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Effect of zinc substitution on the nanocobalt ferrite powders for nanoelectronic devices

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ABSTRACT

Zinc substituted cobalt ferrite powders $\{Co_{(1-x)}Zn_xFe_2O_4\}$ $(0.0 \leqslant x \leqslant 0.5)$ were prepared by the solution combustion method. The structural, morphological, magnetic and electrical properties of as synthesized samples were studied. Powder X-ray diffraction patterns reveals single phase, cubic spinel structure with space group No. $Fd\bar{3}m$ (227). As zinc concentration increases, the lattice constant increases and the crystallite size decreases. The minimum crystallite size of ~12 nm was observed for $x = 0.5$ composition. The synthesized ferrite compounds show ferrimagnetic behavior, with coercivity value of 10779 Oe (Hard ferrite) at 20 K and 1298 Oe (soft ferrite) at room temperature (RT). The maximum saturation magnetization recorded for the $Co_{0.5}Zn_{0.5}Fe_2O_4$ composition was 99.78 emu g^{-1} and 63.83 emu g^{-1} at 20 K and RT respectively. The dielectric parameters such as dielectric constant, loss tangent and AC conductivity were determined as a function of frequency at RT. The magnetic and dielectric properties of the samples illustrates that the materials were quite useful for the fabrication of nanoelectronic devices.

1. Introduction

The miniaturization of magnetic and electronic devices has demanded advanced materials of nanoparticles or thin films with new forms and shapes. Nanoferrites represent an important class of technological materials, due to their remarkable properties which render them suitable for many applications namely switching devices, recording tapes, transducers, actuators, sensors, high quality digital printing, EMI Shielding, biotechnological applications etc. [1–4]. Among various ferrites, $ZnFe_2O_4$ and $CoFe_2O_4$ were extensively studied systems, because they exhibit the typically normal and inverse spinel ferrites respectively. Bulk $ZnFe_2O_4$ shows anti-ferromagnetic below the Neel temperature (T_N) and turns to ferromagnetic or superparamagnetic in nanoscale. In contrast, $CoFe_2O_4$ reveal ferromagnetic where cobalt ions occupy the octahedral sites and Fe^{3+} ions were equally distributed in tetrahedral and octahedral sites. Therefore, Co–Zn mixed ferrite has attracted considerable attention due to the diverse properties of $ZnFe_2O_4$ and $CoFe_2O_4$. Ferrite nanoparticles were conventionally prepared by co-precipitation, ceramic technique, microwave combustion, sol–gel, solvothermal, solid-state and hydrothermal methods [5–7]. Although numerous reports were available on the magnetic and dielectric behavior of cobalt ferrites [8–10] but, less work has been reported on the detailed properties of $Co_{(1-x)}Zn_xFe_{2-}O_4$ prepared by solution combustion (SC) method. SC method has several advantages in preparing multi-component materials for the desired stoichiometry without any contamination. Further, particle size, chemical homogeneity and degree of agglomeration can be appreciably controlled by this method. The prepared samples were characterized using powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The magnetic hysteresis loops and electrical properties such as conductivity, dielectric constant, dielectric loss tangent as a function of frequency with zinc concentration were studied.

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2. Experimental details

Nanocrystalline powders of Zn^{2+} ions doped cobalt ferrites with nominal compositions $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \leqslant x \leqslant 0.5$) were synthesized by a solution combustion technique. The chemicals used for the synthesis were analytical grade cobalt nitrate [$Co(NO_3)_2$], zinc nitrate [$Zn(NO_3)_2$], ferric nitrate [Fe $(NO_3)_3$] and freshly prepared Oxalyl dihydrazine (*ODH*) [$C_2H_6N_4O_2$]. The detailed procedure for synthesis was discussed elsewhere [11]. The chemical reaction of synthesis process was represented by

$$(1-x)Co(NO_3)_2 + 2Fe(NO_3)_3 + 3C_2H_6N_4O_2 + xZn(NO_3)_2 \rightarrow Co_{1-x}Zn_xFe_2O_4 + 9H_2O + 11N_2O + 6CO_2 \quad (1)$$

The X-ray diffraction studies were carried out on powder X-ray diffractometer (PAN analytical XPert Pro) with monochromated Cu Kα radiation ($\lambda = 1.5406$ Å) and Ni filter in the 2θ range of 10–70° at RT. FTIR spectra were taken on Perkin Elmer Spectrometer (spectrum 1000) with KBr pellets in the range 400–4000 cm^{-1}. The surface morphology of the samples were characterized by a scanning electron microscopy (SEM) (JEOL JSM 840A). The magnetic properties were measured using vibrating sample magnetometer (Lakeshore VSM 7410) at RT and low temperature (20 K). The dielectric and impedance measurements were studied with respect to different frequencies from 1 Hz to 1 M Hz at RT.

3. Results and discussion

The powder X-ray diffraction patterns of as-formed $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \leqslant x \leqslant 0.5$) samples were shown in Fig. 1a. All the diffraction patterns were well matched with JCPDS card number 79-1744 [12]. Further, there was no change in peak positions which indicate that the prepared samples were in single phase, cubic structure with space group No. $Fd\bar{3}m$ (227) [13]. The powder diffraction pattern ($x = 0$) was statistically validated by providing necessary structural inputs to FULLPROF suite 2.05 program. Initially, the positions of the peaks were corrected by successive refinements of zero-shift error. Considering the integrated intensity of the peaks as a function of structural parameters, least-squares procedures were adopted for minimization of the difference between the observed and simulated powder diffraction patterns. The minimization of the difference during the simulation was carried out by using the reliability index parameters, weighted residual error and Bragg factor. The background was successfully fitted with a Chebyshev function (χ^2) with a variable number of coefficients depending on its complexity. The fitted profile pattern was shown in Fig. 1b and the estimated parameters were tabulated in Table 1. The inversion parameter (δ) was found to be 0.33, hence the distribution of cations for the composition $x = 0$ is as follows

$$(Co^{2+}_{0.67}Fe^{3+}_{0.33})[Fe^{3+}_{1.67}Co^{2+}_{0.33}]O^{2-}_4$$

The crystal structure was drawn using powder cell program which was shown in Fig. 1c. The average crystallite size (d_{ave}) of the samples were calculated using the Debye–Scherrer formula [14]

$$d_{ave} = k\lambda/\beta\cos\theta \quad (2)$$

where d_{ave} is the average crystallite size derived from the (311), (220), (400), (511) and (440) peaks of the PXRD patterns, k is the sphere shape factor ($k = 0.9$), θ is the Braggs angle, β is the full width at half maxima (FWHM) of the peaks and λ is the wavelength of X-ray ($\lambda = 1.5406$ Å). The variation of d_{ave} with Zn^{2+} ions content was shown in Fig. 2. The crystallite size increases with zinc content showing a maximum value of 18 nm for $x = 0.1$ and thereafter it decreases gradually with increasing Zn content. The average crystallite size of the Zn doped cobalt ferrites were found to be in the range from 12 to 18 nm. Further, it was observed that all the reflections slightly shifting to lower angle with zinc ions content which implies that, the increase in the lattice parameter was due to zinc concentration. The crystallite size and strain present in the material

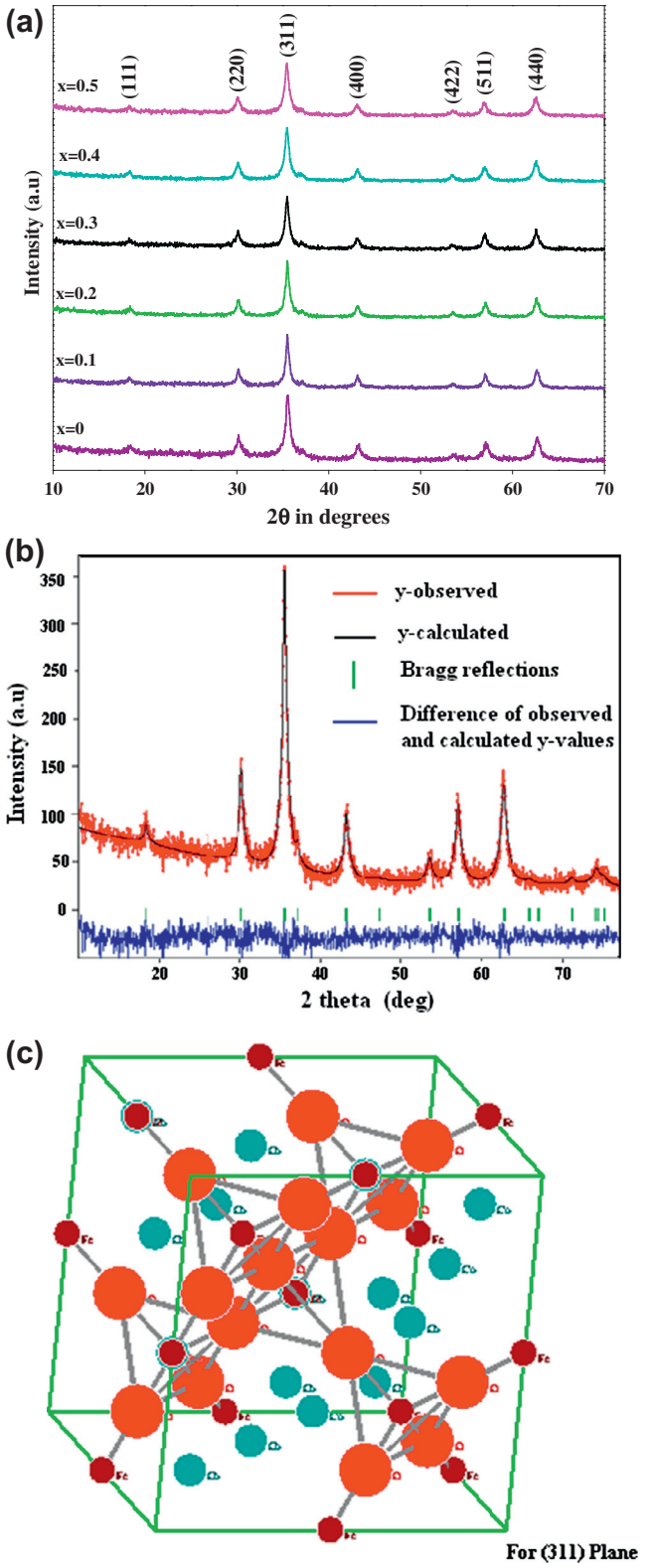

Fig. 1. (a) PXRD patterns of the $Co_{1-x}Zn_xFe_2O_4$ nanoparticles from ($0.0 \leqslant x \leqslant 0.5$), (b) Rietveld refinement of $CoFe_2O_4$ and (c) crystal structure of $CoFe_2O_4$ for (311) plane.

was estimated using the Williamson and Hall (W–H) plots [15] using the relation.

$$\beta\cos\theta = \varepsilon(4\sin\theta) + \lambda/D \quad (3)$$