Research articles

Superior magnetic properties of Ni ferrite nanoparticles synthesized by capping agent-free one-step coprecipitation route at different pH values

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ABSTRACT

In this work, well-dispersed nanoparticles of $NiFe_2O_4$ with diameters less than 10 nm and good crystallinity and excellent magnetic properties were synthesized via a simple one-step capping agent-free coprecipitation route from metal chlorides. The ammonia was used as the precipitating agent and also the solution basicity controller. The effect of pH value during the coprecipitation process was investigated by details through microstructural, optical and magnetic characterizations of the synthesized particles using X-ray diffraction, transmission electron microscopy, Fourier transform infrared and UV–vis spectroscopy, and vibrating sample magnetometer. The results showed that the particle size, departure from the inverse spinel structure, the band gap value and the magnetization of Ni ferrite samples increase with pH value from 9 to 11 indicating the more pronounced surface effects in the smaller nanoparticles.

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1. Introduction

Over the years, the spinel ferrites with general formula of $(M,Fe)_3O_4$ where M is a divalent cation, have drawn considerable attention. This is because of not only their striking physical and chemical properties, but also their technological applications including magnetic storage, magnetic diagnosis, ferro-fluids, electro-communication, microwave devices, gas sensing, and so on [1]. Each application field requires a certain ferrite with specific properties which can be engineered by the preparative conditions. In particular, for biomedicine applications, such as drug delivery or contrast agents in magnetic imaging, the material needs to have room temperature soft ferromagnetic behavior with low eddy current loss at high frequencies, as well as enhanced optical properties and good chemical and physical stability. Among various ferrites studied, it has been found that nano-scale Ni ferrite exhibiting small hysteresis is a good candidate [2].

The spinel ferrites crystallize in a face centered cubic (fcc) structure with space group of Fd3m whose unit cell contains 8 formula units, such that 32 oxygen ions reside at fcc sites and 24 metal cations distribute among two kinds of non-equivalent interstitial sites: 64 tetrahedral (A) and 32 octahedral (B) sites, at which metal cations are surrounded by 4 and 6 oxygen ions, respectively [3,4].

Based on the cation distribution, the structure adopts one of the three types of normal, inverse and mixed spinels. The bulk $NiFe_2O_4$ stabilizes in inverse spinel structure in which 8 Ni^{2+} ions occupy preferentially B sites, whereas 16 Fe^{3+} ions are equally distributed between A and B sites [5,6], i.e. it can be expressed as $(Fe^{3+})_A(Ni^{2+}Fe^{3+})_BO_4$. However, the cation distribution has been turned out to be sensitive to several factors, such as synthesis process. It has been found that the nano-sized $NiFe_2O_4$ is also an inverse spinel [7,8], but a mixed structure has been reported for Ni ferrites nanoparticles smaller than a few nm [9], i.e. some of Ni^{2+} ions occupy A sites by displacing the equal number of Fe3 + ions to B sites. So in general, Ni ferrite can be expressed as $(Ni_{1-i}^{2+} + Fe_i^{3+})_A(Ni_i^{2+} + Fe_{2-i}^{3+})_BO_4$ where "i" is a parameter concerning the inversion grade (0 < i < 1, for the mixed spinel). The degree of inversion may vary with synthesis conditions.

The magnetic properties of ferrites are determined by the cation distribution on the two magnetic sublattices A and B, and their ordering, precisely by the A-O-B superexchange interactions [3]. Furthermore, the magnetic interactions are significantly affected by the surface spin structure, inter-particle interactions and magnetocrystalline anisotropy being controlled by morphology and particle size, i.e. by synthesis conditions. The bulk Ni ferrite is a ferrimagnet as a result of antiparallel spins of cations at A and B sites [1]. The nanoparticles of this material larger than about 15 nm, also exhibit ferrimagnetism, but smaller particles show superparamagnetism [7]. However, at nano-scale level, a reduced particle size is often accompanied by a decrease in the saturation magnetization

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owing to the surface spin-canting effect [10], which limits their practical applications. Ideally, fine nanoparticles of high crystallinity with a high saturation magnetization are needed.

To date, a number of methods have been used to prepare homogenous nano-ferrites, such as sol-gel [7,11], mechanochemical alloying [9], microwave [12], solvothermal [13] and coprecipitation [2,14–16]. The simple and rapid aqueous coprecipitation route continues to be widely used for synthesizing nanoparticles of high crystallinity and homogeneity, as all the reactions occur at the atomic scale. Besides its low synthesis temperature resulting in products of small size, it has the advantage of easily controlling the synthesis conditions and consequently the particle size. The pH value of the solution during the chemical reactions is a crucial factor controlling the structural morphology and particle size and hence the material's physical properties. The previous studies on pH-dependent properties of nanoferrites prepared by this technique show conflicting results: Some observed that increasing the pH value results in larger particles [17], while the opposite trend has been observed in some works [18]. Furthermore, some has reported that increasing pH value leads to a decrease in saturation magnetization [19], while others observed an optimal saturation magnetization value at a certain pH value [17]. However, controlling simultaneously the particle size, crystallinity and the magnetic properties of ferrites through this method is still a challenge under investigation. So, in this work we apply a simple one-step capping agent-free coprecipitation route avoiding high temperature treatment and prolonged processing times to synthesize monodispersed $NiFe_2O_4$ nanoparticles. With the objective of improving their various properties, we investigate the effect of pH value on their structural, morphology, optical and magnetic characteristics. In particular, the optical properties of Ni nanoferrites have been relatively less explored.

2. Experimental methods

2.1. Sample synthesis

The $NiFe_2O_4$ nanoparticles were synthesized by coprecipitation of Ni and Fe chlorides with ammonia aqueous (NH_4OH) as the precipitating agent. The reactant used were stoichiometric amounts of iron III chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and nickel II chloride nonhydrate ($NiCl_2$), all of analytical grade with purity of better than 99% from Merck Co. Each salt was dissolved in 25 ml deionized water under continuous stirring, and then they were mixed together and brought to the reaction temperature of 60 °C on a hot plate for 5 min. Then the aqueous solution was magnetically stirred for about 30 min to obtain a homogenous clear yellow-colored stock solution. It was divided into two nearly equal parts. To regulate the pH of the solution, a diluted ammonia solution was added dropwise. The reactants were continuously stirred till the emulsion's color was changed and precipitate appeared indicating to formation of the compound. It is believed that the formula of $NiFe_2O_4$ is satisfied through the following (unbalanced) chemical reaction:

$$NiCl_2 + FeCl_3.6H_2O + NH_3.nH_2O \rightarrow NiFe_2O_4 + NH_4Cl + N_2 \uparrow + H_2O \tag{1}$$
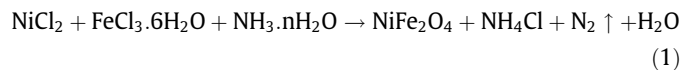
The pH value continuously monitored was set at the selected values of 9 and 11 (low pH value of the reaction medium was not able to precipitate the solution, so only two different pH values were chosen for this study). The two samples were coded as N9 and N11, respectively. After about 30 min, the stirrer was turned off and the particles were allowed to settle down. After the solution was cooled to room temperature, the brownish black magnetic particles precipitated at the bottom of the beaker were collected with the help of a magnet. The resultant product was thoroughly rinsed several times with deionized water and ethanol to remove the traces of nitrogen, chloride ions, unreacted materials and unwanted impurities. For each wash, a magnet collected the magnetic particles at the bottom allowing the residues to float and be decanted. Afterwards, the product was centrifuged for about 5 min at 1000 rpm and then dried in a 100 °C air oven for 10 h to remove the water contents. Finally, the acquired substance was ground in an agate mortar into a fine powder.

2.2. Characterization

The synthesized $NiFe_2O_4$ particles were characterized for structural, chemical, morphological, optical and magnetic properties. The structural characterization of the as-synthesized powders was performed by analyzing the X-ray diffraction (XRD) patterns recorded by a Philips X'pert diffractometer system using a monochromatic Cu-Kα radiation (λ = 1.54056 Å) in the angle range of 2θ = 20–90° at the scan rate of 0.05°/s. The refinement of XRD profiles was carried out by CELREF software.

The morphological characterization of the samples was performed by high resolution transmission electron microscopy (TEM) using a Zeiss EM10 TEM system. For TEM observations, suspensions of the ferrite powders dispersed in ethanol were deposited over some carbon coated Cu grids.

To further investigate the structural and chemical aspects of the samples, their Fourier transform infrared (FTIR) spectra were recorded in 4000–400 cm^{-1} wavenumber range. The spectra were obtained by a Thermo Scientific Nicolet iS10 spectrometer using the pellets of KBr (MERCK Ltd.) with 1 wt% of the ferrite powders.

In order to study the optical properties of the nanoparticles including the energy gap, their optical absorption spectra were recorded at room temperature in the wavelength range of 250–700 nm. The spectra were recorded by a PG Instruments Ltd. T80 UV–vis spectrometer from the ferrite powders dispersed in ethanol by ultrasonic radiation.

The magnetic properties of the samples were explored by analyzing the magnetization hystersis (M-H loop) measurements carried out at room temperature using a homemade vibrating sample magnetometer (VSM, Meghnatis Daghigh Kavir Kashan Co., Iran) under the applied magnetic fields up to ±12 kOe.

3. Results and discussion

3.1. Structural and morphological analysis

The XRD patterns of NiFe2O4 nanoparticles synthesized from the initial solution of pH = 9 and 11 (N9 and N11 samples) are shown in Fig. 1. Both samples are crystalline and single-phased, and no peaks from the starting salts or any secondary phases were detected in the patterns. All the diffraction peaks belong to the expected cubic spinel structure with S.G. Fd3m. The refined lattice parameters are summarized in Table 1. They are comparable with but lower than the value for the bulk compound (JCPDS No. 01-086-2267). The reduced lattice parameters for these nanocrystalline samples with respect to the bulk material is related to the increased number of surface atoms forcing the lattice to shrink to minimize the surface energy [20]. As seen, N11 sample has larger lattice constant. The variation of the unit cell dimensions with pH value can be explained based on various factors, including (1) microstructural aspects in particular defects, and (2) the distribution of cations with different ionic radii among A and B sites. These points will be discussed a little later.

Another remarkable feature in XRD patterns is the relatively broad peaks indicating to the small size of the crystallites. The