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Magnetic and magnetostrictive properties of Cu substituted Co-ferrites

B. Chandra Sekhar [a], G.S.N. Rao [b], O.F. Caltun [c], B. Dhana Lakshmi [d], B. Parvatheeswara Rao [d,*], P.S.V. Subba Rao [d]

[a] Vignan's Institute of Engineering for Women, Visakhapatnam 530046, India
[b] Dr. V.S. Krishna Govt. Degree College, Visakhapatnam, India
[c] Department of Physics, A.I. Cuza University, Iasi, Romania
[d] Department of Physics, Andhra University, Visakhapatnam 530003, India

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ABSTRACT

Copper substituted cobalt ferrite, $Co_{1-x}Cu_xFe_2O_4$ ($x=0.00$–0.25), nanoparticles were synthesized by sol–gel autocombustion method. X-ray diffraction analysis on the samples was done to confirm the cubic spinel structures and Scherrer equation was used to estimate the mean crystallite size as 40 nm. Using the obtained nanoparticles, fabrication of the sintered pellets was done by standard ceramic technique. Magnetic and magnetostrictive measurements on the samples were made by strain gauge and vibrating sample magnetometer techniques, respectively. Maximum magnetostriction and strain derivative values were deduced from the field dependent magnetostriction curves while the magnetic parameters such as saturation magnetization (51.7–61.9 emu/g) and coercivity (1045–1629 Oe) on the samples were estimated from the obtained magnetic hysteresis loops. Curie temperature values (457–315 °C) were measured by a built in laboratory set-up. Copper substituted cobalt ferrites have shown improved strain derivative values as compared to the pure cobalt ferrite and thus making them suitable for stress sensing applications. The results have been explained on the basis of cationic distributions, strength of exchange interactions and net decreased anisotropic contributions due to the increased presence of Co^{2+} ions in B-sites as a result of Cu substitutions.

1. Introduction

Ferrites exhibit a wide range of electromagnetic properties useful for a variety of technological applications. Nickel–zinc and manganese–zinc ferrites are the most explored over a wide frequency range for electronic device applications as they exhibit high permeability, high magnetization, high resistivity and low core losses [1]. Metal bonded cobalt ferrites, on the other hand, with high magnetizations and high values of negative magnetostriction are found promising for magnetomechanical stress/strain sensing and actuating applications [2]. Till recently, high magnetostrictive materials, such as Terfenol, $SmFe_2$ and other rare earth iron compounds are widely used as sensing materials [3,4]. However, the rare earth based composites exhibit magneto-mechanical hysteresis apart from low sensitivity to stress and thus provide only limited scope for sensing due to their high values of anisotropy besides other disadvantages such as poor mechanical stability and high costs [5].

In order to enhance the magnetostrictive performance, current research is focused on obtaining a substituted cobalt ferrite material, which exhibits higher magnetostrictive strains at lower magnetic field strengths (larger strain derivative). Several efforts have been made by exploring different processing and compositional modifications to the cobalt ferrite to obtain better magnetic and magnetostrictive properties. In this connection, it was reported that the annealing of cobalt ferrite can lead to alteration of the cation distribution among the octahedral and tetrahedral sites and there by leads to resulting in useful magnetic properties [6]. Also from the view point of chemical compositional modifications, it was observed that the substitution of Mn for either Fe or Co was seen as a promising measure to bring in structural changes as well as improvements in strain derivative due to corresponding variations in cation distributions [7]. Moreover, it was also shown that the saturation magnetization, coercivity, Curie temperature and magnetostriction of the cobalt ferrite can be desirably altered by adjusting the Mn content [8]. In order to obtain further improvements in strain derivative, it is now aimed at investigating the effects of copper ions when they replace cobalt ions in Co ferrites. Based on the obtained data and analysis, a suitable composition with the desirable characteristics of high strain derivative, moderate values of maximum magnetostriction and saturation magnetization and low Curie temperature as a good sensing material

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* Corresponding author.
E-mail address: bprao250@yahoo.com (B. Parvatheeswara Rao).

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has been proposed.

2. Experimental details

Co–Cu ferrite nanoparticles with the chemical formula, $Co_{1-x}Cu_xFe_2O_4$, where x varies from 0.00 to 0.25 in steps of 0.05, have been prepared by sol–gel autocombustion method. For this purpose, analytical reagent grade cobalt nitrate, copper nitrate, iron nitrate, citric acid and ammonia were used in desired proportions as raw materials. All the chemicals were purchased from Hi-media, Mumbai, India and used as-obtained without any further modifications.

The solutions of the metal nitrate salts and citric acid in desired proportions were prepared separately by using minimum amounts of deionized water and mixed in 1:1 M ratio to form an aqueous solution, a method that maximizes molecular mixing of the components [9]. The pH of the mixed solution was adjusted to 7 using ammonia. The solution was then heated up to 80 °C while stirring to transform the same into dried gel. At this stage, the temperature of the container was further increased to 110 °C only to be ignited at any point of time. Upon ignition, the dried gel burns in a self propagating combustion manner until all the gels were completely burnt out to form ash like flakes. These flakes were then neatly collected and collapsed by using a glass rod or spatula for ultimately making them to be fluffy loose powders. The X-ray diffraction patterns of the obtained samples confirm single phase cubic spinel structures [10]. Fabrication of ferrite pellets using the obtained nanoparticles (crystallites of about 40 nm in size as estimated from Scherrer equation) was done by standard ceramic procedure [11]. The ferrite nanoparticles of all the samples were lightly ground for a few hours in the presence of methanol, air dried and granulated by using 5% poly vinyl alcohol (PVA) as a binder. The granulated powder was then pressed into pellets of 12 mm diameter and 3 mm thickness at a pressure of 150 MPa. The resulting compacts of the ferrite system were then sintered at a temperature of 1050 °C for 4 h in air atmosphere before switching of the furnace and allowing the samples to cool normally.

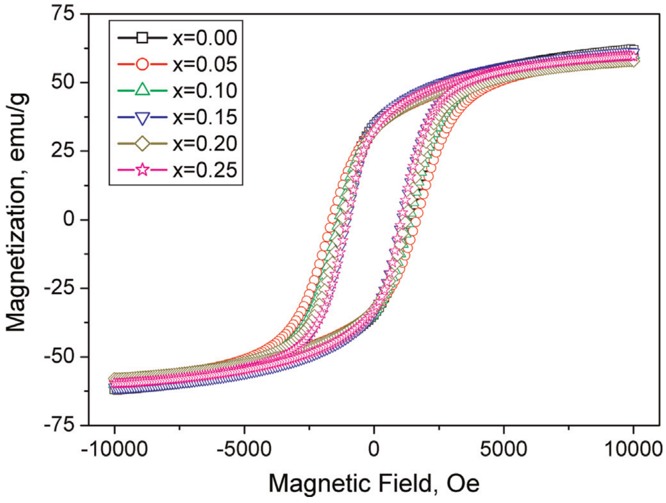

Fig.1. Room temperature magnetic hysteresis loops of $Co_{1-x}Cu_xFe_2O_4$.

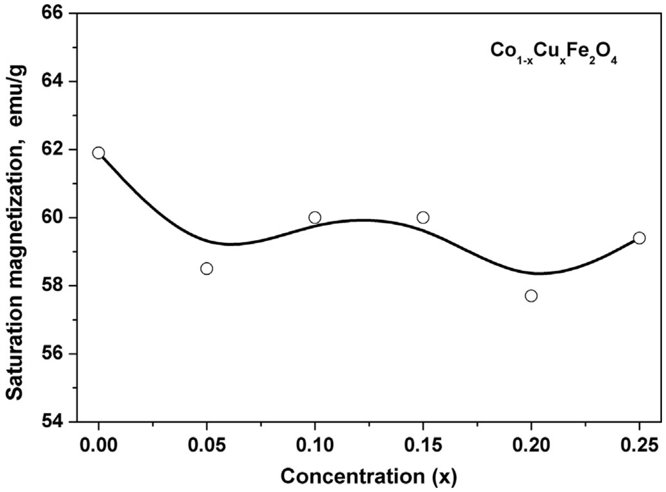

Fig. 2. Variation of saturation magnetization with concentration (x) in $Co_{1-x}Cu_xFe_2O_4$.

3. Results and discussion

3.1. Saturation magnetization

Magnetic hysteresis loops of the Cu substituted cobalt ferrite samples at room temperature are shown in Fig. 1. The curves of all the samples exhibit typical soft ferrimagnetic nature with moderate coercivities.

Saturation magnetization and coercivity values for each sample in the ferrite system has been extracted from the corresponding loop and the variation of saturation magnetization as a function of substituent ion concentration is shown in Fig. 2.

It is evident from the figure that the Cu substitution in $Co_{1-x}Cu_xFe_2O_4$ system throughout the range of concentrations investigated has resulted slightly lower values of saturation magnetization compared to the basic cobalt ferrite. Among different Cu concentrations, the samples with $x=0.05$ and 0.2 are marked by lower values of saturation magnetization.

The observed variations in saturation magnetization as a function of substituent concentration can be explained on the basis of super exchange interactions among tetrahedral (A) and octahedral [B] site ions in the spinel lattice. Generally, in ferrites, Neel [12] considered three kinds of exchange interactions between unpaired electrons of the ions lying (i) both at A-sites (A–A interaction), (ii) both at B-sites (B–B interaction) and (iii) one at A-site and another at B-site (A–B interaction). Out of these three interactions, A–B interaction is predominant over B–B and A–A interactions. These interactions tend to align all the magnetic spins at A-site in one direction and those at B-site in the opposite direction. The net magnetic moment of the lattice is therefore the difference between the magnetic moments of B- and A-sublattices, i.e. $M_B - M_A$. The exchange interactions in the spinel lattice can greatly be influenced by the nature of the ions present at both A- and B-sublattices.

The distribution of cations in tetrahedral and octahedral sites in the spinel structure is necessary to discuss the compositional dependence of the saturation magnetization. It takes a long way to provide the correct distribution of cations from the consideration of our measurements on various properties. Before attaining the accurate cation distribution to the $Co_{1-x}Cu_xFe_2O_4$ system, it is first considered necessary to examine the cation distribution of the $CoFe_2O_4$, which can be represented by:

$$(Co_yFe_{1-y})[Co_{1-y}\,Fe_{1+y}]O_4$$

wherein the value of y is reported to be around 0.19 in many works [13,14].

As per the crystal field stabilization energies for occupation of cations in spinel lattice sites, the Cu^{2+} ions have specific preferences for B-sites [15]. In the present $Co_{1-x}Cu_xFe_2O_4$ system,