

Accepted Manuscript

A novel rhombohedron-like nickel ferrite nanostructure: Microwave combustion synthesis, structural characterization and magnetic properties

G. Suresh Kumar, J. Akbar, R. Govindan, E.K. Girija, M. Kanagaraj

PII: S2468-2179(16)30060-0

DOI: [10.1016/j.jsamd.2016.07.003](https://doi.org/10.1016/j.jsamd.2016.07.003)

Reference: JSAMD 41

To appear in: *Journal of Science: Advanced Materials and Devices*

Received Date: 5 June 2016

Revised Date: 9 July 2016

Accepted Date: 13 July 2016

Please cite this article as: G.S. Kumar, J. Akbar, R. Govindan, E.K. Girija, M. Kanagaraj, A novel rhombohedron-like nickel ferrite nanostructure: Microwave combustion synthesis, structural characterization and magnetic properties, *Journal of Science: Advanced Materials and Devices* (2016), doi: 10.1016/j.jsamd.2016.07.003.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



A novel rhombohedron-like nickel ferrite nanostructure: Microwave combustion synthesis, structural characterization and magnetic properties

G. Suresh Kumar^{a,*}, J. Akbar^a, R. Govindan^b, E.K. Girija^b and M. Kanagaraj^c

^a*Department of Physics, K.S.Rangasamy College of Arts and Science (Autonomous), Tiruchengode 637 215, Tamil Nadu, India.*

^b*Department of Physics, Periyar University, Salem 636 011, Tamil Nadu, India.*

^c*Department of Physics and Electronics, Karpagam University, Coimbatore 641 021, Tamil Nadu, India.*

* *Corresponding author. Tel: + 91 9944429261,*

E-mail address: gsureshkumar1986@gmail.com

A novel rhombohedron-like nickel ferrite nanostructure: Microwave combustion synthesis, structural characterization and magnetic properties

Abstract

Research on nickel ferrite nanostructures has drawn a great interest because of its inherent chemical, physical and electronic properties. In this study, we have synthesized rhombohedron - like nickel ferrite nanostructure by a rapid microwave assisted combustion method using ethylenediaminetetraacetic acid as a chelating agent. X-ray diffraction, Fourier Transform Infrared spectrometer, transmission electron microscope and energy dispersive X-ray microanalyser were used to characterize the prepared sample. The magnetic behaviour was analyzed by means of field dependent magnetization measurement which indicates that the prepared sample exhibits a soft ferromagnetic nature with saturation magnetization of 63.034 emu/g. This technique can be a potential method to synthesize novel nickel ferrite nanostructure with improved magnetic properties.

Keywords: Magnetic materials; Nanomaterials; Microwave synthesis; X-ray diffraction; TEM;

1. Introduction

The recent trends in materials research is shifting towards the nanotechnology which offers a unique approach to overcome the shortcomings of their conventional forms due to their large surface to volume ratio and quantum confinement effects [1,2]. Nickel ferrite nanoparticle have received much attention because it is very important group of magnetic nanomaterial due to its extensive applications in high density magnetic storage devices, gas sensors, telecommunication equipments, microwave devices, magnetic guided drug delivery,

magnetic hyperthermia, magnetic resonance imaging, etc., [3-10]. Nickel ferrite has an inverse spinel structure showing ferrimagnetism that originates from the magnetic moment of anti parallel spins between Fe^{3+} ions at tetrahedral sites and Ni^{2+} ions at octahedral sites of the cubic structure [3-10]. The particle size and morphology of nickel ferrite nanoparticle plays a vital role on the above mentioned applications. Recently, a number of synthesis methods such as sol-gel, co-precipitation, hydrothermal, microwave irradiation, combustion, etc., have been developed to synthesize NiFe_2O_4 nanocrystals with various sizes and shapes [3-12]. Most of these methods have been used to synthesize nanoparticles of the required sizes and shapes, but are difficult to employ on a large scale because of expensive and complicated procedures, high reaction temperatures, long reaction times, toxic reagents, removal of by-products and sophisticated processing [5-10]. Among the various methods, microwave synthesise received much attention for the synthesis of nickel ferrite nanoparticles due to several advantages such as shorter time, rapid heating, fast reaction, easy reproducibility, particle size and shape control, high yield, high purity, efficient energy transformation, volume heating, etc., [4,11-13]. Organic modifiers such as oleic acid, urea, citric acid etc., were often used to control the size and shape of the final product in the synthesis process [4, 11, 14]. To the best of our knowledge, there is no report on the synthesis of nickel ferrite nanoparticles *via* microwave combustion method using ethylenediamminetetraacetic acid (EDTA) as an organic modifier. Here we report a rapid and simple microwave combustion method to synthesize rhombohedron-like nickel ferrite nanostructure with the aid of ethylenediamminetetraacetic acid (EDTA) as a chelating agent.

2. Experimental

The chemicals used were nickel nitrate, ferric nitrate, EDTA and NaOH obtained from Merck. All reagents were used without further purification. Distilled water was employed as the solvent.

In a typical synthesis process, nickel nitrate hexahydrate (2.908 g), ferric nitrate nonahydrate (8.08 g) and EDTA (11.167 g) were dissolved in distilled water. The molar ratio of nickel nitrate and ferric nitrate was 1:2 and nitrates to EDTA were 1:1. Then the pH of the obtained mixture was adjusted above 10 by adding 2M of NaOH solution and magnetically stirred for 2 h at 70°C. Subsequently, the obtained brown mixture was put in a microwave oven (2.45 GHz, Samsung, India) and irradiated with microwave power of 600W for 30 minutes. The mixture initially boiled then undergoes dehydration followed by combustion with the evolution of large amount of gas and turns into a black colour solid cake. Finally, the obtained solid cakes were crushed into powder.

Crystallographic identification of the phases of the sample was done by X-ray diffraction (XRD) which was carried using Rigaku MiniFlex II powder X-ray diffractometer in the range between $20^\circ \leq 2\theta \leq 70^\circ$ with Cu K α monochromatic radiation (1.5406 Å). Fourier Transform Infrared (FT-IR) spectrum of the sample was obtained using Perkin Elmer RX1 FT-IR spectrometer in the range 400 to 4000 cm^{-1} . The morphological feature of the sample was examined using JEOL-JEM 2100 transmission electron microscope (TEM). The elemental analysis was done using Oxford INCA energy dispersive X-ray (EDX) microanalyser. Magnetic measurements (M vs H) at room temperature were carried out using vibrating sample magnetometer module (Lakeshore 7407, USA) in the applied field ranges \pm 15 kOe.

3. Results and discussion

EDTA, a member of the polyamino carboxylic acid family, is a complex reagent and it forms metal–EDTA complexes with metal precursors [15]. Hence nickel and iron precursor were mixed with EDTA, a stable Ni–EDTA and Fe–EDTA complexes were formed and it inhibit the reaction between nickel and iron precursor. The microwave heating is emerging technology as an alternative heat source for rapid volumetric heating with shorter reaction time and higher reaction rate. The energy of a microwave photon at a frequency of 2.45 GHz is only 10^{-5} eV or about 1 J mol^{-1} . Upon microwave heating, the microwave energy is transferred to the reaction mixture by interaction of the electromagnetic field at the molecular level resulted in rapid volumetric heating. Due to this rapid volumetric heating, Ni and Fe ions released from their complexes rapidly and caused the burst homogeneous nucleation in a short period and thus crystal grows in anisotropic manner into rhombohedron-like nanostructure as shown in Fig. 1.

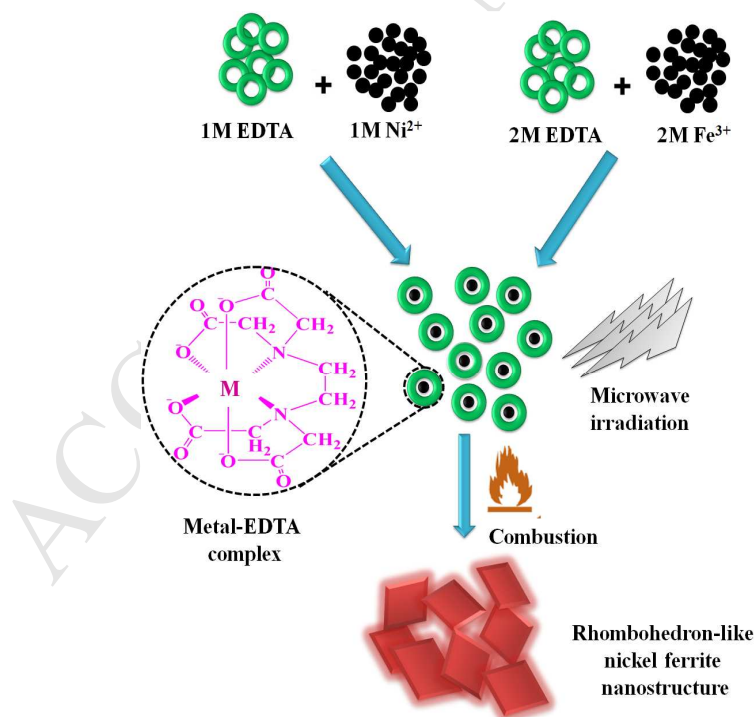


Fig. 1 The schematic of formation of rhombohedron-like nanostructure by microwave combustion method.

The XRD pattern of synthesized sample is shown in figure 2(a). The observed angular positions for the Bragg peaks were compared with Joint Committee on Powder Diffraction Standards (JCPDS) data for NiFe_2O_4 (JCPDS file No. 74–2081). The obtained XRD pattern matched well with the JCPDS data for NiFe_2O_4 which indicates that the prepared sample is mono phase NiFe_2O_4 having cubic inverse spinel structure. XRD pattern exhibits typical reflections from (220), (311), (222), (400), (511), and (440) Miller's planes at $30.14(1)^\circ$, $35.58(3)^\circ$, $37.56(1)^\circ$, $43.20(2)^\circ$, $57.42(1)^\circ$ and $63.20(2)^\circ$, respectively. No secondary phase was observed in XRD analysis of synthesized sample which indicates the phase purity of the synthesized sample. The lattice constants and unit cell volume for the obtained nickel ferrite were calculated as $a = b = c = 8.590 \text{ \AA}$, and $V = 633.83 \text{ \AA}^3$, respectively.

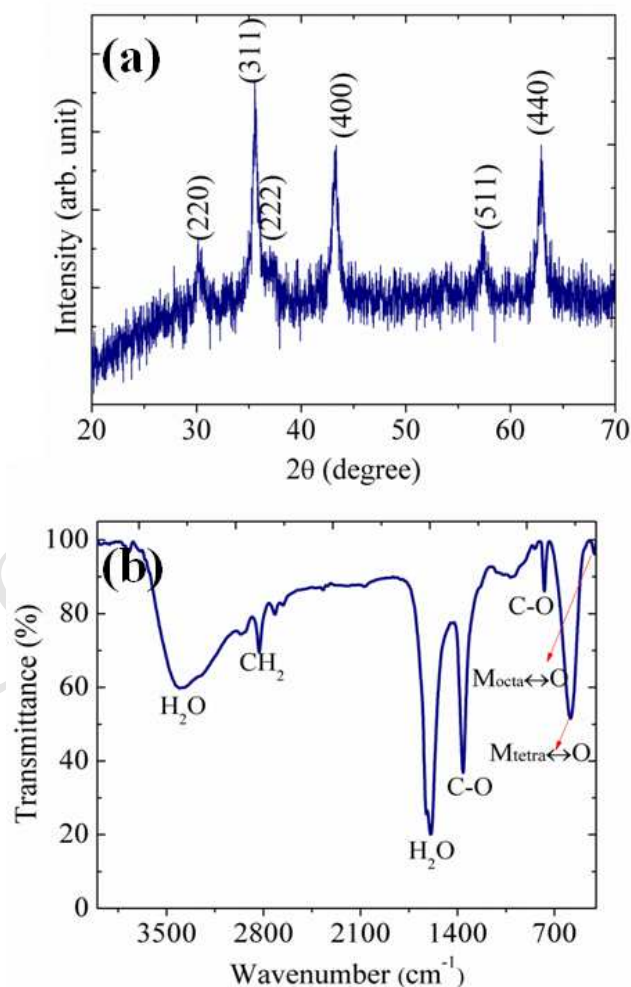


Fig. 2 (a) X-ray diffraction pattern and (b) FT-IR spectrum of the as-synthesized sample.

The formation of the inverse spinel NiFe_2O_4 structure was further supported by FT-IR analysis. Typically two main absorption bands due to metal–oxygen vibration were observed in FT-IR spectrum of ferrites as a common feature of ferrites. The highest one (ν_1) is generally observed in the range $600\text{--}500\text{ cm}^{-1}$ which corresponds to the intrinsic stretching vibration of the metal–oxygen at the tetrahedral site ($\text{M}_{\text{tetra}}\leftrightarrow\text{O}$), whereas the lowest band (ν_2) observed in the range $450\text{--}385\text{ cm}^{-1}$ is attributed to the stretching vibration of the metal–oxygen at octahedral site ($\text{M}_{\text{octa}}\leftrightarrow\text{O}$) of ferrite [3-6]. In the FTIR spectrum of the synthesized sample (figure 2(b)), we have observed a band with high intensity at 585 cm^{-1} and a band with low intensity at 411 cm^{-1} which are due to $\text{M}_{\text{tetra}}\leftrightarrow\text{O}$ and $\text{M}_{\text{octa}}\leftrightarrow\text{O}$ vibration of nickel ferrite, respectively. These two bands are responsible for the vibration of metal ions in the crystal lattices [3]. The bands observed at 1360 cm^{-1} is due to C-O stretching vibration which is originating from organic residue. Also, sharp peaks observed at 2923 and 2852 cm^{-1} are attributed to vibrations of CH_2 group of organic residue [4]. Moreover, a strong band at 1600 cm^{-1} and a broad band around 3400 cm^{-1} were observed in the FT-IR spectrum which are attributed to the stretching and bending vibrations of water molecules adsorbed on the surface of the nickel ferrite [4-10].

Figure 3 (a) and (b) shows the TEM images which indicates that the sample consist of rhombohedron-like nanostructure with size $90\text{--}150\text{ nm}$. Moreover TEM image at high magnification shows the resolved lattice fringes with spacing of 2.91 \AA . The particle size distribution of nanostructure is shown in figure 3 (c). EDX spectrum of the synthesized sample is shown in figure 3 (d). As expected, nickel ($9.29(3)\text{ at.}\%$), iron ($18.54(2)\text{ at.}\%$), oxygen ($33.30(2)\text{ at.}\%$) and carbon ($38.87(3)\text{ at.}\%$) are existed in the as-synthesized sample. The quantitative analysis revealed that the atomic ratio of nickel and iron in the sample is 1:2

which matches the stoichiometric ratio of NiFe_2O_4 and effectively proves the formation of stoichiometric nickel ferrite.

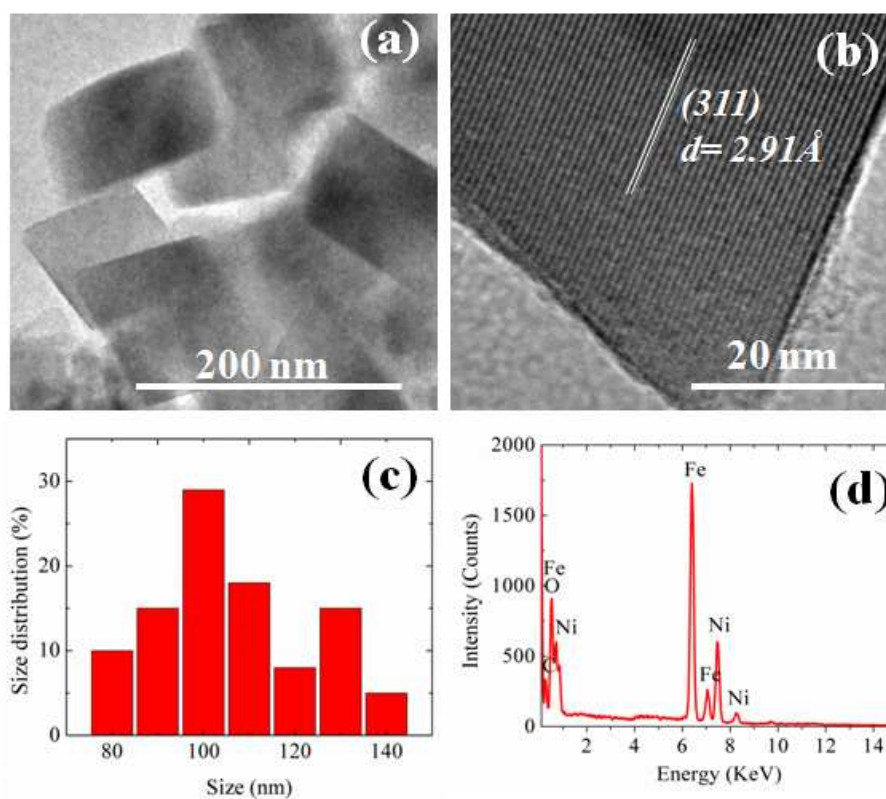


Fig. 3 TEM images (a) low magnification (b) high magnification and (c) particle size distribution and (d) EDX spectrum of synthesized sample.

Magnetic field dependence of dc magnetization curve of the as-synthesized sample is shown in Fig. 4. It clearly indicates the soft ferromagnetic nature of the prepared sample. The saturation magnetization (M_s) and coercivity (H_c) were found as 63.034 emu/g and 275.02 G, respectively. Compared with the nickel ferrite nanoparticles synthesized by other method [3-6], the nickel ferrite nanostructure prepared in the present study possessed high saturation magnetization. Bulk nickel ferrite has an inverse spinel structure with ferrimagnetic order below 850 K. Its magnetic structure consists of two antiferromagnetically coupled sublattices *i.e.* tetrahedral A (denoted as T_d site) and octahedral B (denoted as O_h -sites) sites where Ni^{2+} ions are in octahedral B sites and Fe^{3+} ions are distributed on both the tetrahedral A and the

octahedral B sites equally. According to the crystal field theory, the magnetic moments arise from the local moments of the Ni^{2+} with $3d^8$ electrons and Fe^{3+} with $3d^5$ electrons. The net magnetization comes from the Ni^{2+} ions alone ($\sim 2\mu_B$) since Fe^{3+} moments $\sim 5\mu_B$ in both the A and B sites are antiparallel and cancel with each other. This type of ordering results in a saturation magnetization of $2\mu_B/\text{formula unit (f.u.)}$ or $\sim 50 \text{ emu/g}$ at 0K [16-19]. The value of M_s for obtained nickel ferrite rhombohedron-like nanostructure is comparable to that of theoretical saturation magnetization of 50 emu/g calculated using Neel's sublattice theory and to the reported value of 56 emu/g for the bulk sample [16-19]. M_s is the intrinsic property of magnetic materials, but synthesis method and conditions may affect M_s of the ferrite nanoparticles [3-10]. Luders *et al.* have reported a 250% increase in saturation magnetization due to the cationic interchange in NiFe_2O_4 thin films synthesized by sputtering [19]. It is noteworthy that in comparison to the bulk counterpart, the prepared NiFe_2O_4 rhombohedron-like nanostructure exhibits high coercivity value than the bulk form [16].

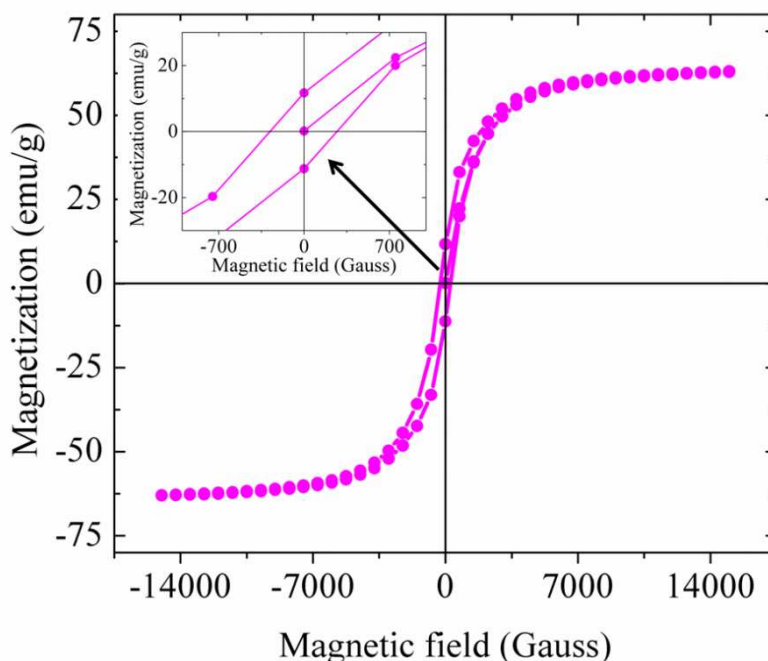


Fig. 4 Magnetic hysteresis curve for the as-synthesized sample measured at room temperature.

4. Conclusion

Nickel ferrite nanostructure with rhombohedron shape was synthesized by microwave assisted combustion method using EDTA as a chelating agent. The prepared nickel ferrite exhibits a soft ferromagnetic behaviour with high saturation magnetization which may find novel application in high density magnetic storage devices, gas sensor, microwave devices, magnetic hyperthermia, magnetic resonance imaging, etc.

Acknowledgement

The authors (G.S.K and J.A) express their sincere thanks to Dr.V. Radhakrishnan, Principal, K.S. Rangasamy College of Arts and Science (Autonomous), Tiruchengode, India, for his constant encouragement to carry out this work. The authors express their special thanks to Prof. B. Viswanathan, Head, NCCR, IIT-Madras, India for providing TEM facility.

References

- [1]. R. Valiev, Materials science: Nanomaterial advantage, *Nature* 419 (2002) 887–89.
- [2]. E. Roduner, Size matters: Why nanomaterials are different, *Chem. Soc. Rev.* 35 (2006) 583–92.
- [3]. H. Hajihashemi, P. Kameli, H. Salamati, The Effect of EDTA on the synthesis of Ni ferrite nanoparticles, *J. Supercond. Nov. Magn.* 25 (2012) 2357–63.
- [4]. D. Wang, J. Zhou, X. Zhou, X. Ke, C. Chen, Y. Wang, Y. Liu, L. Ren, Facile ultrafast microwave synthesis of monodisperse MFe_2O_4 (M: Fe, Mn, Co, Ni) superparamagnetic nanocrystals. *Mater. Lett.* 136 (2014) 401–03.
- [5]. J. Huo, M. Wei, Characterization and magnetic properties of nanocrystalline nickel ferrite synthesized by hydrothermal method. *Mater. Lett.* 63 (2009) 1183–84.

- [6]. P. Sivakumar, R. Ramesh, A. Ramanand, S. Ponnusamy, C. Muthamizhchelvan, Synthesis and characterization of nickel ferrite magnetic nanoparticles, *Mater. Res. Bull.* 46 (2011) 2208–11.
- [7]. D. Chen, X. He, Synthesis of nickel ferrite nanoparticles by sol-gel method, *Mater. Res. Bull.* 36 (2001) 1369–77.
- [8]. S. Thakur, R. Rai, S. Sharma, Structural characterization and magnetic study of NiFe_xO_4 synthesized by co-precipitation method. *Mater. Lett.* 139 (2015) 368-72.
- [9]. D. Chen, D. Chen, X. Jiao, Y. Zhao, M. He, Hydrothermal synthesis and characterization of octahedral nickel ferrite particles. *Powder Tech.* 133 (2003) 247–50.
- [10]. J.Y. Patil, D.Y. Nadargi, J.L. Gurav, I.S. Mulla, S.S. Suryavanshi, Synthesis of glycine combusted NiFe_2O_4 spinel ferrite: A highly versatile gas sensor, *Mater. Lett.* 124 (2014) 144–47.
- [11]. M.H Mahmoud, A.M. Elshahawy, S.A.Makhlouf, H.H. Hamdeh, Mössbauer and magnetization studies of nickel ferrite nanoparticles synthesized by the microwave-combustion method, *J. Magnetism Magnetic. Mater.* 343 (2013) 21–26.
- [12]. M. Sertkol, Y. Koseoglu, A. Baykal, H. Kavas, A. Bozkurt, M.S. Toprak, Microwave synthesis and characterization of Zn-doped nickel ferrite nanoparticles, *J. Alloys Compd.* 486 (2009) 325–29.
- [13]. I. Bilecka, M. Niederberger, Microwave chemistry for inorganic nanomaterials synthesis, *Nanoscale* 2 (2010) 1358–74.
- [14]. D.T.T. Nguyet, N.P. Duong, T. Satoh, L.N. Anh, T.T. Loan, T.D. Hien, Crystallization and magnetic characterizations of DyIG and HoIG nanopowders fabricated using citrate sol-gel, *J. Sci.: Adv. Mater. Dev.* 1 (2016) 193–199.

- [15]. W. A. Norvell and W. L. Lindsay, Reactions of EDTA complexes of Fe, Zn, Mn and Cu with soils, *Soil. Sci. Soc. Am. J.* 33 (1968) 86–91.
- [16]. A. Shan, X. Wu, J. Lu, C. Chen and R. Wang, Phase formations and magnetic properties of single crystal nickel ferrite (NiFe_2O_4) with different morphologies, *Cryst. Eng. Comm.* 17 (2015) 1603–1607.
- [17]. H. Perron, T. Mellier, C. Domain, J. Roques, E. Simoni, R. Drot and H. Catalette, Structural investigation and electronic properties of the nickel ferrite NiFe_2O_4 : a periodic density functional theory approach, *J. Phys.: Condens. Matter* 19 (2007) 346219 (10pp).
- [18]. S. Anjum, G. H. Jaffari, A.K Rumaiz, M.S. Rafique, and S. I. Shah, Role of vacancies in transport and magnetic properties of nickel ferrite thin films, *J. Phys. D: Appl. Phys.* 43 (2010) 265001 (7pp).
- [19]. U. Luders, M. Bibes, J.F. Bobo, M. Cantoni, R. Bertacoo and J. Fontcuberta, Enhanced magnetic moment and conductive behavior in NiFe_2O_4 spinel ultrathin films, *J. Phys. Rev. B* 71 (2005) 134419 (7pp).

Research highlights

- Rapid and facile method to synthesize nickel ferrite
- Novel rhombohedron-like nanostructure
- The obtained product exhibit soft ferromagnetic nature

ACCEPTED MANUSCRIPT