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Preparation and characterization chemistry of nano-crystalline Ni–Cu–Zn ferrite

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ABSTRACT

In submitted research; nanocrystalline powders having elements $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_{2-x}In_xO_4$ with varied amounts of indium ($x = 0.0$, 0.1, 0.2, 0.3 and 0.4) were grown-up by modified citrate to nitrate alchemy. The realism of single phase cubic spinel creation of the synthesized ferrite samples was studied by the DTA-TGA, XRD, SEM, EDX, FT-IR, VSM and dielectric measurements. SEM was applied to inspect the morphological variations and EDX was used to determine the compositional mass ratios. The studies on the dielectric constant (ε'), dielectric loss (ε''), loss tangent ($\tan\delta$), ac conductivity (σ_{ac}), resistive and reactive parts of the impedance analysis (Z' and Z'') at room temperature were also carried out. The saturation magnetizations (Ms) were determined using the vibrating sample magnetometer (VSM). Ms. decreased with the increase In^{3+} doping content, as Fe^{3+} of $5\mu_B$ ions are replaced by In^{3+} of $0\ \mu_B$ ions.

1. Introduction

Spinel ferrite nanoparticles have been the subject of interest in the recent years due to their promising technological applications such as high-density data luggage compartment, ferrofluid, spintronics, sensors, magnetocaloric refrigeration, heterogeneous catalysis, hydrogenation flourishes, magnetically guided drug delivery, magnetic resonance imaging etc. [1–4]. Nanosized ferrite particles exhibit the unusual magnetic properties which are not observed in the bulk material, e.g. single domain behavior, superparamagnetism, and reduced Curie temperature and magnetization [5]. Latest intensification in wireless technology, such as: high-speed wireless network, internet manageable cell phones, has reconnoitred the superficies of real-time intimation during the last few decades. Mutilayer chip inductors (MLCIs) are important components which have greatly benefited the miniaturization of many electronic devices, such as, cellular phone, notebook computer, video camera etc. They are made by putting alternate layers of ferrite material and Ag electrode since Ag is used as an internal conductor of MLCIs due to its high conductivity. The increasing demand of Ni-Cu-Zn ferrite in various applications has led to a growing interest in low temperature sintered ferrites. The Ni-Cu-Zn ferrite is an important material that was used to develop the multilayer chip inductor (MLCIs) in 1980. More recently, Ni-Cu-Zn ferrite nanostructures have been used in the development of miniaturization of electronic components for the application in high frequency region. Ni–Cu–Zn ferrites are famous for their extensive utilization in MLCIs applications in high frequency region. Ni–Cu–Zn ferrite come under the umbrella of soft ferrites and chemically symbolized as MFe_2O_4. For the sake of sharply perusal and exploit the potential and possibilities associated with the nanomaterials, the clef aim is to synthesize well-defined, monodisperse structures of ferrite materials through an ingenious synthesis. The most common synthesis techniques that are used to synthesize the nanomaterials covers; hydrothermal [6], solvothermal [7], mechanical milling [8], sol–gel [9], bacterial synthesis [10] and so on. Most of them have been convened towards the research of particles, with a narrow size distribution in the range of few nanometres. Many research groups have studied the effect of various doping substitution in the Ni-Cu-Zn ferrite matrix to upgrade their structural, electrical and magnetic properties. Yan et al. [11] premeditated the microwave sintering of high-permeability $(Ni_{0.20}Zn_{0.60}Cu_{0.20})Fe_{1.98}O_4$ ferrite at low sintering temperatures, and they initiated that at low frequency domain wall motion plays predominant role in the magnetization process. Effects of impurity Na^+ ions on the structural and magnetic properties of Ni–Zn–Cu ferrite powders were performed by Ailin Xia [12] to reveal that

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the impurity Na^+ ions affect the crystalline structures and magnetic properties greatly. Furthermore, Ref. [13] reported the effect of Mg substitution on electromagnetic properties of $(Ni_{0.25}Cu_{0.20}Zn_{0.55})Fe_2O_4$ ferrite prepared by auto combustion method. Raghvender et al. [14] studied the nanocrystalline Ni–Cu–Zn ferrites prepared by oxalate based precursor method.

It is known that when Fe^{3+} ions are substituted by In^{3+} ions lattice parameters are changed. Large size of In^{3+} tries to increase the lattice parameter and strain produced by its substitution in cell, tries to decrease it [15,16]. Addition of In^{3+} ions into the ferrite samples may produce a change in structural as well as magnetic properties depending on the amount of In^{3+} ions used. Shirsath et al. underline the interesting results as they showed an increase in magnetization with In^{3+} substitution in $NiFe_2O_4$ [17]. In the present work we have used the combustion synthesis, as it is engaged in the field of propellants and explosives, involves an exothermic and self-sustaining chemical reaction between the required metal salts and a proper organic fuel [18]. Since, no reports have been sighted in the literature on the structural, dielectric, impedance, and magnetic phase evolution of nanocrystalline In^{3+} substituted $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_2O_4$ ferrites synthesized by a novel combustion method of synthesis. In the present study we account an effort on the synthesis of $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_{2-x}In_xO_4$ ferrites. In this article we report the low temperature synthesis of Ni–Cu–Zn ferrites and its crystal structure, magnetic and electrical properties.

2. Experimental details

2.1. Method and synthesis

To synthesize the $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_{2-x}In_xO_4$ nanocrystalline ferrite; $Ni(NO_3)_2.6H_2O$, $Cu(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $In(NO_3)_3.9H_2O$, $C_6H_8O_7H_2O$ and $Fe(NO_3)_3.9H_2O$ were used as starting materials. The purity of the constituent elements was 99.9% supplied by Merk, India. In this paper, approximately all regents used were of analytical purity 'AR' and used without further purification. Metal ions were dissolved in 20 mL of distilled water to form a clear solution and assorted overall. The mixture was stirred with a magnetic stirrer until the reactants were dissolved fully. We utilize in the midst of citric acid $C(OH)(COOH)(CH_2COOH)_2H_2O$ (MW 210.14) in this course. Citric acid is a pathetic acid and has three carboxylic and one hydroxyl group for coordinating metal ions, thereby, helps in the homogenous mixing to get segregated from the solutions. A flowchart for the preparation of Ni–Cu–Zn–In spinel ferrite is illustrated in Fig. 1.

Ferrites with different compositions $Ni_{0.5}Cu_{0.25}Zn_{0.25}Fe_{2-x}In_xO_4$ $(0 \leqslant x \leqslant 0.4)$ have been arranged in a polycrystalline form via citrate–nitrate precursor auto combustion using the mixed metal nitrate to the citric acid solution in 1:1 M ratio. The pH value of the clear solution thus obtained was unity. Proper control of the pH is the key factor in synthesizing the ferrites. Therefore, a required amount of ammonia is anthologized into the solution in run time to coordinate the pH cost by 7 in view of the fact that base catalysts are applied to speed up the reaction. Dried gel is formed finally in dehydration process. Then, the mixed solution was poured into a dish and heated and stirred to transform into an aerogel. The gel so formed is kept in an air oven at 100 °C for 36 h in order to remove the adsorbed water. During this process the gel swells into a fluffy mass, which eventually breaks into brittle flakes. The citrate–nitrate precursor auto combustion reaction (for example $x = 0.4$ composition) is as follows:

$$0.5Ni(NO_3)_2 + 0.25Cu(NO_3)_2 + 0.25Zn(NO_3)_2 + 0.4In(NO_3)_3 + 1.6Fe(NO_3)_3 + 3C_6H_8O_7 \rightarrow Ni_0.5Cu_0.25Zn_0.25Fe_1.6In_0.4O_4 + 6N_2 + 4O_2 + 18CO_2 + 12H_2O.$$

This precursor powder was then calcined at 600 °C for 8 h to obtain final product. The rate of heating and cooling was maintained 10°/min. The resultant powders were ground into fine particles using an agate mortar and pestle the powder mixture was pressed into pellets of 13 mm diameter under a uni-axial pressure of 124 MPa. Shielded test leads were used for the electrical connections from the LCR meter to the sample in order to avoid any parasitic impedance. The samples were made in the form of circular pellets. Before starting the measurements the samples were heated at 100 °C for 1 h, so as to homogenize the charge carriers and to remove the moisture content therein. In the present work, the surface of the pellets was cleaned with SiC grinding paper in order to remove any contamination. The surface of the disks was coated on opposite faces with silver paste, thereby forming parallel plate capacitor geometry.

2.2. Characterizations

The sample is in the powder constitution for X-ray investigation. Part of the powder was X-ray examined by using Rigaku X-ray diffractometer (Rigaku Miniflex II) with CuKα radiation (wavelength λ = 1.5406 Å operated at 40 kV and 35 mA). The samples were rotated through an angle of 20–70° at a scanning speed of 2.9×10^{-4} rad/s. The studies of functional groups on as prepared samples were accomplished by Fourier transformed infrared spectroscopy (FTIR) by means of a Shimadzu FTIR-8400S spectrophotometer from 365 to 4000 cm^{-1}, using pressed KBr pellets. For pellets, 0.8 mg of sample and 120 mg of KBr powder were ground to remove any scattering effects, and the powder mixture was pressed to a pellet size apposite for the instrument. The thermal properties of the products were carried out by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) (model DT-40). The measurements were carried out in air and nitrogen atmosphere. Approximately 20 mg of material was placed in a sintered alumina crucible and the temperature was increased from room temperature to 700 °C at a heating rate of 10 °C/min in static air. Room temperature magnetic measurements were carried out with the Quantum Design Model 6000 Vibrating Sample Magnetometer (VSM).

3. Results and discussion

3.1. Thermal analysis

In order to investigate the formation of the spinel structure phase, thermal analysis of the samples was carried out in the temperature range of 30 to 700 °C. Thermal analysis of the precursor citrate combusted powder was carried out in air by using thermo gravimetric (TG) and differential thermal analysis (DTA). Simultaneous TG-DTA spectra for the synthesised sample have been presented in Fig. 2. The endothermic peak in the DTA curve at 316 °C may be the indication of the formation of crystallization of the spinel phase [19,20]. In TG the exothermic peak at 70 °C is attributed to the loss of adsorbed water molecules and other exothermic peaks are because of decomposition of precursor. In TG pattern, the system undergoes a peak between 70 °C and 240 °C, which can be ascribed to the burning of organic material in the sample. The fast decrease in weight between 240 °C and 380 °C of is observed, which is caused by the gradual crystallizing process. During 380–700 °C slow weight loss is detectable, indicating the complete decomposition of the precursor above 380 °C. It is

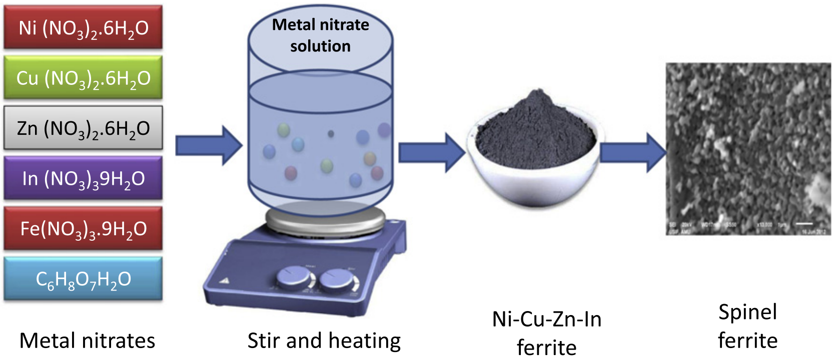

Fig. 1. Flowchart for the preparation of Ni–Cu–Zn–In spinel ferrite by citrate–nitrate precursor auto combustion.