

# Size Dependent Strain Analysis of CaFe<sub>2</sub>O<sub>4</sub> Nano Ceramics

Anand Yadav<sup>1, 2, b)</sup>, Pankaj Choudhary<sup>1, a)</sup>, P. Saxena<sup>1</sup>, S. Patel<sup>1</sup>, V. N. Rai<sup>1</sup>, Meenu Dinesh Varshney<sup>1</sup>, A. Mishra<sup>1</sup>

<sup>1</sup>Material Science Laboratory, School of Physics, Vigyan Bhawan, Devi Ahilya University, Khandwa Road Campus, Indore 452001, India.

<sup>2</sup>Department of Physics, Medi-Caps University, Pigdamber, Indore 453331, India.

<sup>a)</sup>pankaj.7007@rediffmail.com

<sup>b)</sup>anand.212@gmail.com

**Abstract.** CaFe<sub>2</sub>O<sub>4</sub> nano ceramics are successfully prepared by green synthesis technique and the obtained nano-sized powder is annealed at 850° C for 6h. The annealed powder is examined by x-ray diffraction (XRD) measurement at room temperature, which confirms that the diffraction peaks of the annealed CaFe<sub>2</sub>O<sub>4</sub> are well crystalline and correspond to post-spinel orthorhombic structure with space group *Pnma*. Small amount of secondary phase corresponding to CaCO<sub>3</sub> has also been observed. Crystallite size and the strain are estimated by Debye Scherrer [46.81 nm,  $2.46 \times 10^{-3}$ ], Modified Debye Scherrer [50.82 nm,  $2.42 \times 10^{-3}$ ] and Williamson–Hall plot [81.56 nm,  $1.23 \times 10^{-3}$ ] respectively. The change in crystallite size and strain seems to be due to the dislocation and anisotropic nature of CaFe<sub>2</sub>O<sub>4</sub> nano ceramics. This indicates that estimation of crystallite size using least squares technique provides more accurate results that can be applied to minimize sources of errors.

## INTRODUCTION

Nanomaterials have the potential of revolutionizing materials design for many applications. Their novel or unusual physical properties are mainly due to its finite-size effects. Because of the finite-size effects, physical and chemical properties of nanomaterials are normally very different than those of the bulk materials. Recently, ferrite materials in the form of nanoparticles, nano ceramics, bulk, thin films and layered composites are being investigated for various potential applications, such as hard magnets for data storage and soft magnets for magnetic switches, inductors, high-frequency components, gas sensors, super-capacitor, hyperthermia cancer treatment and biotechnological applications [1]. Nanocrystalline CaFe<sub>2</sub>O<sub>4</sub> ceramics have orthorhombic structure with space group *Pnma*. It is important to prepare CaFe<sub>2</sub>O<sub>4</sub> ceramics because the composing metal cations at tetrahedral [Ca<sup>2+</sup> (*d*<sup>0</sup>)] and octahedral [Fe<sup>3+</sup> (*d*<sup>5</sup>)] sites have zero crystal field stabilization energy (CFSE).

Crystallographic orientations in nano materials expand infinitely in all spaces, which may be due to the grain boundaries and triple junctions. Finite size and lattice strain are the two crucial properties, which decide the Bragg peak width, intensity of peak and shift of the  $2\theta$  peak position respectively. Due to the evolution of polycrystalline aggregates, the crystallite size of the particle is not similar as the particle size. The presence of induced strain in nano ceramics also includes lattice deformation stress, stacking faults and phenomena of grain barriers [2].

The aim of the present work is to calculate the crystallite size of CaFe<sub>2</sub>O<sub>4</sub> nano ceramics more accurately from x-ray diffraction data by considering the contributions of other important factors, such as lattice strain effects on the x-ray peak broadening. Micro- structural domain such as lattice strain present in the nano ceramics are estimated based on W–H plot using Williamson–Hall isotropic-strain (W–H-ISM) models. The crystallite size values obtained from Debye Scherrer and W–H methods reveal that there is significant effect of lattice strain and stress.

## EXPERIMENTAL DETAILS

CaFe<sub>2</sub>O<sub>4</sub> nano ceramics were prepared by low temperature based green synthesis route using banana (*Musa paradisiaca*) peel extract (BPE) a non-toxic eco friendly material. Banana peels were washed and dried in the presence of sunlight. Dry peels put in the tubular furnace at temperature 60 °C for 2 hours. The dried peels (10 g) were crushed and mixed in 100 ml distilled water. The extract was filtered through a cheese cloth to remove insoluble fractions and macromolecules. The precipitate was centrifuged at 400 rpm for 30 min. The final extract was used as fuel agent. The stoichiometric ratio of Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and extract banana peels were dissolved in distilled water and placed on magnetic stirrer at 450 rpm for 2 hours. The stirrer temperature raised upto 120 °C to get burned powder. The ash powder was annealed at 850° C for 6 hours to obtain spinel phase.

Structural evolution of nano ceramics was recorded using Bruker D8 advance x-ray diffractometer with Cu-Kα<sub>1</sub> radiation (λ = 1.5406 Å). The data was collected with a step size of 0.02° over the 2θ range (25 ≤ 2θ ≤ 65). X-ray generation was estimated out at 40 kV and 40 mA power settings.

## RESULTS AND DISCUSSION

The x-ray diffraction (XRD) profile of CaFe<sub>2</sub>O<sub>4</sub> nano ceramics is shown in Figure 1. From the XRD pattern, it is observed that CaFe<sub>2</sub>O<sub>4</sub> ceramics crystallizes in orthorhombic symmetry [space group *Pnma*] with distorted spinel (post-spinel) structure. Observed prominent (hkl) planes at (230), (320), (201), (031), (311), (141), (401), (431) and (500) matches well with the JCPDS card No. 72-1199. Small amount of secondary phase corresponding to CaCO<sub>3</sub> is also observed in the profile. The lattice parameters for CaFe<sub>2</sub>O<sub>4</sub> orthorhombic unit cell are estimated to be *a* = 8.768, *b* = 13.250, *c* = 3.413 Å, which are very close to the earlier reported results [3]. The crystallite size of the prepared ceramics was estimated from the full width at half-maxima (FWHM) of the main intense peak (320) profile distribution fitted to Gaussian amplitude function as shown in the inset of Figure 1. Crystallite size (*D*<sub>hkl</sub>) of the sample is ~ 46.81 nm as estimated by the Debye Scherrer equation. Corresponding to (320) plane the calculated value of lattice strain is ~ 2.46 × 10<sup>-3</sup> evaluated using the relation ε = β/4tanθ, where θ is the Bragg angle and β is FWHM in radian.

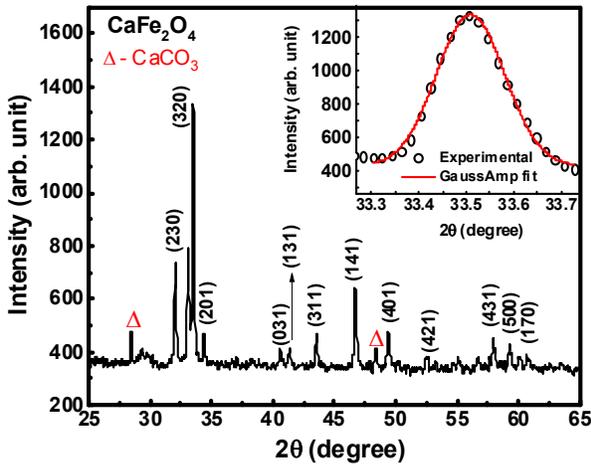


FIGURE 1. XRD pattern of CaFe<sub>2</sub>O<sub>4</sub> nano ceramics. Inset shows Gaussian fit of most intense (320) peak.

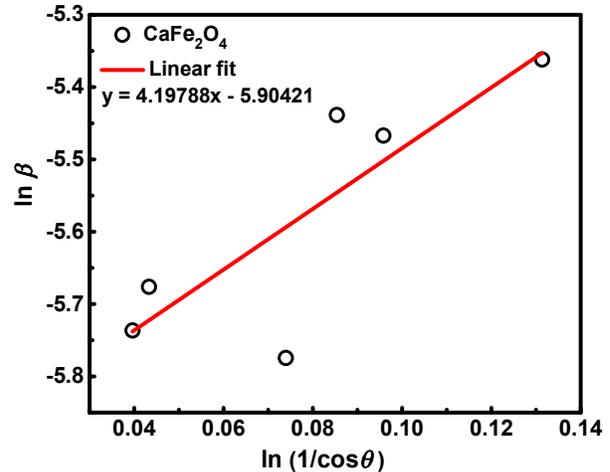


FIGURE 2. Linear plot of modified Scherrer equation of CaFe<sub>2</sub>O<sub>4</sub> nano ceramics.

Modified Scherrer equation is based on the face that we must diminish the errors and obtain the average crystallite size out of all the peaks by using least squares method to mathematically decrease the source of errors.

Scherrer formula can be rewritten as: 
$$\beta = \frac{K \lambda}{D} \frac{1}{\cos \theta}$$

Now taking logarithm on both sides; 
$$\ln \beta = \ln \frac{K \lambda}{D} + \ln \frac{1}{\cos \theta}$$

Figure 2 indicates the plots of ln β vs. ln (1/cosθ) for CaFe<sub>2</sub>O<sub>4</sub> nano ceramics. It is interesting to notice that average crystallite size and calculated strain in prepared nano ceramics is ~ 50.82 nm and ~ 2.42 × 10<sup>-3</sup> respectively.

X-ray peak broadening is represented by the sum of the contributions of crystallite size and strain present in the material. Assuming that the strain present in nano ceramics is uniform and considering the isotropic nature of the crystal, the W–H equation for the total peak broadening is given by:  $\beta \cos \theta = \frac{K \lambda}{D} + 4 \varepsilon \sin \theta$

Figure 3 shows the W-H-ISM plot of  $\text{CaFe}_2\text{O}_4$  nano ceramics. The estimated values of the average crystallite size and lattice strain ( $\varepsilon$ ) are given by  $\sim 81.56$  nm and  $\sim 1.23 \times 10^{-3}$  respectively. The calculated crystallite size ( $D$ ), lattice strain ( $\varepsilon$ ) and dislocation density ( $\delta$ ) values are listed in Table 1. There is a significant difference between estimated crystallite size value by the Debye Scherrer and modified Scherrer analysis. Size-strain related W-H-ISM model results in more accurate estimation of crystallite size compared to Scherrer analysis. Henceforth, it is suggested that the contribution from instrumental effects and lattice strain effect to the x-ray peak broadening need to be considered while calculating the crystallite size value of  $\text{CaFe}_2\text{O}_4$  nano ceramics.

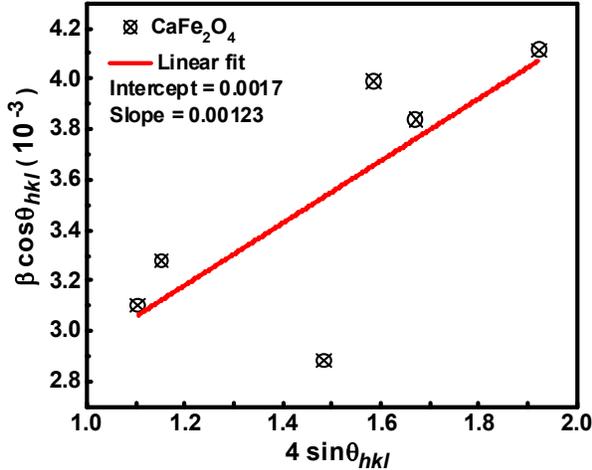


FIGURE 3. W-H-ISM plot of  $\text{CaFe}_2\text{O}_4$  nano ceramics.

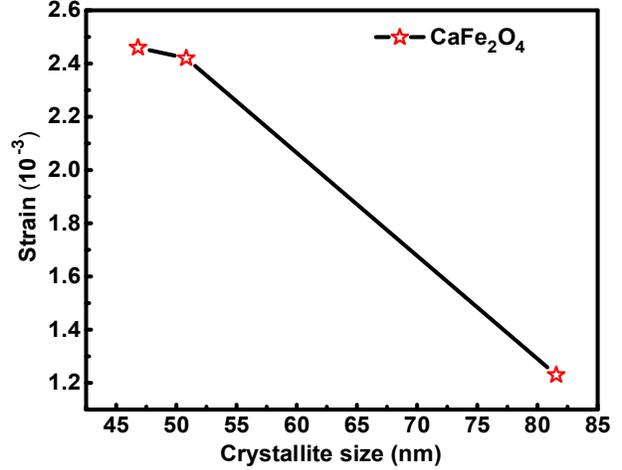


FIGURE 4. Variation of size and strain for  $\text{CaFe}_2\text{O}_4$  nano ceramics.

The crystallite size and the lattice strain values obtained from the W–H-ISM model can be further extended to estimate the dislocation densities present in nano ceramics with more accuracy. Figure 4 clearly shows that as the crystallite size increases the observed strain also decreases. It is due to the presence of lattice defects in the form of oxygen vacancies. Lattice strain is dependent on the porosity and the pore structure of the prepared nano ceramics. Porosity and oxygen vacancy depends on the synthesis technique [4, 5].

TABLE 1. Structural parameters for  $\text{CaFe}_2\text{O}_4$  nano ceramics obtained from XRD data.

Method	$D$ (nm)	Strain ( $\varepsilon$ ) $\times 10^{-3}$	Dislocation density ( $\delta$ ) $\times 10^4$ ( $\text{m}^{-2}$ )
Debye Scherrer	46.81	2.46	4.56
Modified Debye Scherrer	50.82	2.42	3.87
Williamson–Hall	81.56	1.23	1.50

The broadening and narrowing of the diffraction peaks indicate the increase and decrease of the crystallite size as well as lattice strain. Strain-stress varies from different crystallite size and grain size, owing to crystallographic orientations relative to the direction planes and also because of stress concentration at grain contacts during powder ceramics. Even the local strain at the junction points between crystals grains are also affecting the diffraction peak broadening significantly.

## ACKNOWLEDGMENTS

UGC-DAE CSR, Indore as an institute is acknowledged for extending its facilities and financial assistance (Grant No.: CSRIC/BL-22/CRS-119-2014/269).

## REFERENCES

1. P. Choudhary and D. Varshney, *Solid State Comm.* **271**, 89 (2018).
2. K. Venkateswarlu, A. C. Bose and N. Rameshbabu, *Physica B* **405**, 4256 (2010).
3. A. Manohar and C. Krishnamoorthi, *J. Alloy Comp.* **722**, 818 (2017).
4. U. Schubert and N. Husing, *Synthesis of Inorganic Materials* (WILEY-VCH, Weinheim, 2005) 353-354.
5. Y. Zhao and J. Zhang, *J. Appl. Cryst.* **41**, 1095 (2008).