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# 1 Role of dopants (B, P and S) on the stabilization of $\beta$ - $\text{Ca}_2\text{SiO}_4$

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## 12 Abstract

13 The interest in belite ( $\text{Ca}_2\text{SiO}_4$  + 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  $\text{CO}_2$  emission. Belite is also of interest as a biomedical cement.  
16 For the cement industry, stabilization of the  $\beta$ -polymorph is essential since the  $\gamma$ -polymorph  
17 has no hydraulic activity. In order to understand the mechanism of  $\beta$ -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  $\text{Ca}_2\text{SiO}_4$  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  $\beta$ -  
22 polymorph has been established.

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## 23 1 Introduction

24 Dicalcium silicate is used for different applications, such as bioceramics and cement. In  
25 the cement field, belite ( $\text{Ca}_2\text{SiO}_4$ , with impurities or dopants) clinker appears as one of the  
26 most promising route to reduce  $\text{CO}_2$  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  $\alpha$ ,  $\alpha'_H$ ,  $\alpha'_L$ ,  $\beta$  and  $\gamma$  [4]. Unfortunately,  $\gamma$  polymorph, which is stable at  
30 room temperature, does not react with water [5]. The stabilization of water reactive  
31 polymorphs of  $\text{Ca}_2\text{SiO}_4$  ( $\alpha$ ,  $\alpha'_H$ ,  $\alpha'_L$  and  $\beta$ ), is essential in order to ensure reactivity with water  
32 for cement application [6].  $\beta$ -polymorph is the well-known polymorph in the cement field [7].  
33 Recently,  $\beta$ -  $\text{Ca}_2\text{SiO}_4$  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  $\beta$ -structure [13]. Further, Shahsavari et al. [14] suggest the presence of dislocations in  $\beta$ -  
38  $\text{Ca}_2\text{SiO}_4$  which makes the phase the most brittle polymorph.

39 The stabilization during cooling of high temperature polymorphs of  $\text{Ca}_2\text{SiO}_4$  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  $\beta$  polymorph and stimulates  
42 the formation of  $\gamma$  polymorph during cooling [15].  $\beta$ -polymorph is favored by quenching the  
43 clinker [6]. Researchers studied the incorporation of foreign ions inside  $\text{Ca}_2\text{SiO}_4$  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  $\beta$  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  $\beta$ - $\text{Ca}_2\text{SiO}_4$ . Lai et al. [17]  
49 studied the stability of  $\beta$ - $\text{Ca}_2\text{SiO}_4$  doped with ions ( $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  
50  $\text{Ti}^{4+}$ ,  $\text{Mn}^{4+}$ ,  $\text{P}^{5+}$  and  $\text{S}^{6+}$ ) and deduced that the relation between cation radius and  $\beta$   
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  $\beta$  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  $\text{K}_2\text{O}$  or  $\text{Na}_2\text{O}$  lead to the formation of the  $\{001\}$  twins. The role of  
59 impurities upon the microstructure of twin domains and grain boundaries of  $\alpha'$  and  $\beta$   
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  $\beta$ - $\text{Ca}_2\text{SiO}_4$  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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>, 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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>. 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 CO<sub>2</sub>  
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 Ca<sub>2</sub>SiO<sub>4</sub> with different  
81 experimental conditions. It was reported that sulfur addition stabilizes  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> by the  
82 substitution of silicon by sulfur in the structure [33,34]. The maximum content of SO<sub>3</sub> in the  
83 structure of Ca<sub>2</sub>SiO<sub>4</sub> was estimated to be 4.4 wt.% [33]. Different researchers studied  
84 phosphorus addition in Ca<sub>2</sub>SiO<sub>4</sub> structure and they affirmed that the presence of phosphorus  
85 stabilized  $\alpha$ ,  $\alpha'_H$ ,  $\alpha'_L$  and  $\beta$  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.% P<sub>2</sub>O<sub>5</sub> content with respect to SiO<sub>2</sub>, the obtained product was the  $\alpha$ -  
89 Ca<sub>2</sub>SiO<sub>4</sub>/ $\alpha$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> solid solution. Fukuda et al. [37] report the effect of phosphorus  
90 addition upon the microstructure of  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> 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  $\beta$ -polymorph  
93 [19,17,38]. Cuesta et al. [39] claimed that boron stabilized high temperature polymorphs ( $\beta$   
94 and  $\alpha'_L$ ) 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  $\beta$  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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> through poly-  
100 condensation reaction and doped  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> 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<sup>-1</sup>) and ethylene glycol (Fisher Bioreagents CAS: 107-21-1; molar mass:  
104 62.07 g.mol<sup>-1</sup>). The ratio  $R = \frac{m_{resin}}{m_{Ca_2SiO_4}}$  was fixed at 0.9. The calcium precursor was  
105 Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Alfa Aesar CAS: 13477-34-4; molar mass: 236.15 g.mol<sup>-1</sup>). The silicon  
106 precursor was Ludox<sup>R</sup> AS-40 colloidal silica (Aldrich CAS: 7631-86-9. Molar mass of SiO<sub>2</sub>:  
107 60.08 g.mol<sup>-1</sup>, 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-Ca<sub>2</sub>SiO<sub>4</sub> powder.

112 For the solid-state reaction, CaCO<sub>3</sub> (Sigma Aldrich CAS: 471-34-1) and SiO<sub>2</sub> (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 B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> and CaSO<sub>4</sub>. 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 B<sub>2</sub>O<sub>3</sub> or P<sub>2</sub>O<sub>5</sub>, and  $(1 - x)Ca_2SiO_4 + xD$  when D is CaSO<sub>4</sub>  
117 and presented in table 2 (x corresponds to the weight percentage). These elements were  
118 supplied respectively by boric acid H<sub>3</sub>BO<sub>3</sub> (Sigma Aldrich CAS: 10043-53-3), ammonium  
119 phosphate dibasic (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Sigma Aldrich CAS: 7783-28-0) and CaSO<sub>4</sub>·2H<sub>2</sub>O (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<sup>-1</sup>) 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’<sub>H</sub>→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<sub>Kα</sub> radiation (λ<sub>Cu</sub> = 1.54056 Å) 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  $\beta$  polymorph.

139 Differential scanning calorimetry (DSC) was performed on doped  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>. 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 Ca<sub>2</sub>SiO<sub>4</sub> 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 Ca<sub>2</sub>SiO<sub>4</sub> 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 Ca<sub>2</sub>SiO<sub>4</sub> 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 $\beta$ 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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> (BC  
160 on [Figs. 1 and 2](#)). As expected, BS sample prepared by solid state synthesis and without any  
161 dopant presents the  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> polymorph (BS on [Fig. 1](#)) [45]. At 1673 K, the addition of  
162 dopants (P, B and S) leads to the stabilization of  $\beta$ -polymorph (Respectively BSP\_16,  
163 BSB\_16 and BSS\_16 on [Fig. 1](#)). We notice the presence of small intensity peaks related to  $\gamma$ -  
164 polymorph for BSP\_16. Rietveld refinement confirmed the presence of 7 wt% of  $\gamma$ -polymorph  
165 ([Table 4](#)). In addition, we detected a significant quantity of  $\alpha'$ -polymorph, i.e. 22 wt%. For

166 the other samples (BSB\_16 and BSS\_16), we confirmed that the content of  $\beta$ -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  $\gamma$ -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  $\beta$ -polymorph into  $\gamma$ -  
177 polymorph (Table 5). With B doping (BSB\_14) no  $\gamma$ -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  $\beta$  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  $\beta$ -polymorph, the  
183 size increase leads to the formation of  $\gamma$ -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  $\beta$ -polymorph than BSP\_14 and  
190 BSS\_14. This points out the importance of the thermal treatment on stabilization the  $\beta$ -  
191 polymorph.

192 Kim et al. [25] presented the different transformations of  $\text{Ca}_2\text{SiO}_4$  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  $\text{P}_2\text{O}_5$  with respect to  $\text{SiO}_2$ ) and boron (0.13 wt% of  
195  $\text{B}_2\text{O}_3$  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  $\alpha$  polymorph (resp.  $\alpha'_H$  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  $\alpha$  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  $\beta$  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  $\beta$ -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  $\alpha$ -structure is higher than  $\alpha'_H$ -  
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  $\text{Ca}_2\text{SiO}_4$   
215 lattice. They can lower the temperature of formation of  $\alpha$  and  $\alpha'_H$  polymorphs compared to  
216 pure  $\text{Ca}_2\text{SiO}_4$ . During  $\alpha \rightarrow \beta$  cooling, dislocations and defects can appear, which can promote  
217 the stabilization of the  $\beta$  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  $\alpha$  and  $\beta$  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  $\beta$  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  $\gamma_{GB}$  is the GB energy,  $\gamma_S$  is the surface energy and  $\Psi$  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  $\gamma_S$  is  
243 identical for the pure and the P-doped sample (BSP\_16), the increase of  $\Psi$  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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> [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  $\beta$  polymorph and prevents the  $\beta \rightarrow \gamma$  transformation.

#### 262 4.2.2 Twin microstructure modification

263  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> is known to be a heavily twinned structure [12]. Several researchers pretend  
264 that this planar dislocation promotes the stabilization of  $\beta$  polymorph [25]. Besides, the

265 morphology of twin domains is related to the energy of twins [53], and the morphology of  
266 twins in  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> might have an influence upon the stabilization of  $\beta$  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  $\beta$  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  $\beta$  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  $\beta$ -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  $\beta$ -polymorph [25], we can conclude that the formation of the general  
308 morphology might offer better stabilization of  $\beta$ -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  $\gamma$ -polymorph.

#### 311 4.2.3 Surface relief and dislocations

312 In the case of phosphorus addition, the stabilization of  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>, 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  $\beta$  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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> 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  $\beta$ -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  $\beta$  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  $\beta$  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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> compared to  
354 undoped Ca<sub>2</sub>SiO<sub>4</sub> can be related to the formation and motions of linear dislocations (edge and  
355 screw dislocations). In Ca<sub>2</sub>SiO<sub>4</sub>, the increase of the particle size during sintering leads during  
356 cooling to the destabilization of  $\beta$  polymorph and the formation of  $\gamma$  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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>.

### 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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>. 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  $\tau_{PN}$  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  $\tau_{PN}$ , which explain the higher mobility of  
376 dislocation in the case of metal compared to oxide. In the case of  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>, 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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>. 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  $\tau_{PN1}$  and  $\tau_{PN2}$  are the strains of Peierls-Nabarro in Shahsavari's case and in the present  
390 study, respectively. According to this estimation,  $\tau_{PN2}$  is 68 times lower than  $\tau_{PN1}$ , 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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> 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  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>. The  $\alpha \rightarrow \beta$  cooling  
399 stabilizes the  $\beta$ -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  $\beta$ -  
401 Ca<sub>2</sub>SiO<sub>4</sub>. 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  $\beta$  polymorph and  
407 enable its stabilization at room temperature. These modifications might also influence the  
408 mechanical properties and the hydraulicity of  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>. The study of the hydraulicity of  
409 doped  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> 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 CO<sub>2</sub> cements. Finally, the presence of  
412 dislocations can also affect the plasticity of  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>. It could be a good strategy to improve  
413 the grindability of this phase in clinkers to reduce the associated grinding energy.

414

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

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

<sup>a</sup> Virucidal activity in  $\log_{10}$  titer reduction factor recorded after 15 min of contact time at room temperature with an initial RSV of  $1.3 \times 10^7$  TCID<sub>50</sub>/mL (with  $\alpha = \alpha$ -CD,  $\beta = \beta$ -CD,  $\gamma = \gamma$ -CD, *Q* = [DiC<sub>10</sub>][Cl] and *E* = C<sub>12</sub>E<sub>8</sub>). (\*) Minimum virucidal concentration (MVC) = the lowest concentration able to inactivate at least 99.99% of viruses. <sup>b</sup> Calculated according equation 1.

**Table 2.** Physicochemical parameters of [DiC<sub>10</sub>][Cl]/C<sub>12</sub>E<sub>8</sub> (*Q/E*) mixed systems with or without native cyclodextrins ( $\alpha$ ,  $\beta$  and  $\gamma$ ) in aqueous solution at 25 °C compared to [DiC<sub>10</sub>][Cl] and C<sub>12</sub>E<sub>8</sub> alone.<sup>a</sup>

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

<sup>a</sup> All binary or ternary systems are equimolar. <sup>b</sup> CMC = critical micelle concentration,  $D_h$  = hydrodynamic diameter,  $\zeta$ -potential recorded at 10×CMC,  $\alpha$  = the degree of ionization of the micelle. <sup>c</sup> Determined from surface tension modelling using single surfactant/cyclodextrin systems in aqueous solution with dilution experiments. <sup>d</sup> 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*).<sup>a</sup>

	Concentration of each component (μM)								<i>SI</i> <sup>b</sup>	
	20	35	50	75	125	250	500	1000		
HSV-1	(-), $\alpha$ , $\beta$ or $\gamma$	≤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	(-), $\alpha$ , $\beta$ or $\gamma$	≤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>	(-), $\alpha$ , $\beta$ or $\gamma$	≤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>	(-), $\alpha$ , $\beta$ or $\gamma$	≤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

<sup>a</sup> Biocidal or virucidal activity in log<sub>10</sub> titer reduction factor recorded at room temperature after 15 min of contact time for HSV-1 (1.5×10<sup>7</sup> TCID<sub>50</sub>/mL), VACV (1.1×10<sup>7</sup> TCID<sub>50</sub>/mL), *C. albicans* (1.6×10<sup>6</sup> CFU/mL) and 5 min for *P. aeruginosa* (1.0×10<sup>8</sup> CFU/mL). (\*) Minimum virucidal concentration (MVC) = the lowest concentration able to inactivate at least 99.99% of viruses. <sup>b</sup> Calculated according equation 1.

Stabilizing ion	Stabilizer ion source	stabilizer quantity		Firing temperature (K)	Firing time and repetition (Hrs)	Product	Ref.					
B <sup>3+</sup>	H <sub>3</sub> BO <sub>3</sub>	wt% B <sub>2</sub> O <sub>3</sub>	0.24	1708	17	β	[20]					
			0.51	1708	6+2	β						
			1.01	1708	6+2+4.5	β, 3CaO.2SiO <sub>2</sub>						
			3.00	1708	1	3CaO.2SiO <sub>2</sub>						
			5.02	1708	1	3CaO.2SiO <sub>2</sub>						
			7.55	1708	1	3CaO.2SiO <sub>2</sub>						
			0.51	1573	0.5	γ<α' <sub>H</sub> <β		[39]				
			0.76	1573	0.5	α' <sub>H</sub> <β						
			1.02	1573	0.5	α' <sub>H</sub> <β						
			2.05	1573	0.5	α' <sub>H</sub> <β						
			4.15	1573	0.5	β<α' <sub>H</sub>						
			S <sup>6+</sup>	CaSO <sub>4</sub> .2H <sub>2</sub> O	wt% CaSO <sub>4</sub>	0.74			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						
wt% CaSO <sub>4</sub> .2H <sub>2</sub> O	0.06	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						
	P <sup>5+</sup>	-			wt% P <sub>2</sub> O <sub>5</sub>	0.19		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						
5.00			1773	3		α', β	[17]					

Table 1: Effect of the addition of phosphorus, sulfur and boron on the stabilization of different Ca<sub>2</sub>SiO<sub>4</sub>-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)
<b>BC</b>	Poly-condensation	2:1	-	673-1473	3-1
<b>BS</b>	Solid-state	2:1	-	1673	1
<b>BSB_14</b>	-	2:1	Bore-0.2	1473	1
<b>BSP_14</b>	-	2:1	Phosphorus-0.5	1473	1
<b>BSS_14</b>	-	2:1	Sulfur-1	1473	1
<b>BSB_16</b>	-	2:1	Bore-0.2	1673	1
<b>BSP_16</b>	-	2:1	Phosphorus-0.5	1673	1
<b>BSS_16</b>	-	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).

<b>Phase</b>	<b>Code ICSD</b>	<b>Ref.</b>
<b><math>\beta</math>-Ca<sub>2</sub>SiO<sub>4</sub></b>	81096	[40]
<b><math>\gamma</math>-Ca<sub>2</sub>SiO<sub>4</sub></b>	81095	[40]
<b><math>\alpha'</math>-Ca<sub>2</sub>SiO<sub>4</sub></b>	81097	[40]
<b><math>\alpha</math>-Ca<sub>2</sub>SiO<sub>4</sub></b>	182052	[41]
<b>Quartz</b>	77458	[42]
<b>Cristobalite</b>	9008110	[43]
<b>CaO</b>	60199	[44]

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



	$\beta$ -Ca <sub>2</sub> SiO <sub>4</sub>	$\alpha'$ -Ca <sub>2</sub> SiO <sub>4</sub>	$\alpha$ -Ca <sub>2</sub> SiO <sub>4</sub>	$\gamma$ -Ca <sub>2</sub> SiO <sub>4</sub>	SiO <sub>2</sub>	CaO	R <sub>wp</sub>	R <sub>p</sub>	R <sub>exp</sub>
<b>BSP_14</b>	82.3	1.2	-	4.13	1.1	9.1	11.39	7.9	6.9
<b>BSB_14</b>	98.8	0.4	-	-	0.3	0.3	10.7	8.0	6.9
<b>BSS_14</b>	80.2	1.1	-	4.05	2.4	11.5	12.7	9.2	6.9
<b>BSP_16</b>	70.8	22.0	-	7.0	-	-	12.0	8.5	6.8
<b>BSB_16</b>	99.5	-	0.3	-	-	-	12.5	9.0	6.9
<b>BSS_16</b>	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.

	$\Delta a$ (%)	$\Delta b$ (%)	$\Delta c$ (%)	$\Delta \beta$ (%)	$\Delta V$ (%)
<b>BSP_14</b>	-0,01	-0,01	-0,03	-0,03	-0,04
<b>BSB_14</b>	-0,02	-0,01	-0,01	-0,05	-0,08
<b>BSS_14</b>	-0,01	-0,03	-0,01	-0,01	-0,04
<b>BSP_16</b>	-0,05	-0,06	-0,02	-0,03	-0,14
<b>BSB_16</b>	-0,15	-0,01	-0,05	-0,16	-0,20
<b>BSS_16</b>	-0,03	-0,04	-0,01	-0,02	-0,09

Table 5: Variations of  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> unit cell parameters for different samples, calculated using Rietveld refinement, by comparison with the lattice parameters given by Mumme et al. [40] ( $\Delta x = \frac{x_{sample} - x_{reference}}{x_{reference}}$ )