Synthesis of nanocomposite of franklinite (Fe$_2$O$_4$Zn) doped zincite(ZnO) using wet chemical coprecipitation method and rietveld refinement

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Abstract. The nanocomposites of Franklinite (Fe$_2$O$_4$Zn) doped Zincite (ZnO) were synthesized through wet chemical (co-precipitation) technique followed by heat treatment. Metal chlorides and metal oxides are used as precursors for the formation of composites. The asprepared sample composites were subjected to sintering for two hours at the temperature of 300 °C. The detail spectral study and the effect of concentration of precursor salt on the structural parameters were done by using XRD and Rietveld refinement method. The occurrence of two crystalline phases (Fe$_2$O$_4$Zn and ZnO) was estimated from XRD data through Rietveld refinement. It was observed that the Fe$_2$O$_4$Zn have a cubic structure with space group Fd-3m (227), whereas ZnO has hexagonal structure with space group P 63 mc (186). The Wyckoff positions and rietveld refinement parameters like goodness factor, Bragg R factor, $R_p$ value, $R_{exp}$ were calculated. Effect of varying concentration of precursor on development of complete ferrite phase of structure was discussed.

1. Introduction

Thenano scaled magnetic particles have unique properties and this has created much interest in science community because these nano size materials have high surface to volume ratio and make a linkamongst the atoms and bulk system. This shows how the properties of bulk change from the properties of atoms [1]. The physical properties and chemical properties of the surface atoms vary from the same chemically interior atoms. Hence, the various properties of the finite system are depending on surface to volume (S/V) ratio [2].

It is a fact that impact of finite size in bulk system and macroscopic system is negligible.In this range of size, the properties of the system can be described by useful characterization because of occurring one from extensive or intensive in the volume. Generally, the objects of micron size lies in this criteria. But, in case of materials in the range of nano, shows properties of extensive which are not in scale with volume and have intensive properties that depend on size.

Recently K. Ali et al. reported the production of CuFe$_2$O$_4$/ZnO nanocomposites and presented that reaction amongstZnO and CuFe$_2$O$_4$ provides the creation of a network of zinc oxide particles or grain boundaries as a matrix in which the nanoparticles of CuFe$_2$O$_4$ is embedded. They have shown...
that the presence of zinc oxide after a limit enhances the size of grain boundaries and it forms particle size of CuFe₂O₄Is large [3].

K. Ali et al. also reported the variation in value of lattice constant with alteration in the content of zinc oxide. Similarly Kaida, S. et al. reported the formation of ZnFe₂O₄ using powdered zinc oxide and powdered ferric oxide; and showed that change in ZnO content leads to change in lattice constant value [4]. N. M. Derazand others reported that formation of ZnFe₂O₄/ZnO and showed that saturation magnetization (Mₛ) and remnant magnetization (M_r) were depend on the size of constituents of the composite. [5].

From literature study it is also noted that spinel ferrites such as manganese ferrite, nickel ferrite, and zinc ferrite were mostly studied. This was because of having varieties in their structures like mixed spinel, inverse, and normal. They also show good chemical stability, hard in mechanical, less coercivity, best electromagnetic performance, and moderate saturation magnetization. All the said properties make them a best candidate for the soft magnet applications and also for the less/low loss materials at high frequencies [6-8].

In past, researchers shown that the technical properties of ferrites are reliant on the chemical configuration and the dependent nano structural features will be controlled by controlling synthesis process parameters like concentration of precursors, temperature, pressure, pH etc. [9].

In this paper detailed synthesis of nanocomposites of Fe₂O₃/Zn/ZnO through a wet chemical (coprecipitation) method and particle size analysis of the prepared sample through X-Ray Diffraction is discussed. The obtained XRD was then refined using by Full-Prof Software and the Rietveld refinement parameters is reported.

2. Experimental Details

2.1 chemical used
Zinc chloride hexahydrate (ZnCl₂.6H₂O, Sigma-Aldrich), FeCl₃.6H₂O (Sigma-Aldrich), Sodium hydroxide (NaOH, Sigma-Aldrich), Hydrochloric acid (HCl) and ZnO(Sigma-Aldrich). The DI water was used in making all the solutions.

2.2 Methods of preparation
The ZnFe₂O₄/ZnO nanocomposites were synthesized by using Coprecipitation method as described below[10]. The solution of ZnCl₂.6H₂O (0.4M concentration) in 40 ml of HCl (0.4M conc.) and FeCl₃.6H₂O (0.8M conc.) in HCl (40 ml, conc. 0.4M) was added by piezoelectric nozzle (nozzle size: 50 mm, drop rate: 0.01 ml/s) into the NaOH aqueous solution (200 ml, conc. 1.5M) with the help of magnetic stirrer at constant 5000 rpm speed. The temperature during the whole process was at 50°C. The range of pH was controlled on 11 to 12 value only. This was because the sample produced at pH value which was less than 6, not showing the production of phase of spinel ferrites. And the value of pH above the 12 represents the occurrence of mixed phase. In last, the above prepared solution was kept at room temperature. After cooling, the samples were washed several times by using DI water and ethanol in order to eliminate the undesirable impurities. This produces a dark brown homogeneous solution (say-I).

Solution-II was ready by mixing the aqueous solution of Zinc Oxide (50ml, 0.3M) in the solution of NaOH (50ml 0.6M) by using piezoelectric nozzle having drop rate ml/s. This offered Na₂ZnO₃. The above said solution was then mixed in solution of HCl (50ml 0.6M). The final solution comes out in white coloured with ZnO. The obtained solution was stirred on magnetic stirrer for three hour with 5000 rpm speed at temperature 50°C. In last, the final obtained product was washed with DI water for eradicating NaCl completely from the solution number II.

The solution-I and II were mixed smoothly with constant stirring at speed 5000 to 8000 rpm for 6hour. The temperature was maintained at 60°C throughout the system in water jacket reaction vessel by using circulating thermostatic bath. The sample was firstly filtered and then washed. In last, it was dried at temperature 80°C before placing it in vacuum oven at 100 mm pressure of mercury for six hour. The obtained dry powder from oven was then grinded in order to achieved very fine powder.
The programmable furnace was used to heat the sample at 300 °C up to two hour. This way, we obtained Fe$_2$O$_4$Zn in ZnO.

To observe the effect of changing content of ZnO on structural property of resultant composite, the solution–II was prepared with double, triple and four time of its initial concentration and added to solution –I as described above.

3. Result and Discussion

3.1 Analysis of sample by X-Ray Diffraction

X-Ray Diffraction is implemented in order to find the occurrence of crystalline phases of the prepared sample. The XRD pattern of sample from 20 degree to 80 degree was shown in Figure 1. Rietveld refinement was performed on XRD data obtained of heat treated sample as shown in Figure 2.

![XRD diffractogram of heat-treated Fe$_2$O$_4$Zn / ZnO nanocomposites at 300°C (with 1:0.1, 1:0.25, 1:0.5 and 1:1 ratio of Fe$_2$O$_4$Zn:ZnO)](image)

Figure 1. XRD diffractogram of heat-treated Fe$_2$O$_4$Zn / ZnO nanocomposites at 300°C (with 1:0.1, 1:0.25, 1:0.5 and 1:1 ratio of Fe$_2$O$_4$Zn:ZnO)

The XRD data contains peaks amongst 15° and 80°, the peak centred at 2theta-30.14°(220), 35.475°(311), 43.124°(400), 47.48°(331), 57.01°(511) and 62.61°(440). The above data was of zinc ferrite and fully matched with 221086 JCPDS file. The peaks of XRD pattern shows the prepared sample was of FCC crystal structure and having Fd3m space group.

Furthermore, the peaks found at 28.531°, 33.14°, 47.53°, 56.33°, 59.06°, 76.69°, and 79.07° value of 2 theta have planes (111), (200), (220), (311), (222), (331), (420) respectively. These peaks confirm the production of phase of Zinc Oxide and have P63mc space group. This was fully matched with JCPDS card number- 810792. Table 1 and table 2 show the value of plane, FWHM, size of particle, and dislocation density of the nanocomposite Fe$_2$O$_4$Zn/ZnO. Size of nanoparticles (D) was
calculated by equation 1 and the dislocation density (δ) was calculated by the formula (2) as mentioned below:

\[ D = \frac{0.9 \times \lambda}{\text{FWHM} \times \cos \theta} \]  
\[ \delta = \frac{1}{(\text{particle size})^2} \]  

The structural parameters of the ZnO phase and Fe₂O₄Zn phase are shown in table1 and 2 respectively. The average value of particle size was found to be 26.63 nm for ZnO phase and 18.06 nm for phase Fe₂O₄Zn.

| S.no | 2 θ   | d-spacing | Intensity | FWHM | Crystallite Size(nm) | Dislocation Density | (hkl) |
|------|-------|-----------|-----------|------|----------------------|---------------------|-------|
| 1    | 18.205| 4.8691    | 1943.8    | .251 | 33.5                 | 4                   | (111) |
| 2    | 29.944| 2.9817    | 2149.6    | .363 | 23.7                 | 6.57462(022)        |
| 3    | 35.268| 2.5428    | 773.3     | .183 | 47.6                 | 1.602307(113)       |
| 4    | 36.891| 2.4345    | 1022.3    | .384 | 22.7                 | 6.925208(222)       |
| 5    | 46.923| 1.9348    | 374.9     | .176 | 51.4                 | 1.384083(133)       |
| 6    | 53.162| 1.7215    | 633.9     | .263 | 35.3                 | 2.972652(224)       |
| 7    | 56.667| 1.623     | 234.9     | .172 | 54.8                 | 1.207584(115)       |
| 8    | 62.22 | 1.4908    | 951.9     | .545 | 17.8                 | 11.89061(444)       |

Table 1. Structural parameters of ZnO

| S.no | 2 Theta | d-spacing | Intensity | FWHM | Crystallite Size(nm) | Dislocation Density | (hkl) |
|------|---------|-----------|-----------|------|----------------------|---------------------|-------|
| 1    | 31.801  | 2.8116    | 62.2      | 0.93 | 9.28                 | 0.42                | (010) |
| 2    | 34.471  | 2.5997    | 46.6      | .52  | 16.71                | 1.11                | (002) |
| 3    | 36.295  | 2.4732    | 122.2     | .310 | 28.18                | 0.53                | (011) |
| 4    | 47.601  | 1.9088    | 27.2      | 0.68 | 13.34                | 0.20                | (012) |
| 5    | 56.657  | 1.6233    | 42.4      | 1.46 | 6.46                 | 0.87                | (-120)|
| 6    | 62.948  | 1.4754    | 40.6      | 1.14 | 8.54                 | 0.49                | (013) |
| 7    | 68.034  | 1.3769    | 34.3      | 1.14 | 8.79                 | 1                   | (-122)|

Table 2. Structural parameters of Fe₂O₄Zn

The Rietveld refinement for the sample ZnO/ Fe₂O₄Zn 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](image-url)
The isothermal and atomic parameters were shown in table 3 for the prepared sample from the rietveld refinement. The refined profile R-factors of ZnO/ Fe$_2$O$_4$Zn was shown in table no. 4.

### Table 3. Isothermal and atomic parameters for sample ZnO/ Fe$_2$O$_4$Zn

| Phase       | Parameter | $\frac{x}{a}$ | $\frac{y}{b}$ | $\frac{z}{c}$ | Wyne |
|-------------|-----------|----------------|----------------|---------------|------|
| Franklinite | Zn        | 1/8            | 1/8            | 1/8           | 8a   |
|             | Fe        | $\frac{1}{2}$  | $\frac{1}{2}$  | $\frac{1}{2}$ | 16d  |
|             | O         | 0.261          | 0.261          | 0.261         | 32e  |
| Zincite     | Zn        | 1/3            | 2/3            | 0             | 2b   |
|             | O         | 1/3            | 2/3            | 0.378         | 2b   |

### Table 4. Results of the Rietveld refinement for ZnO/ Fe$_2$O$_4$Zn structure

| Phase | Goodness Factor ($X^2$) | Profile R Factor ($R_p$) | Weighted R Factor ($R_{wp}$) | Expected Value ($R_E$) | Bragg R Factor ($R_B$) | $R_F$ Factor |
|-------|-------------------------|--------------------------|------------------------------|-------------------------|-------------------------|---------------|
| 1     | 0.786                   | 51.2                      | 22.0                         | 24.80                   | 23.21                   | 28.64         |
| 2     | 0.786                   | 51.2                      | 22.0                         | 24.80                   | 43.79                   | 45.37         |

4. Conclusion

Wet chemical approach of Coprecipitation was used to fabricate the nanocomposite of ZnO/ Fe$_2$O$_4$Zn. The Fe$_2$O$_4$Zn was found to have a cubic structure. The space group of Fe$_2$O$_4$Zn was obtained as Fd-3m (227) and ZnO has hexagonal structure with space group P6$_3$mc(186). Rietveld refinement of the prepared sample was done fruitfully and obtained R-factors were of small values which conclude that there occurs best agreement amongst the data.

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