Influence of mechanical activation on the synthesis of Sr-Celsian employing a precursor mixture containing coal fly ash

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Strontium aluminosilicate, $\text{SrAl}_2\text{Si}_2\text{O}_8$ (SAS), was synthesized by a solid state reaction using coal fly ash (CFA) as main raw material. A precursor mixture of SrCO_3 , CFA and Al_2O_3 was mechanically-activated for times of up to 12 h using an attrition mill, and subsequently sintered at temperatures of 900-1300 °C. The CFA and the mechanical activation were employed with the aim to promote the transformation from the hexagonal (Sr-Hexacelsian) into the monoclinic (Sr-Celsian) polymorphic form of SAS, since the latter phase is associated with better physical and mechanical properties but the former tends to be the first one to appear. The mean particle size, the crystallite size and the temperature at the end of the curve of weight loss (T_f) decreased, while the specific surface area and the degree of amorphization increased, with increasing milling time. Samples milled for at least 4 h and then sintered at 1100 °C achieved full transformation into Sr-Celsian. The same result was obtained for sintering temperatures higher than 1100 °C, independently of milling time. An increment in both the milling time and the sintering temperature allowed us to improve the densification and the mechanical properties of the synthesized materials.

Keywords: Milling, Synthesis, Refractories, Sr-Celsian, Coal Fly Ash.

Influencia de la activación mecánica sobre la síntesis de Celsiana de Sr empleando una mezcla precursora conteniendo ceniza volante

Aluminosilicato de estroncio, $\text{SrAl}_2\text{Si}_2\text{O}_8$ (SAS), fue sintetizado por reacción en el estado sólido empleando ceniza volante (CFA) como materia prima principal. Una mezcla precursora de SrCO_3 , CFA y Al_2O_3 fue activada mecánicamente por tiempos de hasta 12 h en un molino de atrición, y después sinterizada a temperaturas de 900-1300 °C. El empleo de la CFA y la activación mecánica tuvieron el propósito de promover la transformación polimórfica de la fase hexagonal (Hexacelsiana de Sr) a la monoclinica (Celsiana de Sr) del SAS, ya que esta última se asocia con mejores propiedades físicas y mecánicas pero la primera tiende a aparecer primero. El tamaño promedio de partícula y de cristallita, así como la temperatura al final de la curva de pérdida en peso (T_f), disminuyeron, mientras que el área superficial y el grado de amorfización aumentaron, al incrementar el tiempo de molienda. Las muestras molidas por al menos 4 h y sinterizadas a 1100 °C se transformaron completamente a Celsiana de Sr. Sucedió lo mismo a temperaturas de sinterización mayores a 1100 °C, independientemente del tiempo de molienda. El incremento tanto en el tiempo de molienda como en la temperatura de sinterización permitió mejorar la densificación y las propiedades mecánicas de los materiales sintetizados.

Palabras clave: Molienda, Refractarios, Síntesis, Celsiana de Sr, Ceniza Volante.

1. INTRODUCTION

Strontium aluminosilicate, $\text{SrAl}_2\text{Si}_2\text{O}_8$ (SAS), especially in its monoclinic polymorphic form known as Sr-Celsian, is a very interesting material due to its high resistance toward oxidation and reduction, low dielectric constant, low coefficient of thermal expansion ($2.5 \times 10^{-6}/^\circ\text{C}$), and high melting point ($\sim 1650^\circ\text{C}$) (1-4), and because it is potentially useful as a matrix for ceramic composites with applications at high temperatures (5). However, a hexagonal polymorphic form known as Sr-Hexacelsian tends to be the first phase to appear during the synthesis of SAS, tending to remain metastably at low temperatures. Sr-Hexacelsian is an undesirable phase due to its high coefficient of thermal expansion ($8 \times 10^{-6}/^\circ\text{C}$)

(1, 6), and because it undergoes a reversible transformation into an orthorhombic form in the temperature range of 600-800 °C, which causes a volume expansion of $\sim 3\%$ (1), and this is associated with the generation of microcracks in the material.

Some Sr-Celsian synthesis methods require costly and energy-intensive multi-step processes. For instance, some solid state reaction processes require the employment of temperatures of at least $\sim 1200^\circ\text{C}$ in order to attain full Sr-Hexacelsian to Sr-Celsian conversion (4, 7). Similarly, the glass-ceramics route requires the use of melting temperatures of $\sim 2000^\circ\text{C}$ to obtain the initial glass, which is subsequently

subjected to different thermal treatment cycles in order to promote its crystallization (3, 5).

Since mechanical activation is a well-known way to enhance the reactivity of materials that will participate in a posterior solid state reaction process (8), and coal fly ash (CFA) is an alternative raw material that seems to promote the Hexacelsian to Celsian conversion due to the presence in it of mineralizers such as CaO and TiO₂ (9-11), the influence of the combination of both factors on the synthesis of Sr-Celsian was studied in the present work.

CFA is a by-product of the combustion of coal in power-generation plants (12), which constitutes a rich source of SiO₂ and Al₂O₃. CFA is a very low-cost industrial residue (13) and huge amounts of it are continuously discarded in open landfills worldwide (14). Thus, its use for the synthesis of Sr-Celsian can be additionally seen as a way to contribute to the solution of an important environmental problem, and at the same time a valuable product is obtained from a very cheap raw material, with a potentially important economic impact.

2. EXPERIMENTAL PROCEDURE

2.1. Raw materials

SrCO₃ (Solvay, México, with purity of 97.9 wt.% and mean particle size of 15.5 µm), Al₂O₃ (HPA, SASOL, USA, with purity of 99.99 wt.% and mean particle size of 1.5 µm) and CFA, were used for the preparation of the precursor mixture. The initial CFA was collected from the electrostatic precipitators of a Mexican power-generation plant, and it had a mean particle size of 86 µm. This material was milled for 1 h in a ball mill, attaining a particle size in it of 17 µm. After this, the CFA was subjected to a wet magnetic separation process using a powerful neodymium magnet, which allowed us to reduce in ~53% the content of iron oxides of the as-received material. This was carried out in order to minimize the formation of iron-rich secondary phases with low melting point during the synthesis of Sr-Celsian. The chemical composition of the beneficiated CFA, determined by X-Ray Fluorescence (Bruker AXS S4 Pioneer, XRF apparatus), was (wt. %): 62% SiO₂, 25% Al₂O₃, 3% Fe₂O₃, 3% CaO, 1% MgO, 1% TiO₂, 1% K₂O, and 1% of other oxides (Na₂O, MnO₂, P₂O₅, ZrO₂, PbO and SrO), with a Loss Of Ignition (LOI) of 3% determined by thermogravimetry, which was attributed mainly to the combustion of free carbon present in the CFA. Since the content of SiO₂ + Al₂O₃ + Fe₂O₃ of both the as-received and the beneficiated CFA was higher than 70 wt.%, and their CaO content was relatively low, it was deduced that the used material corresponded to the F class CFA, according to the ASTM C618-03 standard (15).

A precursor mixture of SrCO₃, Al₂O₃ and beneficiated CFA, hereinafter denominated simply as CFA, in weight proportions corresponding to the stoichiometric SAS composition, was prepared. This mixture was composed by (wt.%): 37.4% SrCO₃, 13.6% Al₂O₃, and 49% CFA.

The precursor mixture was milled in a closed chamber laboratory attrition mill fitted with Teflon-lined propellers and container, which was operated at 1600 rpm. Milling was carried out in air at room temperature for 5 min with homogenization purposes (hereinafter this material is sometimes referred to as mixture milled for 0 h, or as reference precursor mixture), or for 4 h, 8 h or 12 h, employing 8 mol %

MgO-partially-stabilized ZrO₂ balls with a diameter of 1.5 mm as milling media, a ball/load mass ratio of 5:1 and ethanol as dispersion medium.

The reference and the mechanically-activated precursor mixtures were uniaxially pressed at 100 MPa into cylinders weighting 1 g and with a diameter of 1.0 cm and a height of ~0.5 cm. The disks were subsequently heat treated in the temperature range of 900-1300 °C, in steps of 100 °C, with a heating rate of 5 °C/min and a holding time of 5 h in all cases.

2.2. Characterization of precursor mixtures

TGA/DTA curves were recorded by using a simultaneous Thermogravimetric/Differential Thermal Analyzer (Perkin Elmer, Pyris Diamond TGA/DTA apparatus). These analyses were performed using 15 mg samples and platinum pans, under air atmosphere from room temperature to above 1200 °C, at a heating rate of 10 °C/min. The derivative DTG curves were also obtained. The mean particle size of all mixtures were determined by the laser diffraction method using a Coulter LS 100Q particle size analyzer. Their specific surface area was calculated from the Brunauer-Emmett-Teller (BET) isotherms determined by the volumetric method using a gas sorption analyzer (Quantachrome, AUTOSORB-1). For this, the samples were degassed at 300 °C and the adsorption of nitrogen was carried out at -195.8 °C. The crystalline phases present in the reference and in the mechanically-activated samples were identified by X-Ray Diffraction (XRD), using a Philips X'Pert 3040 XRD apparatus. The XRD patterns were recorded employing CuKα radiation (λ = 1.54 Å) in the 2θ range of 10-80°, using a scan step of 0.03°, a voltage of 40 kV, and a current of 30 mA.

The degree of amorphization achieved by the SrCO₃ contained in the precursor mixtures as a function of milling time was estimated using a method developed by Ohlberg and Strickler (16, 17), which is based on Equation 1:

$$A = \left[1 - \frac{U_i}{I_i} \times \frac{I_x}{U_x} \right] \times 100 \quad (1)$$

where A denotes the degree of amorphization, U and I denote the background and the integrated intensities, respectively, of the diffraction lines of the reference (i) or the mechanically activated (x) samples in the corresponding XRD patterns.

The average crystallite size (size of the coherently diffracting domains) of SrCO₃ contained in the precursor mixtures was estimated by XRD using Scherrer's equation (18). The main peak of SrCO₃, which corresponded to the (111) plane, was used for this. The Kα₁ and Kα₂ contributions were deconvoluted using the MDI Jade 6 software, which was also employed to determine the position of the peaks. For this, the peak width was fitted to a pseudo-Voigt mathematical function.

2.3. Characterization of sintered materials

The crystalline phases formed in the sintered samples were identified by XRD, using the same equipment and conditions mentioned before. Prior to this, the sintered samples were

milled using a synthetic sapphire mortar and pestle, until a particle size of 25-75 μm was achieved.

The microstructure of the sintered samples was observed by Scanning Electron Microscopy (SEM) using a Philips XL30 ESEM apparatus, employing an acceleration voltage of 20 kV. For this, the sintered samples were cross-sectioned and mounted in cold-cure epoxy resin with the cut surface facing downwards. Then, this surface was ground using SiC papers with successive grit sizes from 80 grit to 2400 grit, which was followed by polishing to a mirror finish using diamond particles with successive sizes of 3, 1 and $\frac{1}{4}$ μm . Prior to their observation on the SEM, the samples were etched for 15 s in a 0.5 wt.% hydrofluoric acid aqueous solution and then graphite-coated using a JEOL JEE-400 vacuum evaporator.

The apparent density (g/cm^3) of the materials was determined by the Archimedes' principle in distilled water, according to the ASTM C 20-00 standard (19). For these measurements, at least 10 replications were carried out per each experimental condition investigated.

The modulus of rupture (MOR) and the Young's modulus (E) of the materials sintered at 1300 $^{\circ}\text{C}$ were determined from the slope of the elastic region of the stress-strain curves obtained from four-point flexural strength tests carried out according to the ASTM C 1161-02c and ASTM C 1352-96 standards (20, 21), using a MTS QTEST/100 mechanical testing machine with a 500 N load capacity, employing a rate of load application (crosshead speed) of 0.05 mm/s until fracture of the specimens. For these tests, prismatic bars with dimensions of 45 mm (length) $\times$ 3 mm (width) $\times$ 4 mm (height) were employed, which were cut using a Struers Accutom 5 diamond saw from sintered prismatic bars with dimensions of 70 mm (length) $\times$ 40 mm (width) $\times$ 30 mm (height), which were obtained by uniaxial pressing using the same load applied to the specimens used to carry out the phase composition studies. Prior to the mechanical tests, the samples were ground and polished in the cut surfaces and borders using the same ceramographic techniques already mentioned in order to avoid possible surface damages. For the mechanical testing of the sintered materials, at least 7 replications were carried out per each experimental condition investigated.

3. RESULTS AND DISCUSSION

3.1. Characterization of precursor mixtures

3.1.1. PHASE COMPOSITION

Figure 1 shows the XRD patterns obtained for the reference and the mechanically-activated precursor mixtures. The main diffraction peaks were attributed to SrCO_3 (JCPDS Card No. 084-1778), $\alpha\text{-Al}_2\text{O}_3$ (Corundum, JCPDS Card No. 46-1212), SiO_2 (Quartz, JCPDS Card No. 33-1161), and $\text{Al}_6\text{Si}_2\text{O}_{13}$ (Mullite, JCPDS Card No. 79-1457). Both quartz and mullite were contained in the CFA. It was observed that with increasing milling time the XRD patterns underwent a reduction in the peak intensities as well as a line broadening, especially in the case of SrCO_3 . It is believed that these changes were caused by a refinement of the crystallite size as well as by a gradual amorphization of the SrCO_3 present in the precursor mixtures. The formation of new phases was not detected at any of the employed milling times.

Figure 1. XRD patterns obtained for the reference and the mechanically-activated precursor mixtures. Key: (O) SrCO_3 , (α) Al_2O_3 , (Q) Quartz, and ($\diamond$) Mullite.

3.1.2. CRYSTALLITE SIZE AND DEGREE OF AMORPHIZATION

As it can be seen in Figure 2, the crystallite size of the SrCO_3 contained in the precursor mixtures decreased steadily, while its degree of amorphization increased steadily, with increasing milling time. The average crystallite size of SrCO_3 was 130 nm for the reference precursor mixture, while the corresponding value obtained for the material milled for 12 h was 54 nm. On the other hand, the degree of amorphization of SrCO_3 achieved a maximum value of 88% for the precursor mixture milled for 12 h.

Figure 2. Crystallite size and degree of amorphization (A) estimated for the SrCO_3 contained in the precursor mixtures as a function of milling time.

3.1.3. MEAN PARTICLE SIZE AND SURFACE AREA

Table I shows that the mean particle size of the precursor mixtures decreased steadily, while their surface area increased steadily, with increasing milling time. The mean particle size was 14.9 μm for the reference precursor mixture, while the corresponding value obtained for the material milled for 12 h was 2.9 μm . On the other hand, the surface area achieved a maximum value of 8.7 m^2/g for the precursor mixture milled for 12 h.

TABLE I. MEAN PARTICLE SIZE AND SURFACE AREA OBTAINED FOR THE PRECURSOR MIXTURES AS A FUNCTION OF MILLING TIME

Milling time (h)	Mean particle size (μm)	Surface area (m^2/g)
0	14.9	3.7
4	4.1	5.4
8	3.2	6.3
12	2.9	8.7

3.1.4. THERMAL ANALYSIS

As examples of the results obtained from the thermal analyses carried out, Figure 3 shows the TGA and DTA curves corresponding to the reference precursor mixture and to the material mechanically-activated for 12 h. Table II gives a summary of the results obtained from the thermal analyses performed for all the studied precursor mixtures. In the case of the DTA curve obtained for the reference material, it was deduced, with the aid of previous literature reports, that peak 1 located at $\sim 935^\circ\text{C}$ corresponds to the orthorhombic to hexagonal phase transition of SrCO_3 . Maitra et al. (22) reported the occurrence of this phase transition at $\sim 925^\circ\text{C}$, while Arvanitidis et al. (23) reported it at $\sim 931^\circ\text{C}$, and Weinbruch et al. (24) at 935°C . The presence of this peak was not evident in the DTA curves obtained for the mechanically-activated precursor mixtures, and this was probably due to the consumption at lower temperatures of most of the SrCO_3 contained in the materials, which was likely

caused by an enhanced reactivity of the latter resulting from their mechanical activation. This is further supported by the results of the TGA/DTG studies carried out.

Referring now to the DTA curves obtained for the material milled for 12 h shown in Figure 3, it was deduced, according to Kobayashi and Inagaki (4), that peak 2 located at $\sim 896^\circ\text{C}$ and peak 3 located at $\sim 963^\circ\text{C}$ corresponded to the crystallization of Sr-Hexacelsian and to the transformation of the latter phase into Sr-Celsian, respectively. Peak 2 coincided in all cases with the temperature (T_f) at the end of the weight loss stage of the TGA curve obtained for the same material, as it can be seen in Table II. Peak 3 was clearly evident only in the case of the material milled for 12 h.

It was observed that T_f decreased with increasing milling time. Figure 3 shows that the material milled for 12 h had a $T_f \sim 894^\circ\text{C}$, which was $\sim 105^\circ\text{C}$ lower than the T_f obtained for the reference sample. This indicates that the kinetics of the solid state reactions involving the participation of SrCO_3 was enhanced by mechanical activation. These chemical reactions gave rise to the formation of phases such as strontium silicates, strontium aluminate and Sr-Hexacelsian, and they were responsible for the weight loss underwent by the precursor mixtures due to the release of CO_2 . These reactions seem to have taken place at much faster rates in the mechanically-activated materials, even at relatively low temperatures, when compared with those occurring in the reference mixture.

This is indeed supported by the results of the DTG studies shown in Figure 4. It can be noticed that three different events

Figure 3. TGA and DTA curves obtained for the reference precursor mixture and for the material mechanically-activated for 12 h. T_f = Temperature at the end of the weight loss curve. Other indicated points are explained in the text.

Figure 4. DTG curves obtained for the reference and the mechanically-activated precursor mixtures. T_f = Temperature at the end of the weight loss curve. Other indicated peaks are explained in the text.

TABLE II. TEMPERATURES ($^\circ\text{C}$) OF OCCURRENCE OF THE MAIN THERMAL EVENTS DETECTED IN THE REFERENCE AND IN THE MECHANICALLY-ACTIVATED PRECURSOR MIXTURES (REFER TO FIGURES 3 AND 4).

Milling time (h)	DTG curves						TGA curves	DTA curves		
	1	2	3	4	5	T_f^a	T_f^a	1 ^b	2	3
0	~ 615	662	836	944	980	~ 1004	~ 999	935	~ 1002	n.d.
4	~ 615	668	867	909	---	~ 939	~ 927	n.d.	~ 939	n.d.
8	~ 615	672	890	917	---	~ 929	~ 925	n.d.	~ 928	n.d.
12	~ 615	672	879	---	---	~ 901	~ 894	n.d.	~ 896	~ 963

^a Temperature at the end of the weight loss curve. ^b Orthorhombic to hexagonal phase transition of SrCO_3 . n.d. = non-detected peak.

happened in the DTG curves when milling time was increased: 1) the number of peaks tended to decrease; 2) the main weight loss stage was shifted toward lower temperatures, with a resultant decreased value of T_p , and 3) the relative importance of some peaks changed; peak 3 gradually became more significant, peak 4 was gradually attenuated until it completely disappeared after 12 h of milling, and peak 5 was found only in the reference material; all these peaks were attributed to weight losses caused by the occurrence of chemical reactions such as those mentioned before. In contrast, peaks 1 and 2 remained relatively unaffected by mechanical activation, and they were attributed to a joint contribution of the release of physically bound water, combustion of free carbon present in the CFA, and incipient formation of strontium silicates.

3.2. Characterization of sintered materials

3.2.1. PHASE COMPOSITION

As examples of the results obtained from the XRD studies carried out for the sintered materials, Figures 5 and 6 show the XRD patterns obtained for the reference and the mechanically-activated precursor mixtures sintered at 900 °C and 1100 °C, respectively. Table III gives a summary of the results obtained from the XRD studies performed for the precursor mixtures subjected to all milling times and sintering temperatures employed.

The formation of Sr-Hexacelsian and Sr-Celsian phases was detected at 900 °C and 1000 °C, at all milling times, with the simultaneous presence of several intermediate secondary phases in all cases. For both sintering temperatures, the relative proportions of Sr-Hexacelsian and Sr-Celsian increased, while those of the secondary phases decreased, with increasing milling time. Sr-Hexacelsian gradually became the predominant phase in the samples when milling time was increased, and this was more accentuated at 1000 °C. However, the formation of the latter phase was practically not detected

at the temperature range of 1100-1300 °C, independently of milling time, since only traces of it were detected in the reference sample sintered at 1100 °C. In contrast, Sr-Celsian predominated in all samples sintered in this temperature range. On the other hand, with increasing milling time and sintering temperature, the relative proportions of all the intermediate phases continued decreasing as the reaction process advanced, until only a small amount of $\text{Sr}_2\text{Al}_2\text{SiO}_7$ was detected as additional phase in the sample milled for 12 h and sintered at 1100 °C. Since only traces of the same secondary phase were detected at 1200-1300°C, thus, all samples sintered at this temperature range were also basically composed by Sr-Celsian, independently of milling time.

Figure 5. XRD patterns obtained for the reference and the mechanically-activated precursor mixtures sintered at 900 °C / 5 h, with prior milling for: a) 0 h, b) 4 h, c) 8 h, or d) 12 h. Key: (H) Sr-Hexacelsian, (M) Sr-Celsian, (O) SrAl_2O_4 , (Q) Quartz, (α) $\alpha\text{-Al}_2\text{O}_3$, ($\square$) SrCO_3 , ($\blacksquare$) SrO , ($\bullet$) SrSiO_3 , ($\dagger$) Sr_2SiO_4 , and ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$.

TABLE III. SUMMARY OF THE RESULTS OBTAINED FROM THE XRD STUDIES CARRIED OUT FOR THE SINTERED MIXTURES, WITH OR WITHOUT PRIOR MECHANICAL ACTIVATION.

Sintering temperature (°C)	Milling time (h)			
	0	4	8	12
900	<u>Main phases:</u> ($\blacksquare$) SrO , ($\dagger$) Sr_2SiO_4 , (Q) Quartz, (O) SrAl_2O_4 <u>Secondary phases:</u> (H) Sr-Hexacelsian, ($\bullet$) SrSiO_3 , (α) $\alpha\text{-Al}_2\text{O}_3$, (M) Sr-Celsian, ($\square$) SrCO_3 , ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$	<u>Main phases:</u> ($\dagger$) Sr_2SiO_4 , (H) Sr-Hexacelsian, (Q) Quartz <u>Secondary phases:</u> (M) Sr-Celsian, ($\bullet$) SrSiO_3 , ($\blacksquare$) SrO , (O) SrAl_2O_4 , (α) $\alpha\text{-Al}_2\text{O}_3$, ($\square$) SrCO_3 , ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$	<u>Main phases:</u> (H) Sr-Hexacelsian, (Q) Quartz <u>Secondary phases:</u> (M) Sr-Celsian, ($\bullet$) SrSiO_3 , ($\dagger$) Sr_2SiO_4 , (α) $\alpha\text{-Al}_2\text{O}_3$, ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, Trace phase: (O) SrAl_2O_4	<u>Main phases:</u> (H) Sr-Hexacelsian <u>Secondary phases:</u> (M) Sr-Celsian, (Q) Quartz, ($\bullet$) SrSiO_3 , ($\dagger$) Sr_2SiO_4 , (α) $\alpha\text{-Al}_2\text{O}_3$, ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, Trace phase: (O) SrAl_2O_4
1000	<u>Main phases:</u> ($\dagger$) Sr_2SiO_4 , (Q) Quartz, (O) SrAl_2O_4 , (H) Sr-Hexacelsian, ($\bullet$) SrSiO_3 , (α) $\alpha\text{-Al}_2\text{O}_3$, (M) Sr-Celsian, ($\square$) SrCO_3 , ($\blacksquare$) SrO , ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$	<u>Main phases:</u> (H) Sr-Hexacelsian, (M) Sr-Celsian, (Q) Quartz, ($\bullet$) SrSiO_3 <u>Secondary phases:</u> (O) SrAl_2O_4 , (α) $\alpha\text{-Al}_2\text{O}_3$, ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, ($\dagger$) Sr_2SiO_4	<u>Main phases:</u> (H) Sr-Hexacelsian, (M) Sr-Celsian, (Q) Quartz, ($\bullet$) SrSiO_3 <u>Secondary phases:</u> (α) $\alpha\text{-Al}_2\text{O}_3$, ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, ($\dagger$) Sr_2SiO_4	<u>Main phases:</u> (H) Sr-Hexacelsian, (M) Sr-Celsian, ($\bullet$) SrSiO_3 <u>Secondary phases:</u> (Q) Quartz, (α) $\alpha\text{-Al}_2\text{O}_3$, ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, Trace phase: ($\dagger$) Sr_2SiO_4
1100	<u>Main phases:</u> (M) Sr-Celsian <u>Secondary phases:</u> (Q) Quartz, ($\bullet$) SrSiO_3 , (O) SrAl_2O_4 , (α) $\alpha\text{-Al}_2\text{O}_3$, ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, Trace phase: (H) Sr-Hexacelsian	<u>Main phases:</u> (M) Sr-Celsian <u>Secondary phases:</u> (Q) Quartz, ($\bullet$) SrSiO_3 , ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, Trace phase: (α) $\alpha\text{-Al}_2\text{O}_3$	<u>Main phases:</u> (M) Sr-Celsian <u>Secondary phases:</u> (Q) Quartz, ($\bullet$) SrSiO_3 , ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$, Trace phase: (α) $\alpha\text{-Al}_2\text{O}_3$	<u>Main phases:</u> (M) Sr-Celsian <u>Secondary phases:</u> ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$
1200	<u>Main phases:</u> (M) Sr-Celsian <u>Trace phase:</u> ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$			
1300	<u>Main phases:</u> (M) Sr-Celsian <u>Trace phase:</u> ($\boxtimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$

Figure 6. XRD patterns obtained for the reference and the mechanically-activated precursor mixtures sintered at 1100 °C/ 5 h, with prior milling for: a) 0 h, b) 4 h, c) 8 h, or d) 12 h. Key: (H) Sr-Hexacelsian, (M) Sr-Celsian, (O) SrAl_2O_4 , (Q) Quartz, (α) $\alpha\text{-Al}_2\text{O}_3$, (♦) SrSiO_3 , and ($\otimes$) $\text{Sr}_2\text{Al}_2\text{SiO}_7$.

Our results show that the use of CFA as main raw material combined with mechanical activation of the precursor mixture for the solid state synthesis of Sr-Celsian is promissory, since many of the publications in this field describe methods that are more energy-intensive and/or involve a larger number of processing steps, when compared with our method.

For instance, Krzmann et al. (7) synthesized SAS by solid-state reaction employing stoichiometric mixtures of reagent-grade SrCO_3 , Al_2O_3 and SiO_2 powders. After homogenization, the mixtures were first pre-reacted at 1000-1200 °C and then at 1300 °C, apparently for 12 h in both cases, in order to enhance the Sr-Hexacelsian to Sr-Celsian transformation as well as the formation of the latter phase, with grinding operations in between the pre-reaction stages. Prior to sintering, the powders were ball-milled until a mean particle size of 1 μm was achieved. Then, the milled powders were uniaxially pressed and sintered at 1500 °C for 12 or 40 h with a final cooling at 0.7 °C/min. The formation of Sr-Hexacelsian was not detected at any treatment temperature employed, and Sr-Celsian only started to appear at 1100 °C, with the presence in the same sample of considerable amounts of secondary phases such as SrSiO_3 , Al_2O_3 , SiO_2 , SrAl_2O_4 and $\text{SrAl}_2\text{SiO}_7$. When temperature was increased to 1200 °C the Sr-Celsian phase started to prevail, but the presence of the SrSiO_3 and Al_2O_3 secondary phases only disappeared at temperatures of at least 1400 °C.

In a work reported by Hyatt and Bansal (3), glasses with stoichiometric SAS composition were melted at temperatures higher than 2000 °C in a continuous electric arc furnace with Mo electrodes using reagent-grade SrCO_3 , Al_2O_3 and SiO_2 powders. Glass flakes were produced by quenching the melt between water-cooled metallic rollers. Glass bars and rods were also fabricated. The glass flakes were wet ground in an attrition mill, until a mean particle size of $\sim 3 \mu\text{m}$ was achieved. Full transformation of the glass into Sr-Celsian occurred at either 1100 °C/1 h or 1050 °C/10 h for powder glass and at either 1250 °C/1 h or 1150 °C/10 h for bulk glass.

Kobayashi and Inagaki (4) synthesized SAS by a solid-state reaction between kaolin and SrCO_3 . These researchers observed that densification of the precursor mixtures started at a temperature close to that of decomposition of SrCO_3 , and that the release of CO_2 during the latter process inhibited the attainment of full densification in the materials. In order to avoid this, the precursor mixtures were calcined at 800 °C/5 h for complete decomposition of the strontium carbonate. The calcined powders were then milled for 1-20 h and uniaxially pressed. This was followed by heat treatment of the compacts in air at temperatures of up to 1200 °C, with holding time of 1 h in all cases. At 900 °C, the sample was completely amorphous. A rapid formation of Sr-Hexacelsian occurred at 950 °C, and its transformation into Sr-Celsian started at 1100 °C, which was completed at 1200 °C.

3.2.2. MICROSTRUCTURE

The SEM micrograph of Figure 7, which corresponds to a sample milled for 12 h and then sintered at 1300 °C, shows that the formed Sr-Celsian crystals had the needle-like morphology that is typical of this phase, as well as an appreciable amount of intergranular porosity. The latter microstructural feature was likely related to the release of CO_2 caused by the decomposition of SrCO_3 during the solid state reaction process, which could have interfered with the densification of the material.

Figure 7. SEM micrograph of a sample milled for 12 h and then sintered at 1300 °C.

3.2.3. APPARENT DENSITY AND MECHANICAL PROPERTIES

Table IV shows the results obtained from the evaluation of apparent density and mechanical properties carried out as a function of milling time for the samples sintered at 1300 °C. It can be seen that the values of apparent density, MOR and E increased with increasing milling time. In this way, the maximum values for these properties were achieved in the samples milled for 12 h, which were: apparent density = $3.05 \pm 0.02 \text{ g/cm}^3$, which was 99% of the theoretical density of Sr-Celsian (3.084 g/cm^3 , according to the JCPDS Card No. 381454), MOR = $88 \pm 4 \text{ MPa}$, and E = $66 \pm 1 \text{ GPa}$.

TABLE IV. VALUES OF APPARENT DENSITY, MOR AND E OBTAINED AS A FUNCTION OF MILLING TIME FOR THE SAMPLES SINTERED AT 1300 °C. THE STANDARD DEVIATIONS OF ALL MEASUREMENTS ARE GIVEN.

Milling time (h)	$\rho_{\text{apparent}} \text{ (g/cm}^3\text{)}$	MOR (MPa)	E (GPa)
0	2.63 ± 0.05	12 ± 1	8 ± 2
4	2.82 ± 0.04	51 ± 4	21 ± 3
8	2.95 ± 0.04	48 ± 2	45 ± 5
12	3.05 ± 0.02	88 ± 4	66 ± 1

4. CONCLUSIONS

The kinetics of formation of Sr-Celsian by solid state reaction, as well as the Sr-Hexacelsian to Sr-Celsian conversion, were enhanced by the use of CFA as main raw material combined with mechanical activation of the precursor mixtures. Full transformation into Sr-Celsian was achieved in the samples milled for at least 4 h and then sintered at 1100 °C. This was also the case for sintering temperatures higher than 1100 °C, independently of milling time. An increment in both the milling time and the sintering temperature allowed us to improve the densification and the mechanical properties of the synthesized materials. The samples milled for 12 h and then sintered at 1300 °C achieved an apparent density = $3.05 \pm 0.02 \text{ g/cm}^3$, MOR = $88 \pm 4 \text{ MPa}$, and E = $66 \pm 1 \text{ GPa}$.

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