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Excerpt

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**Characterization of Materials by X-ray Diffraction (XRD), Scanning Electron  
Microscopy (SEM) and Differential Scanning Calorimetry (DSC)**

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## Synthesis and Determination of Thermodynamical Properties of the Compounds of the system Ca-Mg-Bi

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### ABSTRACT

Bismuth is an element obtained as a sub-product in lead production; Mexico occupies the second position in the world in production of this element. Bismuth is used as iron, aluminum and copper alloying, in the pharmaceutical industry, in the cosmetics industry, etc. Bismuth is separated from lead by the Kroll-Berterton Process in which a Ca-Mg alloy is added to the melting lead to form the intermetallic compounds  $\text{Ca}_3\text{Bi}_2$ ,  $\text{Mg}_3\text{Bi}_2$  and  $\text{Ca}_2\text{MgBi}_2$  which float to the surface of the bath. Unfortunately, there is little thermodynamical information of the compounds of the system Ca-Mg-Bi which can be used to study and optimize the Kroll-Berterton process in a theoretical way. In this work there were synthesized the compounds  $\text{Ca}_3\text{Bi}_2$ ,  $\text{Mg}_3\text{Bi}_2$  and  $\text{CaMg}_2\text{Bi}_2$  using powders of pure elements (Ca, Mg and Bi) in the required amounts and melted under an inert atmosphere. After synthesis, the samples were characterized by X-Ray Diffraction to ensure the formation of the desired compounds. Later, calorimetric technique was used to determine the thermodynamical properties of the compounds. The results obtained by X-Ray Diffraction show the formation of  $\text{Mg}_3\text{Bi}_2$  and  $\text{Mg}_2\text{CaBi}_2$  species; however, there is no crystallographic information of the compound  $\text{Ca}_3\text{Bi}_2$ . The heating curves obtained by calorimetry show endothermic peaks, due to the presence of phase changes as is indicated in the Ca-Bi, Mg-Bi and Ca-Mg-Bi phase diagrams.

**Keywords:** Bi, Mg, Ca, calorimetry, phase equilibria.

### INTRODUCTION

Bismuth is mainly obtained as a sub-product of the refining of lead. This is because the lead and bismuth are elements with similar properties so that mineral deposits are associated with bismuth and lead. The common method for separating bismuth from lead is called “Kroll-Berterton Process” which uses calcium and/or magnesium to remove bismuth from lead bath. Kroll-Berterton Process consists in adding a calcium-magnesium alloy to form intermetallic compounds Ca-Mg-Bi of high melting point and lower density than lead. The standard specification of many countries stipulate a maximum of 0.005% bismuth in the metallic lead, nowadays, this is the most widely used process to recover bismuth from lead. Figure 1 shows the phase diagram Ca-Bi[1] where the compound  $\text{Ca}_3\text{Bi}_2$  is formed with a composition of 60% at. Ca and 40% at. Bi. Figure 2 shows the phase diagram Mg-Bi[2] with the compound  $\text{Mg}_3\text{Bi}_2$  with 60% at. Mg and 40% at. Bi, this compound exhibits an allotropic transformation above 700 °C. Figure 3 shows the phase diagram Ca-Mg-Bi[3] where the ternary compound  $\text{CaMg}_2\text{Bi}_2$  is formed with a composition of 20% at. Ca, 40% at. Bi and 40% at. Mg.

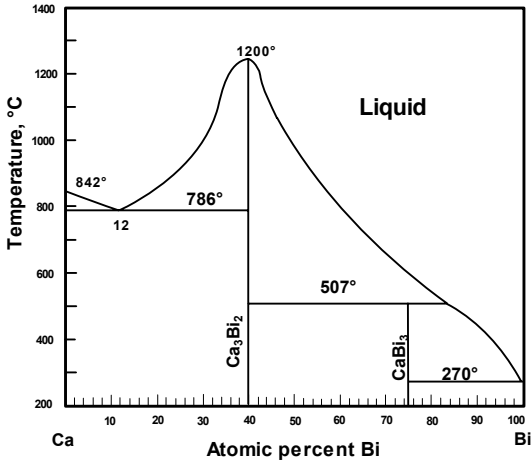


Figure 1. Phases diagrams of the system Ca-Bi [1].

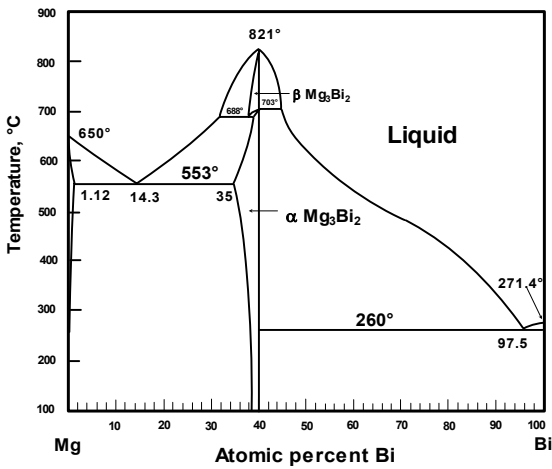


Figure 2. Phases diagrams of the system Mg-Bi [2].

Paliwal and Jung [4] determined the short range ordering behavior of liquid Mg-Bi solution and thermodynamic modeling of the Mg-Bi binary system had been optimized to obtain one set of model parameters for the Gibbs energies of the liquid and all solid phases as functions of composition and temperature. Kim[5] studied the thermodynamic properties of Ca-Bi alloys by electromotive force (emf) measurements at ambient pressure as a function of temperature between 723 K and 1173 K using a  $\text{Ca(s)}|\text{CaF}_2|\text{Ca(inBi)}$  cell for twenty different Ca-Bi alloys spanning the entire range of composition from  $X_{\text{Ca}} = 0$  to 1. Kumar[6] studied the large deviation from the ideal mixture and the concentration dependent asymmetry in the thermodynamic properties of Mg-Bi alloy.

#### Invariant Reactions

- 1000°C  $e_1$ :  $\text{Liq} = \text{Ca}_3\text{Bi}_2 + \text{CaMg}_2\text{Bi}_2$   
 712°C  $e_2$ :  $\text{Liq} = \text{Ca}_3\text{Bi}_2 + \text{CaMg}_2$   
 640°C  $e_3$ :  $\text{Liq} = \text{Ca}_3\text{Bi}_2 + (\text{Mg})$   
 640°C  $e_4$ :  $\text{Liq} = \text{CaMg}_2\text{Bi}_2 + (\text{Mg})$   
 270°C  $e_5$ :  $\text{Liq} = \text{CaMg}_2\text{Bi}_2 + (\text{Bi})$   
 850°C  $p$ :  $\text{Liq} + \text{CaMg}_2\text{Bi}_2 = \text{Mg}_3\text{Bi}_2$   
 630°C  $E_1$ :  $\text{Liq} = \text{CaMg}_2\text{Bi}_2 + \text{Ca}_3\text{Bi}_2 + (\text{Mg})$   
 551°C  $E_2$ :  $\text{Liq} = \text{CaMg}_2\text{Bi}_2 + \text{Mg}_3\text{Bi}_2 + (\text{Mg})$   
 516°C  $E_3$ :  $\text{Liq} = \text{Ca}_3\text{Bi}_2 + \text{CaMg}_2 + (\text{Mg})$   
 445°C  $E_4$ :  $\text{Liq} = \text{Ca}_3\text{Bi}_2 + \text{Ca(HT)} + \text{CaMg}_2$   
 265°C  $E_5$ :  $\text{Liq} = (\text{Bi}) + \text{CaBi}_3 + \text{CaMg}_2\text{Bi}_2$   
 258°C  $E_6$ :  $\text{Liq} = (\text{Bi}) + \text{Mg}_3\text{Bi}_2 + \text{CaMg}_2\text{Bi}_2$   
 490°C  $U$ :  $\text{Liq} + \text{Ca}_3\text{Bi}_2 = \text{CaBi}_3 + \text{CaMg}_2\text{Bi}_2$

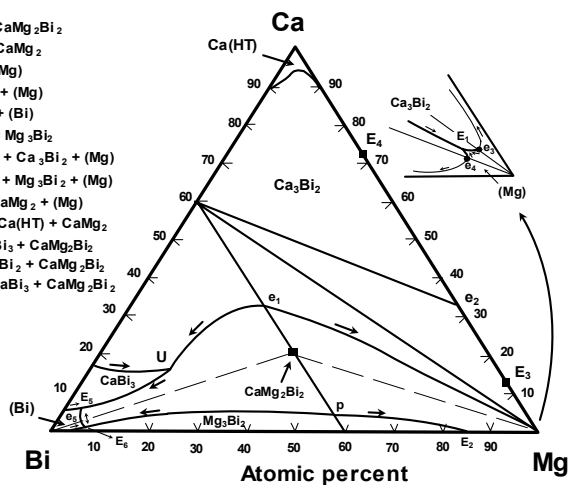


Figure 3. Phases diagrams of the system Ca-Mg-Bi[3].

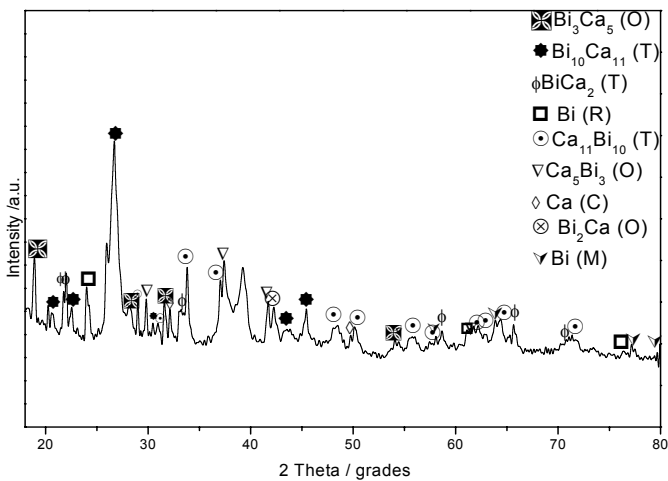
## EXPERIMENTAL PROCEDURE

For the experimental procedure first of all synthesis is defined with high purity powders of Calcium, Magnesium and Bismuth to form the intermetallic compounds  $\text{Ca}_3\text{Bi}_2$ ,  $\text{Mg}_3\text{Bi}_2$  and  $\text{CaMg}_2\text{Bi}_2$  in the required proportions and melted at a temperature of 650° C under inert atmosphere during long time, the next step is the characterization by X-Ray Diffraction to confirm the formation of the intermetallic compounds, later is the determination of thermodynamic properties by calorimetry to determine the phase changes, invariant reactions and thermodynamic properties of the compounds.

## RESULTS AND DISCUSSION

**X-Ray Diffraction**

Figures 4 to 6 show the results of X-Ray Diffraction of the systems Ca-Bi, Mg-Bi and Ca-Mg-Bi using the following conditions: voltage of 30 kV, current of 25 mA, scan speed 2 deg/min and a Cu K $\alpha$  radiation = 1.5406. Figure 4 shows the X-Ray pattern of the sample Ca-Bi, where Ca<sub>11</sub>Bi<sub>10</sub> and Ca<sub>5</sub>Bi<sub>3</sub> are seen as a predominant species. It is also observed the presence of oxidized species and metallic bismuth. The compound Ca<sub>3</sub>Bi<sub>2</sub> could not be detected by this technique since there is no crystallographic information of this compound.



**Figure 4.** X-Ray pattern of the Ca-Bi system.

Figure 5 shows the X-Ray pattern of the Mg-Bi system which shows the presence of the compound Mg<sub>3</sub>Bi<sub>2</sub> and Bi, possibly due to an excess of this element in the preparation of the compound. Figure 6 shows the X-Ray pattern of the Ca-Mg-Bi system where it is observed the formation of the ternary compound CaMg<sub>2</sub>Bi<sub>2</sub> and Bi, possibly there was not a perfect homogenization of the powders and some amount of bismuth did not react.

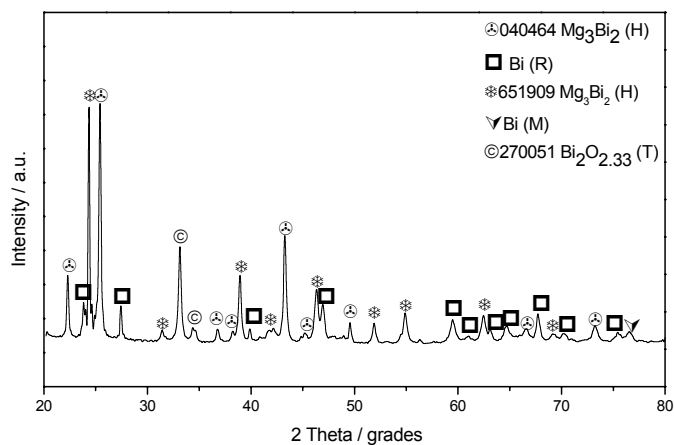


Figure 5. X-Ray pattern of the Mg-Bi system.

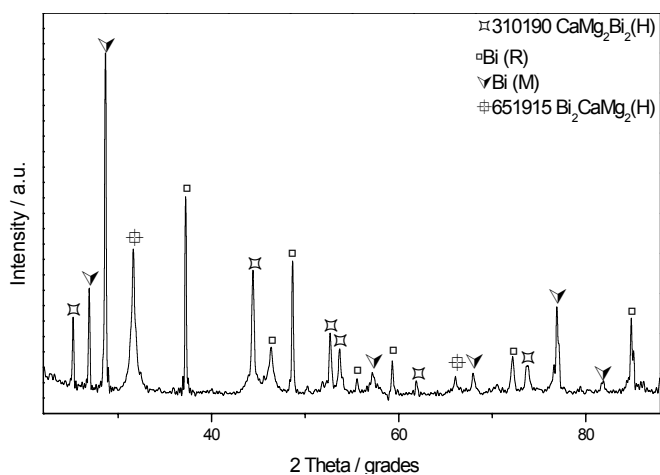
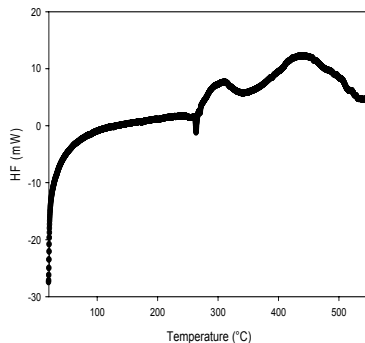
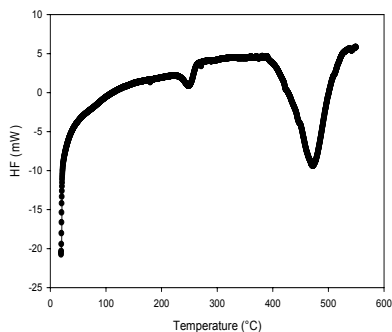


Figure 6. X-Ray pattern of the Ca-Mg-Bi system.

### Differential Scanning Calorimetry

Figures 7 to 10 show the results obtained by differential scanning calorimetry of the compounds of the system Ca-Mg-Bi. The atmosphere used was Ar of high purity and the mass of the samples was between 12 and 264 mg, using alumina crucibles of 70  $\mu$ L. The vertical axis shows the values of electric power in mW, while in the horizontal axis corresponds to the temperature ( $^{\circ}$ C). Figure 8 shows the heating curve of Ca-Bi system where two endothermic peaks are obtained at 270 $^{\circ}$  and 500 $^{\circ}$  C, which belong to the eutectic and peritectic points of Ca-Bi binary diagram of Figure 1, respectively. The intensity of the peaks shows that there is little amount of free bismuth. However it is necessary to improve the preparation technique to avoid the formation of other chemical species and determine only the properties of the compound  $\text{Ca}_3\text{Bi}_2$ .

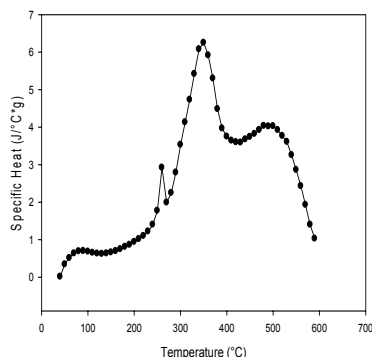
The heating curve of Figure 8 corresponds to the sample  $\text{Mg}_3\text{Bi}_2$  and an endothermic peak is observed at a temperature of 282 $^{\circ}$  C, which may correspond to the melting point of metallic bismuth. This curve also shows a peak at 395 $^{\circ}$  C, however it is not possible to determine the transformation to which corresponds as there is not an invariant reaction or phase change at that temperature in the Mg-Bi phase diagram (Figure 2).



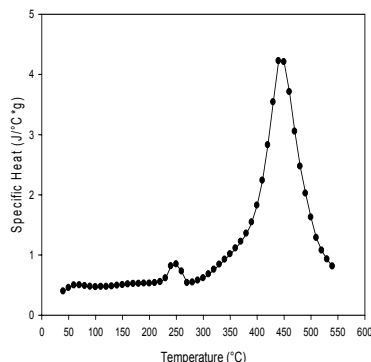
**Figure 7.** Heating curve of the Ca-Bi system.

**Figure 8.** Heating curve of the Mg-Bi system.

The heat capacity of Figure 9 corresponds to the sample  $\text{Mg}_3\text{Bi}_2$ , an exothermic peak is observed at the temperature of 260 $^{\circ}$  C, which corresponds to the melting point of metallic bismuth. This graphic shows a peak at the temperature of 353 $^{\circ}$  C which corresponds to the formation of the intermetallic compound  $\alpha\text{Mg}_3\text{Bi}_2$  if it is related with the phases diagrams of figure 2. The heat capacity of Figure 10 corresponds to the sample  $\text{CaMg}_2\text{Bi}_2$ , two exothermic peaks are observed at the temperatures of 246 $^{\circ}$  C and 446 $^{\circ}$  C, respectively, which correspond to the formation of the invariant reactions in Figure 3.



**Figure 9.** Specific heat versus temperature of  $\text{Mg}_3\text{Bi}_2$  compound.



**Figure 10.** Specific heat versus temperature of  $\text{CaMg}_2\text{Bi}_2$  compound.

## CONCLUSIONS

This work deals with the preparation of compounds of the system Ca-Mg-Bi ( $\text{Ca}_3\text{Bi}_2$ ,  $\text{Mg}_3\text{Bi}_2$  and  $\text{CaMg}_2\text{Bi}_2$ ) as well as their characterization. The main conclusions are:

- The intermetallic compounds  $\text{Mg}_3\text{Bi}_2$  and  $\text{CaMg}_2\text{Bi}_2$  were synthesized and analyzed showing an excess of Bi.
- The intermetallic compound  $\text{Ca}_3\text{Bi}_2$  was not identified by X-Ray Diffraction due to the lack of crystallographic information of this compound.
- The heating curves obtained by calorimetry enables us to detect the phase transformations and associate them with the phase diagrams.
- We are still working with calorimetry technique to obtain the thermodynamical properties of the compounds of the Ca-Mg-Bi system.
- The curves of specific Heat-T were estimated for the  $\text{Mg}_3\text{Bi}_2$  and  $\text{CaMg}_2\text{Bi}_2$  compounds.

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## Study of the Synthesis of Mullite From Kaolin- $\alpha$ - $\text{Al}_2\text{O}_3$ and Kaolin- $\text{Al}(\text{NO}_3)_3$

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### ABSTRACT

The synthesis of mullite from kaolin clay and two precursors of aluminum:  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{Al}(\text{NO}_3)_3$  was investigated. In order to study the temperature effect, the system kaolin- $\alpha$ - $\text{Al}_2\text{O}_3$  was calcined in air in a range of 1200 to 1500°C, for 2 h. For the system kaolin- $\text{Al}(\text{NO}_3)_3$ , the combustion method was employed, using urea as fuel, and calcined in air at 1500°C for 2 h. The products were characterized by X-ray diffraction, scanning electronic microscopy (SEM), energy dispersive spectroscopy and particle size analysis in order to analyze and compare their morphology and structure. The crystallographic study revealed an incomplete reaction between the kaolin and the  $\alpha$ - $\text{Al}_2\text{O}_3$ . Nevertheless, in the system kaolin- $\text{Al}(\text{NO}_3)_3$ , it was obtained mullite with high purity and trace amounts of cristobalite.

**Keywords:** X-ray diffraction, structural, scanning electron microscopy (SEM), Al.

### INTRODUCTION

Mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) is a refractory material which has been investigated by decades due to its high thermal stability, low density, high mechanical strength and good chemical stability [1-4]. In addition, the ability to operate at high temperature and in corrosive environments, allows mullite to be used in a variety of composites [5], as well as in advanced structural and functional ceramics [6]. Nevertheless, mullite is rarely in nature, as it requires high temperatures and low pressures [7]. Therefore, several methods have been proposed in order to obtain crystalline mullite from different starting materials [8-10].

Kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ ), the major kaolin component, is the most common precursor for the synthesis of mullite [7-13] due to its potential and economic application. Nevertheless, the amount of  $\text{SiO}_2$  in kaolinite is higher than in mullite; the excess  $\text{SiO}_2$  together with the impurities in kaolinite forms a glassy phase and cristobalite to accompany the formation of mullite at temperatures higher than 1000°C [13]. The presence of a large amount of glass phase is thus detrimental to the mechanical properties of the mullite prepared from kaolinite [7]. In order to consume the  $\text{SiO}_2$  in the glassy phase,  $\text{Al}_2\text{O}_3$  is generally added so that the reaction product of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is also a mullite phase.

Solid state reaction is a useful method for introducing the  $\text{Al}_2\text{O}_3$  into the kaolinite lattice which consists in the grinding of solids in a medium either dried or wet and their subsequent heat treatment at high temperatures. Parameters of synthesis such as calcination temperature, composition and texture of precursors as same as nature of the solvent, determine the final properties of the product [7, 14].

Furthermore, the implementation of a combustion reaction may improve the synthesis of mullite due to the addition of heat may favor the interaction between the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  so that the interdiffusion rates of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  within the mullite lattice may increase since it is typically slow thus restricts its formation [15]. In order to test this hypothesis, it was carried out the synthesis of mullite by using two methods: solid state reaction (SSR) and combustion-solid state reaction (CSSR) from kaolin extracted from Hidalgo, Mex., which is characterized by containing a significant proportion of quartz and some iron and titanium impurities.

## EXPERIMENTAL PROCEDURE

### Raw material

Kaolin clay (Molinos y Moliendas de Pachuca, S.A. de C.V.), which is extracted from the Tenango Dorian region in Hidalgo State, from Mexico, was used as starting material in the two methods of synthesis. It was processed mechanically using a roll crusher brand Quinn Process Equipment Company and a screen No. 400, in order to get a particle size mineral less than 37  $\mu\text{m}$ . For removing  $\text{SiO}_2$  impurities, a kaolin suspension was prepared with 45% w/w of solids and 1 kg/ton of sodium hexametaphosphate (Aldrich, 96%) as dispersant, milling at 300 rpm by 30 min. Then, deionized water was added to the suspension in order to dilute at 20% w/w and was stirred vigorously. After 30 min, two phases were formed: suspended slurry, which was called dispersed kaolin, and the precipitated one, called assented kaolin.

### Kaolin- $\alpha$ - $\text{Al}_2\text{O}_3$ system

5 g of kaolin clay and  $\alpha$ - $\text{Al}_2\text{O}_3$  (Aldrich, 99.2%), with a molar fraction,  $x = n(\alpha\text{-Al}_2\text{O}_3)/n(\text{Al}_2\text{O}_3\text{2SiO}_2) = 0.5$ , 1 y 2, were added together with 20 mL of ethanol (Aldrich, 99%) to a miller with zirconium balls and mixed at 3600 rpm during 2 h. The product was dried at 100°C and calcined at a temperature range of 1200 to 1500°C.

### Kaolin- $\text{Al}(\text{NO}_3)_3$ system

5 g of kaolin clay was suspended in a solution with  $\text{Al}(\text{NO}_3)_3$  (Aldrich, 99%) using a molar ratio  $n(\alpha\text{-Al}_2\text{O}_3)/n(\text{Al}_2\text{O}_3\text{2SiO}_2) = 0.5$ , and a equivalent of  $\text{CO}(\text{NH}_2)_2$  (Aldrich, 98%) as fuel, varying the solvent amount from 5 to 20 mL. Subsequently, it was carried out combustion at 600°C. The product was calcined at 1500°C.

### Characterization

The composition of the materials were investigated by X-Ray Diffraction (XRD) (Inel, model EQUINOX 2000) and energy dispersive x-ray spectroscopy (EDS) and its microstructure was observed by scanning electronic microscopy (SEM) (Jeol JSM 6300). The average particle size was determined by laser ray analysis (Beckman Coulter, model LS13320).