

## Comparative Study of Influence of Anions on Thermal Behavior of nanosized Alumina

Fadia Shaheen<sup>1\*</sup> Muhammad Irfan<sup>2</sup> Bakht Bahadur Rana<sup>1</sup> Rashad Mahmood<sup>1</sup>  
Muhammad Latif Mirza<sup>3</sup>

1.Glass and Ceramic Research Centre, PCSIR Laboratories Complex, Lahore, Pakistan

2.PITMAEM, PCSIR Laboratories Complex, Lahore, Pakistan

3.Department of Chemistry, University of Sargodha, Sargodha, Pakistan

### Abstract

Nanoalumina precursors homogeneously precipitated from aluminum nitrate and aluminum chloride were investigated for their thermal transitions and structural transformations. From both the monovalent anionic salts under identical reaction conditions, alumina precursors derived were same i.e. pseudoboehmite but their thermal behavior was different. Pseudoboehmite prepared from nitrate was amorphous and prone to dehydroxylation and subsequent calcination while pseudoboehmite prepared from chloride had relatively higher crystallinity and delayed dehydroxylation and calcination. In case of nitrate, life duration of gamma alumina was brief i.e. up to 350°C whereas it in case of chloride it showed off at 375 and persisted up to 800°C. Consequently, complete formation of alpha alumina occurred at 1150°C in the former case while alpha phase was in process of its conversion from theta phase in this temperature regime in the latter case. DTA-TG, XRD, SEM, etc. were carried out for the characterization.

**Keywords:** aluminum hydroxide, boehmite, pseudoboehmite, metastable polymorphs, corundum

### Introduction

Alumina hydrate are common source of alumina. There are two main kinds of alumina hydrate known as aluminum hydroxides and aluminum hydroxydioxes. Alumina trihydrate or aluminum trihydroxide  $[Al(OH)_3 = Al_2O_3 \cdot 3H_2O]$  exist in three crystalline polymorphs named gibbsite or hydrargillite [ $\gamma$ -Al(OH)<sub>3</sub>], bayerite [ $\alpha$ -Al(OH)<sub>3</sub>], and nordstrandite [ $\beta$ -Al(OH)<sub>3</sub>]. Monohydrated alumina or aluminum oxihydroxide  $[AlO(OH) = Al_2O_3 \cdot H_2O]$  is available in two crystalline polymorphs. These are boehmite [ $\gamma$ -AlO(OH)] and diasporite [ $\alpha$ -AlO(OH)]. Thermal dehydroxylation of these alumina hydrates leads to the formation of alpha alumina which involves a number of metastable polymorphs so called transitional aluminas designated by Greek letter to identify i.e. alpha, gamma, delta and others. Each one of these has a different crystalline structure and is stable in a peculiar temperature range. By progressive elevation of the temperature, each transition alumina can suffer transformation into another transition alumina, however, all of them recrystallize into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at higher temperatures which has a very stable crystalline structure and melts at 2050°C (Cardarelli 2008). The transition alumina particularly the  $\gamma$  form has fine particle size and huge surface area with enhanced catalytic surface activity find industrial applications as adsorbant, catalyst or catalyst carrier, coating and soft abrasive (Levin and Brandon 1998). Thermal stability of the transitional aluminas depends on their morphology and crystallite size (Braun et al 1999) which in turn is influenced by the aluminum hydroxide psalt used as starting material (Temuujin et al 2000).

The preparation of nanoalumina powder by solution technique generally involves two stage processes, the formation of metal salt solution and its subsequent decomposition. It is well known that the morphology of the aluminum hydroxide precipitated and its thermal behavior is affected by many factors such as concentration, kind of metal compounds, precipitation reagents, coexistent ions and temperature, etc. (Unuma 1998, Ramanathan 1996; Nagai 1993; Nagai et al 1991; De Hek, H 1978 and Stol 1976). It has been reported (Ada 2003 and Xiao 2007) that aluminum nitrate-urea and aluminum chloride-urea reactions result in sudden formation of gelatinous precipitates at pH 6.5. The monovalent anions NO<sub>3</sub><sup>1-</sup> and Cl<sup>1-</sup> because of their poor coordinate bond forming ability do not interfere in the reaction of hydroxide with aluminum containing polymeric cation growing into the larger charged polymeric species via olation and oxolation within Al-O-Al bridges

In the present study alumina nanopowders were produced from aluminum nitrate and aluminum chloride under identical reaction conditions to study the relative effect of monovalent anions on thermal transition and structural transformation of alumina nanopowders during conversion into alpha alumina. Besides, variation in average particle size of nanopowders was also studied.

### Experimental

Aluminum nitrate nonahydrate Al(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (Fluka) and aluminum chloride AlCl<sub>3</sub>.6H<sub>2</sub>O (Fluka) were used as starting materials. Molar ratios of aluminum salts and urea (NH<sub>2</sub>)<sub>2</sub>CO (Merck) are given in Table 1.

Table 1: Molar compositions of aluminum salt and urea.

| Sr. No | Composition | Symbol | Salt:Urea molar ratio | Aluminum Salt M/3l | Urea M/3l |
|--------|-------------|--------|-----------------------|--------------------|-----------|
| 1.     | AN          | AN3    | 1:3                   | 0.3                | 0.9       |
|        |             | AC3    |                       |                    |           |
|        |             | AN5    | 1:5                   | 0.3                | 1.5       |
| 2.     | AC          | AC5    |                       |                    |           |
|        |             | AN7    | 1:7                   | 0.3                | 2.1       |
|        | AC          | AC7    |                       |                    |           |
|        |             | AN9    | 1:9                   | 0.3                | 2.7       |
|        |             | AC9    |                       |                    |           |

The sols were heated at 90°C temperature with constant stirring and volume was maintained to 6 liters by adding distilled water. The pH of the sols has been monitored throughout the reaction at definite intervals of time. When pH value reached 7, the reaction was stopped. Gels were washed several times using distilled water. A tray type freeze drier of Max series was used to sublime gels at -40°C. Nanopowders collected from freeze drier were consolidated into green bodies. After presintering at 800°C for 2 hours, the powders were damped with 2wt% (related to Al<sub>2</sub>O<sub>3</sub>) polyvinyl alcohol PVA (Hoechst, Frankfurt) and uniaxially pressed into 1X0.3" disks. The prerequisites and parameters of cold compaction are given in Table 2.

The green machined compacts were initially dried overnight at room temperature, heated at 100°C for 1 hour in electric oven and finally thermolysed at 800°C for 1 hour. The digital electric laboratory oven WE 500HA and high temperature rapid heating electric furnace RHF/3 Carbolite, UK were used. Sintering was carried out up to 1400°C at the heating rate 5°C per minute and soaking time 3 hours.

For TDA, specimens with 50 mm length and 20 mm width were fired up to 1600°C @ 20°C per minute in Horizontal Orton Dilatometer DIL 2016 STD.

X-ray diffraction measurements were conducted on Siemen's Diffractometer D5000. X-ray tube operated at 40 kV and 30 mA. Data was collected with a scintillation counter in the 10-70° range with a step of 0.05° and a counting time of 60 s/step.

A Hitachi S-3700, Japan SEM equipped with EDS, was used to acquire image at the accelerating voltage 25 kV, working distance 5 mm, tilt angle 0°. To improve image resolution sample was coated with platinum at 0.1 torr and 20 μA for 2 min which has been found optimum for a thin layer coating.

## Results and Discussion

### Hydrolysis-precipitation of Aluminum Hydroxide

The hydrolysis-precipitation using aluminum salt and urea as precursors undergoes change in pH which is plotted as a function of time in Figure 1. In case of AN3, pH gradually increased from 3 to 5 in about 7.5 hours. At this pH, the turbidity appeared in the sol. The increase in pH value however, was spontaneous in next 1.5 hours and reached 6. This lead to flocculation of sol and the content of vessel turned white. The heating and stirring for further 1 hour accomplished the conversion of sol into gel as the pH value reached 7 i.e. neutral. The behavior of AC3 composition is similar to AN3. It also shows two plateaus in pH curve. The time period however, for the conversion of sol into gel was comparatively little more. There is a difference of about 15 minutes. The physical appearance of two reaction products was different. AN3 gel was transparent, thick and more colloid thus difficult to filter. Relative to AN3, AC3 gel was opaque, thin and easy to filtrate. The reaction mechanism of the formation of aluminum hydroxide includes

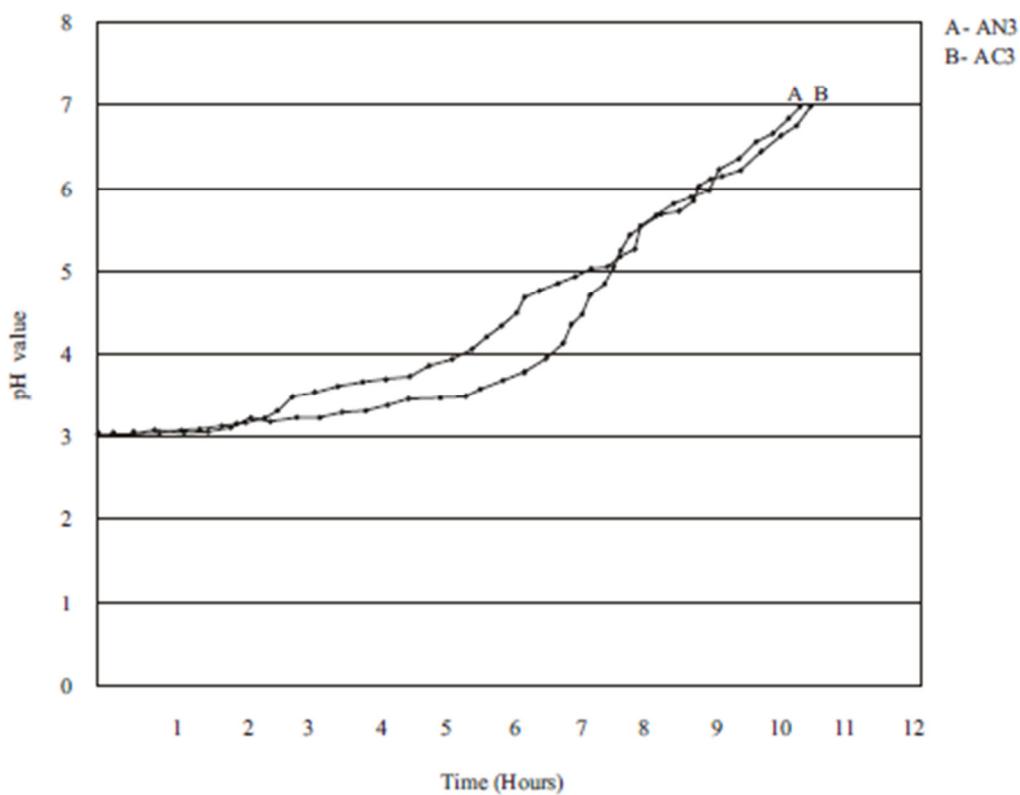
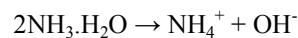
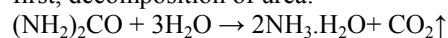
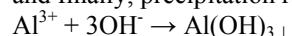


Figure 1 pH plot of AN3 and AC3

first, decomposition of urea:



and finally, precipitation reaction:



Particle profile of freeze dried powders is presented in Figure 2. The figures revealed

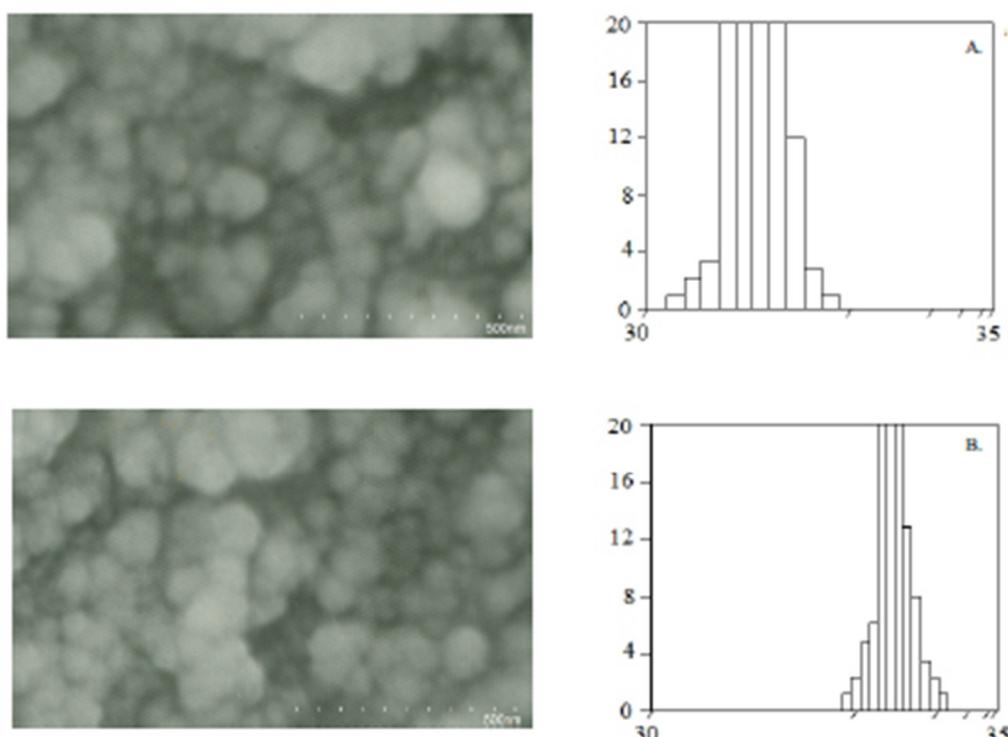


Figure 2 Particle profile of AN3 and AC3

that AN3 and AC3 nanopowders have 31 nm and 32 nm average particle size, respectively which is quite comparable. However, there was difference in particle size distribution. AN3 showed narrower particle size distribution while AC3 relatively wider. Scherrer formula was also applied to measure average size of crystallite and data obtained was in agreement.

In case of both the aluminum salts, average particle size increased with increase in molar concentration of urea and vice versa.

**a) Structural changes and thermal transformations of AN alumina nanopowder**

AN compositions showed same thermal trend. Among these four, AN3 composition was selected for study of structural changes corresponding to thermal transformations.

The XRD diffractogram of AN3 nanopowder presented in Figure 3a, exhibits that the powder is amorphous. The diffractogram however, appears more like an array of amorphous haloes. DSC-TG thermogram of AN3 in Figure 4 shows that the powder undergoes three stages of decomposition with total 45% weight loss. In the first stage, between 30-150°C weight loss is 12% corresponding to a broad endotherm at 150°C which is nevertheless due to the decomposition of volatile compounds. The sample heated at 125°C for 1 hr is shown in Figure 3b. There was no change in diffractogram.

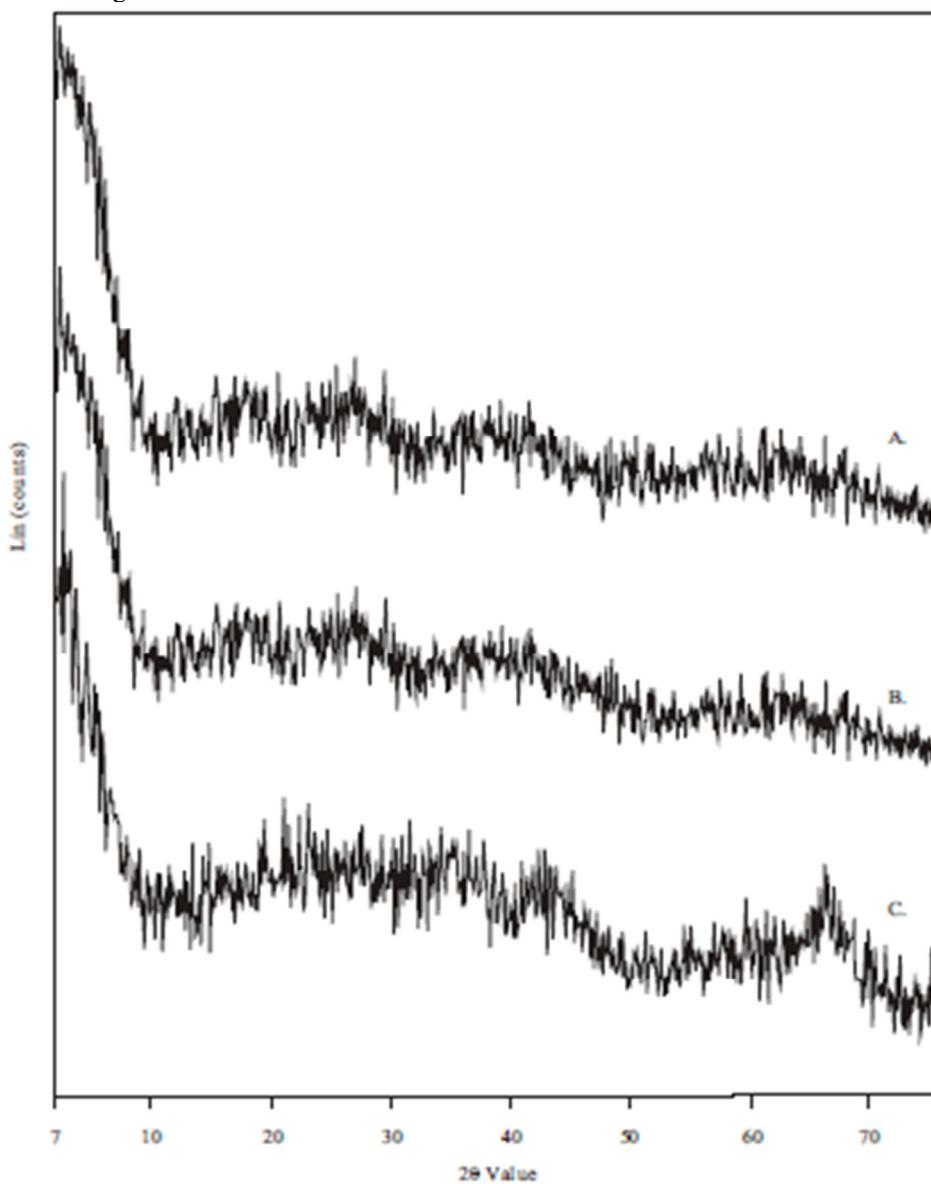


Figure 3 XRD of AN3 at RT 125 and 225C

In the second stage, maximum weight loss occurred i.e. 38% in the temperature regime 150 to 360°C along with a large endothermic peak at 250°C. The sample was heated at 225°C for 1 hr and diffractogram is shown in Figure 3c. It seems that haloes tend to organize themselves into bands. These XRD bands are typical of pseudoboehmite. The bands are not sharp and distinct showing that the powder is still predominantly amorphous.

The endothermic peak at 250°C relates to dehydroxylation of pseudoboehmite.

During thermal transformation, two small endothermic peaks also called humps by Mackenzie (Mackenzie 1957) appeared at 360 and 600°C. According to the general pathway of thermal dehydroxylation of aluminum hydroxide (Antos 2004), pseudoboehmite dehydrates on heating into gamma alumina which on further heating into delta then theta and finally into alpha alumina. Therefore of these two, the low temperature peak corresponding to third and final weight loss of about 2% represents gamma phase while high temperature peak to delta phase of alumina. The medium sized peak at 1150°C accounts for conversion into alpha alumina.

In the temperature region between successive thermal events, two crystalline phases coexist, however their relative proportion varies with temperature (Bennet and Stevens 1998; Braun et al 1999). Based on the fact, the Figure 4 is charted into various temperature zones in order to compare DSC thermal event with XRD structural change. There are two continuous lines in the figure, below first the powder is exclusively pseudoboehmite and beyond latter alpha alumina. The dotted lines show the transformation of crystalline phases. The area beneath two lines depicts the temperature zone where two crystalline phases coexist. The crystalline phase identification in the present study was carried out on the basis of the principle peak, preceding XRD diffractogram, relative proportion of crystalline phases and DSC interpretations.

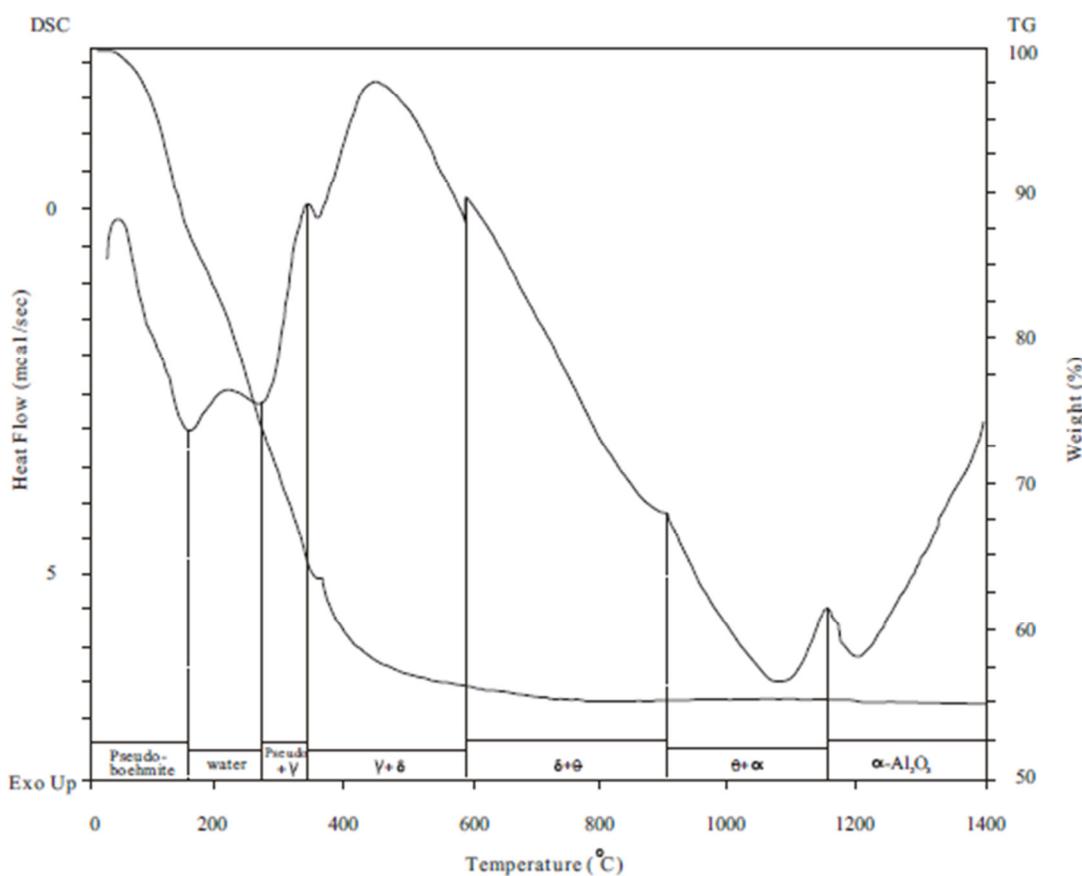


Figure 4 DSC-TG of AN3

XRD peaks of four aluminas under consideration i.e. gamma, delta, theta and alpha alumina lie close to each other. This is due to the fact that oxygen anions in the crystal lattices have fixed positions while distribution of aluminum cations shows difference in structural arrangements. Relative distribution of cations is cubic closed packed c.c.p. in gamma, delta and theta and hexagonal closed packed h.c.p. in alpha alumina thus structural arrangement is quite similar (Levin 1998). Similar d reflexion values of transitional and alpha alumina are given. in Table 2

**Table 2: Similar d reflexion values of transitional and alpha alumina.**

| Gamma | Delta | Theta | Alpha |
|-------|-------|-------|-------|
| 4.55  |       | 4.52  |       |
|       |       | 3.55  | 3.54  |
| 2.87  |       | 2.86  |       |
| 2.73  |       | 2.72  |       |
| 2.43  |       | 2.44  |       |
| 2.27  | 2.28  | 2.26  |       |
|       | 1.99  | 2.02  | 1.99  |
| 1.96  | 1.96  | 1.96  |       |
| 1.80  |       | 1.80  |       |
|       |       | 1.77  | 1.77  |
| 1.61  |       | 1.62  | 1.63  |
|       |       | 1.57  | 1.57  |
|       | 1.54  | 1.54  | 1.54  |
| 1.51  |       | 1.50  |       |
|       |       | 1.43  | 1.43  |
| 1.40  | 1.40  | 1.40  |       |
|       | 1.39  | 1.38  | 1.38  |
| 1.36  |       | 1.36  | 1.36  |
| 1.33  |       | 1.33  |       |
| 1.31  |       | 1.31  | 1.30  |
|       |       | 1.28  | 1.26  |

The sample after heating at 350°C for 1 hr is shown in Figure 5. According to Figure 4,

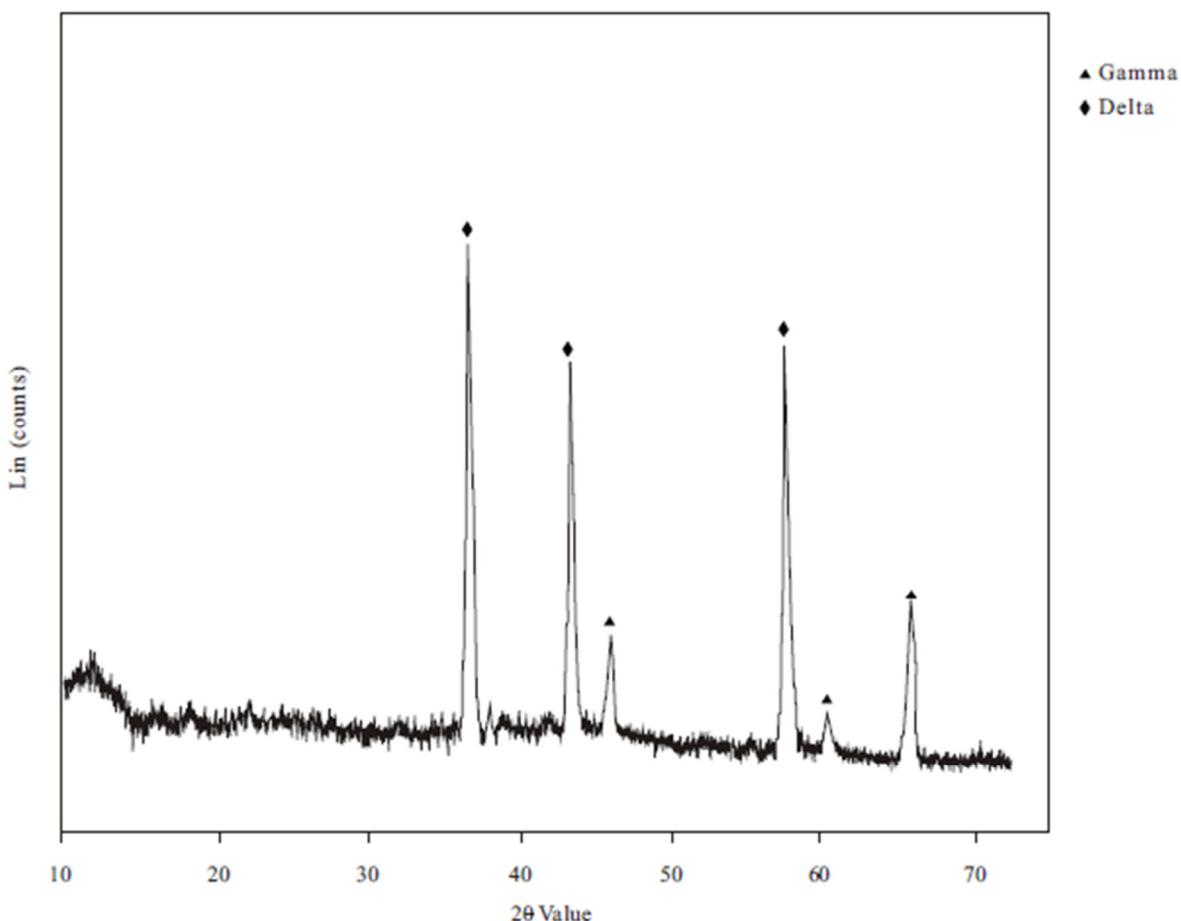


Figure 5 XRD of AN3 at 350  
pseudoboehmite and gamma are the two probable phases in this temperature range, however, XRD diffractogram

identifies delta as principle phase with minor peaks of gamma. This shows that pseudoboehmite had been completely dehydroxylated and gamma is being transformed into delta alumina.

Sample was heated at temperature beyond which weight loss is static i.e. 800°C for 2 hrs. The resulting diffractogram is shown in Figure 6. In accordance with DSC, delta and theta co-exist at this temperature. Two crystalline phases identified were theta and alpha which seems in succession with the preceding XRD graph. The principle peak with d reflexion 2.57 was identified as theta phase besides peaks with d reflexion 2.08, 1.73, 1.57 and 1.50. XRD peak with 1.96 d value depicts either of three transitional alumina phases. This peak is designates as theta and/or delta. Gamma phase had been converted into delta phase at 350°C therefore is nonexistent at 800°C.

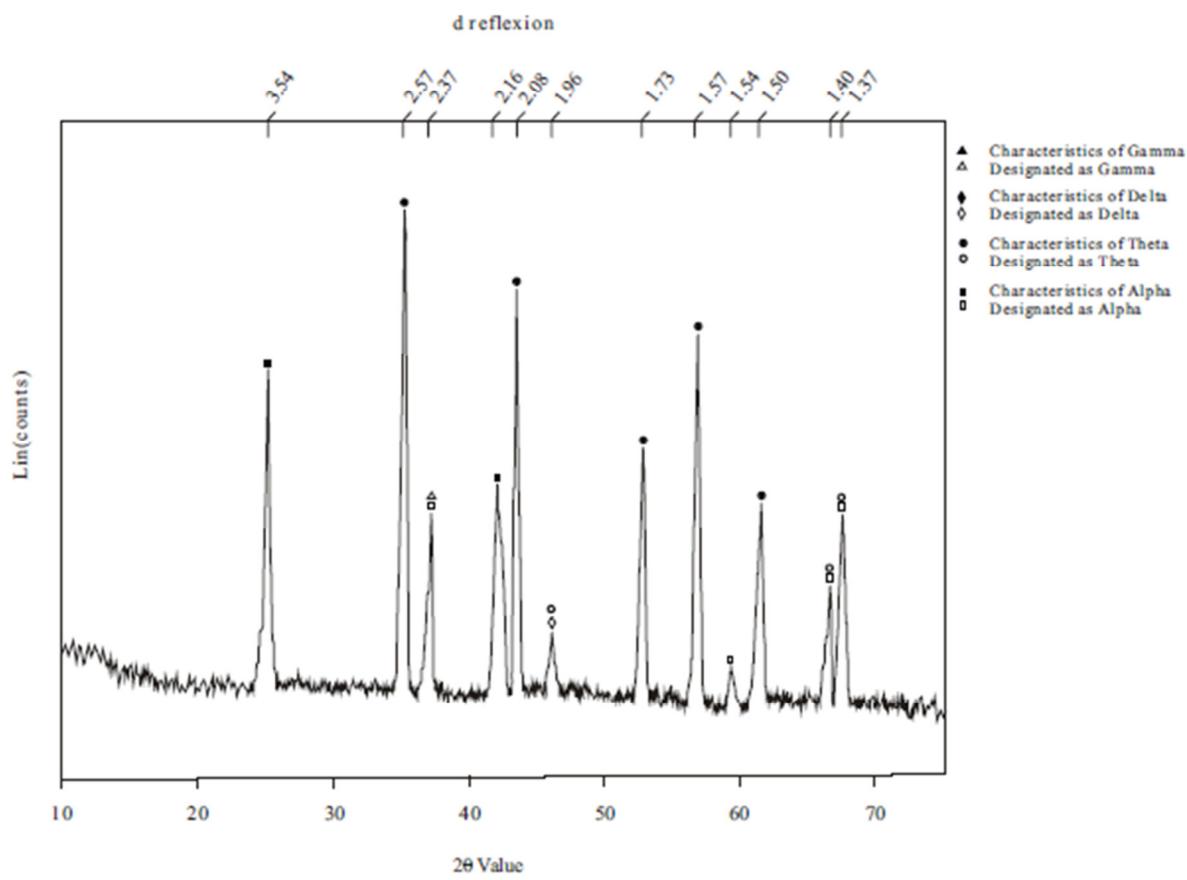


Figure 6 XRD of AN3 at 800C

The second phase i.e. alpha showed its characteristic peaks at 3.54, and 2.16 d reflexions. The peak with 1.54 d value is marked as alpha in the graph though it has equal probability of delta and theta phase. This is due to the reason that the crystalline structure of sample at this stage gives an impression that sample is at the initial stage of conversion from theta into alpha phase. In addition, peak with d value 2.37 is also designated as alpha since the gamma is improbable.

The XRD peak with 1.40 and 1.37 d reflexions could be due to one of the transitional aluminas or alpha alumina. Keeping in view relative proportion of theta and alpha phases, the probability of gamma and theta is nil. However, it is difficult to figure out that which of the remaining two phases, the peaks signify to.

The exothermic peak in DSC thermogram at 1150°C accounts for alpha alumina. The diffractogram of sample obtained after heating at this temperature for 1 hr is shown in Figure 7. It merely shows single crystalline phase i.e. alpha alumina which is in agreement with the DSC thermogram.

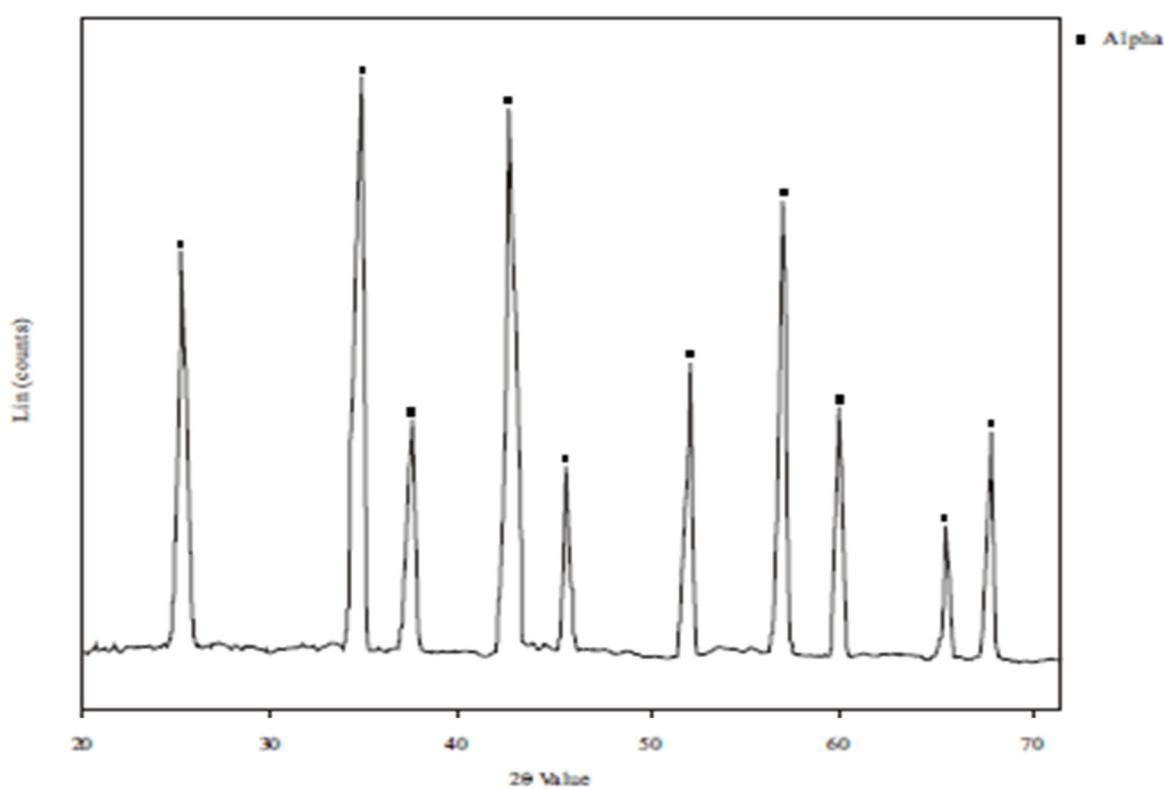


Figure 7: XRD of AN3 at 1150°C

**b) Structural changes and thermal transformations of AC alumina nanopowder**

Thermal behavior of AC compositions had been same with shift of thermal event to higher temperature with increase in average particle size. AC3 composition was chosen to explore structural changes on heating.

DSC-TG thermogram of AC3 shown in Figure 8 is comparable to AN3. TG curve shows 45% weight loss. Up to 150°C temperature, 11.5% weight loss along with a large endothermic peak shows liberation of adsorbed water. Major weight loss i.e. 26.5% from 150 to 375°C with a large endothermic peak at 280°C is associated with dehydroxylation of pseudoboehmite.

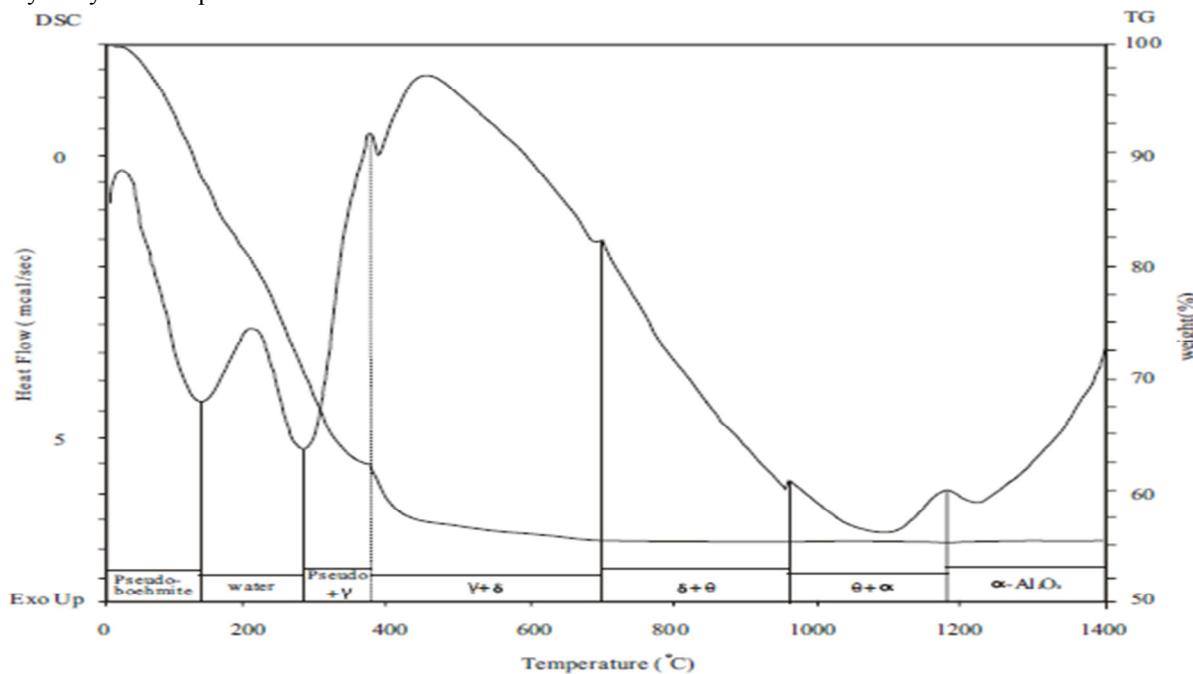


Figure 8: DSC-TG of AC3

Remaining 7% weight loss occurred from 375 to 700°C. No further weight loss was observed. First and the foremost exothermic peak at 375°C shows dehydroxylation of pseudoboehmite into  $\gamma$ -alumina. Two very small exothermic peaks at 700 and 957°C indicate  $\delta$ - and  $\theta$ -alumina, respectively. Last exothermic peak at 1166°C shows transformation into  $\alpha$ -alumina.

Comparison of DSC thermogram of AN3 and AC3 shows that peak for the dehydroxylation of pseudoboehmite is shifted towards higher temperature. The XRD diffractogram of AC3, in Figure 9 has sharp pseudoboehmite bands which show that it has higher crystallinity relative to AN3 powder

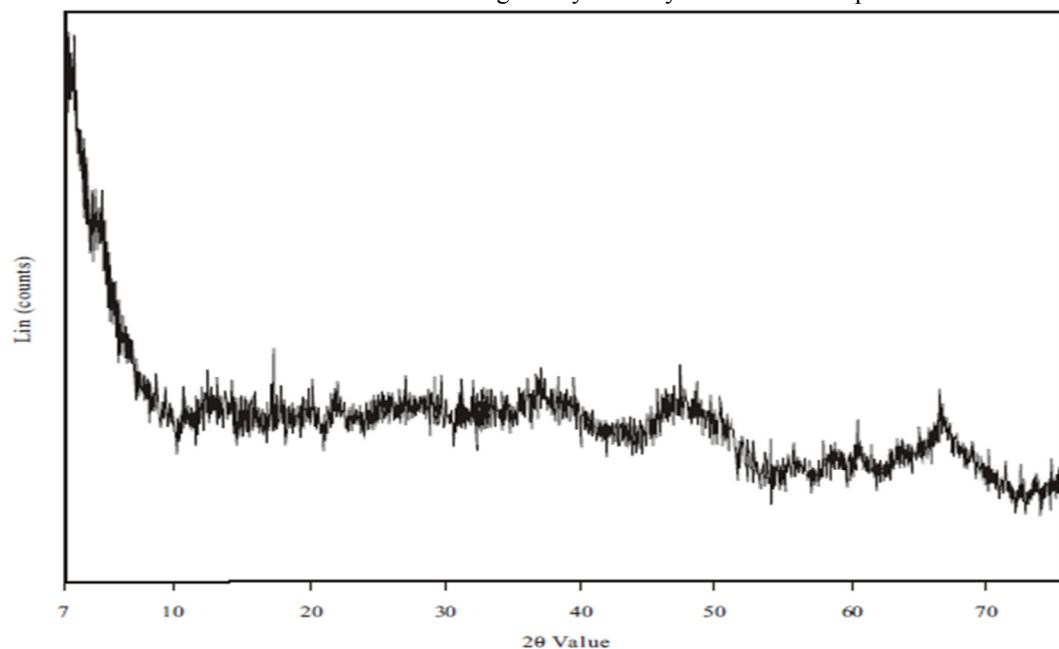


Figure 9: XRD of AC3 at RT

Sample after heating at 375°C for 1 hr is shown in Figure 10. It shows several small peaks of gamma phase emerging out of pseudoboehmite bands. Comparison of Figure 5 and 11 reveals that dehydroxylation of pseudoboehmite is completed at far lower temperature in AN3 than in AC3

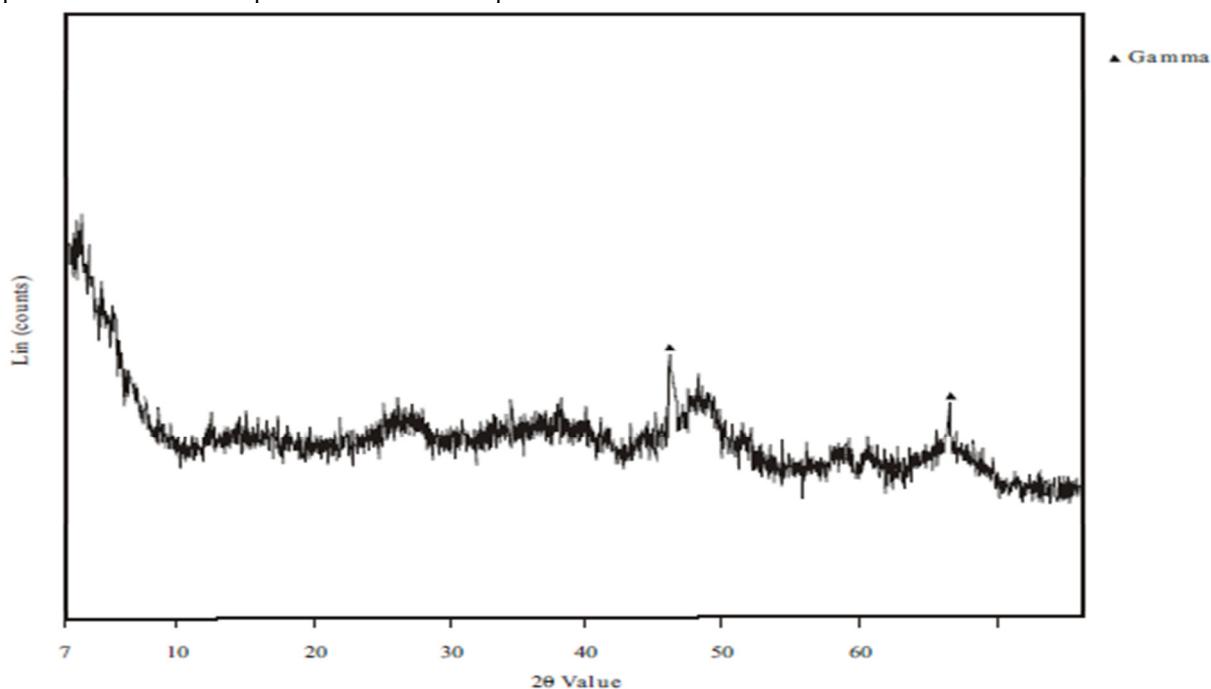


Figure 10 XRD of AC3 at 375

Sample was heated further at 800°C for 2 hrs and its diffractogram is shown in Figure 11.

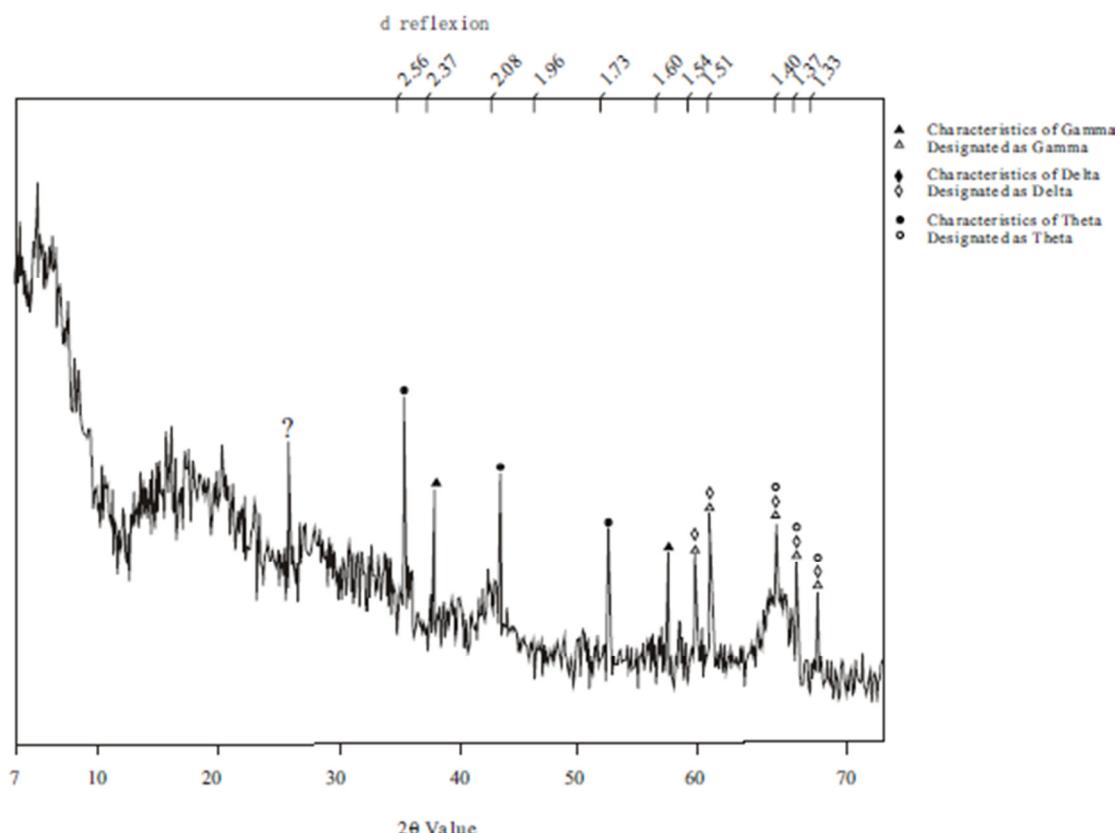


Figure 11 XRD of AC3 at 800°C

DSC thermogram proposes two phases i.e. delta and theta at this temperature. Theta phase was certainly identified as major phase along with minor proportion of delta. In addition to these two phases, gamma phase was encountered found in quite fair proportion. Few bands of pseudoboehmite were also found.

The principle peak with 2.56 besides, peaks with 2.08 and 1.73  $d$  reflexions are characteristics of theta phase. Two peaks with  $d$  reflexion 2.73 and 1.60 are characteristics of gamma phase. XRD peaks with  $d$  values 1.96, 1.54, 1.51 and 1.33 represent gamma and/or delta phase of alumina.

For peaks with 1.40 and 1.37  $d$  values, the presence of amorphous haloes eliminates the possibility of alpha phase however; there are equal chances of each of three transitional aluminas.

The peak with 3.46  $d$  reflexion remained unidentified throughout the crystallographic studies.

Comparison of Figure 7 and 12 reveals that at identical temperature, theta phase just appeared in AC3 whereas it was in transformation into alpha phase in AN3. It would be worth mentioning that there was no change in physical appearance of AC3 sample while AN3 sample appeared as crumpled crisp mass when collected from furnace after soaking temperature 800°C.

Sample heated at 1140°C for 1 hr is shown in Figure 12. The crystalline phases identified were theta and alpha. The principle peak with 2.06  $d$  reflexion is characteristic of theta phase. Three additional peaks for theta phase appeared with  $d$  values 2.56, 1.73 and 1.51. The alpha phase shows its peaks at 2.42 and 1.58  $d$  values.

XRD peaks with 1.40 and 1.37  $d$  values are designated as theta and/or alpha since at such high temperature the existence of gamma and delta phase seems rare.

Sample heated at 1300°C for 1 hr shows alpha phase in Figure 13 which is in accordance with the DSC thermogram.

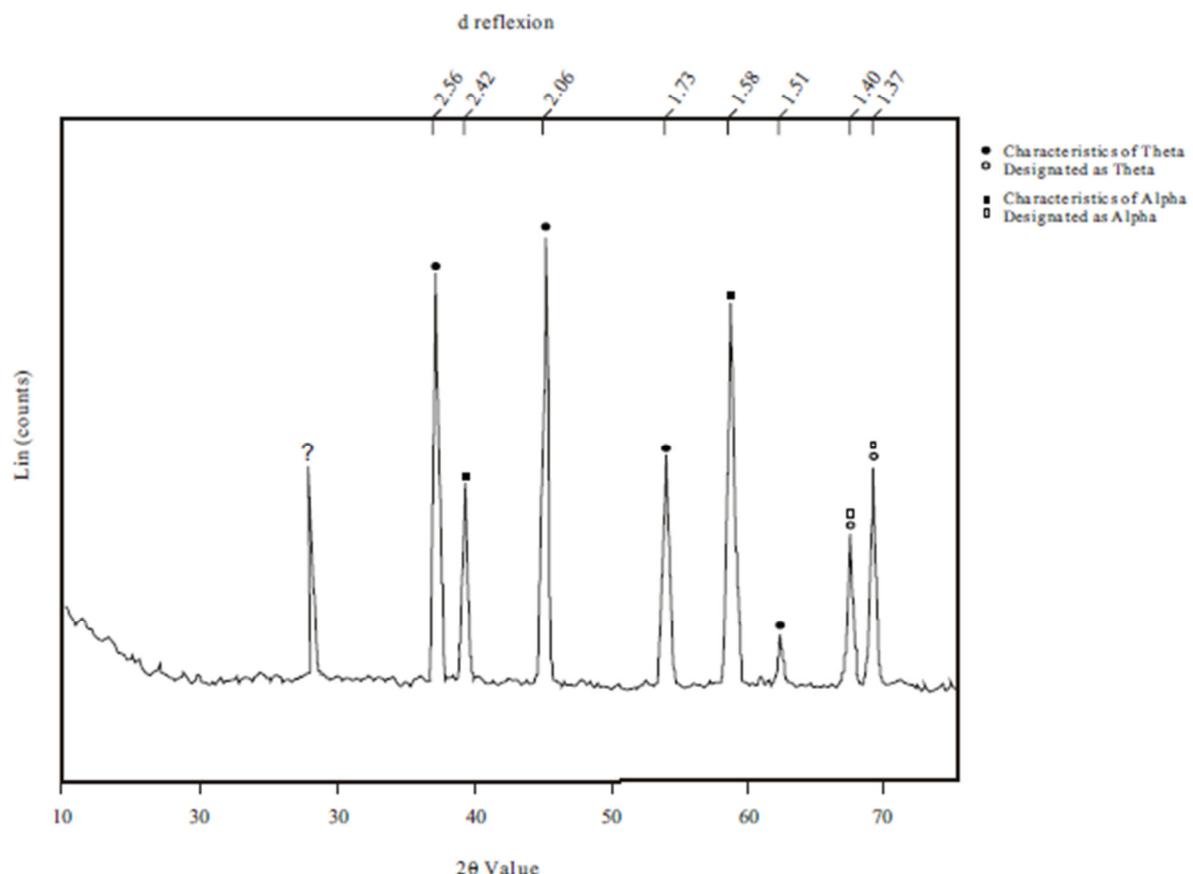


Figure 12 XRD of AC3 at 1140

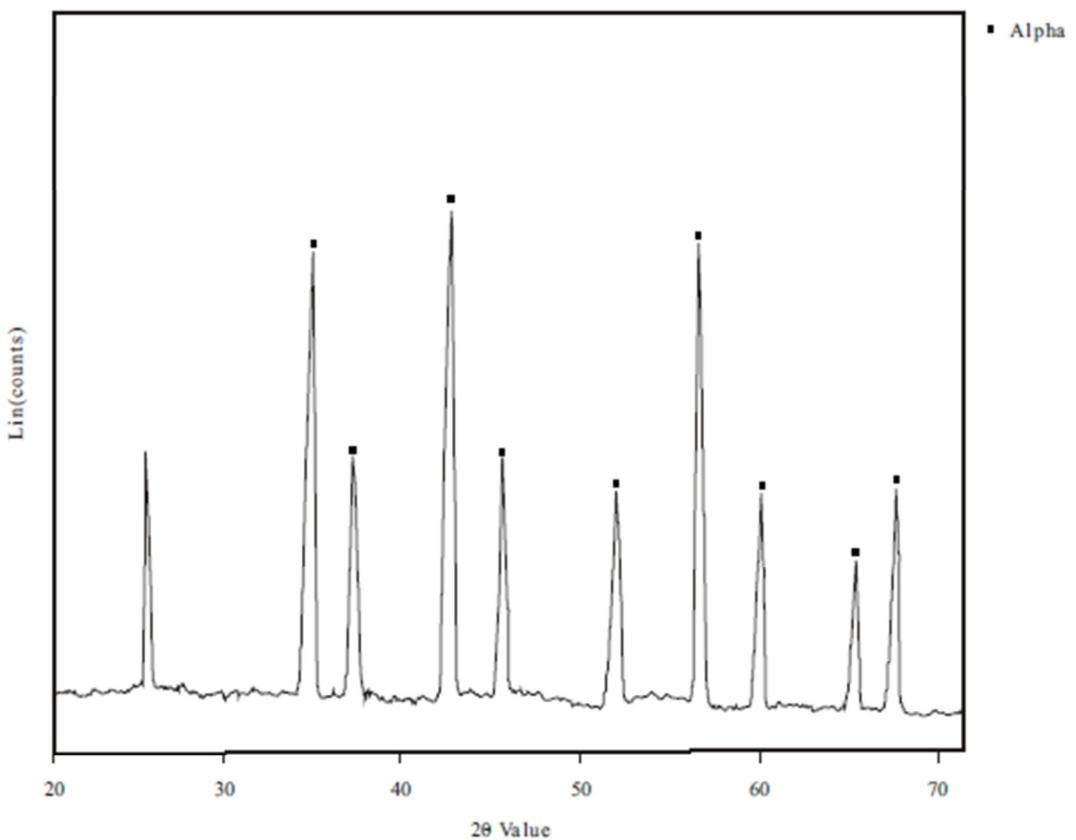


Figure 13 XRD of AC3 at 1300°C

### Conclusion

Nanoalumina precursors prepared from aluminum nitrate and aluminum chloride under identical reaction conditions had comparable average particle size but incomparable thermal transitions and structural transformations which relates to difference in particle size distribution. The precursor in both the cases was pseudoboehmite however, their relative dehydration, dehydroxylation and calcination temperatures were different. Pseudoboehmite obtained from aluminum nitrate has less crystallinity and was more prone to thermal transformations as compared to pseudoboehmite obtained from aluminum chloride. The sequence of thermal transformation was same, i.e. pseudoboehmite → gamma- $\gamma$  → delta- $\delta$  → theta- $\theta$  → alpha- $\alpha$   $\text{Al}_2\text{O}_3$  though temperature ranges and intensities of transitional aluminas and recrystallization into alpha alumina was not same. In case of nitrate, pseudoboehmite was completely dehydroxylated below 350°C and transformed into gamma alumina. Life span of gamma phase was brief, besides theta phase appeared as major phase. On the other hand in case of chloride, pseudoboehmite was not completely dehydroxylated even up to 375°C. Gamma phase was found existent even up to 800°C. In consequence, alpha phase appeared at 1140°C in nanoalumina produced from aluminum nitrate whereas theta co-existed with alpha up till 1150°C in nanoalumina produced from aluminum chloride.

### References:

1. Ada. K., Sarikaya. Y., Alemdaroglu T., 2003. Ceram. Int. 29, 513.
2. Antos, J., Aitani A. M., 2004. Catalytic Naphtha Reforming, second ed. Marcel Dekker, Inc.
3. Braun, S., Appel, L., Zinner L., Schmal M., 1999. Br. Ceram. Trans. 98, 87.
4. Cardarelli, F., 2008. Materials Handbook. Springer-Verlag, London.
5. De Hek, H., Stol, R. J., De Bryun, P. L., 1978. J. Coll. Inter. Sci. 64, 72.
6. Nagai, H., Hirano, K., Kato, A., 1991. Br. Ceram. Trans. 90, 44.
7. Ramanathan, S., Roy, S. K., Bhat, R., Upadhyaya, D. D., Biswas, A. R., 1996. J. Alloy Compd. 243, 39.
8. Stol, R. J., Van Helden, A. K., De Bryun, P. L., 1976. J. Coll. Inter. Sci. 1, 115.
9. Temuujin, J., Jadambaa, Ts., Mackenzie, K. J. D. Angerer, P., Porte, F., Riley, F., 2000. Bull. Mater. Sci. 23, 301.
10. Levin, I., Brandon, D., 1998. J. Am. Ceram. Soc. 81, 1995.
11. Unuma, H., Kato, S., Ota, T., Takahashi, M., 1998. Adv. Powder. Technol. 9, 181.
12. Mackenzie, R. C., 1957. The Differential Thermal Investigation of Clays, Mineralogical Society, Londres.