\{100\}$ and $\{001\}$. Xiuji et al. [13] claimed that the nature of impurities might influence the type of twinning ($\{100\}$ and $\{001\}$) by proving that doping with K_2O or Na_2O lead to the formation of the $\{001\}$ twins. The role of impurities upon the microstructure of twin domains and grain boundaries of α' and β polymorphs was also investigated for the case of phosphorus and barium additions by Ghose et al. [26]. In fact, based on the observation of contrasts by transmission electron microscopy, they proposed that a second phase was formed at the grain boundaries in the P- and Ba-doped β - Ca_2SiO_4 samples. Groves [12] investigated the impact of the thermal treatment of powder upon the microstructure of twin domains and claimed that two types of fast cooling can exist: $\alpha \rightarrow \beta$ and $\alpha'_H \rightarrow \beta$. He claimed that the $\alpha \rightarrow \beta$ transformation lead to more internal strains than the $\alpha'_H \rightarrow \beta$ transformation. Internal strains generated by the $\alpha \rightarrow \beta$ transformation could be sufficient to generate dislocations at the grain boundaries.

Despite some early works on the twinning properties of β - Ca_2SiO_4 , the impact of the nature of stabilizer elements on the morphology of twin domains and grain boundaries has not yet being studied to our knowledge. Therefore, the main goal of this study consists of examining the effect of three stabilizer elements (boron, phosphorus and sulfur) upon the microstructure of the β - Ca_2SiO_4 . The selection of these three dopants is justified below. Sulfur can be part of the raw materials used to produce clinkers containing belite. As an example, belite-rich sulfoaluminate clinkers are a good alternative to Portland clinkers due to the energy savings [27]; calcium sulfate is one of the raw materials and sulfur can be present in belite [28]. Concerning phosphorus, it can be present in the limestone used for clinker manufacture [29] or in other calcium sources such as ash bones which are used to reduce CO_2 emission during the clinkering process [30,31]. Lastly, with respect to boron, its presence in belite-rich sulfoaluminate clinker was found to catalyze the hydration of belite [32]. Table 1 presents the effect of those elements upon the structure of Ca_2SiO_4 with different experimental conditions. It was reported that sulfur addition stabilizes β - Ca_2SiO_4 by the substitution of silicon by sulfur in the structure [33,34]. The maximum content of SO_3 in the structure of Ca_2SiO_4 was estimated to be 4.4 wt.% [33]. Different researchers studied phosphorus addition in Ca_2SiO_4 structure and they affirmed that the presence of phosphorus stabilized α , α'_H , α'_L and β polymorphs [22,35,36]. Poulsen et al. [18] described the mechanism of stabilization, which consisted in the substitution of silicon by phosphorus and charge compensation being maintained by creation of calcium vacancies. Duée et al. [36] said that for a 10 wt.% P_2O_5 content with respect to SiO_2 , the obtained product was the α - $\text{Ca}_2\text{SiO}_4/\alpha$ - $\text{Ca}_3(\text{PO}_4)_2$ solid solution. Fukuda et al. [37] report the effect of phosphorus addition upon the microstructure of β - Ca_2SiO_4 surface. These authors detected the formation of surface relief on the grain surface and related it to a martensitic transformation $\alpha'_\text{L} \rightarrow \beta$. With respect to boron, previous studies evidenced that boron stabilizes the β -polymorph [19,17,38]. Cuesta et al. [39] claimed that boron stabilized high temperature polymorphs (β and α'_L) by substituting silicon and calcium atoms.

In the present study, examination of twin domains, grain boundaries and surface reliefs are carried out in order to refine the understanding of β stabilization at room temperature and its effect on the microstructure of grains.

2 Sample preparation

Two synthesis routes were adopted to prepare pure stable β - Ca_2SiO_4 through polycondensation reaction and doped β - Ca_2SiO_4 through solid-state reaction. For the poly-

condensation reaction, we applied the same experimental protocol as described in a previous study [15]. The resin was prepared by mixing citric acid (Alfa Aesar CAS: 77-92-9; molar mass: 192.124 g.mol⁻¹) and ethylene glycol (Fisher Bioreagents CAS: 107-21-1; molar mass: 62.07 g.mol⁻¹). The ratio $R = \frac{m_{resin}}{m_{Ca_2SiO_4}}$ was fixed at 0.9. The calcium precursor was Ca(NO₃)₂·4H₂O (Alfa Aesar CAS: 13477-34-4; molar mass: 236.15 g.mol⁻¹). The silicon precursor was Ludox^R AS-40 colloidal silica (Aldrich CAS: 7631-86-9. Molar mass of SiO₂: 60.08 g.mol⁻¹, 40 vol% in water). Calcium nitrate and colloidal silica were dissolved in water. This solution was added drop by drop into the resin and then stirred at 363 K for 3 h. The formed gel was cured at 373 K for 24 h to evaporate water and to transform into a foam. It was then calcined at 673 K and gave a brown powder, which was treated at 1473 K for one hour to produce pure β-Ca₂SiO₄ powder.

For the solid-state reaction, CaCO₃ (Sigma Aldrich CAS: 471-34-1) and SiO₂ (Ceradel CAS: 14808-60-7) were mixed intimately, in a 2:1 stoichiometric proportion. Boron, phosphorus and sulfur were supplied by the addition of B₂O₃, P₂O₅ and CaSO₄. Their quantity were adjusted according to prepare the following mix: $(1 - x)Ca_2SiO_4 + \frac{x}{2}D$, where D (which stands for ‘Dopant’) is B₂O₃ or P₂O₅, and $(1 - x)Ca_2SiO_4 + xD$ when D is CaSO₄ and presented in table 2 (x corresponds to the weight percentage). These elements were supplied respectively by boric acid H₃BO₃ (Sigma Aldrich CAS: 10043-53-3), ammonium phosphate dibasic (NH₄)₂HPO₄ (Sigma Aldrich CAS: 7783-28-0) and CaSO₄·2H₂O (Fluka CAS: 10101-41-4). Their percentages were selected according to results from previous works (Table 1). Experimental conditions were chosen to obtain β and to prevent the formation of α’ and γ polymorphs. All mixtures were milled (RETSCH miller) with the addition of a small quantity of ethanol. Disks of 20 mm in diameter and ~ 3.2 mm thickness were pressed (compaction pressure: 2 T). Disks were heated in a platinum crucible at two temperatures, 1473 and 1673 K, for 1 h (heating ramp: 600 Kh⁻¹) and quenched in air at room temperature. These two temperatures were chosen in order to study the two transformations that can occur during cooling, namely α→β and α’_H→β. Table 2 presents the notations and the firing conditions.

3 Characterization techniques

X-Ray diffraction (XRD) data were collected at room temperature on a Bruker D8 Advance X-ray diffractometer with CuK_α radiation (λ_{Cu} = 1.54056 Å) at a step scan of 0.01 ° operated at a voltage 40 kV and an electric current 40 mA. Phase identification was carried

out using EVA program. Rietveld refinement was carried out for all samples to determine unit cell parameters and the quantification of different phases in each sample using TOPASS software. Files from the Inorganic Crystal Structure Database (ICSD) used in this study are presented in Table 3. For each refinement, the Pseudo Voight II profile shape function was used. Instrumental parameters (background, zero), scale factor and cell parameters were refined. Atomic coordination numbers were refined only for the β polymorph.

Differential scanning calorimetry (DSC) was performed on doped β - Ca_2SiO_4 . The DSC scans were taken with Thermo-balance TG-DSC Setsys Setaram 24 apparatus. The firing cycle was the following: heating ramp 10 °C/min up to 1420 °C and cooling ramp 10 °C/min.

Scanning electron microscopy (SEM) was carried out with a FEI Quanta 450 microscope. No conductive layer was deposited on the surface of samples in order to offer the original surface for specific analyses. The specimens were stored in desiccators filled with silica gel before and after examinations to prevent hydration.

High resolution transmission electron microscopy (HR-TEM) was used to study the morphology and the crystallography of different samples. TEM experiments were carried out on a JEOL 2100F- LM microscope operating at 200 kV. Since Ca_2SiO_4 particles react under the electron beam, the observations were carried out at 73 K. Fast Fourier Transform (FFT) was performed and high resolution (HR) images were recorded to investigate crystalline characteristics of Ca_2SiO_4 nanoparticles. Inverse Fast Fourier Transform (IFFT) was studied in some cases to investigate a preferential direction. Selected area electron diffraction (SAED) was performed on Ca_2SiO_4 particle to identify the crystalline structure. Specimens were prepared by dispersing the selected powders in acetone and dropping the suspensions on copper grids coated with carbon support films.

4 Results and discussion

4.1 Effect of dopants on the stabilization of the β polymorph

XRD patterns of the different samples treated at 1673 and 1473 K are presented on Figs. 1 and 2. The sample prepared by chemical route leads the formation of pure β - Ca_2SiO_4 (BC on Figs. 1 and 2). As expected, BS sample prepared by solid state synthesis and without any dopant presents the γ - Ca_2SiO_4 polymorph (BS on Fig. 1) [45]. At 1673 K, the addition of dopants (P, B and S) leads to the stabilization of β -polymorph (Respectively BSP_16, BSB_16 and BSS_16 on Fig. 1). We notice the presence of small intensity peaks related to γ -polymorph for BSP_16. Rietveld refinement confirmed the presence of 7 wt% of γ -polymorph (Table 4). In addition, we detected a significant quantity of α' -polymorph, i.e. 22 wt%. For

the other samples (BSB_16 and BSS_16), we confirmed that the content of β -polymorph is very high (respectively 99.5 and 98.8 wt%). We also record a significant displacement of XRD peaks in the doped samples compared to the pure sample. This fact suggests a change of lattice parameters, which can be due to the incorporation (insertion/substitution) of the dopant into the structure. The calculated variations of lattice parameters using Rietveld refinement, by comparison with the lattice parameters given by Mumme et al. [40], shows that lattice deformations depend on the nature of the dopant (Table 5). Samples prepared by solid-state route and fired at 1473 K contain some unreacted silica and CaO, which can be due to the lower firing temperature. Small peaks related to γ -polymorph are detected despite the presence of P (BSP_14) or S (BSS_14). Phase quantification using Reitveld method confirms the presence of unreacted oxide and small amount of transformed β -polymorph into γ -polymorph (Table 5). With B doping (BSB_14) no γ -polymorph is detected and the XRD peaks are narrow compared to the other samples, namely BSP_14 and BSS_14. To conclude, sintering at 1673 K (followed by quenching at room temperature) leads to a better stabilization of the β polymorph than sintering at 1473 K. The peaks of samples treated at 1673 K are broader than peaks of the samples treated at 1473 K.

With respect to the effect of particle size upon the stabilization of pure β -polymorph, the size increase leads to the formation of γ -polymorph and the increase of the firing temperature leads to the increase of particle size [15]. In the present case, two facts should be pointed out: (i) for each dopant, the increase of firing temperature leads to the broadening of diffraction peaks; though increasing the firing temperature should lead to an increase of particle size (and a narrowing of the diffraction peaks), the broadening observed in the present case could be associated to the existence of deformation in the unit cells, such as strain or dislocations [46]. (ii) BSP_16 and BSS_16 reveal a better stabilization of β -polymorph than BSP_14 and BSS_14. This points out the importance of the thermal treatment on stabilization the β -polymorph.

Kim et al. [25] presented the different transformations of Ca_2SiO_4 as a function of temperature and claimed that the $\alpha \rightarrow \alpha'_H$ transformation occurs at 1693 K. The presence of foreign ions such as phosphorus (1 wt% of P_2O_5 with respect to SiO_2) and boron (0.13 wt% of B_2O_3 with respect to CaO) decreases the temperature of $\alpha \rightarrow \alpha'_H$ transformation from 1693 to 1553 and 1669 K, respectively [26]. In the present case, with the addition of one dopant (P, S or B), the α polymorph (resp. α'_H polymorph) can be formed during sintering at 1673 K (resp. 1473 K). In order to confirm this fact, Fig. 3 shows the evolution of the heat flow during cooling of the doped samples. Indeed, the exothermic peak corresponding to $\alpha \rightarrow \alpha'_H$

transformation occurs below 1673 K and at different temperatures according to the nature of the dopant, which confirms the formation of α polymorph in the case of high temperature firing. However, this transformation doesn't occur in the case of the pure sample. Consequently, the β phase present in the BSP_16, BSS_16 and BSB_16 samples (resp. BSP_14, BSS_14 and BSB_14 samples) is due to the $\alpha \rightarrow \beta$ (respectively $\alpha'_H \rightarrow \beta$) fast cooling. According to XRD results, the $\alpha \rightarrow \beta$ transition leads to a better stabilization of high temperature β -polymorph than the $\alpha'_H \rightarrow \beta$ transition. Fukuda et al. [47] claimed that the solubility of foreign ions, namely iron and aluminum, into α -structure is higher than α'_H -structure. During the cooling, the solubility of foreign ions decreases and these ions can migrate either to the grain surfaces or towards the grain boundaries [48]. This postulate is supported by Groves [26], who interpreted the difference between the two types of cooling by the formation of dislocations at the grain surfaces in the case of $\alpha \rightarrow \beta$ cooling. Therefore, the broadening of XRD peaks, observed for the samples sintered at 1673 K, compared to samples sintered at 1473 K, can be due to the deformation in the unit cells induced by dislocations, which arise in the case of $\alpha \rightarrow \beta$ cooling. To conclude, the dopants can deform the Ca_2SiO_4 lattice. They can lower the temperature of formation of α and α'_H polymorphs compared to pure Ca_2SiO_4 . During $\alpha \rightarrow \beta$ cooling, dislocations and defects can appear, which can promote the stabilization of the β phase. In the next paragraph, SEM and TEM techniques will be used to complete XRD results and to investigate the effect of the presence of dopant element upon the surface of samples.

4.2 Effect of doping elements upon the microstructure

4.2.1 Grain boundary (GB) modifications

The addition of dopant elements (P, B and S) affects the grain boundary (GB) morphology compared with the pure sample as shown in Figs. 4 and 5. In the case of phosphorus addition (BSP_16, Fig. 5), there is a modification of the GB grooves (indicated by white arrows) compared to the pure sample (Fig. 4). This modification was not recorded for the sample fired at 1473 K. In the case of boron addition (BSB_16, Fig. 5), an interphase is present next to the GB (indicated by white arrows); it could be an amorphous phase since no specific XRD peak was recorded. On the other hand, the addition of sulfur (BSS_16, Fig. 5) lead to the deformation of grain boundaries (indicated by white arrows). Lastly, doped samples sintered at 1473 K (BSB_14 and BSS_14, Fig. 5) present no significant difference in the grain boundary microstructure compared with the pure sample (Fig. 4). The apparition of an interphase (case of B doping) in GB and the change of GB grooving (case of P doping) might result from the difference of dopant solubility between α and β polymorphs, which

leads to the segregation of the dopant at the GB during cooling. The absence of such morphology in samples sintered at 1473 K (and fast cooled) can result from the formation of the β polymorph during the $\alpha'_H \rightarrow \beta$ cooling.

The existence of GB grooves influences the GB energy [49], which can be estimated using Mullin's equation [50]:

$$\frac{\gamma_{GB}}{\gamma_S} = 2 \cos\left(\frac{\Psi}{2}\right) \quad (1)$$

where γ_{GB} is the GB energy, γ_S is the surface energy and Ψ is the dihedral angle of GB. According to the SEM observation, the GB grooves, due to the presence of phosphorus ions, leads to the increase of the dihedral angle of GB as presented in Fig. 6. Assuming that γ_S is identical for the pure and the P-doped sample (BSP_16), the increase of Ψ leads to the decrease of the GB energy.

For the deformed microstructure (case of S doping), dislocations are known to be transmitted from one grain to another through GB. Grain boundaries can also act as an obstacle and can be efficient dislocation sinks, which is related to the level of stress of the grain [51]. The consequence is the formation of a piled up deformation at GB [52]. Since dislocations were recorded in the case of β -Ca₂SiO₄ [14], the GB might play the role of an obstacle for the displacement of dislocations leading to the formation of a pile up (indicated by white arrows). In order to confirm the presence of dislocations, BSS_16 sample was examined by TEM. A HR-TEM image was recorded along b axis, which is confirmed by FFT, and presented in Fig. 7. An examination of atom arrangement exhibits the presence of screw dislocation, which is formed by the shearing of (101) planes as presented in the atomic model in Fig. 7. The IFFT pattern with [101], presented in Fig. 7, confirms the presence of deformation. Therefore, those dislocations can migrate to the GB and create such observed deformation.

Different types of GB deformation were recorded, which are related to different causes depending on the nature of dopant element. Therefore, such deformations might have an influence on the energy of GB, by decreasing it comparing to the pure sample, which can contribute to the stabilization of β polymorph and prevents the $\beta \rightarrow \gamma$ transformation.

4.2.2 Twin microstructure modification

β -Ca₂SiO₄ is known to be a heavily twinned structure [12]. Several researchers pretend that this planar dislocation promotes the stabilization of β polymorph [25]. Besides, the

morphology of twin domains is related to the energy of twins [53], and the morphology of twins in β -Ca₂SiO₄ might have an influence upon the stabilization of β polymorph. Therefore, in the present study, the effect of dopants upon the twin morphology was studied. For the interpretation of the observed morphologies, we referred to the description of twins alloys in the literature [53]. According to their morphology, twins can be classified into different types: the crossing twin morphology, the general morphology and the zig-zag morphology [53]. These classifications will be used to interpret our observations.

Given our SEM and TEM observations, the twin morphology of pure samples (BC) seems to be different compared to doped samples. In the present work, only {100}-type twin was studied since all our samples are heavily twinned in the (100) plane, which makes the detection of {001}-type twin very hard. The pure sample has laminates of finite widths (indicated by a white arrow, Fig. 8). The morphology of doped samples differs from the morphology of the pure sample since the laminates are getting thinner compared to BC via branching and variants in each laminate. It results in thin needles close to the interface as presented for the B-doped sample in Fig. 8 (indicated by a black arrow). This morphology is more present in the case of B-doping than in the P- and S-doping cases.

The twin microstructures can be classified as a function of the morphology of ending tips [53]. The crossing twin morphology requires that the width of laminates are positioned in such a way that the twinning planes match exactly at the interfaces and the twin boundary (TB) is coherent [53]. In the case of the pure sample, this condition is not quite fulfilled even with finite widths of domains as presented in Fig. 9 showing the absence of compatibility of TB of two domains at the interface. Therefore, such morphology can be classified as a pseudo-crossing morphology (Fig. 9). The formation of needles (via branching), for doped samples corresponds to the general morphology (Fig. 10). In order to identify the type of observed twin, SAED were recorded for the two different morphologies and both are {100}-type twin. Therefore, this change in morphology cannot be related to a change in twin type. Seiner et al. [53] provided an explanation for the different twinning morphology and how they control the morphology of ending tips of laminates. The apparition of the general morphology, with the presence of dopants, can be explained also by the change of the surface specific energy of twinning plane compared to the pure sample. This change can be related to the insertion of dopant into the β structure. In addition to that, TBs can play the role of sinks for structural defaults and dislocations, similar to GBs behavior, which can leads to the deformation of the morphology of twin domains.

The twin morphology of doped samples treated at 1473 K is similar to the pure sample. It can be explained as follows: (i) the lower quantity of dopant inside the grains of samples sintered at 1473 K compared to samples sintered at 1673 K decreases the density of structural defects. Thus, the morphology of twin domains cannot be deformed; (ii) the low insertion of dopant elements into the β structure compared to the doped samples treated at 1673 K cannot create a significant modification upon the surface specific energy of twinning planes and induce a change in the twin morphology.

In addition to the stabilization of β -polymorph by substitution or/and insertion of the dopant into the structure and according to the link between the formation of twins and the stabilization of β -polymorph [25], we can conclude that the formation of the general morphology might offer better stabilization of β -polymorph compared to the pseudo-crossing twin morphology. This fact can be related to the formation of high energy TB compared to the pure sample, which might act as an obstacle for the germination of γ -polymorph.

4.2.3 Surface relief and dislocations

In the case of phosphorus addition, the stabilization of β -Ca₂SiO₄, fired at 1673 K, is accompanied with the formation of significant deformation of the grain surface (Fig. 11a). It is less important when firing temperature is at 1473 K (Fig. 11b). The orientation of this relief is perpendicular to the twin variants (circled in white in Fig. 11). Such a surface relief, with the stabilization of β polymorph with phosphorus addition, was observed by Fukuda et al. [37], with the same orientation. The surface relief was reported as a deformation generated by the strain produced during the $\alpha' \rightarrow \beta$ and $\alpha \rightarrow \beta$ transitions, which are classified as ferro-elastic martensitic transformation [25]. This strain can deform the surface of the grains when phosphorus is present in the structure [53]. The lower magnitude of surface deformation in sample fired at 1473 K compared to 1673 K might be related to the higher intensity of the generated strain during $\alpha \rightarrow \beta$ compared to $\alpha' \rightarrow \beta$ transformation [25].

In the case of boron addition, grains show slip steps on the surface (see the blue arrows on Figs. 12a and 12b). TEM and SAED observations of BSB_16 in a deformed zone confirm the formation of pure β -Ca₂SiO₄ along $[\bar{3}01]$ without a secondary phase. It corresponds to the formation of slip (indicated by the blue arrows, Fig. 12c). The absence of rings on the SAED pattern confirms the high crystallinity and the absence of an amorphous phase. Compared to P-doped samples, these observations can be related to a deformation coming from the martensitic transformations forming the β -structure. The absence of this deformation in case of sample fired at 1473 K can be due to the difference in the intensity of generated strain

between $\alpha \rightarrow \beta$ and $\alpha' \rightarrow \beta$ transformation. By inspecting BSB_16 sample by HR-TEM, we recorded the formation of defects such as [002](020) edge dislocation (Fig. 13). The inverse of fast Fourier transform with [002] (Fig. 13c) demonstrates clearly the existence an extra half (002) plane. Therefore, the dislocation motion can be at the origin of the formation of these slips as presented in Fig. 13d (e.g. (020) glide) [51]. The motion of dislocations needs energy and the generated strain during the formation of β structure might provide enough energy to move the dislocations to the surface. This morphology is not observed for sample fired at 1473 K since its β transformation provides lower strain energy.

In the case of sulfur addition, the surface morphology is different from boron and phosphorus doped samples. BSS_16 is characterized by the formation of etch pits on the surface of grains with sizes of the order of 10 nm as presented in Fig. 14 (indicated by blue arrows). The formation of these pits can be related to the motion of dislocations, because we note the formation of screw dislocations as presented in section 4.2.1 section and in Fig. 15, which shows the shearing of (020) planes. Hence, the motion of such dislocations might induce the formation of pits on the surface of the grains [54,55].

Lastly, samples treated at 1473 K present a surface microstructure similar to the pure sample, i.e. a smooth surface with low deformation. It suggests that little dislocations are formed. This fact can be related to the low content of dopant inside the structure and to the type of cooling, which is confirmed by the lower variation of unit cell parameters comparing to samples treated at 1673 K (Table 5). This conclusion seems to be coherent with XRD results. Consequently, the broadening of XRD peaks can be explained by the formation of dislocations.

To conclude, the change of the surface microstructure of doped β -Ca₂SiO₄ compared to undoped Ca₂SiO₄ can be related to the formation and motions of linear dislocations (edge and screw dislocations). In Ca₂SiO₄, the increase of the particle size during sintering leads during cooling to the destabilization of β polymorph and the formation of γ polymorph. The addition of dopants (S, B, P) conducts to the formation of dislocations. One of the driving forces of $\beta \rightarrow \gamma$ transformation is the generated strain during previous transformations [6]. The motion of these dislocations might consume part of this strain and contributes to the stabilization of β -Ca₂SiO₄.

4.3 Dislocation motion

The presence of dislocation and their motion were considered as the source of observed deformation on the surface of $\beta\text{-Ca}_2\text{SiO}_4$. The high density of deformation in the case of samples fired at 1673 K, compared to those fired at 1473 K, can be explained by the difference of thermal strain generated by the higher firing temperature, which induces to the motion of dislocations to interfaces such as GB and TB. According to the literature, the motion of dislocations requires a minimum strain, which is proportional to the dislocation characteristics (type, width of deformation) and to the structure density. This relation is described by Peierls-Nabarro's model [56]:

$$\tau_{PN} \approx G e^{-\left(\frac{2\pi w}{b}\right)} \quad (2)$$

where τ_{PN} is the strain of Peierls-Nabarro, G is the shear modulus, w is the width of the deformation due to the presence of edge dislocation and b is the modulus of burger vector. An increase in the width of deformation leads to a decrease of the strain necessary to move a dislocation into the structure. In addition, the decrease of b , associated to the increase of interatomic distance, leads to the decrease of τ_{PN} , which explain the higher mobility of dislocation in the case of metal compared to oxide. In the case of $\beta\text{-Ca}_2\text{SiO}_4$, Shahsavari et al. [14] estimated the strain of Peierls-Nabarro based on experimental observation and ab-initio simulation (Fig. 16). They claimed a very high value of strain (164.44 MPa) necessary to move a dislocation inside $\beta\text{-Ca}_2\text{SiO}_4$. Besides this high value, they announced that the motion of dislocations inside this structure is very difficult and requires a high energy. In the present work, the examination of an edge dislocation in the case of BSB_16 by HR-TEM shows big difference compared to the observation of Shahsavari et al. [14]. As shown in Fig. 16, the presence of an extra half plan leads to a larger area of deformation inside the structure of BSB_16 compared to the case of Shahsavari et al. [14]. In fact, the width of deformation in BSB_16, estimated equal to $10 \times b$, is larger than the previous case which was estimated to be $6 \times b$. Assuming that shear modulus is the same for both cases, the strain of Peierls-Nabarro for both cases can be compared according to equation (3):

$$\frac{\tau_{PN1}}{\tau_{PN2}} \approx \frac{e^{-\left(\frac{2\pi w_1}{b_1}\right)}}{e^{-\left(\frac{2\pi w_2}{b_2}\right)}} \quad (3) \quad \rightarrow \quad \frac{\tau_{PN1}}{\tau_{PN2}} \approx 68,31$$

where τ_{PN1} and τ_{PN2} are the strains of Peierls-Nabarro in Shahsavari's case and in the present study, respectively. According to this estimation, τ_{PN2} is 68 times lower than τ_{PN1} , which involves a much higher mobility of dislocations in our case compared to Shahsavari's case.

This difference can be due to the nature of dopant present and to the thermal treatment. Thus, the contribution of some surface deformations to the presence and the mobility of dislocations can be confirmed by these results.

5 Conclusion

The mechanism of stabilization of β -Ca₂SiO₄ through the addition of dopants seems to be more complicated than described by different previous works [20,33,39]. XRD results show the type of cooling ($\alpha \rightarrow \beta$ and $\alpha'_H \rightarrow \beta$) influences the stability of β -Ca₂SiO₄. The $\alpha \rightarrow \beta$ cooling stabilizes the β -structure better than $\alpha'_H \rightarrow \beta$ cooling. In addition to the effect of particle size, the presence of dopants showed a significant influence effect upon the stabilization of β -Ca₂SiO₄. The mechanism of stabilization needs to be more developed than a simple insertion or substitution inside the lattice. Fig. 17 summarizes the main conclusions of this work. The presence of stabilizer ions can lead to the increase of the density of dislocations and to the change of grain boundary morphology in addition to the lattice deformation. Depending on the thermal treatment, these modifications influence the surface aspect and the properties of twins. Such modifications might lead to the decrease of Gibbs energy of β polymorph and enable its stabilization at room temperature. These modifications might also influence the mechanical properties and the hydraulicity of β -Ca₂SiO₄. The study of the hydraulicity of doped β -Ca₂SiO₄ when general morphology dislocations are present is the next step to look at in order to examine to which extend the hydraulicity could be modified. This point is important for belitic cements classified as low carbon CO₂ cements. Finally, the presence of dislocations can also affect the plasticity of β -Ca₂SiO₄. It could be a good strategy to improve the grindability of this phase in clinkers to reduce the associated grinding energy.

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Figure 1: XRD patterns of samples prepared through solid-state route fired for 1 hour at 1673 K compared to BC sample (Poly-condensation route), which is fired at 1473 for one hour; full line: β -Ca₂SiO₄ and dashed line: γ -Ca₂SiO₄.

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Figure 16: HR-TEM observation of edge dislocation in β -Ca₂SiO₄ structure: 1) observation of Shahsavari et al. [14], 2) observation of BSB_16 (\vec{b} : *burger vector*, w : *width of deformation*).

Figure 17: effect of dopant (B, P and S in the present study) on the structure and microstructure of β -Ca₂SiO₄.

Table 1. Dose-dependent virucidal activity and corresponding synergy index (*SI*) against RSV (enveloped RNA virus).^a

	Concentration of each component (μM)								<i>SI</i> ^b
	20	35	50	75	125	250	500	1000	
(-), α , β or γ	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	-
<i>Q</i>	≤ 1.0	≤ 1.0	2.0	3.2	$\geq 6.5^*$	≥ 6.5	≥ 6.5	≥ 6.5	-
<i>Q/\alpha</i>	≤ 1.0	≤ 1.0	≤ 1.0	1.7	3.3	$\geq 6.5^*$	≥ 6.5	≥ 6.5	2.0
<i>Q/\beta</i>	≤ 1.0	≤ 1.0	≤ 1.0	1.2	2.1	$\geq 6.5^*$	≥ 6.5	≥ 6.5	2.0
<i>Q/\gamma</i>	≤ 1.0	1.2	3.5	$\geq 6.5^*$	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	0.6
<i>E</i>	≤ 1.0	1.1	2.0	3.6	$\geq 6.5^*$	≥ 6.5	≥ 6.5	≥ 6.5	-
<i>E/\alpha</i>	≤ 1.0	≤ 1.0	≤ 1.0	1.2	2.9	$\geq 6.5^*$	≥ 6.5	≥ 6.5	2.0
<i>E/\beta</i>	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	≤ 1.0	3.1	$\geq 6.5^*$	≥ 6.5	4.0
<i>E/\gamma</i>	≤ 1.0	1.2	2.1	3.8	$\geq 6.5^*$	≥ 6.5	≥ 6.5	≥ 6.5	1.0
<i>Q/E</i>	1.2	2.7	$\geq 6.5^*$	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	0.8
<i>Q/E/\alpha</i>	1.6	3.2	$\geq 6.5^*$	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	0.8
<i>Q/E/\beta</i>	2.0	4.2*	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	0.6
<i>Q/E/\gamma</i>	1.9	4.0*	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	≥ 6.5	0.6

^a Virucidal activity in \log_{10} titer reduction factor recorded after 15 min of contact time at room temperature with an initial RSV of 1.3×10^7 TCID₅₀/mL (with $\alpha = \alpha\text{-CD}$, $\beta = \beta\text{-CD}$, $\gamma = \gamma\text{-CD}$, $Q = [\text{DiC}_{10}][\text{Cl}]$ and $E = \text{C}_{12}\text{E}_8$). (*) Minimum virucidal concentration (MVC) = the lowest concentration able to inactivate at least 99.99% of viruses. ^b Calculated according equation 1.

Table 2. Physicochemical parameters of [DiC₁₀][Cl]/C₁₂E₈ (*Q/E*) mixed systems with or without native cyclodextrins (α , β and γ) in aqueous solution at 25 °C compared to [DiC₁₀][Cl] and C₁₂E₈ alone.^a

	Micelles properties ^b				Binding constant (M ⁻¹) ^c			
	CMC (μ M)	D_h (nm)	ζ (mV)	α (%)	K^Q_1	K^Q_2	K^E_1	K^E_2
<i>Q</i>	1,200 ^d	4.0	57.9	61	-	-	-	-
<i>Q/\alpha</i>	5,500 ^d	3.9	60.4	60	26,000 ^d	7,500 ^d	-	-
<i>Q/\beta</i>	5,100 ^d	4.1	54.9	63	9,700 ^d	2,900 ^d	-	-
<i>Q/\gamma</i>	10,200 ^d	4.0	61.7	58	6,860 ^d	-	-	-
<i>E</i>	100 ^d	7.9	0	-	-	-	-	-
<i>E/\alpha</i>	160	8.1	0	-	-	-	7,300 ^d	2,400 ^d
<i>E/\beta</i>	300	7.7	0	-	-	-	17,000 ^d	-
<i>E/\gamma</i>	105	8.0	0	-	-	-	70 ^d	-
<i>Q/E</i>	60 ^d	8.5	35.4	73	-	-	-	-
<i>Q/E/\alpha</i>	90	8.7	38.7	75	26,000 ^d	7,500 ^d	7,300 ^d	2,400 ^d
<i>Q/E/\beta</i>	80	8.6	40.1	76	9,700 ^d	2,900 ^d	17,000 ^d	-
<i>Q/E/\gamma</i>	70	8.4	34.2	72	6,860 ^d	-	70 ^d	-

^a All binary or ternary systems are equimolar. ^b CMC = critical micelle concentration, D_h = hydrodynamic diameter, ζ -potential recorded at 10×CMC, α = the degree of ionization of the micelle. ^c Determined from surface tension modelling using single surfactant/cyclodextrin systems in aqueous solution with dilution experiments. ^d Taken in Leclercq et al., 2013.

Table 3. Dose-dependent biocidal or virucidal activity and corresponding synergy index (*SI*) against enveloped DNA viruses (HSV-1 and VACV), bacterium (*P. aeruginosa*) and fungus (*C. albicans*).^a

		Concentration of each component (μM)								<i>SI</i> ^b
		20	35	50	75	125	250	500	1000	
HSV-1	(-), α , β or γ	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	-
	<i>Q</i>	≤1.0	1.1	1.5	3.7	≥6.5*	≥6.5	≥6.5	≥6.5	-
	<i>E</i>	≤1.0	1.2	2.6	3.5	≥6.5*	≥6.5	≥6.5	≥6.5	-
	<i>Q/E</i>	1.1	3.7	5.7*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	0.8
	<i>Q/E/α</i>	≤1.0	2.2	6.0*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	0.8
	<i>Q/E/β</i>	1.3	4.0*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	0.6
	<i>Q/E/γ</i>	4.1*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	0.3
VACV	(-), α , β or γ	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	-
	<i>Q</i>	≤1.0	≤1.0	≤1.0	≤1.0	1.3	1.9	≥6.5*	≥6.5	-
	<i>E</i>	≤1.0	≤1.0	≤1.0	≤1.0	1.2	1.7	≥6.5*	≥6.5	-
	<i>Q/E</i>	≤1.0	1.2	2.8	4.6*	≥6.5	≥6.5	≥6.5	≥6.5	0.3
	<i>Q/E/α</i>	≤1.0	1.4	3.7	4.9*	≥6.5	≥6.5	≥6.5	≥6.5	0.3
	<i>Q/E/β</i>	≤1.0	1.3	4.0*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	0.2
	<i>Q/E/γ</i>	≤1.0	1.2	5.2*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	0.2
<i>P. aeruginosa</i>	(-), α , β or γ	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	-
	<i>Q</i>	1.7	3.2	4.1*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	-
	<i>E</i>	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	-
	<i>Q/E</i>	1.7	3.6	4.5*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	1.0
	<i>Q/E/α</i>	1.4	2.7	4.5*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	1.0
	<i>Q/E/β</i>	≤1.0	2.1	4.6*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	1.0
	<i>Q/E/γ</i>	1.2	2.1	4.1*	≥6.5	≥6.5	≥6.5	≥6.5	≥6.5	1.0
<i>C. albicans</i>	(-), α , β or γ	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	-
	<i>Q</i>	≤1.0	≤1.0	1.3	4.3*	≥6.0	≥6.0	≥6.0	≥6.0	-
	<i>E</i>	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	≤1.0	-
	<i>Q/E</i>	≤1.0	≥6.0*	≥6.0	≥6.0	≥6.0	≥6.0	≥6.0	≥6.0	0.5
	<i>Q/E/α</i>	≤1.0	≥6.0*	≥6.0	≥6.0	≥6.0	≥6.0	≥6.0	≥6.0	0.5
	<i>Q/E/β</i>	≤1.0	≥6.0*	≥6.0	≥6.0	≥6.0	≥6.0	≥6.0	≥6.0	0.5
	<i>Q/E/γ</i>	≤1.0	≤1.0	4.6*	≥6.0	≥6.0	≥6.0	≥6.0	≥6.0	0.7

^a Biocidal or virucidal activity in log₁₀ titer reduction factor recorded at room temperature after 15 min of contact time for HSV-1 (1.5×10⁷ TCID₅₀/mL), VACV (1.1×10⁷ TCID₅₀/mL), *C. albicans* (1.6×10⁶ CFU/mL) and 5 min for *P. aeruginosa* (1.0×10⁸ CFU/mL). (*) Minimum virucidal concentration (MVC) = the lowest concentration able to inactivate at least 99.99% of viruses. ^b Calculated according equation 1.

Stabilizing ion	Stabilizer ion source	stabilizer quantity		Firing temperature (K)	Firing time and repetition (Hrs)	Product	Ref.
B³⁺	H ₃ BO ₃	0.24	wt% B ₂ O ₃	1708	17	β	[20]
		0.51		1708	6+2	β	
		1.01		1708	6+2+4.5	β, 3CaO.2SiO ₂	
		3.00		1708	1	3CaO.2SiO ₂	
		5.02		1708	1	3CaO.2SiO ₂	
		7.55		1708	1	3CaO.2SiO ₂	[39]
		0.51		1573	0.5	γ<α' _H <β	
		0.76		1573	0.5	α' _H <β	
		1.02		1573	0.5	α' _H <β	
		2.05		1573	0.5	α' _H <β	
		4.15		1573	0.5	β<α' _H	
S⁶⁺	CaSO ₄ .2H ₂ O	0.74	wt% CaSO ₄	1523	2.5	β, CaO	[20]
		0.74		1673	4+1+22	β, γ	
		2.88		1673	2+2	β	
		3.03		1673	3+3	β	
		4.90		1673	2+2+2.5	β	
		0.06	wt% CaSO ₄ .2H ₂ O	1723	2	α<γ<β	[33]
		0.10		1723	2	α<γ<β	
		0.13		1723	2	α<γ<β	
		0.19		1723	2	γ<α<β	
P⁵⁺	-	0.19	wt% P ₂ O ₅	1708	6	β, γ	[20]
		0.40		1708	2	β, γ	
		0.60		1708	1+2	β	
		1.00		1708	8+4+2	β	
		3.00		1708	2+18+2.5	α	
	Ca(PO ₃) ₂	5.00		1773	3	α', β	[17]

Table 1: Effect of the addition of phosphorus, sulfur and boron on the stabilization of different Ca₂SiO₄-polymorphs prepared with different experimental conditions (Stabilizer quantity in wt%, firing temperature and firing repetitions) as described in references [17, 20, 33, 39].

Sample	Synthesis route	Ca:Si (molar ratio)	Impurity-Wt%	Firing temperature (K)	Firing duration (hours)
BC	Poly-condensation	2:1	-	673-1473	3-1
BS	Solid-state	2:1	-	1673	1
BSB_14	-	2:1	Bore-0.2	1473	1
BSP_14	-	2:1	Phosphorus-0.5	1473	1
BSS_14	-	2:1	Sulfur-1	1473	1
BSB_16	-	2:1	Bore-0.2	1673	1
BSP_16	-	2:1	Phosphorus-0.5	1673	1
BSS_16	-	2:1	Sulfur-1	1673	1

Table 2: Experimental conditions of samples preparation through poly-condensation and solid-state routes. BC (resp. BS) refers to samples prepared by a chemical route (resp. solid-state reaction). BSB, BSP and BSS correspond to samples doped with boron (0.2 wt%), phosphorus (0.5 wt%) or sulfur (1 wt%) and sintered at 1473 K (BSP_14, BSP_14, BSS_14) or 1673 K (BSP_16, BSP_16, BSS_16).

Phase	Code ICSD	Ref.
β-Ca₂SiO₄	81096	[40]
γ-Ca₂SiO₄	81095	[40]
α'-Ca₂SiO₄	81097	[40]
α-Ca₂SiO₄	182052	[41]
Quartz	77458	[42]
Cristobalite	9008110	[43]
CaO	60199	[44]

Table 3: Inorganic Crystal Structure Database (ICSD) codes of the different compounds used for Rietveld refinement

	β -Ca ₂ SiO ₄	α' -Ca ₂ SiO ₄	α -Ca ₂ SiO ₄	γ -Ca ₂ SiO ₄	SiO ₂	CaO	R _{wp}	R _p	R _{exp}
BSP_14	82.3	1.2	-	4.13	1.1	9.1	11.39	7.9	6.9
BSB_14	98.8	0.4	-	-	0.3	0.3	10.7	8.0	6.9
BSS_14	80.2	1.1	-	4.05	2.4	11.5	12.7	9.2	6.9
BSP_16	70.8	22.0	-	7.0	-	-	12.0	8.5	6.8
BSB_16	99.5	-	0.3	-	-	-	12.5	9.0	6.9
BSS_16	98.8	0.4	0.3	-	-	-	10.7	8.0	6.7

Table 4: Percentages of phases in the different samples deduced from Rietveld refinement of XRD patterns.

	Δa (%)	Δb (%)	Δc (%)	$\Delta \beta$ (%)	ΔV (%)
BSP_14	-0.01	-0.01	-0.03	-0.03	-0.04
BSB_14	-0,02	-0,01	-0,01	-0,05	-0,08
BSS_14	-0,01	-0,03	-0,01	-0,01	-0,04
BSP_16	-0,05	-0,06	-0,02	-0,03	-0,14
BSB_16	-0,15	-0,01	-0,05	-0,16	-0,20
BSS_16	-0,03	-0,04	-0,01	-0,02	-0,09

Table 5: Variations of β -Ca₂SiO₄ unit cell parameters for different samples, calculated using Rietveld refinement, by comparison with the lattice parameters given by Mumme et al. [40] ($\Delta x = \frac{x_{sample} - x_{reference}}{x_{reference}}$)