Crystallite size determination of barium hexaferrite nanoparticles using WH-plot and WPPM

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Abstract. Scherrer formula and Williamson-Hall plot or WH-plot are the common methods to determine microstructure information from diffraction pattern, a technique with the expenses of the physical meaning of the result. Eventually a Whole Powder Pattern Modeling (WPPM) has been proposed, allowing physical information to be extracted from the diffraction data with the one-step refinement of the experimental pattern. In this paper, we reported the comparison between Williamson-Hall plot and Whole Powder Pattern Modeling to determine the crystallite size of nanoparticle barium hexaferrites which prepared by mechanical alloying and direct ultrasonic destruction.

1. Introduction
Recently nanostructured magnetic materials have become a hot topic due to their unusual properties raised from the surfaces of neighboring grains. The reason is that because of a great surface to volume ratio in the nanostructures system, then any physical phenomena taking place on the grain surfaces would contribute significant effects to the bulk properties. The unusual properties of permanent magnets were claimed for the first time by McCallum et al. \cite{1} that they have developed the isotropic permanent magnet based on nanostructured materials with a remanent magnetization value significantly exceeding the conventional limits based on Stoner and Wohlfarth theory \cite{2}. The enhancement in remanent magnetization is due to the interaction phenomenon since the orientation of the interacting spins becomes partly independent of the different crystallographic directions in each crystallite \cite{3}. In fact, the interaction phenomenon that raised remanent enhancement occurred not only in the single phase nanostructured material \cite{4} but also in the nanocomposite magnet system \cite{5}. The basic principle to gain the effects of exchange grain interaction is the crystallite sizes of magnetic phase in the material must be in nanometer scale size.

Based on this fact, the determination of crystallite size becomes critical. Nanocrystalline barium hexaferrite (BHF) has been a subject of increasing interest due to the potential applications in the various areas like permanent magnets, microwave devices and fast magnetic recording devices \cite{6-8}. Accurate determination of crystallite size is very important for a BHF as a hard magnetic material, leading to reduction in coercivity as it identity \cite{8-11}.
As the latest Scanning Electron Microscopes (SEMs) and Transmission Electron Microscopes (TEMs) easily achieve sub-nanometer resolution, determination of nanocrystalline materials becomes obvious. However, some limitations in analysis were still found such as limitation of analysis to only a few grains [12]. In addition to SEM and TEM, an indirect method like x-ray diffraction would also be possible for crystallite size analysis from the respective powder diffraction pattern. In years, Scherrer formula [13, 14] and Williamson-Hall plot [13, 15] methods have been used to determine the microstructural of the nanocrystalline material. Scherrer observed that the small crystallite size give rise to line broadening and derived a well-known equation for relating the crystallite size to broadening, which is called the Scherrer Formula [14]. Stokes and Wilson also observed that the crystal imperfection and distortion can cause line broadening [16]. Further, Williamson and Hall proposed a method for deconvoluting size and strain contribution by looking the peak width as a function of 2θ which is written in equation 1 [15].

\[
\beta_{hkl}\cos\theta = \frac{k\lambda}{D} + 4\varepsilon\sin\theta
\]  

where \(\beta_{hkl}\) is the full width at half maximum of the line broadening, \(\theta\) is the Bragg angle, \(k\) is the Scherrer constant depends on the how the line profile width is determined and usually not known, \(\lambda\) is the source wavelength, \(D\) is the crystallite size and \(\varepsilon\) is microstrain represents displacements of atoms from their ideal positions, produced by any lattice imperfection (dislocations, vacancies, interstitials, substitutional, and similar defects).

It is clearly seen that the size and strain broadening are independent to each other, which is allowed to be separated when both occur together. The crystallite size was estimated from y-intercept and the strain from the slope. However, Scherrer formula (SF) and Williamson-Hall (WH) plot are strictly valid for Lorenzian peaks only, which are seldom meet a practice condition because some information also contain in Gaussian peaks. The average crystallite size is work well for isotropic domain, but not good enough for anisotropic domain. The microstrain contribution only provides a general term of defects, but does not identify their source [17]. The real obstacle comes from where SF and WH plot are extracted. Structure (Rietveld) refinement and whole powder pattern fitting (WPPF) are two distinct methods implementing the SF and WH-plot in the algorithms. The common tool for Rietveld and WPPF diffraction pattern analysis is shown in equation 2 [12].

\[
y_{ic}(2\theta) = y_{ib} + S\sum_{k} G_{ik} M_{k} L_{k} |F_{k}|^2 P_{k} A_{k} E_{k}
\]

where \(y_{ic}\) is the net intensity calculated at point \(i\) in the pattern, \(y_{ib}\) is the background intensity, \(G_{ik}\) is the normalized peak profile function contained size and strain effects, \(M_{k}\) is the multiplicity factor, \(L_{k}\) is the structure factor, \(P_{k}\) is the preferred orientation, \(A_{k}\) is the absorption correction and \(E_{k}\) is the extinction correction. The profile functions are introduced by modeling the peak profiles with an arbitrary bell-shaped function and further deduce the physical information. This is a two-step method where the result cannot be evaluated a priori.

The diffraction peak profiles are a complex combination of physical and instrumental effects. Constrains by the given analytical function can introduce a systematic (model) errors in correlated with structural and non-structural parameters. As a consequence, the results can be biased and difficult to assess. It also comes to the practical issues that the refinement is very sensitive to minimizing the least-squares of observed and calculated data.

Alternatively, there is a technique proposed to cover all Gauss/Lorentz-type combinations and one of those, called Whole Powder Pattern Modeling (WPPM) [17]. This technique directly refines the entire pattern with the individual parameter corresponding to individual source of broadening. It is able to model such information with a consistency and remarkable agree with the microscopy result [17-19]. It starts from Fourier approach and works in convolutive way where diffraction profiles can be seen in equation 3 [17].

\[
I_{(hkl)}(d^*, d^*_{(hkl)}) = k(d^*) \sum_{hkl} w_{hkl} \int_{-\infty}^{\infty} C_{hkl}(L) \exp(2\pi i L \cdot s_{hkl}) dL
\]
where \( d^* \) is the reciprocal space coordinate (\( d^*_{hkl} \) in Bragg condition), \( k(d^*) \) groups of known geometrical and structural terms, \( w_{d^*} \) is the weight function (dependent on defects present in the material), \( L \) is the length in real space (inversely proportional to \( d^*_{hkl} \)), \( s_{d^*} \) is the distance from peak centroid in the reciprocal space and \( C \) is the Fourier transform (FT) multiplication as explained in equation 4 [17].

\[
C_{(hkl)} = T_{p}\cdot A_{(hkl)}^F \cdot A_{(hkl)}^{iB} \cdot (A_{(hkl)}^{F} + iB_{hkl}^{F}) \cdot (A_{(hkl)}^{iSB} + iB_{hkl}^{iSB}) \cdot (A_{hkl}^{SF} + iB_{hkl}^{SF})
\]

where \( T_{p}\) is the FT of instrumental profile, \( A_{(hkl)}^{F} \) is the FTs for lognormal, \( \Gamma \) or York distribution depends on grain shape and size, \( A_{(hkl)}^{iB} \) is the lattice distortion due to dislocation, \( (A_{(hkl)}^{F} + iB_{hkl}^{F}) \) is the stacking fault broadening, \( A_{(hkl)}^{iSB} \) is the anti-phase broadening, \( (A_{(hkl)}^{iSB} + iB_{hkl}^{iSB}) \) is the grain surface relaxation broadening, \( (A_{hkl}^{SF} + iB_{hkl}^{SF}) \) is the stoichiometric fluctuations broadening and additional line broadening source that can be included due to Fourier Transform of the various effects are multiplied. It is one-step procedure that removed the arbitrary hypotheses by direct modeling the whole diffraction pattern in terms of physical models of the microstructure.

2. Experimental

The nanoparticles BHF was prepared through two successive steps. In the first step, the mechanical alloying of the solid-state reaction method was employed. In this method, stoichiometric quantities of the analytical-graded precursors \( \text{BaCO}_3 \) and \( \text{Fe}_2\text{O}_3 \) from Sigma-Aldrich with 99% purity level were milled in a ball mill apparatus with a ball-powder mass ratio of 10:1 using a jog speed of 160 rpm for 20 hours. Milled powders resulted from mechanical milling were compacted into a cylindrical die of 25 mm diameter under 10 tons load force. The green compact was then sintered at 1100°C for 2 hours leading to fully crystalline bulk sample. The crystalline bulk sample was re-milled for 10 hours and then washed with a light HCl solution to eliminate impurities. In the second step, the fully crystalline re-milled powders were then further treated with direct ultrasonic probe with 5% Vol/Vol of water, at a frequency 20 kilohertz and 60 \( \mu \)m transducer amplitude. X-ray diffraction was performed under a Philips diffractometer using Co-\( \alpha \) radiation due to the fluorescence effect of iron. The crystallite size of powder diffraction data was determined using High Score Plus (HSP) software implementing WH-plot and PM2K software implementing WPPM. Powder XRD data of 5 hours ultrasonically irradiated sample were used in refinements after determining the instrument broadening with Si-standard (SRM-640). The average particle size distributions of powder specimens were determined using Dynamic Light Scattering (DLS) Particle Size Analyzer and Scanning Electron Microscope (SEM).

3. Result and Discussion

Fitted powder XRD patterns of ultrasonic irradiated samples in figure 1(a) shows a typical single phase M-type hexagonal structure of BHF with space group P63/mmc. Strong preferred orientation on \( hhl \) -planes in bulk pattern is a typical of mechanical alloyed BHF sintered between 1000-1250°C [20, 21]. As the ultrasonic irradiation time increased the intensity of diffracted peaks also decreased due to the more random distribution of destructed crystals. The decrease in intensity was followed by line broadening of diffracted peaks. In figure 1(b), broadened peaks of (114) for ultrasonic irradiated powders are compared. It shows the Full Width Half Maximum (FWHM) increased as the ultrasonic irradiation time increased. The longer irradiation time, the higher value of FWHM. It is concluded that the ultrasonic irradiation can reduce the crystallite size. In the previous work, Karina et al. [22] have reported their comprehensive studies on the use of high power ultrasonicator to refine further the mechanically alloyed powders. Prior to irradiation ultrasonically the crystalline mechanically milled \( \text{SrO.6} (\text{Fe}_2\text{O}_3) \) powders which initially have mean particle and crystallite sizes respectively 723 nm and 179 nm, both were progressively reduced the size, though with a different reduction rate after irradiated under an ultrasonic transducer of 55 \( \mu \)m amplitude. After 5 hours irradiation time the polycrystalline particles reduced the size towards monocrystalline particles of about 87 nm. Hence, crystallites in the particle can be further refined.
Figure 1. PXRD patterns of: (a) stacked ultrasonic assisted samples and (b) comparison of 023 peaks.

Figure 2(a) is a plot of particle size distribution of powder sample evaluated by particle size analyzer after ultrasonically irradiated for 5 hours. It shows a bi-modal distribution with a mean size of 51.2 nm and 276.3 nm, respectively. The high mean distribution occurred due to effect of fine particles that tend to agglomerate. It can be seen that the particles of a low mean particle size occupied the largest volumetric distribution by 64 % and that of a high mean particle size occupied by 36%.

SEM micrograph of such agglomerated particles is shown in figure 2(b). It can be clearly seen that the agglomerated particles present as a homogenous spherical shape with size range from a few ten nanometers to a few hundred nanometers. The mean crystallite size and crystallite size distribution of such particles can be evaluated from the respective XRD data.

Figure 2. (a) Particle size distribution and (b) SEM micrograph of ultrasonic irradiated sample.

WH-plot and WPPM analysis of XRD data for the 5 hours ultrasonically irradiated sample is shown in figure 3. Such plot was made of refined XRD data of figure 1(a), from which the refinement result of WH-plot has Rexp 9.0, Rwp 9.2 and GoF 1.1. It indicates a good agreement between data and model. Linear fitting Williamson-Hall plot in figure 3(a) has resulted in a linear relation of $\beta^*\cos\theta = 0.209 + 0.070^*\sin\theta$. Referring to equation (1), it confirms the presence of microstrain 0.018 (3) % of the particles. The mean crystallite size of particles is 42.434(2) nm. The dash-dot linear plot shows 12% ($\pm$ 7 nm) deviation with similar weighted residue to continuous line. The modelled pattern of WPPM has Rexp 5.2, Rwp 5.5 and GoF 1.1 and the refinement parameters are lesser than Rietveld method. It was found the perfect match between data, model and the size distribution.
distribution was modeled by a lognormal distribution as shown in figure 3(b). The result superimposed second peak from DLS graph. Mean size of 49.1 nm is very close to DLS result (49.2 nm), concludes that each particle contained single crystallite. The curve width is about 3 nm narrower than DLS result (7.1 nm), shows a difference between the techniques.

![Figure 3](image_url)

**Figure 3.** (a) Rietveld/WPPF result as WH-plot and (b) WPPM result as a lognormal distribution.

4. Conclusions
A comparison between WH-plot and WPPM method of crystallite size determination at nano particle BHF has successfully performed. It is found that the average crystallite size of WH-plot was very close to the mean crystallite size distribution from WPPM. The size of WH-plot was about 42.4 nm and for WPPM about 49.1 nm. Both results have good agreement with DLS and SEM analysis. WPPM give the advantage of size distribution which is very important information in nano material applications.

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References
[1] McCallum R W, Kadin A M, Clemente G B, Keem J E 1987 J. Appl. Phys. 61 3577
[2] Stoner E C and Wohlfarth E P 1948 Phil. Trans. Roy. Soc. A-240 599
[3] Giselher Herzer 2005 NATO Science Series II: Mathematics, Physics and Chemistry 184
[4] Eds. B. Idzikowski, P. Švec, M. Miglierini (Kluwer Academic, Dordrecht) p 15
[5] Manaf A, Leonowicz M, Davies H A, Buckley R A 1992 Materials Letters 13 194
[6] Manaf A, Buckley R A and Davies H A 1993 J. Magn. Magn. Mater. 128 307
[7] Pullar R C 2012 Prog. Mat. Sci. 57 1191
[8] Sharrock M P and Carlson L W 2002 IEEE Trans. Magn. 31 2871
[9] Manawan M, Manaf A, Soegijono B, Yudi A 2014 Adv. Mat. Res. 896 401
[10] Manaf A, Hafizah M A E, Belyamin, Nainggolan B, Manawan M 2017 Int. J. Tech. 2 37
[11] Ataie A and Zojaji S 2007 J. Alloys Comp. 431 331
[12] Chaudhury S, Rakshit S, Parida S, Singh Z, Mudher K S, Venugopal V 2008 J. Alloys Comp. 455 25
[13] Leoni M 2012 Information on Imperfections, in Uniting Electron Crystallography and Powder Diffraction (Trento: Springe p 173)
[14] Alexander L E and Klug H P 1974 X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials 2nd ed. (New York: Wiley)
[15] Scherrer P 1918 Nachrichten von der Gesellschaft der Wissenschaften, Gottingen. Mathematisch-Physikalische Klasse 2 98
[16] Williamson G K and Hall W H 1953 Acta Metal 1 22
[17] Stokes A R and Wilson A J C 1944 Proc. Phys. Soc. 40 197
[18] Scardi P and Leoni M 2001 Acta Crys. A58 190
[19] Leoni M, Maggio R D, Polizzi S, Scardi P 2004 J. American Cer. Soc. 86 1133
[20] Abdellatif M, Abele M, Leoni M, Scardi P 2013 J. Thin Solid Films 530 44
[21] Wang S, Ding J, Shi Y, Chen Y 2000 J. Magn. Magn. Mater. 219 206
[22] Dho J, Lee E K, Park J Y, Nur N H 2005 J. Magn. Magn. Mater. 285 164
[23] Fitriana K N, Hafizah M A E and Manaf A 2017 Int. J. Tech. 4 644