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Effect of Zn substitution on the structural and magnetic properties of Ni–Co ferrites

K. Raju[a,*], G. Venkataiah[b,1], D.H. Yoon[a]

[a]School of Materials Science and Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea
[b]Department of Physics, Indian Institute of Science, Bangalore 560012, India

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Abstract

A series of ferrite samples with the compositional formula, $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($0 \le x \le 0.5$), was prepared using the citrate based sol–gel method for the better understanding of zinc doping on the structural and magnetic properties. The Rietveld-refined X-ray diffraction data revealed that the samples are having cubic structure with the *Fd-3m* space group. The lattice parameter increased linearly with increasing Zn content. The surface morphology and stoichiometric ratio of the compositional elements were analyzed by scanning electron microscopy equipped with energy dispersive spectroscopy (EDS). EDS showed that the elemental ratios were stoichiometric. An examination of the magnetic properties revealed an increase in saturation magnetization with increasing Zn concentration up to $x=0.3$ and a decrease thereafter. These results could be explained using Neel's collinear two-sub-lattice model and three-sub-lattice non-collinear model suggested by Yafet and Kittel. The magnetic cubic anisotropy constant determined by the law of approach to saturation decreased with increasing Zn content. The underlying mechanism behind observed behavior was discussed qualitatively.

Keywords: A. Sol–gel method; B. X-ray diffraction; C. Magnetic properties; D. Ferrites

1. Introduction

Ferrites with the general compositional formula, $MeFe_2O_4$ (where Me is one or more divalent metallic ions), exhibits a cubic spinel structure. The spinel structure has two types of sub-lattice sites, i.e. tetrahedral and octahedral sites. The net magnetization of the spinel structure is the difference in the magnetization of these sub-lattices. The distribution of the cations at tetrahedral and octahedral sites is an important issue to tune the physical properties of spinel ferrites. Indeed, this distribution depends on several factors, such as the method of preparation, chemical composition, different doped cations, and sintering temperature [1,2].

In general, bulk samples of ferrites are synthesized using conventional solid state reaction methods, which involve high sintering temperatures and longer annealing times to obtain a homogeneous composition. Unfortunately, this preparation method prevents optimization of physical properties of these materials needed for many advanced technological applications due to the poor homogeneity, undesirable phase formation, irregular grain growth, etc. Therefore, wet chemical methods have been used largely to circumvent the limitations in traditional ceramic methods and to produce nanoscale materials. Sintered ferrite samples derived from nanocrystalline powders might exhibit improved magnetic properties [3,4].

Recently, a considerable amount of work has been reported on structural, magnetic and electrical properties of both bulk and nanocrystalline Ni–Zn ferrites [5–13]. In addition, Co–Zn ferrites were also investigated thoroughly because of their appealing magnetic properties for device applications [14–17]. Ni–Zn ferrites possess high resistivity and saturation magnetization, whereas Co–Zn ferrites possess high cubic magnetocrystalline anisotropy.

*Corresponding author. Tel.: +82 538103970; fax: +82 538104628.
E-mail address: raju@ynu.ac.kr (K. Raju).
[1]Present address: School of Physics, University of Hyderabad, Hyderabad 500046, India.

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Research has also been performed on the Ni–Co system with particular focus on enhancing the magnetic properties [18–20]. Unfortunately, less attention has been paid to the synthesis of materials with high saturation magnetization, high resistivity and high crystalline anisotropy, which are essential for device applications. Interestingly, Ni–Co–Zn ferrites fall in this category. The available research on this material [21,22] has been confined to a specific concentration of cobalt and/or zinc. Therefore, a comprehensive study of structural and magnetic properties of Ni–Co–Zn ferrites with systematically varying cobalt and zinc concentrations is needed to exploit these materials for a wide range of applications at room temperature. Therefore, this study demonstrates the structural, magnetic properties of sol–gel synthesized $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($0 \le x \le 0.5$) ferrite system and explained the underlying qualitative mechanism.

2. Experimental

Ferrites with the compositional formula, $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($0 \le x \le 0.5$), were synthesized using a citrate based sol–gel method. The samples were prepared from their corresponding metal nitrates as starting materials. The citric acid dissolved in distilled water was added to all the metal nitrates in solution and the pH was adjusted to approximately 7 by slowly adding an ammonia solution. After obtaining the sol by slow evaporation, a gelating reagent, ethylene glycol was added and heated between 160 and 180 °C to produce gel. Upon further heating, a dry fluffy porous mass (precursor) was produced, which was calcined at 900 °C for 3 h to obtain a nanocrystalline ferrite powder with an average particle size of approximately 100 nm. Subsequently, the calcined powder was pressed into pellets and sintered at 1200 °C for 3 h in air at a rate of 5 °C/min, both in heating and cooling modes. This sintering temperature was found to be the most appropriate for obtaining Zn doped ferrites from powders synthesized using wet chemical methods and displaying homogeneous microstructure, small mean grain size and satisfactory magnetic parameter values, which were comparable to the theoretical values [23]. Table 1 lists the chemical compositions of the samples and their labeling. The samples were characterized structurally by X-ray diffraction (XRD, Philips Xpert) using CuK_α radiation ($\lambda = 1.5406$ Å) between 20° and 80° 2θ with a step size of 0.01° and a scan step time of 0.6 s. The XRD patterns of all the samples clearly revealed the phase formation. The data was analyzed using the FULLPROF Rietveld refinement program [24]. The surface morphology of the sintered samples was examined by scanning electron microscopy (SEM, Inspect S, FEI Company) with an attached energy dispersive X-ray spectrometer (EDS). The room temperature magnetization measurements were performed using a vibrating sample magnetometry (VSM, Lake Shore model no 7460).

3. Results and discussion

3.1. Structural properties

Powder XRD was performed to examine the structural aspects of the materials, and the patterns are shown in Fig. 1

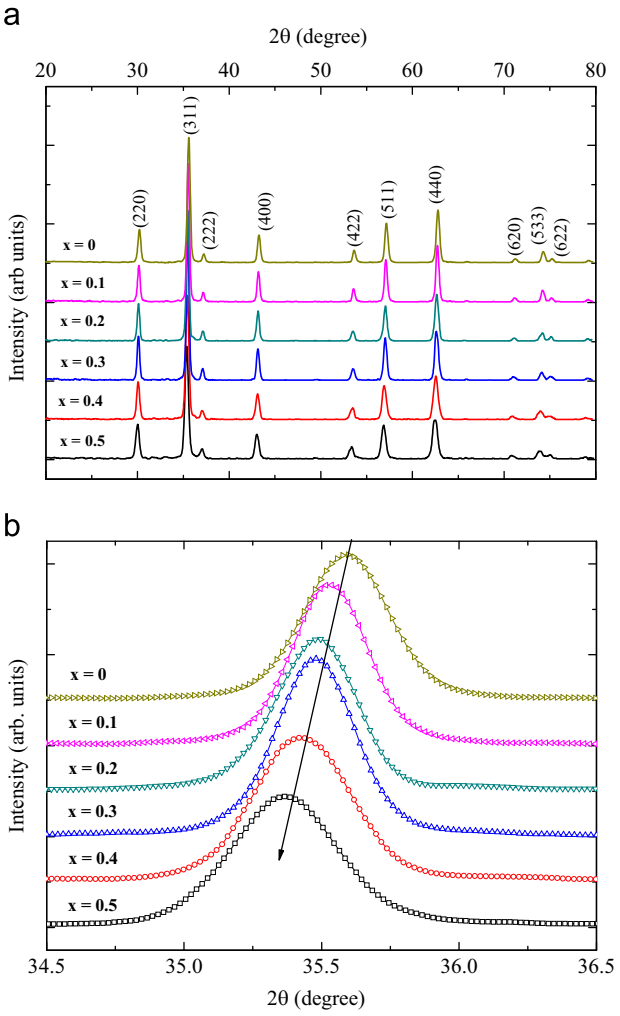

Fig. 1. (a) XRD patterns of all the sintered samples and (b) shift in 2θ at ~35.5° with varying Zn concentration.

Table 1
Structural parameters of the $Ni_{0.5}Co_{0.5-x}Zn_xFe_2O_4$ ($0 \le x \le 0.5$) system.

Sample composition	Sample code	a (Å)	Oxygen parameter ($x=y=z$)	χ^2
$Ni_{0.5}Co_{0.5}Fe_2O_4$	$x=0$	8.3614 (5)	0.2565 (4)	1.24
$Ni_{0.5}Co_{0.4}Zn_{0.1}Fe_2O_4$	$x=0.1$	8.3791(3)	0.2560 (8)	1.15
$Ni_{0.5}Co_{0.3}Zn_{0.2}Fe_2O_4$	$x=0.2$	8.3890 (1)	0.2560 (1)	1.09
$Ni_{0.5}Co_{0.2}Zn_{0.3}Fe_2O_4$	$x=0.3$	8.3982 (4)	0.2555 (5)	1.11
$Ni_{0.5}Co_{0.1}Zn_{0.4}Fe_2O_4$	$x=0.4$	8.4026 (2)	0.2523 (6)	1.21
$Ni_{0.5}Zn_{0.5}Fe_2O_4$	$x=0.5$	8.4068 (5)	0.2505 (1)	1.16

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