Journal of Molecular Structure 1076 (2014) 55–62

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Structural, magnetic, dielectric and optical properties of nickel ferrite nanoparticles synthesized by co-precipitation method

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HIGHLIGHTS

- $NiFe_2O_4$ nanoparticles were synthesized by a co-precipitation method.
- Raman spectroscopy indicates mixed spinel structure for $NiFe_2O_4$.
- M–H loops and ESR spectra suggested strong surface effects in the nanoparticles.
- Photoluminescence study indicates that Ni^{2+} ions occupy both tetrahedral and octahedral sites.

ARTICLE INFO

Article history:
Received 9 June 2014
Received in revised form 16 July 2014
Accepted 17 July 2014
Available online 23 July 2014

Keywords:
Ferrites
Crystal structure
Optical properties
Dielectric properties
Magnetic properties

ABSTRACT

Nickel ferrite nanoparticles were synthesized by wet chemical co-precipitation method and the corresponding temperature dependent structural, magnetic and optical properties of these nanoparticles have been investigated. X-ray diffraction patterns show the single phase cubic spinal crystal structure belonging to the space group Fd3m. The average crystallite size varies in the range 8–20 nm with varying sintering temperature. Raman spectroscopy exhibits a doublet-like peak behaviour which indicates the presence of mixed spinel structure. The saturation magnetization, coercivity and remanence increase with increasing sintering temperature from 250 to 550 °C. The non-saturation and low values of magnetization at high fields indicate the strong surface effects to magnetization in $NiFe_2O_4$ nanoparticles. The *g*-value calculated from electron spin resonance spectrum indicates the transfer of divalent metallic ion from octahedral to tetrahedral site (i.e. mixed spinel structure). The dielectric permittivity, loss tangent and ac conductivity measurements show strong temperature dependence at all frequencies. The observed ac conductivity response suggests that the conduction in ferrite nanoparticles is due to feeble polaron hopping between Fe^{3+}/Fe^{2+} ions. Room temperature UV–vis diffuse spectra indicate that $NiFe_2O_4$ is an indirect band gap material with band gap ranges from 1.27 to 1.47 eV with varying sintering temperature. The photoluminescence study clearly indicates that the Ni^{2+} ions occupy both octahedral and tetrahedral sites confirming mixed spinel structure.

Introduction

Spinal ferrites are the most interesting magnetic oxides widely used due to their interesting magnetic, electrical, and optical properties. Their excellent qualities like high electrical resistivity, high permeability and negligible eddy current losses for high frequency electro-magnetic wave propagation make them suitable for many technological applications such as high density magnetic storage, microwave devices, telecommunication equipments, magnetic fluids, magnetically guided drug delivery and gas sensors. In nano region the properties of ferrites are strongly depends on the particle size. Due to large surface/volume ratio the properties of nanoferrites are different from their bulk counterparts [1–3]. The reduction in the particle size of these ferrites leads to the variation in Neel temperature [4], higher values of coercivity [5], lower values of saturation magnetization and reduced or enhanced magnetic moments [6–8], etc. There are reports available which support that surface structure and magnetic properties are strongly related to each other [9,10].

Among various ferrites nano size nickel ferrite is a soft magnetic material with low coercivity and saturation magnetization but high electrical resistivity. Hence, it is a suitable material for

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http://dx.doi.org/10.1016/j.molstruc.2014.07.048
0022-2860/

magnetic and magneto-optical applications. Nanostructured nickel ferrite exhibits small hysteresis and hence, is considered as a good core material for power transformers and telecommunication applications [11,12]. Nanoparticles of nickel ferrite are also used in gas and humidity sensing, and catalytic applications.

The bulk nickel ferrites have inverse spinel cubic structure [13]. The crystal structure is face centred cubic in which unit cell containing 32 O^{2-}, 8 Ni^{2+} and 16 Fe^{3+}ions. The oxygen ions form 64 tetrahedral (A) and 32 octahedral (B) sites, where 24 cations are placed. In inverse spinel nickel ferrite nanoparticles, the A site is fully occupied by Fe^{3+} ions and B site is occupied by Ni^{2+} and Fe^{3+} ions. Hence, the ferrimagnetism in these materials is a result of anti parallel spins between Fe^{3+} and Ni^{2+} at A and B sites respectively. According to Neel's ferrimagnetic theory, the magnetic moment per formula unit (M) in the μ_B units is given as: $M = M_{oct} - M_{tet}$, where M_{oct} and M_{tet} are the magnetic moments of the octahedral and tetrahedral sites, respectively. From last few years, many physical and chemical methods have been used to synthesize nanosize ferrites. Since structural, magnetic and electrical properties of ferrites depends their composition and microstructure and hence are strongly dependent on the synthesis method and synthesis conditions [14]. Some of these methods are mechanical milling [15], co-precipitation [16,17], hydrothermal reaction [18], micro emulsion method [19] and sol–gel technique [20]. The co-precipitation method is widely used because of its simplicity, low cost, low synthesis temperature and small particle size.

The structural and electronic properties (near and at the surface of the particle) are modified when the particle size of a material is reduced [21]. It has been reported that the electrical conductivity and the dielectric loss decrease with a reduction of grain size in nano-structured nickel ferrites [22,23] and again depends on synthesis route. It is reported that nickel ferrite nano particles exhibit ferrimagnetism, or superparamagnetism depending on the microstructure of the samples [24]. Ferrimagnetism is generally associated with samples with a grain size of 15 nm or more and superparamagnetism with samples of smaller grain size (<10 nm). The metal ions of these materials are surrounded by oxygen atoms and give rise to super-exchange interaction between the tetrahedral and octahedral sub lattices which in turn affects the magnetic properties [25]. The magnetization also depends on the other factors such as magneto crystalline anisotropy, spin canting effect, and dipolar interactions between the moments on the surface of the nanoparticles [26]. Further, the optical properties of nano ferrites are relatively less explored. These properties like magneto-optical properties, optical band gaps etc. are important from technological aspect. The main objective of this work is to study the structural, magnetic, optical and photoluminescence properties of nickel ferrite nanoparticles. In this paper, we report the structural, magnetic, dielectric, optical and photoluminescence properties for $NiFe_2O_4$ nanoparticles sintered at different temperatures.

Experimental

$NiFe_2O_4$ nanoparticles were synthesized by co-precipitation method. Nickel nitrate, ferric nitrate and sodium hydroxide were used as starting materials. Oleic acid was used as surfactant. Aqueous solutions of ferric nitrate and nickel nitrate were prepared in de-ionized water and NaOH solution was added to it slowly and the solution were stirred continuously using a magnetic stirrer until a pH level of 10–11 was reached. This solution was heated at 80 °C for an hour. 5 ml of oleic acid was added for surface coating and the solution was further heated at 90 °C for half an hour. This product was later cooled to room temperature followed by the addition of few drops of HNO_3 to yield the precipitate. The precipitate was thoroughly washed with distilled water and acetone to remove traces of sodium and nitrates. It was kept overnight for drying. The obtained powder was grounded and kept for calcination at different temperatures i.e. 250 °C, 350 °C, 450 °C, and 550 °C for 2 h and were coded as N1, N2, N3 and N4 respectively.

The structural characterization of all the samples were done by X-ray Diffraction (XRD 6000, Shimadzu) using CuKα radiation (λ = 1.54059 Å) at 40 kV and 30 mA. Scanning was performed from 20° to 70° at a step size of 0.02 °/s. Fourier Transform infrared (FTIR) spectra were obtained on Spectrum BX-II spectrometer (Perkin Elmer) using pallet of KBr with (ratio of sample and KBr is 1:100) and without samples. Raman spectra have been recorded on Argon ion T64000, HORIBA JOBIN YVON spectrometer. The morphological information was gathered using high resolution transmission electron microscope (HRTEM, Technai G20-stwin, 300 kV). The system was equipped with super twin lenses having point resolution of 1.44 Å and line resolution 2.32 Å and the measurements were taken on samples deposited over carbon coated copper grids. For the dielectric measurements, the calcined powders at 550 °C were palletized and were sintered at 550 °C for 2 h. The dielectric measurements were carried out on silver coated pellet which was sintered at 550 °C for 2 h by using LCR meter (PSM 1735) in the temperature range (40–400 °C) with room temperature and at few selected temperatures at various frequencies with step size of 5 °C, data acquisition was fully automated by giving heating rate of 2 °C/min. Magnetic properties were explored by magnetization hysteresis (M–H) measurements which were carried out at room temperature by using Vibrating Sample Magnetometer (VSM, Lakeshore 7400 series). A X-band (f = 9.878 GHz, Bruker Biospin GmbH) electron spin resonance (ESR) spectrometer employing an AC magnetic field (100 kHz) modulation technique was used to record the first derivative absorption signal of Ni ferrite nanopowder. Band gap variation with temperature was found by using UV-Diffuse Reflectance on (Ocean optics UV–Visible 4000). The photoluminescence spectrum was measured on LS-55 Luminescence spectrometer (Perkin Elmer).

Result and discussion

Structural analysis

XRD studies

XRD patterns of N1, N2, N3, and N4 samples are shown in Fig. 1. The patterns show the formation of single phase cubic spinal

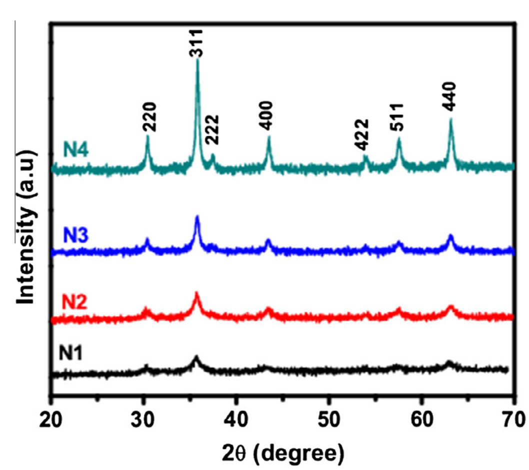

Fig. 1. XRD patterns for $NiFe_2O_4$ nanoparticles sintered at 250 °C (N1), 350 °C (N2), 450 °C (N3) and 550 °C (N4).