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Electrical transport properties of nano crystalline Li–Ni ferrites

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Abstract

Nickel substituted lithium nano ferrites with the chemical composition $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ ($0.0 \leq x \leq 1.0$) were prepared by Citrate-gel method. The single phase cubic spinel structure of the ferrites was confirmed by X-ray diffraction analysis. Surface morphology and particle size of the samples was studied using Transmission Electron Microscopy (TEM). The TEM micrographs reveal that the particle size of the samples was in the nanometric range confirming the nano crystalline nature. The FTIR spectra shows the two significant absorption bands in the wave number range of 400–600 cm^{-1} arising due to the inter-atomic vibrations in the tetrahedral and octahedral coordination compounds. The dielectric parameters like dielectric constant (ε'), dielectric loss tangent ($\tan\delta$) and AC conductivity (σ_{ac}) of the samples were measured using LCR meter at room temperature in the frequency range 20 Hz–2 MHz ε', $\tan\delta$ and σ_{ac} of the samples show a normal dielectric behavior of ferrites with frequency which indicates the fact that the dielectric dispersion is due to the hopping of electrons between the Fe^{2+} and Fe^{3+} ions. Thermo Electric Power (TEP) studies of Li–Ni ferrites were measured using differential method in the temperature range of 473–873 K. Seebeck coefficient (S) of the prepared ferrites was increased with increasing temperature.

Keywords: Ferrites; Citrate gel method; X-ray diffraction; Dielectric behavior; Thermo electric power

1. Introduction

Ferro-spinels have interesting structural, electrical and magnetic properties. They are widely used in many important applications such as microwave devices like circulators, phase shifters, memory cores, magnetic recording media, transformers, choke coils, high frequency instruments, data storage, noise filters and recording heads, owing to their high magnetic permeability and low magnetic loss [1]. The usefulness of a ferrite material for microwave devices is influenced by physical and chemical properties which in turn depend on the method of preparation [2]. For obtaining the required properties, selection of the ferrite composition and nature of substituent ion is most important besides sintering temperature and time. The valence state of doping ions in the selected ferrite composition influences the structural, electrical and magnetic properties of ferrite material.

Ferrite materials are low mobility semiconducting iron oxides. Unlike most materials, they possess high permeability and moderate permittivity at different frequencies. Due to their small eddy current losses, they possess wide range of electronic applications in terms of energy production, transmission and telecommunication applications. At present, 'nano ferrites' has been the subject of many scientists all over the world because of novel properties exhibited by nano-particles. The properties of bulk material vary drastically when their size approaches the nano-scale [3]. In ferrites, grain size reduction and grain boundary modifications results in high frequency properties such as resistivity and quality factors. Smaller grain size will provide large number of grain boundaries as barriers for the electron hopping between the different ions so as to increase the resistivity and decrease the eddy current losses in ferrites [4].

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Lithium ferrites and substituted Lithium ferrites have become most attractive materials for microwave applications especially as a replacement for garnets. Mixed lithium ferrites have low cost, square hysteresis loop, high Curie temperature that make them promising materials for microwave applications [5–7].

Nano-crystalline ferrite materials can be synthesized by various preparation techniques including glass-ceramic method [8], hydrothermal method [9], sol–gel method [10], co-precipitation method [11], and citrate-gel method [12]. Many scientists have studied the frequency dependence on the dielectric properties of Li–Co [13], Li–Mg [14], Li–Ge [15]. Among the various preparation methods citrate-gel auto-combustion method has attracted the attention of solid state chemist, physicist and material scientist etc. due to the fact that the product with high purity, good homogeneity and low particle size can be obtained. This is because the mixing of constituent cations takes place on atomic scale in the precursor itself, thereby lowering the sintering temperature during the formation of required ferrites. Moreover, novel properties for the product were observed in this method of preparation [16]. Some authors have synthesized nickel substituted lithium ferrites by ceramic method with high sintering temperature [17]. However, there is no detail report on Ni substituted Lithium nano ferrites prepared by citrate-gel auto combustion method with low sintering temperature.

In the present work, the authors report the structural properties of Li–Ni nano crystalline ferrites with XRD, TEM and FTIR analysis with the detailed investigation of the composition. Frequency dependence of the dielectric properties and thermo electric power studies of the samples with the results were discussed.

2. Experimental

Ni substituted Lithium ferrites with compositional formula $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ (where x = 0.0 to 1.0) with a step increment of 0.2 have been prepared by low temperature citrate gel auto combustion method with the following raw materials as starting chemicals:

(i) Ferric nitrate ($Fe(NO_3)_2 9H_2O$)
(ii) Nickel nitrate ($Ni(NO_3)_2 6H_2O$)
(iii) Lithium nitrate ($LiNO_3$)
(iv) Citric acid ($C_6H_8O_7 \cdot H_2O$) and Ammonia solution (NH_3).

The detailed procedure for the preparation of ferrites by citrate-gel auto-combustion method was explained in our earlier publication [18]. The synthesized powders were sintered at 500 °C for 4 h in air at a slow heating rate of 5 °C/min and then furnace cooled. X-ray diffraction analysis of the prepared ferrite powders were performed by using Philips X-ray diffractometer with Cu K_α radiation of wavelength 1.5405 A°. The average crystallite size of the ferrites was determined from the measured width of their diffraction pattern using the Debye Scherer's formula

$$D = \frac{0.91\lambda}{\beta \cos\theta} \quad (1)$$

Where λ-the wavelength of the x-ray used for diffraction,

β – full width half maximum (FWHM) in radians.
θ – diffraction angle.

The lattice constant 'a' was calculated using the following relation

$$a = d\left(h^2 + k^2 + l^2\right)^{1/2} \quad (2)$$

where d-inter planar distance, hkl-miller indices

Hopping length for tetrahedral site (d_A) and octahedral site (d_B) can be calculated using

$$d_A = 0.25a\sqrt{3}A^0 \quad \& \quad d_B = 0.25a\sqrt{2}A^0 \quad (3)$$

The morphology of prepared ferrites was investigated using Transmission Electron Microscopy with a JEOL 2000 electron microscope operating at 200 kV.

The FTIR spectra of the ferrite samples as pellets in KBr were recorded by SHIMADZU FTIR spectrophotometer in the frequency range of 400–600 cm^{-1}

For the thermo electric power measurements, the synthesized powders were made in the form of circular pellets (diameter – 13 mm and thickness – 2 mm) using 2% polyvinyl alcohol (PVA) as binder under a pressure of 5 tons for 1–2 min. These pellets were finally sintered at 500 °C for 4 h and then slowly cooled to room temperature. Pellets were then coated on either side with a thin layer of silver paste to have good electrical contact.

Agilent E4980A Precision LCR meter was used for the dielectric measurements of the prepared pellets by using bellow formulae [19,20].

$$\text{Real part of dielectric constant } (\varepsilon') = C\,d/A\,\varepsilon_0 \quad (4)$$

$$\text{Imaginary part of dielectric constant } \varepsilon'' = (\varepsilon')\tan\delta \quad (5)$$

$$\text{AC conductivity} \quad \sigma_{ac} = 2\pi f\,\varepsilon_o(\varepsilon')\tan\delta \quad (6)$$

Where C – capacitance of the pellet in faraday

$\tan\delta$ – dielectric loss tangent.
ε_0 – permittivity of free space = 8.85×10^{-12} F/m
f – frequency

Thermo electric power measurement studies on the prepared pellets were carried out by differential method from 320 K to well beyond Curie temperature. The pellet was kept between the hot and cold junctions of the method. The temperature difference between two ends of the sample was kept at 10 K throughout the measured temperature range. The thermo emf was produced across the sample as the charge carriers (electrons or holes) diffused from the hot junction to the cold junction due to the temperature gradient ΔT in degree Kelvin maintained across the sample.