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Emerson Pérez
Gerson Marquez
Vicente Sagredo

Effect of Calcination on Characteristics of Nickel Ferrite Nanoparticles Synthesized by Sol-Gel Method

Departamento de Física,
Universidad de Los Andes,
Mérida, VENEZUELA

Nanosized nickel ferrite compound was synthesized by using sol-gel method. Significant differences in the particle size were obtained after two different calcination cycles at 873 and 1073 K. The average particle size of sample calcinated at 873K was found to be ~ 25 nm which increases up to 120 nm on calcination at 1073 K. Low-field magnetization data show at room temperature an strong irreversibility between zero field cooled(ZFC) and field cooled(FC) cycles without a clear blocking temperature. The FC data shows a behavior typical for strongly coupled system because of the interaction particle-particle favored by the agglomeration of particles observed by the SEM micrographs. The effective magnetic moment per molecule evaluated from hysteresis loops at magnetic field of 5.5 Tesla is slightly smaller than 2μB.

***Keyword*:** Nickel ferrite; Nanoparticles; Sol-gel method; Low-field magnetization
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1. Introduction

During the last decades, there has been an increasing interest in spinel nanoferrites because of their remarkable magnetic properties and their unique electric, dielectric and optical properties, owing to both the broad applications in several technological fields [1]. Nickel ferrite ($NiFe_2O_4$) is a cubic ferrimagnetic oxide which has attracted attention because of their large permeability at high frequency and high electrical resistivity [2-6]. Nickel ferrite nanoparticles are important because experimental evidence for surface spin disorder have been reported in several previous studies [2]. The spinel structure of nickel ferrite as the well-known ferrites posseses the general formula AB_2O_4 where A refers bivalent cations in tetrahedral sites and B trivalent cations in octahedral sites. A more general formula $(A_{1-\lambda}B_{\lambda})(A_{\lambda}B_{2-\lambda})O_4$ represents many others intermediary distributions for the cations, where λ is called inversion parameter [4].

Due to its increasing uses in many new applications, especially magnetic, magneto-optic and gas sensors, synthesis and preparation of nickel ferrite were the goals of many research works and studies during the last two decades [7,8]. Moreover, its capability to host another metal within its molecular structure, such as Zn, Cu, Co, Mn and Cu, has encouraged researchers to find many other fields not easily introduced with the original structure [1-3]. As well, capping the surface of nickel ferrite structures with organic or organometallic agents made them good candidates for ferrofluids, magneto-optics, spintronics, biomedical applications and anodes for batteries [9-13].

This compound was prepared as thin films or powders by several different methods and techniques. The most common ones are sol-gel methods [14,15], the ball-milling technique [16], co-precipitation [17], electrospinning method [18,19], the hydrothermal method [20], the reverse micelles process [21], and the micro-emulsion method [22].

Nickel ferrite nanostructures exhibit featured magnetic properties compared to the larger scale structures [23-26]. Therefore, the interest in synthesizing these nanostructures has increased drastically within the last decade to overcome some technological problems in many modern industries [27-30]. The importance of magnetic measurement and testing applications will continue to rise corresponding to technological trends such as electric mobility, robotics, miniaturization and automation technologies, as well as promising magnetic materials among which nickel ferrite is one of the best [31-36].

In this work, we present results of structure and magnetic study of nickel ferrite nanoparticles synthesized by sol-gel method throughout the x-ray diffraction, scanning electron micrographs, infrared spectroscopy and magnetization as a function of temperature and magnetic field.

2. Experimental Work

Nickel ferrite nanoparticles were synthesized via sol-gel method. Analytical grade nickel nitrate, and iron nitrate were dissolved in deionized water forming solution (a). Solution (b) was formed dissolving citric acid in Ethylen glycol. This mixture was stirred at room temperature for 12 hours in order to obtain a transparent solution. Later both solutions were mixed and stirred at different temperatures 318-363 K during different time periods, from 30 minutes to 4 hours. The obtained product at this step

looks as a dark brown resin. This product was heated in an oven in air atmosphere at 423 K for 48 hours. The gels were placed in a furnace and thermally treated at 873 or 1073 K in air for 2.5 hours [37]. These samples will be called sample (a) and sample (b), respectively. The characterizations of the samples were done by crystallographic phase identification performed on INEL CPS 120 diffractometer with Cu Kα radiation, a graphite monochromator on the diffracted beam and scintillation counter. The morphology and particles sizes of the as prepared samples are determined by scanning electron microscope (JEOL 6400 SEM). Fourier-transform infrared (FTIR) spectra were recorded in the spectral range 380-4000 cm^{-1} using a Perkin-Elmer spectrophotometer on pellets obtained by dispersing the samples in KBr. Magnetic measurements were carried out at room temperature (RT) and 2 K by using a SQUID Quantum Design MPMSXL-7 magnetometer in the temperature range 2-300 K and magnetic field up to 50 kOe.

3. Results and Discussion

The x-ray diffractograms of as-obtained samples of $NiFe_2O_4$ calcinated at 873 K and 1073 K are shown in Fig. (1). All characteristic peaks of $NiFe_2O_4$ are present in the diffraction pattern (JCPDS: 10-0325). It is clear that the diffractogram of sample (a) presents two additional marked peaks, attributed to α-Fe_2O_3 [38]. However, these peaks almost disappear when the calcination temperature increases as shown in Fig. (1b). It is also possible to observe that the diffraction peaks become narrower and sharper, suggesting that particle size increases and crystallinity improves [39].

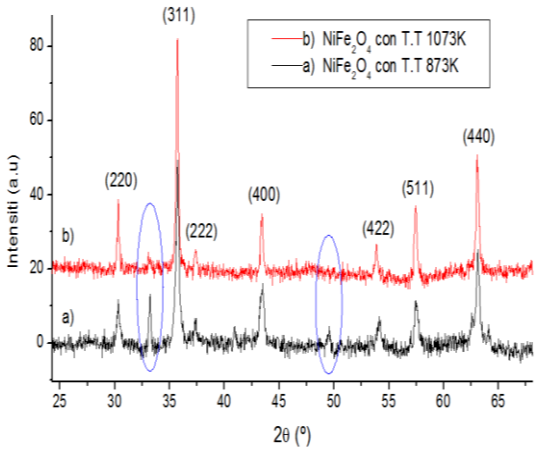
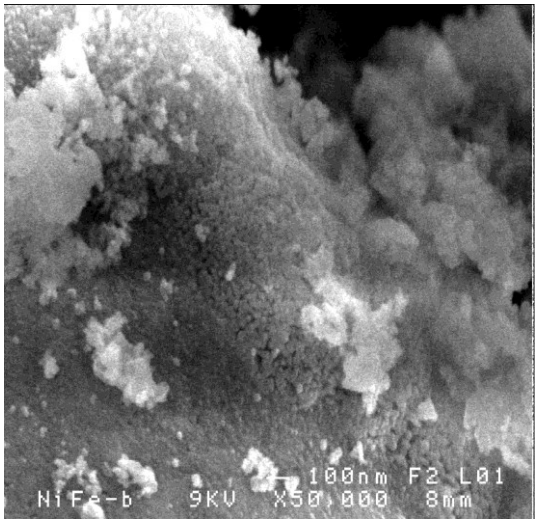
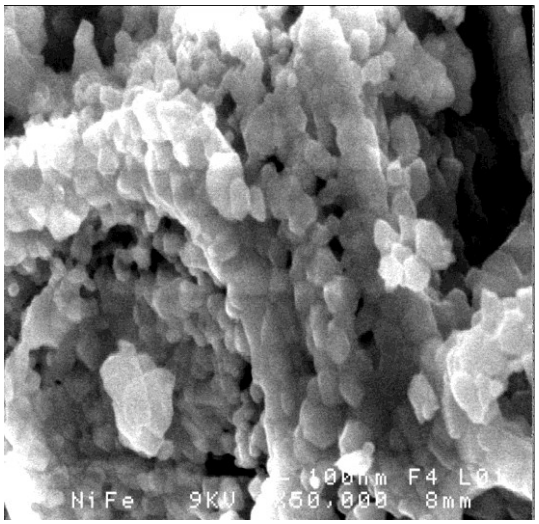


Fig. (1) XRD patterns of nickel ferrite nanoparticles for two calcination temperatures

The SEM micrographs of the samples with different calcination temperatures are shown in Fig. (2). It is possible to notice that – for both samples – the micrographs show agglomerated particles ranging from 20 to 150 nm. However, nickel ferrite is one of the few ternary compounds that the particle size of their nanostructures remains approximately constant when extracted from the nonmetallic substrates on which they are deposited [40,41].



(a)



(b)

Fig. (2) SEM images of nickel ferrite nanoparticles synthesized in this work with two different calcination temperatures (a) 873 K and (b) 1073 K

The observed FTIR spectra of nickel ferrite nanoparticles in the wavenumber range of 380-4000 cm^{-1} are shown in Fig. (3). The spectra of samples calcinated at 873 K and 1073 K present bands at similar wavenumber: about 3411; 1619; 2334; 588 and 408 cm^{-1}. The two first bands can be ascribed to the stretching modes of the free and absorbed water [42,43]. The third band indicates the presence of traces of CO_2. Two characteristics bands at ~590 and 400 cm^{-1} confirm the presence of metal oxides. The band at ~590 cm^{-1} corresponds to intrinsic stretching vibrations of the metal at the tetrahedral sites (Fe ↔ O), whereas the band at ~400 cm^{-1} can be associated to metal vibrations in octahedral sites (Ni ↔ O) [42] (Maensiri et al, 2007).

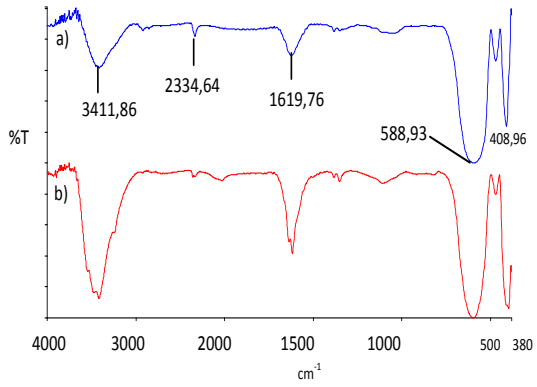


Fig. (3) FTIR spectra of nickel ferrite nanoparticles calcinated at (a) 873 K and (b) 1073 K

Figure (4) shows the experimental DC magnetization measured in the ZFC and FC modes with H= 50 Oe for the heat treated samples. The obtained results are characteristic for superparamagnetic particles with blocking temperature above room temperature. However, the FC data does not show large increase as the temperature decreases as usually happened in an uncoupled system. In the present case, the agglomeration of particles, observed by SEM, suggests the presence a strongly coupled system because of particle-particle interactions which stabilize the spins and prevent alignment with the field [44]. The saturation magnetization and coercitivity for both samples measured at 300 K under the same applied magnetic field are given in Table (1). From these values, it is clear the influence of the calcination temperature on the crystallinity of the ferrite and naturally on the related magnetization.

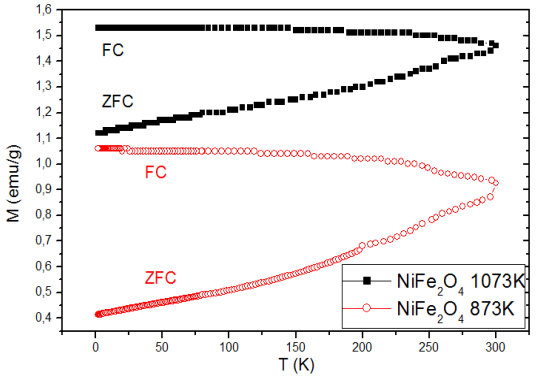


Fig. (4) Temperature dependency of the magnetization obtained in ZFC and FC cycles

The hysteresis loops are shown in Fig. (5) and (6), the inserts in these figures show the magnified view of the M-H curve with small values of H. It is possible to see that the coercitivity (H_c) decreases as the temperature increases from 2 K. It is important to mention that the saturation magnetization of the nanosized nickel ferrite drastically decreases with the decreases in the calcination temperature.

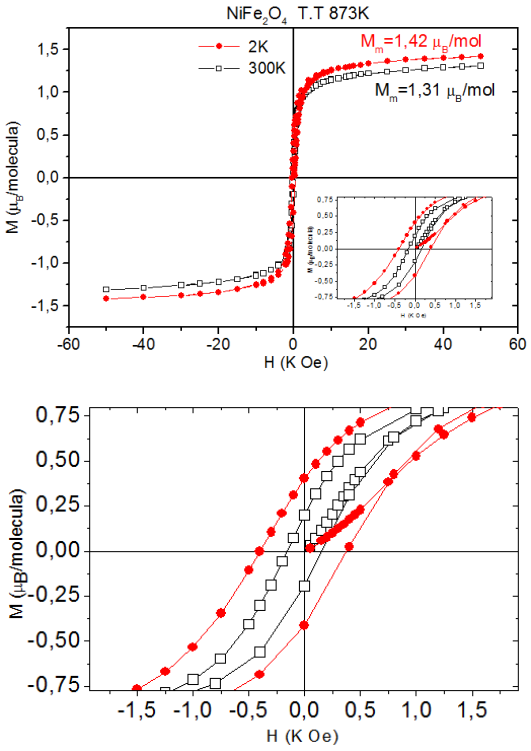


Fig. (5) The M-H curves of the nickel ferrite nanopowder (a) sample at room temperature (RT) and 2 K

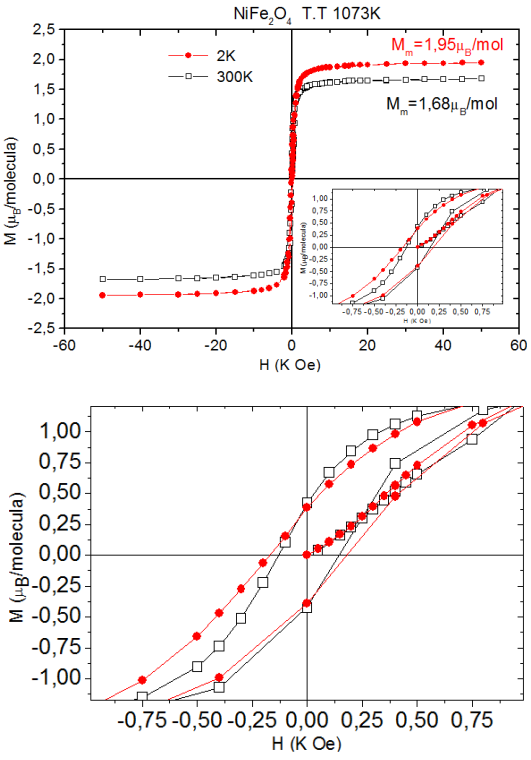


Fig. (6) The M-H curves of the nickel ferrite nanopowder (b) sample room temperature (RT) and 2 K

Table (1) Structural and magnetic parameter of $NiFe_2O_4$ nanoparticles synthesized in this work

Parameter	873 K	1073 K
Cell parameter (Å)	8.327 (1)	8.3334 (9)
Particle size (nm)	~ 20-30	~ 100-150
Measurement T (K)	2	2
	300	300
M_m ($\mu_{B/mol}$)	1.95	1.42
	1.68	1.31
M_r ($\mu_{B/mol}$)	0.388	0.403
	0.423	0.199
H_c (Oe)	170	397
	114	150

4. Conclusions

$NiFe_2O_4$ nanoparticles have been synthesized by the sol-gel method. The calcination step was done at two different temperatures: 873 K and 1073 K in order to study its influence on the structural and magnetic properties. The average size of the synthesized particles was 25 and 125 nm, respectively. The field and temperature dependent magnetization measurements show that the obtained nickel ferrites nanoparticles are superparamagnetic below room temperature. It is clear that the magnetization does not complete saturation even at the highest magnetic field (5.5 T).

References

[1] J. Wang et al., "Synthesis and magnetic properties of $Zn_{1-x}Mn_xFe_2O_4$ nanoparticles", Physica B: Cond. Matt., 349(1-4) (2004) 124-128.

[2] J.G. Duque et al., "Magnetic properties of NiF_2O_4, nanoparticles produced by a new chemical method", Physica B: Cond. Matt., 398(1-2) (2007) 287-290.

[3] D.S. Mathew and R.-S. Juang, "An overview of the structure and magnetism of spinel ferrite nanoparticles and their synthesis in microemulsions", Chem. Eng. J., 129(1-3) (2007) 51-65.

[4] J.L. Gunjakar, A.M. More, K.V. Gurav and C.D. Lokhande, "Chemical synthesis of spinel nickel ferrite ($NiFe_2O_4$) nano-sheets", Appl. Surf. Sci., 254(18) (2008) 5844-5848.

[5] A. Baykal, N. Kasapoglu, Y. Koseoglu, M. Toprak and H. Bayrakdar, "CTAB-assisted hydrothermal synthesis of $NiFe_2O_4$ and its magnetic characterization", J. Alloys Compd., 464(1-2) (2008) 514-518.

[6] F.S. Tehrani, V. Daadmehr, A.T. Rezakhani, R.H. Akbarnejad and S. Gholipour, "Structural, magnetic, and optical properties of zinc- and copper- substituted nickel ferrite nanocrystals", J. Supercond. Nov. Mag., 25(7) (2012) 2443-2455.

[7] G. Dixit, J.P. Singh, R.C. Srivastava, H.M. Agrawal and R.J. Chaudhary, "Structural, magnetic and optical studies of nickel ferrite thin films", Adv. Mat. Lett., 3(1) (2012) 21-28.

[8] A. Alarifi, N.M. Deraz and S. Shaban, "Structural, morphological and magnetic properties of $NiFe_2O_4$ nano-particles", J. Alloys Compd., 486(1-2) (2009) 501-506.

[9] O.A. Hamadi, "Characteristics of CdO-Si Heterostructure Produced by Plasma-Induced Bonding Technique", Proc. IMechE, Part L, J. Mater.: Design and Appl., 222(5) (2008) 65-71.

[10] A.K. Yousif and O.A. Hamadi, "Plasma-Induced Etching of Silicon Surfaces", Bulg. J. Phys., 35(3) (2008) 191-197.

[11] O.A. Hamadi, N.J. Shakir and F.H. Hussain, "Magnetic Field and Temperature Dependent Measurements of Hall Coefficient in Thermal Evaporated Tin-Doped Cadmium Oxide Thin Films", Bulg. J. Phys., 37(4) (2010) 223-231.

[12] O.A. Hammadi, M.K. Khalaf and F.J. Kadhim, "Fabrication of UV Photodetector from Nickel Oxide Nanoparticles Deposited on Silicon Substrate by Closed-Field Unbalanced Dual Magnetron Sputtering Techniques", Opt. Quant. Electron., 47(12) (2015) 3805-3813.

[13] O.A. Hammadi, M.K. Khalaf and F.J. Kadhim, "Fabrication and Characterization of UV Photodetectors Based on Silicon Nitride Nanostructures Prepared by Magnetron Sputtering", Proc. IMechE, Part N, J. Nanomat. Nanoeng. Nanosys., 230(1) (2016) 32-36.

[14] S. Prasad and N.S. Gajbhiye, "Magnetic studies of nanosized nickel ferrite particles synthesized by the citrate precursor technique", J. Alloys Compd., 265(1-2) (1998) 87-92.

[15] H. R. Dehghanpour, "Physical and Chemical Properties of $NiFe_2O_4$ Nanoparticles Prepared by Combustion and Ultrasonic Bath Methods", Russian J. Appl. Chem., 89(1) (2016) 80-83.

[16] I.A. Abdel-Latif, "Fabrication of Nano-Size Nickel Ferrites for Gas Sensors Applications", J. Phys., 1(2) (2012) 50-53.

[17] Y. Shi, J. Ding, X. Liu and J. Wang, "$NiFe_2O_4$ ultrafine particles prepared by coprecipitation/mechanical alloying", J. Magn. Magn. Mater., 205(2-3) (1999) 249-254.

[18] X. Tan, G. Li, Y. Zhao and C. Hu, "Effect of Cu content on the structure of $Ni_{1-x}Cu_xFe_2O_4$ spinels", Mater. Res. Bull., 44 (2009) 2160-2168.

[19] K. Nejati and R. Zabihi, "Preparation and magnetic properties of nano size nickel ferrite particles using hydrothermal method", Chem. Centr. J., 6 (2012) 23-28.

[20] M. Salavati-Niasari, F. Davar and T. Mahmoudi, "A simple route to synthesize nanocrystalline nickel ferrite ($NiFe_2O_4$) in the presence of octanoic acid as a surfactant", Polyhedron, 28(8) (2009) 1455-1458.

[21] K. Maaz, S. Karim, A. Mumtaz, S.K. Hasanain, J. Liu and J.L. Duan, "Synthesis and magnetic

characterization of nickel ferrite nanoparticles prepared by coprecipitation route", J. Magn. Magn. Mater., 321(12) (2009) 1838-1842.

[22] H. Kavas, N. Kasapoglu, A. Baykal and Y. Kaseoglu, "Characterization of $NiFe_2O_4$ nanoparticles synthesized by various methods", Chem. Papers., 63(4) (2009) 450-455.

[23] H. Nathani, S. Gubbala and R.D.K. Misra, "Magnetic behavior of nanocrystalline nickel ferrite: Part I. The effect of surface roughness", Mater. Sci. Eng. B, 121(1-2) (2005) 126-136.

[24] P. Sivakumar, R. Ramesh, A. Ramanand, S. Ponnusamy and C. Muthamizhchelvan, "Synthesis and characterization of $NiFe_2O_4$ nanoparticles and nanorods", J. Alloys Comp., 563 (2013) 6-11.

[25] R.H. Kodama, A.E. Berkowitz, J.E.J. McNiff and S. Foner, "Surface Spin Disorder in $NiFe_2O_4$ Nanoparticles", Phys. Rev. Lett., 77(2) (1996) 394-397.

[26] H. Nathani and R.D.K. Misra, "Surface effects on the magnetic behavior of nanocrystalline nickel ferrites and nickel ferrite-polymer nanocomposites", Mater. Sci. Eng. B, 113(3) (2004) 228-235.

[27] A.B. Nawale, N.S. Kanhe, K.R. Patil, S.V. Bhoraskar, V.L. Mathe and A.K. Das, "Magnetic properties of thermal plasma synthesized nanocrystalline nickel ferrite ($NiFe_2O_4$)", J. Alloys Compd., 509(12) (2011) 4404-4413.

[28] A. Pradeep, P. Priyadharsini and G. Chandrasekaran, "Production of single phase nano size $NiFe_2O_4$ particles using sol-gel auto combustion route by optimizing the preparation conditions", Mater. Chem. Phys., 112(2) (2008) 572-576.

[29] Yu.A. Mirgorod, N.A. Borshch, V.M. Fedosyuk and G.Yu. Yurkov, "Magnetic Properties of Nickel Ferrite Nanoparticles Prepared Using Flotation Extraction", Inorg. Mater., 49(1) (2013) 109-113.

[30] Z. Shi, J. Zhang, D. Gao, Z. Zhu, Z. Yang, Z. Zhang and D. Xue, "Magnetic resonance of the $NiFe_2O_4$ nanoparticles in the gigahertz range", Nanoscale Res. Lett., 8 (2013) 404-408.

[31] O.A. Hammadi, "Photovoltaic Properties of Thermally-Grown Selenium-Doped Silicon Photodiodes for Infrared Detection Applications", Photonic Sensors, 5(2) (2015) 152-158.

[32] O.A. Hamadi, "Characterization of SiC/Si Heterojunction Fabricated by Plasma-Induced Growth of Nanostructured Silicon Carbide Layer on Silicon Surface", Iraqi J. Appl. Phys., 12(2) (2016) 9-13.

[33] O.A. Hammadi and N.E. Naji, "Electrical and spectral characterization of CdS/Si heterojunction prepared by plasma-induced bonding", Opt. Quant. Electron., 48(8) (2016) 375-381.

[34] O.A. Hammadi, "Characteristics of Heat-Annealed Silicon Homojunction Infrared Photodetector Fabricated by Plasma-Assisted Technique", Phot. Sens., 6(4) (2016) 345-350.

[35] O.A. Hammadi, M.K. Khalaf and F.J. Kadhim, "Silicon Nitride Nanostructures Prepared by Reactive Sputtering Using Closed-Field Unbalanced Dual Magnetrons", Proc. IMechE, Part L, J. Mater.: Design and Appl., 231(5) (2017) 479-487.

[36] O.A. Hammadi, "Fabrication of High-Quality Microchannels for Biomedical Applications Using Third-Harmonic Radiation of Nd:YAG Laser", J. Laser Sci. Eng., 10(2) (2018) 61-64.

[37] S. Mitra, K. Mandal and P. Anil Kumar, "Temperature dependence of magnetic properties of $NiFe_2O_4$ nanoparticles embeded in SiO_2 matrix", J. Magnet. Mag. Mater., 306(2) (2006) 254-259.

[38] Y. Cheng et al., "Synthesis and magnetic properties of nickel ferrite nano-octahedra", J. Solid State Chem., 178(7) (2005) 2394-2397.

[39] L.A. Garcia-Cerda and S.M. Montemayor, "Synthesis of $CoFe_2O_4$ nanoparticles embedded in a silica matrix by the citrate precursor technique", J. Magnet. Mag. Mater., 294(2) (2005) e43-e46.

[40] O.A. Hammadi, "Production of Nanopowders from Physical Vapor Deposited Films on Nonmetallic Substrates by Conjunctional Freezing-Assisted Ultrasonic Extraction Method", Proc. IMechE, Part N, J. Nanomat. Nanoeng. Nanosys., DOI: 10.1177/2397791418807347, Online: 4 November 2018

[41] O.A. Hammadi, "Nanostructured CdSnSe Thin Films Prepared by DC Plasma Sputtering of Thermally Casted Targets", Iraqi J. Appl. Phys., 14(4) (2018) 33-36.

[42] S. Maensiri et al., "A simple route to synthesize nickel ferrite $NiFe_2O_4$ nanoparticles using egg white", Scripta Materialia, 56(9) (2007) 797-800.

[43] O.A. Hammadi and N.E. Naji, "Fabrication and Characterization of Polycrystalline Nickel Cobaltite Nanostructures Prepared by Plasma Sputtering as Gas Sensor", Phot. Sens., 8(1) (2018) 43-47.

[44] A.F. Gross et al., "Controlling Magnetic Coupling between Cobalt nanoparticles through Nanoscale Confinement in Hexagonal mesoporous Silica", J. Phys. Chem. B, 107(23) (2003) 5475-5482.

