# Synthesis, Characterization and Evaluation of δ-Al₂O₃ Nanoparticles Prepared by Chemical Method with Variation of pH

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This research aims to analyze nanoparticles made by adjusting the pH value in the coprecipitation synthesis process with the help of aluminum chloride. The prepared samples are pH adjusted using ammonium hydroxide. The samples are calcined at 650 °C and the pH values of the synthesized samples are 8, 9, 9.5 (S1, S2, S3). X-ray diffraction (XRD) analysis of the prepared samples confirms their orthorhombic structure. The average crystal size of the prepared δ-Al₂O₃ samples is 3.650, 2.741 and 2.806 nm for S1, S2 and S3, respectively. The lattice parameter is in the range of 5.59 to 5.63 for $a$, 5.57 to 5.69 for $b$, and 23.75 to 23.79 for $c$, pH = 8, 9, and 9.5, respectively, according to XRD analysis. The volume is 740 to 759 Å³, dislocation density ($D$) is in the range from 2.020 to 3.353 and mechanical characteristics (strain) are among the parameters provided. The Williamson-Hall and size-strain plots are both examined extensively. The results are compared showing that the crystal size of the sample is in the range of 2.2 to 2.8 nm and the strain is between 0.0193 to 0.0702 as per the W-H plots, and for the SS plots, the crystal size is in the range of 0.97 to 1.35 nm and the strain is between 0.314 to 0.409.

**Keywords:** Aluminum oxide, Nanoparticles, XRD, W-H plot, SS plot.

## 1. INTRODUCTION

These days, metal oxide nanoparticles have many uses in engineering, medicine, and materials [1]. Al₂O₃ nanoparticles are used in various adsorbent and catalyst applications, including catalyst adsorption in polyethene production, hydrogen peroxide synthesis, and as a selective adsorbent to remove different chemicals from gas streams such as gas streams arsenic and fluoride. Aluminum oxides are commonly used in ceramics, refractories, and abrasives because of their hardness, chemical inertness, high melting point, non-volatility, and resistance to oxidation and corrosion [2]. The importance of alumina as a catalyst or catalytic support in various chemical processes has also been widely acknowledged [3]. Because of its transparency and a wide variety of properties, alumina film can also be utilized in optics [4].

As seen from Fig. 1, aluminum oxide is an amphoteric oxide of aluminum with the chemical formula Al₂O₃. It is also known as alumina in the mining, ceramics, and materials research communities. There are two forms of anhydrous Al₂O₃ that is $\alpha$-Al₂O₃ and $\gamma$-Al₂O₃. $\alpha$-Al₂O₃ is stable at high temperatures, but infinitely metastable at low temperatures. It is obtained by heating $\gamma$-Al₂O₃ or any hydrous oxide to temperatures exceeding 1000 °C. It occurs naturally as the mineral corundum. $\alpha$-Al₂O₃ is a hard substance that can withstand hydration and acid attack [5], with a hexagonal close-packed (HCP) array of anions, the density of $\alpha$-Al₂O₃ is only around 0.595 g/cm³. The anions are topologically arranged so that they appear to be in the closest packing, but they are not in contact with one another. $\gamma$-Al₂O₃ is made by dehydrating hydrous oxides at temperatures below 450 °C. The cubic spinel structure of metastable-form alumina is cation deficient.

The letters alpha, beta, gamma and delta are in order. Alumina is a typical catalyst and catalyst support that is reasonably affordable. It is also used as a starting material in the manufacture of Al₂O₃-based ceramics [5].
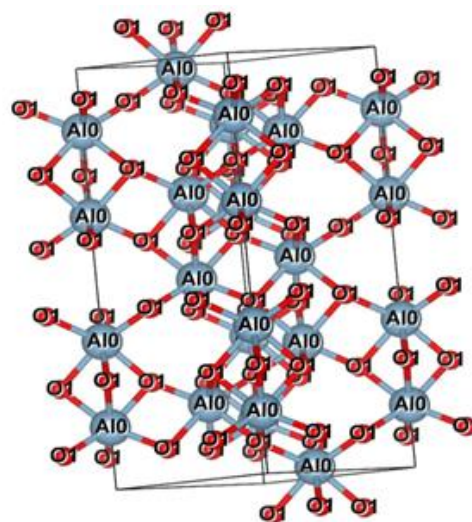


**Fig. 1** – Alumina's molecular structure

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Alumina is widely used in various applications due to its unique properties, including chemical and thermal stability, relative strength, excellent wear resistance, high hardness, high melting point, good electrical and chemical resistance. This material can also act as a mediator in some chemical processes. Alumina particles have been synthesized using a variety of processes, which can be divided into two groups. Chemical methods include sol-gel processing [6], hydrothermal [7], precipitation [8], combustion techniques [9], micro emulsion [10] and vapor deposition [11]. Physical methods include mechanical milling [11], laser ablation [12], solid state reaction [2, 13].

In this work, we reported on $\delta$-Al$_2$O$_3$ by a simple chemical route by the co-precipitation method. The structural properties are studied in detail by X-ray diffraction. The W-H plot and size strain plots (SSP) are extensively studied, and the results are compared. The lattice parameters, unit cell volume, dislocation density ($\rho D$) and mechanical properties (strain) are also reported.
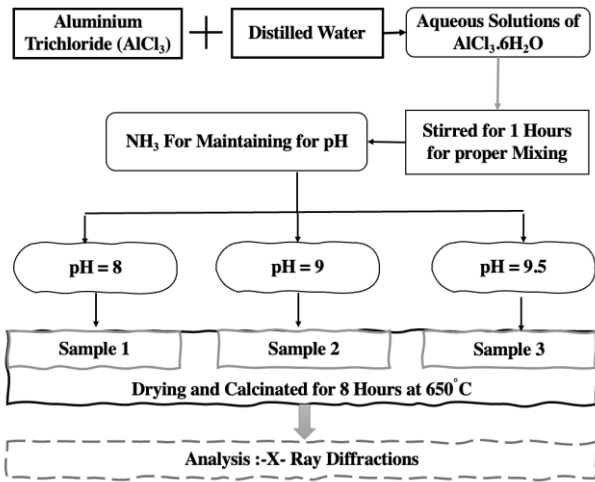


**Fig. 2** – Flow chart for synthesis of Al$_2$O$_3$

## 2. EXPERIMENTAL METHODS OF PREPARATION

### 2.1 Synthesis of Alumina by Co-Precipitation Method

The staring materials were aluminum trichloride (AlCl$_3$). First, AlCl$_3$ was dissolved in 200 ml of distilled water added to get a transparent solution. In the next step, NH$_3$ was added to the stirred AlCl$_3$.6H$_2$O solution drop by drop until pH (8, 9, 9.5) was maintained to get white precipitation as gelation of Al cations in the form of hydroxides Al(OH)$_3$. This precipitate was filtered in Whatman filter paper to get nanoparticles. These wet particles were separated and then collected for heating at 650 °C for 8 h which is shown in Fig. 2. A white fine alumina nanopowder was obtained for characterization.

### 2.2 Characterization

#### 2.2.1 Structural Analysis

The synthesized $\delta$-Al$_2$O$_3$ was studied utilizing X-ray diffraction technique with Cu-K$\alpha$ radiation ($l = 1.54$ Å), the scan range was 05° to 90°.
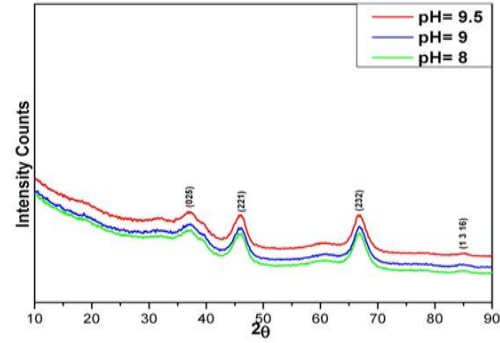


**Fig. 3** – X-ray diffraction patterns

## 3. RESULTS AND DISCUSSION

Fig. 3 depicts the X-ray diffraction patterns of the powders. Broad delta picks appeared as the pH value increased, as illustrated in Fig 3. The calcination temperature of $\delta$-Al$_2$O$_3$ manufactured samples was 650 °C, and the picks shown correspond to the (2 2 1), (1 3 16), (2 3 2), (2 5 0) and (0 4 0) of the orthorhombic structure of $\delta$-Al$_2$O$_3$, which were identified by standard JCPDS card data. The mean size of the ordered $\delta$-Al$_2$O$_3$ nanoparticles was calculated using the full width at half maximum (FWHM) and the Debye-Scherrer formula [14] as follows:

$$D = \frac{0.9\lambda}{B\cos\theta} ,\qquad (1)$$

where $K = 0.9$ is the shape factor, $B$ is the line broadening at half the maximum intensity (FWHM) in radians, $\lambda$ is the X-ray wavelength and $\theta$ is the Bragg angle.

The mean size of the as-prepared Al$_2$O$_3$ nanoparticles was around 3.036 nm, according to the Debye-Scherrer equation, and Table 1 includes the computed characteristics such as lattice constant, crystallite size, cell volume micro strain, and dislocation density.

$$\frac{1}{d_{hkl}^2} = \frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2} ,\qquad (2)$$

where $a$, $b$, $c$ are the lattice parameters, $d$ is the interplanar spacing, $hkl$ are the Miller indices.

X-ray diffraction confirms the orthorhombic structure with lattice parameters $a = a$, $b = 2a$, $c = 1.5a$ and space group P212121, but for both P21212 and P212121 it is suggested as candidate space groups for the orthorhombic structure due to these two orthorhombic models with symmetry and lattice parameters $a = 5.49$ to 5.63 Å, $b = 5.57$ to 5.63 Å, $c = 23.75$ to 23.63 Å [18]. The unit cell volume was determined using equation (3) and the results are tabulated in Table 1.

$$V = (a \times b \times c),\qquad (3)$$

where $a$, $b$, $c$ are the lattice parameters.

### 3.1 Williamson-Hall Analysis (W-H Plot) and Size-Strain Plot (SSP) Analysis

We assume that size and broadening are the two components that affect the Bragg peak integral width.

As a result, strain broadening and size are both additive components of the total. In a study by Williamson and Hall [15], a distinct angle (*q*) dependent on each effect laid the groundwork for the separation between dimensions and strain broadening.

$$\beta_{hkl}\cos\theta = \frac{k\lambda}{D} + 4\varepsilon\sin\theta \; . \qquad (4)$$

Fig. 4 depicts the difference between $\beta\cos\theta$ vs. $\sin\theta$ (W-H analysis). Because of the linear plot of $\beta\cos\theta$ vs. $\sin\theta$, the equation gives (linear form) $y = mx + c$, where *m* is the strain and $c = 1/D$.
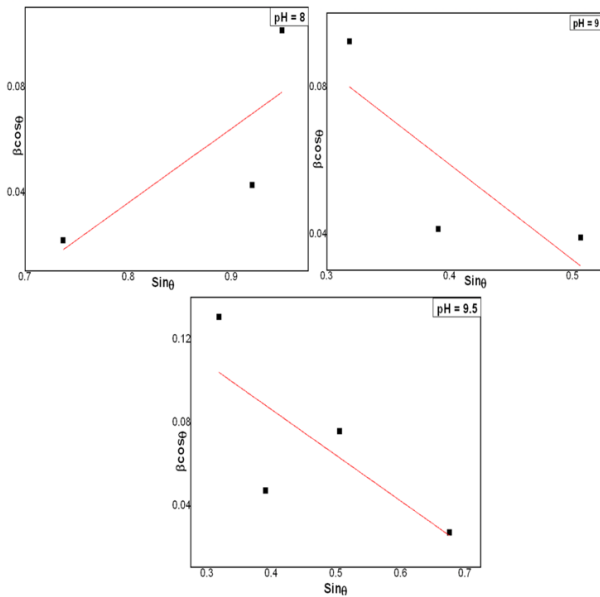


**Fig. 4** – Williamson-Hall analysis (W-H plot) for $\delta$-Al$_2$O$_3$

The SSP is a tool for interpreting the quantity of isotropic nature and microstrain contribution, with the benefit of giving less weight to data from high-angle reflections, as illustrated in Fig. 5. We assume the Lorentzian function for the crystallite size profile and the Gaussian function for the strain profile in this approximation [16, 17]. Accordingly, we have

$$\left(d_{hkl}\beta_{hkl}\cos\theta\right)^2 = \frac{K\lambda}{D}\left(d_{hkl}^2\beta_{hkl}\cos\theta\right)+\left(\frac{\varepsilon}{2}\right)^2 . \qquad (5)$$
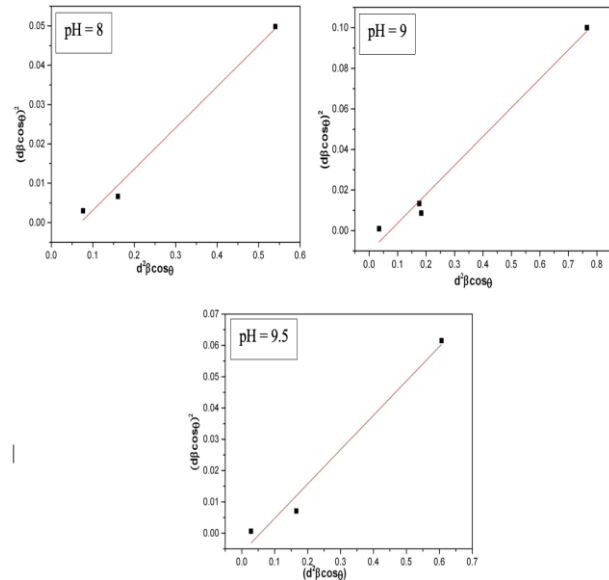


**Fig. 5** – Size-strain analysis (SSP) for $\delta$-Al$_2$O$_3$

In Fig. 5, similarly to the Williamson-Hall plot analysis, the term $(d\beta\cos\theta)^2$ is plotted with respect to $(d^2\beta\cos\theta)$ for all the orientation peaks of Al$_2$O$_3$ samples with the orthorhombic structure [18, 19]. In this case, the crystalline size and strain are calculated for both W-H plot and SSP, as reported in Table 2.

**Table 1** – Summary of XRD measurements for Al$_2$O$_3$ prepared by co-precipitation method

| pH | Crystal size (nm) | Microstrain | Lattice constant, Å | | | Volume *V*, Å³ | Dislocation density (m$^{-2}$)×10$^{17}$ |
|----|-------------------|-------------|------|------|--------|----------------|-------------------------------------------|
|    |                   |             | *a*  | *b*  | *c*    |                |                                           |
| 8  | 3.650             | 0.0158      | 5.598 | 5.576 | 23.755 | 741.499        | 2.631                                     |
| 9  | 2.7413            | 0.0175      | 5.496 | 5.663 | 23.798 | 740.685        | 3.353                                     |
| 9.5 | 2.806            | 0.0143      | 5.637 | 5.698 | 23.635 | 759.147        | 2.020                                     |

**Table 2** – W-H plot and SSP for *d*-Al$_2$O$_3$

| pH value | W-H plot | | SSP | |
|----------|----------------------|--------|----------------------|--------|
|          | Crystallite size (*D*) | Strain | Crystallite size (*D*) | Strain |
| **8**   | 2.24 nm  | 0.0193 | 1.16 nm | 0.314 |
| **9**   | 2.825 nm | 0.0199 | 0.97 nm | 0.409 |
| **9.5** | 2.850 nm | 0.0702 | 1.35 nm | 0.314 |

ture with lattice parameters $a = 5.49$ to $5.63$ Å, $b = 5.57$ to $5.63$ Å, $c = 23.75$ to $23.63$ Å and average crystallite size of 3.06 nm. We also calculated the dislocation density, the mechanical property of the sample. The W-H plots and SSP were extensively studied, and the results were correlated. Thus, a chemical method such as the coprecipitation method is desirable to obtain the $\delta$-Al$_2$O$_3$ nanopowder.

## 4. CONCLUSIONS

The $\delta$-Al$_2$O$_3$ (aluminum oxide) nanopowders were successfully synthesized by the co-precipitation method. Structural properties were investigated using X-ray diffraction analysis showing the orthorhombic struc-

## ACKNOWLEDGEMENTS

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# Синтез, характеристика та оцінка наночастинок δ-Al₂O₃, отриманих хімічним методом зі зміною pH

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　　　Дослідження спрямоване на аналіз наночастинок, отриманих шляхом коригування значення pH в процесі синтезу співосадження за допомогою хлориду алюмінію. Підготовлені зразки кориговані pH за допомогою гідроксиду амонію. Зразки прожарюють при 650 °C, і значення pH синтезованих зразків становлять 8; 9; 9,5 (S1, S2, S3). Рентгенодифракційний (XRD) аналіз підготовлених зразків підтверджує їх ромбічну структуру. Середній розмір кристалів підготовлених зразків δ-Al₂O₃ становить 3,6; 2,7 та 2,8 нм для S1, S2 та S3 відповідно. Параметр решітки знаходиться в діапазоні від 0,559 до 0,563 нм для $a$, від 0,557 до 0,569 нм для $b$ і від 2,375 до 2,379 нм для $c$, pH складає 8, 9 і 9,5 відповідно до XRD аналізу. Об'єм становить від 740 до 759 Å³, густина дислокацій ($D$) знаходиться в діапазоні від 2,020 до 3,353, механічні характеристики (деформація) входять до числа параметрів, що надаються. Графіки Вільямсона-Холла (W-H) та розмірно-деформаційні (SS) графіки детально досліджуються. Результати порівнюються, показуючи, що розмір кристала зразка знаходиться в діапазоні від 2,2 до 2,8 нм, а деформація приймає значення від 0,0193 до 0,0702 для графіків W-H, а для графіків SS розмір кристала зразка знаходиться в діапазоні від 0,97 до 1,35 нм, і деформація приймає значення в діапазоні від 0,314 до 0,409.

**Ключові слова:** Оксид алюмінію, Наночастинки, XRD, Графік W-H, Графік SS.