SYNTHESIS OF COBALT FERRITE NANOPARTICLES USING MICROEMULSION METHOD: STRUCTURE, MORPHOLOGY, AND MAGNETIC PROPERTIES

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ABSTRACT

Cobalt ferrite nanoparticles were prepared by the microemulsion method. Different values of pH of the microemulsion were maintained to find out the optimum pH to prepare cobalt ferrite nanoparticles. Prepared nanoparticles were characterized using X-ray Powder Diffraction (XRD), Vibrating Sample Magnetometer (VSM), and Scanning Electron Microscope (SEM). Rietveld refinement was used to analyze the crystal structure of the prepared cobalt ferrite nanoparticles. The crystallite size of prepared nanoparticles has been found from XRD in the range of 13.79 nm to 30.40 nm. The saturation magnetization, remanent magnetization, and coercivity have been found to be 12.05 emu/g, 0.77 emu/g, and 118.912 Oe respectively from VSM measurements.

Keywords: Cobalt ferrite nanoparticles, Rietveld refinement, Scanning Electron Microscope (SEM), Vibrating Sample Magnetometer (VSM), and X-ray Powder Diffraction (XRD).

1. INTRODUCTION

Nanotechnology deals with the fabrication, study, and applications of materials with at least one dimension of 1 to 100 nm. The unique physical and chemical properties of nanomaterials are strongly related to their size and exhibit novel properties compared with their bulk counterparts having similar chemical composition. The ratio of the number of surface atoms to bulk atoms increases with decreasing the size of nanomaterials and introduces significant changes in properties (Mathew & Juang, 2007; Méndez-Vilas, 2013). Magnetic nanoparticles are being extensively studied due to their strong sensitivity to the applied magnetic field and the capability to get functionalized and/or encapsulated with drug molecules (Agnieszka Z. Wilczewska, Katarzyna Niemirowicz, Karolina H. Markiewicz, 2012; Bamrungsap et al., 2012; H. Maeda, J. Wu, T. Sawa, Y. Matsumura, 2000; Patra et al., 2018; Yu et al., 2015). Applications of Magnetic nanoparticles include but are not limited to the data storage systems, magnetic fluids, catalysis, and bioapplications like detection of biological entities, magnetic bioseparation, clinic diagnosis and therapy (such as magnetic resonance imaging (MRI) and hyperthermia), targeted and controlled drug delivery, and biological labels (Foroughi et al., 2015; Mathew & Juang, 2007; Wu et al., 2008). Among different types of magnetic nanoparticles, biocompatible iron oxide nanoparticles have received considerable attention for their potential applications as an enhancing agent in MRI, active agent in drug delivery, tissue repair, cell separation, etc. (Angelique Y. Louie, Martina M. Hüber, Eric T. Ahrens, Ute Rothbächer, Rex Moats, Russell E. Jacobs, Scott E. Fraser, 2000; Gupta & Gupta, 2005; Jun et al., 2005; Mohapatra et al., 2011; Perez et al., 2004; Wu et al., 2008). However, due to their high chemical activity, the bare iron oxide nanoparticles are easily oxidized in air, resulting in loss of magnetism and dispersibility (Wu et al., 2008). Furthermore, the low coercivities of pure iron oxides restrict their applications in the high-density recording. Modification with cobalt enhances the coercivities of iron oxides (Sharrock, 1989; V. Pillai, 1996). Spinel cobalt ferrite (CoFe2O4) has high coercivity (Hc) and moderate magnetization (Ms) with immense physical and chemical stability, which make CoFe2O4 nanoparticles suitable for high-density digital recording (Chinnasamy et al., 2003; Houshiar et al., 2014; Mohapatra et al., 2011; Shafi et al., 1998). Moreover, applications of cobalt ferrite nanoparticles in therapeutic applications add several benefits due to their large magnetic anisotropy (Cannas et al., 2006; Fortin et al., 2007; Mohapatra et al., 2011). In the lattice structure of cobalt ferrite, the octahedral sites are occupied by the Co2+ ions and half of the Fe3+ ions, while tetrahedral sites are occupied by the other half of the Fe3+ ions, which is a complete inverse spinel structure (Goldman, 2006; Verwey & Heilmann, 1947; Zeng et al., 2017).

The method of formation of cobalt ferrite nanoparticles has an effect on the size, size distribution, shape, and consequently on the final properties of the fabricated nanoparticles. Moreover, the change of properties is not regular. While the ferromagnetic CoFe2O4 nanoparticles have prospect in permanent magnetic applications, the
superparamagnetic \( \text{CoFe}_2\text{O}_4 \) nanoparticles have prospect in biomedical applications (Duong et al., 2021). So, further research work on the fabrication method of cobalt ferrite nanoparticles is required. The available methods of fabricating cobalt ferrite nanoparticles are solid-state reaction (Khedr et al., 2006), reverse micelles (Calero-DdeLC & Rinaldi, 2007), chemical co-precipitation (Zi et al., 2009), hydrothermal method (Chen et al., 2009), sol-gel (Gul & Maqsood, 2008), combustion (Franco et al., 2011), and microemulsion (A. Bee, R. Massart, 1995; Sinkó et al., 2012), etc. Every method has its pros and cons. For example, the thermal decomposition method generates highly monodispersed particles with a narrow size distribution, but the fabricated nanoparticles are usually capable of dissolving only in nonpolar solvents. Co-precipitation method produces nanoparticles with a wide size distribution, consequently it needs particles separation process after fabrication (Wu et al., 2008). Among the formation methods of cobalt ferrite nanoparticles, the microemulsion is a promising method due to the better control of shape and size of the nanoparticles, but, careful investigation is needed to find the effect of process parameters on the properties of nanoparticles. In this research report, the synthesis of the nanoparticles was done by the microemulsion method and the characterization of the nanoparticles was performed by XRD, SEM, and VSM. The Rietveld analysis was used to analyze the structure of the fabricated nanoparticles.

2. METHODOLOGY

Beakers, measuring cylinder, glass rod, mortar pestle were washed and cleaned in an ultrasonic cleaner. After cleaning, the instruments were dried at 90 °C for several minutes in a dryer. Ferric chloride hexahydrate \( (\text{FeCl}_3 \cdot 6\text{H}_2\text{O}) \), cobalt chloride hexahydrate \( (\text{CoCl}_2 \cdot 6\text{H}_2\text{O}) \), and sodium hydroxide \( (\text{NaOH}) \) were weighed using electric balance up to two decimal numbers. Distilled water and oleic acid were measured using a measuring cylinder. 3.25 ml of 0.4 M iron chloride \( (\text{FeCl}_3 \cdot 6\text{H}_2\text{O}) \) solution and 25 ml of 0.2 M cobalt chloride \( (\text{CoCl}_2 \cdot 6\text{H}_2\text{O}) \) solution were taken in a beaker; distilled water was added to make the solution 100 ml followed by mixing thoroughly. Pellets of sodium hydroxide were crushed to smaller particles using a mortar pestle for quick dissolution. 2.3 M sodium hydroxide solution was made by mixing 9.6 gm of crushed sodium hydroxide pellets in 100 ml distilled water. Sodium hydroxide was added drop by drop to the solution maintaining continuous stirring to increase the pH and different pH level (12, 12.5, and 13) was tried to find out the optimum level of pH to prepare the nanoparticles (Figure 1). It is noteworthy that the nanoparticles were obtained at pH level 13.

![Figure 1: Adjusting pH and the solution after adjusting pH.](image)

Oleic acid (40 ml) was added as a surfactant and after that precipitation was found. The precipitated liquid was stirred continuously for 2 hrs at 85 °C and then the liquid was cooled slowly to room temperature. The solid precipitate was separated by filtration and the precipitate was washed with 1:1 ethanol and distilled water to remove impurities. Supernate was poured out and subsequently centrifuge operation for 20 min at 4500 rpm was applied to remove the remaining liquid with the particles.

Prepared black particles were dried in an oven at 120 °C for 24 hrs. After grounding into fine powders, the particles were annealed at 900 °C for 11 hrs maintaining a firing schedule (Figure 2). The temperature was increased from room temperature to 900 °C within 5 hrs. This temperature was held for 1 hr. Then the sample was cooled back to room temperature (25 °C) within 5 hrs.
3. RESULTS AND DISCUSSION

3.1 Structural Properties Analysis

The crystallographic structure of the powder was characterized by x-ray diffraction (XRD) and the XRD pattern shows that both the peaks of cobalt ferrite and cobalt chloride are present (Figure 3). The reasons for cobalt chloride inclusion may be the raw materials that didn’t take part in the reaction. Improper nucleation may be the reason behind this phenomenon too. The diffraction peaks of (1 1 1), (2 2 0), (2 2 2), (3 1 1), (4 0 0), (4 1 1), (4 4 0) and (5 3 1) planes are corresponding to spinel cobalt ferrite. The average crystallite size was calculated from the XRD data using Scherer equation (Cullity, 1978). The crystallite size of prepared cobalt ferrite ranged from 13.79 nm to 30.40 nm and the second phase of cobalt chloride was from 13.44 nm to 42.72 nm.

Rietveld Refinement

Rietveld refinement is a technique described by Hugo Rietveld to characterize the crystal structure of materials. Using a least-squares approach, this method processes a theoretical line to match the measured profile (M. R.
Gauna, M. S., Conconi, S. Gomez, G. Suarez, E. F. Aglietti, 2015; Rietveld, 1969). The following graph of intensity vs. 2θ shows the Rietveld refinement of the prepared cobalt ferrite nanoparticles (Figure 4).

![Figure 4: Rietveld Refinement of the XRD pattern for (a) cobalt ferrite and (b) cobalt chloride phases (Inset shows the crystal structure of the corresponding phases).](image)

The black part of the curve indicates the prepared cobalt ferrite nanoparticles and the green part shows the standard Bragg position of corresponding phase (Figure 4 (a). The red line expresses the mismatch between the prepared sample and the standard one. The reason behind this mismatch between the curves is the presence of unwanted phases like cobalt chloride which is shown in Figure 3. However, the Rietveld refined parameters of the XRD patterns are included in Table 1.

The bond length between necessary atoms was also measured in the Rietveld refinement process. The bond lengths measured here are, Fe-O = 2.45 Å, Co-O = 2.45 Å, O-O = 2.45 Å. The density of the prepared sample was 5.04 gm/cm³.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Space group</th>
<th>Lattice constants (Å)</th>
<th>Unit cell volume (Å³)</th>
<th>Reliability factors (%)</th>
<th>GoF</th>
<th>Bragg R Factor</th>
<th>RF Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt ferrite</td>
<td>Fd-3m</td>
<td>a = 2.80636</td>
<td>22.102</td>
<td>Rp = 37.2</td>
<td>2.2</td>
<td>92.2</td>
<td>72.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 2.80636</td>
<td></td>
<td>Rwp = 43.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 2.80636</td>
<td></td>
<td>Rexp = 21.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cobalt chloride</td>
<td>R-3m</td>
<td>a = 3.24408</td>
<td>158.021</td>
<td>Rp = 34.6</td>
<td>2.0</td>
<td>99.4</td>
<td>93.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b = 3.24408</td>
<td></td>
<td>Rwp = 21.4</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c = 17.33810</td>
<td></td>
<td>Rexp = 20.5</td>
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</tr>
</tbody>
</table>

3.2 Magnetic Property Analysis

Room temperature magnetic properties of the cobalt ferrite were measured using a vibrating sample magnetometer (VSM). The saturation magnetization (Mₛ), remnant magnetization (Mᵣ), and coercivity (H_c) were determined from obtained hysteresis loops. Magnetization vs magnetic field (M-H) curve up to 10,000 Oe at room temperature shows the hysteresis loop and the loop forms S-shaped (Figure 5). The obtained S-shaped hysteresis loop is thinner compared to other works in literature in which cobalt ferrite nanoparticles were prepared in solid state and Solvothermal Processes (Duong et al., 2021; Khedr et al., 2006). This may happen due to the presence of cobalt chloride phase. Saturation magnetization is the maximum magnetization, after reaching it, magnetization does not increase with increasing magnetic field. The saturation magnetization (Ms) of the sample is 12.05 emu/g. The upward part of the sample is 12.05 emu/g and the downward part is -12.05 emu/g. The value of Ms is smaller in nano-sized materials than the bulk material (Gu et al., 2008). The required field to demagnetize the sample is known as the coercive field. From the hysteresis loop, we can see the coercive fields of the prepared sample are 136.09 Oe and -101.74 Oe. The average coercive field of the prepared cobalt ferrite nanoparticles sample is 118.92 Oe. The value of magnetization after removing the magnetic field is known as remanent. The downward part remanence of the sample is -0.91 emu/g and the upward part remanent of the sample is 0.63 emu/g. The average remanence magnetization of cobalt ferrite nanoparticles sample is 0.77 emu/g. It is clearly visible that the remanent of the prepared sample is very low.
means that it is easy to magnetize and demagnetize the sample by applying an external field. These are the properties of soft ferrimagnetic materials.

3.3 Morphological Analysis

To reveal the morphology of the fabricated cobalt ferrite nanoparticles, scanning electron microscope images were taken. The images of Figure 6 show particles with some agglomerations. The reason for agglomerations might be unwanted phases like cobalt chloride. This unwanted phase might be generated due to the unreacted raw materials.

4. CONCLUSIONS

The synthesis of the cobalt ferrite nanoparticles was done by the microemulsion method. Different pH (12, 12.5, and 13) was maintained to prepare cobalt ferrite nanoparticles and the nanoparticles were prepared only at pH 13. The drying temperature was 120°C and the firing temperature was 900°C. The prepared cobalt ferrite nanoparticles were blackish in color and the crystal structure was inverse spinel. The crystallite size was between 13.79 nm and 30.40 nm. The hysteresis loop was S-shaped. The VSM result showed that average coercivity was 118.92 Oe, average remanent magnetization was 0.77 emu/g and average saturation magnetization was 12.05 emu/g. The remanent of the prepared particles was very low which indicates the property of ferrimagnetic material.

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REFERENCES
