Original Article

Synthesis And Characterisation Of Cobalt And Nickel Ferrite Magnetic Nanoparticles

Sudha Thotakura, Anantha Lakshmi Vadivelu, Padmakar Rao Gogada, Lakshmi Bhavisetti and Suryakala Duvvuri*

Department of Chemistry, GITAM School of Science, GITAM (Deemed to be University), Visakhapatnam, Andhra Pradesh, INDIA.

DOI: 10.47750/pnr.2023.14.03.287

Abstract

Cobalt and nickel ferrite magnetic nanoparticles have been synthesized using a co-precipitation method. The samples are annealed at 600°C. The morphological, structural and magnetic properties of the nanoparticles are characterized by FTIR, X-ray diffraction, scanning electron microscopy and TEM. The annealing temperature has effect on the grain size, the lattice parameter, the degree of inversion, the cationic distribution is studied. FTIR studies proved the respective functional groups of the ferrites. The X-ray diffraction measurements describe the average grain size. Scanning electron microscopy shows that the particles have spherical shapes but not homogeneous sizes. TEM provides the detailed morphological composition of the obtained crystalline nano ferrites.

Keywords: Cobalt ferrite, Nickel ferrite, chemical co-precipitation method, nanoparticles, magnetism, characterization studies

INTRODUCTION:

Spinel ferrites have received increased attention in the fundamental research due to their electrical, magnetic, optical and catalytic properties. Hence finding applications in a variety of industrial sectors[1-3]. Among the spinel system, cobalt and nickel ferrite (MFe_2O_4 M= Co,Ni) is found to be one of the most extensively studied. They possesses an AB_2O_4 structure with tetrahedral A site occupied by metal ions and octahedral B site with Fe^{3+} ions in a face-centered cubic unit cell [4]. This arrangement describes good catalytic activity, great chemical stability and high electromagnetic performance, These properties are strongly influenced by morphology, agglomeration and particle size, which can be controlled very well in co precipitation method [5-8]. Though several studies have been performed using a variety of wet chemistry techniques, such as hydrothermal, sol-gel, sol-gel auto-combustion, polymeric precursor method, polyol and coprecipitation. Coprecipitation is one of the most widely used methods for the synthesis of magnetic ferrite nanoparticles [9-10]. This method consists of mixing aqueous solutions of metal salts at certain molar ratios in highly basic solutions, either at room temperature or at elevated temperature. The nanoparticles morphology and size depend on the type of salt used, ionic strength, pH and other reaction parameters such as stirring rate, dropping speed of basic solution, etc.[11-12]. However, the main challenge in this approach lies on the control of particles aggregation, once strong dipole-dipole magnetic interactions lead to a wide distribution in crystal sizes and coalescence effects caused by the thermal treatment can significantly affect the material efficiency[13]. In this route, we explore structural and morphological aspects of the zinc and nickel ferrite nanoparticles. The structural and morphological characteristics of the nanoparticles were evaluated by means of various analytical techniques such as X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), scanning (SEM) and transmission electron microscopy (TEM) and thermal analysis. The obtained results demonstrate that zinc and nickel ferrite crystals synthesized are good potent to apply in other applications as adsorbent [14].

Experimental Synthesis:

All chemicals used, $FeCl_3 \cdot 6H_2O$, $CoCl_2$, $NiCl_2$, NaOH are of analytical grade, purchased from SigmaAldrich and used as received. Cobalt ferrite and nickel ferrite samples have been prepared by co precipitation methods[14].

For the preparation of cobalt ferrite sample a mixed aqueous solution was prepared by dissolving 3.3637 g of $FeCl_3 \cdot 6H_2O$ and 0.8481 g of $CoCl_2$ in 3 mL of distilled water. Then 10 mL of 4.97 mol L^{-1} NaOH (precipitating agent) was added drop wise. An aliquot of the formed suspension was centrifuged.The main suspension was transferred to an alumina tube and heated to 150 °C for 15 h, under static conditions. An aliquot of the resulting material was separated, centrifuged and the solid named as cobalt ferrite. The sample is washed with distilled water, centrifuged at 6000 rpm and dried at 100 °C for 8 h.

The second series consists of nickel ferrite nanoparticles synthesized by means of the traditional co-precipitation method. In this case, the synthesis procedure is similar to the above described method.

RESULTS

STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATIONS

FTIR:

Infrared spectrum of the samples is obtained through FTIR, for better understanding of the magnetic ferrite nanoparticles.

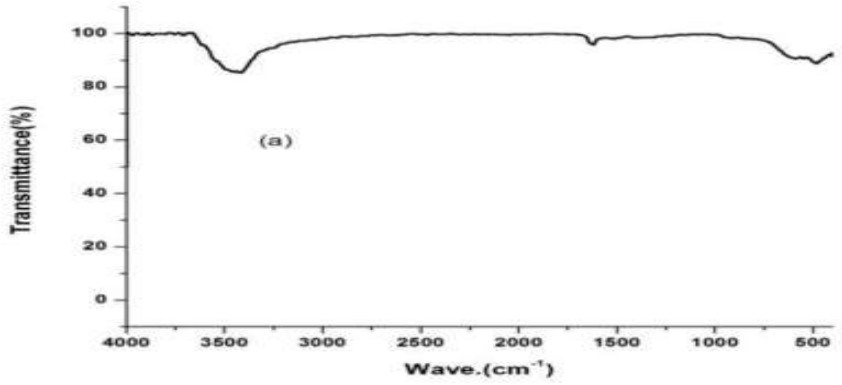

Figure 1: FTIR of cobalt ferrite nano particles

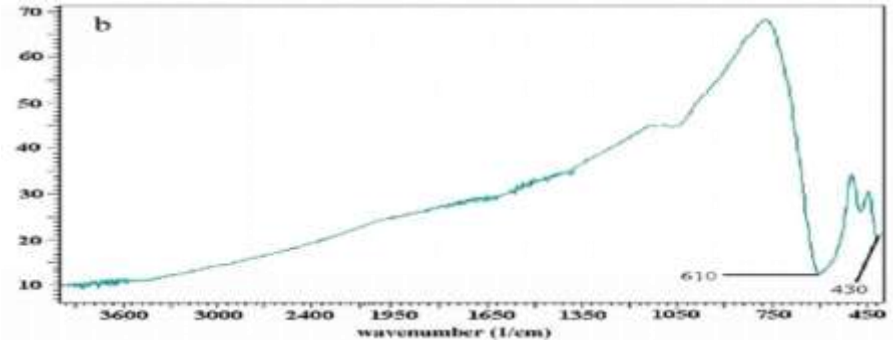

Figure 2: FTIR of nickel ferrite nano particles

XRD analysis:

The samples were characterized by X-ray diffraction (XRD) in order to identify the crystalline phases. The measurements were obtained with an X-ray diffractometer (Shimadzu DRX-7000), using Cu-Kα radiation, with 40 kV voltage and 30 mA current. The diffractograms were obtained in the 2θ range ranging from 10 to 80 degrees in 5 °C/min steps. To identify the crystalline phase (s), the X´Pert High Score version 4.8 software is used. These results were used to calculate the average crystalline size of samples through Sherror equation.

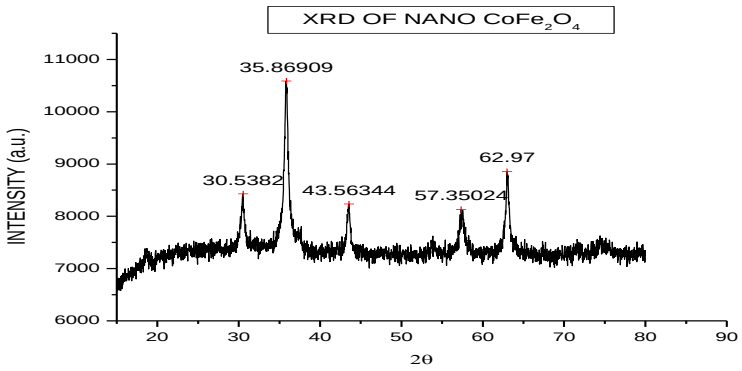

Figure 3: XRD of nano cobalt ferrite

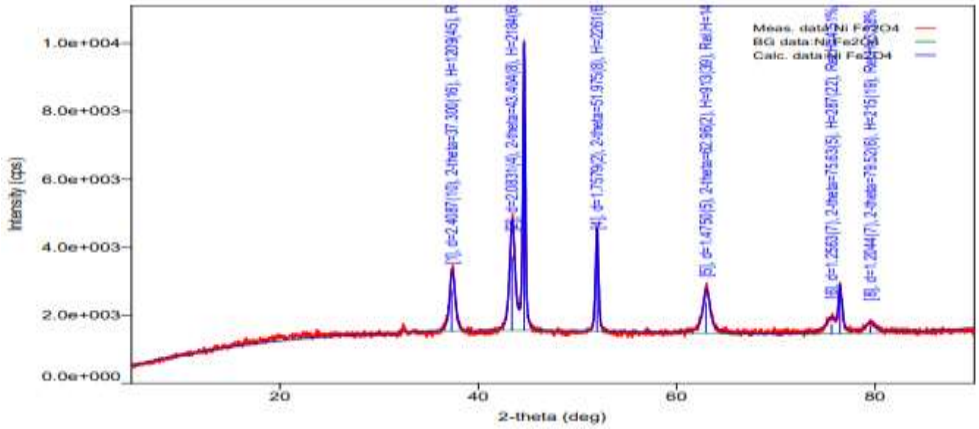

Figure 4: XRD of nano nickel ferrite

The morphology of the samples was evaluated by field emission scanning electron microscopy (SEM) (MEV-FEG) (Carl Zeiss, Auriga model) coupled with dispersive energy spectrometer (EDS), which was used for Chemical composition analysis, which was also obtained by X-ray Fluorescence Spectroscopy, using an EDX-7000 Shimadzu detector spectrometer. The enlargements were performed on a scale of 1 micrometer (1 µm) and / or 200 nanometers (200 nm).

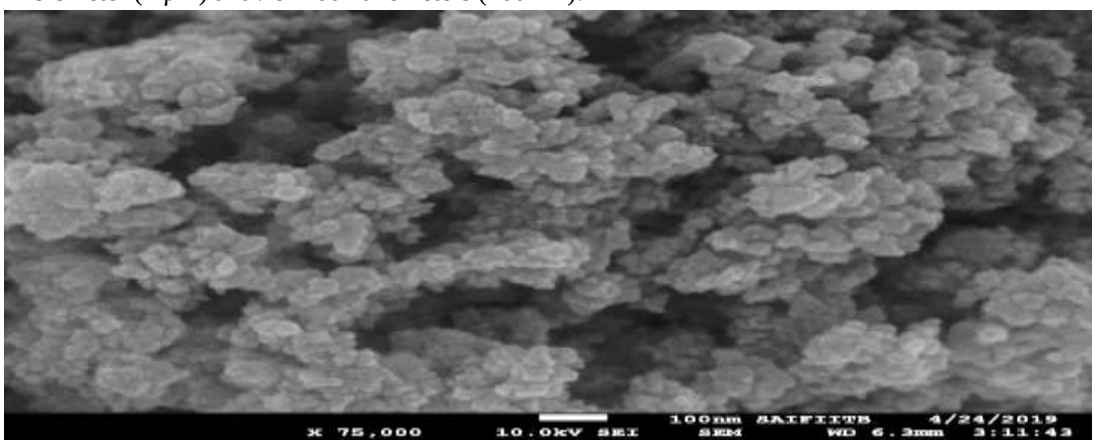

Figure 5: SEM image of nano cobalt ferrite

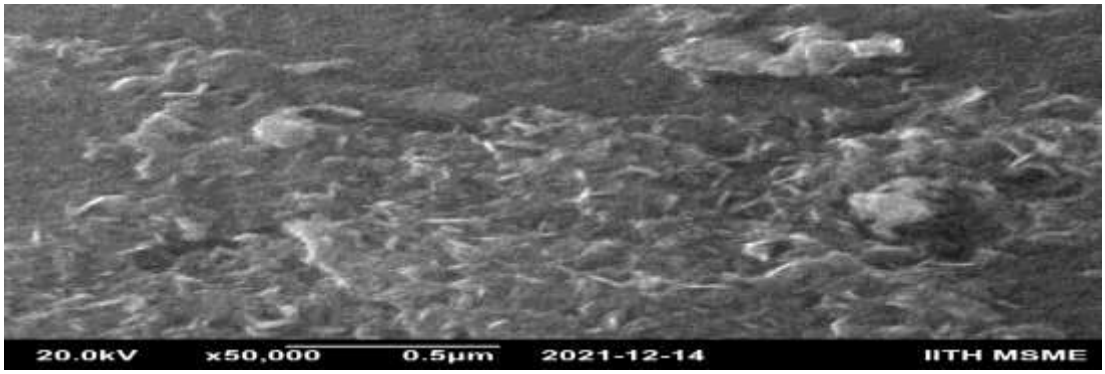

Figure 6: SEM image of nano nickel ferrite

Using Brunauer-Emmett-Teller (BET) surface analysis with nitrogen (N_2) adsorption-desorption isotherms. The BET surface area and the particle size for cobalt and nickel ferrite are measured. The resultant average pore volume and pore diameter indicate the presence of nano-crystalline meso-porous composite particles.

TEM analysis:

TEM studies measured by a High-Resolution Transmission Electron Microscope (HR-TEM) (JEM-4010, JEOL, Peabody, MA, USA)).

DISCUSSION

Cobalt ferrite nanoparticles:

The synthesis of cobalt ferrites ($CoFe_2O_4$) materials with reasonable size and tunable magnetic properties is used for the promising industrial and biomedical applications. These cobalt ferrites nanoparticles have been synthesized by co-precipitation technique[15-16]. FTIR spectroscopy showed the formation of ferrite phase with high and low frequency bands at 573 cm^{-1} and 455 cm^{-1}, respectively. The transition metal is obtained at 420 cm^{-1}. XRD analysis revealed that the average crystallite size of synthesized powder is 69 nm using (311) peaks, and it has exhibited polycrystalline structure. The TEM images exposed that the materials have been well agglomerated along with spherical-shaped nanoparticles[17-18]. EDX study confirmed the presence Co, O, Fe and C with stoichiometric composition and no more impurity detected in the spectrum. In addition, the magnetic anisotropy increases (19.05 → 344.84 erg/g) when Co is added with Fe_3O_4. This confirmed the ferromagnetic behavior of composites[19-20].

Nickel ferrite nanoparticles:

FTIR spectral analysis of nickel ferrite helps to confirm the formation of spinel structure in ferrite samples. The FTIR spectra of the investigated $NiFe_2O_4$ samples the wavenumber range of 1000–300 cm^{-1}, two main broad metal–oxygen bands are seen in the infrared spectra of all spinels, especially ferrites. The higher one is generally observed in the range 600–550 cm^{-1}, is caused by the stretching vibrations of the tetrahedral metal– oxygen bond. The lowest band usually observed in the range 450–385 cm^{-1}, is caused by the metal–oxygen bond. X-ray density is observed to be greater than physical density of Ni-ferrite which is in accordance with literature [21-22]. Calculated values of lattice parameter of Niferrite samples are are in close agreement with standard data (8·34 Å). From SEM and TEM analysis co-precipitation derived particles are of irregular shape with a wide particle size distribution of 60 to 80nm and gives Ni-ferrite particles of moderate size and a narrow particle size distribution[23-25].

CONCLUSION

Co-precipitation technique is used to synthesize $CoFe_2O_4$ and $NiFe_2O_4$ nanoparticles. The method produces single phase cubic Ni-ferrite nanoparticles and also hematite (Fe_2O_3) phase. Co-precipitation gives particles of very small size with a wide size variation and super paramagnetic nature. Ni-ferrite particles of comparatively larger size with small size variation and ferrimagnetic nature. At this annealing temperature, particle size and saturation magnetization are found to increase. Co-precipitation is better for the preparation of pure and homogeneous form. Co-precipitation is suitable for the synthesis of

ferrites with very small size and super paramagnetic nature. At the same $NiFe_2O_4$ nanoparticles exhibit less hysteresis loss with almost same saturation magnetization.

REFERENCES

1. Zhao G, Xu JJ, Chen HY. Fabrication, characterization of Fe3 O4 multilayer film and its application in promoting direct electron transfer of hemoglobin. Electrochemistry Communications. 2006;8(1):148-154.

2. Zhang T, Tian B, Kong J, Yang P, Liu B. A sensitive mediator-free tyrosinase biosensor based on an inorganic-organic hybrid titania sol-gel matrix. Analytica Chimica Acta. 2003;489(2):199-206.

3. Chu X, Jiang D, Zheng C. The preparation and gas-sensing properties of NiFe2 O4 nanocubes and nanorods. Sensors and Actuators B: Chemical. 2007;123(2):793-797.

4. Rana S, Srivastava RS, Sorensson MM, Misra RDK. Synthesis and characterization of nanoparticles with magnetic core and photocatalytic shell: Anatase TiO2 -NiFe2 O4 system. Materials Science and Engineering: B. 2005;119(2):144-151.

5. Raikher YL, Stepanov VI, Depeyrot J, Sousa MH, Tourinho FA, Hasmonay E, et al. Dynamic optical probing of the magnetic anisotropy of nickel-ferrite nanoparticles. Journal of Applied Physics. 2004;96(9):5226-5233.

6. Cunningham CH, Arai T, Yang PC, McConnell MV, Pauly JM, Conolly SM. Positive contrast magnetic resonance imaging of cells labeled with magnetic nanoparticles. Magnetic Resonance in Medicine. 2005;53(5):999-1005.

7. Yoon TJ, Kim JS, Kim BG, Yu KN, Cho MH, Lee JK. Multifunctional nanoparticles possessing a "magnetic motor effect" for drug or gene delivery. Angewandte Chemie (International ed). 2005;44(7):1068-1071.

8. Li H, Wu H, Xiao G. Effects of synthetic conditions on particle size and magnetic properties of NiFe2 O4 . Powder Technology. 2010;198(1):157-166.

9. Sivakumar P, Ramesh R, Ramanand A, Ponnusamy S, Muthamizhchelvan C. Preparation of sheet like polycrystalline NiFe2 O4 nanostructure with PVA matrices and their properties. Materials Letters. 2011;65(9):1438-1440.

10. Chen L, Dai H, Shen Y, Bai J. Size-controlled synthesis and magnetic properties of NiFe2 O4 hollow nanospheres via a gelassistant hydrothermal route. Journal of Alloys and Compounds. 2010;91(1-2):L33-L38.

11. Bao N, Shen L, Wang Y, Padhan P, Gupta A. Facile Thermolysis Route to Monodisperse Ferrite Nanocrystals. Journal of the American Chemical Society. 2007;129(41):12374-12375.

12. Patange SM, Shirsath SE, Jadhav SS, Lohar KS, Mane DR, Jadhav KM. Rietveld refinement and switching properties of Cr3+ substituted NiFe2 O4 ferrites. Materials Letters. 2010;64(6):722- 724.

13. Cross WB, Affleck L, Kuznetsov MV, Parkin IP, Pankhurst QA. Self-propagating high-temperature synthesis of ferrites MFe2 O4 (M = Mg, Ba, Co, Ni, Cu, Zn); reactions in an external magnetic field. Journal of Materials Chemistry. 1999;9(10):2545-2552.

14. Sivagurunathan P, Gibin SR. Preparation and characterization of nickel ferrite nano particles by co-precipitation method with citrate as chelating agent. Journal of Materials Science: Materials in Electronics. 2016;27(3):2601-2607.

15. Guo L, Shen X, Meng X, Feng Y. Effect of Sm3+ ions doping on structure and magnetic properties of nanocrystalline NiFe2 O4 fibers. Journal of Alloys and Compounds. 2010;490(1-2):301- 306.

16. Deb P, Basumallick A, Das S. Controlled synthesis of monodispersed superparamagnetic nickel ferrite nanoparticles. Solid State Communications. 2007;142(12):702-705.

17. Ahmed MA, Mansour SF, El-Dek SI. Investigation of the physico-chemical properties of nanometric NiLa ferrite/PST matrix. Solid State Ionics. 2010;181(25-26):1149-1555.

18. Aliahmad M, Noori M, Hatefi Kargan N, Sargazi M. Synthesis of nickel ferrite nanoparticles by co-precipitation chemical method. International Journal of Physical Sciences. 2013;8(18):854-858. 1

19. Zhang X, Niu Y, Li Y, Hou X, Wang Y, Bai R, et al. Synthesis, optical and magnetic properties of α-Fe2 O3 nanoparticles with various shapes. Materials Letters. 2013;99(2013):111-114.

20. Straumal BB, Mazilkin AA, Protasova SG, Myatiev AA, Straumal PB, Goering E, et al. Amorphous grain boundary layers in the ferromagnetic nanograined ZnO films. Thin Solid Films. 2011;520(4):1192-1194.

21. Sagadevan S, Arunseshan C. Dielectric Properties of Cadmium Selenide (CdSe) Nanoparticles synthesized by solvothermal method. Applied Nanoscience. 2014;4(2):179-184.

22. Sagadevan S. Studies on the dielectric properties of CdS nanoparticles. Applied Nanoscience. 2014;4(3)325-329.

23. Sagadevan S. Synthesis and Electrical Properties of TiO2 Nanoparticles Using a Wet Chemical Technique. American Journal of Nanoscience and Nanotechnology. 2013;1(1):27-30.

24. Sagadevan S. Synthesis, structural and dielectric properties of zinc sulfide nanoparticles. International journal of Physical Sciences. 2013;8(21):1121-1127.

25. Sagadevan S. Study of Structural, Surface Morphological and Dielectric Properties of Cu-doped Tin Oxide Nanoparticles. Journal of Nano Research. 2015;34:91-97.