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Effect of composition on structural and magnetic properties of nanocrystalline $Ni_{0.8-x}Zn_{0.2}Mg_xFe_2O_4$ ferrite

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ABSTRACT

Nanocrystalline magnetic particles of $Ni_{0.8-x}Zn_{0.2}Mg_xFe_2O_4$ ferrites with x lying between 0.0 and 0.8 were synthesized using metal nitrates and freshly extracted egg-white. The synthesized powders were characterized using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and transmission electron microscopy (TEM). With increasing magnesium concentration, the lattice constant increases while X-ray density decreases. The average crystallite size determined from XRD data using Scherrer formula lie in the range of 35–59 nm. TEM image shows spherically agglomerated particles with average crystallite size agreed well with that obtained from XRD. Magnetic properties measured at room temperature by vibrating sample magnetometer (VSM) reveal a decrease in saturation magnetization up to Mg content of 0.6. In agreement with FT-IR results, the unexpected increase in the magnetization at Mg content of 0.8 can be attributed to the tendency of Mg^{2+} ions to occupy the tetrahedral site. The decrease in the value of coercivity with increasing magnesium content can be explained based on the magneto-crystalline anisotropy.

1. Introduction

Spinel ferrites nanocrystals have been widely investigated in the recent years due to their remarkable electrical and magnetic properties and wide practical applications in information storage system, ferrofluid technology, magneto-caloric refrigeration and medical diagnosis [1].

To meet the demand of high performance devices, an important step is to synthesize ferrite crystals in nanoscale forms with narrow particle size distribution and minimum particles agglomeration. Below the critical size these crystals exist in a single domain state so the domain wall resonance is avoided and the material can work at higher frequencies [2]. Many techniques have been provided for the synthesis of the nano-sized ferrites. These methods include sol–gel [3], organic precursors [4], hydrothermal [5], co-precipitation [6], cathodic electrophoretic deposition (EPD) [7], mechanochemical synthesis [8], reverse micelle [9], and electrochemical deposition [10]. More recently, a simple, cost effective and environmentally friendly method utilizing egg-white is also used [11–13].

Zinc substitution plays a decisive role in determining the ferrite properties. Mixed Zn ferrites and especially Ni–Zn ferrites are the most important magnetic materials, which offer a broad range of frequency suppression in the MHz band frequency. They posses a unique combination of desirable properties such as large magnetic permeability at high frequencies, electrical resistivity, mechanical hardness, chemical stability in addition to the reasonable cost [14]. They have a wide range of applications [15] in microwave absorbance, electronic devices such as radio and TV sets, integrated nonreciprocal circuits, high frequency transformers, memory core devices, rod antennas, read-write heads for high-speed digital tape or disk recording, telecommunication applications, excellent catalysts for alkylation of aromatics and in gas sensing.

$MgFe_2O_4$ [16] is a partially inverse cubic spinel. It can be considered as a collinear ferrimagnet whose degree of inversion is sensitive to the sample preparation history. Magnetic properties of ferrites are strongly dependent on their chemical compositions and additives or substitutions. Small amount of foreign ions in the ferrite can dramatically change the properties of ferrites.

In the literature very few studies on the Mg substituted Ni–Zn ferrites are present. El Hiti [17] studied the dc conductivity of $Zn_xMg_{0.8-x}Ni_{0.2}Fe_2O_4$ system, with $x = 0.0$, 0.2, 0.4, 0.6 and 0.8, as a function of temperature and composition. The dc conductivity was found to increase with increasing temperature, while it decreases with increasing Zn content. The Curie transition temperature decreases, while the activation energy for conduction increases by increasing Zn content.

$Ni_{0.2}Zn_xMg_{0.8-x}Fe_2O_4$ ferrites; $0 \leqslant x \geqslant 0.8$ were studied using X-ray diffraction and Mössbauer spectroscopy [18]. The samples proved to have a single-phase cubic spinel structure. The

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dependence of the lattice constants and intercationic distances on Zn content was studied. According to the Mössbauer studies, the samples with $x = 0.0–0.4$ are magnetically ordered while others are paramagnetic. The cation distributions were deduced and supported by X-ray studies.

$Ni_{1-x}Mg_xFe_2O_4$ ferrites ($0 \leqslant x \leqslant 1$) were prepared by the co-precipitation method [19]. The samples were characterized by XRD. The crystallite size variation is within the range 10–13 nm. The Curie temperature was determined using AC magnetic susceptibility data and the observed variation is explained based on cations distribution among tetrahedral and octahedral sites.

The properties of ferrites are highly sensitive to the cation distribution, which in turn is controlled by preparation conditions and substitution of different metals. Accordingly, the present work is aimed at the preparation of $Ni_{0.8-x}Zn_{0.2}Mg_xFe_2O_4$ ferrites with $x = 0.0–0.8$ using egg-white method. The produced nano-sized ferrites were characterized using thermogravimetry (TG), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and transmission electron microscopy (TEM) techniques. The change in the magnetic properties of the investigated system was measured using vibrating sample magnetometer (VSM). To the best of our knowledge, the influences of magnesium substitution on the structural and magnetic properties of Ni–Zn ferrites have seldom been reported.

2. Experimental

Precursors of the mixed ferrite samples were prepared, using stoichiometric ratios of the metal nitrate and freshly extracted egg-white, according to egg-white method as previously described [12,13].

The dried precursors were ground and calcined in a muffle furnace at 550 °C for 2 h.

Thermogravimetric analysis (TG) was carried out, using Perkin–Elmer thermal analyzer on precursors up to 600 °C at a heating rate of 5 °C min^{-1} in air.

X-ray powder diffraction analysis was conducted on D8 Advance diffractometer using Cu Kα radiation (operated at 40 kV and 35 mA).

Fourier transform infrared spectroscopic analysis, using KBr pellets, was carried out in the range 200–4000 cm^{-1} using a Jasco model FT-IR 310 spectrometer.

Transmission electron microscopy was performed using Jeol 2010 transmission electron microscope with an accelerating voltage of 100 kV. A drop of diluted sample in alcohol was dripped on the TEM grid and dried, which was then used to examine the grain size and morphology of synthesized sample.

The characteristic hysteresis loops of the system were measured at room temperature, up to a maximum external field of ±8 kOe, by using vibrating sample magnetometer (VSM; Lake Shore 7404). Parameters like specific saturation magnetization (M_s), coercive force (H_c) and remanence (M_r) were evaluated.

3. Results and discussion

The TG analysis was conducted to determine the temperature at which the egg-white content can decomposed completely and to identify the proper calcination temperature for obtaining ferrites. Fig. 1 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the dried egg-white precursor with $x = 0.4$. The thermal decomposition follows five major steps. These steps are attributed to the dehydration followed by the decomposition of the anhydrous precursor to form the spinel ferrite. The first step starts with the removal of the adsorbed water and ends at about 100 °C. This is followed by the decomposition of the anhydrous precursor through successive steps which are finished at 500 °C giving an overall weight loss of 73%. No weight loss can be observed after this temperature. Accordingly, the egg-white precursors were calcined at 550 °C.

Fig. 2 shows XRD patterns of the investigated egg-white precursors annealed at 550 °C. The observed diffraction peaks for all the samples are perfectly indexed to cubic spinel phase (JCPDS card No. 88-1940 and 08-0234), and no impurities are detected in the XRD patterns. The diffraction peaks can be indexed to the planes of (2 2 0), (3 1 1), (2 2 2), (4 0 0), (5 1 1) and (4 4 0). The observed broadening of diffraction peaks indicates the nano-crystallinity of the samples.

The particle size of the synthesized ferrite samples was estimated from X-ray peak broadening of diffraction peaks using Scherrer formula [20]. The values of the particle size, lattice constant and X-ray density as deduced from the X-ray data are given in Table 1.

The average particle size for $Ni_{0.8-x}Zn_{0.2}Mg_xFe_2O_4$ gradually increases with increasing Mg content. A slight decrease was observed

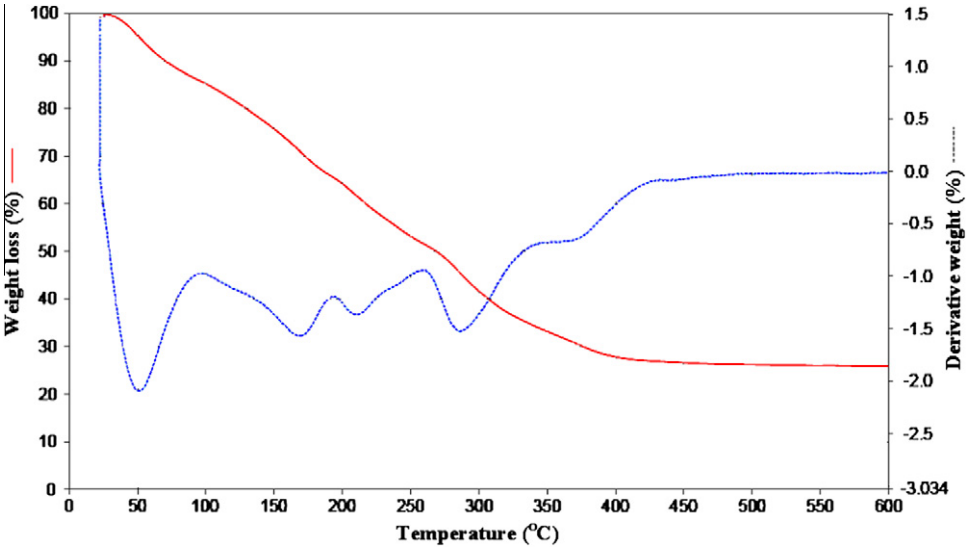

Fig. 1. TG–DTG curves in air of precursor with Mg content of 0.4. Heating rate = 5 °C min^{-1}.