Synthesis, Characterization, and Magnetic Behavior of Cobalt-Ferrite Nanoparticles under Variant Temperature Conditions

M. A. Alotaibi\textsuperscript{a}, I. Ud Din\textsuperscript{a,*}, A. I. Alharthi\textsuperscript{a}, P. Ahmad\textsuperscript{b}, A. Naeem\textsuperscript{c}, I. A. ElSayed\textsuperscript{a}, and G. Centi\textsuperscript{d}

\textsuperscript{a} Department of Chemistry, College of Science and Humanities, Prince Sattam Bin Abdulaziz University, P.O. Box 173, Al-Kharj, 11942 Saudi Arabia
\textsuperscript{b} Department of Physics, University of Azad Jammu and Kashmir, Muzaffarabad, 13100 Pakistan
\textsuperscript{c} National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar, Pakistan
\textsuperscript{d} University of Messina, ERIC aisbl and CASPE/INSTM, Departments ChiBioFarAm and MIFT, Messina, 98166 Italy

* e-mail: drisraf@yahoo.com

Received November 11, 2020; revised November 11, 2020; accepted November 20, 2020

Abstract—Wet chemical method was applied for the synthesis of cobalt-ferrite nanoparticles. The physico-chemical properties were investigated by number of analytical techniques. TGA revealed the thermal stability of synthesized cobalt-ferrite nanoparticles. X-ray diffraction studies displayed the nanoparticles crystalline nature. Structure of cobalt-ferrite nanoparticles was confirmed via infrared spectroscopy by manifesting Co and Fe ions absorption peaks. Morphological studies showed synthesis of nanoparticles of cobalt-ferrite by employing field emissions scanning electron microscopy. The magnetic properties of cobalt-ferrite nanoparticles were investigated by vibrating sample magnetometer (VSM). The X-ray photoelectron spectroscopy studies confirmed the synthesis of cobalt-ferrite by displaying the oxidation of Co as Co\textsuperscript{2+} and Fe as Fe\textsuperscript{3+}, respectively. The VSM results revealed that the magnetic characteristics of cobalt-ferrite nanoparticles were completely changed by the variation of temperature.

Keywords: ferrite nanoparticles, VSM, temperature effect, magneton number, anisotropy constant

DOI: 10.1134/S106378342104003X

1. INTRODUCTION

Spinel-type cobalt-ferrite (CoFe\textsubscript{2}O\textsubscript{4}) nanoparticles have gained a great research interest for the last two decades [1, 2]. Cobalt-ferrite nanoparticles have been recorded as having good electromagnetic properties, high coercive force, and moderate saturation magnetization [3, 4]. Similarly, profile of cobalt-ferrite nanoparticles has reported excellent chemical stability, high resistance to corrosion, and good mechanical stability [5]. Due to all these features, cobalt-ferrite nanoparticles have a versatile potential for applications in a variety of technological equipments.

Cobalt-ferrite nanoparticles are equipped with potential application in many areas like drug delivery, storage devices, medical appliances, and magnetic resonance imaging [6–10]. Nevertheless, their application as magnetic materials have been investigated very extensively. The magnetic properties of cobalt-ferrite nanoparticles vary with a number of parameters like particle size, annealing temperature, and synthesis method. Many methods have been reported for the synthesis of cobalt-ferrite nanoparticles [8, 11]. However, wet chemical route, because of its simplicity and low cost, provides an easy option to synthesize cobalt-ferrite nanoparticles. Amongst all other factors, magnetic properties of cobalt ferrite are also dependant on the temperature. This is because of the fact that temperature tend to modify the Co and Fe ionic distribution in cobalt ferrite. Due to the different distribution of ions in a crystal structure, the magnetic profile of cobalt ferrite varies with the temperature.

Magnetic profile of cobalt ferrite has been extensively investigated. However, literature regarding the magnetic profile of cobalt ferrite is more concentrated in the temperature range below the room temperature. The literature regarding the magnetic studies of cobalt ferrite in the temperature range above the room temperature is very limited. The significance of the current work is the investigations of magnetic behavior of cobalt-ferrite nanoparticle in the temperature range of 50 to 300\textdegree C.

This work reports synthesis of cobalt-ferrite nanoparticles by wet chemical method. The formation of cobalt-ferrite nanoparticles was confirmed by vari-
ety of analytical techniques. The temperature-dep- 
edant magnetic properties in temperature zones of 
room temperature up to 300°C were studied by vibrat-
ing sample magnetometer (VSM).

2. EXPERIMENTAL
2.1. Materials
Both nitrate salts of cobalt hexahydrate 97% extra 
pure and ferric nonahydrate 98% pure purchased from 
Loba Chemie Pvt. Ltd were utilized as precursor 
materials for the synthesis of cobalt-ferrite nanoparti-
cles. Ammonium hydroxide was used to adjust the 
basic reaction medium during the synthesis of cobalt-
ferrite nanoparticles. Oleic acid purchased from 
Albright and Wilson Asia Pvt. Ltd., Singapore was 
added to the reaction as a surfactant in the current 
work.

2.2. Synthesis of Cobalt–Ferrite Nanoparticles
In this work, wet chemical route was employed for 
the syntheses of cobalt–ferrite nanoparticles [12, 13]. 
0.04 mol of cobalt nitrate hexahydrate was dissolved in 
100 mL of distilled water. Upon dissolution of cobalt 
salt, 0.08 mol of ferric nitrate nonahydrate was added 
to the solution. Solution temperature was raised and 
small quality of surfactant was added. Solution pH was 
adjusted to 12 by drop-wise adding ammonium 
hydroxide to the stirring solution. The slurry was 
stirred for one hour at 85 to 90°C for 1 h. Centrifuga-
tion of the precipitates at 2000 rpm for 30 min. isolated 
the cobalt-ferrite nanoparticles. Thus obtained 
cobalt-ferrite nanoparticles were oven-fried overnight 
and calcined at 450°C for 4 h. The calcined cobalt fer-
rite was designated as CoFe450.

2.3. Characterization of Cobalt–Ferrite Nanoparticles
Libra TG 209 F1 analyzer was employed to assess 
the thermo-gravimetric analysis (TGA) of cobalt–fer-
rite nanoparticles. The X-rays diffraction technique 
was used to study the crystallographic properties of 
cobalt–ferrite nanoparticles. This was carried out by 
Rigaku Japan model Ultima IV. Room-temperature 
XRD profile was measured from 10° to 80° with 2θ 
Bragg angle.

Crystallite size of cobalt–ferrite nanoparticles was 
calculated by Debye–Scherrer formula, given as below 
[9, 10]:

\[
d = \frac{0.9\lambda}{\beta \cos \theta},
\]

where \( \lambda \) is X-ray wavelength (CuK\( \alpha \) = 0.154 nm), \( d \) is 
crystallite size in nanometers, \( \beta \) is full width at half 
maximum (FWHM) of chosen peak (311) in radians, 
and \( \theta \) represents peak angle.

Synthesis of cobalt–ferrite nanoparticles was 
affirmed by infrared spectroscopy. Thermo Scientific 
iD5 ATR spectrometer was employed for this study.

Field emissions scanning electron microscopy 
(FESEM) was used to investigate morphology and 
particle size of cobalt–ferrite nanoparticles. FEI 
Quanta FEG 250 model was used in the current work.

The X-ray photoelectron spectroscopy (XPS) was 
utilized to measure the surface chemistry of cobalt–ferrite 
nanoparticles. Thermo Scientific model 
K-ALPHA Surface Analysis was used in the current 
study.

Electromagnetic properties of cobalt–ferrite 
nanoparticles were investigated by VSM. MicroSense 
model FCM-10 Magnetic field control module was 
employed in the current study.

Magneton number \( n_B \) was calculated as [14]

\[
n_B = \frac{MW \times M_s}{5585},
\]

where \( MW \) is molecular weight of cobalt ferrite, \( M_s \) is 
magnetization saturation in emu/g.

Anisotropy constant \( K \) was calculated as [15]

\[
K = \frac{H_C M_s}{0.96},
\]

where \( H_C \) represents coercivity.

3. RESULTS AND DISCUSSION
3.1. Thermo-Gravimetric Analysis
To assess the thermal stability of synthesized 
cobalt–ferrite nanoparticles, TGA was performed in 
the temperature range of 25 to 1000°C. The TGA 
curve of synthesized cobalt–ferrite nanoparticles is 
presented in Fig. 1.

The TGA curve of cobalt–ferrite nanoparticles 
showed weight loss in three different temperature 
regions. First weight loss was observed up to 150°C. 
This weight loss indicated the loss of water molecules 
from the cobalt–ferrite nanoparticles. A second steep 
weight loss was recorded between 150 and 350°C. This 
weight loss indicated the loss of water molecules 
from the cobalt–ferrite nanoparticles. A second steep 
weight loss was observed between 150 and 350°C. This 
weight loss was assigned to the decomposition of

![Fig. 1. TGA curve of cobalt–ferrite nanoparticles.](image-url)
nitrates used as Co and Fe precursor materials during the synthesis of cobalt-ferrite nanoparticles. A third weight loss was documented beyond 360°C with a tail at about 870°C. This high-temperature weight loss could be due to the phase and magnetic transitions, as reported in the literature [16].

In summarizing the TGA results, the study concluded synthesis of highly thermally stable cobalt-ferrite nanoparticles.

3.2. XRD Study

The XRD pattern of calcined cobalt-ferrite nanoparticles is shown by Fig. 2.

The XRD pattern displayed lines at 2θ = 18°, 30°, 35°, 37°, 43°, 54°, 57°, 63°, and 74°. These diffraction lines corresponded to (111), (220), (311), (222), (400), (422), (511), (440), and (533) Bragg’s reflections, respectively. This diffraction pattern indicated the cubic spinel structure of synthesized cobalt-ferrite nanoparticles with JCPDS card no. 89-1009 [17]. The Debye–Scherrer size calculation revealed 36-nm crystallite size of the annealed cobalt-ferrite nanoparticles.

3.3. Structure Analysis

Synthesis of cobalt-ferrite nanoparticles was further confirmed by infrared analysis. Infrared spectrum of synthesized cobalt-ferrite nanoparticles is displayed in Fig. 3.

The FTIR spectrum exhibited absorption bands at two regions. The FTIR absorption bands were observed between 400 and 500 cm⁻¹ for cobalt-ferrite nanoparticles. These absorption bands represent the octahedral metal stretching vibrations of cobalt-ferrite nanoparticles. Likewise, another FTIR absorption bands recorded around 592 cm⁻¹ in the current study for cobalt-ferrite nanoparticles. Such FTIR absorption bands have been reported for the intrinsic metal stretching vibrations at the tetrahedral site [18–20]. Thus FTIR absorption bands observed in lower wave-length region indicates the presence of cobalt ions, as they generally occupy the octahedral site. Similarly, the FTIR absorption bands at higher wavelength region correspond to the presence of Fe ions, as they tend to occupy both octahedral and tetrahedral sites.

In conclusion, FTIR analysis confirmed the synthesis of cobalt-ferrite nanoparticles by displaying the respective metal ions absorption bands, as reported in the literature. Thus, FTIR findings supported the XRD studies for the formation of cobalt-ferrite nanoparticles.

3.4. Morphological Studies of Cobalt-Ferrite Nanoparticles

FESEM studies revealed the morphology and average particle size of cobalt-ferrite nanoparticles. As depicted in Fig. 4, well dispersed cobalt-ferrite nanoparticles were observed in the FESEM image.

The FESEM image confirmed synthesis of homogenous, size-controlled cobalt-ferrite nanoparticles. The average size of cobalt-ferrite nanoparticles was observed to be 40 nm (Fig. 5).
The slight discrepancy in the size of cobalt-ferrite nanoparticles measured by FESEM and XRD methods can be well apprehended by the fact that FESEM measures particle size, whereas XRD gives crystallite size. In brief, FESEM investigations supported the findings of XRD regarding synthesis of cobalt-ferrite nanoparticles.

3.5. XPS Investigations

XPS measurements were carried out to investigate the electronic state of cobalt and iron metals in cobalt-ferrite nanoparticles. The XPS spectra are displayed in Fig. 6.

It is clear from the spectrum in Fig. 5a that Co 2p showed two spin-orbit doublets peaks situated at ~780 and ~795 eV representing Co 2p3/2 and Co 2p1/2 [21, 22]. These two doublets are associated with shakeup satellites peaks. The presence of shakeup peaks indicates the oxidation state of Co as Co2+ state, which confirms the valence state of cobalt in cobalt-ferrite nanoparticles.

Similarly, Fig. 5b shows the XPS spectrum of iron in the cobalt-ferrite nanoparticles. By closer look at Fe 2p spectrum, it is demonstrated with two XPS peaks originating at ~711 and ~725 eV indicating the occurrence of Fe 2p3/2 and Fe 2p1/2 doublets [23, 24]. Thus XPS spectrum of Fe 2p indicates the presence of iron in Fe3+ state, confirming valence state of Fe in cobalt-ferrite nanoparticles.

By concluding the XPS findings the Co and Fe metals were found in 2+ and 3+ oxidation states, respectively. This confirms the successful synthesis of cobalt-ferrite nanoparticles in the current study.

3.6. Electromagnetic Properties of Cobalt-Ferrite Nanoparticles

The magnetic properties of the prepared cobalt ferrite were studied using VSM in applied field range up to ±18 kOe from room temperature up to 300°C. Figure 7 shows the hysteresis loops for the sample at different temperatures.

The coercivity was observed as decaying exponentially with temperature, as expected [25]. The hysteresis loop gradually flattens as the temperature increases toward the Curie temperature. Magnetic ferrite nanoparticles are characterized by the presence of a non-collinear spin structure (spin canting).

Spin canting is an indicator of magnetic disorder at the particle surface [26, 27]. The hysteresis loop gradually flattens as the temperature increases toward the Curie temperature. At a high temperature (300°C), the sample shows no hysteresis with lower magnetic saturation (more disorder and spin canting) while at lower temperature (50°C) it shows a sort of hysteresis with higher magnetic saturation. These results confirm the previous work done on ferromagnetic nanoparticles and how the particles size affect the spin canting which produce magnetic disorder at the particle surface [27].

The structure of the hysteresis loops gives some interesting information. The hysteresis loops at the temperature of 50 and 100°C indicates hard character cobalt-ferrite nanoparticles. This can also be well apprehended by higher retentivity, larger coercivity, and higher remnant magnetization as compared to the hysteresis loops of the cobalt-ferrite nanoparticles at higher temperature as documented by tabulated data (Table 1).
Such characteristic of the materials are required in the devices applications like audio recording, credit cards, and computer disk drives. However, magnitudes of all these magnetic parameters were decreased with increasing temperature. This can be justified by the fact that anisotropy energy dominates thermal energy as system temperature is dropping. This decreasing trend in magnetic perimeters as a consequent of increasing temperature is in line with the literature [28].

On the other hand, the same materials displayed narrower hysteresis loops in high temperature regions. Subsequently, the magnitudes of retentivity, coercivity, and remnant magnetization were reduced with the increasing temperature. Materials with such profile are very useful in electrical machinery where minimal energy dissipation is required. Applications of such materials are found in transformers and electric motors as less energy is wasted in the form of heat. The magnitude of magneton numbers were also observed to decrease as the temperature of magnetization is increased. Magneton number, being magnetic moment per formula unit is decreased with temperature. This is quite understandable, as the magnetic moments were declined with increasing temperature. Likewise, $M_r/M_s$ ratio was continuously declined with increasing temperature due to drastic decrease and in $M_s$ with temperature. The magnetic anisotropy $K$ values recorded at various temperatures are documented in Table 1. As a general rule, the magnitude of magnetic anisotropy are temperature-dependant and declining with temperature in the current study. Similar magnitude of magnetic anisotropy were recorded elsewhere [15].

| Temperature, °C | $H_c$, Oe  | $M_s$, emu g⁻¹ | $M_r$, emu g⁻¹ | $M_r/M_s$ | $n_B$ | $K$, 10⁵ emu Oe g⁻¹ |
|----------------|----------|---------------|---------------|-----------|------|------------------|
| 50             | 936.68   | 57            | 15.83         | 0.28      | 39   | 55               |
| 100            | 396.14   | 53            | 8.43          | 0.16      | 16   | 22               |
| 150            | 185.53   | 48            | 4.36          | 0.09      | 07   | 09               |
| 200            | 80.14    | 42            | 1.90          | 0.05      | 03   | 04               |
| 250            | 28.33    | 36            | 0.58          | 0.02      | 01   | 01               |
| 300            | 7.13     | 30            | −0.02         | 0         | 0.2  | 0.2              |

Fig. 7. VSM hysteresis loops of cobalt-ferrite nanoparticles at different temperature.
CONCLUSIONS

In the current work, cobalt-ferrite nanoparticles were prepared by wet chemical method. Physico-chemical profile of synthesized cobalt-ferrite nanoparticles was extensively investigated by number of analytical techniques. The magnetic investigations revealed temperature-dependant magnetic behavior of synthesized cobalt-ferrite nanoparticles.

ACKNOWLEDGMENTS

This project was supported by the Deanship of Scientific Research at Prince Sattam bin Abdulaziz University under the research project no. 2019/01/10916. The research facilities provided by the Chemistry Department of College of Science and Humanities at Prince Sattam bin Abdulaziz University are also acknowledged.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. M. Houshiar, F. Zebhi, Z. J. Razi, A. Alidoust, and Z. Askari, J. Magn. Magn. Mater. 371, 43 (2014).
2. Z. Mahhouti, H. El Moussaoui, T. Mahfoud, M. Hamedoun, M. El Marssi, A. Lahmar, A. El Kenz, and A. Benyoussef, J. Mater. Sci.: Mater. Electron. 30, 14913 (2019).
3. T. Prabhakaran, R. Mangalaraja, J. C. Denardin, and J. A. Jiménez, J. Alloys. Compd. 716, 121269 (2020).
4. A. Franco, Jr. and F. C. e Silva, Appl. Phys. Lett. 96, 172505 (2010).
5. S. Martinez-Vargas, A. I. Mtz-Enriquez, H. Flores-Zuñiga, A. Encinas, and J. Oliva, Synth. Met. 264, 116384 (2020).
6. D. D. Andhare, S. R. Patade, J. S. Kounsalye, and K. M. Jadhav, Phys. B (Amsterdam, Neth.) 583, 412051 (2020).
7. X. Pineda, G. C. Quintana, A. P. Herrera, and J. H. Sánchez, Mater. Chem. Phys. 2020, 122778 (2020).
8. A. F. L. Moreira, F. L. O. Paula, A. F. C. Campos, and J. Depeyrot, J. Solid State Chem. 286, 121269 (2020).
9. K. Vasundhara, S. N. Achary, S. K. Deshpande, P. D. Babu, S. S. Meena, and A. K. Tyagi, J. Appl. Phys. 113, 194101 (2013).
10. M. Abbas, B. P. Rao, M. N. Islam, K. W. Kim, S. M. Naga, M. Takahashi, and C. G. Kim, Ceram. Int. 40, 3269 (2014).
11. I. U. Din, S. Tasleem, A. Naeem, M. S. Shaharan, and G. M. Al Kaisy, Austral. J. Basic. Appl. Sci. 7, 154 (2013).
12. I. U. Din, S. Tasleem, A. Naeem, M. S. Shaharan, and Q. Nasir, Synth. React. Inorg. Metal-Organ. Nano-Met. Chem. 46, 405 (2016).
13. G. Chandra, R. C. Srivastava, V. R. Reddy, and H. M. Agrawal, J. Magn. Magn. Mater. 427, 225 (2017).
14. A. Mohammad, S. M. Aliridha, and T. Mubarak, Digest J. Nanomater. Biostimul. 13, 615 (2018).
15. L. Ajroudi, N. Mliki, L. Bessais, V. Madigou, S. Villain, and C. Leroux, Mater. Res. Bull. 59, 49 (2014).
16. A. V. Ravindra, M. Chandrika, C. Rajesh, P. Kollu, S. Ju, and S. D. Ramaraoo, Eur. Phys. J. Plus 134, 296 (2019).
17. R. Jabbar, S. H. Sabeeh, and A. M. Hameed, J. Magn. Magn. Mater. 494, 165726 (2020).
18. M. Kurian, S. Thangachan, D. S. Nair, E. K. Aswathy, A. Babu, and A. Thomas, and K. T. Binu Krishna, J. Adv. Ceram. 4, 199 (2015).
19. H. Kumar, J. P. Singh, R. Srivastava, P. Negi, H. Agrawal, and K. Asokan, J. Nanosci. Nanotech. 2014, 862415 (2014).
20. R. Yadav, I. Kuritka, J. Vilčáková, J. Havlíca, J. Mášilko, L. Kalina, J. Tkacz, J. Švec, V. Enev, and M. Haiduchová, Adv. Natur. Sci.: Nanosci. Nanotechnol. 8, 045002 (2017).
21. W. P. Wang, H. Yang, T. Xian, and J. L. Jiang, Mater. Trans. 53, 1586 (2012).
22. J. L. Ortiz-Quinonez, U. Pal, and M. S. Villavenue, ACS Omega 3, 14986 (2018).
23. M. Fantauzzi, F. Secci, M. Sanna Angotzi, C. Passiu, C. Cannas, and A. Rossi, RSC Adv. 9, 19171 (2019).
24. A. Murtaza, S. Yang, M. T. Khan, A. Ghani, C. Zhou, and X. Song, Mater. Chem. Phys. 217, 278 (2018).
25. B. Martinez, X. Obradors, L. Balcells, A. Rouanet, and C. Monty, Phys. Rev. Lett. 80, 181 (1998).
26. E. Lima, Jr., A. Brandl, A. Arellaro, and G. Goya, J. Appl. Phys. 99, 083908 (2006).
27. A. Nairan, M. Khan, U. Khan, M. Iqbal, S. Riaz, and S. Naseem, Nanomaterials 6 (4), 73 (2016).