Phase evaluation of Li^+ substituted $CoFe_2O_4$ nanoparticles, their characterizations and magnetic properties

R.H. Kadam [a], Suresh T. Alone [b], Maheshkumar L. Mane [c], A.R. Biradar [a], Sagar E. Shirsath [d],*

[a] Materials Science Research Lab, Shrikrishna Mahavidyalaya Gunjoti, Osmanabad, Maharashtra, India
[b] Department of Physics, RS Art's, Science and Commerce College, Pathri, Aurangabad, Maharashtra, India
[c] Department of Physics, Rajarshi Shahu Mahavidyalaya, Latur, Maharashtra, India
[d] Spin Device Technology Center, Department of Information Engineering, Shinshu University, Nagano 380-8553, Japan

ARTICLE INFO

ABSTRACT

Li^+ substituted $CoFe_2O_4$ with the chemical formula $Li_{3x}CoFe_{2-x}O_4$ were synthesized by sol–gel auto combustion method. The synthesized samples were annealed at 600 °C for 4 h. X-ray diffraction data were used to evaluate the structure of the prepared samples. Spinel ferrite phase of $CoFe_2O_4$ changes to ordered like lithium ferrite phase with increase in L^{i+} substitution. Lattice constant increases whereas particle size found to decrease with Li^+ substitution. Infrared spectroscopy also confirmed the phase transition of $CoFe_2O_4$ after the incorporation of lithium ions. Substitution of Li^+ ions for Fe^{3+} caused a decrease in the saturation magnetization from 69.59 emu/g to 47.71 emu/g and the coercivity increased from 647 Oe to 802 Oe. Resistivity and dielectric properties shows inverse relation to each other.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Even after more than half of the century the scientist, researchers, technologist, and engineers are still excited in various types of bulk as well as nanocrystalline ferrite materials. The recent trend is focused on the doped ferrites prepared using various synthesis techniques with different cation concentrations which in turn affects the various properties like, electrical, dielectric, and magnetic behavior [1]. It is known that the intrinsic parameters of ferrites, such as magnetization, low dielectric losses, Curie temperature and resistivity, depend on the chemical composition, heat treatment and type of additive or substituted ions. In addition, the rectangularity of B–H loop is also found to increase with increasing defects that hinder the magnetic domain wall motion within the grains. It is interesting to note that the electromagnetic properties of spinel ferrites can be tailored by controlling the type and amount of transition metallic substitutes. Until now, several investigations have been carried out to make further improvements in the electric, dielectric and magnetic properties of substituted lithium ferrites.

Cobalt ferrite shows the good magnetostrictive properties, magnetocrystalline anisotropy, high coercivity and moderate saturation magnetization among all the ferrite family [2]. The magnetoelastic properties of Co^{2+} in spinel ferrites are most commonly seen in magnetocrystalline anisotropy and relaxation effects. In general, Co^{2+} ions are stabilized in octahedral sites which give rise to a degenerate or near-degenerate orbital ground state. As a result, the strong spin–lattice interaction that arises from the unquenched orbital angular momentum has served to explain the high spin wave line widths [3]. Lithium (Li^+) and Li-substituted ferrites have been found to be excellent materials in high density recording media and absorbers and microwave devices due to their low cost, high saturation magnetization, high Curie temperature and hysteresis loop properties, which offer advantageous performances over other spinel structures [4,5]. However, no reports have been found in the literature on the properties of Li-substituted cobalt ferrites. The purpose of the present work is to study the structural, magnetic and electrical properties of Li^+ substituted $CoFe_2O_4$ with a chemical formula $Li_{3x}CoFe_{2-x}O_4$ (where $x=0.0$, 0.1, 0.2 and 0.3).

2. Experimental procedure

Ferrite powders of composition $Li_{3x}CoFe_{2-x}O_4$ (where $x=0.0$, 0.1, 0.2 and 0.3) were synthesized by the sol–gel auto-combustion method. A.R. grade citric acid ($C_6H_8O_7 \cdot H_2O$), lithium nitrate ($LiNO_3$), cobalt nitrate ($Co(NO_3)_2 \cdot 3H_2O$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were dissolved in distilled water to obtain a mixed solution. The reaction procedure was carried out in an air

* Corresponding author. Tel.: +81 8048186605.
  E-mail addresses: shirsathsagar@hotmail.com,
sagarshirsath@gmail.com (S.E. Shirsath).

atmosphere without the protection of inert gases. The molar ratio of metal nitrates to citric acid was 1:3. The metal nitrates were dissolved together in the minimum amount of double-distilled water needed to obtain a clear solution. An aqueous solution of citric acid was mixed with the metal-nitrate solution, and ammonia solution was slowly added to adjust the pH to 7. The mixed solution was placed on a hot plate with continuous stirring at 90 °C. During evaporation, the solution formed a very viscous brown gel. When all of the water molecules were removed from the mixture, the viscous gel began to froth. After few a minutes, the gel ignited and burnt with glowing flints. The decomposition reaction continued until the entire citrate complex was consumed. The auto-combustion was completed within a minute, yielding brown-colored ashes referred to as the precursor. The as-prepared powders of all the samples were sintered at 600 °C for 4 h to obtain the final product.

The samples were powdered for X-ray investigation. One portion of the powder was examined using a Phillips X-ray diffractometer (Model 3710) with Cu-$K\alpha$ radiation ($\lambda = 1.5405$ Å). The scanning step was 2 °/min and scanning rate was 0.02°. A 1-D detector was used for the XRD measurement. The X-ray generator was operated at 40 kV and 30 mA. A specially processed Si powder sample was used as the instrumental standard. The (1 1 1) reflection of Si at 28.5° indicates that the instrumental broadening is very small (0.5 Å). Particle size and particle size distribution is characterized by transmission electron microscopy (TEM) (Philips, Model CM 200). The infrared spectrum of each sample was recorded at room temperature in the range of 300 cm^{-1} to 900 cm^{-1} using a Perkin Elmer infrared spectrophotometer. The magnetic measurements were performed at room temperature using a commercial PARC EG&G VSM 4500 vibrating sample magnetometer. The DC electrical resistivity of each sample was measured using the two-probe technique in the temperature range 300–800 K on a disc-shaped pellet of 10 mm diameter and 3 mm thickness. The dielectric properties, i.e. the dielectric constant (ε') and dielectric-loss tangent ($\tan\delta$) as a function of temperature were studied using LCR-Q meter.

3. Results and discussion

3.1. Structural analysis

The phase identification and the lattice constant determination were performed on an X-ray diffraction pattern (XRD). The X-ray diffraction (XRD) patterns of the $Li_{3x}CoFe_{2-x}O_4$ ferrite system with $x = 0.0$–0.3, in the steps of 0.1 are shown in Fig. 1. The XRD pattern for $CoFe_2O_4$ ($x = 0.0$) indicate well-defined peaks of crystalline FCC phase which confirm spinel cubic structure formation for the samples (JCPDS card # 01-1121). No additional impurity reflections were observed ensuring the phase purity. It was evident from the XRD pattern that the second phase peaks were dominant at $x \geq 0.2$ Li$^+$ substitution. This second phase shows the transition of single phase cubic spinel structure of $CoFe_2O_4$ to order like lithium ferrite phase. It may be quite likely that Li$^+$ substitution goes beyond its solubility limit in the spinel lattice, forming a second phase. The second phase was identified as lithium ferrite (JCPDS card # 82-1436). The second phase corresponds to superstructures peaks are evidence that this sample has ordered spinel type structure. These superstructure lines arise from ordering of the lithium sublattice and are seen for conventionally prepared materials that have reached thermodynamic equilibrium [6,7]. Here it is to be noted that the two separate crystallographic forms of $Li_{0.5}Fe_{2.5}O_4$ have been isolated; a superstructured form in which the lithium and iron atoms are ordered and a disordered form in which lithium and iron have a random statistical distribution over all the

octahedral positions. The ordered i.e. superstructure form of $Li_{0.5}Fe_{2.5}O_4$ has an inverse spinel structure (space group $Fd3m$), with Fe^{3+} resides at tetrahedral 8a positions and Li$^+$ and Fe^{3+} randomly distributed over the 16d octahedral sites. Samples have the cubic spinel structure with a small amount of α-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ [8,9].

The diffraction peak shifts towards the lower angle a little with Li$^+$ substitution (Figs. 1 and 2). The diffraction angles (2θ) and lattice parameters (a) of $Li_{3x}CoFe_{2-x}O_4$ ferrite as a function of Li$^+$ substitution (x) are shown in Fig. 2. The lattice constant (a) of all the samples was determined by using the equation discussed elsewhere [10]. Variation of the lattice constant indicates an increasing trend with increasing Li$^+$ substitution. The radius of the Li$^+$ ion (0.78 Å) is bigger than that of the Fe^{3+} (0.67 Å) thus, the shift in diffraction peak towards lower is caused by the substitution of Li$^+$ ions for Fe^{3+} ions. Meanwhile, Li$^+$ ion enter into the octahedral-site (B site) which swells the lattice, and then enlarges the lattice parameter.

The morphologies and particle sizes of the samples were studied by transmission electron microscopy (TEM). Fig. 3 shows the typical TEM image of the sample $x = 0.1$. From the figure, it is clear that the particles are spherical in shape and are agglomerated to some extent. This agglomeration can be attributed to the magnetic dipole interactions arising between ferrite particles [11]. The average crystallite size (t) was determined using the line broadening of most intense (3 1 1) diffraction peak using the
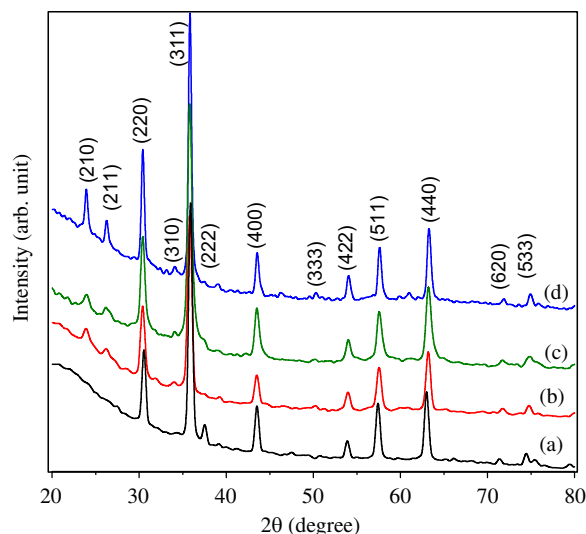

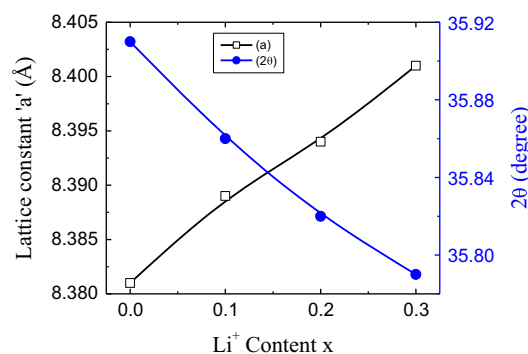**Fig. 1.** X-ray diffraction patterns of $Li_{3x}CoFe_{2-x}O_4$ where (a) = 0.0, (b) = 0.1, (c) = 0.2 and (d) = 0.3.

Fig. 2. Variation of lattice constant and 2θ position for (3 1 1) plane with Li content x.