Synthesis of monoclinic Celsian from Coal Fly Ash by using a one-step solid-state reaction process

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Abstract

Monoclinic (Celsian) and hexagonal (Hexacelsian) Ba$_{1-x}$Sr$_x$Al$_2$Si$_2$O$_8$ solid solutions, where $x = 0, 0.25, 0.375, 0.5, 0.75$ or 1, were synthesized by using Coal Fly Ash (CFA) as main raw material, employing a simple one-step solid-state reaction process involving thermal treatment for 5 h at 850–1300 °C. Fully monoclinic Celsian was obtained at 1200 °C/5 h, for SrO contents of $0.25 < x < 0.75$. However, an optimum SrO level of $0.25 < x < 0.375$ was recommended for the stabilization of Celsian. These synthesis conditions represent a significant improvement over the higher temperatures, longer times and/or multi-step processes needed to obtain fully monoclinic Celsian, when other raw materials are used for this purpose, according to previous literature. These results were attributed to the role of the chemical and phase constitution of CFA as well as to a likely mineralizing effect of CaO and TiO$_2$ present in it, which enhanced the Hexacelsian to Celsian conversion.

Keywords: (A) Powders: solid-state reaction; (B) X-ray methods; (E) Thermal applications; Celsian

1. Introduction

Due to its high resistance to oxidation and reduction [1], low dielectric constant [2] and low thermal expansion coefficient [3], barium aluminosilicate (BaAl$_2$Si$_2$O$_8$, or BAS$_2$) is a valuable material for the matrix of ceramic composites [4,5], as well as for protective coatings [6]. BaAl$_2$Si$_2$O$_8$ has three polymorphic forms: monoclinic (usually denominated either as Celsian or as Monocelsian), hexagonal (Hexacelsian) and orthorhombic [3,7]. The melting point of stoichiometric BaAl$_2$Si$_2$O$_8$ is 1760 °C. Hexacelsian is the stable phase below 1590 °C and Celsian is stable below 1590 °C. However, Hexacelsian may exist metastably below the latter temperature due to a sluggish hexagonal to monoclinic conversion [8]. Hexacelsian is an undesirable phase due to its high mean thermal expansion coefficient of $8 \times 10^{-6}/°C$ (300–1000 °C) [3,9], when compared to the value of $2.26 \times 10^{-6}/°C$ (20–1000 °C) reported for Celsian [3,10]. Besides, Hexacelsian transforms into the orthorhombic form at 300 °C, which is accompanied by a volume change of ~3–4%, with a consequent microcracking of the material. Thus, successful employment of BaAl$_2$Si$_2$O$_8$ requires a previous stabilization of its monoclinic form. It is well-known that the hexagonal to monoclinic conversion is greatly enhanced by the addition of mineralizers such as Li$_2$O, MgO, CaO, NaF and TiO$_2$ [11,12]. On the other hand, I.G. Talmy and D.A. Haught, as quoted by Bansal et al. [13], showed that partial substitution of BaO by SrO in polycrystalline BaAl$_2$Si$_2$O$_8$ facilitates the Hexacelsian to Celsian transformation and, under certain conditions, Hexacelsian may never form.

Generally BaAl$_2$Si$_2$O$_8$ is synthesized from stoichiometric mixtures of Al$_2$O$_3$, SiO$_2$ and BaCO$_3$ reagent-grade powders.
However, a variety of other alternative raw materials can also be used for this purpose, among which Coal Fly Ash (CFA) is one of the less frequently employed [14]. CFA is a byproduct of coal-burning power plants, whose main chemical constituents are SiO₂ and Al₂O₃, and whose main mineralogical components are quartz, mullite (Al₇Si₂O₁₃) and a highly reactive amorphous phase [15]. Millions of Tons of CFA are produced all over the world each year, most of which are discarded, with minimum use mainly as additive for Portland cement. As a result, an abundant and cheap potential source of SiO₂ and Al₂O₃ is in the CFA. Yet, to date, only researchers to have used CFA as raw material for the synthesis of Celsian have been Amritphale et al. [14], who are up to now the only researchers to have used CFA as raw material for the synthesis of Celsian BaAl₂Si₂O₈ containing ceramics. It is worth mentioning that Amritphale et al. [14], who are up to now the only researchers to have used CFA as raw material for the synthesis of Celsian BaAl₂Si₂O₈-containing ceramics, did not study either the Hexacelsian to Celsian transformation or the effect of SrO doping on the latter transformation in their materials. In fact, the chemical compositions studied by these authors differ greatly from those studied in the present work, in such a way that completely different phase compositions and microstructures were obtained in both cases, and for different intended applications.

A further objective of this work was to develop a relatively low-temperature solid-state synthesis process which was simpler and of shorter duration than those recommended in previous literature reports [16] for the production of Celsian.

2. Experimental procedure

Ba₁₋ₓSrₓAl₂Si₂O₈ solid solutions, where x = 0, 0.25, 0.375, 0.5, 0.75 or 1, were synthesized by using a simple one-step solid-state reaction process, employing suitable mixtures of Coal Fly Ash (CFA), BaCO₃ (purity of 99.43 wt.%, Alkem, México), SrCO₃ (purity of 97.86 wt.%, Solvay, México) and Al₂O₃ (HPA-0.5, purity of 99.99 wt.%, Sasol, USA). Monoclinic and hexagonal solid solutions, with SrO contents in the range of 0.25 ≤ x ≤ 0.75, are hereinafter denominated as Celsian and Hexacelsian, respectively. The limiting compositions with monoclinic structure are denominated as Ba₃-Celsian BaAl₂Si₂O₈, for x = 0, and Sr-Celsian SrAl₂Si₂O₈, for x = 1.

CFA was collected directly from the cyclone precipitators of Coalburning power plants, whose main chemical constituents are quartz, mullite (Al₇Si₂O₁₃) and a highly reactive amorphous phase [15]. Millions of Tons of CFA are produced all over the world each year, most of which are discarded, with minimum use mainly as additive for Portland cement. As a result, an abundant and cheap potential source of SiO₂ and Al₂O₃, which is already fine and which does not require to be extracted or mined, is basically wasted.

Thus, this work was focused on the synthesis of Celsian, with and without SrO doping, using CFA as main raw material, with particular attention given to the reaction mechanism, as well as to a likely mineralizing effect of impurities contained in the CFA on stabilization of the monoclinic phase. It is worth mentioning that Amritphale et al. [14], who are up to now the only researchers to have used CFA as raw material for the synthesis of Celsian BaAl₂Si₂O₈-containing ceramics, did not study either the Hexacelsian to Celsian transformation or the effect of SrO doping on the latter transformation in their materials. In fact, the chemical compositions studied by these authors differ greatly from those studied in the present work, in such a way that completely different phase compositions and microstructures were obtained in both cases, and for different intended applications.

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<table>
<thead>
<tr>
<th>X</th>
<th>Sample code</th>
<th>CFA</th>
<th>Al₂O₃</th>
<th>BaCO₃</th>
<th>SrCO₃</th>
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<tbody>
<tr>
<td>0</td>
<td>BAS</td>
<td>42.62</td>
<td>13.40</td>
<td>44.07</td>
<td>-</td>
</tr>
<tr>
<td>0.25</td>
<td>B7S2</td>
<td>43.78</td>
<td>13.76</td>
<td>33.99</td>
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<tr>
<td>0.375</td>
<td>B6S3</td>
<td>44.42</td>
<td>13.97</td>
<td>28.72</td>
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<tr>
<td>0.5</td>
<td>B5S5</td>
<td>45.07</td>
<td>14.17</td>
<td>23.31</td>
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<tr>
<td>0.75</td>
<td>B2S7</td>
<td>46.44</td>
<td>14.60</td>
<td>12.60</td>
<td>26.95</td>
</tr>
<tr>
<td>1.0</td>
<td>SAS</td>
<td>47.87</td>
<td>15.07</td>
<td>-</td>
<td>37.06</td>
</tr>
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</table>

Table 2
Composition of green powder mixtures (wt.%) with expected crystalline Ba₁₋ₓSrₓAl₂Si₂O₈ after heat treatment.
Table 3
Parameters of the departure model used for the refinements. Space Group C2/m (no. 12). Cell parameters \(a = 8.633(6) \, \text{Å}, \quad b = 13.063(8) \, \text{Å}, \quad c = 7.214(5) \, \text{Å}, \quad \beta = 115.17(5)^\circ\).

<table>
<thead>
<tr>
<th>Name</th>
<th>Mult.</th>
<th>Wyckoff</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{iso})</th>
<th>Occ.</th>
<th>Species</th>
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<td>(i)</td>
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<td>0.0000</td>
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<td>Ba</td>
</tr>
<tr>
<td>Tl</td>
<td>8</td>
<td>(j)</td>
<td>0.00832</td>
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<td>0.22450</td>
<td>0.0167</td>
<td>1.00</td>
<td>Si/Al</td>
</tr>
<tr>
<td>T2</td>
<td>8</td>
<td>(j)</td>
<td>0.20313</td>
<td>0.38148</td>
<td>0.34697</td>
<td>0.0165</td>
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<tr>
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<td>0.0192</td>
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</tr>
<tr>
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<td>(j)</td>
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<td>0.39700</td>
<td>0.0245</td>
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Table 4
Chemical analysis of CFA (wt.%).

<table>
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<tr>
<th></th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
<th>TiO(_2)</th>
<th>Other oxides*</th>
<th>LOI</th>
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<td>24.93</td>
<td>7.13</td>
<td>1.97</td>
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<td>0.69</td>
<td>0.60</td>
<td>0.85</td>
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<tr>
<td>Beneficiated</td>
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<td>25.73</td>
<td>7.37</td>
<td>2.12</td>
<td>0.48</td>
<td>0.46</td>
<td>0.37</td>
<td>0.59</td>
<td>1.11</td>
<td>1.94</td>
</tr>
</tbody>
</table>

* SrO, ZrO\(_2\), CuO, NiO, SO\(_3\) and PO\(_4\).

3. Results and discussion

3.1. Characterization of CFA

To back up the reaction mechanism proposed, free energy computations for all possible reactions between BaO, SiO\(_2\), SrO and Al\(_2\)O\(_3\) were performed using HSC [20]. This is a computing package that offers an exhaustive thermochemical database and includes enthalpy (H), entropy (S) and heat capacity (C) data for chemical compounds.
that of CaO remained relatively unchanged in a level close to 2 wt.%. The Loss On Ignition (LOI) of ~2 wt.% corresponded basically to free carbon present in the CFA, whose level was only slightly reduced by the beneficiation process.

Fig. 1 shows the XRD pattern of beneficiated CFA. Only quartz and mullite crystalline phases plus a large proportion of amorphous phase were detected. Amorphous phase is visible in the intense broad background (centre: ca. 23°, 2θ), which is a characteristic feature of this phase.

Dissolution of CFA with HF acid [21,22], followed by ICP chemical analysis of the resulting solution, allowed us to estimate that CFA contains ~75 wt.% of amorphous phase, with a chemical composition of 74 wt.% SiO₂ and 18 wt.% A_2O_3 (balance corresponding to Fe_2O_3, CaO plus other minor impurities). These calculations were carried out assuming that the impurities were basically contained in the glassy phase. Impurities such as Fe_2O_3, remaining in the CFA after the beneficiation process, were not detected by XRD because a part of them was present as crystalline phases with a level below the detection limit of the technique employed, while another part was contained in the amorphous phase, also in a low level.

SEM analysis showed that the as-received CFA was composed predominantly by small spherical particles, which were either solid or hollow (cenospheres and plenospheres). Some flake-like particles were also observed.

Table 5. Calculated compositions are given inside the parentheses. Small differences observed between the calculated and the analyzed compositions can be attributed to small errors in sample preparation and chemical analysis, as well as to the presence of impurities in the CFA. However, in all cases the analyzed SiO₂/AI₂O₃ and SiO₂/BaO weight ratios were very close to the theoretical ones.

The phase evolution of the BAS₂ and B7S2 nominal compositions as a function of temperature can be followed from the XRD patterns shown in Figs. 2 and 3, respectively. The chemical analyses of heat-treated materials are shown in Table 5. Calculated compositions are given inside the parentheses. Small differences observed between the calculated and the analyzed compositions can be attributed to small errors in sample preparation and chemical analysis, as well as to the presence of impurities in the CFA. However, in all cases the analyzed SiO₂/AI₂O₃ and SiO₂/BaO weight ratios were very close to the theoretical ones.

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The phase evolution of the BAS₂ and B7S2 nominal compositions as a function of temperature can be followed from the XRD patterns shown in Figs. 2 and 3, respectively. The BAS₂ material was fully transformed into Ba₂Al₂Si₂O₈, mainly in its monoclinic form, after thermally treated at 1300 °C/5 h. On the other hand, the B7S2 nominal composition, Fig. 3, achieved full transformation into monoclinic Celsian at 1200 °C/5 h. The same result was obtained for the B6S3 and B5S5 nominal compositions, according to Table 6, which gives a summary of the XRD results obtained for all nominal compositions and temperatures studied. In contrast, the B2S7 and SAS nominal compositions achieved a full transformation into monoclinic Celsian at 1300 °C/5 h, with the presence of traces of Hexacelsian and strontium aluminate in SAS.

These results indicate that both undoped and SrO-doped monoclinic Celsian can be obtained at relatively low
temperatures and short thermal treatments using a simple one-step process when CFA is employed as the main raw material. In general, doping the BaAl$_2$Si$_2$O$_8$ composition with SrO in the range of 0.25 ≤ x ≤ 0.75, resulted in a reduction of 100°C in the temperature required for full transformation of Hexacelsian into Celsian. These synthesis conditions represent a significant improvement over the higher temperatures, longer times and/or multi-step processes needed for full conversion when other raw materials (either amorphous or crystalline, and either mineral or reagent-grade) are used for the synthesis of BaAl$_2$Si$_2$O$_8$, with or without SrO doping, according to previously published literature, as described below.

Regarding the synthesis of Celsian BaAl$_2$Si$_2$O$_8$ without SrO doping, Meyn Corral and Verdich [3] obtained this phase by solid-state reaction of mixtures of kaolin and BaCO$_3$ at 1350°C/24 h. Talmy and Haught [23] synthesized the same phase from BaCO$_3$, Al$_2$O$_3$ and amorphous SiO$_2$ at 1500°C for 100 h. Bansal et al. [13] obtained full monoclinic BaAl$_2$Si$_2$O$_8$ from cold isostatically pressed and sintered (1300°C/20 h) glass powders. Lastly, Lee and Aswath [16] synthesized Celsian BaAl$_2$Si$_2$O$_8$ using a three-step process, with or without the addition of Li$_2$O. In the first step, SiO$_2$ and BaCO$_3$ were reacted at 1150°C/4 h in order to form barium silicate, avoiding in this way the formation of barium aluminate, which is much less reactive than barium silicate and, thus, delays the formation of Celsian. In the second step, barium silicate was reacted with Al$_2$O$_3$ at 1200°C/6 h in order to form Hexacelsian. In the third step, Hexacelsian was ground, encouraging in this way the formation of monoclinic Celsian nucleus, and then heat treated at 1200-1530°C for 4-50 h, in order to promote its conversion into Celsian. Pure Celsian was obtained when ground pre-synthesized Hexacelsian was doped with 0.4 wt.% Li$_2$O, followed by thermal treatment at 900°C/4 h.

Regarding the use of SrO doping for the synthesis of monoclinic Ba$_1$-$x$Sr$_x$Al$_2$Si$_2$O$_8$. Fu et al. [17] obtained this phase by solid-state reaction of mixtures of BaCO$_3$, SrCO$_3$, Al$_2$O$_3$, and SiO$_2$ reagent-grade powders, observing an increase in the Hexacelsian to Celsian conversion with increasing SrO content, achieving a maximum conversion of ~40% for x = 0.375 after calcination at 950°C/4 h, which was followed by heat treatment at 1040°C/4 h. Bansal [24] obtained Celsian with chemical composition of Ba$_{0.75}$Sr$_{0.25}$Al$_2$Si$_2$O$_8$ by solid-state reaction of a suitable mixture of Al$_2$O$_3$, SiO$_2$, BaCO$_3$ and SrCO$_3$ reagent-grade powders, which was first calcined at ~900–910°C for 24 h and then ground, following this by hot pressing at 1300°C for 2–3 h under a pressure of 27.5 MPa. Krzmanc et al. [25] synthesized a material with the same composition by solid-state reaction at 1100°C/12 h, using similar raw materials, obtaining a mixture of Hexacelsian and Monocelsian, in which the first phase predominated. Bansal [26], on the other hand, was able to achieve full conversion of Hexacelsian into Celsian for a monolithic specimen containing 90 wt.% BaAl$_2$Si$_2$O$_8$ glass and 10 wt.% SrAl$_2$Si$_5$O$_8$ glass, either after hot pressing at 1300°C for 10 min at 13.8 MPa, followed by annealing at 1200°C/2 h, or after hot pressing at 1300°C/2 h under 13.8 MPa. Lastly, Bansal et al. [13] obtained full monoclinic Celsian from cold isostatically pressed and sintered (above 900°C for 20 h) BaAl$_2$Si$_2$O$_8$ glass powders doped either with 9.87 or with 18.6 wt.% SrO. In Refs. [13, 26], the initial glasses were obtained by melting suitable mixtures of BaCO$_3$, SrCO$_3$, Al$_2$O$_3$ and SiO$_2$ reagent-grade powders at temperatures of ~2000–2100°C.

As for the case of undoped and SrO-doped BaAl$_2$Si$_2$O$_8$ compositions, the conditions employed in this work for the synthesis of Celsian SAS represent also a significant improvement over the higher temperatures, longer times and/or multi-step processes needed for full conversion of Hexacelsian into Celsian, according to previous literature reports. For instance, Kobayashi and Inagaki [27] obtained full monoclinic Celsian SAS by solid-state reaction of stoichiometric mixtures of kaolin and SiC, which were calcined at 900°C for several hours, then milled for 1–20 h and uniaxially pressed at 98 MPa, following this by heat treatment at 1200°C/1 h. On the other hand, Bansal et al. [13] obtained full monoclinic Celsian SAS from cold isostatically pressed and sintered (1100°C/20 h) glass powders.

### 3.3. Reaction mechanism for the formation of Celsian

In order to obtain additional information regarding the reaction mechanism for the formation of Celsian, for the case of the BaAl$_2$Si$_2$O$_8$ nominal composition studied, TGA/DTA...
For samples having a Ba:Si molar ratio of either 2:1 or 1:1, the decomposition of $	ext{BaCO}_3$ to the formation of barium silicates is strongly and irreversibly with SiO$_2$, forming various barium silicates and Hexacelsian without appreciable formation of barium aluminates, which appeared only at temperatures $\geq 900$ °C. Lee and Aswath [16] emphasized that, for the case of BaCO$_3$–Al$_2$O$_3$ mixtures, the reaction path leading to the formation of Hexacelsian occurs via the initial formation of barium silicates. In this way, Hexacelsian can be formed at relatively low temperatures. This agrees with the results obtained from the XRD and TGA/DTA analyses carried out in the present work. The use of CFA as main raw material, which contains Al$_2$O$_3$ and SiO$_2$ already chemically combined forming mullite and amorphous phases, as well as a large amount of free SiO$_2$ (quartz), facilitated the occurrence of solid-state reactions leading to the initial formation of transient barium silicates instead of barium aluminates, and this in turn led to an easy formation of Hexacelsian, which was subsequently relatively easily transformed into Celsian.

From the XRD and TGA/DTA results obtained, it was deduced that, for the case of the BaAl$_2$Si$_2$O$_8$ nominal composition studied, the likely reaction path was as follows:

(a) The reaction between BaCO$_3$ and silica starts at $T > 850$ °C through a series of exothermic reactions. The formation of Ba-silicates as transient phases can be produced by reactions (1)–(6). Reaction (2) has the lowest Gibbs free energy and therefore is the most viable. However, as it is obvious, this reaction does not happen until BaO is available once BaCO$_3$ decomposes.

\[
\begin{align*}
\text{BaCO}_3 + \text{SiO}_2 & = \text{BaSiO}_3 + \text{CO}_2, \\
\Delta G^{900 \degree C} & = -19.61 \text{ kcal} \tag{1} \\
2\text{BaCO}_3 + \text{SiO}_2 & = \text{Ba}_2\text{Si}_2\text{O}_5 + 2\text{CO}_2(g), \\
\Delta G^{900 \degree C} & = -31.12 \text{ kcal} \tag{2} \\
\text{BaCO}_3 + 2\text{SiO}_2 & = \text{Ba}_2\text{Si}_2\text{O}_5 + \text{CO}_2(g), \\
\Delta G^{900 \degree C} & = -23.5 \text{ kcal} \tag{3} \\
\text{BaSiO}_3 + \text{BaCO}_3 & = \text{Ba}_2\text{Si}_2\text{O}_5 + \text{CO}_2(g), \\
\Delta G^{900 \degree C} & = -5.35 \text{ kcal} \tag{4} \\
2\text{BaSiO}_3 + \text{SiO}_2 & = \text{Ba}_2\text{Si}_3\text{O}_8, \quad \Delta G^{900 \degree C} = -5.82 \text{ kcal} \tag{5}
\end{align*}
\]
Ba$_2$Si$_2$O$_5$ + SiO$_2$ = 2BaSi$_2$O$_5$, $\Delta G^{900\,^\circ C} = -1.85$ kcal (6)

The presence of barium silicates (Ba$_2$SiO$_4$, BaSiO$_3$ and Ba$_2$Si$_2$O$_5$) was detected by XRD after thermal treatment of the samples in the temperature range of 850–1000 °C, so a fast reaction between BaO/BaCO$_3$ and SiO$_2$ for the formation of barium silicates was assumed to occur at these temperatures. Indeed, other researchers [31,32] have stated that BaSiO$_3$ is the first barium silicate to form. BaSiO$_3$ led later on to the formation of both Ba$_2$SiO$_4$ (reaction (4)) and Ba$_2$Si$_2$O$_5$ (reaction (6)) barium silicates, during holding time at this temperature. All quartz contained in the CFA was consumed mainly for the formation of barium aluminates (reactions (1)–(3), (5) and (6)). It is worth mentioning that formation of Ba$_2$Si$_2$O$_5$ directly from BaSiO$_3$ has not been reported in the literature, thus, although the intermediate Ba$_2$Si$_2$O$_5$ barium silicate could be formed (10), probably this compound was not detected by XRD due to a fast rate for reactions (5) and (6).

(b) Formation of Hexacelsian in the temperature interval 850–1100 °C as a metastable phase can take place by the following reactions:

$$\text{Al}_2\text{Si}_2\text{O}_{13} + 3\text{BaCO}_3 + 4\text{SiO}_2 = 3\text{BaAl}_2\text{Si}_2\text{O}_8 + 3\text{CO}_2,$$

$$\Delta G^{900\,^\circ C} = -103.49 \text{ kcal} \quad (7)$$

$$\text{BaSi}_2\text{O}_5 + \text{Al}_2\text{O}_3 = \text{BaAl}_2\text{Si}_2\text{O}_8, \quad \Delta G^{900\,^\circ C} = -12.05 \text{ kcal} \quad (8)$$

Thermodynamic calculations indicate that reaction (7) has the lowest Gibbs free energy; hence, it is the most favourable. Similarly, the amorphous phase contained in the CFA was consumed for the formation of Hexacelsian (reaction (9)):

$$[m\text{SiO}_2\,n\text{Al}_2\text{O}_3]_{\text{Amorphous}} + (m/2-n)\text{Al}_2\text{O}_3 + (m/2)\text{BaCO}_3 = (m/2)\text{BaAl}_2\text{Si}_2\text{O}_3 + (m/2)\text{CO}_2 \quad (9)$$

Due to a lack of thermodynamic data for the amorphous phase contained in the CFA, the Gibbs free energy of reaction (9) could not be calculated. However, since such an amorphous phase is considered to be highly reactive, it is very likely that reaction (9) was thermodynamically favourable.

(c) Between 900 and 1100 °C formation of Hexacelsian continued via reaction (8), with additional amounts of this phase formed at the expense of the remaining Al$_2$O$_3$ and some of the barium silicates previously formed (reaction (10)).

$$\text{BaSi}_2\text{O}_5 + \text{Al}_2\text{O}_3 = \text{BaAl}_2\text{Si}_2\text{O}_8, \quad \Delta G^{1000\,^\circ C} = -12.6 \text{ kcal} \quad (10)$$

(d) The formation of BaAl$_2$O$_4$ by reaction of previously formed barium silicates or by direct reaction of Al$_2$O$_3$ with BaCO$_3$ or BaO is not thermodynamically viable (reactions (11)–(13)). Thus, the formation of barium aluminates was probably due to the presence of areas enriched in aluminum and barium in the sample.

$$2\text{BaSi}_2\text{O}_3 + \text{Al}_2\text{O}_3 = \text{BaAl}_2\text{Si}_2\text{O}_8 + \text{BaAl}_2\text{O}_4,$$

$$\Delta G^{900\,^\circ C} = +38.6 \text{ kcal} \quad (11)$$

$$\text{Ba}_2\text{Si}_2\text{O}_5 + \text{Al}_2\text{O}_3 = \text{BaAl}_2\text{O}_4 + \text{BaSiO}_3,$$

$$\Delta G^{1000\,^\circ C} = +40.1 \text{ kcal} \quad (12)$$

$$\text{BaCO}_3 + \text{Al}_2\text{O}_3 = \text{BaAl}_2\text{O}_4 + \text{CO}_2(g),$$

$$\Delta G^{900\,^\circ C} = +24.6 \text{ kcal} \quad (13)$$

$$\text{BaO} + \text{Al}_2\text{O}_3 = \text{BaAl}_2\text{O}_4, \quad \Delta G^{900\,^\circ C} = +5.6 \text{ kcal} \quad (14)$$

Lee and Aswath [16] mentioned that once BaAl$_2$O$_4$ is formed, this compound tends to remain even after thermal treatment at 1530 °C/50 h, due to a pretty low reaction rate of BaAl$_2$O$_4$ with SiO$_2$ to form Hexacelsian. In this work, traces of barium aluminates were detected on the SEM but not by XRD in samples heat treated at 1300 °C, probably because at this temperature the content of barium aluminates was below the detection limit of the XRD technique employed. This sample shows a homogeneous microstructure with randomly distributed clusters of Ba-aluminates. No diffusion or reaction within the clusters and the rest of the sample occurred probably because the coarse Ba-aluminates were in equilibrium at local level with Celsian, and thus, it was not possible to eliminate them by heat treatment. However, most of the BaAl$_2$O$_4$ formed by the mechanism explained above was slowly consumed by reaction (15) in the temperature range of 900–1300 °C, involving the participation of free crystalline quartz and SiO$_2$ contained in the glassy phase, both of them present in the CFA.

$$\text{BaAl}_2\text{O}_4 + \text{SiO}_2 = \text{BaAl}_2\text{Si}_2\text{O}_8, \quad \Delta G^{900\,^\circ C} = -60.08 \text{ kcal} \quad (15)$$

At ~1300 °C the last BaSi$_2$O$_5$ remaining could be also completely consumed by Al$_2$O$_3$ contained in the remnant glassy phase of the CFA, according to reaction (8).

(e) Lastly, between 1100 and 1300 °C, the Hexacelsian to Celsian conversion continued, in such a way that the latter phase became predominant at 1200 °C. It is worth mentioning that small deviations from the Celsian stoichiometry within the samples could induce the development of small quantities of transitory liquid phases in the vicinity of the eutectic point of the subsystem Ba$_2$Si$_2$O$_5$–BaSiO$_3$–SiO$_2$ at 1122 °C [33]. These liquid phases could also enhance the polymorphic transformation of Hexacelsian to Celsian. However, this effect was considered to be small and it was not evaluated.
solid solutions with monoclinic structure, i.e., the formation of the same phases took place following a similar sequence for all nominal compositions studied, with or without SrO doping, except for the case of the B2S7 material, for which strontium silicates and aluminate were formed instead of the corresponding barium compounds. This suggests that, at relatively low SrO concentrations, this oxide participated predominantly in the formation of $\text{Ba}_2\text{Al}_2\text{Si}_3\text{O}_8$ solid solutions, instead of reacting with $\text{Si}_2\text{O}_3$ and/or $\text{Al}_2\text{O}_3$ for the formation of strontium silicates and/or strontium aluminate. However, at SrO levels of 0.75 $\leq x \leq 1$, the formation of the latter compounds predominated, at all treatment temperatures employed. Krzman et al. [25] obtained similar results for SrO concentrations in the range of $0.6 < x < 1$.

The most important difference observed between the undoped and SrO-doped Celsian compositions was that in the latter case all reactions started at lower temperatures. In this case, the Hexacelsian to Celsian conversion started in the temperature range of 900–1000 °C, with an increased proportion of the latter phase with increasing SrO content at 1000 °C. The proportion of Celsian also increased with increasing temperature for a given SrO level, becoming the predominant phase at 1100 °C. At 1200 °C, all the SrO-doped materials were composed entirely of Celsian, except for the B2S7 nominal composition, which contained additional traces of strontium aluminate.

In the case of the $\text{Sr}_2\text{Al}_2\text{Si}_3\text{O}_8$ composition, a reaction mechanism similar to that deduced for the $\text{Ba}_2\text{Al}_2\text{Si}_3\text{O}_8$ material was also followed, although in the case of the first composition the mullite present in the CFA completely disappeared only at 900 °C, probably due to reactions (16) and (17):

\begin{align}
\text{Al}_2\text{Si}_2\text{O}_13 + 3\text{SrCO}_3 + 4\text{SiO}_2 &= 3\text{SrAl}_2\text{Si}_2\text{O}_8 + 3\text{CO}_2, \\
\Delta G^{900°C} &= -103.5 \text{ kcal} \\
\text{Al}_2\text{Si}_2\text{O}_13 + 2\text{SrSiO}_3 &= 2\text{SrAl}_2\text{Si}_2\text{O}_8 + \text{Al}_2\text{O}_3, \\
\Delta G^{900°C} &= -27.6 \text{ kcal} \\
\text{SrCO}_3 + \text{SiO}_2 &= \text{SrSiO}_3 + \text{CO}_2, \\
\Delta G^{900°C} &= -20.8 \text{ kcal} \\
2\text{SrCO}_3 + \text{SiO}_2 &= 2\text{SrSiO}_4 + 2\text{CO}_2, \\
\Delta G^{900°C} &= -30.9 \text{ kcal}
\end{align}

The formation of metastable Sr-silicates ($\text{SrSiO}_3$, $\text{Sr}_2\text{Si}_4\text{O}_9$) was detected by XRD at 900 °C (reactions (18) and (19)):

\begin{align}
\text{SrCO}_3 + \text{SiO}_2 &= \text{SrSiO}_3 + \text{CO}_2, \\
\Delta G^{900°C} &= -20.8 \text{ kcal} \\
2\text{SrCO}_3 + \text{SiO}_2 &= 2\text{SrSiO}_4 + 2\text{CO}_2, \\
\Delta G^{900°C} &= -30.9 \text{ kcal}
\end{align}

Another difference observed with respect to the $\text{Ba}_2\text{Al}_2\text{Si}_3\text{O}_8$ material was the formation of a strontium aluminosilicate ($\text{Sr}_2\text{Al}_2\text{Si}_3\text{O}_9$, $\text{s}_2\text{AS}$), different in chemical composition to Celsian SAS, additionally to the formation of strontium silicates, strontium aluminate and Hexacelsian occurring at 900 °C (reactions (20)–(24)). $\text{Sr}_2\text{Al}_2\text{Si}_3\text{O}_8$ disappeared later on at 1200 °C.

\begin{align}
\text{SrO} + \text{Al}_2\text{O}_3 &= \text{SrAl}_2\text{O}_4 \\
\text{Sr}_2\text{Si}_2\text{O}_4 + \text{Al}_2\text{O}_3 &= \text{Sr}_2\text{Al}_2\text{Si}_4\text{O}_9 \\
2\text{SrSiO}_3 + 2\text{Al}_2\text{O}_3 &= \text{Sr}_2\text{Al}_2\text{Si}_2\text{O}_6 + \text{SrAl}_2\text{O}_4
\end{align}

The Gibbs free energy of reactions (20)–(24) could not be calculated due to a lack of thermodynamic data for some of the chemical species involved in them. However, since the formation of all their chemical products were indeed detected by XRD, it can be safely assumed that all of these reactions are thermodynamically favourable at temperatures ≥900 °C.

Lastly, Celsian SAS was the predominant phase at 1300 °C, with the presence of only trace amounts of Hexacelsian and strontium aluminate at this temperature.

Although the proposed reaction mechanism can help us to explain the evolution of phases observed in our materials as a function of treatment temperature, it is worth mentioning that there is also a likely mineralizing effect caused by some of the impurities present in the CFA, particularly CaO and TiO$_2$ [12], which could promote an easy stabilization of Celsian at a relatively low temperature. This will be discussed further in the following section.

### 3.4. Mineralizing effect of some impurities present in the CFA on the stabilization of Celsian

Besides the SrO dopant added in order to promote the Hexacelsian to Celsian transformation, many of the impurities contained in the CFA, namely Na$_2$O, CaO, TiO$_2$, MgO and K$_2$O, Table 4, are also known to greatly enhance the kinetics of this conversion. Among these oxides, CaO and TiO$_2$ are the most important ones in terms of their concentration and mineralizing effect in the materials synthesized in this work.

According to Lee and Aswath [12], both CaO and TiO$_2$ are more efficient mineralizers than SrF$_3$. These authors established that the minimum treatment temperature required for full conversion of Hexacelsian into Celsian, for a constant dopant addition of 10 mol.%., is: ~1200 °C for CaO, ~1250 °C for TiO$_2$, and ~1300 °C for SrF$_3$. On the other hand, the minimum dopant amount required to achieve full conversion at 1250°C/4 h, is: ~2 mol. % for either CaO or TiO$_2$, and ~12 mol. % for SrF$_3$. The minimum concentration of 2 mol.% is equivalent either to 0.3 wt.% of CaO or to 0.43 wt.% of TiO$_2$. Table 5 shows that in our materials the CaO concentration varied from 1.31 to 1.62 wt.%, while that of TiO$_2$ varied from 0.45 to 0.61 wt.%. This means that all synthesized materials had a concentration of both impurities above the minimum values required for full stabilization of Celsian, according to Ref. [12]. Thus, in this work, a synergistic mineralizing effect of CaO and TiO$_2$ present in the CFA, which acted in combination with the SrO dopant added, could account for the observed stabilization of Celsian at relatively low temperatures. This is supported by the SEM/EDS results obtained, which are given in Fig. 5 and Table 7. Points 2 and 3 indicated in the micrographs of Fig. 5 correspond to Celsian ($\text{Ba}_2\text{Al}_2\text{Si}_3\text{O}_8$) grains containing Fe$_2$O$_3$, CaO, Na$_2$O and TiO$_2$ as impurities, according to Table 7. On the other hand, points 1 and 4 correspond to elongated needle-like
barium aluminate grains, which contained Fe$_2$O$_3$, MgO and K$_2$O as impurities. Thus, the CFA impurities known to have a strong mineralizing effect on the Hexacelsian to Celsian transformation tended to concentrate in the phase with nominal chemical composition of Ba$_{1-x}$Sr$_x$Al$_2$Si$_2$O$_9$.

Lee and Aswath [12] mentioned that the addition of mineralizers induces the generation of oxygen and barium vacancies in Hexacelsian, by assisting the braking of its Ba–O or (Al, Si)–O bonds, and thus promoting in this way its transformation into Celsian. In the case of mineralizers with cationic radii of $\sim$0.99 Å, such as CaO, this transformation is likely promoted by formation of an interstitial solid solution in which the Ca$^{2+}$ cations reside in the double six-ring (D6R) sites of the hexagonal cell, with the consequent creation of Ba$^{2+}$ vacancies, according to the reaction:

$$\text{CaO} = \text{Ca}^{2+} + \text{V}_{\text{Ba}}^{+} + \text{O}^{2-} + \text{V}^{X} \quad (25)$$

It has also been mentioned [34] that the addition of CaO enhances the Hexacelsian to Celsian transformation by promoting the formation of Celsian nuclei with a plate-like morphology on the basal planes of the Hexacelsian structure.

In the case of mineralizers with cationic radii of $\sim$0.66 Å, such as TiO$_2$, the Hexacelsian to Celsian transformation is likely promoted by substitution of the host Al$^{3+}$ (or Si$^{4+}$) ions by the guest Ti$^{4+}$ ions, also with a consequent creation of Ba$^{2+}$ vacancies, according to the reaction:

$$2\text{TiO}_2 = 2\text{TiAl}^{0} + \text{V}_{\text{Ba}}^{+} + 4\text{O}^{2-} + 2\text{V}^{X} \quad (26)$$

Lastly, for the case of SrO-doped materials, Lee and Aswath [12] mentioned that the Sr$^{2+}$ ions could reside in both the Ba$^{2+}$-host sites and the D6R interstitial sites of Hexacelsian. However, the fact that Ca$^{2+}$ is a much more dopant than Sr$^{2+}$ [34], could indicate that the Sr$^{2+}$ ions reside mainly in the Ba$^{2+}$-host sites of Hexacelsian.

Table 7
Results of SEM/EDS analyses (wt.%) carried out in BAS$_2$ specimens of Fig. 5.

<table>
<thead>
<tr>
<th>Analyzed point</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>BaO</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>MgO</th>
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<tr>
<td>1</td>
<td>2.41</td>
<td>55.74</td>
<td>30.26</td>
<td>2.69</td>
<td>1.16</td>
<td>2.47</td>
<td>3.31</td>
<td>1.97</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>28.8</td>
<td>19.59</td>
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<td>1.17</td>
<td>0.75</td>
<td>2.47</td>
<td>3.31</td>
<td>2.91</td>
<td></td>
</tr>
<tr>
<td>3</td>
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<td>46.97</td>
<td>0.66</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
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<td>16.43</td>
<td>9.91</td>
<td>0.88</td>
<td>2.4</td>
<td>2.66</td>
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<td></td>
</tr>
</tbody>
</table>

Fig. 5. SEM micrographs of HF-etched BAS$_2$ specimens heat treated at 1300 °C/5 h. (a) Backscattered electrons image, (b) secondary electrons image.

Fig. 6. Hexacelsian to Celsian conversion fraction as a function of SrO added, after heat treatment at 1100 or 1200 °C for 5 h.
3.5. Hexacelsian to Celsian conversion fraction

According to Fig. 6, a maximum Hexacelsian to Celsian conversion fraction of ~96% was achieved for \( x = 0.375 \) at 1100 °C/5 h, while full conversion was achieved by doping the BaAl2Si2O8 composition with SrO in the range of \( 0.25 \leq x \leq 0.75 \) at 1200 °C/5 h. As already mentioned, these conversion levels are much higher than those reported by Fu et al. [17], who achieved a maximum conversion of ~40% for \( x = 0.375 \), after calcination at 950 °C/4 h followed by heat treatment at 1040 °C/4 h. For the case of undoped BaAl2Si2O8, it can be seen that the conversion fraction is increased from ~12 to ~62% by increasing temperature from 1100 to 1200 °C.

These results show that the optimum conditions to achieve full Hexacelsian to Celsian conversion appear to involve the addition of a suitable amount of SrCO3 to the initial mixture of CFA, Al2O3, SiO2 and BaCO3 employed in the present work, in order to have a SrO concentration in the range of \( 0.25 \leq x \leq 0.75 \) in the materials thermally treated at 1200 °C/5 h. However, the most recommended addition level within the mentioned range will ultimately depend on how it influences other properties of the materials, such as liquidus temperature and thermal expansion coefficient, which are two of the most important properties when structural applications at high temperatures are envisaged. Bansal et al. [13] reported only a small variation in both properties as a function of SrO content, for SrO-containing BaAl2Si2O8 glasses. However, Fu et al. [17] found, for materials synthesized by the solid-state reaction route, that the average thermal expansion coefficient decreased with increasing SrO content, from ~16 x 10^{-6}/°C for BaAl2Si2O8 with no added SrO, to a minimum value of ~7 x 10^{-6}/°C for SrO concentrations of 0.25 \( \leq x \leq 0.475 \), in the temperature range of 25-400 °C. These authors recommended an optimum SrO addition level of \( x = 0.375 \). Based on these results, as well as on those obtained in the present work, the optimum SrO level recommended by us is \( 0.25 \leq x \leq 0.375 \).

3.6. Rietveld refinement of synthesized materials

Before starting the Rietveld refinements, the instrumental broadening of the diffractometer was determined with the aid of a LaB6 NIST standard with a known narrow crystal lattice size distribution. The peak shape model employed was the one of Thompson–Cox–Hastings (TCA). For asymmetry corrections, the model of Béhar–Baldinozzi [35] was employed. The background was fitted to a 20 degree polynomial. With these premises, the Pawley refinements were initiated setting free the zero shift of the goniometer 2θ scale, asymmetry, crystallite size, lattice strain, cell parameters and background coefficients. The Cagliotti coefficients (\( w_1, w_2, w_3 \)) and X and Y coordinates of the TCA peak shape were always kept constant since they determine the instrumental broadening. After a few cycles, the refinements converged. In a second stage, the Rietveld refinements were initiated using as starting values the ones found in the first stage. The occupancy of large Ba/Sr cations were first set free, on top of the parameters refined by the

<table>
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<tr>
<th>Sample code</th>
<th>( R_{wp} )</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>( \beta )</th>
<th>Ba occ.</th>
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</thead>
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<td>7.119</td>
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</table>

<table>
<thead>
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<th>b</th>
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Table 8
Agreement factor, cell parameters (Å) and occupancies after the Rietveld refinements. The errors of cell parameters are ±0.004. The errors associated to the occupancy are ±0.03.

Table 9
Crystallographic data for the studied compositions, according to the corresponding JCPDS cards [38].

Pawley method [36], doing then the same with the atomic positional parameters, the preferential orientation parameters according to the model of Rietveld-Toraya [37], and, finally, the global isotropic Debye-Waller factor. The statistics of the diffraction pattern due to the presence of other phases and the limitations of the instrument did not allow the determination of individual isotropic Debye–Waller factors. When attempted, some of the ionic species attained meaningless physical values. The rest of the refined parameters reached acceptable values, including the atomic coordinates of all ion species.

The most relevant parameters found after the Rietveld refinements are shown in Table 8. All cell parameters are very similar to those reported in the JCPDS cards [38] for SrAl2Si2O8 and BaAl2Si2O8 (with and without Sr content), as shown in Table 9. This implies that the materials synthesized in the present work were chemically and structurally similar to those obtained from reagent-grade raw materials, whose cell parameters are reported in the JCPDS cards.

Some minor amounts of Ti and Fe were present in the analyzed samples, most likely as Ti4+ and Fe3+ partially substituting the small Al3+ and Si4+ ions. Since X-rays do not allow to discriminate between ionic species such as Si4+, Al3+, Fe3+ and Ti4+, it was assumed as a good approximation that the population of Ba2+ found for Celsian without Sr could be used to determine the small M2+/M4+ cation ratio, simply from a balance of charges. For the rest of the Celsian samples, it was supposed that the M2+/M4+ ratio was the same and therefore the number of vacancies at that site was considered to be constant. With this hypothesis in mind, the Ba/Sr proportions were estimated for the whole series.

For the occupancy analysis of large cations in site 4(i) only Ba ions were considered, since the Rietveld module of MS4 does not allow the presence of two different species in the same site. To calculate the Ba/Sr ratio for the Sr-containing specimens, the scattering factors for Ba2+ and Sr2+ were
Table 10
Proportion of barium in the specimens as a function of the refined occupancy ($p$).

<table>
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<tr>
<th>X</th>
<th>Value1</th>
<th>Value2</th>
<th>Value3</th>
<th>Value4</th>
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<td>0.938</td>
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<td>0.792</td>
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<td>0.616</td>
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</tr>
</tbody>
</table>

Fig. 7. Variation of cell volume of Celsian samples analyzed as a function of Ba content. A straight line was fitted and its statistic parameters are shown as an inset.

The linear increase of the cell size. Indeed, if the content of small cations in sites T1 and T2 remains constant, the cell parameters should vary in a linear fashion as a function of Ba or Sr content. In Fig. 7, the trend of the cell variation can be appreciated. The cell volume has been plotted against Ba content. The linear increase of the cell volume with composition, from SrAl$_2$Si$_2$O$_8$ to BaAl$_2$Si$_2$O$_8$, indicates that Vegard's rule is obeyed. These results also confirm the formation of Ba$_{1-x}$Sr$_x$Al$_2$Si$_2$O$_8$ solid solutions over the entire concentration range $0 \leq x \leq 1$ [24].

4. Conclusions

Monoclinic (Celsian) and hexagonal (Hexacelsian) Ba$_{1-x}$Sr$_x$Al$_2$Si$_2$O$_8$ solid solutions were synthesized by using Coal Fly Ash (CFA) as main raw material, employing a simple one-step solid-state reaction process. The Ba$_{0.625}$Sr$_{0.375}$Al$_2$Si$_2$O$_8$ composition showed the largest Hexacelsian to Celsian conversion (96%) at 1100 °C/5 h, while full conversion was achieved at 1200 °C/5 h for materials with SrO contents in the range of 0.25 ≤ $x$ ≤ 0.75. An optimum SrO level of 0.25 ≤ $x$ ≤ 0.375 was recommended for stabilization of Celsian at the latter temperature, based on the effect of SrO on the liquidus temperature and thermal expansion coefficient of these materials, reported by other researchers. Chemical analyses and Rietveld refinements showed that the synthesized materials were chemically and structurally similar to analogous materials obtained from reagent-grade powders in previously published literature. The easy stabilization of Celsian at a relatively low temperature and short time, when compared to previously published data, can be attributed to the joint contribution of two main factors: (a) presence of Al$_2$O$_3$ and SiO$_2$, already chemically combined forming mullite and an amorphous phase, together with a large content of free SiO$_2$ in the CFA employed; this resulted in a reaction path leading to the formation of transient barium silicates (BaSiO$_3$, Ba$_2$SiO$_4$ and BaSi$_2$O$_5$) in the temperature range of 850–1100 °C; the formation of barium aluminates was also detected at temperatures higher than 900 °C; all of this led in turn to an easy formation of Hexacelsian, (b) a likely synergistic mineralizing effect of impurities present in the CFA, particularly CaO and TiO$_2$, which could act in combination with the added SrO, greatly facilitating the Hexacelsian to Celsian conversion. Lastly, thermodynamics calculations were used to validate the detailed model for the reaction sintering mechanism. It can be appreciated that the theoretical predictions agree with the sequential appearance of phases. Namely, ΔG computations for the formation of BaAl$_2$Si$_2$O$_8$, BaSiO$_3$, Ba$_2$SiO$_4$, Ba$_2$Si$_2$O$_6$, Ba$_2$Si$_2$O$_7$ and BaAl$_2$O$_4$ confirm the much lower ΔG value for BaAl$_2$Si$_2$O$_8$ in the whole range of temperatures considered. Consequently, its appearance as the first phase during reaction is fully justified.

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