



Cr-substitution effect on the structural and magnetic properties of nano-sized NiFe_2O_4 prepared via novel chitosan route



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ABSTRACT

Nano-crystalline Cr-substituted nickel ferrites; $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ ($x=0.0-1.0$) were prepared using chitosan template method. Differential thermal analysis–thermogravimetric measurements revealed the complete combustion of the gel precursor at 220 °C. X-ray diffraction (XRD) of the as-prepared precursors exhibited the presence of secondary phases besides the entire ferrites. XRD of the calcined precursors at 500 °C indicated single-phase cubic spinel structure for all the prepared samples. The lattice parameter are slightly changed with increasing Cr-content while the particle size and X-ray density gradually decreases. Vibrating sample magnetometer measurements confirmed that Cr-substitution caused a decrease in the saturation magnetization while increasing coercivity. The higher magnetizations obtained compared with other methods in literature enhances using of chitosan as a template for the preparation of other systems. The relatively high coercivity values suggested higher demagnetization magnetic field of the investigated samples. The expected chitosan complexation mechanism as well as the auto-combustion reaction were discussed. A proper cation distribution of the investigated system was suggested through structural data and was confirmed by magnetization studies.

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1. Introduction

Nickel and substituted nickel ferrites have attracted the attention of many scientists for a long time because of their wide technological applications. Nickel ferrite have been extensively used in many electronic devices because of its large permeability, remarkably high electrical resistivity, mechanical hardness, chemical stability and cost effectiveness [1]. On the other hand, substituted nickel ferrites are widely used as magnetic materials and can be offer performance advantage over other spinel structures due to their high electrical resistivity, low eddy current and dielectric losses [2].

Ferrites are particularly interesting systems in which the gradual changes in their chemical composition could produce clear variations in the cation distribution, which in turn drastically affects the physical and chemical properties. The cation distribution was also found to be dependent on atomic sizes, valences and crystal field of substituting ions [3].

In the literature a very few works are reported for the Cr-substituted nickel ferrites [4–9]. Generally, it was found that, the substitution with the magnetic Cr ion introduces magnetic

dilution in the ferrite systems similar to that produced by the non-magnetic substitutions, which may induce interesting magnetic properties in the system.

Many methods were approved for the preparation of nano-crystalline ferrite [10–16]. These methods are strongly affecting the different properties of the produced ferrites. However, most of these methods are time and energy consuming, and are not environment-friendly, and in sometimes involved multi-step syntheses.

An alternative route to synthesize nanoparticles can be achieved using chitosan template method. Chitosan is the deacetylated form of the naturally polysaccharide called chitin. It is well known as a nontoxic and biodegradable linear copolymer, which can be prepared by treating shrimp and other crustacean shells such as crab, lobster and squid with alkali sodium hydroxide [17]. It has been used as a template for the synthesis of mesoporous Ti, Al and Si oxides [18] and CeO_2 nanospheres [19]. To the best of our knowledge, there are no reports in the literature for synthesizing nano-crystalline ferrites using chitosan as template. This makes this method novel and versatile for the preparation of these types of materials.

In the present work, $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ ($0 \leq x \leq 1$) ferrites were prepared using chitosan template method. The effect of magnetic dilution on the structural and magnetic properties was estimated using DTA–TG, XRD, FT-IR, TEM and VSM techniques. The impact of the present preparation method on the different properties was discussed.

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2. Experimental procedure

2.1. Materials

Nano-crystalline $\text{NiFe}_{2-x}\text{Cr}_x\text{O}_4$ ferrites ($x=0.0\text{--}1.0$) were prepared using chitosan as template [19,20]. Stoichiometric amounts of the respective metal nitrates were dissolved in 100 ml distilled water. A solution of 1.6 g of chitosan, dissolved in 100 ml of acetic acid (3%, v/v), was added drop wisely under stirring to the nitrates solution. The temperature was raised to 60 °C and kept for 30 min. NH_4OH solution (50%, v/v) was then added drop wisely to obtain pH of 8. The gel formed was evaporated at 100 °C until complete combustion and the obtained powders are taken the name; as-prepared chitosan precursor.

Parts of the samples are further calcined at 500 °C for 1 h in an electric furnace. The calcined precursors were then quenched and kept in a dessicator.

2.2. Techniques

Simultaneous differential thermal analysis–thermogravimetry (DTA–TG) experiments were carried out using a Perkin Elmer thermal analyzer up to 600 °C at a heating rate of 5 °C min^{−1} in flowing air atmosphere.

The structure and phases formation were characterized through X-ray diffraction analysis (XRD) with a Bruker D8 Advance X-ray diffractometer with $\text{CuK}\alpha 1$ irradiation source ($\lambda=0.154$ nm). The patterns were recorded in the 2θ range of 10°–80° with scanning rate 1°/min.

Fourier transform infrared (FT-IR) spectra were recorded with a Perkin Elmer FTIR in KBr medium in the range of 700–200 cm^{−1}.

The morphology of the obtained ferrites was examined using a JEOL 2010 TEM operating at an accelerating voltage of 100 kV.

Magnetic measurements were performed using a vibrational sample magnetometer (VSM-9600M) at room temperature with maximum applied magnetic field of 5 kOe.

3. Results and discussion

3.1. Complexation mechanism

Chitosan is a linear non-starch polysaccharide biopolymer composed of randomly distributed β -(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine (Fig. 1) [21,22]. The amino groups besides the hydroxyl groups are acting as a dentate for the metal ions which facilitate their close proximity and increase the amenability for their efficient reaction and easy production of ferrites.

The solubility of chitosan in aqueous solution is pH dependent and increases with increasing acidity. This why chitosan solution was prepared using acetic acid (pH~5). In the presence of metal ions, the pH of solution must be adjusted at about 8, using ammonium hydroxide, so that the negatively charged amino and hydroxyl groups can be considered as potential binding sites for the metal ions and consequently gel formation.

Heating this gel in the presence of nitrate ions, initiate an auto combustion reaction in which the chitosan moiety acts as a fuel and the nitrates behave as an oxidant [23]. Such exothermic

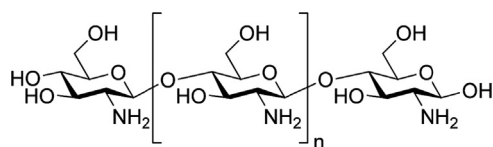


Fig. 1. Structure of chitosan.

reaction can be resulted in the decomposition of the high molecular weight organic matter into CO_2 and NO_x with the formation of ferrites nanoparticles.

3.2. DTA–TG studies

The thermal study was performed for gel-precursor to obtain information about decomposition reaction and the ideal conditions for ferrite formation. Fig. 2 shows DTA–TG curves for the thermal decomposition of gel-precursor in air. From the figure it is appeared that the decomposition occurs through three TG steps while DTA curve shows one endothermic and one sharp exothermic peaks.

The first two steps occur in the temperature range of 30–180 °C and are accompanied with a broad endothermic DTA peak. This weight loss can be attributed to the loss of water. The third step starts at about 200 °C and can be considered as the main decomposition step. The decomposition is steep and accompanied by a sharp exothermic DTA peak which due to the combustion reaction between nitrates and the chitosan moiety. The obtained weight loss can be assigned to the liberation of water, CO_2 and NO_x . Almost no weight loss can be observed above 220 °C indicates the completion of gel decomposition.

3.3. X-ray diffraction

Identification of the single-phase spinel structure was estimated through X-ray diffraction measurements. Fig. 3 shows X-ray diffraction patterns of the as-prepared precursors. Analysis of the patterns revealed the presence of secondary phases besides the entire ferrites. These phases can be assigned to Fe_2O_3 (JCPDS file No.: 89-0598) and awaruite; Ni_3Fe (JCPDS file No.: 88-1715). The appearance of these phases indicates that the auto-combustion reaction is not sufficient for the complete formation of ferrites and further calcination must be preceded.

Fig. 4 illustrates XRD patterns of the precursors calcined at 500 °C for 1 h. From the figure, it is clear that all the samples have a single-phase face centered cubic (fcc) structure with no additional lines corresponding to any other phase. The experimental lattice parameters (a_{Exp}) calculated using d -values and plane reflections (hkl) (Table 1), are observed to be slightly changed with increasing chromium content (x). This can be attributed to the smaller difference between the ionic radii of Fe^{3+} ions (0.645 Å) and the substituent Cr^{3+} ions (0.63 Å) [24].

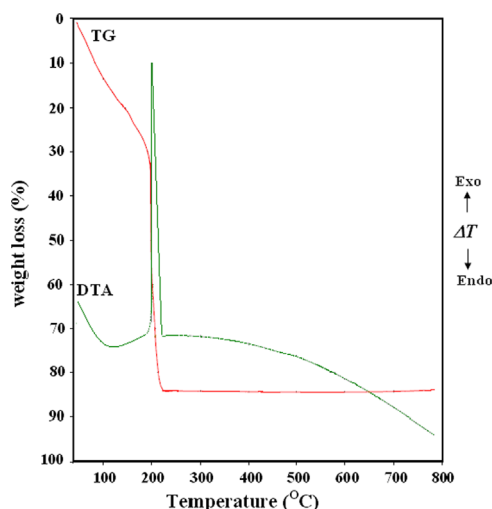


Fig. 2. DTA–TG curves in air of the gel-precursor with $x=0.0$. Heating rate=5 °C min^{−1}.

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