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# Structural Transitions in Alumina Nanoparticles by Heat Treatment

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**Abstract.** γ-alumina nanoparticles were annealed sequentially at 800°C, 950°C and 1100°C and structural transitions as a function of heat treatment were studied by X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and $^{27}$Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS–NMR) methods.. XRD studies found that γ-$Al_2O_3$ is stable upto a temperature of at least 950°C and transforms to the thermodynamically stable α-phase after annealing at 1100°C. MAS–NMR revealed that γ–alumina contains $AlO_4$ and $AlO_6$ structural units in the ratio 1: 2, while α–phase contains only $AlO_6$ units. DSC confirmed that γ→ α transition initiates at 1060°C.

**Keywords: Alumina nanoparticles, XRD, DSC, MAS–NMR.**
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## INTRODUCTION

Aluminum oxide commonly known as alumina ($Al_2O_3$), is one of the most interesting ceramic materials both for its numerous applications and excellent physical properties [1]. Alumina exists in a several metastable polymorphs, the so-called transition alumina (such as γ, δ, θ, χ and κ) as well as its thermodynamically stable α-$Al_2O_3$ phase [2].

The metastable alumina polymorphs show structural transitions upon heating, with transformation sequence irreversibly ending in the α-phase at temperatures in the range of 1100 to 1200°C. The α-alumina transformation temperature is however, relatively high, and it is possible to form many of the metastable phases at synthesis conditions between room temperature and 1000 °C [3].

The metastable phases such as γ-alumina find use in numerous applications. The low surface energy and therefore the inherent high surface areas of γ-alumina have made it useful for catalysis applications. Furthermore, thin films of amorphous alumina have proved to be very useful as optical coatings and as a dielectric layers in microelectronics devices [4].

In this work, we report the study of phase transformations in γ–alumina nanoparticles. Nanoparticles were annealed at three temperatures and characterized by X-ray diffraction (XRD), Differential Scanning Calorimetry (DSC) and $^{27}$Al MAS-NMR.

## EXPERIMENTAL METHODS

γ-alumina nanopowder (Aldrich Inc., 99.9% particle size <50 nm) weighing 2 g was taken as a starting material. The powder was ground in an agate motor-pestle and subjected to heat treatment in the temperature range of 800-1100°C. X-ray diffraction and $^{27}$Al MAS-NMR were performed after each annealing treatment to study the phase transformation properties. The initial sample (labelled as γ-Alumina-RT) was analysed by DSC to determine the temperature of structural transitions. Details of heat treatment of nanoparticles are given in Table 1.

X-ray diffraction studies were performed on Bruker D8 Focus X-ray diffractometer with Cu $K_\alpha$ radiation (λ =1.54056 Å) in the 2θ range of 10°-70°. Thermal studies were performed on the initial γ-$Al_2O_3$ sample on SETARAM SETSYS Evolution-1750 system in the temperature range of 200-1500°C at a heating rate of 10°C $m^{-1}$ and airflow rate of 20 ml $m^{-1}$ in Pt pans. $^{27}$Al

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MAS-NMR spectra were collected with a 3.2 mm Varian MAS probe at room temperature on a Varian NMR spectrometer operating at 16.4 T corresponding to the Larmor frequency of 182.42 MHz for $^{27}Al$ nuclei. Chemical shifts was referenced to 1 M $Al(NO_3)_3$ (aq).

## RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of alumina nanoparticles annealed upto a maximum temperature of 1100°C.

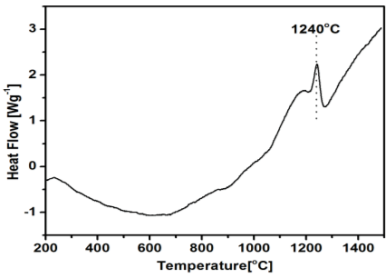


**FIGURE 2.** DSC thermogram of γ-$Al_2O_3$-RT sample.

**TABLE 1**: Details of annealing treatment of γ-$Al_2O_3$ powder and fraction of $^{[4]}Al$, $^{[5]}Al$ and $^{[6]}Al$ species as measured by $^{27}Al$ MAS-NMR.

| Sample Code | Annealing Temperature [°C] | $^{[4]}Al$ | $^{[5]}Al$ | $^{[6]}Al$ |
|---|---|---|---|---|
| γ–Alumina-RT | - | 0.330 | 0.022 | 0.646 |
| γ–Alumina–800 | 800 | 0.343 | 0.020 | 0.635 |
| γ–Alumina–950 | 950 | 0.357 | 0.017 | 0.625 |
| γ–Alumina–1100 | 1100 | 0 | 0.022 | 0.978 |

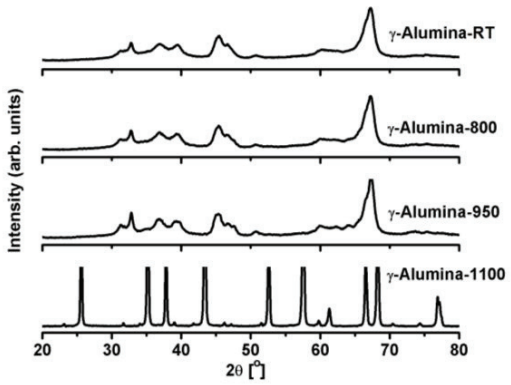


**FIGURE 1.** XRD patterns of initial γ–alumina powder (Sample Code: γ-Alumina-RT) and annealed samples.

XRD pattern of the initial $Al_2O_3$ powder (γ-Alumina-RT) shows two prominent but broad peaks centered at 45.9° and 67.1° corresponding to γ-alumina [5]. XRD patterns of the samples annealed at 800°C and at 950°C, do not show any significant changes and match with those of the initial γ-$Al_2O_3$ sample (Figure 1), whereas after annealing at 1100°C, sharp peaks are detected due to its transformation to α-$Al_2O_3$ [6]. Peak positions in the XRD patterns of all samples are presented in Table 2.

DSC studies confirm that transition of γ-alumina into α-phase occurs at 1240°C with onset point of 1064°C. Hence the transformation to α-phase after heat treatment at 1100°C can be understood [Figure 2].

$^{27}Al$ MAS-NMR spectra are shown in Figure 3. The spectra consist of four peaks centered at ~8, 14, 35 and 70 ppm. Peaks at ~8 ppm and ~14 ppm are due to $AlO_6$ structural units, $AlO_5$ and $AlO_4$ produce resonance peaks at ~35 and 70 ppm respectively [7]. The initial sample (γ–Alumina-RT) has two peaks at ~8 and 70 ppm due to γ–phase, that is normally formed by thermal decomposition of aluminum oxy-hydroxide at 400°C [7]. The fractions of tetra, penta and hexa coordinated Al-O units are determined from the tatios of areas under the resonance peaks and their values are given in table 1.

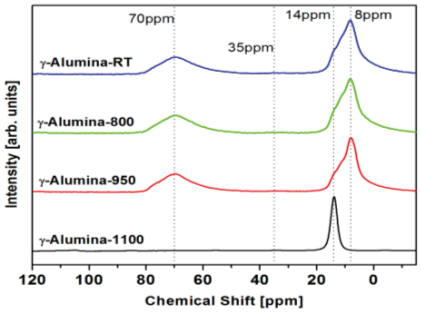


**FIGURE 3.** $^{27}Al$ MAS-NMR spectra of γ–alumina powder heat-treated upto 1100°C.

**Table 2:** XRD peak positions of γ–Alumina-RT and the sample annealed at 1100°C. Corresponding crystalline phases are also listed

| Sample no. | 2θ [°] | Crystalline phases |
|---|---|---|
| γ-Alumina-RT | 32.7 | γ |
| | 36.8 | γ |
| | 39.5 | γ |
| | 45.4 | γ |
| | 67.2 | γ |
| | 84.6 | γ |
| | 100.7 | |
| γ-Alumina-1100 | 25.6 | α |
| | 35.2 | α |
| | 37.8 | α |
| | 43.4 | α |
| | 52.6 | α |
| | 57.5 | α |
| | 61.3 | α |
| | 66.5 | α |
| | 68.2 | α |
| | 76.9 | α |
| | 77.1 | α |
| | 80.7 | α |

From the data given in table 1, it can be concluded that the initial γ-$Al_2O_3$ nanoparticles contain 33% of $AlO_4$ units and 66% of six-coordinated, $AlO_6$ units. On annealing γ-$Al_2O_3$ powder upto 950°C, no significant changes take place in the concentration of short-range structural units. After annealing at 1100°C, the sample contains ~98% of $AlO_6$ units. Hence, the initial γ-$Al_2O_3$ powder transforms almost completely to the rhombohedral α-phase of $Al_2O_3$ with heat treatment at 1100°C for 6 h.

## CONCLUSIONS

γ–Alumina nanoparticles were heated in the temperature range of 800-1100°C. Phase transitions after heat treatment at 800, 950 and 1100°C are studied by XRD and $^{27}Al$ MAS-NMR. Sharp peaks in XRD pattern of the sample annealed at 1100°C confirm the transformation to the thermodynamically stable α–phase. The fraction of $AlO_6$ units is maximizes in this sample. The exothermic peak at ~1240°C in the DSC thermogram is due to γ → α transition.

## REFERENCES


1. A. Boumaza, L. Favaro, J. Lédion, G. Sattonnay, J.B. Brubach, P. Berthet, A.M. Huntz, P. Roy and R. Tétot, Journal of Solid State Chemistry 182, 1171-1176 (2009).
2. S. Cava, S.M. Tebcherani, I.A. Souza, S.A. Pianaro, C.A. Paskocimas, E. Longo and J.A. Varela, Materials Chemistry and Physics 103, 394-399 (2007).
3. S. Kim, C. Kim and Y. Oh, Journal of Materials Science Letters 16, 257-259 (1997).
4. L.D. Laude, K. Kolev, M. Brunel and P. Deleter, Applied Surface Science 86, 368-381 (1995).
5. PDF File # 10-0425, ICDD: Newtown Street, PA, USA.
6. PDF File # 10-0173, ICDD: Newtown Square, PA, USA.
7. L.A. O'Dell, S.L.P. Savin, A.V. Chadwick and M.E. Smith, Solid State Nuclear Magnetic Resonance 31, 169-173 (2007).