

The thermal behavior of some polymeric precursors used in $\text{CaAl}_{12}\text{O}_{19}$ synthesis

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Abstract $\text{CaAl}_{12}\text{O}_{19}$ was synthesised using three different precursors: (a) a polyester type precursor resulted from the traditional Pechini method; (b) a polyester type precursor resulted from the reaction between citric acid and calcium and aluminum nitrates; and (c) a polymeric type precursor resulted from the reaction between acrylic acid and calcium an aluminum nitrates. The thermal behavior of the three precursors used in the $\text{CaAl}_{12}\text{O}_{19}$ synthesis was monitored to underline the thermal effects associated to the $\text{CaAl}_{12}\text{O}_{19}$ formation. Thermal analyses performed on precursors do not reveal clear differences regarding the thermal effects assigned to calcium aluminates formation, at temperatures over 800 °C. In contrast, thermal analysis of samples pre-fired at 200 °C, and especially at 600 °C, show clear differences between samples obtained in different ways. It is noted that in samples obtained from acrylic acid and nitrates, and citric acid and nitrates, CA_6 is practically single phase after calcination at 1,200 °C. However, in the sample obtained from citric acid, ethylene glycol, and nitrates, calcined at 1,200 °C, CA_6 is present along with CA_2 and $\alpha\text{-Al}_2\text{O}_3$.

Keywords Calcium aluminates · Polymeric precursor method · Thermal analysis

Introduction

Over time, the binary compounds of the $\text{CaO-Al}_2\text{O}_3$ system were studied with interest for the valuable features

owned by them. These compounds have been extensively analyzed due to their refractory and hydraulic proprieties and are also candidate materials for a wide range of technological applications because of their optical, electrical, thermal, and mechanical properties.

Calcium hexaaluminate $\text{CaAl}_{12}\text{O}_{19}$ or $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$ (CA_6), known as hibonite, has high refractory and a series of interesting electrical and optical properties. As a result, CA_6 synthesis is the subject of a large number of papers [1–5]. Since the formation of CA_6 through ceramic method runs difficult and requires very high temperatures (1,650 °C), the attention of researchers turned to various unconventional methods of synthesis, aiming the temperature decrease for the CA_6 synthesis.

Ianoș and his team [1] prepared single-phase CA_6 by low-temperature combustion synthesis, using a mixture of urea and β -alanine as fuel, no further ignition being necessary. Altay et al. [2] obtained CA_6 at 1,175 °C starting from a mixture of stoichiometric proportions of calcium and aluminum nitrates into 5 wt% aqueous solution of poly(vinyl alcohol). A new eco-friendly fabrication process for porous ceramics using hydraulic alumina and water was developed by Nagaoka et al. [3]; in this way they obtained CA_6 as single crystalline phase at 1,600 °C for 2 h. Using aluminum sulfate solutions and calcium nitrate as starting reagents, Singh and Sharma [4] obtained calcium hexaaluminate in the temperature range of 1,000–1,400 °C. Hexagonal $\text{CaAl}_{12}\text{O}_{19}$ powders have been obtained at 1,200 °C for 2 h by a reverse micelle process [5].

Some calcium aluminate compounds were formed using as a raw material a hazardous waste from tertiary aluminum industry. The first aluminate formed was C_{12}A_7 which at 838–848 °C had a transition to CA_2 , and then it was transformed to CA at 1,000–1,034 °C [6].

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By the combustion method [7], europium-doped calcium aluminate phosphor was obtained at temperatures around 500 °C. The $\text{CaAl}_{12}\text{O}_{19}:\text{Eu}$ phosphor was then investigated for its photoluminescence and thermoluminescence properties.

Cinibulk [8] assigned in his work the structure of magnetoplumbite for CA_6 , which consists of conduction layers and spinel blocks. Calcium hexaaluminate has shown a promise as an interface phase in fiber-reinforced ceramic oxide composites because of its preferred basal-plane cleavage properties. Considering this behavior, Asmi and Low [9] studied the physical and mechanical behavior of alumina composites containing 5–50 wt% CA_6 .

CA_6 is also used as reinforcing material in alumina composites because of its chemical compatibility and mechanical and thermal expansion properties. For this purpose, alumina–calcium hexaaluminate composites were synthesized by the sol–gel technique [10].

Doping hibonite with Ni^{2+} ions, Costa et al. [11] obtained a new turquoise blue ceramic pigment, similar to that of V-doped zircon and Ni-doped willemite pigments.

$\text{CaAl}_{12}\text{O}_{19}$ was successfully used as a doping phase for $\text{CaAl}_{12}\text{O}_{19}:\text{Mn}^{4+}$ [12], which further can be modified by co-doping with different contents of Mg^{2+} [13, 14]. It was observed that increasing the content of MgO in the synthesis process, the red phosphor $\text{CaAl}_{12}\text{O}_{19}:\text{yMn}^{4+}$ ($y = 0.001\text{--}1.5\%$) enhanced its photoluminescence efficiency.

Nie et al. [15] reported Cr^{3+} ion as a co-dopant to modify the unpractical photon cascade emission properties of Pr^{3+} in $\text{CaAl}_{12}\text{O}_{19}$ phosphors.

The polymeric precursors, especially those obtained with citric acid, were used for the synthesis of different compounds [16–19] in advantage conditions.

The purpose of this paper is to establish optimal conditions to achieve thermal analysis, to highlight the characteristic thermal effects associated to solid state reactions of CA_6 formation.

Experimental

The starting reagents were of analytical purity: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Chimopar, Romania), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Scharlau Chemie S.A., Spain), citric acid (S.C. Silal Trading SRL, Romania), ethylene glycol (Chimopar, Romania), acrylic acid (Reactivul, Romania), and benzoyl peroxide (Merck, Germany).

The studied sample compositions are presented in Table 1.

Polymeric precursor method, also called Pechini method relies on the synthesis of polyester resins starting from calcium and aluminum nitrates, citric acid, and ethylene glycol. Sample A_1 was prepared by this method. Sample A_2

Table 1 Studied sample compositions

| Sample | Raw materials | Molar ratio | Phase composition after annealing at/°C |
|--------------|----------------------------|-------------|--|
| A_1 | $\text{Ca}(\text{NO}_3)_2$ | 1 | 600 Amorphous |
| | $\text{Al}(\text{NO}_3)_3$ | 12 | 1,000 $\gamma\text{-Al}_2\text{O}_3$ |
| | Citric acid | 38 | 1,200 CA_2 , $\alpha\text{-Al}_2\text{O}_3$, CA_6 |
| | Ethylene glycol | 38 | |
| A_2 | $\text{Ca}(\text{NO}_3)_2$ | 1 | 600 Amorphous |
| | $\text{Al}(\text{NO}_3)_3$ | 12 | 1,000 $\gamma\text{-Al}_2\text{O}_3$ |
| | Citric acid | 38 | 1,200 CA_6 , $\alpha\text{-Al}_2\text{O}_3$ (traces) |
| A_3 | $\text{Ca}(\text{NO}_3)_2$ | 1 | 600 Amorphous |
| | $\text{Al}(\text{NO}_3)_3$ | 12 | 1,000 $\gamma\text{-Al}_2\text{O}_3$ |
| | Acrylic acid | 57 | 1,200 CA_6 , $\alpha\text{-Al}_2\text{O}_3$ (traces) |

was prepared following the same steps, but without ethylene glycol. Stoichiometric amount of citric acid necessary for chelating Ca^{2+} and Al^{3+} was calculated taking into account the $\text{CaAl}_{12}\text{O}_{19}$ structure, which means 38 mol citric acid to obtain a mole of calcium hexaaluminate. Based on the literature information [20], we worked with an excess of citric acid using the molar ratio citric acid/ $\text{Ca}^{2+}/\text{Al}^{3+} = 38/1/12$. The molar ratio citric acid/ethylene glycol was determined to insure the esterification of all $-\text{COOH}$ groups provided by the citric acid excess.

In the aqueous solution of citric acid, calcium and aluminum nitrates were added and after complete dissolution, a clear solution was obtained at 60–70 °C. Ethylene glycol was added to this solution and then further heated.

After gradual evaporation of water, the reaction mass is subject of the polycondensation process with formation of a resin, that became a crumbly brown to black mass when heated at 200 °C. This resin represents the precursor for the CA_6 formation after subsequent annealing.

Sample A_3 was prepared in the same way as sample A_2 , but the difference consists in the replacement of citric acid with acrylic acid. For the synthesis it was used an excess of 50 % acrylic acid.

Benzoyl peroxide was added for the initiation of the polymerization process. The amount of benzoyl peroxide was calculated as 0.3 wt% referred to acrylic acid.

After complete dissolution and partial evaporation of water, a rubber like material was formed and became a brittle black mass after ignition at 200 °C.

Thermal analyses (TG and DTA) were carried out using a NETZSCH-STA 449 instrument, using Pt crucibles, in air, with a heating rate of 10 K min^{-1} . Tests were conducted on both type of precursors, resulted from the polycondensation reactions (samples A_1 and A_2), and polymerization (sample A_3), respectively, and also on the samples annealed at 200 °C and at 600 °C as well. Phase composition of samples annealed at 600, 1,000, and

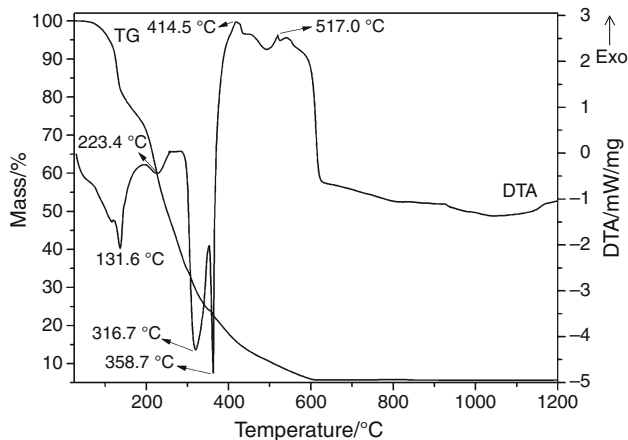


Fig. 1 TG and DTA curves of sample A₁

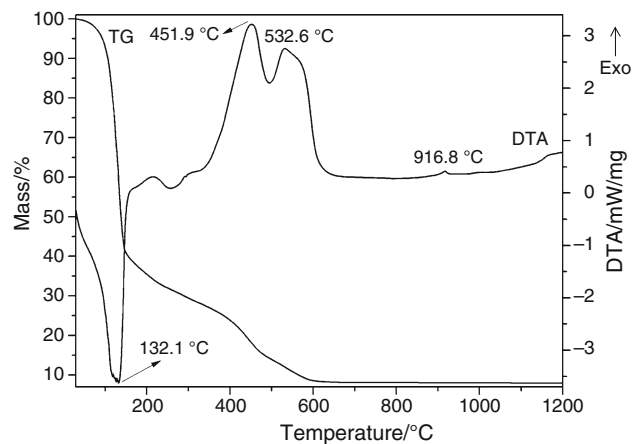


Fig. 3 TG and DTA curves of sample A₃

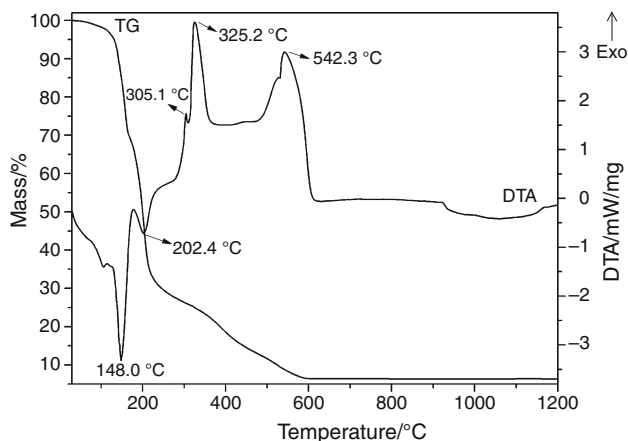


Fig. 2 TG and DTA curves of sample A₂

1,200 °C was determined by X-ray diffraction, using a DRON 3 diffractometer, $\text{CuK}\alpha$ radiation.

Results and discussion

The samples as resulted in the polyesterification and polymerization processes, respectively, were subjected to thermal analysis. Thermal analysis of samples A₁–A₃ are shown in Figs. 1–3.

A sequence of successive processes assigned to the degradation of precursor resin was distinguished in all samples.

It is noted that the endothermic processes in the sample A₁ extend nearly to 400 °C, while in sample A₂ and A₃ they are completed before 300 °C. This can be explained by a higher thermal resistance of polyester resin resulted in the sample A₁ after polycondensation reaction between citric acid with ethylene glycol.

The endothermic processes are followed by successive exothermic processes for all the samples.

It may be noted that the exothermic effects pointed out on the DTA curve of sample A₂, closely resemble to those of citric acid, suggesting the presence of citric acid, derived from the excess used in the recipe, and unprocessed in a resin in the absence of ethylene glycol.

The total mass loss for all samples, A₁–A₃ is very high (94.27, 93.59, and 91.86 %); this loss corresponds to the degradation of organic component of the resin. Very small amount of oxide sample (represented by CaO and Al₂O₃) is left after the degradation of resin, which makes it practically impossible to track any interactions between the two oxides through thermal effects.

For this reason, the samples were previously subjected to heat treatment at 200 °C, to assure the partial degradation of the resin along with a significant mass loss. Thermal analyses performed on these samples are presented in Figs. 4–6. All the pre-fired samples show a much smaller mass loss (27.3 % for sample A₁, 40.5 % for the sample A₂, and 36.04 % for sample A₃, respectively).

Thermal analysis of samples A₁–A₃ are similar, regarding the development of some exothermic processes over 300 °C and attributed to oxidative degradation of precursor resin accompanied by mass loss.

In the case of sample A₁, this process ends at 760 °C, while for sample A₂, this is extended up to 950 °C and even up to 1,000 °C for sample A₃. Sample A₁ is distinguished from samples A₂ and A₃ because between 760 and 850 °C a slight (0.73 %) increase of mass is recorded on the TG curve, which may be due to the presence in the sample of the CaCO₃ and CaO that reacts with the CO₂ resulted from the thermal degradation of the resin. The simultaneous presence of CaO and CaCO₃ in the sample at 850 °C is supported by the mass loss ($\Delta m_{850-950\text{ °C}} = -3.24\%$).

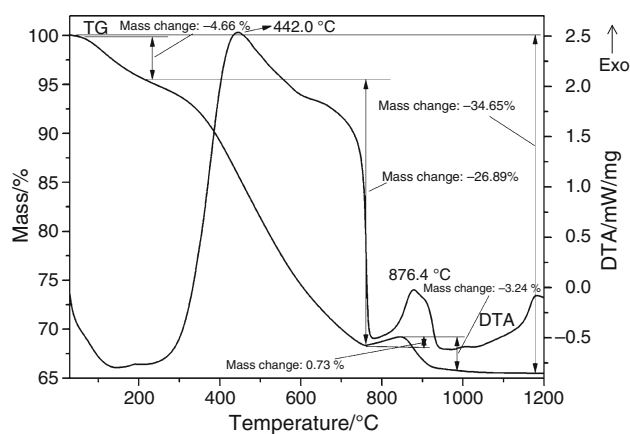


Fig. 4 TG and DTA curves of sample A₁ pre-fired at 200 °C/1 h

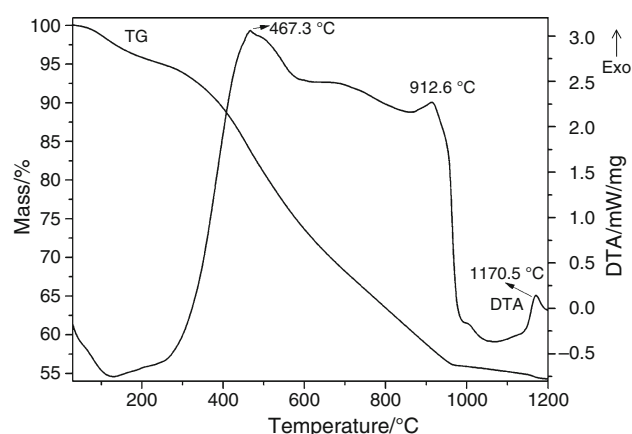


Fig. 6 TG and DTA curves of sample A₃ pre-fired at 200 °C/1 h

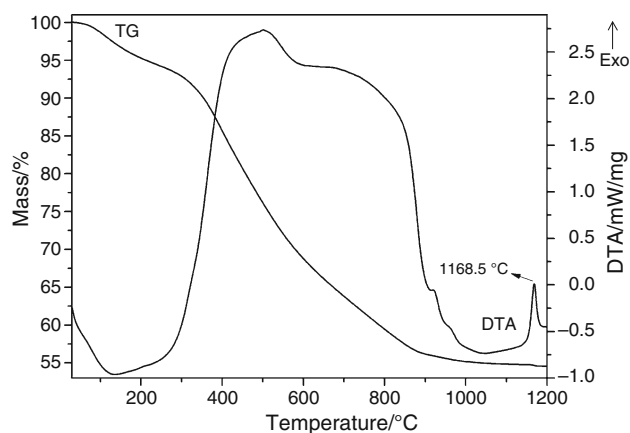


Fig. 5 TG and DTA curves of sample A₂ pre-fired at 200 °C/1 h

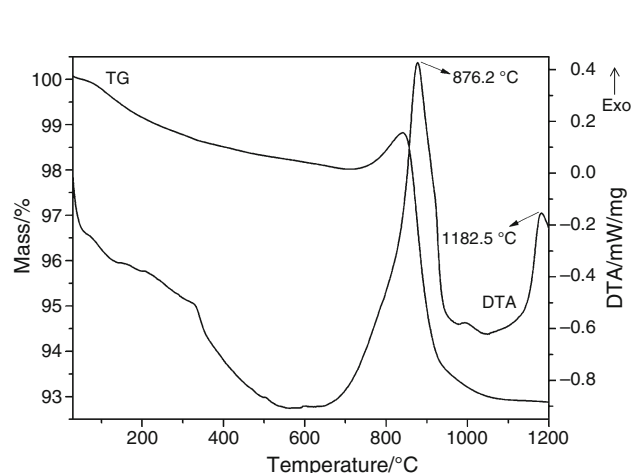


Fig. 7 TG and DTA curves of sample A₁ pre-fired at 600 °C/1 h

Taking into account the stoichiometry of the mixture and the final mass of the sample, in the absence of CaO, the mass loss due to decarbonation should be 4.17 %.

Exothermic process with maximum at 876.4 °C accompanied by mass loss can be possibly attributed to the overlap of the crystallization process of γ -Al₂O₃ over the decarbonation of CaCO₃.

The exothermic effect without mass variation over 1,100 °C is attributed to the formation of CA₆.

For a better highlighting of these processes, the samples were subjected to previous annealing at 600 °C before performing the thermal analyses (Figs. 7–9).

In this case, the exothermic effects are clearly outlined: sample A₁ shows an exothermic effect relatively strong with a peak at 876.2 °C. On the TG curve, the exothermic effect is preceded by an increase of mass as in the case of sample A₁ pre-fired at 200 °C.

Samples A₂ and A₃ show on DTA curve similar effects at higher temperatures, i.e., at 920.9 and 919.4 °C, respectively that are not preceded by the increase of mass.

These exothermic effects are attributed to the solid state reaction between CaO and Al₂O₃. Mass loss that

accompanies these processes can be attributed to decomposition of CaCO₃ present in the sample.

Even if sample A₃ was also pre-fired at 600 °C/1 h, it shows a maximum at 472.8 °C. This can be explained by the lack of the necessary amount of oxygen, present in the sample, to accomplish a complete burn of the resin.

Mass loss of samples, resulting in parallel with the crystallization process can be partially attributed to decomposition of CaCO₃, formed during thermal degradation, and to the degradation of the organic components from the resin.

It should be noted that in this case, the presence of CaCO₃ as calcite at temperatures below 800 °C was not obvious, as had happened in the synthesis of other calcium aluminate by the same method [21]. The lack of calcite in these samples can be explained by the difficulty of its crystallization in samples consisting mainly of Al₂O₃ and low CaO contents, respectively.

Sample A₁ shows a relatively weak exothermic effect with a maximum at 1182.5 °C, and practically no mass

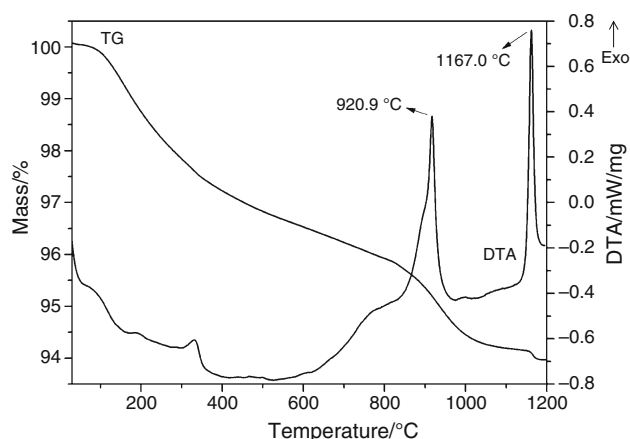


Fig. 8 TG and DTA curves of sample A₂ pre-fired at 600 °C/1 h

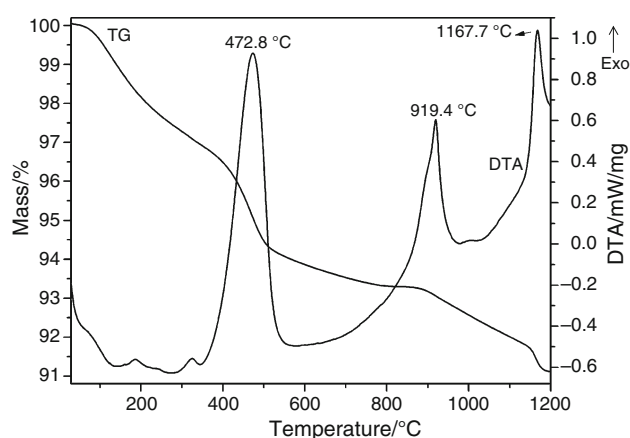


Fig. 9 TG and DTA curves of sample A₃ pre-fired at 600 °C/1 h

variation. For sample A₂, similar exothermic effect that runs at slightly lower temperature (1,167.0 °C) is stronger, narrower, and with a clear mass variation even if it is very small (0.23 %). In the case of sample A₃, the exothermic effect occurs at 1,167.7 °C with a mass variation of 0.72 %. These exothermic effects suggest reactions in solid state between CaO and Al₂O₃ or more likely between CA₂ and Al₂O₃.

X-ray diffraction patterns of samples A₁–A₃ annealed at 600 °C show that all the samples are amorphous (Table 1).

XRD patterns of samples A₁–A₃ after annealing at 1,000 °C show an almost identical phase composition: weak crystallized γ -Al₂O₃ phase (Table 1). This phase composition, confirms the assignment of the exothermic effect around the temperature of 900 °C to the crystallization process of γ -Al₂O₃.

Figure 10 shows the XRD patterns of samples A₁–A₃ after annealing at 1,200 °C. The net difference between the sample A₁–A₃ is obvious. In the sample A₁, the main phase is CA₂, with unreacted α -Al₂O₃ and only low proportion of the designed compound CA₆. For samples A₂ and A₃, the

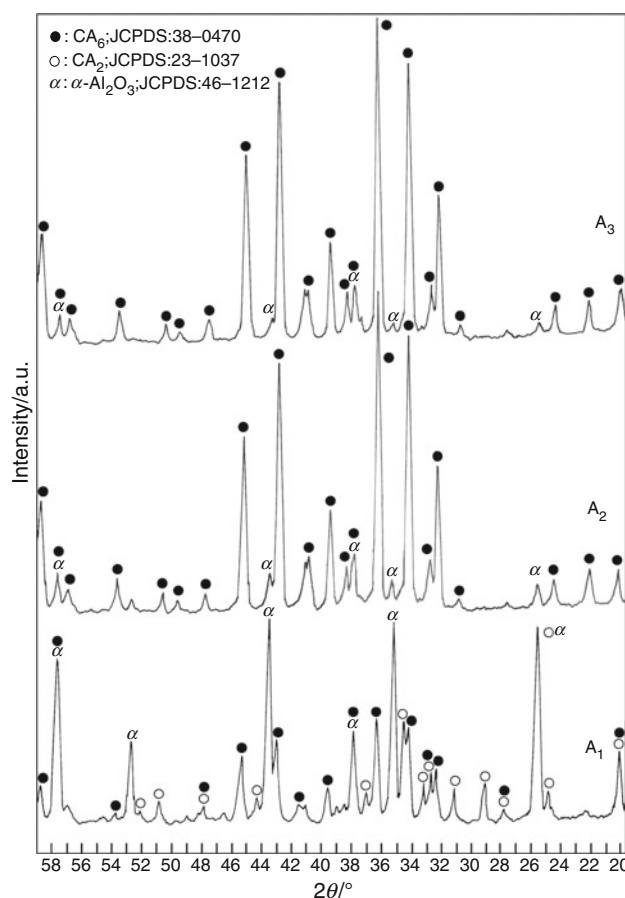
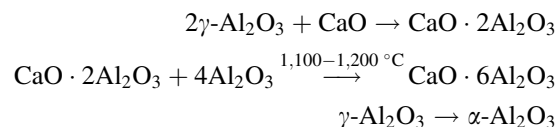


Fig. 10 XRD patterns of samples A₁–A₃ annealed at 1,200 °C/1 h

main phase is the designed compound CA₆, and a low proportion of α -Al₂O₃ that can be considered just traces.

Correlating the thermal analysis with X-ray diffraction patterns of the samples annealed at 1,000 and 1,200 °C, the exothermic effect at 876–920 °C can be assigned to the γ -Al₂O₃ crystallization and the exothermic effect at 1,167–1,182 °C to the formation of CA₆.

The evolution of the phase composition of the studied samples between 1,000 and 1,200 °C suggests the following succession of the calcium aluminates formation:



Showing a net difference on the forming capability of the designed compound, CA₆, between the samples can be concluded:

- For sample A₁, prepared according to traditional Pechini method, the designed compound (CA₆) is formed only in small proportion after annealing at 1,200 °C.

This finding confirms the difficult formation of this compound, which requires higher temperatures. To preserve the distinctive advantages of unconventional methods, the solution of temperature increase is uninteresting.

- For sample A₂, free of ethylene glycol, there are surprisingly observed, much more favorable conditions for obtaining the designed compound.
- For sample A₃ prepared with acrylic acid the obtained results are similar with the one obtained in the case of sample A₂.

Conclusions

CA₆ formation through ignition at 1,200 °C depends on the nature of the used precursors:

- The polyester-type precursor obtained from citric acid, ethylene glycol, and calcium and aluminum nitrates, leads to the formation of CA₆ along with CA₂ and α -Al₂O₃ (sample A₁).
- The precursor obtained from citric acid and calcium and aluminum nitrates leads to the formation of CA₆ and just traces of α -Al₂O₃ (sample A₂).
- The polymeric type precursor derived from acrylic acid and calcium and aluminum nitrates leads to the formation of CA₆ and just traces of α -Al₂O₃ (sample A₃).

Rational choice of the conditions for prior heat treatment of the samples, to achieve thermal analysis, allows the highlighting of the exothermic processes that accompany the formation of CA₆. The information provided by thermal analysis are confirmed by phase composition through X-ray diffraction.

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