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Study by DTA/TG of the formation of calcium aluminate obtained from an aluminium hazardous waste

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Abstract A Spanish hazardous waste from tertiary aluminium industry was used as a raw material for the synthesis of calcium aluminate. An amorphous precursor was obtained by a hydrothermal method at different values of pH. The transformation of the precursor in a crystalline aluminate was followed by TG/DTA up to 1300 °C. At temperatures between 719 and 744 °C, the precursors evolve towards the formation of $C_{12}A_7$ which becomes CA at circa 1016 °C. Mass spectrometry coupled to thermal analyser allowed the identification of the decomposition products.

Keywords Aluminium waste · Calcium aluminate · TG/DTA

Introduction

Calcium aluminate compounds, $CaAl_2O_4$ (CA), $CaAl_4O_7$ (CA_2) and $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) are widely used as hydraulic binders in the cement industry. CA is the main component of calcium aluminate cements and also plays an important role in the processing and manufacturing of macrodefect-free ceramic cements [1, 2]. CA is also used as a refractory material in the steel industry.

Traditionally pure calcium aluminate phases are synthesized using solid-sate reactions. These reactions involve the sintering of mixtures of oxides or carbonates at high temperature and long time. Recently sol–gel methods and self-combustion or polymeric precursor methods are used as an alternative way to prepare homogeneous precursor phases [3–5]. In these methods, pure reactants (salts, oxides) are employed as starting materials.

In this article, the synthesis and the characterization of an amorphous calcium aluminate precursor obtained by hydrothermal treatment, at different values of pH, from an aluminium hazardous waste (AHW), was studied. The formation of CA from the amorphous precursor was followed by Differential Thermal Analysis, DTA, Thermogravimetric Analysis, TG, and Mass Spectrometry, MS.

The AHW, a very fine powdery solid, generated by the tertiary industry of aluminium, is a complex material which consists of Al_{metal}, corundum, spinel, aluminium nitride, quartz, calcite, iron oxide, other metal oxides, chlorides and other salts [6]. Slag produced in the secondary industry is profitable for the tertiary industry by means of milling, shredding and granulometric classification processes yielding different fractions which are commercialized according to the aluminium content. The finest fraction constitutes the “AHW” referred to above which is stored in safety containers. The European directive on waste, 2008/98/EC [7] defines the waste as H12 because of in the presence of water or humidity, AHW generates toxic gases as hydrogen, ammonia, methane and hydrogen sulphide.

Processes described for the treatment of AHW-related-materials aimed, generally, to render inert products [8–10]. Recently, several procedures have been developed to recover the aluminium content as valuable products, and so the production of glasses [11], glass–ceramics [12] and boehmite [6] are reported.

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The aim of this work is to study by means of TG/DTA, the formation of monocalcium aluminate, CA, using a hazardous waste as Al-bearing product and CaO. A low temperature hydrothermal method was employed to obtain the precursor phase.

Experimental

Materials

A sample of AHW, supplied by a tertiary aluminium industry (Recuperaciones y Reciclajes Roman S.L. Fuenlabrada, Madrid, Spain) was used as source material for Al_2O_3. The major mineralogical composition of the AHW is as follows: 31.2% Al_{metal}, 20.0% Al_2O_3 (corundum), 15.0% $MgAl_2O_4$ (spinel), 8.4% AlN, 8.0% SiO_2 (quartz), 8.2% $CaCO_3$ (calcite), 1.8% Fe_2O_3 (haematite), 1.5% TiO_2, 1.5% chloride (Na/K), 0.7% Al_2S_3 and other minor compounds (metal oxides). Pure CaO (Panreac 97%), 10% v/v HCl solution and 1-M NaOH solution were also used.

Synthesis of precursor

Aluminate precursors were synthesized by a hydrothermal process which consisted of the following stages: In the first one, a 10% v/v HCl solution was used to dissolve the acid-soluble compounds of aluminium content in the AHW, fundamentally metallic aluminium and aluminium nitride. A suspension was obtained which was centrifuged and the Al^{3+} solution was separated of the insoluble solid. This acidic Al^{3+} solution was subjected to the second stage. In this one, a 1-M NaOH solution was added dropwise to a magnetically stirred Al^{3+} solution up to values of pH of 7, 8 and 10 were reached. A gel started to precipitate from the first drop and when the corresponding pH value was achieved, CaO, in the stoichiometric rate Al/Ca to form the monocalcium aluminate was added. The suspension was aged with continuous stirring for 24 h. Then the solid was separated by centrifugation and washed with deionized water until total chloride removing. The solid was dried at 60 °C during 4 days and then it was crushed in a mortar to get a fine powder and it was heated at 90 °C for 24 h. The solid products obtained—aluminate precursors—were characterized by XRD and SEM. Then, they were subjected to thermal treatment to obtain the calcium aluminate and TG/DTA analysis was performed to study their evolution to calcium aluminate.

Analysis and characterization

The samples were chemically analysed by Atomic Absorption Spectroscopy (AAS, Varian Spectra model AA-220FS) and micro X-ray Fluorescence Spectroscopy (XRF, Bruker S8 Tiger model with W tube, LiF crystal analyser and 4 kW of voltage) for Ca- and Al-specific content. C was determined by oxygen combustion in an induction furnace (Leco model CS-244). The identification of phases by X-ray diffraction (XRD) was performed by Bruker D8 Advance diffractometer at 2θ interval between 2° and 70°, with $Cu_{K\alpha}$ radiation ($\lambda = 1.5405$ Å). The morphological characterization of samples was performed by scanning electron microscopy (SEM, Field emission Jeol JSM 6500F). For observation, a powdered sample was embedded into a polymeric resin. A coating of graphite was used to get conducted sample. The Brunauer–Emmett–Teller (BET) surface area of the samples was obtained from nitrogen-adsorption isotherms obtained in a Coulter SA 3100 system, at relative pressure range of 0.04–0.20. Samples were degassed for 4 h before measurement at 300 °C.

The thermal analysis was performed by simultaneous TG/DTA (SETARAM DTA-TG Setsys Evolution 500), at a heating rate of 20 °C min^{-1}, in He atmosphere up to 1300 °C. Alumina crucibles with 30 mg of sample were used. The outlet of the TGA was connected, through a capillary tube held at 200 °C, to the mass spectrometer. In such a configuration, evolved gas products by the thermal treatment could be simultaneously analysed by quadrupolar mass spectroscopy (QMS).The ion detection was performed through secondary electron multiplier which detects very low pressures within Chaneneltron detector. A mass range between 40 and 130 atomic mass unit was studied.

Results and discussion

Precursor characterization

The Ca/Al ratio of the precursors obtained at pH 7, 8 and 10 are: 0.654, 0.757 and 0.896, respectively. The Ca/Al ratio increases with the pH value. The theoretical Ca/Al ratio for the stoichiometric CA is 0.743. The Ca/Al ratio for precursor obtained at pH 8 is most nearly at the theoretical Ca/Al ratio.

Figure 1 shows the XRD patterns of the precursors obtained at different pH values. The pattern of precursor obtained at pH 7 can be assigned to $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$ (JCPDS 35-0105) which is a hydrated calcium aluminate with partial substitution of oxygen by chloride. The presence of this phase reveals the formation of reactive aluminate phases in the early stage of precursor formation, when CaO is added to the oxy-hydroxide aluminium gel [13]. The same phase is observed as the unique crystalline phase for precursor at pH 10. However, the XRD pattern of precursor obtained at pH 8 showed two phases: the above

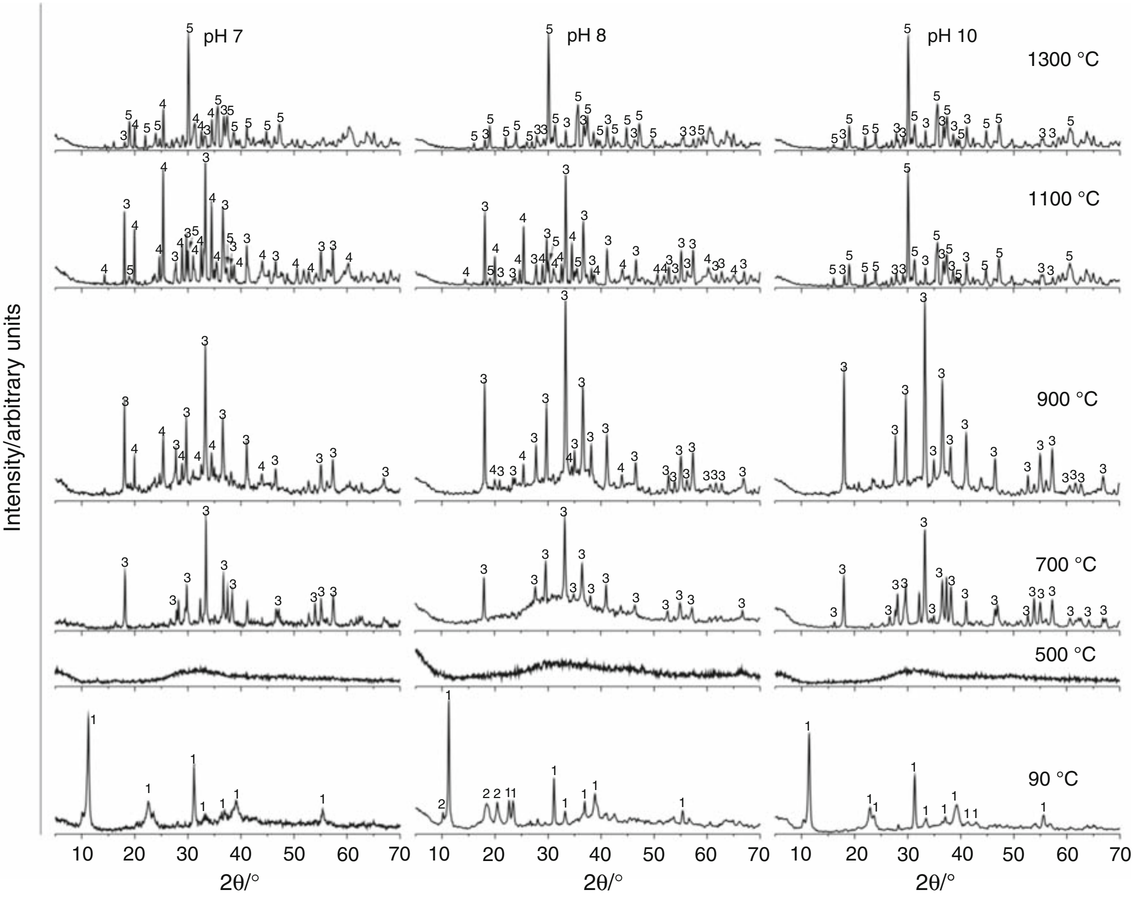

Fig. 1 XRD patterns of calcium aluminate precursors obtained at pH 7, 8 and 10, and samples obtained at different temperatures by thermal treatment of the corresponding precursor. *1* $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ (JCPDS 35-0105), *2* $Ca_2Al_2O_5 \cdot 6H_2O$ (JCPDS 12-0008), *3* C12A7 (JCPDS 48-1882), *4* CA2 (JCPDS 72-0767), *5* CA (JCPDS 70-0134)

one and $Ca_2Al_2O_5 \cdot 6H_2O$ (JCPDS 12-0008). Finally, some differences in crystallinity are observed between patterns and so for pH 8 the reflections are better defined.

Thermal treatment and XRD/SEM studies

Precursors were heat treated at 150, 300, 500, 700, 900, 1100 and 1300 °C for 5 h. At 150 °C (patterns not included), all samples exhibited XRD diffractograms similar to those corresponding to precursors, this means that at this temperature and from the crystallographic point of view, there are not any transformation. At 300 °C (patterns not included), all samples exhibited XRD diffractograms characteristic of amorphous materials. Thus, at this temperature, the crystallinity of the precursors is lost and the structural reorganization of elements starts. At 500 °C, the patterns show that samples are still amorphous (Fig. 1).

The morphological aspect of the sample obtained at pH 8 and 500 °C can be seen at Fig. 2a, in which grains constituted by nanoparticles aggregates can be observed, this being characteristic of poor crystalline materials.

Figure 2b shows a zone in which several crystallites start to growth, accordingly, this is the transition temperature between amorphous and crystalline calcium aluminate forms.

At 700 °C, the diffraction maxima of C12A7 (JCPDS 48-1882) are observed for pH 8 and 10, in this last sample the crystallinity of this phase is higher than in the first one. C12A7 is obtained as unique crystalline phase at a relatively low temperature and its formation is favoured in the case of the precursor obtained at the highest pH value. In the case of pH 7 sample, the diffraction peaks fit much better to the phase JCPDS file 45-0568 which corresponds to C12A7 with partial substitution of oxygen atoms by chloride atoms (1O/2Cl). Thus, the generated solid solution can be formulated as $Ca_{12}Al_{14}O_{32}Cl_2$.

At 900 °C, the evolution of C12A7 to CA2 is observed for samples obtained at pH 7 and 8. Both the phases coexist at this temperature. This situation is not clearly identified for sample of pH 10, and thus, the peaks corresponding to CA2 were not observed at this temperature. For this sample the transformation of C12A7 to CA starts to be produced

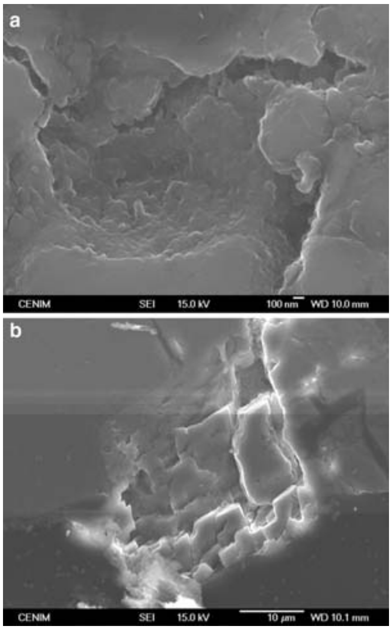

Fig. 2 SEM images of pH 8 precursor heated at 500 °C **a** amorphous zone, **b** zone of crystalline growth

directly at 1100 °C (Fig. 1). For samples of pH 7 and 8, CA reflections are also observed at this temperature along with reflections of CA2 and C12A7.

Figure 3a shows a crystal of C12A7 developed from the nanoparticles aggregates, obtained at 900 °C from pH 10 sample. Figure 3b, corresponds to pH 7 heated at 1100 °C, two zones are clearly differenced at low magnification, C2A (zone 1) and C12A7 (zone 2). In Fig. 4, the morphological aspect of C12A7 is shown, it is observed as a microstructure (Fig. 4a), formed by dendritical aggregate of nanospheres (Fig. 4b).

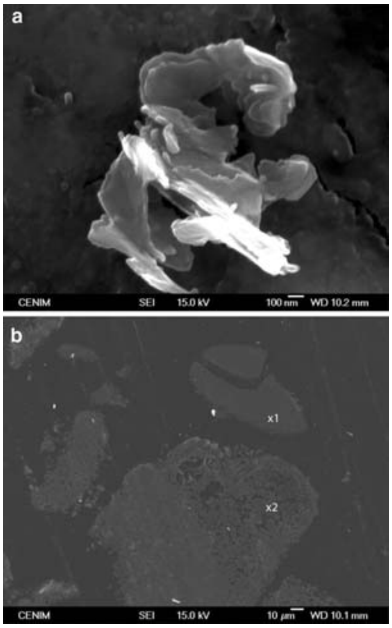

Fig. 3 SEM images **a** C12A7 crystal developed from nanoparticles aggregate obtained at pH 10 and 900 °C, **b** C2A (zone 1) and C12A7 (zone 2), obtained at pH 7 and 1100 °C

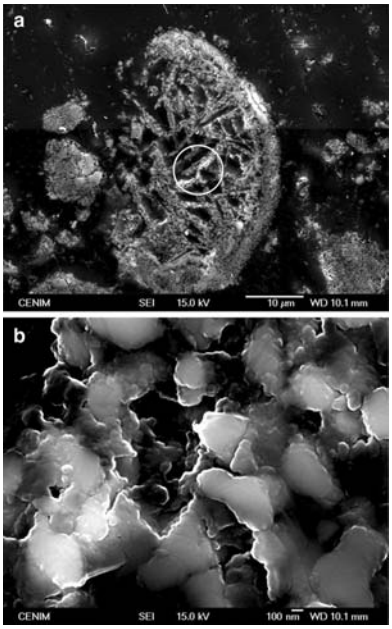

Fig. 4 SEM images of **a** microstructure of C12A7 **b** magnification of a dendrite zone

A specific surface area, S_{BET}, of 175.3, 150.6 and 135.7 $m^2\ g^{-1}$ was obtained for the precursors at pH 7, 8 and 10, respectively. When samples are heated a drastic decreasing of S_{BET} was observed and so the specific surface area for the same samples heated at 1300 °C was 0.28, 0.40 and 0.29 $m^2\ g^{-1}$ for samples of pH 7, 8 and 10, respectively. This indicates a high sinterization of samples with temperature.

Table 1 Parameters determined by DTA and DTG (Fig. 5)

Sample	Temperature range DTA/°C	DTA peak area/μV s/mg	Mass variation limit/°C	Mass variation/%
pH 7	74.7–184.7	23.89	59.8–188.1	−3.58
	184.7–407.8	195.34	188.1–456.1	−23.05
	661.5–742.7	6.96	456.1–779.1	−4.29
	817.1–896.6	2.14	779.1–900	−2.63
	996.6–1079.4	2.69		
pH 8	65.9–167.8	12.54	75.8–176.3	−0.72
	167.8–241.3	3.39	176.3–534.9	−24.14
	242.2–404.6	131.48	538.7–751.6	−3.16
	712.3–770.7	4.13	753.6–1275	−3.06
	944.0–1054.0	8.80		
pH 10	98.2–186.8	26.33	71.7–190.0	−4.57
	186.8–396.1	187.03	190.1–450.1	−20.65
	800.4–888.1	4.97	453.9–779.1	−4.71
	971.0–1092.9	2.15	781.2–1285.5	−2.90

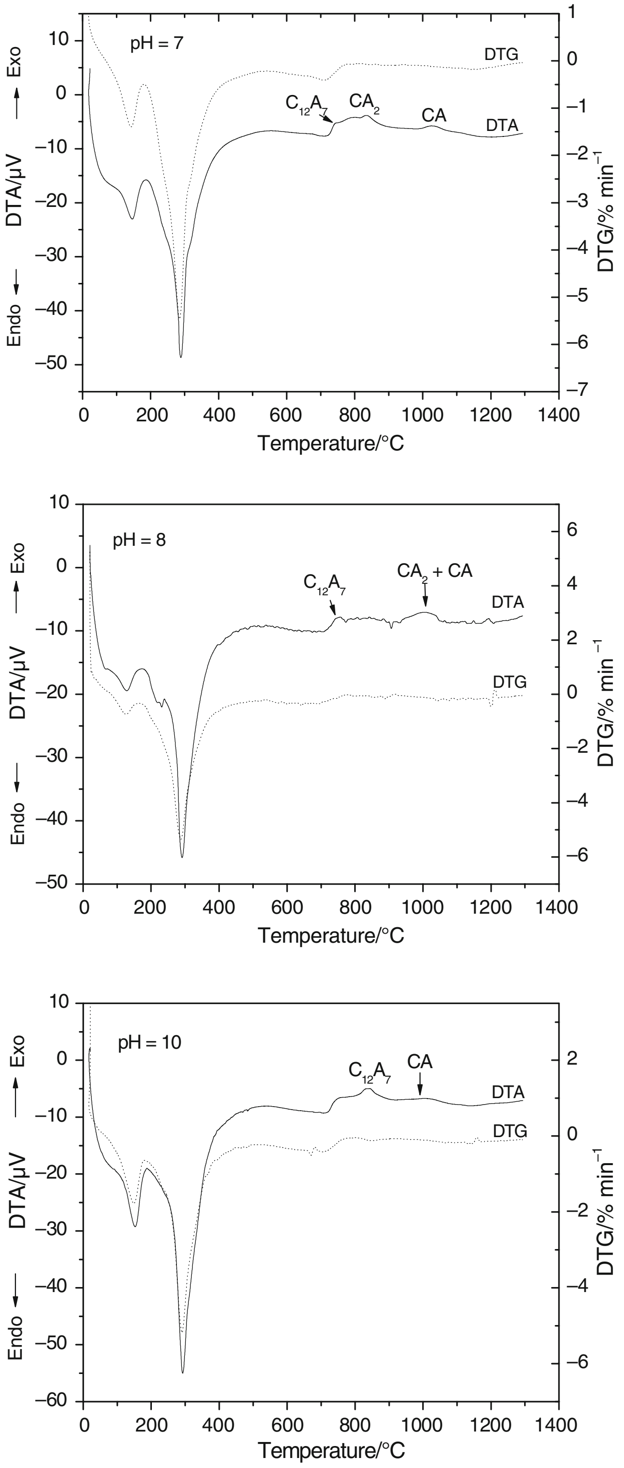

Fig. 5 DTA and DTG curves of samples obtained at pH 7, 8 and 10

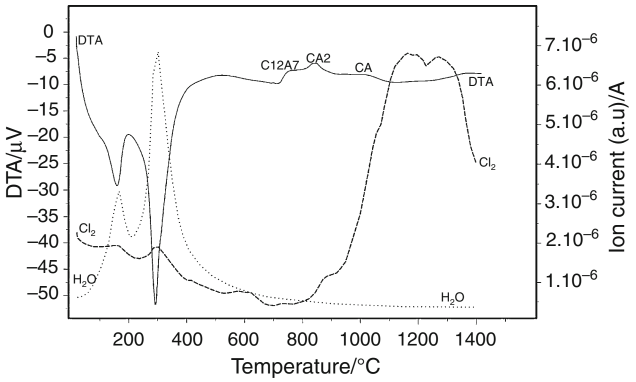

Fig. 6 DTA curve of sample obtained at pH 7 and curves of emission of Cl_2 and H_2O obtained by mass spectrometry

TG/DTA analysis

The thermal behaviour of all the samples in non-isothermal conditions was studied between 25 and 1300 °C. Table 1 collects the results of DTA and TG which includes the values of the temperature range and the peak area from DTA signal and the mass variation associated to the different thermal effects observed. The peak integration was performed using the software SETSOFT 2000 (vs.3.0.6) with a linear baseline from first to last point.

The DTA and the derivative TG (DTG) curves for all samples are shown in Fig. 5. Three zones can be clearly differenced in this figure. In the first zone, from room temperatures to 409, 405 and 396 °C (for pH 7, 8 and 10, respectively), several endothermic effects are observed and they can be attributed to the loss of water, including the dehydration and dehydroxylation processes. Two effects are observed for sample obtained at pH 7 and 10, but in the case of sample obtained at pH 8, a third effect can be clearly distinguished. This agrees with the XRD results which indicate that this sample consists of two different phases of hydrated calcium aluminate. Mass variation around 25% for samples of pH 8 and 10 and slightly higher, 26.6%, for sample of pH 7 was calculated from TG. The second zone stars at 662, 712 and 800 °C for samples of pH 7, 8 and 10, respectively, and it attributed to the formation of C12A7 and CA2. The higher pH value, the higher starting temperature of aluminate formation. Finally, in the last zone, at temperature higher than 900 °C a lower than 1100 °C, the CA formation occurs according to DTA. The formation of the different aluminate phases agrees to the XRD results and the bibliographic data [13, 14].

Mass spectrometry was used to confirm the presence of chlorine in the sample obtained at pH 7. Figure 6 shows the DTA curve of sample obtained at pH 7 along with the curves of emission of Cl and H_2O. The initial precursor in this case, and according to XRD was identified as the phase $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$. The elimination of water takes place principally at temperature lower than 400 °C, in agreement with XRD and DTA results, but residual chlorine is eliminated mostly at temperature higher than 900 °C.

Conclusions

A hazardous waste from tertiary aluminium industry can be used as a raw material for the synthesis of calcium aluminate. An amorphous precursor was obtained by a hydrothermal method at different values of pH. The transformation of the precursor in a crystalline aluminate was followed by TG/DTA up to 1300 °C. All the techniques used to characterize the samples give similar or complementary results, so as conclusion the calcium aluminates precipitated from 700°. The first aluminate formed is C12A7. This aluminate has a transition to CA2 at 838–848 °C and then is transformed to CA at 1000–1034 °C, which coexists with the previous one. The phase C12A7 was obtained as unique crystalline phase, at 900 °C, in the case of precursor obtained at pH 10.

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