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# Synthesis of α-alumina powder obtained from irradiated pseudoboehmites

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**Abstract**. The alumina powder was obtained through a technique based on firing irradiated pseudoboehmites powder to study the radiation effects in the alumina properties. The electron beam radiation effect in a pseudoboehmite produced by sol-gel synthesis was investigated, using aluminum chloride and ammonium hydroxide as precursors. The addition of poly(vinyl alcohol) ($[C_2H_3OH]_n$) solution (8 wt% in water) was also analyzed. The aluminum chloride solution was mixed with the polyvinyl alcohol and the mixture was dropped into an ammonium hydroxide solution. The work presents the effects of pseudoboehmite radiation in the structure of alumina. The alumina was obtained by pseudoboehmite calcinations. The milky-white colloidal pseudoboehmite precipitate obtained by sol-gel method was filtered, washed with distilled water, dried at 70°C, and powdered in a mortar. The sample acquired was calcined 4 hours at 1100°C, and after that X-ray powder diffraction was performed. The well defined α-alumina crystal was obtained from 1100°C treatment for some samples. The X-ray powder diffraction data shows that in some irradiated samples calcined at 1100° C for four hours presented θ-alumina and α-alumina. The powder dried at 70° C was also examined by thermal analysis. The Thermo Gravimetric Analysis (TG) and Differential Thermal analysis (DTA) were used to evaluate mass loss and the pseudoboehmite endothermic and exothermic transformations. The samples were analyzed through scanning electron microscopy technique.

## Introduction

The sol-gel synthesis is a promising process for obtaining pseudoboehmite and high surface area alumina with controlled pore diameter [1]. The structure of pseudoboehmite is similar to the structure of boehmite. They have similar peak positions on their diffraction patterns. The structure of boehmite consists of double layers of oxygen octahedra partially filled with Aluminum cations. Boehmite has the same structure as lepidocrocite (γ -FeO-(OH)). It is orthorhombic with space group *Amam* (a = 3.6936 Å, b = 12.214 Å, c = 2.8679 Å). The difference between boehmite and pseudoboehmite are related to additional water molecules in the pseudoboehmite, which unit cell is larger as compared to the boehmite ones. Water molecules usually are considered to be introduced in the interlayer space [2]. According to Moroz et al [3], the changes in the local structure of layers of pseudoboehmite structure seem to be due the formation of new bonds between the molecules of water and ions of the layers.

γ-aluminas are widely used as catalyst, supports of catalysts, adsorbents, while α-alumina is applied in mechanical parts, refractors, insulators, abrasives, etc. The preparation of α-alumina by heating aluminum hydroxides can produce a finely divided powder constituted by micrometer sized particles. This α-alumina powder is an important material in Traditional and Advanced ceramics, for high temperature applications as well as aggressive chemical environments

Aluminum oxides do not transform directly to the stable hexagonal corundum structure (α-alumina). Aluminum salts decompose to transition aluminas, metastable phases, before transforming into α-alumina. These phase transformation sequences for aluminum trihydrate, $Al(OH)_3$, transformation in aluminas, as the mineral gibbsite and in the form of bayerite obtained in the Bayer process and for AlOOH both as boehmite and diaspore is γ→δ→θ→α-alumina. Under hydrothermal condition, gibsite and bayerite first decomposes to boehmite (AlOOH) and them to γ→δ→θ→α-alumina. The dehydration around 250° C produces high specific surface area alumina. Further decomposition of this phase reduces the surface area and then finally the transformation of θ→α-alumina occurs via nucleation and growth finishing the transformations of alumina.

The irradiation of materials with electrons, especially polymers, with the purpose of improvement of the properties of the material, is growing recently [4]. The effect of irradiation in pseudoboehmite obtained from aluminum nitrate was already studied in the literature [5]. So the aim of this paper is to study the effect of a huge radiation dose of 200 kGy in the gel of pseudoboehmite obtained from aluminum chloride. We report the study of the effect of irradiation in the characteristics of pseudoboehmite and aluminas obtained from irradiated pseudoboehmite.

## Experimental

The used reagents were: aluminum chloride solution obtained using $AlCl_3.6H_2O$, ammonium hydroxide ($NH_4OH$) water solution (28wt%) and polyvinyl alcohol ($[C_2H_4O]n$) water solution (8 wt%), which was used to increase the viscosity of the aluminium chloride solution. The aluminium chloride solution was mixed with the polyvinyl alcohol and the mixture was dropped into an ammonium hydroxide solution. All chemicals used in the experiments are of analytical purity and used directly without any further purification. All the solutions were prepared with deionized water. All the eight experiments were carried using batch technique. The products of each reaction were divided into 2 parts and one sample was irradiated. After irradiation of the eight samples, the sixteen samples (8 irradiated and 8 not irradiated) were filtered and washed with water during filtration. Thereafter the product of filtration was dried at 70° C for 24 hours in air. The parameters used in the reactions are showed in Table 1 and the factorial $2^n$ experimental design [6] is showed in Table 2. The irradiation procedure was with electron beam, from electrons accelerator of the DYNAMITRON, with energy of the order of 1.5MeV and tax of dose of 11.3kGy/s, in the dose of 200kGy.

Table 1: Studied parameters in the reactions

| Variable | level (-) | level (+) |
|---|---|---|
| A Synthesis temperature | 23° C | -5° C |
| B $AlCl_3$solution:polyvinyl alcohol solution | ∞ | 2.5:1 |
| C [$AlCl_3$] | 2M | 0.2M |
| D Radiation dose | 0 | 200kGy |

*Characterization of the samples:*

The pseudoboehmites and the aluminas obtained by calcination of the pseudoboehmite in different temperatures were characterized by several techniques.

*Thermal analyses*: The thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed in Netzsch-STA409C equipment; heating from room temperature to 1300° C, with 20° C $min^{-1}$ heating rate and 50$cm^3$/min $N_2$ flow.

Table 2: Matrix of the full factorial $2^4$ experimental design.

| Experiment | A | B | C | D |
|---|---|---|---|---|
| 1 | - | - | - | - |
| 2 | + | - | - | - |
| 3 | - | + | - | - |
| 4 | + | + | - | - |
| 5 | - | - | + | - |
| 6 | + | - | + | - |
| 7 | - | + | + | - |
| 8 | + | + | + | - |
| 9 | - | - | - | + |
| 10 | + | - | - | + |
| 11 | - | + | - | + |
| 12 | + | + | - | + |
| 13 | - | - | + | + |
| 14 | + | - | + | + |
| 15 | - | + | + | + |
| 16 | + | + | + | + |

*X-rays powder diffraction*: The not irradiated samples dried at 70° C were analyzed by x-ray diffraction. For the irradiated and not irradiated samples calcined at 1100° C for 4 hours were collected diffraction data with a Rigaku MultiFlex difractometer with a fixed monocromator. The experimental conditions were: 40kV, 20mA, $20^o \leq 2\theta \leq 80^o$, $\Delta 2\theta = 0.02^o$, $\lambda_{CuK\alpha}$, divergence slit = 0.5°, reception slit = 0.3 mm and step time 6 s. The Rietveld analysis was performed with the Rietveld refinement program GSAS [7]

*Specific surface area*: The specific surface area was measured with a Quantachrome NOVA 1200 Brunauer–Emmett–Teller BET surface analysis instrument, based on adsorption of $N_2$. The samples were calcined at 500° C for this analysis.

*Scanning electron microscopy*: Scanning electron microscopy (SEM) images were taken with a Jeol JSM 840A equipment, using secondary electron detector. The powder was placed upon SEM stubs covered with double-face tape and covered with gold in an Edwards Sputter Coater model S150B. The images were registered under several magnifications from 100X to 10000X.

**Results and discussion**

It was observed that samples 11, 12, 15 and 16 became yellow after the irradiation procedure, probably due to the presence of PVAl in these samples.

*Thermal analyses*: DTA and TG analysis: A typical DTA curve was observed for samples 1,2,5,6, 9,10,13,14 shows an endothermic curve near 100°C, due to the water vaporization, and an endothermic curve around 400°C due to decomposition of pseudoboehmite to γ-alumina. The DTA and the DTG data shows that in the irradiated samples the two endothermic transformations occur in higher temperatures than in the not irradiated samples. This was already observed in pseudoboehmites synthesized from aluminium nitrate [5]. The decomposition of PVAl and the dehydration of pseudoboehmite at the same range temperature of DTA analysis resulted in complex peaks in this region for the other samples. In the thermal analysis at 1200°C is observed a sharp peak for samples 1, 2, 5, 6, 9, 10, 12, 13 and 14 probably due to the transformation of the last metastable phase of alumina to α-alumina(θ→α-alumina). It was observed comparing DTA results of samples 1 and 2 with the corresponding irradiated samples (9 and 10), that there was a significant increase in the temperature of the θ→α-alumina transformation (Table 3). For the same conditions, but with diluted aluminum chloride solution, samples 5 and 6 and the corresponding irradiated samples 13 and 14, there is no big difference in the temperature of θ→α-alumina transformation.

Table 3 Temperature of the last exothermic peak observed at the DTA analysis

| Sample | T(°C) | Sample | T(°C) |
|---|---|---|---|
| 1 | 1184 | 9 | 1222,8 |
| 2 | 1206,6 | 10 | 1238,6 |
| 5 | 1198 | 13 | 1193,4 |
| 6 | 1226 | 14 | 1217 |

Figure 1 shows the TG and DTG analysis for sample 15. It is observed tree peaks in the DTG analysis probably to water desorption, PVAl decomposition and to the pseudoboehmite→γ-alumina phase transformation.

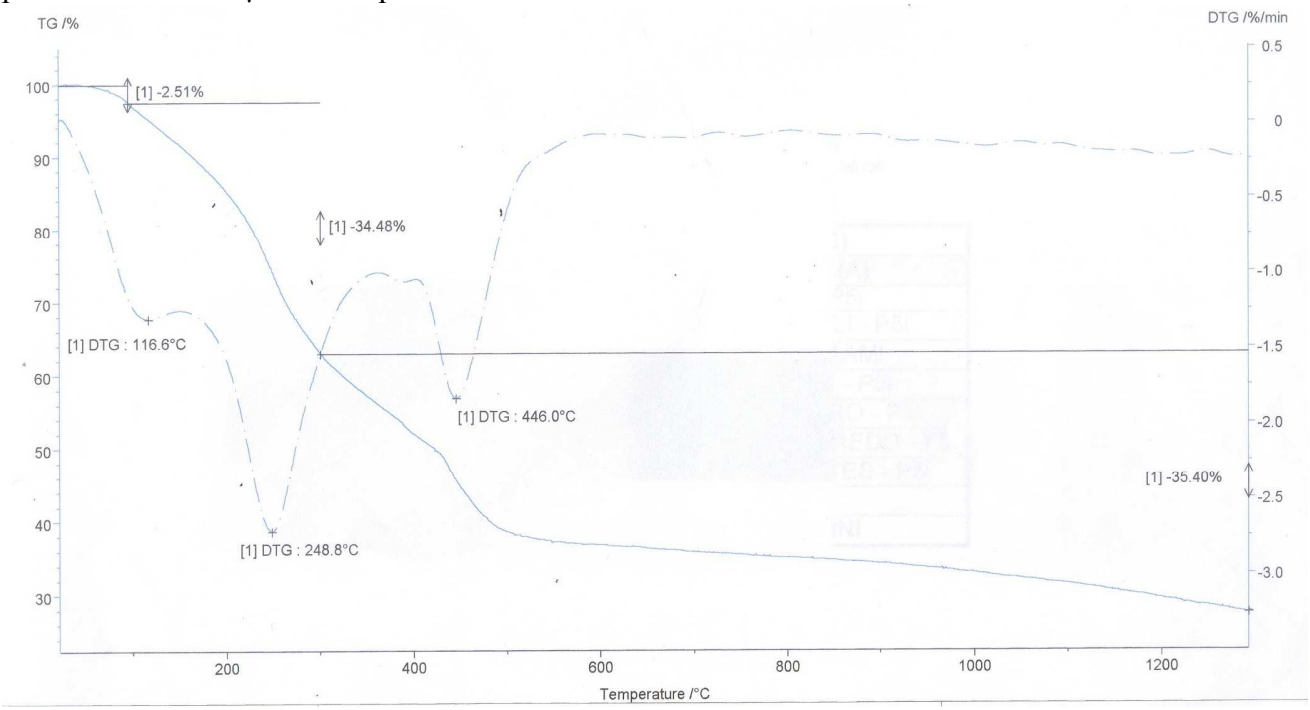


Figure 1: TG and DTG of sample 15.

*Specific surface area:* The data of the specific surface area (Table 4) shows that for the samples synthesized in the presence of PVAl in diluted $AlCl_3$ solution (0.2M), the non-irradiated samples have a bigger specific surface area than the irradiated samples.

Table 4: Specific surface area of the 16 samples.

| Sample | Specific surface area($m^2$/g) | Sample | Specific surface area($m^2$/g) |
|---|---|---|---|
| 1 | 240.8 | 9 | 252.9 |
| 2 | 228.4 | 10 | 252 |
| 3 | 281.6 | 11 | 348.2 |
| 4 | 277.5 | 12 | 302.2 |
| 5 | 87.4 | 13 | 64.3 |
| 6 | 283.7 | 14 | 181.9 |
| 7 | 217 | 15 | 55.6 |
| 8 | 166.5 | 16 | 42 |

For the samples synthesized with diluted $AlCl_3$ solution (0.2 M), samples 5, 6, 7, 8 and samples 13, 14, 15, 16, the medium value of the specific surface area of the irradiated samples present a lower result than the not irradiated samples.

For the variable specific surface area, using the data of Table 4 and the factorial experimental design, the Table 5 was obtained.

By the analysis of the effects of the variables in the specific surface area (Table 5) we conclude that the $AlCl_3$ concentration in the solution is the principal variable with influence in the specific surface area data. With the 0.2M solution of $AlCl_3$ there is a reduction in the specific surface area of the samples. It is observed that the irradiation of the samples decreased the specific surface area of the samples calcined at 500º C. This was already observed with the pseudoboehmite synthesized with aluminum nitrate [5]. This means that the irradiated samples present a smaller specific surface area than the non-irradiated samples. The two ways interaction CD equal to -67 also confirm that these 2 variables (C and D) are the one with great influence in the specific surface area. The two way interaction AB with a value equal to -52 plays also an important role in the specific surface area. When both variables A and B are in the same level (- - or + +) there is a reduction in the specific surface area. When they are in different levels (- + or + -) there is an increase in the specific surface area.

Table $5.2^4$ experimental factorial designs –Estimated effects and coefficients for the data of Table 4.

| Term | Estimated Value |
|---|---|
| Constant | 205 |
| Main effects: | |
| A-synthesis temperature | 23 |
| B– $AlCl_3$solution:PVAlsol. | 12 |
| C – [$AlCl_3$] | -136 |
| D – Radiation dose | -35 |
| 2-way Interactions AB | -52 |
| AC | 39 |
| AD | -9 |
| BC | -46 |
| BD | -13 |
| CD | -67 |
| 3-way interactions - ABC | -43 |
| ABD | 8 |
| ACD | -1 |
| BCD | -27 |
| 4-way interactions - ABCD | 21 |

*Scanning electron microscopy:* From the (SEM) micrographs it is observed that the γ-$Al_2O_3$ crystallites (samples of pseudoboehmite calcined at 500ºC) of not irradiated samples present a more homogeneous surface than the irradiated samples. From these SEM it is observed that the irradiation promote the beginning of the agglomeration of the small grains into big crystallites (Fig. 2). Probably due to this there is a reduction in the specific surface area for the irradiated samples.

*X-rays powder diffraction:* The x-ray diffraction data of the not calcined samples shows the broad peaks characteristic of pseudoboehmite at $2\theta=13^o$ (020) and $2\theta=28^o$ (021).

A first comparative overview of powder diffraction data from all samples shows that those calcined at 1100ºC present the θ-alumina and α-alumina structures (see Table 6). The samples contain only these two phases of alumina and no other observable impurities were detected. The average intensity in the diffraction data of the irradiated samples is smaller than that of the non-irradiated samples, which could indicate that the radiation decrease the crystallinity.

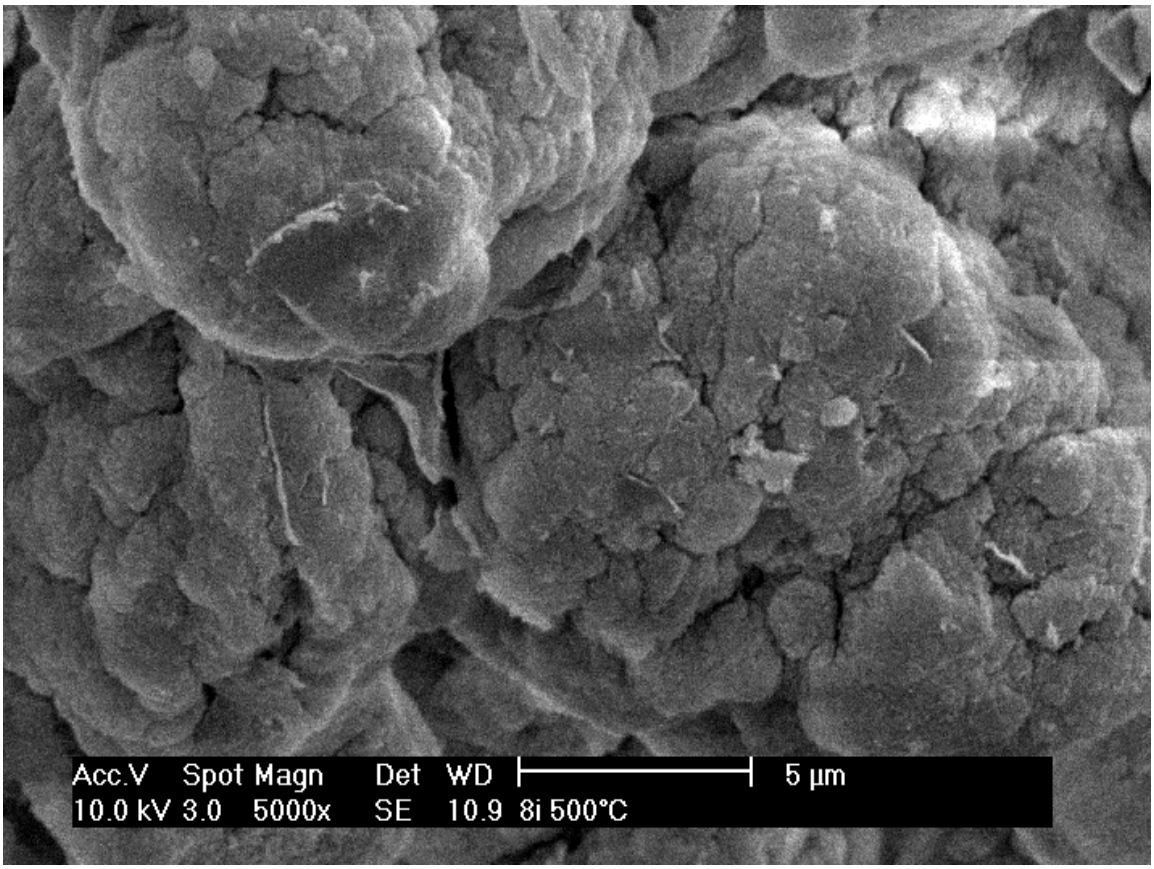


Figure 2. Micrograph of sample 16 calcined at 500° C: magnification of 5000X

Table 6: Results of phase quantification by Rietvelt method.

| Sample | α-alumina | Theta-alumina | Sample | α-alumina | Theta-alumina |
|---|---|---|---|---|---|
| 1 | 100% | | 9 | 67,9% | 32,1% |
| 2 | 96,3% | 3,7% | 10 | 58,7% | 41,4% |
| 3 | 40,6% | 59,4% | 11 | 51,3% | 48,7% |
| 4 | 35,4% | 64,6% | 12 | 28,3% | 71,7% |
| 5 | 100% | - | 13 | 100% | - |
| 6 | 100% | - | 14 | 100% | - |
| 7 | 39,7% | 60,3% | 15 | 24,7% | 75,3% |
| 8 | 56,7% | 43,3% | 16 | 36,4% | 63,6% |

Table 7 shows the results of the experimental design results, estimated effects and interactions, using the amount of α-alumina as the variable of study.

The more important effects are the ratio $AlCl_3$solution:PVAl solution, the radiation dose, the $AlCl_3$ concentration and the interactions with these 3 variables (BC and BCD). The more important effect is associated with the $AlCl_3$solution: polyvinyl alcohol solution (-51,2%). When the synthesis of pseudoboehmite is made with a $AlCl_3$solution: polyvinyl alcohol solution equal to 2.5:1 there is a big reduction of the α-alumina concentration in the calcined samples. When the samples are irradiated in general there is a reduction in the concentration of α-alumina and when we change the $AlCl_3$ concentration from 2M to 0,2M there is an increase in the amount of α-alumina in the calcined sample. Figure 3 shows the x-ray diffraction data of sample 5. It is observed the presence of α-alumina predominantly.

Table 7. $2^4$ experimental factorial designs -Estimated effects and coefficients for the data of Table 6

| Term | Estimated value |
|---|---|
| Constant | 64,7 |
| Main effects | |
| A-synthesis temperature | -1,6 |
| B– $AlCl_3$solution:PVAl sol. | -51,2 |
| C – [$AlCl_3$] | 9,9 |
| D – Radiation dose | -12,7 |
| 2-way Interactions AB | 1,7 |
| AC | 8,7 |
| AD | -3,6 |
| BC | -9,4 |
| BD | 4,8 |
| CD | 3,8 |
| 3-way interactions - ABC | 5,5 |
| ABD | -2,2 |
| ACD | 2,3 |
| BCD | -13,6 |
| 4-way interactions - ABCD | 0,9 |

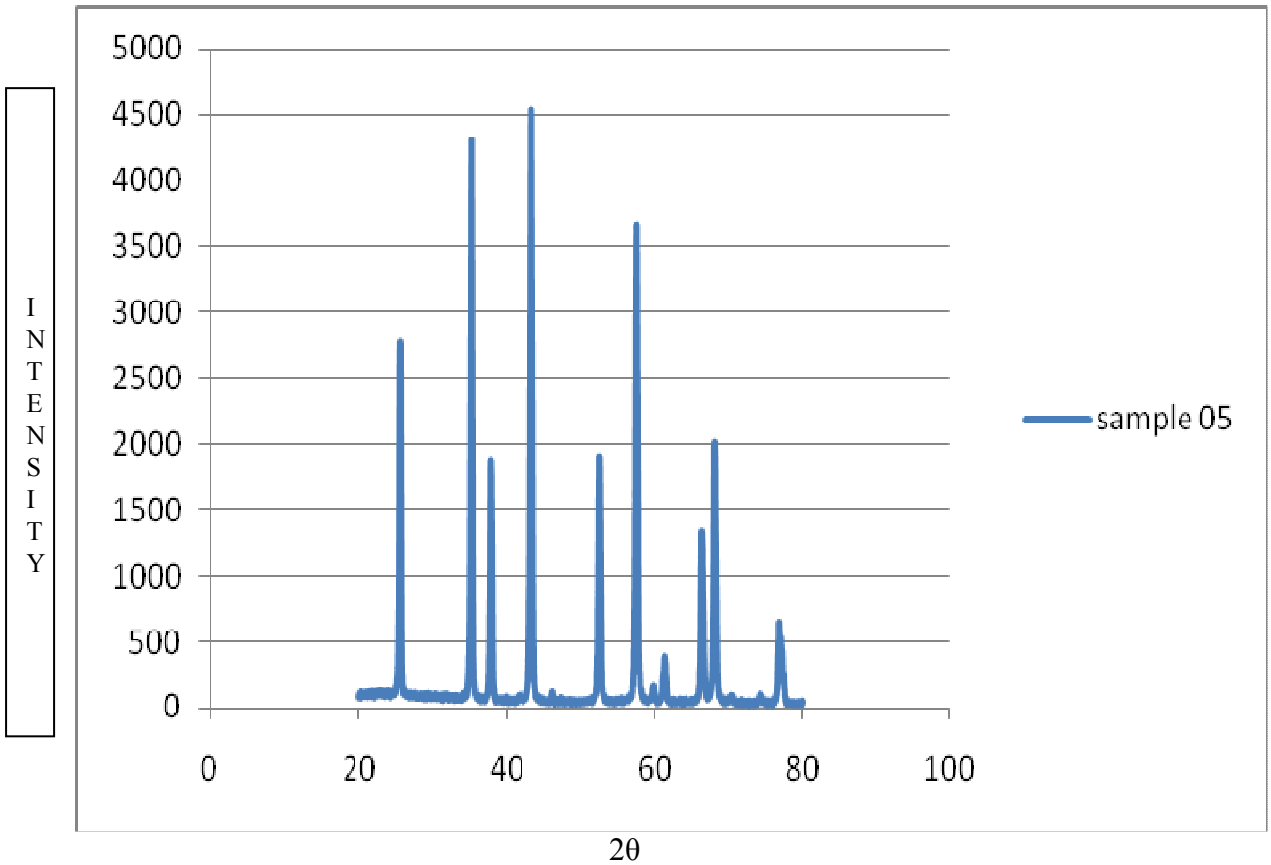


Figure 3 X-ray diffraction data of sample 5.

The x-ray diffraction data shows that samples 1 and 2 have 100% and 96.3% of α-alumina. The samples obtained in the same conditions but irradiated, samples 9 and 10 have only 32.1 and 41.4% of α-alumina. Probably this explains the difference in the temperature observed in DTA analysis for the θ→α-alumina transformation. For the samples 5 and 6 and the samples obtained in the same reactions conditions but irradiated, samples 13 and 14, there is no significant difference in

the amount of α-alumina and probably this explains the small difference in the temperature of θ→α-alumina transformation observed in the DTA analysis.

**Conclusions**:
From the experimental design we conclude that for the conditions of study that the synthesis of pseudoboehmite with a diluted solution of the aluminium chloride 0.2[M] and the irradiation of the samples promoted the reduction of the specific surface area of the γ-alumina. These are the main variables with influence in the specific surface area variable. The observation by Scanning Electron Microscopy shows that the surface of the not irradiated sample seems more porous and homogeneous than the irradiated samples. The full factorial experimental design data analysis shows that the addition of PVAl in the synthesis of pseudoboehmite and the irradiation of the pseudoboehmite samples has influence in the phase transformation of θ→α-alumina. The precipitation of pseudoboehmite with PVAl addition reduces the concentration of the α-alumina in the product obtained by calcination of pseudoboehmite at 1100$^{o}$ C. The radiation dose also influences the θ→α-alumina transformation.

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