Structural characterization and rietveld refinement of CeO$_2$/CoFe$_2$O$_4$ nanocomposites prepared via coprecipitation method

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Abstract: The CeO$_2$/CoFe$_2$O$_4$ nanocomposites were synthesized through the co-precipitation approach followed by heat-treatment. As-prepared samples were sintered at temp 600°C and 800°C for two hours. To study the structural characterization of the prepared samples X-ray diffraction (XRD) technique was used. The obtained XRD data was further refined through the Rietveld method by using the fullprof suit software. The heat-treated samples exhibit two crystalline phases namely CeO$_2$ and CoFe$_2$O$_4$. The refinement confirmed that all the samples are cubic structure. The CoFe$_2$O$_4$ was found to have an fcc cubic structure with space group Fd-3m(227), whereas the crystal structure of CeO$_2$ has fcc structure with space group Fm-3m(225). In this paper, the lattice parameters, bond length, bond angle, particle size, lattice strain, dislocation density were studied in detail. The Wyckoff positions and interatomic distance have been calculated.

Keywords: CeO$_2$/CoFe$_2$O$_4$, Nanocomposites, Coprecipitation, particle size, lattice strain, dislocation density.

1. INTRODUCTION

From last few decades magnetic nano ferrites of type MFe$_2$O$_4$ have become the source of interest, because of their unique structural, electrical, magnetic, and catalytic properties, where M represents any transition metal ions like Co, Zn, Ni etc. Nano ferrites have found uses in various fields such as magnetic resonance imaging, drug delivery, biomedicine etc [1]. Among the various ferrite materials, cobalt ferrite (CoFe$_2$O$_4$) with inverse spinel structure in nano form is well known to have some special properties i.e it shows high coercivity, high chemical stability, moderate saturation magnetization (Ms) value, high magnetic anisotropy and mechanical hardness [2]. These strange properties of cobalt ferrite make it fundamental to use in many technological applications such as high-density recording media, cancer treatment and drug delivery, magnetic fluids, magnetic refrigerants [3] etc. To explore the properties of CoFe$_2$O$_4$ in diverse fields it becomes necessary to dope with other metal ions and metal oxide. Ion doping has a great impact on the physicochemical properties of ferrite nanoparticles which leads to the structural disorder, change in particle size, lattice strain and cation redistribution. In past researcher shows that by surface modification, the surface characteristics of ferrite nanoparticles are greatly changed, which will result in some novel performances and applications. Literature reveals that the doping of Gd$^3+$ in nickel ferrite gives a finite variation in structural and magnetic properties of nickel ferrite [4]. Similarly a change in crystal structure parameter, grain size, saturation magnetization (Ms) and BET surface area of ZnFe$_2$O$_4$ nanoparticles is observed when Ce$^{3+}$ is substituted in ZnFe$_2$O$_4$ [5]. Besides, some ferrite composite materials are synthesized to vary surface
properties and develop new applications using a surface modification method [6]. So to tune the properties of CoFe2O4, it becomes necessary to make the composites of cobalt ferrite with metal oxide.

In recent year CeO2 doped cobalt ferrite nanocomposites has attracted much interest. Cerium is one of the most generous rare earth elements and its oxide (CeO2) has high dielectric constant and band gap [7]. Nanostructured CeO2 has superior physical and chemical properties which make it to widely used in various fields such as catalysis to controlling emissions from vehicles, solar cells, gas sensor etc.[8] The development of nanocomposites of CeO2 with magnetic nanoparticles could extend the possible application of these materials, for example, the CeO2 doped CuFe2O4 nanocomposites are widely used in energy storage applications [9]. Similarly, Fe3O4/CeO2 nanocomposites can be used as a magnetically separable catalyst [10]. CoFe2O4 shows strong magnetic behavior so together with CeO2 it is can used to produce very strong magnet [11]. Recently CeO2/CoFe2O4 nanocomposites is used as a magnetically separable catalyst [12]. Till now, CeO2/CoFe2O4 is less studied systems among researchers. A little work has been reported on successful synthesis of CeO2/CoFe2O4 nanocomposites. Successful preparation of the CeO2/CoFe2O4 nanocomposites by coupling homogeneous precipitation with hydrothermal method was reported by Wetchakun et al. [13]. They have shown that controlled precursors ratios of CoFe2O4 in CeO2 can control the particle size and specific surface area of resultant composite (CeO2/CoFe2O4).

So here we have synthesized CeO2/CoFe2O4 nanocomposites using coprecipitation method. In past many techniques like sol-gel, hydrothermal, solid-state reaction, co-precipitation, radiofrequency thermal plasma, etc. were used by the researchers for the synthesis of CeO2 and CeO2 doped nanocomposites [14]. Among these methods the coprecipitation method was proved to be less costly, environment-friendly, less time consuming, and easy scale-up [15-16]. Beside synthesis we have also reported the detailed structural characterization of CeO2/CoFe2O4 nanocomposites. We have used XRD to investigate the structural analysis of prepared samples and the accurate resolve of nanostructural parameters has been done using Rietveld analysis. Since, Rietveld refinement is the best method of nanostructure characterization which is able to calculate the reciprocal lattice parameters, lattice strain, change in atomic and direct lattice parameters of relative phase abundances of all the phases in a multiphase scale factor, lattice shift constant, half-width profile parameters, atoms position of nano-crystalline materials, etc. Keeping above facts Rietveld’s refinement of X-ray diffraction data has been adopted here. The refinement clearly shows the change in parameters in terms of the bond length, bond angles, and different atomic positions [17-18]. The positions of different atoms create change in the behavior of the same materials and these parameters can be seen behind refinement. However, in the history decade the number of publications which used Rietveld refinement for quantitative phase investigation but to the best of author’s knowledge there are limited investigations which report the Rietveld refinement of CeO2/CoFe2O4 nanocomposites.

2. EXPERIMENTAL:

CeO2/CoFe2O4 nanocomposites with 20wt% of CeO2 were prepared by the coprecipitation method. We have used FeCl3, CeCl3, 7H2O, CoCl2·6H2O and NaOH as precursors. Magnetic stirring! is used to mix these raw materials in their stoichiometric amounts and using deionized water as a solvent. After agitating well, NaOH aqueous solution was added drop wise to this mixed solution. During this drop wise addition the pH of the medium was maintained at 11. This will produce precipitate in the solution mixture [19]. Then, the precipitation was aged at 50°C for 2h. After that the precipitates were washed several times with deionized water and ethanol to remove the water-soluble impurities and free reactants and then dried at 80°C overnight. The obtained sample was then powdered using agate mortar. This powdered sample was then heated in a muffle furnace at 600°C (2h) and 800°C (2h).
3. RESULTS AND DISCUSSION:

XRD analysis and Rietveld Refinement

XRD is used to determine the presence of crystalline phases of the prepared sample. The XRD pattern has shown in Figure 1. The sample was scanned from 20 degrees to 80 degrees. Rietveld refinement of the XRD data has focused, the phases and structures of the prepared composite sample were determined to investigate the crystal structure which is depicted in Figure 2.

Figure 1. XRD pattern of CeO$_2$/CoFe$_2$O$_4$ nanocomposites (C1) as-prepared (C2) Heat-treated at 600$^\circ$C (C3) Heat-treated at 800$^\circ$C

The X-ray diffraction (XRD) pattern of powdered sample was obtained at room temperature by using a Philips X ray diffractometer having GIXRD geometry. The diffractometer was operated with a wavelength of radiation 1.5418Å. The diffraction pattern consists of well resolved peaks between 15$^\circ$ and 80$^\circ$ angle indexed as (220),(311),(400),(331),(511),(440) corresponding $2\theta$-30.14$^\circ$, 35.475$^\circ$, 43.124$^\circ$, 47.48$^\circ$, 57.01$^\circ$ and 62.61$^\circ$ respectively are well matched with the CoFe$_2$O$_4$ ferrite, JCPDS file no. 221086. All the peaks of said diffraction pattern reveals the formation of FCC Cubic structure with space group Fd3m(227) [JCPDS card no-221086].

Further, the peak centred at 2theta- 28.531$^\circ$ (111), 33.14$^\circ$ (200), 47.53$^\circ$ (220), 56.33$^\circ$ (311), 59.06$^\circ$ (222), 76.69$^\circ$ (331), 79.07$^\circ$ (420) give the confirmation of the formation of CeO$_2$ phase with space group Fm3m(225) (JCPDS file no.810792). The (hkl) plane, $\theta$, d-spacing, full width at half maxima, particle size (D), dislocation density (\(\delta\)) and micro-strain (\(\varepsilon\)), for the nanocomposite CeO$_2$/CoFe$_2$O$_4$ obtained from X-Ray diffraction analysis were shown in table 1 particle size (D) was determined by the scherrer equation (1) and dislocation density (\(\delta\)) was calculated by the formula (2) are given bellow:

\[
D = \frac{(0.9*\lambda)}{(FWHM*Cos\theta)} \quad (1)
\]

\[
\delta = \frac{1}{D^2} \quad (2)
\]
The average particle size was found to be 43.09 nm for CeO\(_2\) phase and 68.89 nm for CoFe\(_2\)O\(_4\) phase. Lattice parameter of cubic CeO\(_2\) with various concentrations of dopant were calculated using relation \(a = \left[ d^2(h^2+k^2+l^2) \right]^{1/2}\) (results are listed in Table 1). Upon increasing the temperature, lattice parameter values tended to decrease because of replacement or may be due to defect formation due to Co ions in the CeO\(_2\) lattice. To observe the effect of Ce doping in Co, Rietveld refinement was done using full prof suit software. Co doping cause lattice contraction as lattice parameter decreases with doping. This contraction occur due to smaller ionic radii of Co\(^{2+}\) (0.65-0.9 Å) than that of Ce\(^{4+}\) (0.97 Å). The Rietveld refinement for the sample CeO\(_2\)/CoFe\(_2\)O\(_4\) has been shown in Figure 2 by using the FullProf suit software. It could be seen that the profile for observed and calculated ones are matching to each other.

**Figure 2.** Rietveld refinement of the XRD pattern of CeO\(_2\)/CoFe\(_2\)O\(_4\) nanocomposite

![Rietveld refinement of the XRD pattern of CeO\(_2\)/CoFe\(_2\)O\(_4\) nanocomposite](image)

**Figure 3.** Structure diagram of A (CeO\(_2\)) and B (CoFe\(_2\)O\(_4\))

![Structure diagram of A (CeO\(_2\)) and B (CoFe\(_2\)O\(_4\))](image)

Figure 3 shows the crystal structure of CeO\(_2\) (A) and CoFe\(_2\)O\(_4\) (B). The crystal structure of CeO\(_2\) refined in a FCC cubic crystal geometry (phase 1) with space group Fm3m and the crystal structure of CoFe\(_2\)O\(_4\) successfully refine in FCC cubic crystal geometry (phase 2) with space group Fd3m. The
refined direct cell parameters for CeO$_2$ are found to be $a = b = c = 5.4089$, $a = \beta = \gamma = 90^\circ$. The direct cell volume of CeO$_2$ are found to be $587.0496$ and the refined direct cell parameters for CoFe$_2$O$_4$ are found to be $a = b = c = 8.3732$, $a = \beta = \gamma = 90^\circ$ and refined direct cell volume for CoFe$_2$O$_4$ are found to be $587.0496$ which is shown in Table 2. The Fractional atomic co-ordinates and isothermal parameter of different atoms obtained from the rietveld analysis of XRD patterns for the sample CeO$_2$/CoFe$_2$O$_4$ is shown in table 3. The appropriate value of goodness of fit parameters are found to be $\chi^2 = 0.242$, $R_p = 69.7$, $R_{wp} = 34.7$, $R_{exp} = 70.51$, and bragg R factor for CoFe$_2$O$_4$ is $27.44$ and for CeO$_2$ is $48.41$ and Rf factor for CoFe$_2$O$_4$ is $36.07$ and for CeO$_2$ is $57.14$ which is shown in table 4. The bond length and bond angles obtained for CoFe$_2$O$_4$ and CeO$_2$ phase are shown in table 5 and table 6 respectively.

Table 1. Crystal Structure parameters of CeO$_2$/CoFe$_2$O$_4$ obtained from X-ray Diffraction Pattern

| 2 theta (degree) | Particle size (nm) | d-spacing [Å] | (hkl) | FWHM | Cell parameter (a) | dislocation density (nm$^{-2}$) | Strain |
|------------------|--------------------|----------------|-------|------|-------------------|-------------------------------|--------|
| 28.547           | 76.55198           | 3.124          | (111) | 0.107| 5.41              | 0.184842884                  | 0.00045|
| 30.14            | 68.50795           | 2.963          | (220) | 0.12 | 5.92              | 0.168918919                  | 0.000506|
| 33.08            | 75.97182           | 2.7057         | (200) | 0.109| 5.4114            | 0.184795062                  | 0.00045|
| 35.475           | 71.84931           | 2.5284         | (311) | 0.116| 8.3857            | 0.119248961                  | 0.00048|
| 43.124           | 105.3803           | 2.096          | (400) | 0.081| 8.384              | 0.119274809                  | 0.000329|
| 47.486           | 90.33987           | 1.913          | (331) | 0.096| 8.3385            | 0.119224582                  | 0.000384|
| 57.018           | 120.458            | 1.632          | (222) | 0.12 | 5.41              | 0.184842884                  | 0.000456|
| 59.06            | 76.03488           | 1.562          | (440) | 0.089| 8.3834            | 0.119283346                  | 0.000332|
| 62.616           | 104.4059           | 1.482          | (331) | 0.116| 5.412             | 0.184774575                  | 0.00039 |
| 76.691           | 87.27148           | 1.2416         | (420) | 0.092| 5.411              | 0.184808723                  | 0.00031 |

Table 2. Rietveld refinement. Cell parameters for CeO$_2$/CoFe$_2$O$_4$ nanocomposite

| Materials | System configuration and space group | Direct cell parameters | Direct and reciprocal cell volume | Reciprocal lattice parameter |
|-----------|-------------------------------------|------------------------|----------------------------------|-----------------------------|
| CoFe$_2$O$_4$ | FCC (Fd3m) | $a=b=c=8.3732$ | $a=\beta=\gamma=90.000$ | $\alpha^{*}=\beta^{*}=\gamma^{*}=0.1194$ 29 |
| CeO$_2$ | FCC (Fm3m) | $a=b=c=5.4089$ | $a=\beta=\gamma=90.000$ | $\alpha^{*}=\beta^{*}=\gamma^{*}=0.1848$ 81 |

Table 3. Fractional atomic co-ordinates and isothermal parameter of different atoms obtained from the rietveld analysis of XRD patterns for the sample CeO$_2$/CoFe$_2$O$_4$

| Materials | Atom | Wyck. | Site | x/a | y/b | z/c |
|-----------|------|-------|------|-----|-----|-----|
| CoFe$_2$O$_4$ (Fd3m) | O | 32e | .3m | 0.38000 | 0.38000 | 0.38000 |
| Co | 8a | -43m | 0 | 0 | 0 |
| Fe | 8a | -43m | 0 | 0 | 0 |
| Co | 16d | -3m | 5/8 | 5/8 | 5/8 |
| CeO$_2$ (Fm3m) | O | 8c | -43m | 1/4 | 1/4 | 1/4 |

Table 4. Result of retiveld refinement for CeO$_2$/CoFe$_2$O$_4$

| Phase | $\gamma^2$ | RP | Rwp | RE | Rb | RF |
|-------|------------|----|-----|----|----|----|
| CoFe$_2$O$_4$ | 0.242 | 69.7 | 34.7 | 70.51 | 27.44 | 36.07 |
| CeO$_2$ | 0.242 | 69.7 | 34.7 | 70.51 | 48.41 | 57.14 |
Table 5. Bond lengths (Å) and selected angles (degree) of CoFe₂O₄

| Atom1 | Atom2 | Atom3 | D 1,2 | D 1,3 | Angle |
|-------|-------|-------|-------|-------|-------|
| O     | fe    | co    | 1.8853| 2.0523| 123.611|
| O     | fe    | co    | 1.8853| 2.0523| 123.611|
| O     | fe    | co    | 1.8853| 2.0523| 123.611|
| O     | fe    | co    | 2.0523| 2.0523| 92.313 |
| O     | fe    | co    | 2.0523| 2.0523| 92.313 |
| fe    | O     | O     | 1.8853| 1.8853| 109.471|
| fe    | O     | O     | 1.8853| 1.8853| 109.471|
| fe    | O     | O     | 1.8853| 1.8853| 109.471|
| fe    | O     | O     | 2.0523| 2.0523| 92.361 |
| fe    | O     | O     | 2.0523| 2.0523| 92.361 |
| fe    | O     | O     | 2.0523| 2.0523| 92.361 |
| fe    | O     | O     | 2.0523| 2.0523| 92.361 |
| fe    | O     | O     | 2.0523| 2.0523| 92.361 |

Table 6. Bond lengths(Å) and selected angles (degree) of CeO₂ phase

| Atom1 | Atom2 | Atom3 | D 1,2 | D 1,3 | Angle |
|-------|-------|-------|-------|-------|-------|
| Ce    | O     | O     | 2.3418| 2.3420| 70.529|
| Ce    | O     | O     | 2.3418| 2.3420| 70.529|
| Ce    | O     | O     | 2.3418| 2.3420| 70.529|
| Ce    | O     | O     | 2.3418| 2.3420| 70.529|
| Ce    | O     | O     | 2.3418| 2.3420| 70.529|
| Ce    | O     | O     | 2.3420| 2.3420| 109.471|
| Ce    | O     | O     | 2.3420| 2.3420| 109.471|
| Ce    | O     | O     | 2.3420| 2.3420| 109.471|
| Ce    | O     | O     | 2.3420| 2.3420| 109.471|
| Ce    | O     | O     | 2.3420| 2.3420| 109.471|
| O     | Ce    | Ce    | 2.3420| 2.3420| 109.471|
| O     | Ce    | Ce    | 2.3420| 2.3420| 109.471|
| O     | Ce    | Ce    | 2.3420| 2.3420| 109.471|
| O     | Ce    | Ce    | 2.3420| 2.3420| 109.471|
| O     | Ce    | Ce    | 2.3420| 2.7045| 54.736 |
| O     | Ce    | Ce    | 2.3420| 2.7045| 54.736 |
| O     | Ce    | Ce    | 2.3420| 2.7045| 54.736 |

4. CONCLUSION:

CeO₂/CoFe₂O₄ nanocomposites were synthesized through coprecipitation method. The structural characterization of composite had done using XRD and Rietveld Refinement. The crystal structure of CeO₂ has Fcc cubic geometry with space group Fm3m and the crystal structure of CoFe₂O₄ has cubic geometry with space group Fd3m. The(hkl) plane, 2 theta, d-spacing, FWHM, particle size, Lattice strain and dislocation density value of nano sized CeO₂/CoFe₂O₄ phase was estimated. The goodness factor parameters of our samples are found to be $\chi^2=0.242$, Rp= $69.7$, Rwp=$34.7$, Rexp=$70.51$ and
bragg R factor for CoFe$_2$O$_4$ is 27.44 and for CeO$_2$ is 48.41 and Rf factor for CoFe$_2$O$_4$ is 36.07 and for CeO$_2$ is 57.14. The agreement factors (R-factors) and $\chi^2$ using fullproof program shows good fitting. The structural refinement of CeO$_2$/CoFe$_2$O$_4$ samples is in good agreement with XRD results.

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