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Study of structural and magnetic properties of Li–Ni nanoferrites synthesized by citrate-gel auto combustion method

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Abstract

An attempt has been made to prepare nanocrystalline nickel substituted lithium ferrites, having chemical composition $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (where $x=0.0$–1.0 with a step increment of 0.2) by a citrate-gel auto combustion method. Structural characterization of the synthesized samples was carried out by X-ray diffraction analysis (XRD) and field emission scanning electron microscopy (FESEM). Magnetic measurements were carried out using vibrating sample magnetometer (VSM) and Mossbauer spectroscopy. From these measurements it is observed that Ni^{2+} substitution in lithium ferrites has strong influence on magnetic properties. Hysteresis loops indicate that the saturation magnetization values were decreased from 56 emu/gm to 28 emu/gm by increasing the Ni^{2+} content in the Li–Ni ferrite samples. This signifies the fact that the lesser magnetic Ni^{2+} ions are substituted for the magnetic Fe^{3+} ions in the octahedral sub-lattice of the ferrites. Field Cooled (FC) and Zero Field Cooled (ZFC) magnetization measurements under an applied field of 100 Oe and 1000 Oe in the temperature range of 5–375 K were performed on two samples $Li_{0.1}Ni_{0.8}Fe_{2.1}O_4$ and $NiFe_2O_4$. The magnetization as a function of an applied field 10 T was carried out at two different temperatures 5 K and 310 K. These measurements showed the blocking temperature of the two samples at around 350 K above which the materials show super-paramagnetic behavior where the coercivity and remanence magnetization are almost zero.

Keywords: Magnetic properties; Nanocrystalline ferrites; X-ray diffraction; FC & ZFC studies; Hysteresis loops

1. Introduction

The development of the novel nanocrystalline magnetic materials and the study of their tunable electromagnetic properties has become one of the most important research areas of the 21st century. Ferrites are the ferri-magnetic semiconducting materials composed of iron oxides and metal oxides. These are superior and excellent magnetic materials that are widely used in high frequency microwave applications like isolators, circulators, gyrators and phase shifters [1]. Ferrites in nanoregime exhibit excellent properties than in bulk form. Nanoferrites showcase high electrical resistivity and excellent magnetic properties that are not found in any other magnetic materials. In addition to these properties, they have very high degree of compositional variability. It is because, the crystal structure of ferrites is such that it can accommodate different cations at available sites with different valence states. Depending on the occupancy of cations between the different sites, spinel ferrites are of three types viz., normal spinel, inverse spinel and mixed spinel. In the inverse spinel structure, A-sites are occupied by the Fe^{3+} ions whereas the B-sites are occupied by the divalent metal cations and Fe^{3+} ions in equal proportions. The angle A–O–B is closer to 180° than the angles B–O–B and A–O–A.

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Therefore the pair (Fe–Fe) has a strong anti-ferromagnetic interaction.

Lithium ferrite belongs to inverse spinel category, the structure of which allows the easy incorporation of different transition metal ions. The substitution of different metal cations in the structure of ferrites, considerably affect their electrical and magnetic properties. This is mainly due to the magnetic interaction between the cations that are distributed among the tetrahedral and octahedral sites, thereby changing the structure of the lithium ferrites from inverse spinel to the mixed spinel. Lithium ferrites and substituted lithium ferrites are equally important materials in the field of microwave technology due to their low cost, high Curie temperature, squareness ratio of hysteresis loop and low dielectric loss [2–5].

The substitution of other metals for Fe in lithium ferrites has been proposed to tailor the structural, electrical and magnetic properties. Transition metal ion doping in semi conducting material is expected to enhance its performance for various applications. A variety of metal ions substitution like Zn^{2+}, Mg^{2+}, Cr^{2+}, Cd^{2+}, Co^{2+}, Al^{3+} has been done by various researchers in $Li_{0.5}Fe_{2.5}O_4$ so as to optimize their structural, electrical and magnetic properties [6–10]. The crystal structure and sole presence of Fe^{3+} ions in the host material has allowed changing of the exchange interactions giving rise to its ferromagnetic order. The subsequent substitution with either magnetic or non-magnetic cations has allowed analysis of different magnetic states that are arising due to the perturbed exchange interactions between the magnetic ions [11].

The microstructure and the properties of ferrite materials are very sensitive to several factors including route of synthesis, composition of constituents, grain size or grain structure, type and amount of metal ion substitution [12]. Nanocrystalline ferrites prepared by variety of techniques have been studied by large number of researchers in the past decade. Synthesis of pure and substituted ferrites was carried out by several methods, such as co-precipitation technique, thermal decomposition at 900–1100 °C, electro spinning technique, auto- combustion method etc. Among these techniques, auto-combustion method is characterized by high temperatures, fast heating rates, short reaction times and results in very low sized particles. These novel features make auto-combustion method, an attractive method for the synthesis of nanocrystalline materials compared with conventional solid state reaction method. The control of the electrical and magnetic properties at high frequencies has been attracting the attention of researchers in recent years [13].

Various researchers reported that the $Li_{0.5}Fe_{2.5}O_4$ ferrites synthesized by different synthesis processes show different values of magnetic parameters like M_s (saturation magnetization), M_r(remanence), and H_c (coercivity) [14–17]. The sintering temperature of the lithium ferrite is around 1100 °C, at which Li_2O is volatile and stoichiometry of the material is not maintained [18]. It is observed that there is a significant change in the properties of lithium ferrites by substitution of different metal cations. This fact motivated the authors to synthesize nickel substituted lithium ferrites by the citrate-gel auto combustion method with low sintering temperature to maintain the stoichiometry of the material. The present paper reports the synthesis, structural and magnetic properties of Ni substituted lithium ferrites with the chemical composition $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ by the citrate-gel auto-combustion method. The effect of nickel substitution on magnetic properties was investigated by Mossbauer and FC & ZFC studies.

2. Experimental

2.1. Preparation of $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ nanoferrite particles

Nanocrystalline $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (x=0.0, 0.2, 0.4,.6, 0.8 and 1.0) ferrites were synthesized by the citrate gel auto-combustion method using high purity Lithium nitrate-$LiNO_3$, Ferric nitrate $Fe(NO_3)_29H_2O$, Nickel nitrate-$Ni(NO_3)_26H_2O$, and citric acid-$C_6H_8O_7 \cdot H_2O$ [99% pure Sigma Aldrich Company Chemicals] as raw materials. The calculated quantities of metal nitrates and citric acid were weighed and dissolved separately in minimum quantity of double distilled water. The individual solutions were mixed together with continuous stirring by placing it on a magnetic stirrer with hot plate, and pH of the mixed solution was maintained at 7 by adding ammonia. Then the temperature was increased to 100 °C with continuous stirring. When the volume of the solution is reduced to one-third of the initial volume indicated by gel formation, the temperature was increased to 180 °C. The gel has burnt and undergone combustion in a self propagating manner resulting in the formation of ferrite powder. The resultant powder was ground and sintered at 500 °C for four hours in a muffle furnace. The overall reactions for formation of $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ ferrites for x=0.0, 0.4 and 1.0 values are given by:

$$0.5LiNO_3 + 2.5Fe(NO_3)_3 \cdot 9H_2O + 3C_6H_8O_7 \rightarrow$$
$$Li_{0.5}Fe_{2.5}O_4 + 4N_2 + 18CO_2 + 7H_2 + 27.5H_2O$$

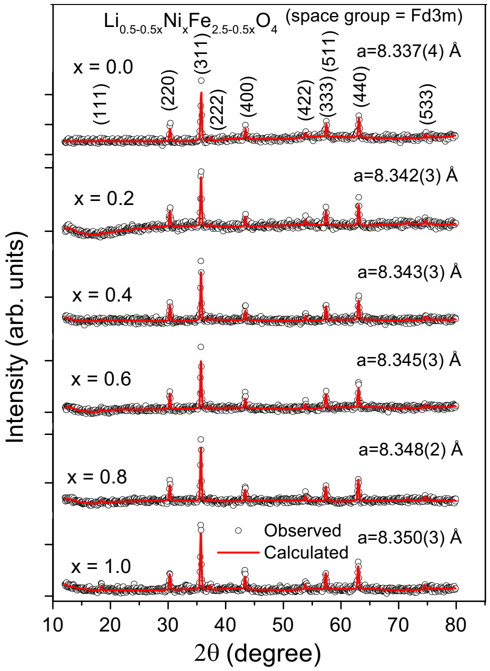

Fig. 1. Rietveld refined X-ray diffraction patterns of $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (x=0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) ferrite NPs.