J Therm Anal Calorim (2011) 105:427–434
DOI 10.1007/s10973-010-1246-2

The use of thermal analysis in the study of $Ca_3Al_2O_6$ formation by the polymeric precursor method

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ESTAC2010 Conference Special Issue

Abstract Single-phase $Ca_3Al_2O_6$ was prepared via polymeric precursor method. The influence of the reactants nature in the $Ca_3Al_2O_6$ synthesis was investigated. For this purpose, citric acid and soluble salts of calcium (nitrate, chloride, carbonate) and aluminium (nitrate, chloride, acetate) were used as starting materials, in the presence and, respectively, in the absence of ethylene glycol. $Ca_3Al_2O_6$ resulted as single-phase after annealing at 1050 °C for 1 h only starting from calcium nitrate or carbonate and aluminium nitrate or acetate as salts precursor for Ca^{2+} and Al^{3+} cations. The formation of $Ca_3Al_2O_6$ is not conditioned by the ethylene glycol presence in these mixtures. Using calcium and aluminium chlorides, the phases present at 1050 °C are $Ca_{12}Al_{14}O_{33}$ and unreacted CaO.

Keywords Calcium aluminates · Pechini method · Polymeric precursor method · Thermal analysis

Introduction

Tricalcium aluminate, $Ca_3Al_2O_6$ or $3CaO{\cdot}Al_2O_3$ (C_3A) is one of the important mineralogical compounds in the Portland cement composition. Beside the wide use of C_3A in the cement technology, recently has been reported the possibility to produce a novel red light-emitting material $Ca_3Al_2O_6{:}Eu^{3+}$, in which the activator Eu^{3+} is hosted in the lattice of $Ca_3Al_2O_6$ [1]. Tricalcium aluminate has also been successfully used as doping phase for improving the bioactivity and biocompatibility of the calcium aluminate bone cement [2] and nickel support as catalyst for methane partial oxidation to syngas (CO and H_2) [3].

The preparation of C_3A via conventional methods based on annealing mechanical mixtures of oxides, hydroxides and/or salts, requires high temperatures (1200–1400 °C) and is always preceded by the formation of various intermediate phases such as $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) or $CaAl_2O_4$ (CA) [4–6].

To avoid the disadvantages of the conventional route, many chemical unconventional methods have been developed for the C_3A synthesis [7–29].

Stephan and Wilhelm [7] used the sol–gel method for the C_3A synthesis. Only after three annealing cycles of 14 h at 1260 °C with intermediate grindings they obtained C_3A together with insignificant amounts of CaO and $C_{12}A_7$.

Douy and Gervais [8] prepared pure C_3A at 1230 °C using spray-drying of calcium and aluminium nitrates aqueous solution.

The use of some complex combinations as precursors for preparing C_3A has been also attempted [9, 10]. Using as precursor the complex combination resulted by oxidation of ethylene glycol by calcium and aluminium nitrates, Lazău et al. [9] prepared C_3A as single-phase at 1000 °C.

A solution-polymerization route, based on polyvinyl alcohol as polymer carrier [11–13] represents another alternative for preparing C_3A.

The combustion method was also investigated for the calcium aluminate synthesis [14–19]. Taş reported [16] the synthesis of pure C_3A after annealing the powders at 1050 °C for 48–72 h using urea, carbohydrazide or glycine as fuel. The use of fuel mixtures in the combustion method represents a significant innovation noticed by Ianoş et al. [17–19]. This new approach allows obtaining pure C_3A,

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directly from the combustion reaction, without any further annealing, using a mixture of urea and β-alanine as fuel [19].

In the past years, Pechini method (also known as the citrate route or polymeric precursor method) has been widely reported for the synthesis of many oxide powders [20–24].

Invented by Pechini [25], this process involves a polyester-type resin formation which represents the polymeric carrier for the pre-ceramic powder. In this route, citric acid acts as a chelating agent of the dissolved metal cations. The cation sources are soluble salts, usually nitrates. By heating the solution of these chelates and a polyhydroxy alcohol (usually ethylene glycol) at temperatures between 150 and 250 °C, the polycondensation reaction takes place and results in the resin formation, in which the metal cations are uniformly distributed.

This method was also investigated for the synthesis of different calcium aluminates [26–29]. Using nitrates salts and a molar ratio citric acid/total cations = 1, Gaki et al. [26] obtained pure C_3A after annealing at 1000 °C for 3 h. Starting from aluminium nitrate and calcium carbonate, Yuan et al. [29] studied the influence of the molar ratio citric acid/total cations on the C_3A formation. For molar ratio citric acid/total cations = 1, respectively, 2, the annealing temperature for obtaining C_3A was 1100 °C for 2 h, whilst when using a molar ratio citric acid/total cations = 4, single-phase C_3A was obtained after annealing at 1000 °C for 2 h.

The article deals with a systematic and original study regarding the influence of the reactants nature in the C_3A synthesis using the polymeric precursor's method.

The behaviour of the polymeric precursor depending on the thermal treatment conditions has been also investigated.

Experimental

The raw materials used were: $Ca(NO_3)_2 \cdot 4H_2O$ (Reactivul, Romania), $CaCl_2 \cdot 2H_2O$ (Reactivul, Romania), $CaCO_3$ (Reactivul, Romania), $Al(NO_3)_3 \cdot 9H_2O$ (Merck, Germany), $AlCl_3 \cdot 6H_2O$ (Reactivul, Romania), $Al(OH)(CH_3COO)_2$ (Riedel de Haën, Germany), citric acid (Chimopar, Romania) and ethylene glycol (Reactivul, Romania). The compositions of the studied samples are presented in Table 1.

The difference between the samples 1, 3 and 4 was the nature of the salts used as the source for the Ca^{2+} and Al^{3+}cations, in order to emphasize the role that they play in obtaining C_3A as single-phase. The molar ratio Ca^{2+}/Al^{3+} for all the four samples was the same, 3/2, in order to result C_3A.

Starting from the literature data [29], the citric acid was taken in excess over the stoichiometric amount needed. We worked with the molar ratio citric acid/Ca^{2+}/Al^{3+} = 15/3/2. The molar ratio citric acid/ethylene glycol was established in order to ensure the esterification of all –COOH groups by the citric acid excessively used.

The polymeric precursor for the four samples was prepared by the following procedure: the calcium and aluminium salts, in the molar ratios presented in Table 1, were dissolved in the aqueous solution of citric acid at the temperature of 60–70 °C, resulting in a homogeneous solution. Ethylene glycol was added (sample 2 excepted) to the obtained solution under continuous heating.

After complete water evaporation, the reaction mass undergoes a polycondensation process. The resulted resin represents the precursor for the C_3A formation after thermal treatments at temperatures between 600 and 1050 °C.

Investigations regarding the mechanism of C_3A synthesis were performed via thermal analysis using a NETZSCH-STA 449C instrument. The TG/DTA curves were recorded in the range 25–1200 °C with a heating rate of 10 K min^{-1}, using platinum crucibles. The experiments were carried out in nitrogen atmosphere and also in artificial air at a flow rate of 20 mL min^{-1}. Samples were also characterized by means of IR spectroscopy. FTIR spectra were carried out using a Shimadzu Prestige-21 spectrometer in the range 400–4000 cm^{-1}, using KBr pellets and resolution of 4 cm^{-1}.

The phase composition evolution of the samples was monitored by XRD using a DRON 3 diffractometer with $Cu_{K\alpha}$ radiation. BET surface area measurements were performed using a Micromeritics ASAP 2020 instrument and nitrogen as adsorption gas.

Results and discussion

The mixture of raw materials corresponding to sample 1 (solution) was subjected to thermal analysis in nitrogen atmosphere (Fig. 1).

The strong endothermic effect at 146.4 °C accompanied by large mass loss on TG curve can be assigned to the removal of the free water and crystallization water. The second endothermic effect at 223.0 °C accompanied also by mass los was assigned to the removal of the water resulted from the polycondensation processes. A small endothermic effect follows on DTA curve, accompanied by mass loss at 400 °C, associated with some degradation processes of the precursor resin. Between 400 and 600 °C, weak exothermic effects may be noticed which can be assigned to some oxidative degradation processes of the precursor resin. These oxidative degradation processes rely on the existing oxygen in the resin composition.

It has to be noted that the sample mass remaining after the water removal from the solution subjected to the thermal analysis was very small and therefore, the processes that took place over 400 °C were insufficiently

Table 1 Compositions of the studied samples

Sample no.	Reactants				Molar ratio
1	$Ca(NO_3)_2$	$Al(NO_3)_3$	Citric acid	Ethylene glycol	3:2:15:16.5
2	$Ca(NO_3)_2$	$Al(NO_3)_3$	Citric acid	–	3:2:15
3	$CaCl_2$	$AlCl_3$	Citric acid	Ethylene glycol	3:2:15:16.5
4	$CaCO_3$	$Al(OH)(CH_3COO)_2$	Citric acid	Ethylene glycol	3:2:15:16.5

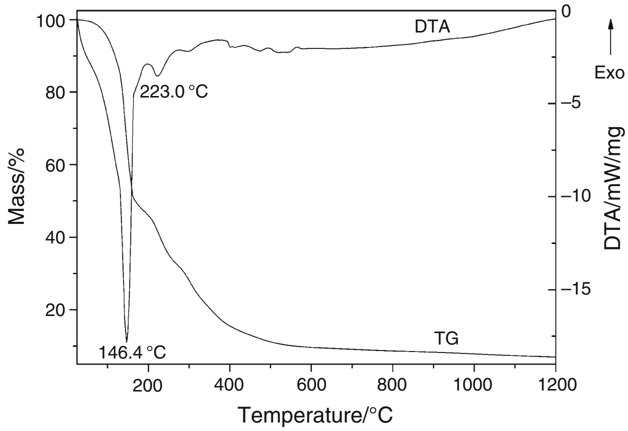

Fig. 1 TG and DTA curves of the mixture of raw materials corresponding to sample 1, recorded in nitrogen atmosphere

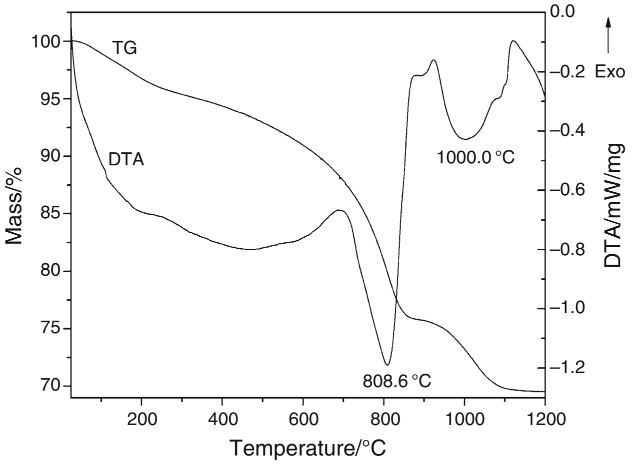

Fig. 2 TG and DTA curves of the precursor 1, pre-fired at 400 °C/1 h, recorded in nitrogen atmosphere

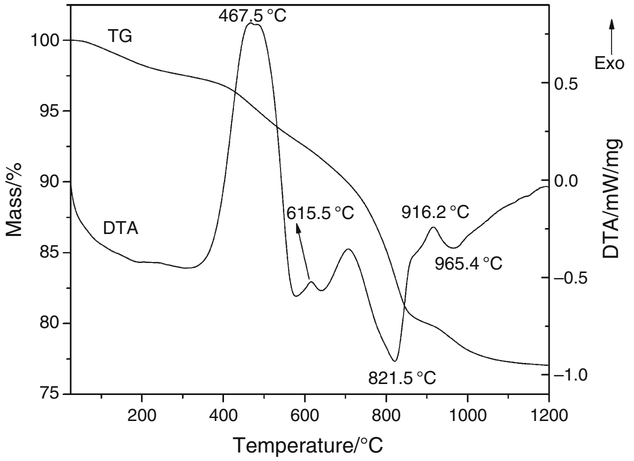

Fig. 3 TG and DTA curves of the precursor 1, pre-fired at 400 °C/1 h, recorded in air atmosphere

emphasized. To get more information regarding the processes development at higher temperatures, the sample was pre-fired at 400 °C for 1 h and only afterwards subjected to thermal analysis.

Figure 2 shows the TG and DTA curves of the precursor 1, pre-fired at 400 °C/1 h, recorded in nitrogen atmosphere.

As result of pre-firing the sample at 400 °C, in the range 20–500 °C, TG curve shows a low and continue mass loss associated with some resin residues decomposition and accompanied on the DTA curve by a small but large endothermic effect.

The strong endothermic effect at 808.6 °C accompanied by a significant mass loss was associated with the decomposition of $CaCO_3$ resulted from the polymeric resin degradation. The large endothermic effect between 950–1100 °C, accompanied by mass loss on TG curve, could be assigned to the unoxidative degradation of the last organic residues from the resin.

The results of the FTIR analysis shown below evidence the presence of organic residue in the samples annealed at 600 and 850 °C.

The behaviour of the polymeric resin 1, pre-fired at 400 °C, subjected to thermal analysis in air atmosphere (Fig. 3) essentially differ in the range 350–650 °C compared with its behaviour in nitrogen atmosphere.

In this case, the DTA curve (Fig. 3) shows a large exothermic effect between 400 and 580 °C, accompanied by mass loss on TG curve. This effect is due to the combustion reactions of the organic residues resulted from the resin degradation, reactions favoured by the presence of the oxygen in the working atmosphere. The weak exothermic effect at 615.5 °C, accompanied also by mass loss, is associated with the burning of organic carbon left behind by the resin degradation. $CaCO_3$ decomposition is in this case also pointed out on the DTA curve at 821.5 °C, accompanied by mass loss.

In the 850–1200 °C range, the sample behaviour is similar, whether the working atmosphere was nitrogen or air. The endothermic effect above 850 °C is pointed out in both nitrogen and air atmosphere. The endothermic effect which appears in nitrogen atmosphere between 930 and 1100 °C can be also observed in air atmosphere but, in this case, the endothermic effect and the mass loss are smaller.

The thermal analysis in air atmosphere of samples 2–4, pre-fired at 400 °C are shown in Figs. 4, 5, 6.

From the comparative analysis of the four samples thermal behaviour, the following conclusions result: all the samples present on the DTA curve, the endothermic effect associated with the $CaCO_3$ decomposition to CaO and CO_2 (at 821.5 °C—sample 1, 807.6 °C—sample 2, 822.5 °C—sample 3 and 844.8 °C—sample 4); therefore, regardless the used calcium salt (nitrate, chloride, carbonate), the C_3A obtaining is preceded by the CaO formation. Relatively low decomposition temperature of $CaCO_3$, around 820 °C, suggests that the resulted CaO is present in a fine dispersed and highly reactive form.

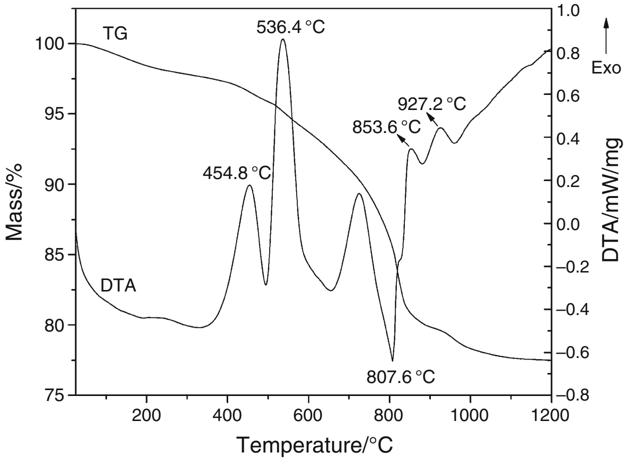

Fig. 4 TG and DTA curves of the precursor 2, pre-fired at 400 °C/1 h, recorded in air atmosphere

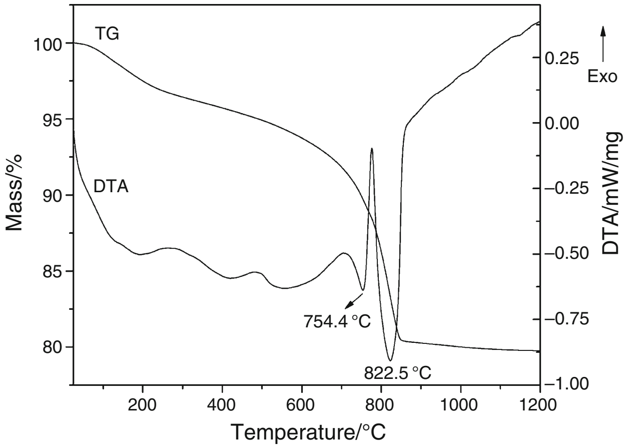

Fig. 5 TG and DTA curves of the precursor 3, pre-fired at 400 °C/1 h, recorded in air atmosphere

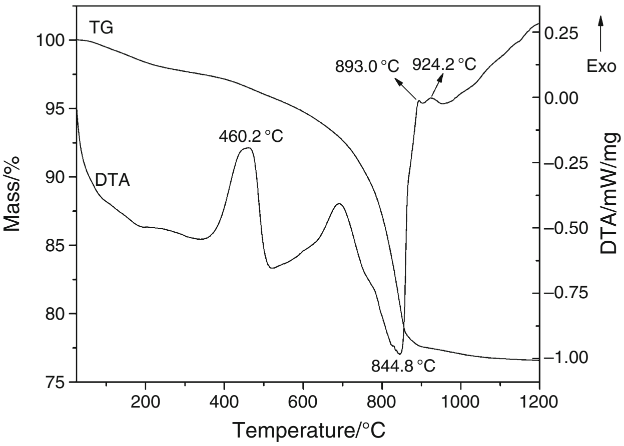

Fig. 6 TG and DTA curves of the precursor 4, pre-fired at 400 °C/1 h, recorded in air atmosphere

The $CaCO_3$ presence in the samples annealed at 600 °C is supported by the XRD results (Fig. 7).

In all the samples annealed at 600 °C, the single crystalline phase present is $CaCO_3$ (calcite). The explanation for the presence of this phase is the reaction between the CaO and CO_2 (resulted from the resin degradation) forming $CaCO_3$. The decomposition of $CaCO_3$ at temperatures below 850 °C is also supported by RX diffraction analysis—that shows the lack of $CaCO_3$ (calcite) at this temperature for all the samples (Fig. 8).

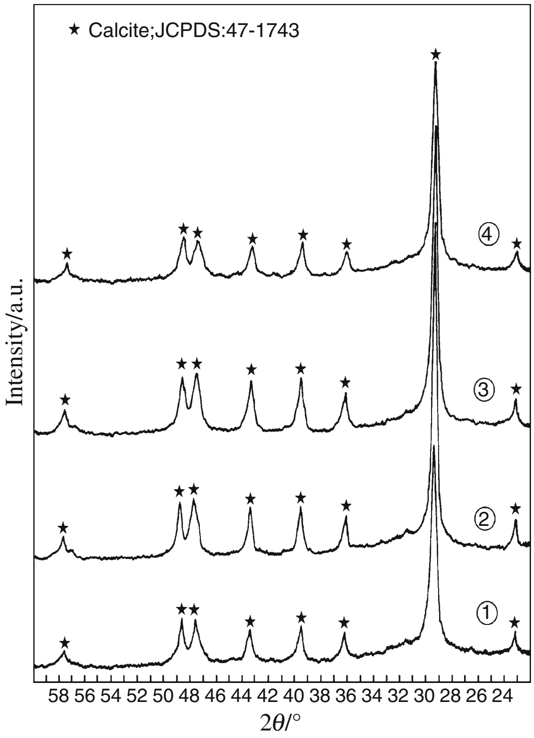

Fig. 7 XRD patterns of samples 1, 2, 3, and 4 annealed at 600 °C/1 h

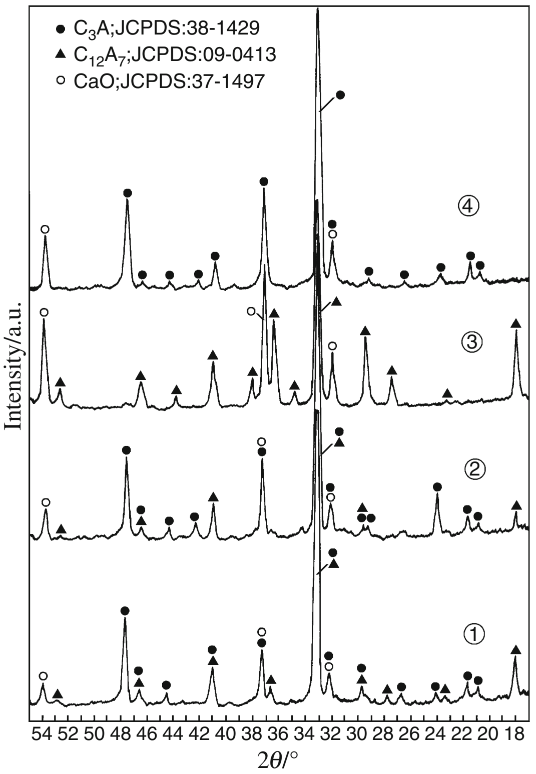

Fig. 8 XRD patterns of samples 1, 2, 3 and 4 annealed at 850 °C/1 h

In the temperature range 350–650 °C, the behaviour of samples 1 and 4 is similar. Sample 2, differing from sample 1 only by the lack of ethylene glycol, shows two distinct exothermic effects between 350 and 650 °C, unlike sample 1 presents a single large exothermic effect. This behaviour could be explained by the fact that the ethylene glycol present in sample 1 participates at polycondensation processes with the carboxyl groups by the citric acid excessively used, resulting a resin in which the Ca^{2+} and Al^{3+} cations distribution is statistical.

Unlike samples 1, 2 and 4, which present strong exothermic effects between 350 and 650 °C, sample 3 presents only a weak exothermic effect between 420 and 550 °C with a small mass loss. This behaviour can be explained by the fact that, the resin degradation during the sample prefiring at 400 °C was more advanced for sample 3 (starting from chlorides) compared with samples 1, 2 and 4.

The weak exothermic processes between 850 and 930 °C for samples 1, 2 and 4 are associated with the reaction between the newly formed CaO and the Al_2O_3 present in the mixture, forming $C_{12}A_7$ and after that, the reaction between $C_{12}A_7$ and CaO, resulting C_3A. These effects lack in the case of sample 3.

Over 930 °C, the DTA curves of samples 2 and 4 point out weak exothermic effects with a small mass loss, similar to sample 1.

Assigning these effects to the unoxidative resin degradation is supported by the observation made on samples removed from the platinum crucible: even after reaching the temperature of 1000 °C samples were grey at the bottom, whilst the colour at the top was pure white. The presence and the possible influence of the highly dispersed residual carbon on the C_3A formation should not be neglected. This residual carbon could prevent the Al_2O_3 crystallization process during the temperature rise, keeping it into a reactive form which enters in reaction with the very reactive CaO resulted from the $CaCO_3$ decomposition. This assumption is supported by the existing observations in literature, according to which, the excess of citric acid favours the formation of C_3A [29].

Unfortunately, the XRD analysis do not reveals the presence of a crystallized aluminium precursor for any of the samples. For this reason, one can only make suppositions based on the thermal analysis results regarding the aluminium precursor that reacts with CaO forming C_3A.

The results of the phase analysis for the samples annealed at 850 °C show differences depending on the source of Ca^{2+} and Al^{3+} cations. In samples 1 and 2 (where nitrates of calcium and aluminium were used) and also in sample 4 (where calcium carbonate and basic aluminium acetate were used), C_3A is already present alongside $C_{12}A_7$ and CaO. In sample 3, at 850 °C was revealed only $C_{12}A_7$ and CaO whilst C_3A is absent.

At 1050 °C, the XRD analysis (Fig. 9) shows the presence of a single-phase C_3A only in the samples 1, 2 and 4. As the phase composition of sample 3 annealed at 600 °C proves the presence of $CaCO_3$ as in the case of the other samples, and the thermal analysis (Fig. 5) shows its decomposition at 822.5 °C, results that, the difference in case of sample 3 is the precursor for the Al^{3+} cations. At 1050 °C, the phase analysis of sample 3 does not change compared to the phase analysis at 850 °C, what means that C_3A was not formed.

Taking into account that a large part of diffraction maximum of $C_{12}A_7$, C_3A and CaO overlap, the clear delimitation of these phases was made based on the following peaks at: $2\theta = 18.126°$ (only for $C_{12}A_7$), $2\theta = 47.626°$ and $2\theta = 59.272°$ (only for C_3A), $2\theta = 53.856°$ (only for CaO).

The FTIR spectra of the samples 1–4 annealed at 600, 850 and 1050 °C are shown in Figs. 10, 11, 12, 13.

The results of the FTIR spectra are in accordance with the statements made on the bases of the thermal analysis and XRD spectra.

- At 600 °C, all the samples present the specific bands of CO_3^{2-} ions from $CaCO_3$: 712, 880–860,1450–1410,1795 cm^{-1} [30, 31]. The broad band located at 3450–3500 cm^{-1} is due to –OH stretching vibration (intermolecular hydrogen bond) of the organic residue

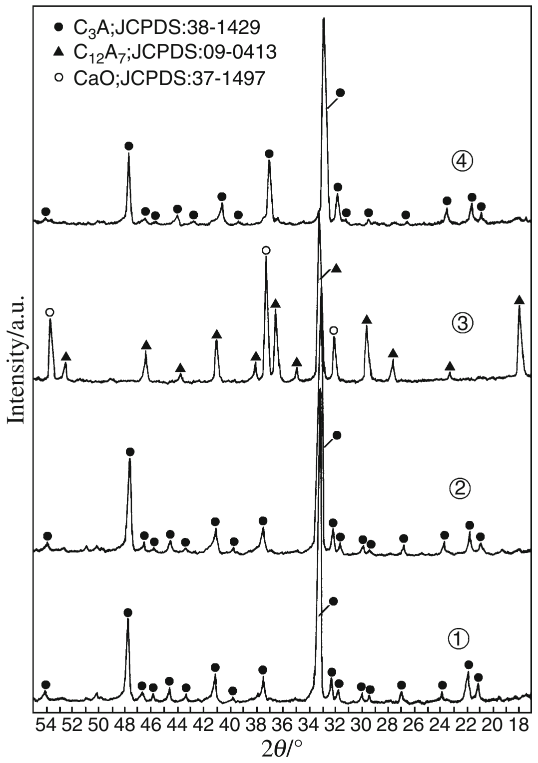

Fig. 9 XRD patterns of samples 1, 2, 3 and 4 annealed at 1050 °C/1 h

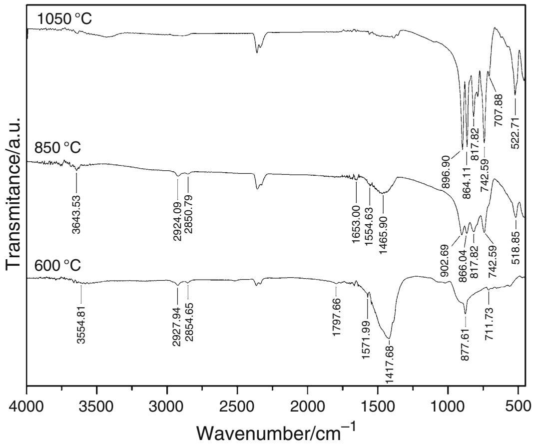

Fig. 10 FTIR spectra of sample 1, annealed at 600, 850 and 1050 °C/1 h

[31]. The two bands located in the region 2850–2927 cm^{-1} are assigned to the asymmetrical and symmetrical stretching vibrations of CH_2 [31].

- At 850 °C, in all samples spectra, the intensity of characteristic bands of CO_3^{2-} ions decreases; the two bands located in the region 2850–2927 cm^{-1} are present; instead of a broad band located at 3450–3500 cm^{-1}, a sharp band appears, located at 3643 cm^{-1} and assigned to free (monomeric) –OH [31]. The specific bands of calcium aluminates appear in the region 500–909 cm^{-1}.

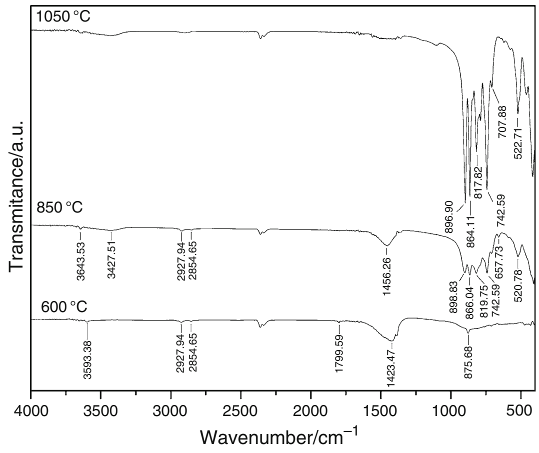

Fig. 11 FTIR spectra of sample 2, annealed at 600, 850 and 1050 °C/1 h

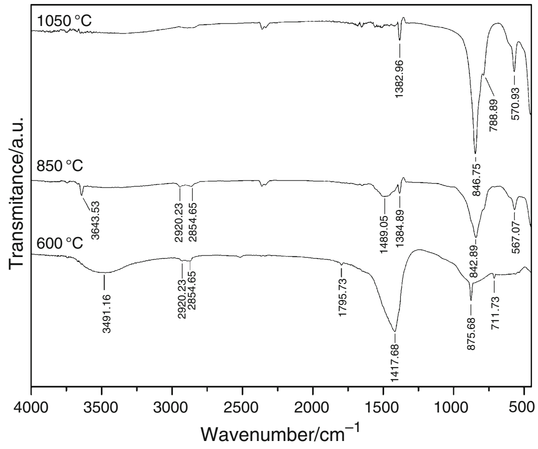

Fig. 12 FTIR spectra of sample 3, annealed at 600, 850 and 1050 °C/1 h

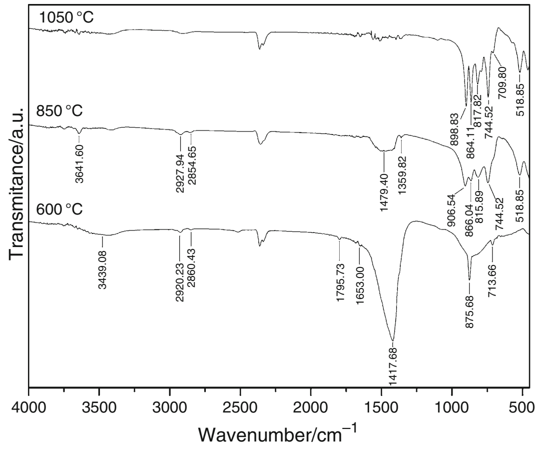

Fig. 13 FTIR spectra of sample 4, annealed at 600, 850 and 1050 °C/1 h

- At 1050 °C, all the samples show the characteristic bands of calcium aluminates. Between samples 1, 2 and 4 on one side and sample 3 on other side, there is a major difference, in full agreement with the XRD spectra: samples 1, 2 and 4 show the characteristic bands for C_3A [32], whilst sample 3 shows the characteristic bands for $C_{12}A_7$. The sharp band located at 1382.96 cm^{-1} may be assigned to –OH group, resulted by the interaction of $C_{12}A_7$ or CaO with atmospheric moisture.

For samples 1, 2 and 4, annealed at 1050 °C, containing single-phase C_3A, the specific surface area was performed. The obtained values were: 4.34 $m^2\ g^{-1}$ for sample 1, 3.69 $m^2\ g^{-1}$ for sample 2 and 3.31 $m^2\ g^{-1}$ for sample 4. These values are comparable with those reported by Gülgün et al. [13] (4.2 $m^2\ g^{-1}$) at the C_3A preparation starting from low polymerization degree PVA.

The larger specific surface area of sample 1 compared with sample 2 may be explained by the ethylene glycol presence in the precursor resin and the higher gas volume resulted in the resin degradation process. Comparing the specific surface area of samples 1 and 4, it can be noticed that the specific surface area of C_3A depends also by the salt used as the source of the two cations. The smaller specific surface area of sample 4 suggests the starting of the C_3A formation at a lower temperature than for sample 1 and at the temperature rise up to 1050 °C, a more advanced crystallization process takes place in sample 4.

Conclusions

The results of thermal analysis corroborated with the XRD investigations provided valuable information regarding the underlying processes for the C_3A synthesis using the polymeric precursor method. It was proved that $CaCO_3$ (calcite) is the intermediate compound formed by the resin degradation in all the studied cases.

The synthesis of C_3A as single-phase using the polymeric precursor method was conditioned by the raw materials used. C_3A resulted as single-phase after annealing at 1050 °C for 1 h only starting from calcium nitrate or carbonate and aluminium nitrate or acetate as salts precursor for Ca^{2+} and Al^{3+} cations. The obtaining of C_3A is preceded by the formation of $C_{12}A_7$ and CaO, which leads to C_3A according to the reaction:

$$C_{12}A_7 + 9\ CaO\ = 7C_3A$$

Even if, using calcium and aluminium chlorides, the homogeneity of the Ca^{2+} and Al^{3+} cations in the precursor resin was performed at ionic scale, C_3A was not obtained. In this case, at 1050 °C, the only present phases were $C_{12}A_7$ and CaO. This shows that the two phases formed in the presence of chlorides have a lower reactivity.

The lack of ethylene glycol in the reaction mixture did not affect the C_3A formation. This shows that –COOH and –OH, by the citric acid used in excess, lead to the formation of a resin, in a proportion which ensures the formation of C_3A at 1050 °C.

Acknowledgements This study was partially supported by the strategic grant POSDRU/88/1.5/S/50783, Project ID50783 (2009), co-financed by the European Social Fund—Investing in People, within the Sector Operational Programme Human Resources Development 2007–2013.

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