



Effect of doping of manganese ions on the structural and magnetic properties of nickel ferrite



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ARTICLE INFO

Article history:

Received 14 October 2015

Received in revised form

21 December 2015

Accepted 25 January 2016

Available online 28 January 2016

Keywords:

Ferrites

Nanocrystalline materials

Magnetization

Mossbauer spectroscopy

Raman spectroscopy

ABSTRACT

We report the synthesis of Mn doped nickel ferrite having the generic formula $Ni_{1-x}Mn_xFe_2O_4$ ($x = 0.05, 0.10, 0.15$) through chemical co-precipitation technique. The samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, dc magnetization studies and Mössbauer spectroscopy. XRD measurements showed the formation of pure spinel phase with particle size homogeneity. Rietveld refinement of the diffraction patterns using GSAS showed the presence of cationic vacancies in the sample. The analysis of the Williamson-Hall plot indicated the presence of strain in all the samples. Raman spectroscopy indicated the coexistence of an additional tetragonal phase $P4_122$ in addition to the cubic phase $Fd\bar{3}m$ in the samples. Dc magnetization studies showed the sample possessed negligible coercivity coupled with ferrimagnetic nature, corroborated by the Mössbauer measurement. The Mössbauer studies gave evidence of distortion in the crystal structure due to the dopant ions and the presence of cationic vacancies. The samples possessing low magnetocrystalline anisotropy along with ferrimagnetic behavior are a potential candidate for biomedical industries.

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1. Introduction

Ferrites have been extensively studied for their excellent magnetic properties since Neel laid the foundation of magnetism in ferrites [1]. Their basic characteristics such as coercivity, electrical conductivity, saturation magnetisation can be tailored to suit specific applications. Recently ferrites have gained special attention in the biomedical industry owing to their novel characteristics such as zero coercivity and high saturation magnetisation [2]. It makes them a potential candidate for targeted drug delivery and magnetic resonance imaging (MRI) techniques opening up new avenues in disease diagnostics and their treatment [3–5]. Recently the Mn–Zn ferrites have been found as suitable candidates for hyperthermia and MRI contrast agents. They are characterized by small remnant magnetisation and a low magnetocrystalline anisotropy. The system of nickel ferrites is suitable for hyperthermia applications owing to their soft magnetic nature [6–8]. A low value of coercive field is desirable since it indicates minimum energy loss during the

switching of the magnetic field. These particles form the basis of ferrofluids which have important applications in rocket propulsion and optical filters [9–11].

The properties of nano-ferrites are dependent on the synthesis route undertaken for such as sol–gel, chemical co-precipitation, high energy milling, pulsed laser deposition and many others [12,13]. Chemical co-precipitation offers the advantage of preparation of particles with maximum purity and high degree of particle size homogeneity [14,15]. The particle size can be controlled depending upon the use of suitable capping agents which permit the growth of particles as small as 2 nm. The properties of ferrites are strongly co-related to their particle size; a change in particle size alters the surface to volume ratio of the particle thereby altering the chemical coordination of the compound [16,17].

Nickel ferrite has been a subject of widespread investigation due to its excellent magnetic and dielectric properties. The compound Ni ferrite has an inverse spinel cubic structure. The crystal comprises two interpenetrating sub-lattices A and B which are tetrahedrally and octahedrally coordinated respectively. The tetrahedral site is occupied by Fe^{3+} ions while the B site consists of an equal distribution of Fe^{3+} and Ni^{2+} ions. The ferrimagnetic nature arises from the anti-parallel alignment of spins of unequal magnitude at

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the A site and the B site. The doping of a transition metal such as Co, Mn, leads to a remarkable change in the magnetic properties of the compound [18]. The magnetic property is a complex interplay of the cationic distribution and magnetic disorder in the crystal. The dopant shows a site preference for the tetrahedral or the octahedral site depending upon the dopant concentration and symmetry of bond formation [19]. The site preference of the dopant can be determined by Mössbauer studies since it is sensitive to the presence of iron ions whose site occupancy will be affected by the addition of dopant ions [20]. Difference in the ionic radius of the dopant and the parent cations may induce a stress in the lattice which can be verified by the X-ray diffraction along with the purity of the phase formed.

There have been fewer reports which deal with the effect of doping of Mn ions on the various properties of the nickel ferrite synthesized through chemical coprecipitation technique. In the present work, we have synthesized a series of Mn doped Ni ferrite samples having the generic formula $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$, with 'x' taking the values 0.05, 0.10 and 0.15. The samples have been synthesized by standard chemical co-precipitation route to ensure particle size uniformity and purity of phase. X-ray diffraction studies were carried out to study the structural changes in the crystal. The analysis of vibrational modes and the short range ordering of the lattices were carried out using Raman spectroscopy. We have conclusively shown that doping of Mn into Nickel ferrite leads to a loss of symmetry of the octahedral site which has not been reported for these ferrites in the literature yet. The magnetisation studies show the particles have negligible coercive field coupled with ferrimagnetic behavior. The detailed Mössbauer studies helped to determine the occupancy of Fe ions at the sub-lattices and confirmed the ferrimagnetic behavior of the sample. The low coercivity (<15 Oe) coupled with a high saturation magnetisation (>61 emu/g) make it an attractive candidate for medical and ferrofluid applications. The value of saturation magnetisation obtained in our studies is higher than previous reports [21,22]. In this manuscript we develop a cogent theory to investigate the relation between the structural and magnetic properties of the synthesized ferrites.

2. Experimental procedure

The samples of Mn doped Ni ferrite $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ were synthesized via the standard chemical co-precipitation technique. The reagents $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, FeCl_3 , $\text{Mn}(\text{Cl})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in a stoichiometric ratio in de-ionized water. The solution was stirred using a magnetic stirrer while NaOH was added drop by drop till the pH of the solution reached 7 with the appearance of precipitate. The pH was increased to 10 so as to enable complete precipitation. The solution was digested at 80 °C for 2 h so that no component was left un-reacted. It was washed dried and ground into fine powder. The ground sample was fired at 1100 °C in a furnace and slowly cooled to obtain fine black particles of the ferrite. All the characterizations were done with these powders.

The X-ray diffraction of the samples $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.05, 0.10, 0.15$) were carried out using Bruker D8 Advance X-Ray Diffractometer at room temperature (300 K). The source of radiation was $\text{Cu-K}\alpha$ having a wavelength of 1.5406 Å with the data collected at a scanning speed of 0.02° per sec in the angular range of $15^\circ \leq 2\theta \leq 70^\circ$. The TEM images for studying the morphological characteristics of the samples were taken with a JEOL200 high resolution microscope. Raman spectroscopy of the polycrystalline samples was carried out by spectrometer from Renishaw Instruments at room temperature using 514.5 nm line of Argon ion laser in the frequency range $100 \text{ cm}^{-1} - 1000 \text{ cm}^{-1}$ to study the vibrational and structural details of the crystal. The magnetic measurements of the samples were carried out using Quantum

Design SQUID magnetometer at room temperature upto a field of 7 T. The Mössbauer spectroscopy measurements were carried out using a constant acceleration Mössbauer spectrometer calibrated using a 12 μm high purity Fe foil at room temperature. The spectra were measured in zero magnetic field and fitted using LGFIT2 program [23].

3. Results and discussions

3.1. XRD report

The X-ray diffraction patterns of the all the samples (Mn5, Mn10 and Mn15) were matched with the standard reference pattern of NiFe_2O_4 (JCPDS card no. 10–325). The samples belonged to the space group $Fd\bar{3}m$ and the peaks were indexed with the corresponding planes of the unit cell. The absence of additional peaks indicated the presence of single phase. The diffraction profiles were fitted using GSAS by Rietveld refinement technique [24]. The peak shapes were modeled using pseudo-Voigt function with Finger, Cox and Jephcoat correction for reflection asymmetry due to axial divergence [25]. χ^2 was used as a measure of goodness of fit of the refined profiles. The values of chi-square lay between 1.2 and 1.7 while the values of reliability factors (R_{wp} and R_p) were less than 0.1 indicating a strong agreement between the experimental patterns and the calculated patterns (Fig. 1). The Williamson–Hall graph (Fig. 2) was plotted for all the samples and the value of crystallite size was extracted from the plots using Scherrer's equation as shown in Table 1.

Analysis of the diffraction peaks showed that the average size of the crystallite of all the samples lie in the range 43–50 nm indicating size homogeneity. The lattice constant shows a slight increase with increasing Mn ion concentration in the sample. The lattice expansion can be explained on the basis of replacement of the smaller Ni^{2+} ions (0.79 Å) by the larger Mn^{2+} ions (0.83 Å). The refinement of the samples indicated the presence of cation vacancies in the crystal. Analysis of the Williamson–Hall plot indicates the presence of strain in the sample which may be attributed to the difference in ionic radii of the Fe^{3+} and Mn^{2+} as well as the presence of cation vacancies.

3.2. TEM studies

Fig. 3 shows the microstructure of Mn5 sample. The particles appear to be spherical in shape with a size of around 50 nm. This is in agreement with the crystallite size calculated from the refinement of the XRD data. The chemical coprecipitation ensures uniform particle size distribution which can be observed from the nearly monodispersed particles in the microstructure image. Further, it is observed that the particles are single grain crystals without any intraparticle structure. It indicates the highly crystalline nature of the nanoparticles. A small degree of agglomeration is observed on account of the increase in the surface energy of the particles as their size is reduced to nano dimensions. The inset shows the FFT image carried out on a small cluster of nanoparticles. The bright diffraction spots arise out of the 311 and 220 planes which can be seen clearly in the image. The results of TEM and XRD are in excellent agreement with each other.

3.3. Raman analysis

Fig. 4 shows the Raman spectra of all the samples. Nickel ferrite belonging to the space group $Fd\bar{3}m$ (O_h^7) crystallizes in an inverse spinel structure. The crystal consists of two interpenetrating sub-lattices which have tetrahedral coordination and octahedral coordination. The tetrahedral site consisting of Fe ions belongs to T_d

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