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Effects of annealing temperature variation on the evolution of structural and magnetic properties of $NiFe_2O_4$ nanoparticles synthesized by starch-assisted sol–gel auto-combustion method

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ABSTRACT

Evolution of the structural and magnetic properties of $NiFe_2O_4$ nanoparticles synthesized by starch-assisted sol–gel auto-combustion method, and exposed to further annealing at 200 °C, 400 °C, 600 °C, 800 °C and 1000 °C, was evaluated in detail and correlation of these properties explored. The ferrite nanoparticles were characterized by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy, Raman Spectroscopy, Fourier Transform Infrared Spectroscopy, X-ray Photoelectron Spectroscopy and Vibrating Sample Magnetometer. The X-ray diffraction patterns demonstrated single phase formation of $NiFe_2O_4$ spinel ferrite nanoparticles at different annealing temperature 200 °C, 400 °C, 600 °C, 800 °C and 1000 °C. The change in crystallite size with increase of annealing temperature is observed. The FE-SEM analysis also indicated an increase of particle size with increase of higher annealing temperature. The change in Raman modes and infrared absorption bands were noticed with change of particle size. The X-ray photoelectron spectroscopy revealed the presence of Ni^{2+} and Fe^{3+} at octahedral and tetrahedral sites in $NiFe_2O_4$ nanoparticles. The representative sample $NiFe_2O_4$ nanoparticles annealed at 400 °C, have mixed cation distribution $(Ni^{+2}_{0.23}Fe^{+3}_{0.52})[\ Ni^{+2}_{0.77}Fe^{+3}_{1.48}]O_4$. The highest value of coercivity 62.35 Oe and saturation magnetization 34.10 erg/g were obtained at annealing temperature 600 °C and 1000 °C, respectively.

1. Introduction

Recently, magnetic nanoparticles are the focus of much research and development due to its applications in magnetic resonance imaging (MRI) enhancement, magnetically guided drug delivery, magnetic recording media, magnetic fluids for the storage and retrieval of information, catalysis, sensors, etc. [1–5]. In particular, spinel ferrite nanoparticles have been an important subject of research as they exhibit unique properties, different from those of bulk materials. The magnetic properties are mainly affected at the nanoscale, because when the particle size decreases down to the nanoregime, each particle can behave as a single magnetic domain. When the particle size is decreased into the nanoregime, the properties of the material are also altered as the surface area becomes very large in comparison to the bulk material. The electron spins on the surface of a magnetic material are canted (or disordered) because of reduced spin–spin exchange near the surface [6]. An extensive amount of research has been focused on learning how changes in grain size, cation distribution, and surface properties affect the magnetic properties of a ferrite magnetic nanoparticles. Ferrites crystallize in a spinel-type cubic structure, which is traditionally divided into two different ideal structure types, namely, normal and inverse. In normal spinels, M ions of ferrites MFe_2O_4 are solely located on tetrahedral (8a) sites and Fe ions solely on octahedral (16d) sites within the $Fd\bar{3}m$ space group. Inverse spinels have half of the Fe ions residing on tetrahedral sites, while the rest of the Fe ions and all the M ions occupy the octahedral sites. At the nanoscale, the cation distribution is often found to be mixed (between these two ideal structure types), and this is then quantified by the inversion parameter, which corresponds to the fraction of M ions residing on the octahedral sites [7].

Nickel ferrite ($NiFe_2O_4$) is one of the most important materials in the inverse spinel family exhibiting ferrimagnetic properties

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combined with relatively low electrical properties and it displays low eddy current loss in alternating current applications. It has been widely used in electronic devices because of the large permeability at high frequency and high electrical resistivity [8]. Recently, it has been used as magnetic resonance imaging contrast agents, as anode material for lithium ion batteries [9,10]. Bulk $NiFe_2O_4$ have an inverse spinel structure with Ni^{2+} ions located on octahedral sites and Fe^{3+} ions located on the octahedral and tetrahedral sites equally [11]. On the other hand, the nanosized counterpart has a mixed cation distribution $(Ni_{1-\gamma}Fe_{\gamma})[Ni_{\gamma}Fe_{2-\gamma}]$,where the inversion parameter γ is found to vary, depending on the sample preparation method and the thermal treatment. Since the peculiar properties of ferrites are strictly related to the distribution of cations between octahedral and tetrahedral sites in the spinel structure, the control of cation distribution provides a means to tailor their properties. The changes in the particle size can influence physical properties due to change in cation distribution [12].

There are several synthesis techniques, such as sol–gel, coprecipitation, microemulsion, sol–gel combustion, hydrothermal treatment, ballmilling, mechanosynthesis and electrospinning for synthesis of $NiFe_2O_4$ nanoparticles [13–21]. In these synthesis techniques, sol–gel auto combustion method is a unique combination of the combustion and the chemical gelation processes. This sol–gel auto combustion method is based on simple route of preparation and cheap precursors. The obtained product from this method are found ultra fine and homogeneous. This method involves an exothermic and self-sustaining chemical reaction between the metal salts and a suitable organic fuel, namely, urea, citric acid, glycine, hydrazides and DL-Alanine [17,22–28]. To the best of our knowledge no attempt was made earlier to use starch as fuel for synthesis of nickel ferrite nanoparticles. Starch (from potato) is a common bio-polymer used as a fuel to achieve nickel ferrite nanoparticles. This paper reports detailed study of influence of annealing temperature on strucrural and magnetic properties of nickel ferrite nanoparticles synthesized by starch-assisted sol–gel auto-combustion method. Azadmanjiri et al. [26] reported formation of $NiFe_2O_4$ nanoparticles by citric acid assisted sol–gel auto-combustion process. This research group observed the formation of $NiFe_2O_4$ spinel phase as well as α-Fe_2O_3 phase at 800 and 900 °C. However, with increasing the calcination temperature at 1000 °C, the inclusion phase (α-Fe_2O_3) was decreased. The synthesized $NiFe_2O_4$ nanoparticles at 1000 °C were spherical in morphology. The crystallite size of $NiFe_2O_4$ nanoparticles formed at 1000 °C was 72 nm. In our work, we noticed single phase formation of $NiFe_2O_4$ nanoparticles formed by use of starch as fuel in sol–gel auto-combustion method and further annealed at lower temperature 200 °C. At this temperature, the particles are spherical having crystallite size 16.5 nm. However, at higher temperature 1000 °C, we observed $NiFe_2O_4$ nanoparticles of 56.9 nm crystallite size with hexagonal morphology.

2. Experimental section

2.1. Materials

The following chemicals were used for the synthesis of Nickel ferrite nanoparticles by starch-assisted sol–gel auto-combustion method: Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) were purchased from Alfa Aesar GmbH & Co KG, Germany. Starch Soluble $(C_6H_{10}O_5)_n$ (from potatoes) was purchased from Lach-Ner, Czech Republic. All chemicals were used as received without any further purification.

2.2. Synthesis

The following protocol was used for the synthesis of Nickel ferrite nanoparticles by starch-assisted sol–gel auto-combustion method. The Stoichiometric amount of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were dissolved in distilled water to obtain a mixed solution. The molar ratio of nickel nitrate to iron nitrate was 1:2. The metal nitrates were dissolved together in the minimum amount of double-distilled water needed to obtain a clear solution. An aqueous solution of Starch $(C_6H_{10}O_5)_n$ (from potatoes) was mixed with the metal-nitrate solution. The mixed solution was placed on a hot plate with continuous stirring at 100 °C. During evaporation, the solution formed a very viscous gel. Then the gel was heated to 200 °C to initiate a self-sustaining combustion reaction and produce as-burnt ferrite powder. The following equation represents the decomposition of metal-starch ferrite gel precursor into nickel ferrite

$$Ni(NO_3)_2.6H_2O + 2Fe(NO_3)_3.9H_2O + \left[(C_6H_{10}O_5)_n\right] \xrightarrow{200\ ^oC} NiFe_2O_4 + 8NO_2(g) + 15H_2O + xO_2(g) + (nC + nH_2)$$

Finally, the as-burnt powders were additionally annealed in a furnace in air atmosphere at 200, 400, 600, 800 and 1000 °C, for 2 h.

2.3. Characterization of product

The crystal structure of $NiFe_2O_4$ ferrite nanoparticles annealed at different temperature were characterized through PANalytical Empyrean X-ray diffractometer with CuKα radiation (1.5406 Å). Raman Spectra of $NiFe_2O_4$ ferrite nanoparticles annealed at different temperature were measured using a confocal microscope with a spectrometer “Nanofinder-S” (SOLAR TII, Ltd.). Fourier transform infrared (FT-IR) spectra were recorded using Nicolet iS 50 FTIR spectrometer by the ATR method. The morphology and size of $NiFe_2O_4$ ferrite nanoparticles annealed at different temperature were examined using a field emission gun Scanning Electron Microscope (FEG-SEM) Model-JEOL JSM-7600F. The chemical state and cation distribution at octahedral and tetrahedral site in spinel $NiFe_2O_4$ ferrite nanoparticles were studied by X-ray Photoelectron Spectroscopy (XPS) using Kratos Analytical Axis Ultra DLD. Magnetic measurements of $NiFe_2O_4$ ferrite nanoparticles annealed at different temperature were performed using a vibrating sample magnetometer (VSM 7407, Lake Shore) at room temperature with maximum applied magnetic field of 10 kOe.

3. Result and discussion

3.1. Structural studies

The X-ray diffraction (XRD) patterns of $NiFe_2O_4$ nanoparticles synthesized by starch-assisted sol–gel auto-combustion method with further annealing at 200, 400, 600, 800 and 1000 °C, are shown in Fig. 1. It can be seen that the XRD patterns present peaks at reflection planes indexed (220), (311), (222), (400), (422), (511) and (440) for all samples therefore proving the formation of the single phase cubic spinel structure. All the reflection peaks of $NiFe_2O_4$ nanoparticles were compared with standard powder diffraction cards of $NiFe_2O_4$ and found to be fully compatible with standard reflection peaks. The peaks becoming sharper and narrower with increase of annealing temperature indicates the improvement of crystallinity with increase of annealing temperature.

The crystallite size can be measured by the Scherrer equation which is expressed as [29]: