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Synthesis of chemically and structurally modified dicalcium silicate

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Abstract

This paper describes the synthesis of cements, chemically and structurally related to Ca_2SiO_4. Silica was obtained from rice hull after heating at 600 °C. Calcium oxide and small amounts of barium chloride were mixed in order to obtain a final (Ca/Si) or (Ca + Ba)/Si ratio equal to 1.95, 1.90, and 1.80, which is lower than in the conventional cement. The solids were mixed and ultrasonically treated for 1 h with a water/solid ratio of about 20. After drying and grinding, the mixtures were heated up to 1100 °C. It was possible, in some cases, to obtain a cementitious material. These cements are structurally related to β-Ca_2SiO_4 and the lower (Ca + Ba)/Si ratio obtained was 1.95. The initial chemical compositions of these cements are: $(Ca_{1.83} + Ba_{0.12})SiO_4$ and $(Ca_{1.79} + Ba_{0.16})SiO_4$. A further lowering in the (Ca + Ba)/Si ratio changes the nature of the silicates.

Keywords: Cement; Ca_2SiO_4; Cement manufacture; Characterization; Chemistry

1. Introduction

There is a growing interest in the synthesis of β-Ca_2SiO_4 to be used as a cementitious material motivated by economic implications and environmental concerns. The total or partial replacement of conventional Portland cement by Ca_2SiO_4 presents many positive aspects, such as energy and raw material savings as well as the possible higher durability [1–4]. Also, according to Davidovits [5], the cement industry is responsible for approximately 6% of total CO_2 emissions. In order to minimize this problem, recent works presented alternative cements containing higher amounts of β-Ca_2SiO_4 in its composition. The use of by-products or residues generated from other activities seems to be a good approach to solve both economic and environmental issues related to cement production [6–8]. Recently, the use of rice hull ash as raw material for the synthesis of Ca_2SiO_4 has been presented [9–11]. In these works, the synthesis of β-Ca_2SiO_4 was achieved at relatively low temperatures and it was observed that the replacement of small amounts of Ca by Ba into the crystalline structure was needed to stabilize the β-phase. A more detailed discussion is presented in Ref. [9].

On the other hand, it is well known that β-Ca_2SiO_4 hydrates much slowly than Ca_3SiO_5, and this is the probably the most significant limitation for the use of this kind of cement [12,13]. This hydration behavior may be related to the cell unity volume of both silicates (2.280 and 0.387 nm^3 for Ca_3SiO_5 and β-Ca_2SiO_4, respectively). Of course, the overall hydration is strongly affected by many other important experimental conditions, such as the water/cement ratio, particle size distribution, presence of admixtures, temperature, etc.

It is well known that the presence of defects in crystalline structures can modify physical and/or chemical property [14]. In fact, many important technological applications arise from defects in crystalline structure. Although the presence of structural defects is almost inevitable, these defects can be artificially introduced during the material preparation [15]. Vacancies, the absence of atoms or a group of atoms in the crystal structure, play a very important role in the structure/properties relationship.

This work describes the synthesis of cements with variable chemical composition. These cements are chemically and structurally related to β-Ca_2SiO_4. However, two major differences should be stressed: (1) the partial replacement of Ca by Ba atoms, in progressive amounts, in

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Table 1
Nominal chemical composition of the desired silicates prepared with a Ca/Si or (Ca + Ba)/Si ratio of 1.95

Chemical composition	Chemical composition
$Ca_{1.95}SiO_4$	$(Ca_{1.83} + Ba_{0.12})SiO_4$
$(Ca_{1.91} + Ba_{0.04})SiO_4$	$(Ca_{1.79} + Ba_{0.16})SiO_4$
$(Ca_{1.87} + Ba_{0.08})SiO_4$	$(Ca_{1.75} + Ba_{0.20})SiO_4$

order to facilitate the formation of the cementitious material, and (2) the preparation of cements with Ca/Si or (Ca + Ba)/Si ratios <2.0. The subtraction of CaO from the original stoichiometry is expected to modify some physical and chemical properties. The viability of the synthesis of cements with calcium and oxygen-deficient non-stoichiometry is studied. The subtraction of such atoms may lead to crystalline structures that are more "open" than found in usual cement, which is expected to accelerate the hydration. Of course, there is a limit to the synthesis of these cements, regulated by the energy cost of creating excess holes.

2. Methods

Rice hull ash was obtained by heating the rice hull at 600 °C in an open furnace. The resulting material is white powder with a surface area of 21 $m^2\ g^{-1}$, identified as cristobalite [16].

CaO (analytical grade reagent; Mallinckrodt) was heated to 1000 °C prior to use. In some preparations, CaO was obtained by a thermal decomposition of $CaCO_3$ at 1000 °C. $BaCl_2{\cdot}2H_2O$ (Synth), an analytical grade reagent, was used without further purification. After hand mixing, water was added to the solids, creating a suspension that was ultrasonically treated for 60 min in an ultrasonic cleaner (25 kHz; Thornton) at room temperature. The water/solids ratio was kept approximately 20:1. After this treatment, an intermediate silicate was obtained, with a Ca/Si ratio ≈ 1.6, along with the hydroxides. The suspension was dried and ground. The solid mixtures were heated from 500 to 1100 °C. The process was followed by FT-IR spectroscopy (Perkin-Elmer Spectrum One) and X-ray diffraction (powder method; Shimadzu).

Tables 1–3 list the nominal chemical composition of the cements. For the sake of simplicity, they are presented in the form of the desired silicates, although in many cases the synthesis was not fully completed. Three possible "families" of cements were investigated, with Ca/Si or (Ca + Ba)/Si ratios of 1.95, 1.9, and 1.80. The compositions presented take into account the original Ca_2SiO_4 stoichiometry.

Table 2
Nominal chemical composition of the desired silicates prepared with a Ca/Si or (Ca + Ba)/Si ratio of 1.90

Chemical composition	Chemical composition
$Ca_{1.9}SiO_4$	$(Ca_{1.78} + Ba_{0.12})SiO_4$
$(Ca_{1.86} + Ba_{0.04})SiO_4$	$(Ca_{1.74} + Ba_{0.16})SiO_4$
$(Ca_{1.82} + Ba_{0.08})SiO_4$	$(Ca_{1.70} + Ba_{0.20})SiO_4$

Table 3
Nominal chemical composition of the desired silicates prepared with a Ca/Si or (Ca + Ba)/Si ratio of 1.80

Chemical composition	Chemical composition
$Ca_{1.8}SiO_4$	$(Ca_{1.68} + Ba_{0.12})SiO_4$
$(Ca_{1.76} + Ba_{0.04})SiO_4$	$(Ca_{1.64} + Ba_{0.16})SiO_4$
$(Ca_{1.72} + Ba_{0.08})SiO_4$	$(Ca_{1.60} + Ba_{0.20})SiO_4$

3. Results and discussion

The samples were divided into three "families" accordingly to the Ca/Si or (Ca + Ba)/Si ratio. The results presented here are limited only to some samples belonging to each family. However, they do represent the general behavior, unless otherwise stated. These families were prepared in order to have Ca/Si or (Ca + Ba)/Si ratios of 1.95, 1.9 and 1.8.

After ultrasonic treatment, the intermediate silicates were heated up to 1100 °C and the effect of heating was followed by FT-IR spectroscopy. The spectra are shown in Figs. 1–3.

The broad bands at around 1440 cm^{-1} in the FT-IR spectra are due to the presence of CaO. Its disappearance indicates that temperature induces chemical modifications, although not necessarily the formation of the desired calcium silicate. In fact, in most of the cases, there is a formation of two or more components. However, FT-IR spectra are very useful as a first check of the synthesis, since they are a fast and reliable technique.

The main peaks attributed to β-Ca_2SiO_4 are the stretching modes of Si–O located at 900 and 1000 cm^{-1}, and the Si–O bending mode at 460 cm^{-1} [17–19]. As expected, for samples with a (Ca + Ba)/Si ratio of 1.80, the peak at 460 cm^{-1} is absent or it presents a very small relative intensity, indicating that at this stoichiometry, the desired silicate is not obtainable or its concentration is very small. The other peaks are usually present in calcium silicates. These observations are valid to this family, regardless of the amount of barium used in the synthesis.

Samples with (Ca + Ba)/Si ratios of 1.90 and 1.95 show a different picture. According to the composition and temperature, it is possible to identify all the peak characteristics of the desired calcium silicate. However, it should be pointed out that for a sample with a ratio of 1.95, the synthesis appears to be complete at 800 °C, while for a ratio of 1.90, the temperature is higher at 1000 °C.

Some selected X-ray diffraction patterns for each family, after heating at 800 °C, are presented in Figs. 4–7.

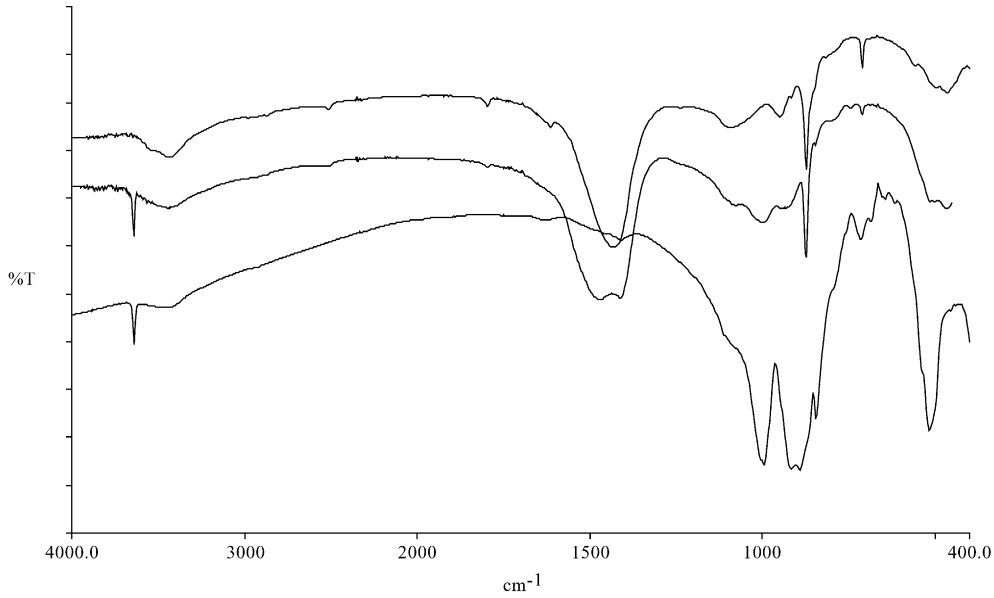

Fig. 1. Silicates with a (Ca + Ba)/Si ratio of 1.95. FT-IR spectra of the sample $(Ca_{1.75} + Ba_{0.20})SiO_4$ after heating at 500, 600, and 800 °C (from the top to the bottom).

The diffraction patterns presented in Figs. 4 and 5 show that cements with a (Ca + Ba)/Si ratio of 1.90 or 1.80 cannot be obtained at 800 °C using the methodology described. In both cases, a mixture of silicates was obtained, without the presence of a crystalline structure similar to β-Ca_2SiO_4. Also, this behavior is similar to samples within the same families but having different chemical compositions.

For better visualization, Figs. 6 and 7 present the X-ray diffraction for the family having a Ca/Si or (Ca + Ba)/Si ratio of 1.95, after heating to 800 °C.

In Fig. 6, where the samples were prepared with a small addition or no addition of barium chloride, the X-ray diffraction patterns show that the cement is not present. Similar results were obtained earlier, although in that case the heating temperature was 700 °C.

A different picture is observed when higher amounts of barium chloride are added to the initial mixture of solids. Three samples were selected (Fig. 7); as a general trend, it was possible to synthesize cements with a (Ca + Ba)/Si ratio of 1.95. The samples $(Ca_{1.83} + Ba_{0.12})SiO_4$ and $(Ca_{1.87} +$

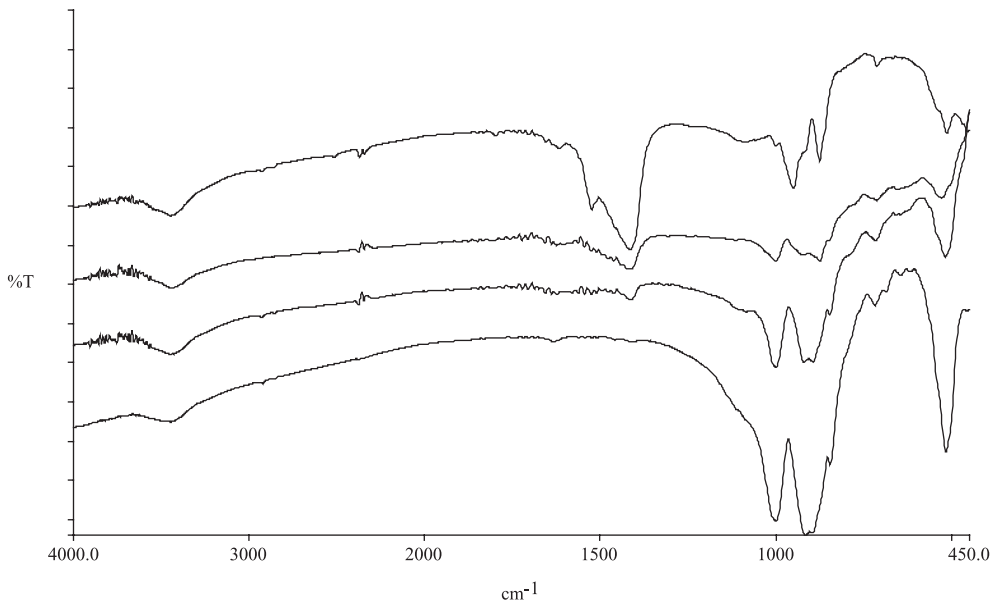

Fig. 2. Silicates with a (Ca + Ba)/Si ratio of 1.90. FT-IR spectra of the sample $(Ca_{1.78} + Ba_{0.12})SiO_4$ after heating at 500, 600, 700, and 1000 °C (from the top to the bottom).

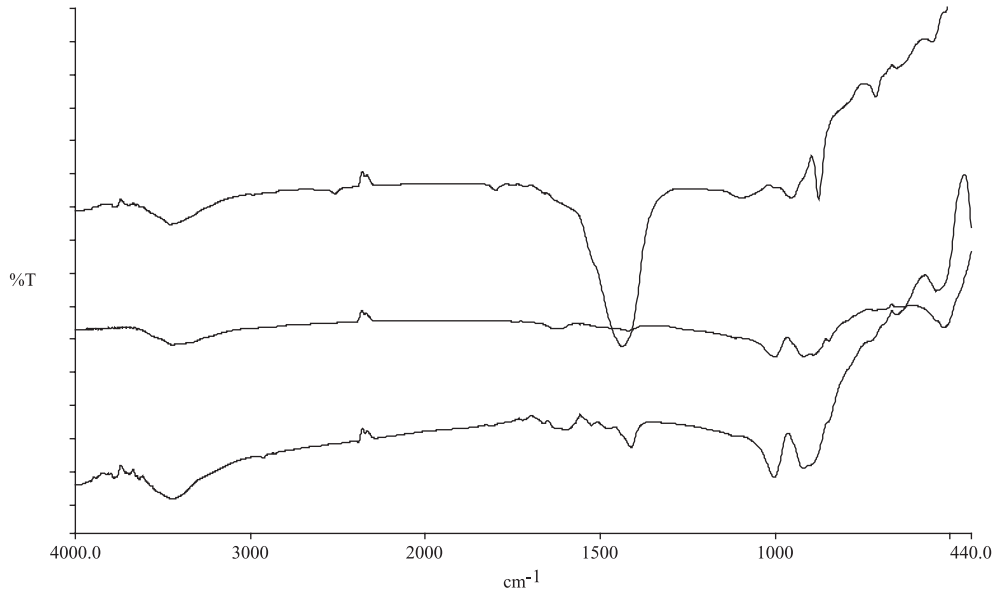

Fig. 3. Silicates with a (Ca + Ba)/Si ratio of 1.80. FT-IR spectra of the sample $(Ca_{1.68} + Ba_{0.12})SiO_4$ after heating at 500, 600, and 700 °C (from the top to the bottom).

$Ba_{0.08})SiO_4$ show a structure very close to β-Ca_2SiO_4 (in agreement with file 9-351, I-33-B3 from JCPDS) without the presence of other phases in appreciable amounts. Also, a further addition of barium in the structure leads to the formation of residual CaO.

4. Conclusions

This paper describes the synthesis of cements related to β-Ca_2SiO_4. The major difference is the possibility of synthesizing cements with a (Ca + Ba)/Si ratio < 2. The nominal chemical composition is described by $(Ca_{1.83} + Ba_{0.12})SiO_4$ and $(Ca_{1.87} + Ba_{0.08})SiO_4$. These cements were obtained at 800 °C, without the presence of residual CaO. The synthesis of structurally modified cements, as presented in this paper, opens the possibility for new studies on the relationship between structure and property in the cement chemistry.

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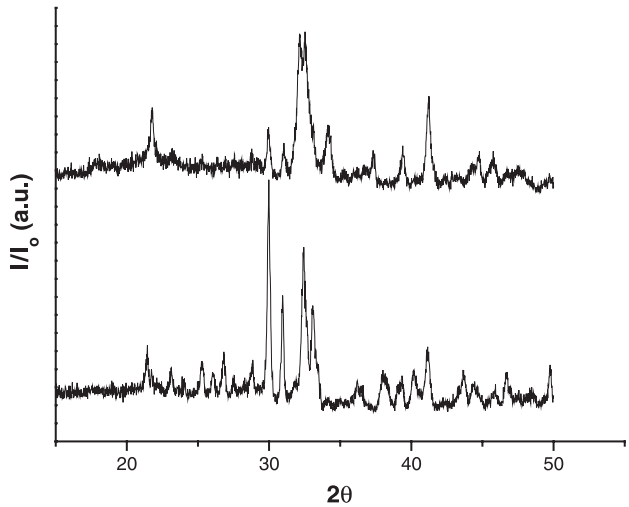

Fig. 4. X-ray diffraction for samples with a (Ca + Ba)/Si ratio of 1.90 after heating to 800 °C. Upper: $(Ca_{1.74} + Ba_{0.16})SiO_4$; lower: $(Ca_{1.70} + Ba_{0.20})SiO_4$.

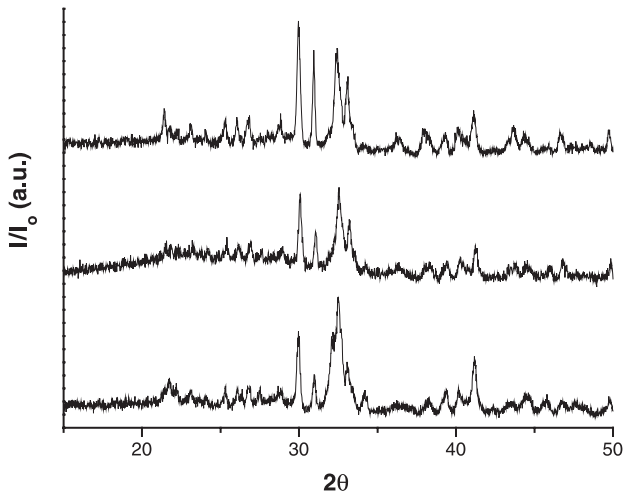

Fig. 5. X-ray diffraction for samples with a (Ca + Ba)/Si ratio of 1.80 after heating to 800 °C. Upper: $(Ca_{1.68} + Ba_{0.12})SiO_4$; middle: $(Ca_{1.64} + Ba_{0.16})SiO_4$; lower: $(Ca_{1.60} + Ba_{0.20})SiO_4$.

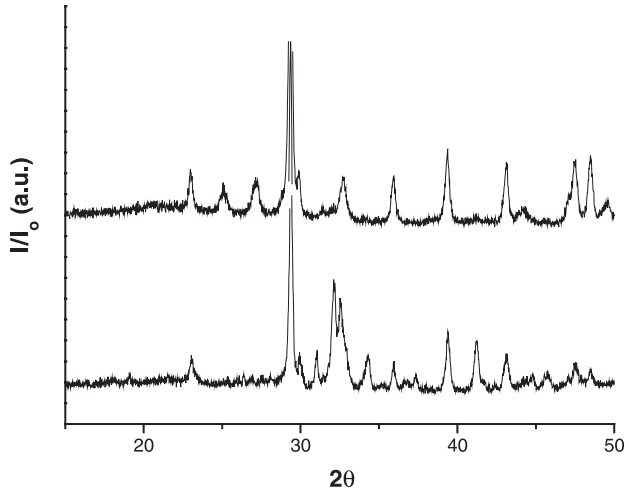

Fig. 6. X-ray diffraction for samples with a (Ca + Ba)/Si ratio of 1.95 after heating to 800 °C. Upper: $Ca_{1.95}SiO_4$; lower: $(Ca_{1.91} + Ba_{0.04})SiO_4$.

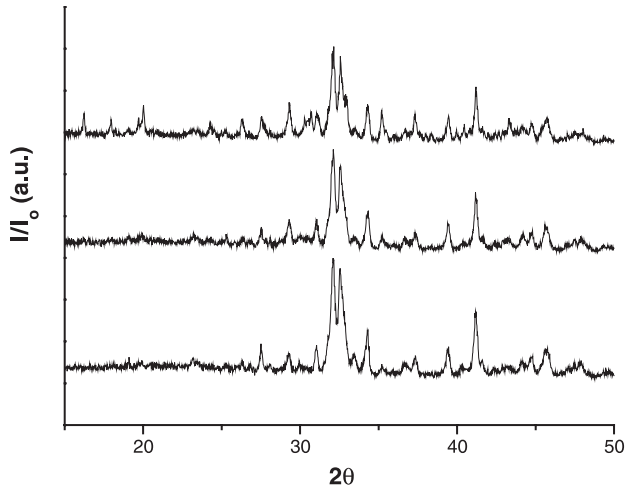

Fig. 7. X-ray diffraction for samples with a (Ca + Ba)/Si ratio of 1.95 after heating to 800 °C. Upper: $(Ca_{1.79} + Ba_{0.16})SiO_4$; middle: $(Ca_{1.83} + Ba_{0.12})SiO_4$; lower: $(Ca_{1.87} + Ba_{0.08})SiO_4$.

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