



HAL
open science

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

Sofien Saidani, Agnès Smith, Youssef El Hafiane, Lotfi Ben Tahar

► To cite this version:

Sofien Saidani, Agnès Smith, Youssef El Hafiane, Lotfi Ben Tahar. Role of dopants (B, P and S) on the stabilization of β -Ca₂SiO₄. Journal of the European Ceramic Society, 2020, 10.1016/j.jeurceramsoc.2020.07.037 . hal-02935782

HAL Id: hal-02935782

<https://unilim.hal.science/hal-02935782v1>

Submitted on 24 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

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

2 Sofien SAIDANI^{1,2,3}, Agnès SMITH¹, Youssef EL HAFIANE¹ and Lotfi BEN TAHAR^{2,3,4}

3 ¹) *Université de Limoges, Institute of Research on Ceramics, IRCER - UMR 7315, Centre Européen de*
4 *la Céramique, 12 rue Atlantis, 87068 Limoges cedex, France*

5 ²) *University of Carthage, Laboratoire des composés hétéro-organiques et des matériaux*
6 *nanostructurés-LR18 ES11, Faculty of Sciences of Bizerte, Jarzouna 7021, Tunisia*

7 ³) *University of Tunis El Manar, Faculty of Sciences of Tunis, 2092 Tunis, Tunisia*

8 ⁴) *University of Northern Border, College of Science of Arar, P.O. Box 1231, Arar 91431, Kingdom of*
9 *Saudi Arabia*

10 ¹: corresponding author (agnes.smith@unilim.fr)

11

12 Abstract

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

23 1 Introduction

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

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

39 The stabilization during cooling of high temperature polymorphs of Ca_2SiO_4 depends on
40 three parameters: particle size [15], thermal treatment [16] and the presence of impurities
41 [17]. The increase of particle size leads to the destabilization of β polymorph and stimulates
42 the formation of γ polymorph during cooling [15]. β -polymorph is favored by quenching the
43 clinker [6]. Researchers studied the incorporation of foreign ions inside Ca_2SiO_4 structure
44 [17,18,19,20]. The mechanism of stabilization was also investigated and different theories
45 were established [21]. Pritts and Daugherty [22] developed a β polymorph stabilization model
46 involving the charge and the radius of the foreign ions to explain the mechanism of
47 stabilization. Xiuji and Shizong [23] proposed that the ability of ion polarization might be an
48 important factor to estimate the effect of element on the stability of β - Ca_2SiO_4 . Lai et al. [17]
49 studied the stability of β - Ca_2SiO_4 doped with ions (Li^+ , K^+ , Na^+ , Sr^{2+} , Mn^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} ,
50 Ti^{4+} , Mn^{4+} , P^{5+} and S^{6+}) and deduced that the relation between cation radius and β
51 stabilization was complicated.

52 Twin domains can contribute to surface energy of particles and thus the stability of
53 specific crystallographic structure [24]. Twins domains of β polymorph were studied by
54 different researchers [13,12,25,26]. During the $\alpha'_L \rightarrow \beta$ transformation, twin domains are
55 formed thus consuming the strain energy provided during the transition [25,6]. Kim et al.
56 [25] claimed the presence of two types of twins: $\{100\}$ and $\{001\}$. Xiuji et al. [13] claimed
57 that the nature of impurities might influence the type of twinning ($\{100\}$ and $\{001\}$) by
58 proving that doping with K_2O or Na_2O lead to the formation of the $\{001\}$ twins. The role of
59 impurities upon the microstructure of twin domains and grain boundaries of α' and β
60 polymorphs was also investigated for the case of phosphorus and barium additions by Ghose
61 et al. [26]. In fact, based on the observation of contrasts by transmission electron microscopy,
62 they proposed that a second phase was formed at the grain boundaries in the P- and Ba-doped
63 β - Ca_2SiO_4 samples. Groves [12] investigated the impact of the thermal treatment of powder
64 upon the microstructure of twin domains and claimed that two types of fast cooling can exist:
65 $\alpha \rightarrow \beta$ and $\alpha'_H \rightarrow \beta$. He claimed that the $\alpha \rightarrow \beta$ transformation lead to more internal strains than
66 the $\alpha'_H \rightarrow \beta$ transformation. Internal strains generated by the $\alpha \rightarrow \beta$ transformation could be
67 sufficient to generate dislocations at the grain boundaries.

68 Despite some early works on the twinning properties of β -Ca₂SiO₄, the impact of the
69 nature of stabilizer elements on the morphology of twin domains and grain boundaries has not
70 yet being studied to our knowledge. Therefore, the main goal of this study consists of
71 examining the effect of three stabilizer elements (boron, phosphorus and sulfur) upon the
72 microstructure of the β -Ca₂SiO₄. The selection of these three dopants is justified below.
73 Sulfur can be part of the raw materials used to produce clinkers containing belite. As an
74 example, belite-rich sulfoaluminate clinkers are a good alternative to Portland clinkers due to
75 the energy savings [27]; calcium sulfate is one of the raw materials and sulfur can be present
76 in belite [28]. Concerning phosphorus, it can be present in the limestone used for clinker
77 manufacture [29] or in other calcium sources such as ash bones which are used to reduce CO₂
78 emission during the clinkering process [30,31]. Lastly, with respect to boron, its presence in
79 belite-rich sulfoaluminate clinker was found to catalyze the hydration of belite [32]. [Table 1](#)
80 presents the effect of those elements upon the structure of Ca₂SiO₄ with different
81 experimental conditions. It was reported that sulfur addition stabilizes β -Ca₂SiO₄ by the
82 substitution of silicon by sulfur in the structure [33,34]. The maximum content of SO₃ in the
83 structure of Ca₂SiO₄ was estimated to be 4.4 wt.% [33]. Different researchers studied
84 phosphorus addition in Ca₂SiO₄ structure and they affirmed that the presence of phosphorus
85 stabilized α , α'_H , α'_L and β polymorphs [22,35,36]. Poulsen et al. [18] described the
86 mechanism of stabilization, which consisted in the substitution of silicon by phosphorus and
87 charge compensation being maintained by creation of calcium vacancies. Duée et al. [36] said
88 that for a 10 wt.% P₂O₅ content with respect to SiO₂, the obtained product was the α -
89 Ca₂SiO₄/ α -Ca₃(PO₄)₂ solid solution. Fukuda et al. [37] report the effect of phosphorus
90 addition upon the microstructure of β -Ca₂SiO₄ surface. These authors detected the formation
91 of surface relief on the grain surface and related it to a martensitic transformation $\alpha'_L \rightarrow \beta$.
92 With respect to boron, previous studies evidenced that boron stabilizes the β -polymorph
93 [19,17,38]. Cuesta et al. [39] claimed that boron stabilized high temperature polymorphs (β
94 and α'_L) by substituting silicon and calcium atoms.

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

98 2 Sample preparation

99 Two synthesis routes were adopted to prepare pure stable β -Ca₂SiO₄ through poly-
100 condensation reaction and doped β -Ca₂SiO₄ through solid-state reaction. For the poly-

101 condensation reaction, we applied the same experimental protocol as described in a previous
102 study [15]. The resin was prepared by mixing citric acid (Alfa Aesar CAS: 77-92-9; molar
103 mass: 192.124 g.mol⁻¹) and ethylene glycol (Fisher Bioreagents CAS: 107-21-1; molar mass:
104 62.07 g.mol⁻¹). The ratio $R = \frac{m_{resin}}{m_{Ca_2SiO_4}}$ was fixed at 0.9. The calcium precursor was
105 Ca(NO₃)₂.4H₂O (Alfa Aesar CAS: 13477-34-4; molar mass: 236.15 g.mol⁻¹). The silicon
106 precursor was Ludox^R AS-40 colloidal silica (Aldrich CAS: 7631-86-9. Molar mass of SiO₂:
107 60.08 g.mol⁻¹, 40 vol% in water). Calcium nitrate and colloidal silica were dissolved in water.
108 This solution was added drop by drop into the resin and then stirred at 363 K for 3 h. The
109 formed gel was cured at 373 K for 24 h to evaporate water and to transform into a foam. It
110 was then calcined at 673 K and gave a brown powder, which was treated at 1473 K for one
111 hour to produce pure β-Ca₂SiO₄ powder.

112 For the solid-state reaction, CaCO₃ (Sigma Aldrich CAS: 471-34-1) and SiO₂ (Ceradel
113 CAS: 14808-60-7) were mixed intimately, in a 2:1 stoichiometric proportion. Boron,
114 phosphorus and sulfur were supplied by the addition of B₂O₃, P₂O₅ and CaSO₄. Their quantity
115 were adjusted according to prepare the following mix: $(1 - x)Ca_2SiO_4 + \frac{x}{2}D$, where D
116 (which stands for ‘Dopant’) is B₂O₃ or P₂O₅, and $(1 - x)Ca_2SiO_4 + xD$ when D is CaSO₄
117 and presented in table 2 (x corresponds to the weight percentage). These elements were
118 supplied respectively by boric acid H₃BO₃ (Sigma Aldrich CAS: 10043-53-3), ammonium
119 phosphate dibasic (NH₄)₂HPO₄ (Sigma Aldrich CAS: 7783-28-0) and CaSO₄.2H₂O (Fluka
120 CAS: 10101-41-4). Their percentages were selected according to results from previous works
121 (Table 1). Experimental conditions were chosen to obtain β and to prevent the formation of α’
122 and γ polymorphs. All mixtures were milled (RETSCH miller) with the addition of a small
123 quantity of ethanol. Disks of 20 mm in diameter and ~ 3.2 mm thickness were pressed
124 (compaction pressure: 2 T). Disks were heated in a platinum crucible at two temperatures,
125 1473 and 1673 K, for 1 h (heating ramp: 600 Kh⁻¹) and quenched in air at room temperature.
126 These two temperatures were chosen in order to study the two transformations that can occur
127 during cooling, namely α→β and α’_H→β. Table 2 presents the notations and the firing
128 conditions.

129 3 Characterization techniques

130 X-Ray diffraction (XRD) data were collected at room temperature on a Bruker D8
131 Advance X-ray diffractometer with Cu_{Kα} radiation ($\lambda_{Cu} = 1.54056 \text{ \AA}$) at a step scan of 0.01 °
132 operated at a voltage 40 kV and an electric current 40 mA. Phase identification was carried

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

139 Differential scanning calorimetry (DSC) was performed on doped β -Ca₂SiO₄. The DSC
140 scans were taken with Thermo-balance TG-DSC Setsys Setaram 24 apparatus. The firing
141 cycle was the following: heating ramp 10 °C/min up to 1420 °C and cooling ramp 10 °C/min.

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

146 High resolution transmission electron microscopy (HR-TEM) was used to study the
147 morphology and the crystallography of different samples. TEM experiments were carried out
148 on a JEOL 2100F- LM microscope operating at 200 kV. Since Ca₂SiO₄ particles react under
149 the electron beam, the observations were carried out at 73 K. Fast Fourier Transform (FFT)
150 was performed and high resolution (HR) images were recorded to investigate crystalline
151 characteristics of Ca₂SiO₄ nanoparticles. Inverse Fast Fourier Transform (IFFT) was studied
152 in some cases to investigate a preferential direction. Selected area electron diffraction (SAED)
153 was performed on Ca₂SiO₄ particle to identify the crystalline structure. Specimens were
154 prepared by dispersing the selected powders in acetone and dropping the suspensions on
155 copper grids coated with carbon support films.

156 4 Results and discussion

157 4.1 Effect of dopants on the stabilization of the β polymorph

158 XRD patterns of the different samples treated at 1673 and 1473 K are presented on [Figs.](#)
159 [1 and 2](#). The sample prepared by chemical route leads the formation of pure β -Ca₂SiO₄ (BC
160 on [Figs. 1 and 2](#)). As expected, BS sample prepared by solid state synthesis and without any
161 dopant presents the γ -Ca₂SiO₄ polymorph (BS on [Fig. 1](#)) [45]. At 1673 K, the addition of
162 dopants (P, B and S) leads to the stabilization of β -polymorph (Respectively BSP_16,
163 BSB_16 and BSS_16 on [Fig. 1](#)). We notice the presence of small intensity peaks related to γ -
164 polymorph for BSP_16. Rietveld refinement confirmed the presence of 7 wt% of γ -polymorph
165 ([Table 4](#)). In addition, we detected a significant quantity of α' -polymorph, i.e. 22 wt%. For

166 the other samples (BSB_16 and BSS_16), we confirmed that the content of β -polymorph is
167 very high (respectively 99.5 and 98.8 wt%). We also record a significant displacement of
168 XRD peaks in the doped samples compared to the pure sample. This fact suggests a change of
169 lattice parameters, which can be due to the incorporation (insertion/substitution) of the dopant
170 into the structure. The calculated variations of lattice parameters using Rietveld refinement,
171 by comparison with the lattice parameters given by Mumme et al. [40], shows that lattice
172 deformations depend on the nature of the dopant (Table 5). Samples prepared by solid-state
173 route and fired at 1473 K contain some unreacted silica and CaO, which can be due to the
174 lower firing temperature. Small peaks related to γ -polymorph are detected despite the
175 presence of P (BSP_14) or S (BSS_14). Phase quantification using Reitveld method confirms
176 the presence of unreacted oxide and small amount of transformed β -polymorph into γ -
177 polymorph (Table 5). With B doping (BSB_14) no γ -polymorph is detected and the XRD
178 peaks are narrow compared to the other samples, namely BSP_14 and BSS_14. To conclude,
179 sintering at 1673 K (followed by quenching at room temperature) leads to a better
180 stabilization of the β polymorph than sintering at 1473 K. The peaks of samples treated at
181 1673 K are broader than peaks of the samples treated at 1473 K.

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

192 Kim et al. [25] presented the different transformations of Ca_2SiO_4 as a function of
193 temperature and claimed that the $\alpha \rightarrow \alpha'_H$ transformation occurs at 1693 K. The presence of
194 foreign ions such as phosphorus (1 wt% of P_2O_5 with respect to SiO_2) and boron (0.13 wt% of
195 B_2O_3 with respect to CaO) decreases the temperature of $\alpha \rightarrow \alpha'_H$ transformation from 1693 to
196 1553 and 1669 K, respectively [26]. In the present case, with the addition of one dopant (P, S
197 or B), the α polymorph (resp. α'_H polymorph) can be formed during sintering at 1673 K (resp.
198 1473 K). In order to confirm this fact, Fig. 3 shows the evolution of the heat flow during
199 cooling of the doped samples. Indeed, the exothermic peak corresponding to $\alpha \rightarrow \alpha'_H$

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

220 4.2 Effect of doping elements upon the microstructure

221 4.2.1 Grain boundary (GB) modifications

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

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

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

$$239 \quad \frac{\gamma_{GB}}{\gamma_S} = 2 \cos\left(\frac{\Psi}{2}\right) \quad (1)$$

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

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

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

262 4.2.2 Twin microstructure modification

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

265 morphology of twin domains is related to the energy of twins [53], and the morphology of
266 twins in β -Ca₂SiO₄ might have an influence upon the stabilization of β polymorph. Therefore,
267 in the present study, the effect of dopants upon the twin morphology was studied. For the
268 interpretation of the observed morphologies, we referred to the description of twins alloys in
269 the literature [53]. According to their morphology, twins can be classified into different
270 types: the crossing twin morphology, the general morphology and the zig-zag morphology
271 [53]. These classifications will be used to interpret our observations.

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

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

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

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

311 4.2.3 Surface relief and dislocations

312 In the case of phosphorus addition, the stabilization of β -Ca₂SiO₄, fired at 1673 K, is
313 accompanied with the formation of significant deformation of the grain surface (Fig. 11a). It
314 is less important when firing temperature is at 1473 K (Fig. 11b). The orientation of this relief
315 is perpendicular to the twin variants (circled in white in Fig. 11). Such a surface relief, with
316 the stabilization of β polymorph with phosphorus addition, was observed by Fukuda et al.
317 [37], with the same orientation. The surface relief was reported as a deformation generated by
318 the strain produced during the $\alpha' \rightarrow \beta$ and $\alpha \rightarrow \beta$ transitions, which are classified as ferro-elastic
319 martensitic transformation [25]. This strain can deform the surface of the grains when
320 phosphorus is present in the structure [53]. The lower magnitude of surface deformation in
321 sample fired at 1473 K compared to 1673 K might be related to the higher intensity of the
322 generated strain during $\alpha \rightarrow \beta$ compared to $\alpha' \rightarrow \beta$ transformation [25].

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

331 between $\alpha \rightarrow \beta$ and $\alpha' \rightarrow \beta$ transformation. By inspecting BSB_16 sample by HR-TEM, we
332 recorded the formation of defects such as [002](020) edge dislocation (Fig. 13). The inverse
333 of fast Fourier transform with [002] (Fig. 13c) demonstrates clearly the existence an extra half
334 (002) plane. Therefore, the dislocation motion can be at the origin of the formation of these
335 slips as presented in Fig. 13d (e.g. (020) glide) [51]. The motion of dislocations needs energy
336 and the generated strain during the formation of β structure might provide enough energy to
337 move the dislocations to the surface. This morphology is not observed for sample fired at
338 1473 K since its β transformation provides lower strain energy.

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

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

353 To conclude, the change of the surface microstructure of doped β -Ca₂SiO₄ compared to
354 undoped Ca₂SiO₄ can be related to the formation and motions of linear dislocations (edge and
355 screw dislocations). In Ca₂SiO₄, the increase of the particle size during sintering leads during
356 cooling to the destabilization of β polymorph and the formation of γ polymorph. The addition
357 of dopants (S, B, P) conducts to the formation of dislocations. One of the driving forces of
358 $\beta \rightarrow \gamma$ transformation is the generated strain during previous transformations [6]. The motion
359 of these dislocations might consume part of this strain and contributes to the stabilization of
360 β -Ca₂SiO₄.

361 4.3 Dislocation motion

362 The presence of dislocation and their motion were considered as the source of observed
363 deformation on the surface of β -Ca₂SiO₄. The high density of deformation in the case of
364 samples fired at 1673 K, compared to those fired at 1473 K, can be explained by the
365 difference of thermal strain generated by the higher firing temperature, which induces to the
366 motion of dislocations to interfaces such as GB and TB. According to the literature, the
367 motion of dislocations requires a minimum strain, which is proportional to the dislocation
368 characteristics (type, width of deformation) and to the structure density. This relation is
369 described by Peierls-Nabarro's model [56]:

$$370 \quad \tau_{PN} \approx G e^{-\left(\frac{2\pi w}{b}\right)} \quad (2)$$

371 where τ_{PN} is the strain of Peierls-Nabarro, G is the shear modulus, w is the width of the
372 deformation due to the presence of edge dislocation and b is the modulus of burger vector. An
373 increase in the width of deformation leads to a decrease of the strain necessary to move a
374 dislocation into the structure. In addition, the decrease of b , associated to the increase of
375 interatomic distance, leads to the decrease of τ_{PN} , which explain the higher mobility of
376 dislocation in the case of metal compared to oxide. In the case of β -Ca₂SiO₄, Shahsavari et al.
377 [14] estimated the strain of Peierls-Nabarro based on experimental observation and ab-initio
378 simulation (Fig. 16). They claimed a very high value of strain (164.44 MPa) necessary to
379 move a dislocation inside β -Ca₂SiO₄. Besides this high value, they announced that the motion
380 of dislocations inside this structure is very difficult and requires a high energy. In the present
381 work, the examination of an edge dislocation in the case of BSB_16 by HR-TEM shows big
382 difference compared to the observation of Shahsavari et al. [14]. As shown in Fig. 16, the
383 presence of an extra half plan leads to a larger area of deformation inside the structure of
384 BSB_16 compared to the case of Shahsavari et al. [14]. In fact, the width of deformation in
385 BSB_16, estimated equal to $10 \times b$, is larger than the previous case which was estimated to
386 be $6 \times b$. Assuming that shear modulus is the same for both cases, the strain of Peierls-
387 Nabarro for both cases can be compared according to equation (3):

$$388 \quad \frac{\tau_{PN1}}{\tau_{PN2}} \approx \frac{e^{-\left(\frac{2\pi w_1}{b_1}\right)}}{e^{-\left(\frac{2\pi w_2}{b_2}\right)}} \quad (3) \quad \rightarrow \quad \frac{\tau_{PN1}}{\tau_{PN2}} \approx 68,31$$

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

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

395 5 Conclusion

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

414

415 *References*

- 416 [1] F. Ma, A. Sha, P. Yang, Y. Huang, The Greenhouse Gas Emission from Portland Cement Concrete
417 Pavement Construction in China, *Int. J. Environ. Res. Public. Health*, 13 (2016), doi:
418 10.3390/ijerph13070632.
- 419 [2] F. P. Glasser, L. Zhang, High-performance cement matrices based on calcium sulfoaluminate–belite
420 compositions, *Cem. Concr. Res.*, 31 (2001) 1881-1886, doi: 10.1016/S0008-8846(01)00649-4.
- 421 [3] E. Gartner, Industrially interesting approaches to “low-CO₂” cements, *Cem. Concr. Res.*, 34 (2004)
422 1489-1498, doi: 10.1016/j.cemconres.2004.01.021.
- 423 [4] S. N. Ghosh, P. B. Rao, A. K. Paul, K. Raina, The chemistry of dicalcium silicate mineral, *J. Mater. Sci.*,
424 14 (1979) 1554-1566, doi: 10.1007/BF00569274.
- 425 [5] R. Trettin, G. Oliev, C. Stadelmann, W. Wieker, Very early hydration of dicalcium silicate-polymorphs,
426 *Cem. Concr. Res.*, 21 (1991) 757-764, doi: 10.1016/0008-8846(91)90171-D.
- 427 [6] G. W. Groves, Phase transformations in dicalcium silicate, *J. Mater. Sci.*, 18 (1983) 1615-1624, doi:
428 10.1007/BF00542054.
- 429 [7] H. F. W. Taylor, *Cement Chemistry*. Thomas Telford, (1997).

- 430 [8] S. Fu, W. Liu, S. Liu, S. Zhao, Y. Zhu, 3D printed porous β -Ca₂SiO₄ scaffolds derived from preceramic
431 resin and their physicochemical and biological properties, *Sci. Technol. Adv. Mater.*, 19 (2018) 495-506,
432 doi: 10.1080/14686996.2018.1471653.
- 433 [9] Z. Gou, J. Chang, Synthesis and in vitro bioactivity of dicalcium silicate powders, *J. Eur. Ceram. Soc.*, 24
434 (2004) 93-99, doi: 10.1016/S0955-2219(03)00320-0.
- 435 [10] H. Zhong, L. Wang, Y. Fan, L. He, K. Lin, W. Jiang, J. Chang, L. Chen, Mechanical properties and
436 bioactivity of β -Ca₂SiO₄ ceramics synthesized by spark plasma sintering, *Ceram. Int.*, 37 (2011)
437 2459-2465, doi: 10.1016/j.ceramint.2011.03.037.
- 438 [11] Z. Gou, J. Chang, W. Zhai, Preparation and characterization of novel bioactive dicalcium silicate
439 ceramics, *J. Eur. Ceram. Soc.*, 25 (2005) 1507-1514, doi: 10.1016/j.jeurceramsoc.2004.05.029.
- 440 [12] G. W. Groves, Twinning in β -dicalcium silicate, *Cem. Concr. Res.*, 12 (1982) 619-624, doi: 10.1016/0008-
441 8846(82)90023-0.
- 442 [13] F. Xiuji, W. Lan, L. Shizong, W. Yanguo, Investigation of β -C₂S twins, *Cem. Concr. Res.*, 18 (1988)
443 753-757, doi: 10.1016/0008-8846(88)90099-3.
- 444 [14] R. Shahsavari, L. Chen, L. Tao, Edge dislocations in dicalcium silicates: Experimental observations and
445 atomistic analysis, *Cem. Concr. Res.*, 90 (2016) 80-88, doi: 10.1016/j.cemconres.2016.09.012.
- 446 [15] S. Saidani, A. Smith, Y. El Hafiane, L. Ben Tahar, Re-examination of the $\beta \rightarrow \gamma$ transformation of Ca₂SiO₄,
447 *J. Eur. Ceram. Soc.*, 38 (2018) 4756-4767, doi: 10.1016/j.jeurceramsoc.2018.06.011.
- 448 [16] P. Fierens, J. Tirloq, Effect of synthesis temperature and cooling conditions of beta-dicalcium silicate on
449 its hydration rate, *Cem. Concr. Res.*, 13 (1983) 41-48, doi: 10.1016/0008-8846(83)90126-6.
- 450 [17] G.-C. Lai, T. Nojiri, K. Nakano, Studies of the stability of β -Ca₂SiO₄ doped by minor ions, *Cem. Concr.*
451 *Res.*, 22 (1992) 743-754, doi: 10.1016/0008-8846(92)90097-F.
- 452 [18] S. L. Poulsen, H. J. Jakobsen, J. Skibsted, Incorporation of Phosphorus Guest Ions in the Calcium Silicate
453 Phases of Portland Cement from ³¹P MAS NMR Spectroscopy, *Inorg. Chem.*, 49 (2010) 5522-5529, doi:
454 10.1021/ic100140j.
- 455 [19] D. Koumpouri, G. N. Angelopoulos, Effect of boron waste and boric acid addition on the production of
456 low energy belite cement, *Cem. Concr. Compos.*, 68 (2016) 1-8, doi: 10.1016/j.cemconcomp.2015.12.009.
- 457 [20] Y. M. Kim, S.-H. Hong, Influence of Minor Ions on the Stability and Hydration Rates of β -Dicalcium
458 silicate, *J. Am. Ceram. Soc.*, 87 (2004) 900-905, doi: 10.1111/j.1551-2916.2004.00900.x.
- 459 [21] D. V. Lopatin, V. M. Chizhikova, Crystal-chemical stabilization of dicalcium silicate, *Steel Transl.*, 37
460 (2007) 191-195, doi: 10.3103/S0967091207030035.
- 461 [22] I. M. Pritts, K. E. Daugherty, The effect of stabilizing agents on the hydration rate of β -C₂S, *Cem. Concr.*
462 *Res.*, 6 (1976) 783-795, doi: 10.1016/0008-8846(76)90008-9.
- 463 [23] F. Xiuji, L. Shizong, Investigation of the effect of minor ions on the stability of β -C₂S and the mechanism
464 of stabilization, *Cem. Concr. Res.*, 16 (1986) 587-601, doi: 10.1016/0008-8846(86)90097-9.
- 465 [24] A. G. Evans, N. Burlingame, M. Drory, W. M. Kriven, Martensitic transformations in zirconia—particle
466 size effects and toughening, *Acta Metall.*, 29 (1981) 447-456. doi: 10.1016/0001-6160(81)90170-X.
- 467 [25] Y. J. Kim, I. Nettleship, W. M. Kriven, Phase Transformations in Dicalcium Silicate: II, TEM Studies of
468 Crystallography, Microstructure, and Mechanisms, *J. Am. Ceram. Soc.*, 75 (1992) 2407-2419, doi:
469 10.1111/j.1151-2916.1992.tb05593.x.
- 470 [26] A. Ghose, S. Chopra, J. F. Young, Microstructural characterization of doped dicalcium silicate
471 polymorphs, *J. Mater. Sci.*, 18 (1983) 2905-2914, doi: 10.1007/BF00700771.
- 472 [27] W. Dienemann, D. Schmitt, F. Bullerjahn, M. Ben Haha, Belite-Calciumsulfoaluminate-Ternesite (BCT) -
473 A new low-carbon clinker Technology, *Cem. Int.*, 11 (2013) 100-109.
- 474 [28] K. Quillin, Performance of belite-sulfoaluminate cements, *Cem. Concr. Res.*, 31 (2001) 1341-1349, doi:
475 10.1016/S0008-8846(01)00543-9
- 476 [29] F. C. Holanda, H. Schmidt, V. A. Quarcioni, Influence of phosphorus from phosphogypsum on the initial
477 hydration of Portland cement in the presence of superplasticizers, *Cem. Concr. Compos.*, 83 (2017)
478 384-393, doi: 10.1016/j.cemconcomp.2017.07.029.
- 479 [30] F. Osawa, N. Shirahama, M. Yamashita, H. Tanaka, Effects of phosphorus oxide in clinker and cement on
480 the properties of high content belite cement, *Cem. Sci. Concr. Technol.*, 69 (2015) 23-28, doi:
481 10.14250/cement.69.23.
- 482 [31] T. Ifka, M. T. Palou, Z. Bazelová, The influence of CaO and P₂O₅ of bone ash upon the reactivity and the
483 burnability of cement raw mixtures, 56 (2012) 76-84.
- 484 [32] A. J. M. Cuberos, A. G. De la Torre, G. Álvarez-Pinazo, M. C. Martín-Sedeño, K. Schollbach, H.
485 Pöllmann, M. A. G. Aranda, Active Iron-Rich Belite Sulfoaluminate Cements: Clinkering and Hydration,
486 *Environ. Sci. Technol.*, 44 (2010) 6855-6862, doi: 10.1021/es101785n
- 487 [33] T. Staněk, P. Sulovský, Dicalcium silicate doped with sulfur, *Adv. Cem. Res.*, 24 (2012) 233-238, doi:
488 10.1680/adcr.11.00021.

- 489 [34] F. R. D. Andrade, S. D. Gomes, M. Pecchio, Y. Kihara, F. M. S. Carvalho, J. R. Matos, Effect of sulfur on
490 the polymorphism and reactivity of dicalcium silicate of Portland clinker, *Cerâmica*, 57 (2011) 129-135,
491 doi: 10.1590/S0366-69132011000100017.
- 492 [35] Y. M. Kim, S. H. Hong, Influence of Minor Ions on the Stability and Hydration Rates of β -Dicalcium
493 Silicate, *J. Am. Ceram. Soc.*, 87 (2004) 900-905, doi: 10.1111/j.1551-2916.2004.00900.x.
- 494 [36] C. Duée, C. Bourgel, E. Véron, M. Allix, F. Fayon, F. Bodéan, J. Poirier, Phosphorus speciation in
495 dicalcium silicate phases: Application to the basic oxygen furnace (BOF) slag, *Cem. Concr. Res.*, 73
496 (2015) 207-214, doi: 10.1016/j.cemconres.2015.03.012
- 497 [37] F. Koichiro, T. Hiroyuki, N. Yasuteru, O. Toshitaka, Surface Relief Induced by Martensitic
498 Transformation in Phosphorus-Bearing Dicalcium Silicate, *J. Am. Ceram. Soc.*, 83 (2000) 2097-2099,
499 doi: 10.1111/j.1151-2916.2000.tb01521.x.
- 500 [38] P. Fierens, J. Tirlocq, Nature and concentration effect of stabilizing elements of beta-dicalcium silicate on
501 its hydration rate, *Cem. Concr. Res.*, 13 (1983) 267-276, doi: 10.1016/0008-8846(83)90110-2
- 502 [39] A. Cuesta, E. R. Losilla, M. Aranda, J. Sanz, A. De la Torre, Reactive belite stabilization mechanisms by
503 boron-bearing dopants, *Cem. Concr. Res.*, 42 (2012) 598-606, doi: 10.1016/j.cemconres.2012.01.006
- 504 [40] W. G. Mumme, R. J. Hill, G. Bushnell-Wye, E. R. Segnit, Rietveld crystal structure refinements, crystal
505 chemistry and calculated powder diffraction data for the polymorphs of dicalcium silicate and related
506 phases, *Neues Jahrbuch fuer Mineralogie - Abhandlungen*, 169 (1995) 35-68.
- 507 [41] J. Barvier, B. G. Hyde, The Structures of the Polymorphs of Dicalcium Silicate, Ca_2SiO_4 , *Acta Cryst.*, B41
508 (1985) 383-390, doi: 10.1107/S0108768185002348
- 509 [42] M. B. Smirnov, Lattice dynamics and thermal expansion of quartz, *Phys. Rev. B*, 59 (1999) 4036, doi:
510 10.1103/PhysRevB.59.4036
- 511 [43] J. G. Thomson, R. L. Withers, S. R. Palethorpe, A. Melnitchenko, Cristobalite-Related Oxide Structures,
512 *Journal of Solid State Chemistry*, 15 (1998) 29-49, doi: 10.1006/jssc.1998.7903
- 513 [44] J. M. Valverde, P. E. Sanchez-Jimenez, L. A. Perez-Maqueda, Limestone Calcination Nearby Equilibrium:
514 Kinetics, CaO Crystal Structure, Sintering and Reactivity, *J. Phys. Chem. C*, 119 (2015) 1623-1641, doi:
515 10.1021/jp508745u
- 516 [45] M. A. Bredig, Polymorphism of Calcium Orthosilicate, *J. Am. Ceram. Soc.*, 33 (1950) 188-192, doi:
517 10.1111/j.1151-2916.1950.tb12789.x.
- 518 [46] C. Suryanarayana, M. G. Norton, *X-Ray Diffraction: A Practical Approach*, Springer US, (1998).
- 519 [47] K. Fukuda, I. Maki, S. Ito, Remelting Reaction within Belite Crystals during Cooling, *J. Am. Ceram. Soc.*,
520 75 (1992) 2896-2898, doi: 10.1111/j.1151-2916.1992.tb05528.x.
- 521 [48] K. Fukuda, I. Maki, S. Ikeda, S. Ito, Microtextures Formed by the Remelting Reaction in Belite Crystals,
522 *J. Am. Ceram. Soc.*, 76 (1993) 2942-2944, doi: 10.1111/j.1151-2916.1993.tb04046.x.
- 523 [49] G. S. Rohrer, Grain boundary energy anisotropy: a review, *J. Mater. Sci.*, 46 (2011) 5881, doi:
524 10.1007/s10853-011-5677-3.
- 525 [50] W. W. Mullins, Theory of Thermal Grooving, *J. Appl. Phys.*, 28 (1957) 333-339, doi: 10.1063/1.1722742.
- 526 [51] B. P. Uberuaga, L. J. Vernon, E. Martinez, A. F. Voter, The relationship between grain boundary structure,
527 defect mobility, and grain boundary sink efficiency, *Scientific Reports*, 5 (2015) 9095, doi:
528 10.1038/srep09095.
- 529 [52] M. W. Grabski, R. Korski, Grain boundaries as sinks for dislocations, *Philos. Mag. J. Theor. Exp. Appl.*
530 *Phys.*, 22 (1970) 707-715, doi: 10.1080/14786437008220941.
- 531 [53] H. Seiner, L. Straka, O. Heczko, A microstructural model of motion of macro-twin interfaces in Ni-Mn-
532 Ga 10M martensite, *J. Mech. Phys. Solids*, 64 (2014) 198-211, doi: 10.1016/j.jmps.2013.11.004.
- 533 [54] R. Scheuplein, P. Gibbs, Surface Structure in Corundum: I, Etching of Dislocations, *J. Am. Ceram. Soc.*,
534 43 (1960) 458-472, doi: 10.1111/j.1151-2916.1960.tb13698.x.
- 535 [55] Y. N. Picard, M. E. Twigg, J. D. Caldwell, C. R. Eddy, M. A. Mastro, R. T. Holm, Resolving the Burgers
536 vector for individual GaN dislocations by electron channeling contrast imaging, *Scr. Mater.*, 61 (2009)
537 773-776, doi: 10.1016/j.scriptamat.2009.06.021.
- 538 [56] B. Joós, M. S. Duesbery, The Peierls Stress of Dislocations: An Analytic Formula, *Phys. Rev. Lett.*, 78,
539 (1997), 266- 269, doi: 10.1103/PhysRevLett.78.266.
- 540

List of figures

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.

Figure 2: XRD patterns of samples fired at 1473 K with addition of stabilizing elements; *full line: β -Ca₂SiO₄, dashed line: γ -Ca₂SiO₄ and (S) SiO₂.*

Figure 3: The evolution of the heat flow as function of temperature of β -Ca₂SiO₄ stabilized by dopants, showing the exothermic peak of $\alpha \rightarrow \alpha'_H$ transformation.

Figure 4: SEM observation of pure sample (BC) showing the morphology of twin domain (black arrow) and grain boundaries (white arrow).

Figure 5: SEM observation of the morphology of grain boundary (white arrows) as a function of the nature of dopant and the type of cooling.

Figure 6: Effect of the presence of phosphorus upon the grain boundary grooving compared to the pure sample (BC) and change of dihedral angle according to SEM observation with the addition of phosphorus (BSP_16).

Figure 7: HR-TEM image of BSS_16 sample along [010] axis showing the presence of screw dislocation, which is formed by the shearing of (101) planes. The atomic model sketches the mechanism of deformation.

Figure 8: SEM images of the twin boundaries (TB) ending tips of the pure and the B-doped sample showing the formation of branching near the GB by adding the dopant.

Figure 9: SEM observation of an interface between two domains (GB) for the pure sample, showing incoherent twin boundaries at the interface (TB of domain 1-blue are not compatible with TB of domain 2-red).

Figure 10: TEM images and SAED pattern along [011] axis of the pure and the B-doped samples showing the change of the {100} twin microstructure (dotted with black arrows).

Figure 11: SEM observation of BSP_16 and BSP_14 showing the formation of surface relief (marked with circle) perpendicular to the twin domains.

Figure 12: a) and b) SEM observation of BSB_16 surfaces showing the formation of slips on the surface grains (dotted with blue arrows). c) TEM observation of BSB_16 showing the formation of slip accompanied with the SAED pattern along β [$\bar{3}01$].

Figure 13: (a) HR-TEM image and (b) FFT pattern of BSB_16 sample confirming the presence of β -Ca₂SiO₄ along [200]. (c) Inverse of Fast Fourier Transform showing the existence of extra (002) half plane. (d) Schematic representation of the edge dislocation along the [002] direction leading to the formation of an edge.

Figure 14: SEM image of BSS_16 showing the presence of etch pits on the surface grains.

Figure 15: HR-TEM images of BSS_16 showing the presence of screw dislocations.

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]	
				1708	6+2	β		
				1708	6+2+4.5	β, 3CaO.2SiO ₂		
				1708	1	3CaO.2SiO ₂		
				1708	1	3CaO.2SiO ₂		
				1708	1	3CaO.2SiO ₂		
		1573	0.51	wt% B ₂ O ₃	1573	0.5	γ<α' _H <β	[39]
					1573	0.5	α' _H <β	
					1573	0.5	α' _H <β	
					1573	0.5	α' _H <β	
					1573	0.5	α' _H <β	
					1573	0.5	β<α' _H	
					1573	0.5	β<α' _H	
S⁶⁺	CaSO ₄ .2H ₂ O	wt% CaSO ₄	1523	2.5	β, CaO	[20]		
			1673	4+1+22	β, γ			
			1673	2+2	β			
			1673	3+3	β			
			1673	2+2+2.5	β			
			1673	2+2+2.5	β			
	1723	0.06	wt% CaSO ₄ .2H ₂ O	1723	2	α<γ<β	[33]	
				1723	2	α<γ<β		
				1723	2	α<γ<β		
				1723	2	α<γ<β		
				1723	2	γ<α<β		
P⁵⁺	-	wt% P ₂ O ₅	1708	6	β, γ	[20]		
			1708	2	β, γ			
			1708	1+2	β			
			1708	8+4+2	β			
			1708	2+18+2.5	α			
			1773	3	α', β		[17]	
			1773	3	α', β			

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] ($\Delta x = \frac{x_{sample} - x_{reference}}{x_{reference}}$)