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Estimation of lattice stress and strain in Cobalt ferrite nanoparticles by Williamson-Hall and size-strain plot methods

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ABSTRACT

Cobalt ferrite nanoparticles ($CoFe_2O_4$) were synthesized by chemical co-precipitation method and characterized by powder X-ray diffraction analysis (PXRD). The PXRD results revealed that the sample product was crystalline with mixed type spinel with cubic structure. The crystalline development in the $CoFe_2O_4$ was investigated by X-ray peak broadening. The Williamson-Hall (W-H) analysis and size-strain plot method (SSP) were used to study the lattice strain and crystalline size of $CoFe_2O_4$. The physical parameters such as strain, stress and energy density values were calculated more precisely for all the reflection peaks of PXRD using modified forms of the W-H plot assuming a uniform deformation model (UDM), uniform stress deformation model (USDM), uniform deformation energy density model (UDEDM) and SSP method. The results of mean particle size slightly differ due to non-uniform strain distribution.

Keywords: Nano particles, X-ray techniques, W-H analysis, co-precipitation

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1. Introduction

A perfect crystal would extend infinitely in all directions, so no crystals are perfect due to their finite size. This deviation from perfect crystallinity leads to a broadening of the X-Ray diffraction peaks. X-ray profile analysis is a simple and powerful tool to estimate the crystallite size and lattice strain [1]. Crystallite size is a measure of the size of coherently diffracting domains. Lattice strain is a measure of the distribution of lattice constants arising from crystal imperfections, such as lattice dislocations [2]. Crystallite size and lattice strain affect the Bragg peak and increase the peak width and intensity and shift the 2θ peak position accordingly. Williamson-Hall (W-H) analysis is a simplified integral breadth method where both size-induced and strain-induced broadening are deconvoluted by considering the peak width as a function of 2θ [3]. In this study, the strain due to lattice deformation was estimated by modified forms of W-H and SSP methods provide information on the stress-strain relation and the strain (ε) as a function of energy density (u). A chemical co-precipitate method was used to prepare $CoFe_2O_4$ nanoparticles as in Yue Zhang et.al [4]. The resulting material was calcinated at 800°C for 5 h.

2. Results and discussion

The XRD pattern of the prepared sample is shown in Fig. 1. The entire detectable peak indexed with the standard reference data (JCPDS: 22-1086). It was clearly seen that the reflection peaks became sharper indicating the enhancement of crystallinity.

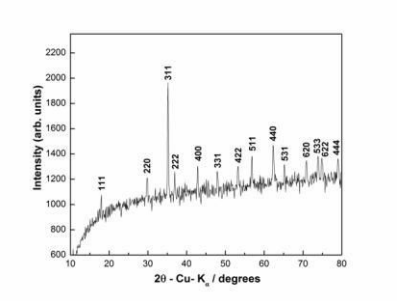

Fig.1 XRD pattern of $CoFe_2O_4$ nanoparticles calcinated at 800^{0}C for 5 hrs.

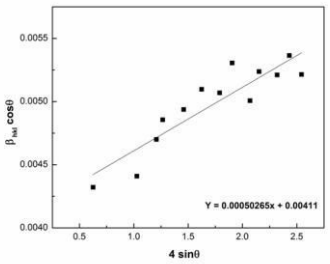

Fig.2 Uniform deformation model (UDM) Plot.

Particle size and strain

The particle size of the $CoFe_2O_4$was determined by the X-ray line broadening method using the Debye-Scherrer equation

$$D = K\lambda/\beta_D \cos\theta \quad (1)$$

Where D is the particle size (nm), λ is the wavelength (A^0), K is a constant (0.9), β_D is the peak width at half-maximum intensity and θ is the peak position. The breadth of the Bragg peak is a combination of both instrument and sample dependent effects. To decouple these contributions, it is necessary to collect a diffraction pattern from the line broadening of a standard material such as silicon to determine the instrumental broadening. The instrument-corrected broadening [5] β_D corresponding to the diffraction peak of $CoFe_2O_4$was estimated using the relation:

$$\beta_D = [(\beta^2)_{measured} - (\beta^2)_{instrumental}]^{1/2} \quad (2)$$

2.1 Williamson-Hall methods

The Strain induced in powders due to crystal imperfections and distortion was calculated using the formula

$$\varepsilon = \beta_s/4\tan\theta \quad (3)$$

From equations (1) & (3) it is confirmed that peak width varies for crystallite size as 1/cosθ and strain as tanθ. This fundamental difference allows that

size and strain broadening are additive components of the total integral breadth of a Bragg peak [6].

$$\beta_{hkl} = \beta_s + \beta_D \quad (4)$$

$$\beta_{hkl} = (4\varepsilon\tan\theta) + (K\lambda/D\cos\theta) \quad (5)$$

Rearranging Eq. (5) gives

$$\beta_{hkl}\cos\theta = (K\lambda/D) + (4\varepsilon\sin\theta) \quad (6)$$

A plot is drawn (Fig.2) with $4\sin\theta$ along the x-axis and $\beta_{hkl}\cos\theta$ along the y-axis. From the linear fit to the data, the crystalline size was estimated from the y-intercept, and strain from the slope of the fit. Eq. (6) represents the UDM, where the strain was assumed to be uniform in all crystallographic directions.

A generalized Hooke's law refers, linear proportionality between the stress and strain as given by $\sigma = Y\varepsilon$, where σ is the stress and Y is the Young's modulus. Applying the Hooke's law approximation to Eq. (6) yields

$$\beta_{hkl}\cos\theta = (K\lambda/D) + (4\sigma\sin\theta/Y_{hkl}) \quad (7)$$

The uniform stress can be calculated from the slope line plotted between $4\sin\theta/Y_{hkl}$ and $\beta_{hkl}\cos\theta$, and crystallite size from the intercept as shown in Fig.3. Eq. (7) represents USDM and strain can be measured if Y_{hkl} of cubic $CoFe_2O_4$ nanoparticles is known. For samples with a cubic crystal phase, Y_{hkl} is related to their elastic compliances S_{ij} as

$$1/Y_{hkl} = S_{11} - 2\,[(S_{11} - S_{12}) - \tfrac{1}{2}\,S_{44}]\,(l^2m^2 + m^2n^2 + n^2l^2) \quad (8)$$

Where S_{11}, S_{12}, S_{44} are the elastic compliances of $CoFe_2O_4$ nanoparticles and l, m, n are the cosines of the angles between the direction to which Y is referred and the crystal axes [7]. S_{11}, S_{12}, S_{44} are related to their elastic stiffness as follows

$$C_{14} = 1/S_{44}, \quad C_{11} - C_{12} = (S_{11} - S_{12})^{-1}, \; C_{11} + 2C_{12} = (S_{11} + 2S_{12})^{-1} \quad (9)$$

The values of elastic stiffness C_{11}, C_{12}, C_{14} for spinel ferrite are 275 GPa, 104 GPa, 95.5 GPa respectively [8].

In Eq. (7), the assumption of homogeneity and isotropy is not justified. Moreover, the constants of proportionality associated with the stress-strain relation are no longer independent when the strain energy density u is considered. According to Hooke's law, the energy density as a function of strain and calculated from

$$u = (\varepsilon^2 Y_{hkl})/2 \quad (10)$$

Eq. (7) modified as

$$\beta_{hkl}\cos\theta = (K\lambda/D) + [4\sin\theta(2u/Y_{hkl})^{1/2}] \quad (11)$$

Plot of $\beta_{hkl}\cos\theta$ versus $4\sin\theta\ (2u/Y_{hkl})^{1/2}$ was constructed and the data fitted to line. The anisotropic energy density was estimated from the slope and crystallite size from the y-intercept. Eq. (11) represents UDEDM and it is shown in Fig. 4.The estimated values of lattice strain, stress, energy density and particle size were in Table 1.

2.2 Size-Strain Plot method

In isotropic line broadening, a better evaluation of the size-strain parameters can be obtained by considering an average ''size-strain plot", which has the advantage that less weight is given to data from reflections at high angles. In this approximation, it is assumed that the ''crystallite size" profile is described by a Lorentzian function and the ''strain profile" by a Gaussian function [9]. Accordingly, we have

$$(d_{hkl}\beta_{hkl}\cos\theta)^2 = K(d^2_{hkl}\beta_{hkl}\cos\theta)/D + (\varepsilon/2)^2 \quad (12)$$

Where K is a constant equal to 4/3 for spherical particles and d is the lattice parameter. $(d_{hkl}\beta_{hkl}\cos\theta)^2$ is plotted with respect to $(d^2_{hkl}\beta_{hkl}\cos\theta)$ and it is shown in Fig 5. The particle size is determined from the slope of the linearly fitted data and root of the y-intercept gives strain.

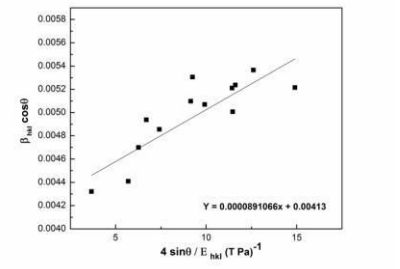

Fig.3 Uniform stress deformation model (USDM) Plot

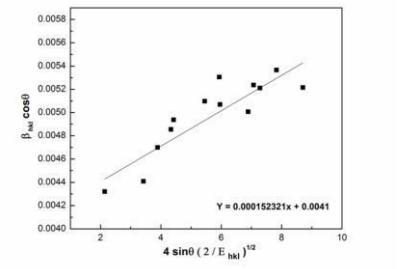

Fig.4 Uniform deformation energy density model (UDEDM) Plot.

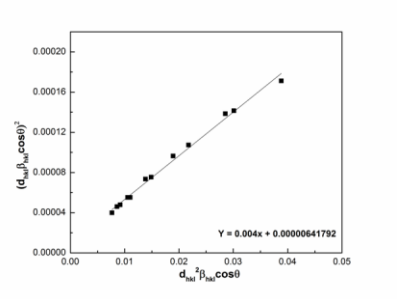

Fig.5 Size-strain plot (SSP).

3. Conclusion

$CoFe_2O_4$ nanoparticles were synthesized by co-precipitation process and characterized by PXRD. The PXRD indicated that $CoFe_2O_4$ nanoparticles were crystalline with mixed type spinel with cubic structure. The line broadening of $CoFe_2O_4$ nanoparticles was due to the small crystallite size and lattice strain. This broadening was analyzed by the Scherrer formula, modified forms of W-H analysis and SSP method. From the results, it was observed that the values of lattice strain, stress and energy density calculated from the W-H analysis is in agreement with the SSP method, but

the crystallite size was slightly deviated. The crystallite size calculated from Scherrer formula also differs from the results of W-H method and SSP method. This variation in particle size reveals that the distribution of non-uniform strain in the particles.

Acknowledgment

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Table 1

Geometric parameters of $CoFe_2O_4$ nanoparticles calcinated at 800^0C for 5 hrs

Williamson-Hall method									Size-Strain Plot method			
UDM		USDM			UDEDM							
D (nm)	ε x 10^{-4} (no unit)	D (nm)	ε x 10^{-4} (no unit)	σ (MPa)	D (nm)	ε x 10^{-4} (no unit)	σ (MPa)	u (KJ/m^3)	D (nm)	ε x 10^{-4} (no unit)	σ (MPa)	u (KJ/m^3)
35.24	5.027	35.06	4.854	89.11	35.32	5.0272	92.3	23.2	33.33	5.066	93.02	23.56