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Research articles

Cobalt substituted nickel ferrites via Pechini's sol–gel citrate route: X-band electromagnetic characterization

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ABSTRACT

Cobalt substituted nickel spinel ferrites were synthesized in the form of $Ni_{1-x}Co_xFe_2O_4 (x = 0–1, \Delta x = 0.15)$ via Pechini's sol–gel citrate method with final sintering at 1000 °C for 6 h. Structural purity of the prepared ferrites is examined by using X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Thermo-gravimetric and differential thermal analysis (TG-DTA) show that the formation of spinel phase is completed upto 700 °C. Lattice constant, cationic distribution and cationic site parameters are estimated from XRD data. For the first time, lattice parameter (a) is determined using four different methods and quite similar values are obtained in those. Characteristic peaks of nickel ferrites are observed in the Raman spectrum of each ferrite composition. Grain size (80–95 nm) is observed to be higher than crystallite size (26.2–31.8 nm) due to agglomeration of grains. Mössbauer spectra recorded at 300 K temperature show the presence of iron in only +3 valency. Variations of isomer shift, hyperfine field, quadrupole splitting and line width are analyzed with the amount of doped cobalt. This paper also presents the electromagnetic and shielding properties of these Ni–Co ferrites in X-band (8.2–12.4 GHz) frequency range using vector network analyzer (VNA). The analysis of shielding effectiveness shows that increasing the amount of cobalt in nickel ferrites results in increase in shielding efficiency of the ferrites which proves the utility of this specific doping.

1. Introduction

Ferrites are ferrimagnetic oxides in which metal cations and oxygen anions arrange themselves, in the crystal lattice, in order to generate different geometric configurations [1]. Ferrites possess combined features of magnetic materials as well as dielectric materials. On one side, they offer useful ferrimagnetic properties, while on other side they show high electrical resistivity [2]. Ferrites can be broadly classified in four categories: spinel ferrites, hexagonal ferrites, garnets and orthoferrites. Among these, spinel ferrites have substantial importance for the ferrite researchers due to their interesting properties including high saturation magnetization, large magnetocrystalline anisotropy, low coercivity, high electric resistivity, high permeability and high Curie temperature [3–5]. These spinel ferrites have composition Fe_2O_3–MO, where M is divalent transition metal ion (nickel, zinc, iron, cobalt, manganese, magnesium, chromium etc.). Out of these, nickel ferrite ($NiFe_2O_4$) is a well-known cubic spinel ferrite due to its numerous applications in fields such as electronic devices, magnetic storage media, magnetic refrigeration, magnetic adsorbents, medical instruments, telecommunication, catalysts, high frequency transformer, microwave absorbers, computer memories [6–10], to cite a few. Ni-ferrite belongs to the class of inverse spinels with complete structural formula $(Fe^{3+}_{\delta})[Ni^{2+}Fe^{3+}_{2-\delta}]O^{2-}_4$, where parentheses and square brackets indicate tetrahedral and octahedral cationic sites respectively and δ represents the degree of inversion. Inverse spinel structure means Ni^{2+} cations are present at octahedral sites and Fe^{3+} cations are present at both tetrahedral (A) and octahedral (B) sites. The ratio of division of ferric ion between A and B sites is indicated by degree of inversion (δ).

In order to prepare ultra-fine ferrite particles, various synthesis techniques including solid state [4], chemical co-precipitation [7–8], sol–gel [3,9], hydrothermal [11], cetyltrimethylammonium (CTAB) assisted hydrothermal [12], micro-emulsion [13], chemical reduction [14] have been developed in the previous times. Out of these, sol–gel auto-combustion method is considered to be a simple, conveniently operated, excellent composition controlled and highly reproducible method. This method needs low processing time and low external energy consumption. Along with modifying the synthesis process, the researchers have also explored different substitution possibilities in pure nickel ferrites, few of which are magnesium [4], zinc [5], calcium [8], zirconium [13], chromium [15], cobalt [16], tin [17] etc.

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Significant variation in structural and magnetic properties of these ferrites have been observed with the doping. Doping of cobalt in nickel ferrite increases the coercivity and saturation magnetization (M_S) due to higher magnetocrystalline anisotropy and higher magnetic moment of cobalt ion. Ni–Co ferrite also exhibits high resistivity in addition to excellent magnetic properties. Babu et. al. reported that frequency of operation of spinel ferrites is directly proportional to square of saturation magnetization (M_S) and electrical resistivity (ρ) and is inversely proportional to grain size [2]. Thus, in the present study, modified sol-gel method named Pechini's sol-gel auto-combustion method (to obtain nano-sized particles) is adopted to dope cobalt (to increase M_S and ρ) in nickel ferrite. It is of interest to note that $Ni_{1-x}Co_xFe_2O_4$ ferrites prepared using other methods have been reported earlier. Kamble and his co-workers reported the structural, magnetic, dielectric and electrical properties along with impedance spectroscopy studies of Ni–Co ferrites prepared using standard ceramic technique [6,18]. Ati et. al. investigated the structural and magnetic properties of the same composition prepared using co-precipitation method for magnetic recording applications [7]. K. Khan prepared Ni–Co ferrite in the shape of nano-rods using co-precipitation and explored the microwave absorption properties in 2–3 GHz frequency range [16]. Gibin et. al. prepared these ferrites using co-precipitation method with citrate as chelating agent. Cyclic voltammetry, X-ray photoelectron spectroscopy and Dynamic light scattering analysis were performed in order to propose these ferrites for super-capacitance applications [19].

In the present study, eight compositions of cobalt ion (Co) doped nickel (Ni) ferrites have been prepared using Pechini's sol–gel auto-combustion method with citric acid as fuel. Firstly, the synthesis technique adopted has been discussed along with the instrument specifications. Then, different properties of the prepared ferrites have been presented along with their discussion: thermal properties using DTA/TGA, structural properties using XRD and Raman spectroscopy, morphological properties using SEM and EDS and X-band electromagnetic and absorption properties using VNA.

2. Experimental procedure

2.1. Preparation of nano-sized ferrite powders

Pechini's sol–gel auto-combustion method has been adopted to prepare cobalt substituted nickel spinel ferrites $Ni_{1-x}Co_xFe_2O_4$ (x = 0.00, 0.15, 0.30, 0.45, 0.60, 0.75, 0.90, 1.00), involving citric acid as fuel. This wet synthesis method has been utilized successfully by different researchers for preparing nano-sized ferrite materials [20–26]. Preparation has been done as per following stoichiometric equation:

$$(1-x)Ni(NO_3)_2 + xCo(NO_3)_2 + 2Fe(NO_3)_3 \xrightarrow{\text{Citric Acid, Ethylene glycol}} Ni_{1-x}Co_xFe_2O_4$$

This Pechini's sol–gel method is basically an electrochemical reduction process involving metal nitrates (as oxidants), citric acid (as fuel) and ethylene glycol (as polymerizing agent) [24,27], which involves hydrolysis of constituent molecular precursors and subsequently polycondensation to gel like material. Two chemical reactions are involved in this method: a complex formation between citric acid and metals, and a sterification between citric acid and ethylene glycol [28]. The detailed process of synthesis is as follow:

All the starting chemicals viz. nickel nitrate (Sigma Aldrich 97%), cobalt nitrate (Loba Chemie 99%), ferric nitrate (Loba Chemie 99–101%) and citric acid (Loba Chemie 99.5%) were of an analytical grade. Stoichiometric amounts of metal nitrates and citric acid were dissolved in minimum amount of distilled water. Citric acid to whole metal nitrate molar ratio was chosen to be 1:1 in order to ensure complete combustion of nitrate ions [23,28]. The mixture was continuously stirred on magnetic stirrer followed by addition of ethylene glycol and hydrogen peroxide. Ethylene glycol was added as a polymerizing agent to reduce any segregation of cations. H_2O_2 was added to decompose any unreacted chemical [25–26]. The mixture was stirred and heated slowly on a water bath until brown fumes of NO_x were completely ceased. Further heating resulted in transformation of liquid mixture in the viscous gel. The gel was further heated at 80 °C for 1.5 h leading to brownish black ashes. The desired ferrites were obtained after slightly grinding the ashes by pestle mortar. The resulting powder was finally sintered in air at 1000 °C for 6 h in linear programmable furnace [28].

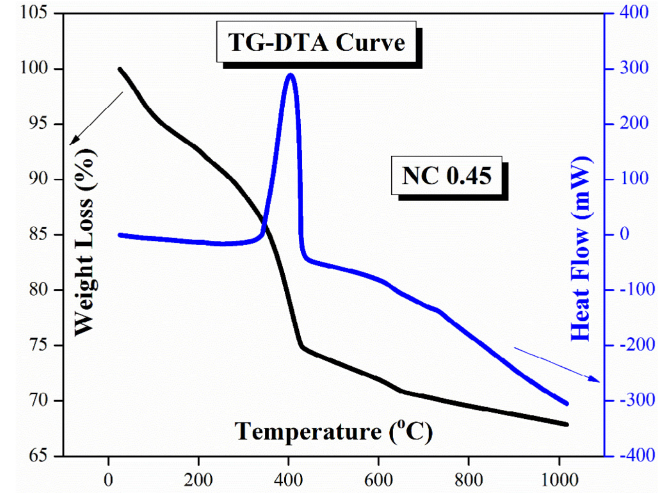

Fig. 1. TGA curve for the prepared spinel ferrite with composition.$Ni_{0.55}Co_{0.45}Fe_2O_4$

2.2. Apparatus details

Thermo gravimetry-differential thermal analysis (TG-DTA) in the temperature range 30–1000 °C at the rate of 10 °C/min in air of the composition NC 0.45 was done using thermal analyzer (Model: EXSTAR 6300). The phase confirmation of the ferrites was done using PANanalytical X'Pert-PRO X-ray Diffractometer (45 kV–40 mA) using Cu-K_α radiation (λ = 1.54056 Å) in 2θ range of 10°–90°. Raman scattering studies were performed on Renishaw InVia Reflex micro-Raman spectrometer, which uses 488 nm argon ion laser (50 mW), 2400 lines/mm diffraction grating and Peltier cooled CCD detector. Measurements were done in wave number range 100–1500 cm^{-1} in backscattering geometry and un-polarized mode. The morphology and elemental composition were investigated using scanning electronic microscope (ZEISS, SUPARA 5) operating at 20 kV. Mössbauer spectra (MS) at room temperature were recorded with a conventional spectrometer operated in constant acceleration mode in transmission geometry with Co^{57} source of 45 mCi in Rh matrix. The recorded MS were fitted using the WinNormos site fit program. The calibration of the velocity scale was done by using an enriched α-^{57}Fe metal foil. The isomer shift values are relative to Fe metal foil (δ = 0.0 mm s^{-1}). For microwave characterization, the powders were granulated using 3–5% solution of polyvinyl alcohol (PVA) to reduce the brittleness. PVA added powders were pressed into the pellets of rectangular shape under uniaxial pressure of 75 kN/m^2. The pellets formed were finally cured at 100 °C for 1.5 h and polished to fit exactly in X-band waveguide (WR-90). X-band (8.2–12.4 GHz) electromagnetic and absorption properties were determined using vector network analyzer (Agilent N5225A PNA series) accompanied by material software (Agilent 85071).