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STRUCTURAL AND THERMAL ANALYSIS OF CALCIUM ALUMINATE OBTAINED BY THE SOL-GEL PROCESS

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Abstract:

This paper aims to characterize structurally and thermally the calcium aluminate synthesized with the ethylenediamine tetraacetic acid (EDTA) by the sol-gel process. Structural analysis were made with Fourier Transform Infrared Spectroscopy and X-ray diffraction and thermal analysis were performed as thermogravimetric and differential thermical analysis. It was observed that structural aluminate features were controlled by the synthetic and thermal conditions.

Introduction

Calcium aluminate ($CaAl_2O_4$) is a refractory compound belonging to the binary system Al_2O_3-CaO with a melting point of 1600 ^oC. $CaAl_2O_4$ has been extensively used in the fielded

advanced ceramics, such as, optical ceramics, catalytic support, industrial concrete and cements, refractory materials and structural ceramics [1,2].

Synthesis of aluminate powders is often performed as oxides, where several synthetic routes are utilized, such as solid state reactions, sol-gel process, ceramic powder manufacturing, , polyacrylamide gel, urea solution, hydroxides precipitation, polymerization route and combustion synthesis [3,4,5]. Solid state reactions are based on mixture and sintering of thin oxide powders at high temperature (1500–1700 ℃) [5,6]. Those reactions ae very simple, but such process shows several disadvantages such as high reaction temperatures, large particle size, a limited degree of chemical homogeneity, and low sintering capability [5,7].

Due to this fact a synthesis method is used to obtain thinner and more homogenous powder, particularly, the sol-gel process. Such process is also called the modified Pechini method [8,9] or gel method [10]. Such process produces pure and ultrathin powders at low temperatures, high crystallinity, high homogeneity of the matrix and activating agents, stable and versatile processing, in addition the reactants are easily mixed up, small size particles are produced, and a high and efficient luminosity is obtained with the absence of non-luminous phases and with a controlled porosity combined with the ability to form extensive surface area at low temperature [9,11,12,13,14,15,16]. Another important advantage of this method is kinetic and mechanism control of chemical reactions [17]. By the end of synthesis employing sol-gel process it can be formed powders, fibers, coatings, monolithic products, among others, depending of the way the synthesis was conducted [17]. During the synthesis it is necessary to control the pH, the stoichiometry of the reagents, the gelling temperature, the metal charge, the removing of the solvent and the pre-treatment conditions [16]. By appropriately controlling the conditions the formation of the materials with different structures is avoided.

In the synthesis of the calcium aluminate by the gel method employed in this work the chelating agent ethylenediamine tetraacetic acid (EDTA) was employed. EDTA has two nitrogen atoms and four oxygen atomos with free electrons to bind the central atom, making it the a polydentate ligand (hexadentated) [18,19]. Due to these chemical bonds with the central atom, EDTA possesses a facility to form complexes with most metallic ions in solution in the proportion 1:1 (metal:EDTA), but for this occurs the solution pH must be appropriately adjusted.

When the pH solution prepared with EDTA is low, EDTA is protonated instead of forming complexes. An example is the formation of the [Ca^{2+} (-EDTA) complex, where the pH must

be 8, otherwise at lower values the chemical complex will not be fully formed and the EDTA will be protonated [20].

This paper aims to characterize structurally and thermally the calcium aluminate synthesized with the ethylenediamine tetraacetic acid (EDTA) by the sol-gel process.

Methodology

➢ Calcium aluminate synthesis

The methodology employed was based on the work of Xu et al. (2003) [3] and adapted to our necessities as described in Figure 1. The ethylenediamine tetraacetic acid (EDTA) was dissolved in a solution of ammonium hydroxide (NH_4OH), following the addition of calcium nitrate ($Ca(NO_3)_{3)}$ and aluminum nitrate ($Al(NO_3)_3$). Metals were added with the ratio 1:1, with the ratio metal-EDTA equals 1:1 and 1:2. After the addition of the respective nitrates, the final pH solution decreased [3]. Such mixture was put on a heating plate under continuous stirring for around 2 h at 80 ^oC to promote water evaporation. After this time, a solution of nitric acid (HNO_3) at 10 % aimed at reducing the pH solution to 0.5. Subsequently, the continuous stirring of the solution was kept for around 1:10 h at 140 ^oC or until the solution gets viscous and form a gel.

The addition of HNO_3 forms an unidentified white precipitate; however, when the addition happens in a continuous way avoid the precipitate formation. The 80 ^oC temperature must be kept before the addition of HNO_3 because in case the temperature be inferior to this value the precipitate formed after the addition o HNO_3 will not be dissolved making difficult the resin formation ate the end of the experimental procedure.

In current work three types of chemical synthesis was used, the first with the ratio metal/EDTA 1:1, where the formed solid was carbonized, pulverized and calcined; in the second reaction the ratio metal/EDTA was also 1:1, but the formed solid was only pulverized and calcined. In the third type of synthesis with a metal/EDTA ratio is 1:2 and the formed solid is pulverized and calcined. The calcination in all ratios of metal/EDTA was done with a temperature ramp of 20 ^oC/min for 2 h at 800 ^oC and conducted to obtain calcium aluminate ($CaAl_2O_3$). Figure 1 show the steps of the synthesis in an schematic way.

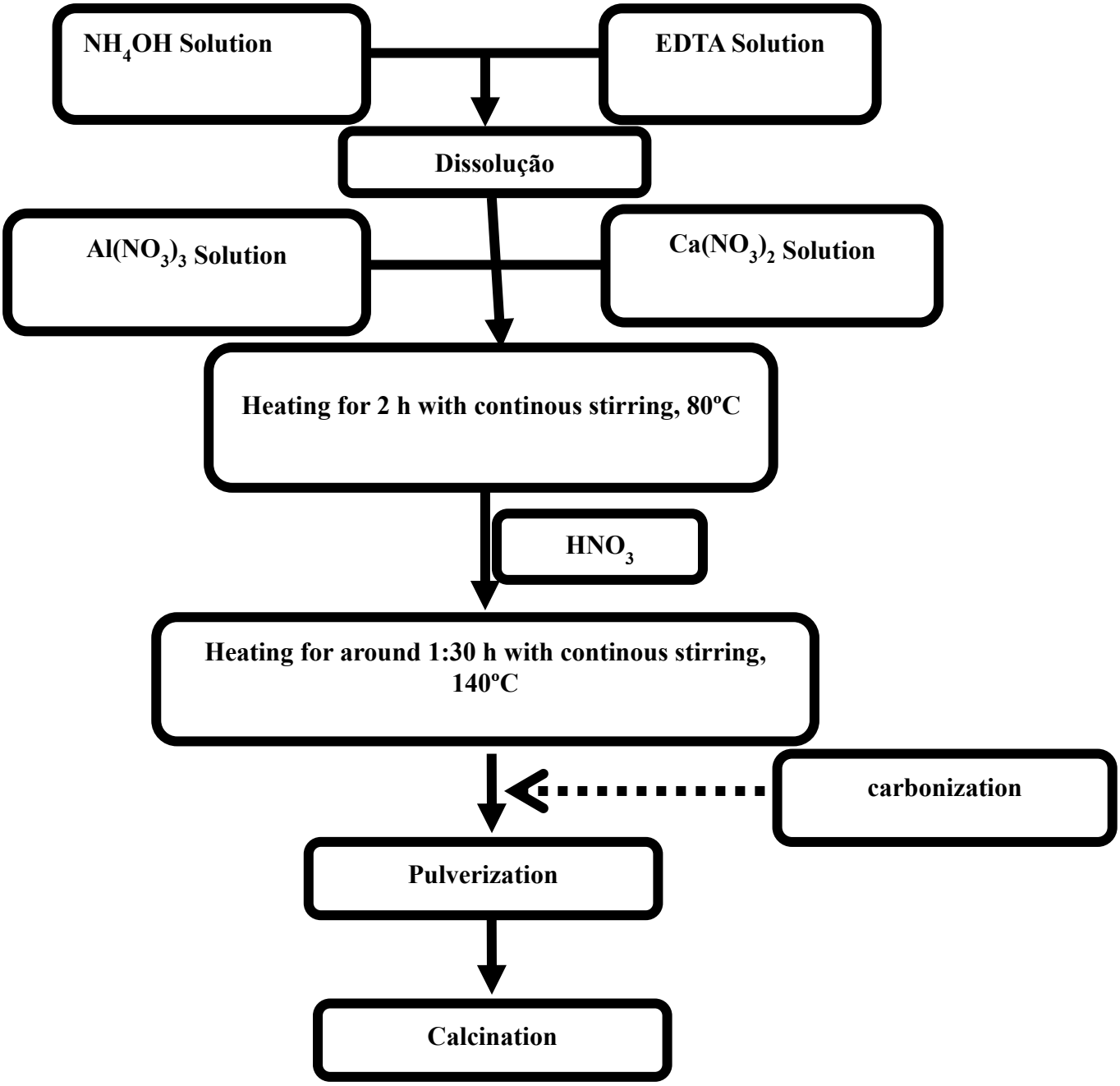

Figura 1 – Flowchart of the synthesis of the calcim aluminate

Characterization

The analytical methods used to characterize the samples of calcium aluminate were thermogravimetric analysis, differential scanning calorimetry, and for the calcined calcium aluminate Fourier transform infrared spectroscopy (FTIE) and X-ray diffraction.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were employed aimed at to determine the calcination temperature for the calcium aluminate powder. To

characterize the precursor of this powder an equipment DTG-60 from Shimadzu , located at the laboratory of research and innovation of advanced materials at the Universidade Estadual de Santa Cruz (UESC). The sample was put in a crucible and heat at the rate of 15 ℃/min under a nitrogen stream of 50 mL/min. Bothe thermal analysis was done in the range 20 – 1220 ℃.

For the FTIR analyis, the sample of calcium aluminate previously synthesized were diluted and pressed to form tablets. A manual press from SPECAC with 10 tons was used for this purpose. The spectra were obtained through a spectrometer model Spectrum 400 Ft-IR/Ft-NIR from Perkin Elmer in the wavenumber range 4000 – 450 cm^{-1} with 10 scans. Such analyses were conduct at the laboratory of biology of fungi from UESC.

X-ray diffraction was done using a Philips system with PW generator – 1830 and a difratometer controller PW – 1840, with a graphite monocromator and radiation CuKα, located at the associate laboratory for materials and sensors (LAS) from the national institute for space research (INPE). The collected spectra have a 0.02^{o} steps with an integration equals 2,0. The 2 θ values were from 10 to 70 ^{o}. For the quantitative analysis of the diffractograms the *American Mineralogist Crystal Structure Database* databank was used.

Results and Discussion

Thermal Analysis

Thermogravimetric analysis and differential scanning calorimetry from the precursors of the calcium aluminate ($CaAlO_4$) with different ratios metal/EDTA, 1:1 (carbonized material), 1:1 (material without carbonization) and 1:2 are shown in Figure 2. Such kind of thermal analysis gives information about the temperature of decomposition of the materials obtained by the synthesis method [21]

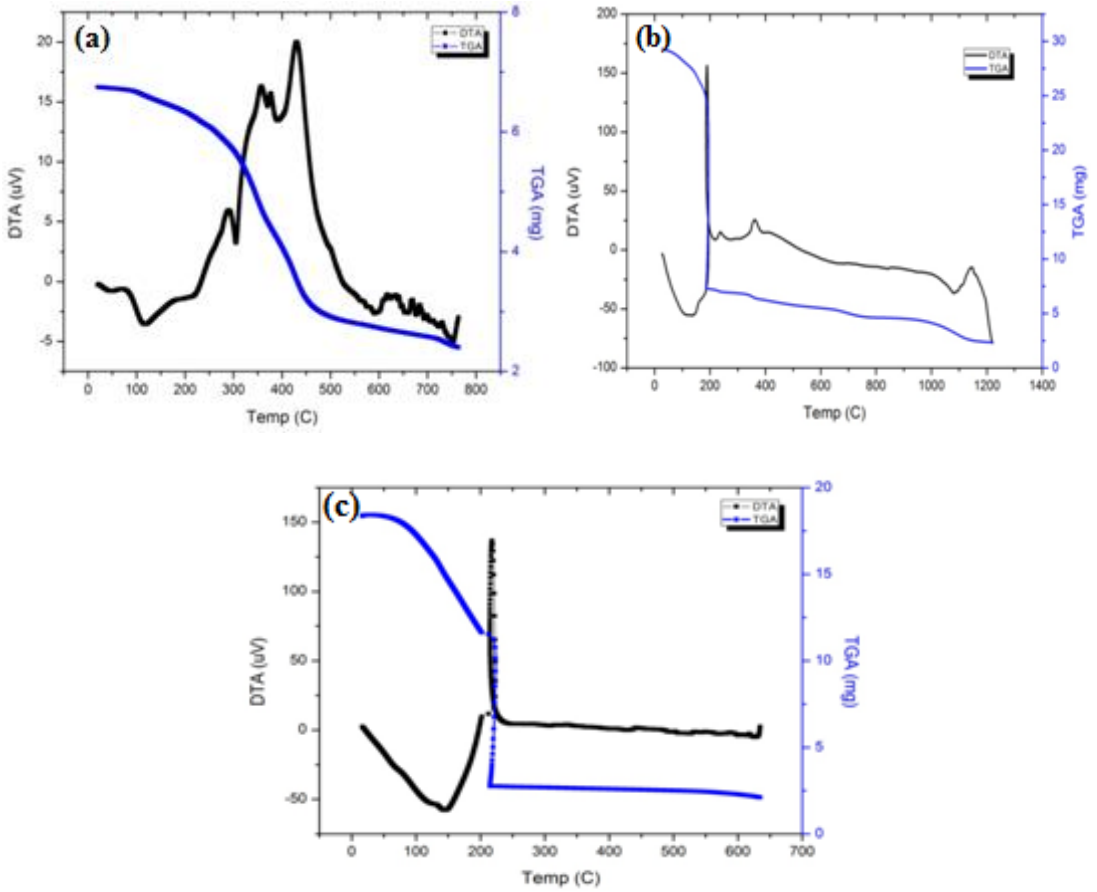

Figure 2 – TG and DTA curves for the precursor of the pure calcium aluminate ($CaAl_2O_4$). (a) $CaAl_2O_4$ with the ratio metal/EDTA 1:1 carbonized; (b) $CaAl_2O_4$ with the ratio metal/EDTA 1:1 without carbonization; (c) $CaAl_2O_4$ with the ratio metal/EDTA 1:2

In the three curves TG or DTA (Figure 2 A, B and C) it is observed a deep loss of material mass, indicating that the precursos of calcium aluminate absorbs water from the environment. For the DTA curve, the exothermic peak from the Figure 2 A occurs within a medium band of 400 ^{o}C. This peak can be related to the formation of calcium aluminate at a lower temperature than previously expected.

The DTA curves described in the Figures 2 B and C, around 200 ^{o}C shown endothermic peaks followed by a strong weight loss. Such loss can be due to the separation of the compounds from EDTA yielding carbonates and nitrates, as well volatilization of NH_4NO_3 and elimination of residues of CO_3^{2-} e NO_3^{-} [3].

As can be observed in the Figures 2 B and C there is no exothermic peak as those found in the Figure 2A. This fact indicates that the calcium aluminate was formed during the synthesis reaction in the respective figures.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was done with calcined samples and the spectra was shown in the Figure 3 to 5

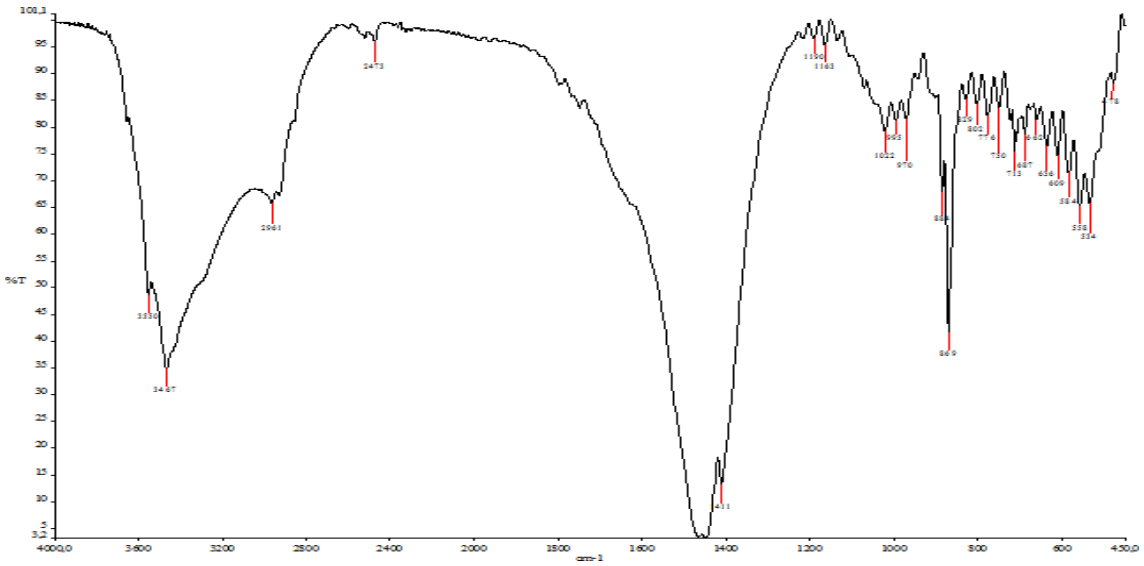

Figure 3 – FTIR spectrum of the pure calcium aluminate at the ratio 1:1, where the material was carbonized

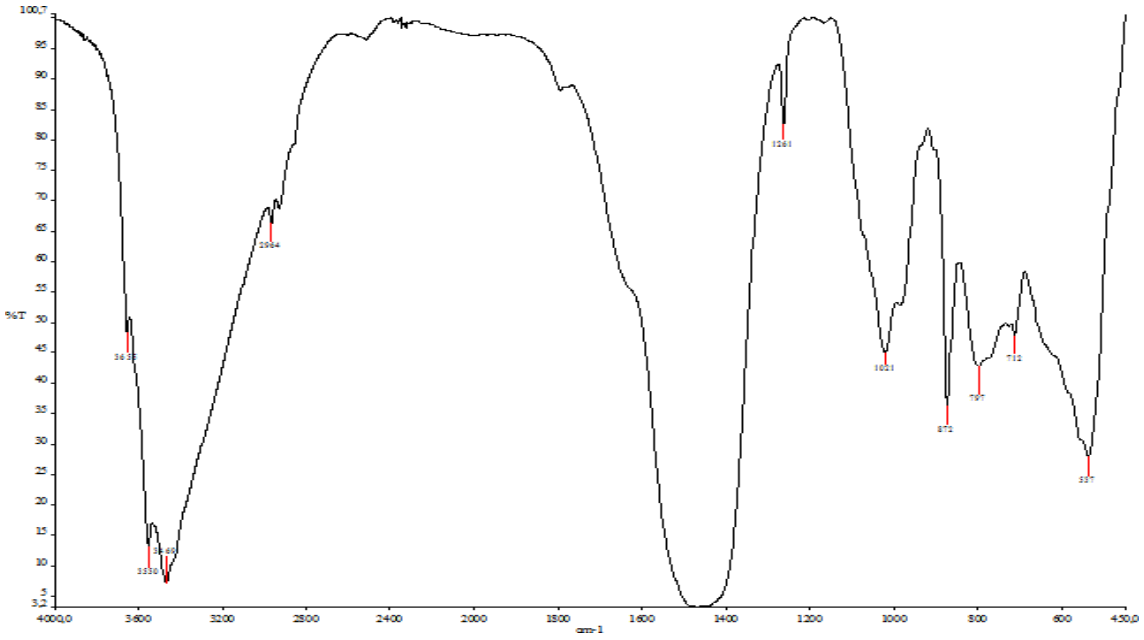

Figure 4 – FTIR spectrum of the pure calcium aluminate at the ratio 1:1, without carbonization

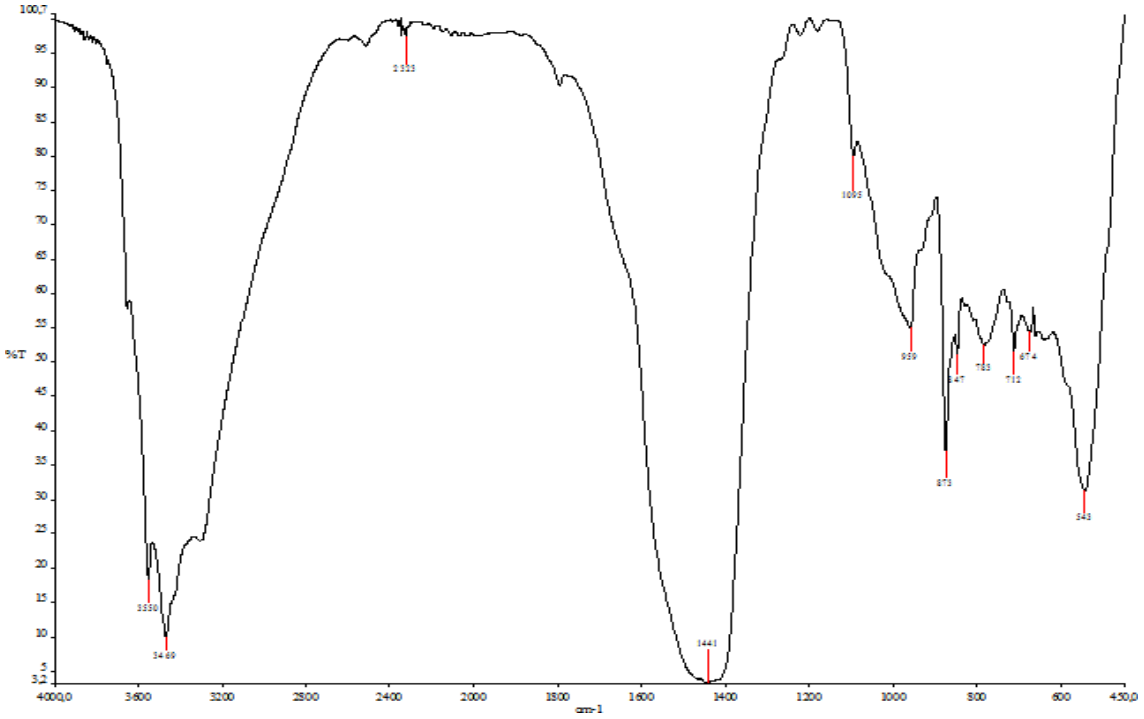

Figure 5 – FTIR spectrum of the pure calcium aluminate at the ratio 1:2

One ́s can observe that in the Figures 3 to 5 the FTIR spectra possess band at the same wavenumber. Hence, the spectral bands between 500 and 900 cm^{-1} probably correspond to the intrinsic vibrations of the tetrahedral sites of the Al-O bonds and octahedral sites of the Ca-O bonds characteristics of spinel. The band around 1450 cm^{-1} can be attributed to the vibrations of carboxylate ions and the two spike peaks around 3450 and 3600 cm^{-1} can be associated with the OH stretching vibrations for the carboxylic acid from the EDTA or from water.

Such results were confirmed by Gaki et al. (2006) when the synthesis of calcium aluminate were done using the synthesis route employing polymeric precursors and nitric acid as a complexing agent [2]

However, these authors did not find the band around 3450 and 3600 cm^{-1} because they did not used the EDTA agent. This vibrational band was confirmed by compared the referred spectrum, found in the article from Zheng and Xiong (2006) [22]. In this paper, the authors synthesized a polyelectrolyte functionalizing it with EDTA, and those was prepared by a covalent bond of polyallylamine hydrochloride (PAH) and EDTA and characterized in the infrared region by FTIR the polyelectrolyte PAH-EDTA by comparing the FTIR spectra of his material with those from PAH and EDTA [22].

X-Ray Diffraction

The X-ray diffraction technique was utilized to confirm if powder of the calcium aluminate was synthesized. Here we present the X-ray analysis of the pure calcium aluminate with the ratio metal/EDTA 1:2, calcined for 2 h at 800 described in the Figure 6.

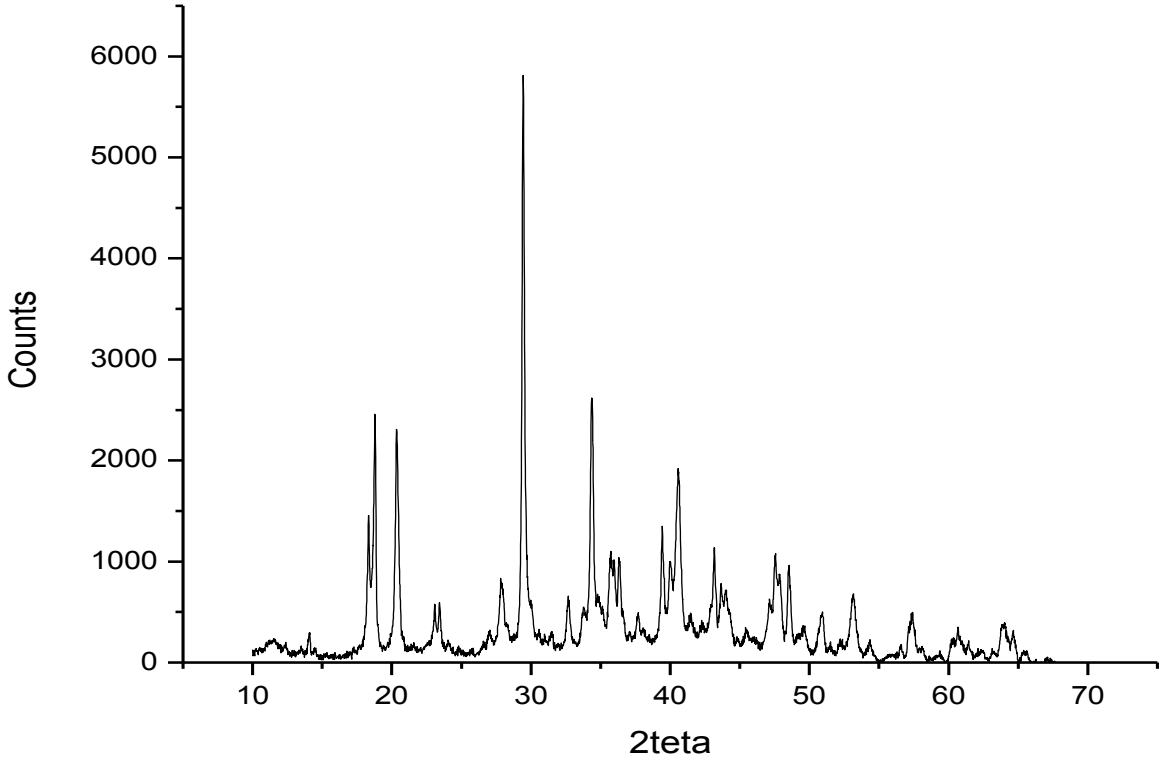

Figure 6 – Diffractogram of pure calcium aluminate with ratio 1:1

The X-ray diffraction of the calcium aluminate with ratio 1:2 suggest the formation of the phase $CaO.Al_2O_3$, characterized by the peaks located at the position 18,869^o, 29,487^o and 35,993^o. Meanwhile, the arising of a broad band under the diffraction peaks between 20^o and 40^o indicate the presence of the amorphous phase in the material. Such results are confirmed by [2], where it was obtained the $CaO.Al_2O_3$ samples at 1400 ^{o}C, using the Pequini synthesis method and the solid state reaction methods.

Conclusions

The obtained results showed that gel route is quite efficient to synthesize calcium aluminate powders. TG and DTA analysis of the calcium aluminate powders with the ratio metal/EDTA 1:1, with carbonized, 1:1 with non-carbonized material and 1:2 showed a strong mass loss of the materials at 200 ^{o}C, except for the carbonized calcium aluminate, where the mass loss

occurred at 300 ^{o}C. It was also observed that in those curves that the aluminate was formed in the following conditions: in the ratio metal/EDTA 1:1, non-carbonized and in the ratio 1:2.

The FTIR analysis for the calcium aluminate showed vibrational bands with similar wavenumbers. The X-ray diffraction analysis of the calcium aluminate in the ratio 1:2 showed a very satisfactory diffractograms, confirming the efficient synthesis of the aluminate.

Acknowledgements

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