

# Study on Synthesis of Superparamagnetic Spinel Cobalt Ferrite Nanoparticles as Layered Double Hydroxides by Co-precipitation Method<sup>1</sup>

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**Abstract**—Cobalt ferrite layered double hydroxide (LDH) nanoparticles with cubic structure were synthesized by the co-precipitation method: addition of NaOH solution to a solution of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$ . Formation of nanoparticles was confirmed by XRD, SEM, TEM, PSA, FT-IR, TGA, DSC, and magnetic characteristics were measured using VSM. Crystals produced by calcination at 900°C possessed high coercivity and pronounced physical and chemical stability. Nanoparticles of  $\text{CoFe}_2\text{O}_4$  formed outer layers with poor crystallization on the surface of cobalt ferrite nanocrystals.

**Keywords:** magnetic materials, chemical synthesis, X-ray diffraction, magnetic properties

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## INTRODUCTION

Layered double hydroxides (LDHs) are solid base catalysts of high potential that have the general formula  $[\text{M}_{1-x}^{\text{II}} \text{M}_x^{\text{III}}(\text{OH})_2]^{z+} \text{A}_{z/n}^{n-} \cdot y\text{H}_2\text{O}$ , where M(II) and M(III) are metal cations,  $x$  is defined as  $\text{M}^{\text{II}}/(\text{M}^{\text{II}} + \text{M}^{\text{III}})$  ratio generally varies from 1 to 5. The layer charge is  $z = x$  when the  $\text{M}^{\text{II}}$  is a divalent cation and  $z = 2x - 1$  when  $\text{A}^{n-}$  denotes anions. LDHs consist of brucite-like layers in which M(II) cations are partially substituted by M(III) cations resulting in a net positive charge which is compensated by interlayer anions of the hydrated interlayer region. The basic properties of LDHs and materials derived from those can be tailored by altering nature of the cations in the layers, M(II)/M(III) ratio, nature of anions, and activation conditions [1].

Recently application of spinel ferrites has been intensively studied in such areas as high-density

information storage system [2], ferrofluid technology [3], magnetocaloric refrigeration [4], medical diagnostics [5], magnetic resonance imaging enhancement [6], and gas sensors [7]. Generally, magnetic properties of ferrite are highly dependent on particles microstructure and volume, surface to volume ratio, intra- and intergranular pores [8].

Among spinel ferrites cobalt ferrite  $\text{CoFe}_2\text{O}_4$  is of considerable interest due to its large magnetocrystalline anisotropy ( $2.65 \times 10^6$ – $5.1 \times 10^6$  erg  $\text{cm}^{-3}$ ) [9], high coercivity at 4.3 kOe at room temperature [10], moderate saturation magnetization ( $M_s = 80$  emu  $\text{g}^{-1}$ ) [11], large magnetostrictive coefficient [12], chemical stability, and mechanical hardness. It exhibits higher coercivity than the other spinel ferrites [13–15].  $\text{CoFe}_2\text{O}_4$  Has an inverse spinel structure in which oxygen atoms make up an FCC lattice with half of  $\text{Fe}^{3+}$  ions occupying the tetrahedral A sites and the other half together with  $\text{Co}^{2+}$  ions located at the octahedral B sites.

<sup>1</sup> The text was submitted by the authors in English.

LDHs can be easily synthesized by co-precipitation of a solution of bivalent and trivalent metal salts with a base (NaOH or KOH) [16]. Generally, supersaturation conditions are reached by controlling pH of the solution [17]. High catalytic activity of particles is related directly with their surface and structural properties such as small size, high surface area, shape and size distributions of pores [18]. Various synthesis strategies for magnetic nanoparticles had been studied [19–26]. Co-precipitation is the simplest method for spinel iron nanoparticles with size range 5–180 nm [27]. This can be the most promising method due to its simplicity, efficiency, and simple control of size and shape of particles. The latter depends on the type of iron salts used (chlorides, sulfates, nitrates, perchlorates, etc.),  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio [28], presence of oxygen gas, reaction rate and temperature [18].

In this study  $\text{CoFe}_2\text{O}_4$  particles have been synthesized by chemical co-precipitation method under different temperatures. XRD has been used to evaluate crystalline structure and purity of the prepared phases. Magnetic characters of the samples have been evaluated.

## EXPERIMENTAL

**Materials and methods.** Suppliers of the chemicals:  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , 98%, Belami Fine Chemicals (India);  $[\text{FeCl}_2 \cdot 4\text{H}_2\text{O}]$ , 99%, ACROS Chemicals (USA-Belgium);  $[\text{FeCl}_3 \cdot \text{H}_2\text{O}]$ , min. 99%, Riedel-Dehaen–Sigma Aldrich Chemicals (Switzerland).

Cobalt spinel ferrite nanoparticles were synthesized as follows:  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{FeCl}_3 \cdot \text{H}_2\text{O}$  with molar ratio of cations  $\text{Co}^{2+} : \text{Fe}^{2+} : \text{Fe}^{3+} = 1.9 : 1 : 2$  were dissolved together in de-ionized water (18.2 MΩ cm). Aqueous solution of NaOH (1.5 mol/L) was added drop wise under  $\text{N}_2$  to pH 7.0 to ensure complete precipitation. The slurry formed was removed from a three neck flask and stored at 40°C for 4 h to improve crystallinity. The precipitate was filtered off, washed with deionized water and ethanol and dried at 50°C under vacuum for 24 h. The resulting LDHs precursor was calcinated at 900°C for 2 h to give  $\text{CoFe}_2\text{O}_4$  LDHs nanoparticles.

**Instruments.** pH Was measured by a single electrode pH-meter (Denver Instrument Co., USA). X-ray diffraction analysis was carried out with Shimadzu-XRD-7000 Diffractometer (Japan), at room temperature with  $\text{CuK}_\alpha$  radiations of wavelength ( $\lambda = 1.5406 \text{ \AA}$ ), generated at 30 kV–30 mA for cobalt ferrite nanoparticles. The nanoparticle size distribution was

measured by Beckman Coulter N5 submicron particle size analyzer, USA. Morphology of the synthesized powders was studied by SEM scanning electron microscope (JEOL JSM-6360 LA, Japan) with a power supply of 30 kV. The composition and elemental studies of  $\text{CoFe}_2\text{O}_4$  nanoparticles were carried out by EDAX combined with the scanning electron microscopy and TEM transmission electron microscope (JEOL JEM 1230, Japan) with Max. Mag. 600k $\times$  and resolution 0.2 nm. FT-IR spectra were recorded by FTIR spectrophotometer Shimadzu-8400 S (Japan) in KBr tablets. Thermal characteristics were measured by TGA-50H, Shimadzu (Japan) with heating rate 10°C/min (30 mL/min) up to 600°C under  $\text{N}_2$ . DSC was performed with a heat flux Shimadzu DSC-60 A, (Japan) in  $\text{N}_2$  atmosphere, flow rate 30 mL/min, temperature range 30–600°C and heating rate 10°C/min. Magnetic characteristics were measured by VSM (Lake Shore-7410 vibrating sample magnetometer), magnetic field up to 20 kOe and magnetic moment sensitivity up to 1  $\mu\text{emu}$ .

## RESULTS AND DISCUSSION

**Effect of pH on synthesis of  $\text{CoFe}_2\text{O}_4$ -LDHs nanoparticles.** pH Of the initial reactant solution was 2.2, upon slow addition of NaOH it increased steadily to 2.7 and then rapidly to 6.6. Evidently, pure  $\text{CoFe}_2\text{O}_4$  was synthesized at pH 7. The method of NaOH addition had a significant influence on the nucleation rate. High concentration of  $\text{OH}^-$  could lead to lower nuclei concentration of  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$ .

On the basis of pH titration curves of the mixed salt solutions by NaOH the hydroxide ion reacted with aqueous  $\text{M}^{\text{II}}$  ions at higher pH to give the LDH. Generally the LDHs are thermodynamically unfavorable for mixtures of metal hydroxides, but mass action effects associated with the high concentration of an anion drive the system towards the LDH [17].

**Effect of calcinations temperature on preparation of  $\text{CoFe}_2\text{O}_4$  nanoparticles.** *Structure and properties of magnetic core  $\text{CoFe}_2\text{O}_4$  nanoparticles.* **XRD.** According to powder X-ray diffraction (XRD) all three precursors had the characteristic structure of hydroxalcalite-like compounds. The synthesized  $\text{CoFe}_2\text{O}_4$  had the structure similar to that of  $\text{MgFe}$ -LDH with Mg : Fe ratio 1 : 2. It exhibited crystallinity poorer than that with Mg : Fe ratio 2 : 1 or 1 : 1 due to higher charge density in the layers [18]. Spinel phase diffraction peaks were registered within shorter time

upon higher concentration of  $\text{MFe}_2\text{O}_4$ . The mean crystals size was calculated from the diffraction peak width by the Scherrer's equation [29].

$$L = k\lambda/(\beta \cos \theta), \quad (1)$$

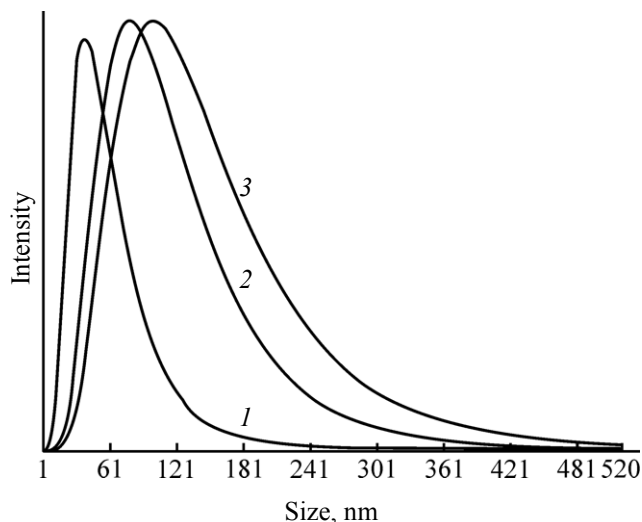
where ( $L$ ) crystals size, ( $\lambda$ ) wavelength of the X-ray radiation, ( $\beta$ ) the line width at half-height, ( $\theta$ ) diffraction angle, ( $k = 0.89$ ) shape factor for spherical particles.  $\text{CoFe}_2\text{O}_4$  Structure is typical to that of the inverse spinel group with the general formula  $\text{A}(\text{B}_2)\text{O}_4$ . The peaks at  $18.2^\circ$ ,  $30.0^\circ$ ,  $35.4^\circ$ ,  $37.2^\circ$ ,  $43.47^\circ$ ,  $57.1^\circ$ , and  $62.72^\circ$  were attributed to (111), (220), (311), (222), (400), (511), and (440) reflections of the spinel phase of  $\text{CoFe}_2\text{O}_4$ .

The peaks stood for the cubic structure (space group:  $Fd\bar{3}m$ ) typical for  $\text{CoFe}_2\text{O}_4$  crystals (JCPDS no. 003-0864). In accordance with the Sherrer's formula size of spinel crystals was about 10–12 nm (Table 1), space group  $Fd\bar{3}$ . Its amorphous character vanished and the diffraction peak of (311) crystal plane showed up. The diffraction peak matched the JCPDS standard card, but it was relatively broad which indicated that  $\text{CoFe}_2\text{O}_4$  crystallization remained incomplete with crystal defects and smaller crystals size ca 23.1 nm. At  $900^\circ\text{C}$  the peak was relatively narrow and high, which indicated that the crystals growth progressed and completed. The crystalline phase was stable [30]. The average crystals size grew accordingly [31, 32].

**Particles size.** Calcination at  $800^\circ\text{C}$  resulted in formation of ca 44 nm particles that grew up to 1.1  $\mu\text{m}$  at  $1000^\circ\text{C}$  (Fig. 1). At the higher end of that range the resulting cobalt ferrite particles growth rate exceeded the nucleation rate. The size of particles increased linearly with calcination temperature growth.

SEM images of  $\text{CoFe}_2\text{O}_4$  have uniform spherical structure morphology (Fig. 2) with spherical particles of narrow size distribution (52–90 nm) at  $900^\circ\text{C}$ . The element analysis detected the following elements: Co (11.31%), Fe (25.52%), and O (63.18%) corresponding to  $\text{CoFe}_2\text{O}_4$ .

**TGA and DSC.** The TGA curve demonstrated three stages of weight loss. The first stage at  $25$ – $120^\circ\text{C}$  was associated with dehydration of the sample (weight loss 7.8%), the second one between 120 and  $270^\circ\text{C}$ , was attribute to decomposition of nitrates (7.2% weight loss) and start of cobalt ferrite crystallization and the third stage between 269 and  $600^\circ\text{C}$  corresponded to the loss of structural water. Above  $600^\circ\text{C}$  no weight



**Fig. 1.** Particle size distributions of  $\text{CoFe}_2\text{O}_4$ -LDHs nanopowders calcined at (1)  $800^\circ\text{C}$ , (2)  $900^\circ\text{C}$ , and (3)  $1000^\circ\text{C}$  for 2 h.

loss was observed and crystallization process was completed.

In DSC the exothermic peak with maximum at  $113.23^\circ\text{C}$  was attributed to hydration and loss of water with specific 30.13 J/g.

**IR spectra.** A band centered around  $1383\text{ cm}^{-1}$  indicated the presence of  $\text{NO}_3^-$  ions [33] and C–H bond in the gel [34]. The metal-oxide vibration band characteristic to cobalt ferrite ( $580$  and  $370\text{ cm}^{-1}$ ) was attributed to the spinel structure.

**VSM.** Magnetic properties of as-prepared  $\text{CoFe}_2\text{O}_4$  nanoparticles and those calcinated at  $900^\circ\text{C}$  were studied with a quantum magnetometer VSM at 300 K ( $T > T_B$ ) with maximum applied field up to 20 kOe (Fig. 3). The coercivity ( $H_c$ ) was about 0.0237 and 1.2506 kOe. Saturation magnetization ( $M_s$ ) values were ca. 13.6 and 70.628 emu/g and indicative of strong soft magnetic properties [18] with the remnant

**Table 1.** XRD and yield results of as prepared and calcined  $\text{CoFe}_2\text{O}_4$

| Sample | Calcination temperature, $^\circ\text{C}$ | Crystalline size <sup>a</sup> , nm | Particle size <sup>b</sup> , nm | Yield after calcinations, % |
|--------|-------------------------------------------|------------------------------------|---------------------------------|-----------------------------|
| 1C     | 0                                         | —                                  | 11.5                            | —                           |
| 1C2    | 600                                       | 19.59                              | 23.1                            | 73.55                       |
| 1C5    | 900                                       | 37.57                              | 87.4                            | 69.33                       |

<sup>a</sup> Calculated by the Scherrer equation. <sup>b</sup> Determined by particle size analyzer.

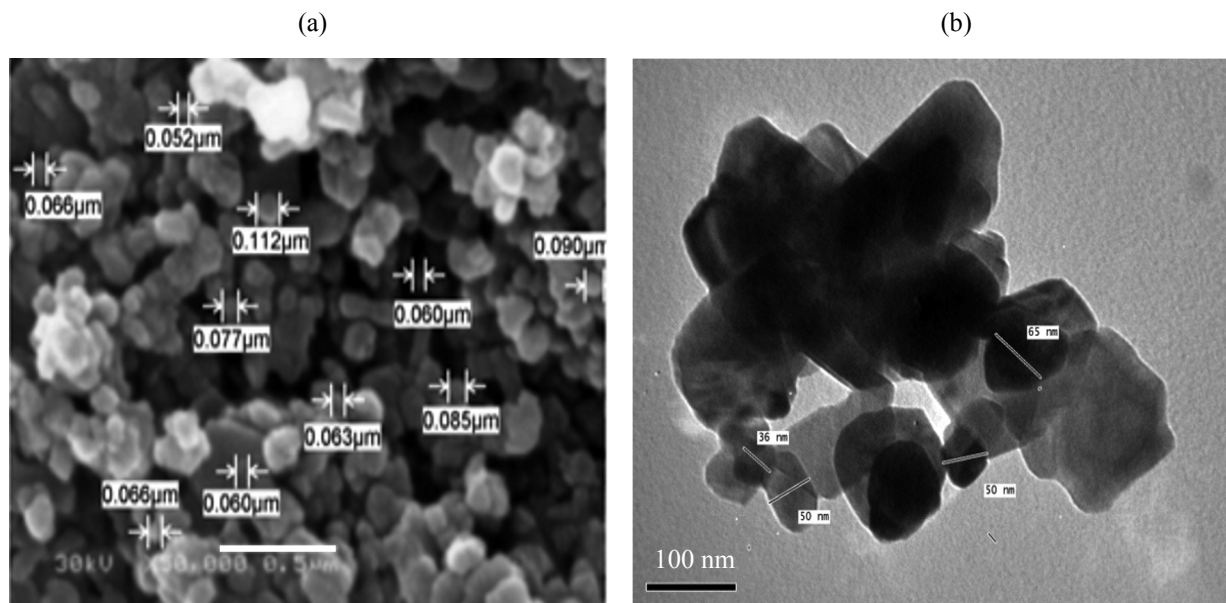


Fig. 2. (a) SEM and (b) TEM micrograph as calcined  $\text{CoFe}_2\text{O}_4$ -LDHs nanoparticles at  $900^\circ\text{C}$ .

magnetization ( $M_r$ ), 0.3 and 29.49 emu/g. The magnetic structure of crystals was unstable and in disorder. The magnetic moment could not be maintained consistent with the external field. The crystal structure did not change under the action of magnetic field and pressure applied [36].

According to reversibility of the M-H curve recorded at room temperature the sample was superparamagnetic.  $\text{CoFe}_2\text{O}_4$  Crystals of less than 14 nm size demonstrated superparamagnetic character at room temperature.

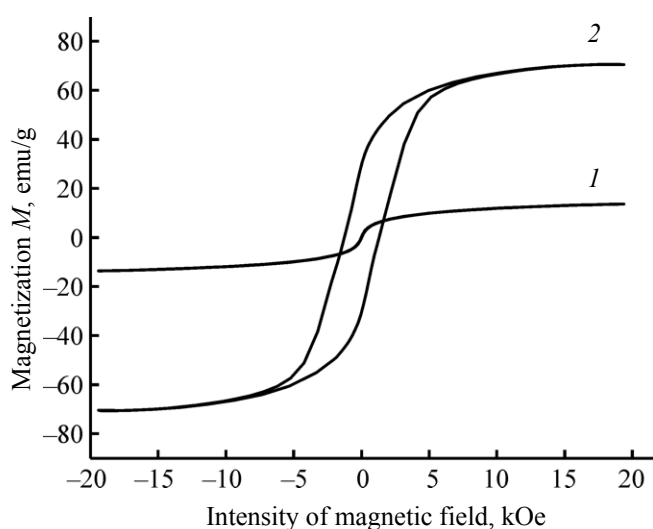
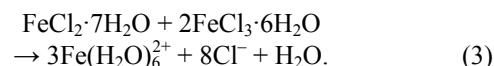
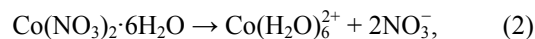


Fig. 3. Magnetization vs. magnetic field of (1) as prepared  $\text{CoFe}_2\text{O}_4$ -LDHs nanoparticle and (2) as calcinated at  $900^\circ\text{C}$ .

The remanence ratio 0.41 for calcinated cobalt ferrite was close to the expected one (0.5) for a system of non-interacting single domain particles with uniaxial anisotropy though cobalt ferrite itself had the cubic structure [32]. Effectively uniaxial anisotropy in magnetic nanoparticles was attributed to surface effects as evidenced by simulations of nanoparticles [37].

**Reaction mechanism.** The reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with a solution of NaOH at pH 7 may follow three possible pathways [38].

(1) Dissolving of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in water (liquid phase synthesis).



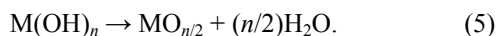
The first path is a homogeneous phase reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  [Eqs. (2), (3), (8)–(10)] [39] that leads to homogeneous precipitation. Upon saturation the process reaches a point of nucleation. Particles growth progresses due to diffusion of atoms onto the nuclei and irreversible aggregation of nuclei.

This overall reaction proceeds in two steps: hydrolysis of the metal cations and subsequent dehydration to form oxides [40]

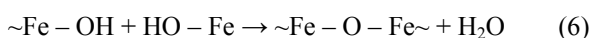


**Table 2.** Magnetic properties of as prepared CoFe<sub>2</sub>O<sub>4</sub> and calcined at 900°C

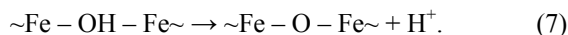
| Sample | Corecivity<br>$H_c$ , kOe | Remnant mag-<br>netization $M_r$ ,<br>emu/g | Saturation<br>magnetization<br>$M_s$ , emu/g |
|--------|---------------------------|---------------------------------------------|----------------------------------------------|
| 1C     | 0.02                      | 0.3                                         | 13.6                                         |
| 1C5    | 1.25                      | 29.49                                       | 70.63                                        |



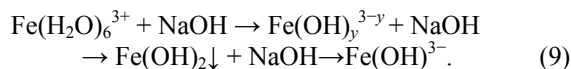
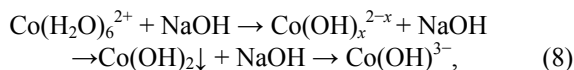
**Dehydration.** The second step involves formation of oxygen bridges between the metal cations. Mechanism of this step is unclear. However, it is assumed to be a reaction between two hydroxide ligands [40]



or a deprotonation reaction

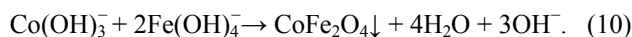


(2). *Transformations of the reactant solution combined with NaOH solution*

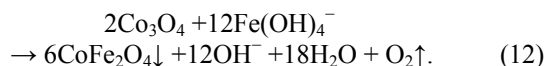


The second path is a solid–liquid two-phase phase reaction. CoFe<sub>2</sub>O<sub>4</sub> is formed in the reaction of Co<sub>3</sub>O<sub>4</sub>, FeCl<sub>2</sub>·4H<sub>2</sub>O with Fe Cl<sub>3</sub>·6H<sub>2</sub>O in supercritical water [Eqs. (2)–(5), (11), (12)]:

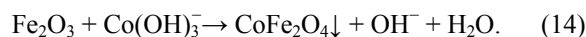
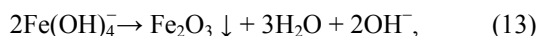
(3) *Reaction (I)*



(4) *Reaction (II)*



(5) *Reaction (III)*



The third path is synthesis of CoFe<sub>2</sub>O<sub>4</sub> from Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O [Eqs. (2)–(5), (13), (14)].

## CONCLUSIONS

In summary, CoFe<sub>2</sub>O<sub>4</sub> LDHs nanoparticles with spinel structure were synthesized by the co-precipitation method at pH = 7 and calcinated at 900°C

and exhibited high superparamagnetic properties, physical and chemical stability. The crystallization, saturation magnetization, coercivity and remnant magnetization increased along with calcination temperature.

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## REFERENCES

1. Zhang, H., Qi, R., Evans, D.G., and Duan, X., *J. Solid State Chem.*, 2003, vol. 177, p. 772.
2. Zolio, R.F., US Patent no. 474, 1984, p. 866.
3. Raj, K., Moskowitz, B., and Casciari, R., *J. Magn. Magn. Mater.*, 1995, vol. 149, p. 174.
4. Mamiya, H., Terada, N., Furubayashi, T., Suzuki, H.S., and Kitazawa, H., *J. Magn. Magn. Mater.*, 2010, vol. 322, nos. 9–12, p. 1561.
5. Bulte, J.W.M., *J. Magn. Reson. Imaging*, 1994, vol. 4, p. 497.
6. Kim, D., Zeng, H., Ng, T.C., and Brazel, C.S., *J. Magn. Magn. Mater.*, 2009, vol. 321, no. 23, p. 3899.
7. Patil, J.Y., Nadargi, D.Y., Gurav, J.L., Mulla, I.S., and Suryavanshi, S.S., *Mater. Lett.*, 2014, vol. 124, no. 1, p. 144.
8. Xiao, S.H., Xu, H.J., Huc, J., Li, L.Y., and Li, X.J., *Physica E*, 2008, vol. 40, p. 3064.
9. Melikhov, Y., Snyder, J.E., Jiles, D.C., Ring, A.P., Paulsen, J.A., Lo, C.C.H., and Dennis, K.W., *J. Appl. Phys.*, 2006, vol. 99, p. 08R102.
10. Chinnnasamy, C.N., Jeyadevan, B., Perales-Perez, O., Shinoda, K., Tohji, K., and Kasuya, A., *IEEE Trans. Magn.*, 2002, vol. 38, p. 2640.
11. Cullity, B.D., *Introduction to Magnetic Materials*, New York: Addison–Wesley, 1972.
12. Mohaideen, K.K. and Joy, P.A., *Curr. Appl. Phys.*, 2013, vol. 13, no. 8, p. 1697.
13. Cao, X., J. Meng, J., Mi, F., Zhang, Z., and Sun, J., *Solid State Commun.*, 2011, vol. 151, no. 9, p. 678.
14. Imine, S., Schoenstein, F., Merccone, S., Zaghruiou, M., Bettahar, N., and Jouini, N., *J. Eur. Ceram. Soc.*, 2011, vol. 31, no. 15, p. 2943.
15. Ayyappan, S., Philip, J., and Raj, B., *Mater. Chem. and Phys.*, 2009, vol. 115, p. 712.
16. Xu, Y., Zhang, H., Duan, X., and Ding, Y., *Mater. Chem. Phys.*, 2009, vol. 114, nos. 2–3, p. 795.
17. Jing, H., Min, W., Li, B., Kang, Y., David, G.E., and Xue, D., *Struct. Bond*, 2006, vol. 119, p. 89.

18. Hui, Z., Rong, Q., David, G. E., and Xue, D., *J. Solid State Chem.*, 2004, vol. 177, p. 772.
19. Philip, J., Jaykumar, T., Sundaram, P.K., and Raj, B., *Meas. Sci. Technol.*, 2003, vol. 14, p. 1289.
20. Sharifi, I., Shokrollahi, H., Doroodmand, M.M., and Safi, R., *J. Magn. Magn. Mater.*, 2012, vol. 324, no. 10, p. 1854.
21. Ahmed, S.R. and Kofinas, P., *Mater. Res. Soc. Symp. Proc.*, 2001, 661, KK 10.10.1.
22. Everett, E.C., *PhD Thesis (Chem.)*, Louisiana, USA, 1994.
23. Ibrahim, A.M., Abd El-Latif, M.M., and Mahmoud, M.M., *J. Alloy and Comp.*, 2010, vol. 506, p. 201.
24. Philip, J., Shima, P.D., and Raj, B., *J. Appl. Phys.*, 2007, vol. 91, p. 203108.
25. Pitaa, M., Abad, J.M., Vaz-Dominguez, C., Briones, C., Mateo-Martí, E., Martín-Gago, J.A., Morales, P., and Fernandez, V.M., *J. Colloid Interface Sci.*, 2008, vol. 321, p. 484.
26. Beck, H.P., Eiser, W., and Haberkorn, R., *J. European Ceramic Soc.*, 2001, vol. 21, p. 687.
27. Gupta, A.K. and Gupta, M., *Biomaterials*, 2005, vol. 26, p. 3995.
28. Liu, Z.L., Wang, H.B., and Lu, Q.H., *J. Magn. Magn. Mater.*, 2004, vol. 283, p. 258.
29. Buzby, S.E., *PhD Thesis (Materials Science and Engineering)*, Delaware, USA, 2005.
30. Zhao, L.J. and Jiang, Q., *J. Magn Magn Mater.*, 2010, vol. 322, p. 2485.
31. Sort, J., Surmach, S., Munoz, J.S., and Baro, M.D., *Phys. Rev. B*, 2002, vol. 65, p. 174420.
32. Maaz, K., Arif, M., Hasanaina, S.K., and Ceylan, A., *J. Magn. Magn. Mater.*, 2007, vol. 308, p. 289.
33. Xiao, S.H., Xu, H.J., Hu, J., Long, Y.L., and Xin, J.L., *Physica E*, 2008, vol. 40, p. 3064.
34. Hoffmann, M.R., Martin, S.T., Choi, W., and Bahne-mann, D.W., *Chem. Rev.*, 1995, vol. 95, p. 96.
35. Cot, F., Larbot, A., Nabias, G., and Cot, L., *J. Eur. Ceram. Soc.*, 1998, vol. 18, p. 2175.
36. Cornell, R.M. and Schwertmann, U., *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, New York: VCH Publishers, 1996.
37. Kodama, R.H., Berkowitz, A.E., McNiff, E.J., and Foner, S., *Phys. Rev. Lett.*, 1996, vol. 77, p. 394.
38. Beydoun, D. and Amal, R., *J. Mol. Catal. A: Chem.*, 2002, vol. 180, p. 193.
39. Spanhel, L., Haase, M., Weller, H., and Henglein, A., *J. Am. Chem. Soc.*, 1987, vol. 109, p. 5649.
40. Blesa, M.A. and Matijevic, E., *Adv. Colloid Interface Sci.*, 1989, vol. 29, p. 173.