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Influence of Co^{2+} on structural and electromagnetic properties of Mg–Zn nanocrystals synthesized via co-precipitation route

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Abstract

Co-precipitation method was used to synthesize the nanoparticles of cobalt substituted zinc–magnesium ferrites having formula "$Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$" where $0.00 \leq x \leq 0.25$. Fabricated samples were annealed at 750 °C for 6 h. The cubic spinel structure of $Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$ nanocrystals was confirmed by Fourier transformed infra-red (FTIR) and X-ray diffraction (XRD). Lattice parameter, crystalline size, cell volume, X-ray density, bulk density and porosity were also determined using XRD data. Lattice parameter exhibits overall decreasing trend (0.824–0.817 nm) with cobalt content; it is due to the substitution of cobalt (having smaller ionic radii) with magnesium and zinc ions. Cation distribution among A and B sites were studied by FTIR spectrum. Vibrating sample magnetometery (VSM) was used to investigate magnetic properties of as prepared nanoparticles. Coercivity exhibits the inverse relation to crystalline size. Lowest value of coercivity (47.722 Oe) was obtained for the sample having $x=0.15$. Dielectric constant, dielectric loss and dielectric tan loss were inversely related with the frequency.

Keywords: Nano-ferrites; XRD; Dielectric parameters; Coercivity

1. Introduction

Magnesium–zinc ferrites are very helpful for reducing hysteresis loses [1], high frequency devices fabrication [2–4], high density media storage devices, magnetic reading and recording data [4], sensor devices[1,2], and bio-medical applications [3]. Nanoparticles of spinel ferrites are potential candidates with respect to research as well as industrial point of view due to their distinctive and remarkable magnetic, electrical, dielectric and structural properties [3]. As compared to other ferrites, spinel ferrites having chemical formula "MFe_2O_4" (where M is a divalent metal ions) are important magnetic material because they have high resistivity, low dielectric losses [2], good thermal stability [4] and high saturation magnetization.

Magnetic parameters of Mg–Zn ferrites strongly depend on particle size which depends on sintering time, sintering temperature and grown techniques [5]. Because of unquenched orbital angular momentum, Co^{2+} ions are recognized to transform the magneto-crystalline anisotropy. Therefore the substitution of cobalt in Mg–Zn ferrites makes some important modification which enhances magnetic and dielectric properties [6]. Lodhi et al. described that magnetic and dielectric properties of Mg–Zn–Co ferrites depend upon chemical composition and cation distribution between octahedral and tetrahedral sites [3]. It is already reported that magnetic and electrical properties of ferrites have inverse relation with crystalline size [7]. To synthesize ferrites in nano-scale, there are a number of synthetic approaches

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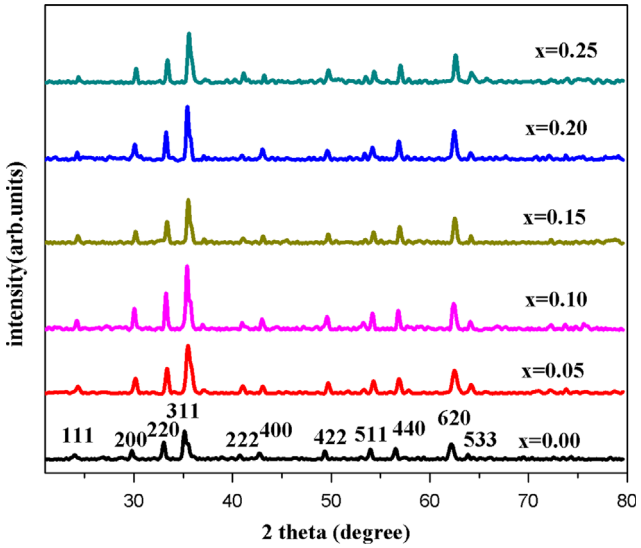

Fig. 1. XRD patterns Nano-precipitate of $Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$.

to synthesize nanoferrites such as sol–gel [8–11], micro-emulsion [3], solid state [12], micro wave sintering [13], novel combustion [14], two step direct micro-emulsion [15], co-precipitation [16,17], hydrothermal [18], mechano-chemical [19], etc.

In this present work, we choose, co-precipitation route to prepare magnesium–zinc–cobalt ferrites having chemical formula "$Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$" where $0.00 \le x \le 0.25$ (with step size 0.05) because it is less toxic, economic and environment friendly growth technique. Effect of cobalt doping on Mg–Zn ferrites has been studied to enhance the magnetic and electrical properties to make these nanoferrites suitable for high frequency electronic devices.

2. Experimental

2.1. Synthesis

"$Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$" where $0.00 \le x \le 0.25$ (with step size 0.05) nano-ferrites were fabricated by using the co-precipitation method [16,20]. The following chemicals were used for the fabrication of $Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$ ferrites nanoparticles; aqueous ammonia NH_4OH (BDH, 35%), $(CH_3COO)_2Mg \cdot 4H_2O$ (BDH, 99%), $(CH_3COO)_2Co \cdot 4H_2O$ (BDH, 98%), $ZnCl_2$ (Merck Germany, 98%), and $[Fe(NO_3)]_3 \cdot 9H_2O$ (Merck Germany, 98%). 0.1 M solutions of Mg, Zn and Co was prepared in distilled water, on the other hand 0.2 M solution of Fe was also prepared. These solutions were mixed according to calculated ratio and placed on hot plate for stirring and heated up to 55 °C. Initially, all solutions were acidic having pH about 2–3. Furthermore, heating of solutions was stopped and pH of all reactions was raised to 10 to form basic media by adding aqueous ammonia in the solutions. After achieving basic media, all mixtures were put on magnetic stirring for 6 h at room temperature. After completing the process of stirring, all mixtures were left as such for 12 h; the precipitates were formed and settled down. All the six types of particles, thus grown were washed with distilled water (H_2O) until all mixtures became neutral, having pH level approximately equal to 7.0. All beakers containing different compositions were placed in oven at 80 °C for drying. Grown precipitates were grinded with mortar and pestle. Grinded nanoparticles of all samples were sintered at 750 °C for 6 h by using fully controlled and automatic Muffle Furnace Vulcan A-550.

2.2. Analysis and characterization

Fabricated nanocrystalline ferrites having chemical formula "$Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$" were characterized by various techniques. Formation of single phase spinel structure and related properties were evaluated by X-ray diffractometer (model Philips PW 1710 using Cu K_α radiation having wavelength 1.5414 Å) and fourier transform infrared spectrometer (Nexus 470). Magnetic properties were studied by vibrating sample magnetometery (Lakeshore-74071) at 300 K whereas LCR meter (Wayne Ker WK6500B) was used to investigate dielectric parameters in frequency range 1–3 MHz at room temperature.

3. Results and discussion

3.1. XRD

X-ray diffraction patterns of cobalt substituted Mg–Zn ferrites are shown in Fig. 1. In the XRD patterns, prominent peaks were observed from following planes (111), (200), (220), (311), (222), (400), (422), (511), (440), (620) and (533); which confirm that all grown samples are comprised of single phase FCC spinel structure without showing any other additional phase. Such diffraction peaks were already reported for face centered cubic spinel ferrites in literature [3,6,21].

Grain sizes of nanoferrites were evaluated by using well known formula named after a physicist P. Scherrer [3,6,22]

$$Crystallite\ size = \frac{0.9 \times \lambda}{\beta \cos \theta} \quad (1)$$

where λ is wavelength of X-ray (1.5414 Å), β is full width half maxima (FWHM) of intense peak and φ is diffraction angle of that peak. It has been observed from Table 1 that grain size decreases with cobalt contents "x" and it reaches minimum

Table 1
Grain size, lattice constant, cell volume, bulk density, X-ray density and porosity of $Mg_{0.6-0.5x}Zn_{0.4-0.5x}Co_xFe_2O_4$.

Cobalt content "x"	$x=0.00$	$x=0.05$	$x=0.1$	$x=0.15$	$x=0.2$	$x=0.25$
Lattice constant (A)	8.246	8.246	8.246	8.246	8.246	8.246
Cell volume (A^3)	560.695	560.695	560.695	560.695	560.695	560.695
Bulk density (g/cm^3)	3.31	3.31	3.31	3.31	3.31	3.31
X-ray density (g/cm^3)	5.13	5.13	5.13	5.13	5.13	5.13
Porosity	0.355	0.355	0.355	0.355	0.355	0.355
Grain size (nm)	37.9	37.9	37.9	37.9	37.9	37.9