Microstructural evaluation of CoAl$_2$O$_4$ nanoparticles by Williamson–Hall and size–strain plot methods

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**ABSTRACT**

CoAl$_2$O$_4$ nanoparticles were prepared by a Pechini method using chelating agent citric acid. CoAl$_2$O$_4$ nanoparticles were synthesized at different calcination temperatures of 600–900°C. The crystalline spinel cubic phase was confirmed by X-ray diffraction results. High-resolution scanning electron microscopy (HRSEM) revealed that nanoparticles of CoAl$_2$O$_4$ morphology showed spherical forms with a certain degree of agglomeration. The Williamson–Hall (W–H) method and size–strain method to evaluate the size of crystallites and strain in the CoAl$_2$O$_4$ nanoparticles’ peak broadening were applied. Physical parameters such as strain and stress values were calculated for all XRD reflection peaks corresponding to the cubic spinel phase of CoAl$_2$O$_4$ in the range of 20°–70° from the modified plot shape by the W–H plot assuming a uniform deformation model (UDM), uniform stress deformation model (USDM), uniform deformation energy density model (UDEDM), and by the size–strain plot (SSP) method. The crystal size of the CoAl$_2$O$_4$ NPs calculated on the W–H plots and the SSP method are in good agreement with the HRSEM and Scherrer method.

**KEYWORDS**

CoAl$_2$O$_4$, Pechini method; W–H analysis; SSP method

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**1. Introduction**

Spinel oxide type AB$_2$O$_4$, where A and B represent two different ionic comparable cations, are a class of chemically and thermally stable materials that are suitable for a wide-ranging applications such as catalyst and magnetic materials. In the spinel structure, oxygen ions form a cubic closed structure and cations A and B occupy two different crystallographic sites: tetrahedral and octahedral sites [1–4]. In the distribution of cations A and B, these two sites are influenced by the combination and nature of the two cations and is strongly dependent on the preparation and processing conditions. Spin cation distribution has been given a lot of attention because it allows understanding of the correlations between the structure and properties such as color, diffusivity, magnetic behavior, and optical properties, which are heavily based on better occupation with these two metal sites [5,6].

In the class of nanomaterials, cobalt aluminate nanocrystalline spinel (CoAl$_2$O$_4$) is known as blue Thenard, commonly used as a catalyst, color filter for automotive lamps, and a pigment layer on luminescent materials due to their optical properties, thermal chemical, peculiar stability, and photochemistry [7–12]. In recent years, much work has been done on the preparation of nanoscale CoAl$_2$O$_4$ for optical properties [13–19]. A variety of methods such as combustion [13], Pechini method [14], sol-gel [15,17], and micro-emulsion [16] have been successfully performed for the preparation of CoAl$_2$O$_4$ nanoparticles.

The crystallite size and strain are of a pattern that the two main key factors lead to the expansion of XRD diffraction peaks [20,21]. The crystallite size introduced for the first time by Scherrer in 1918 [20] is of a single crystal inside the particles or grains, and it is different from the particle size or grain size where the single particle or grain can be comprised of several crystal aggregates. The lattice strain is affected by crystal imperfection such as dislocations and point defects [22]. Two other types are lattice strains in a crystal, that is, uniform and nonuniform strains. However, only the nonuniform strain will cause the broadening of the peak [23].

There are some methods for deformation sizing in materials represented by Scherrer [20,24], Williamson–Hall (W–H) [25,26], strain–size plot (SSP), and Warren–Averbach methods [27,28]. Scherrer and W–H methods set both maximum half width (FWHM) values and integral breaths, while the Warren–Averbach method refers to the Fourier coefficient profile [29]. The Warren–Averbach method is a bit of time method and mathematically cumbersome [27,30].

In this study, CoAl$_2$O$_4$ nanoparticles were prepared by the Pechini method. X-ray diffraction analysis (XRD) and high-resolution scanning electron microscopy (HRSEM) have been used to examine
the structural and morphological behavior of CoAl$_2$O$_4$ nanoparticles. The X-ray peak profile (XPPA) analysis was determined to calibrate the size of the crystallites and strain of CoAl$_2$O$_4$ nanoparticles based on UDM, USDM, and UDEDM models. This work discusses the importance of W–H models and the SSP method in the calibration of crystalline size and strain parameters of CoAl$_2$O$_4$ nanoparticles.

2. Materials and experimental

CoAl$_2$O$_4$ nanoparticles were synthesized using Co (NO$_3$)$_2$.6H$_2$O (LOBA Chemie Ltd), Al (NO$_3$)$_3$.9H$_2$O (Merck), citric acid, and deionized water. All the above chemicals were of analytical grade and were used directly without further purification.

CoAl$_2$O$_4$ nanoparticles were prepared by a Pechini method using citric acid as a chelating agent. First, a certain amount of cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O) and aluminum nitrate (Al(NO$_3$)$_3$.9H$_2$O) was dissolved in deionized water. After that, an appropriate amount of citric acid was added to the above solution with magnetic stirring. The molar ratio of metal ions to citric acid was 1:2. The mixed solution was continuously stirred for 1 h and then heated to 80°C until highly viscous gels were formed. Then, the gels were dried in an oven at 110°C and then calcined at desired temperatures (600–900°C) for 5 h.

X-ray diffraction (XRD) was performed on a Bruker D8 Advance X-ray diffractometer. Morphological analysis and energy dispersion X-ray analysis were performed using an EDAX instrument attached to a high-resolution scanning electron microscope (HRSEM, FEI, Quanta 200F).

3. Results and discussions

3.1 Powder XRD analysis

The crystalline structure of the prepared samples was determined by XRD models with 2θ between 20° and 70°. Figure 1 shows the XRD spectra of CoAl$_2$O$_4$ nanoparticles annealed at 600–900°C for 5 h. Different diffraction peaks are observed for the model and the location of these peaks is very well matched that of spinel cubic CoAl$_2$O$_4$ (JCPDS Card No. 10-458), indicating cobalt aluminate phase formation. The intensity of the diffraction peaks increases with the increase in the annealing temperature, which is associated with increased crystallinity. No peaks corresponding to any other materials or elements are observed, which means that the firing temperature used (900°C) was sufficient for the preparation of high purity CoAl$_2$O$_4$. Strong, sharp, and narrow diffraction peaks have shown that the synthesized product was well crystallized.

3.2 Crystallite size and strain determination

3.2.1 Scherrer method

In general, X-ray diffraction analysis by peak width is due to instrumental amplification, an increase in crystallite size, and lattice strain due to dislocation [31]. Unbundling these contributions must collect a diffraction pattern of a standard material such as silicon to determine instrumental enlargement [32]. The corrected instrumental broadening $\beta_{hkl}$ [33] corresponding to peak CoAl$_2$O$_4$ diffraction was estimated using the equation,

$$
\beta_{hkl} = \left[ \left( \beta_{hkl} \right)_{\text{measured}}^2 - \beta_{\text{instrumental}}^2 \right]^{1/2}
$$

(1)

It is well known that the Scherrer formula provides only the lower limit of crystallite size. The size of crystalline nanoparticles is estimated using the Scherrer formula,

$$
D = \frac{K\lambda}{\beta\cos\theta}
$$

(2)

where $D$ is the volume weighted crystallite size (nm), $k$ is the shape factor ($k = 0.94$), $\lambda$ is the X-ray wavelength (1.54056 Å), $\theta$ is the diffraction angle of Bragg, and $\beta$ is the expanded diffraction peak measured at FWHM (in radians). The sizes of crystallites of CoAl$_2$O$_4$ nanoparticles are shown in Table 1.
3.2.2 W–H method

3.2.2.1 Uniform deformation model (UDM). In many cases, X-ray diffraction patterns are influenced not only by the size of crystallites, but possibly also by lattice strain and lattice defects. W–H analysis is a simplified integral breath method, clearly differentiates the armature size- and strain-induced deformation peak considering the broadening of the peak width as a function of $2\theta$. Individual contribution to the line broadening of a Bragg reflection line can be expressed as:

$$\beta_{hkl} = \beta_s + \beta_D$$  \hspace{1cm} (3)

where $\beta_{hkl}$ represents the full width at half maximum (FWHM) of a radiant peak, and $\beta_s, \beta_D$ are the width due to the size–strain, respectively. In the W–H relation, it is assumed that the strain is uniform throughout the crystallographic direction, which is given by $\beta_{hkl}$

$$\beta_{hkl} = \frac{K\lambda}{D\cos \theta} + 4\varepsilon \tan \theta$$  \hspace{1cm} (4)

Rearranging Equation (4) gives

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta$$  \hspace{1cm} (5)

Here, $D$ and $\varepsilon$ correspond to the value of the crystallite size and the value of the microstrain, respectively. By potting $4\sin \theta$, the average size of the crystallites and the strain can be estimated by the Y-intercept extrapolation and the slope of the line; see Figure 2.

$$D = \frac{K\lambda}{Y \text{ Intercept}}$$  \hspace{1cm} (6)

$$\varepsilon = \text{slope}$$  \hspace{1cm} (7)

3.2.2.2 Uniform stress deformation model (USDM). According to Hooke’s law, within the elastic limit, there exists a linear proportionality relation between the stress ($\sigma$) and strain ($\varepsilon$)

$$\sigma = E\varepsilon$$  \hspace{1cm} (8)

where $E$ is the elasticity modulus or Young’s modulus. This equation is an approximation that is valid for the significantly small strain. Hence, it is assumed that the lattice deformation stress is uniform in the second term of equation signifying UDM and is replaced by $\varepsilon = (\sigma/E)$ and the modified Equation (5) is given by

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\frac{\sigma \sin \theta}{E_{hkl}}$$  \hspace{1cm} (9)

Here, $E_{hkl}$ is Young’s modulus in the direction normal to the set of $(hkl)$ planes. The slope of the straight line between $4\sin \theta/E_{hkl}$ and $\beta_{hkl}\cos \theta$ gives the uniform stress and the crystallite size $D$ easily.
determined from the intercept (Figure 3). Young’s modulus $E_{hkl}$ for samples with a cubic crystal phase is related to their elastic compliances $S_{ij}$ for $\text{CoAl}_2\text{O}_4$, $S_{11} = 6.07$, $S_{12} = -3.83$ and $S_{44} = 7.22$ TPa$^{-1}$ as [34]:

$$E_{hkl} = S_{11}/C_{02}S_{11}/C_{02}S_{12}/C_{02}0.5S_{44}(10)$$

where $m_1 = h(h^2+k^2+l^2)^{-0.5}$, $m_2 = k(h^2+k^2+l^2)^{-0.5}$, and $m_3 = l(h^2+k^2+l^2)^{-0.5}$.

The Young’s modulus $E_{hkl}$ value for cubic $\text{CoAl}_2\text{O}_4$ NPs was calculated to be 2.44 TPa. Figure 3 shows the plot of $\beta_{hkl}\cos\theta$ values as a function of $4\sin(\theta)/E_{hkl}$, the uniform deformation stress can be calibrated from the slope.

3.2.2.3 Uniform deformation energy density model (UDEDM). The following model that can be used to find the energy density of a crystal is called the Uniform Deformation Energy Density Model (UDEDM). Previously, it was assumed that crystals are homogeneous and isotropic. Although in many cases, the assumption of homogeneity and isotropy is not justified. In addition, the proportional constants for the strain–stress relationship are not widely independent when studying the deformation energy density ($u$). For an elastic system that follows Hooke’s law, the energy density (unit energy) can be calculated from the relation $u = (\varepsilon^2 E_{hkl})/2$. Thus, Equation (9) can be rewritten according to the energy and strain relationship, that is,

$$\beta_{hkl}\cos\theta = \left(K\lambda/D\right) + 4\sin(\theta)\left(2u/E_{hkl}\right)^{1/2}$$

The plot of $\beta_{hkl}\cos\theta$ versus $4\sin\theta(2u/E_{hkl})^{1/2}$ is shown in Figure 4. The anisotropic energy density ($u$) is estimated from the slope, and the crystallite size ($D$) of the Y-intercept.

3.2.3 SSP method

The W–H plot showed that the line broadening was essentially isotropic. This indicates that the diffraction domains were isotropic and there was also a microstrain contribution. However, in the case of isotropic line broadening, it is possible to obtain a better evaluation of the size–strain considering that an average “size–strain plot” (SSP), which has relatively less weight gain, is given to high-angle reflections, where accuracy is generally lower. In this approach, the “crystalline dimension” profile is assumed to be described by a Lorentz function and the “strain profile” of a Gaussian function [35]. As a result, we have:
where $K$ is a constant dependent on the shape of the particles; for spherical particles, it is given as 03/04. In Figure 5, similar to W–H methods, the term $(d_{hkl} \beta_{hkl} \cos \theta)^2$ is plotted with respect to $d_{hkl}^2 \beta_{hkl} \cos \theta$ for all CoAl$_2$O$_4$-NPs' orientation peaks. In this case, the particle size is determined by the slope of the linearly fitted
data and the intercepted root yields strain. The size of crystallites ($D$) varies with the result of the calcination temperature obtained by the Scherrer formula, W–H (UDM, USDM, and UDEDM) models and SSP methods shown in Figures 6–8.

### 3.3 Morphological studies

The morphology of cobalt aluminate synthesized nanoparticles was studied by high-resolution scanning electron microscopy (HRSEM). From Figure 9, it can be clearly demonstrated that the obtained nanoparticles are of spherical shape with some groups present in aggregation of spheres. It can be seen from micrographs that the granulometry ranges from 18.76 to 24.95 nm. This is in good agreement with the results obtained from the XRD measurements.

The values of the average crystallite size of different calcined temperatures of CoAl$_2$O$_4$-NPs obtained from different models are more or less similar, implying that the inclusion of strain in various shapes has a slight variation in the average size of crystallites. By inspecting all the graphs, it is clear that the result of the SSP method is more accurate than UDM, USDM, and UDEDM, since data are more accurately set in this method, with all high-intensity points touching linear adaptation. A. Khorsand Zak et al. (2011) reported the X-ray analysis of ZnO nanoparticles using W–H (UDM, USDM and UDEDM) models and SSP methods. They concluded that the SSP method is more suitable method to estimate the crystallite size and strain of ZnO nanoparticles [36]. Thus, it may be concluded that these models are more realistic in the present study; the SSP method is concluded as more close-fitting for evaluating both the crystallite size and strain of CoAl$_2$O$_4$ nanoparticles. The geometric parameters of CoAl$_2$O$_4$ nanoparticles are shown in Table 1.
4. Conclusion

CoAl$_2$O$_4$ nanoparticles have been prepared by the Pechini method and are characterized by powder XRD and HRSEM analysis. From the powder XRD analysis, the peak line broadening of CoAl$_2$O$_4$ nanoparticles due to finite crystallite size and strain were analyzed by the Scherrer formula, W–H method based on UDM, UDSM, and UDEDM models, and SSP method. The W–H plot has been worked out and established to determine the crystallite size- and strain-induced broadening due to lattice deformation. The W–H analysis based on the UDM, UDSM, and UDEDM models are very helpful in calculating the crystallite size and strain. W–H has been developed and established to determine the size of crystallites and the elongated induced deformation due to deformation of the network. UDM-based U-DMS, UDSM, and UDEDM analyses are useful for calculating dimension estimation and deformation of crystallites. The size of crystallites and strain evaluated by the XRD powder measurements are in good agreement with the HRSEM results. The elastic properties of the Young $S_{ij}$ ($E_{hkl}$) module were estimated by the values of the plane of the lattice ($h$, $k$, $l$). The methods discussed above were very useful in determining the average size of deformation crystals, stress, and energy density value, including the size–strain method; it is highly preferable to set crystal perfection.

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Disclosure statement

No potential conflict of interest was reported by the authors.
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