Investigation of annealing temperature on the synthesis of zincite doped cobalt ferrite using Rietveld refinement.

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Abstract. Co-precipitation technique is used for preparing the composites of CoFe₂O₄/ZnO. The effect on the variation on the size of the crystals of CoFe₂O₄ is studied by varying the annealing temperature over the range from 500°C to 900°C. The structure of composite powder obtained after annealing was studied by Rietveld refinement and XRD. The estimation of the crystalline phases of the sample is done by XRD though Rietveld refinement. The space group and structure of zinc oxide was observed as P63mc(186) and hexagonal while that for the cobalt ferrite was Fd3m(227) and cubic. The values of all R factors was calculated and the effect of annealing temperature on the size of the crystal was discussed.

1. Introduction
Ferrite forms an important class of magnetic materials; it is due to the fact that magnetic properties of these ferrites are highly dependent on the morphology and crystallite size of the nano-ferrites. The various properties of the ferrites can be controlled by different techniques of preparation as well as substitutions and doping [1]. Ferrites are of four types as Orthoferrites, Hexagonal ferrites, Garnets, and the spinel ferrites. In the recent past due to wide applications in industries like microwave, electrical and water treatment industries, the researcher have focused more on spinal ferrites [2]. The nanoparticles of metal ferrites is expressed as XFe₂O₄, where X represent divalent ion of a transition metal like cobalt, nickel, zinc, copper, iron etc. [3]. The properties like high electrical resistivity, modest saturation magnetisation, extremely high hardness, chemical stability and huge anisotropy will make cobalt ferrites a versatile ferrite. This ferrite is used in variety of applications ranging from ecological applications to the recording of high-density system [4].

D Deepali et al. prepared the nanoparticle of cobalt ferrites doped with zinc by co-precipitation method and found that when the nanoparticle sintered at 900°C then the magnetic properties like remanent magnetisation, saturation magnetisation etc. were decreased with increasing concentration of Zn²⁺[5].

Zaki H.K. et al. prepared the nano particle of Co₀.₅Cu₀.₅AlₓFe₂₋ₓO₄ by co-precipitation method and they observed that the saturation magnetisation and coercivity deceases with increasing concentration of aluminium [6].

Gangaswamy D.R.S. et al. studied that in the magnetic composite of Ni-Zn which is Ni₀.₅₇₋₀.₃₀Co₂Zn₀.₅Mg₀.₆₈Fe₂O₄ the magnetic permeability increases while the saturation magnetisation and Curie temperature decreases with increase in the concentration of cobalt [7].
Rohilla S. et al. prepared the ferrites of cobalt in the matrix of silica by co-precipitation method. They have observed that on annealing the sample the size of the nanocrystals will increase with increase in the temperature[8].

2. Experimental Details

2.1 Chemical Used
The chemical used in the preparation of the required composites uses the following compounds: Ferric chloride hexahydrate (FeCl3·6H2O; Aldrich 99.99%), Cobalt chloride hexahydrate (CoCl2·6H2O; Aldrich 99.99%), zinc chloride anhydrous (ZnCl2; Aldrich 99.99%), HCl (35%) and sodium hydroxide (NaOH; Aldrich 99.99%) and doubly distilled water.

2.2 Preparation of zincite doped Cobalt ferrite
The composite of the zincite doped with cobalt ferrite is done in three steps as discussed below:

Step 1: Suspension of CoFe2O4
The method of preparing suspension of CoFe2O4 is same as it was in our previous report [10]

Step 2: Suspension of ZnO
The suspension of ZnO was prepared in a similar way as it was in our previous report [9].

Step 3: The composite of CoFe2O4/ZnO
The mixing of the two solutions obtained in the above two steps is described [8]. As par the process the grade 5 Whatman paper was used to filter the white coloured resultant precipitate and is dried in vacuum oven for around five hours at a temperature of around 70°C once it was first washed many times using double distilled water. The precipitate of the resultant sample was crushed to microscopic form. It was finally heated to temperature range from 500°C to 900°C for a duration 2h in a preheated muffle.

3. Result and Discussion

3.1 XRD analysis of zincite doped cobalt ferrite
The investigation of the structure of the composite annealed between 500°C to 900°C were done by X-ray diffraction and the diffractogram so obtained is shown in figure 1. In the diffractogram, some of the peaks were obtained at 2θ(hkl) as 30.16(202), 35.51(311), 37.15(222), 43.13(400), 53.49(422), 57.02(511) and 62.66(404). This data reveals the structure of CoFe2O4 as cubic structure with phase space as Fd-3m and in accordance with JCPDS file number 021045.

The series of the peaks at 2θ(hkl) at 18.38(111), 35.51(311), 37.15(222), 43.13(400), 53.49(422), 57.02(511) and 62.66(404) confirms the production of the zinc oxide phase which is P63mc phase group and is matching with JCPDS card number-810792. The data mentioned in table 1 and table 2 shows the values of various required parameters and the average crystallite size of the prepared nanocomposite was obtained as 34.21 nm for CoFe2O4 and 64.33 nm for ZnO by using Scerener’s formula.

\[ D = 0.9 \times \frac{\lambda}{FWHM} \times \cos \theta \]  
\[ \delta = \frac{1}{(\text{particle size})^2} \]
Figure 1. The XRD diffractogram of the heat-treated CoFe$_2$O$_4$/ZnO from 500°C to 900°C

Table 1. Zinc Oxide Structural parameters

| S.no | 2θ   | d-spacing | Intensity | FWHM  | Crystallite Size(nm) | Dislocation Density | (hkl) |
|------|------|-----------|-----------|-------|----------------------|---------------------|-------|
| 1    | 18.38| 4.8231    | 111.0     | 0.4400| 31.90958652          | 9.82104377          | 111   |
| 2    | 31.54| 2.8345    | 300.55    | 0.2000| 72.01044228          | 1.928452931         | -100  |
| 3    | 34.25| 2.6163    | 170.44    | 0.2000| 72.51497881          | 1.901711143         | -002  |
| 4    | 36.03| 2.4904    | 621.82    | 0.2000| 72.87253345          | 1.883095144         | 101   |
| 5    | 47.36| 1.9181    | 85.26     | 0.2000| 75.67130903          | 1.746375003         | 012   |
| 6    | 56.38| 1.6306    | 146.97    | 0.2400| 65.52180953          | 2.329315058         | 511   |
| 7    | 68.87| 1.3622    | 79.97     | 0.2800| 60.01686105          | 2.776217227         | 201   |

Table 2. Cobalt ferrite structural parameters

| S.no | 2θ   | d-spacing | Intensity | FWHM  | Crystallite Size(nm) | Dislocation Density | (hkl) |
|------|------|-----------|-----------|-------|----------------------|---------------------|-------|
| 1    | 30.16| 2.9604    | 298.71    | 0.4400| 32.6234368           | 9.39594742          | 202   |
| 2    | 35.51| 2.5259    | 1000.0    | 0.4000| 36.3829493           | 7.554473426         | 311   |
| 3    | 37.15| 2.4185    | 72.30     | 0.3600| 40.6157777           | 6.061923518         | 222   |
| 4    | 43.13| 2.0955    | 191.09    | 0.4000| 37.258017            | 7.203781435         | 400   |
| 5    | 53.49| 1.7116    | 78.90     | 0.3600| 43.1122224           | 5.380209402         | 422   |
| 6    | 57.02| 1.6139    | 236.41    | 0.3200| 49.28967             | 4.11612143          | 511   |
3.2 Rietveld Refinement of the sample

The XRD data of the at 900°C is refined and the Full-proof software was used for the Rietveld refinement of the sample and shown in figure-2. It confirms the Wyckoff position of cobalt (Co) at 16c (1/8, 1/8, 1/8); iron (Fe) at 8b (½, ½, ½) and that for oxygen atom(O) at 32e (0.257, 0.257, 0.257). The refined curve is shown in figure 2. The Rietveld refinement is used for calculating the parameters of the cell structure and values calculated are: a = b = c = 0.83814nm, α = β = γ =90° and the cell volume was calculated as 0.58878nm³. The reciprocal cell parameters are a* = b* = c* = 0.119197, α* = β* = γ* =90° and the reciprocal cell volume is 0.00169356 nm³.

![Rietveld Refine diffractogram of CoFe₂O₄/ZnO heat treated at 900°C](image)

Figure 2- Rietveld Refine diffractogram of CoFe₂O₄/ZnO heat treated at 900°C

The table-3 presents the data obtained from the Rietveld refinement of the zincite doped cobalt ferrite for the atomic and isothermal parameter and table-4 reflects the profile R-factors of the refined profile of zincite doped cobalt ferrite.

| Phase     | Parameter | x  | y  | z  | Wycc |
|-----------|-----------|----|----|----|------|
| CoFe₂O₄   | Co        | 1/2| 1/2| 1/2| 8b   |
|           | Fe        | ½  | ½  | ½  | 8b   |
|           | O         | 0.257 | 0.257 | 0.257 | 32e |
|           | Fe        | 1/8 | 1/8 | 1/8 | 16c |
|           | Co        | 1/8 | 1/8 | 1/8 | 16c |
| ZnO       | Zn        | 1/3 | 2/3 | 0  | 2b   |
|           | O         | 1/3 | 2/3 | 0.345 | 2b |

Table 3. Isothermal and atomic parameters for sample CoFe₂O₄/ZnO

| Phase     | Goodness Factor (X²) | Profile Factor (R_p) | Weighted Factor (R_wp) | R Expected Value (R_E) | Bragg Factor (R_B) | R R_ Factor |
|-----------|----------------------|----------------------|------------------------|------------------------|-------------------|-------------|
| 1         | 0.142                | 0.890                | 1.86                   | 4.93                   | 3.13              | 2.56        |
| 2         | 0.142                | 0.890                | 1.86                   | 4.93                   | 10.4              | 8.24        |
4. Conclusion
The composite CoFe$_2$O$_4$/ZnO was prepared by the Co-precipitation method. The developed structure of cobalt ferrite is cubic while that of zinc oxide is hexagonal. The space group of cobalt ferrites was confirmed as Fd$ar{3}$m (227) while that of zinc oxide as P6$_3$mc (186). The values of R factors are small and are in sync with the data.

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