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Structural and DC electrical resistivity, magnetic properties of $Co_{0.5}M_{0.5}Fe_2O_4$ (M= Ni, Zn, and Mg) ferrite nanoparticles

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ABSTRACT

Inverse spinel structured nanoparticles of cobalt ferrite partially substituted by divalent cations of Ni, Zn, and Mg have been synthesized through sol-gel auto combustion route. Structural parameters are studied by powder X-ray diffraction at the diffraction angle range of 10–80°; and FT-IR spectroscopy in the wavenumber range of 1600–400 cm^{-1}. Lattice parameters were calculated from the (hkl) values of the diffraction planes and interplanar spacing and found to be in the range of 8.3659–8.4197 Å. The surface morphology and crystalline nature are studied using scanning electron microscopy and also using HRTEM. The magnetic properties are analyzed through vibrating sample magnetometer. High saturation magnetization of 90.12 emu/g has been achieved from Co-Zn sample whereas high coercive force of 883.45 Oe is achieved in Co-Ni sample. A two-probe DC resistivity was measured in temperature ranges of 300–450 K.

1. Introduction

There has been an increased application of nanoparticles of mixed ferrites for microelectronics, drug delivery, electronic memory devices, transformer cores, and biomedical applications. Currently, the focus is on nano technology as nanoparticles exhibit quite different properties than their counterparts. Such exceptional properties are the key functions in large scientific interest and application of ferrites in different areas. Basically, such large applications of ferrites emanate from their interesting electrical and magnetic properties besides being at nanoscales [1–3].

Ferrites are ferrimagnetic materials exhibiting spontaneous magnetizations where the spin-exchange interaction of the cations at two different sublattices result in non-zero magnetic moments. Thus we can measure the saturation magnetization in certain magnetic field, and also calculate their coercive field and remnant magnetization. Moreover, based on their magnetization ferrites could be soft or hard. Soft ferrites which are characterized by low coercive force are used in electromagnetic cores and radio frequency inductors; and these include lithium ferrite, nickel ferrite, manganese ferrites, etc. Hard ferrites whose signature is high retentivity and coercive field are used in permanent magnets. The ferrites at nanoscales could exhibit superparamagnetism and also are usually described by single domain structure [4–7].

In terms of their electrical properties, ferrites are considered as insulators at low temperature and also could be considered as semiconductors at relatively high temperature. But most significantly their dielectric properties have lead to be used in microwave and high frequency devices [8,9]. All such electrical, magnetic and structural properties of ferrites depend on the synthesis methods. The synthesis methods and chemical compositions in turn determine the microstructures such as grain size, porosity, so forth and these microstructures significantly determine the physical properties of materials. Nanoparticle synthesis of these materials could be possible through sol-gel, hydrothermal, and co-precipitation routes. Moreover, the cation site occupations at the tetrahedral and octahedral sub lattices also determine important properties of ferrites [10,11].

In this present work, we report $Co_{0.5}M_{0.5}Fe_2O_4$ (M = Ni, Zn, and Mg) ferrite nanoparticles, which are synthesized through sol-gel auto combustion method using metal nitrate and citric acid as fuel. From this study, a comparative analysis of the structural, morphological, magnetic, and DC electrical resistivity properties are presented.

2. Experimental details

The starting materials are analytical grade (AR) with 99% purity. The materials are cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$), Magnesium nitrate hexahydrate ($Mg(NO_3)_2$.6H2O) Ferric Nitrate

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($Fe(NO_3)_3{\cdot}9H_2O$) & citric acid monohydrade ($C_6H_8O_7{\cdot}H_2O$). Citric acid helps for the homogenous distribution and segregation of the metal ions. During water dehydration, it suppresses the precipitation of metal nitrates because it has electronegative oxygen atoms interacting with electropositive metal ions. Therefore, at a relative low temperature the precursors can form a homogenous single phase ferrite. The mixed solution is neutralized to pH-7 by adding ammonia; it helps for the well formation of gel and improves the solubility of metal ions. Metal nitrates taken in the required stoichiometric ratio are dissolved in an optimum amount of distilled water and mixed together. Then the citric acid is added to the nitrate solution in 1:1 M ratio. The analytical grade liquid ammonia is added drop by drop to the nitrate solution under constant stirring to maintain the pH value 7. The resulting solution is constantly heated on the magnetic stirrer around 150 °C to allow gel formation. The resultant gel is kept in open air environment to remove the absorbed water and the precursor powder is sintered under the constant heating conditions at 1000 °C for 3 h to obtain the final product. The resultant powder is ground into fine particles by an agate mortar and pestle. Finally, the fine power is pressed into pellets with the help of hydraulic press by applying the 5 tons pressure.

The structural properties of samples are studied by Rigaku X-ray diffractometer (Rigaku Miniflex II) using the CuKα radiation (wavelength = 1.5406 Å). Scanning electron microscopy (SEM) images are obtained using a TESCAN, MIRA II LMH microscope. The composition is determined by energy dispersive X-ray spectroscopy (EDX, Inca Oxford, attached to the SEM). High Resolution Transmission Electron Microscopes (HRTEM) is determined by JEOL 3010 with a UHR pole piece operates at an accelerating voltage 300 kV. FT-IR analysis is carried out and the magnetic properties are studied by using vibrating sample magnetometer (EZ VSM model) at room temperature. A two-probe DC resistivity technique was also employed.

3. Results and discussion

3.1. XRD studies

As shown in Fig. 1, the powder X-ray diffraction patterns of the so synthesized materials reveal the cubic spinel structures of ferrites [12]. The sharp diffraction peaks confirm the crystalline structure of the materials [13]. The lattice parameters are calculated using the formula:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

where, d is the interplanar spacing, (hkl) are the Miller indices, and a is the lattice parameter. The obtained lattice parameters are in the range of 8.3659–8.4197 Å. Using the most intense peak (311), the crystallite sizes have been calculated with the Scherrer's formula:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where, β is the peak full width at half maximum (in radians) at the observed peak angle 2θ, k is the crystallite shape factor (is considered 0.94) and λ is the X-ray wavelength. Thus the calculated values of crystallite sizes vary from 29.01 to 42.68 nm. These results confirm that the synthesized materials are at the nanoscale level. The theoretical densities of the samples are also calculated using the formula:

$$d_x = \frac{8M}{N_A a^3}$$

where, M is the molecular weight of the sample, N_A is Avogadro's number, and a is the lattice parameter. These all structural parameters are summarized in Table 1.

3.2. FESEM with EDS studies

The surface morphology and nature of the texture are studied using scanning electron microscopy. As can be observed from Fig. 2(a)–(c), clear grain and crystalline nature of the sample are shown. Grain boundaries and pores are also visible and these microstructures determine the magnetic and electrical properties of the materials synthesized.

Table 1
Lattice parameters and ionic radii data of $Co_{0.5}M_{0.5}Fe_2O_4$ (M = Ni, Zn and Mg) ferrite nanoparticles.

Compound	a (Å)	Cell Volume (Å)^3	Crystallite size (nm)	Space Group
Co-Ni	8.3659	585.5112	42.68	*Fd-3m*
Co-Zn	8.4197	596.8938	29.01	*Fd-3m*
Co-Mg	8.3936	591.3541	38.83	*Fd-3m*

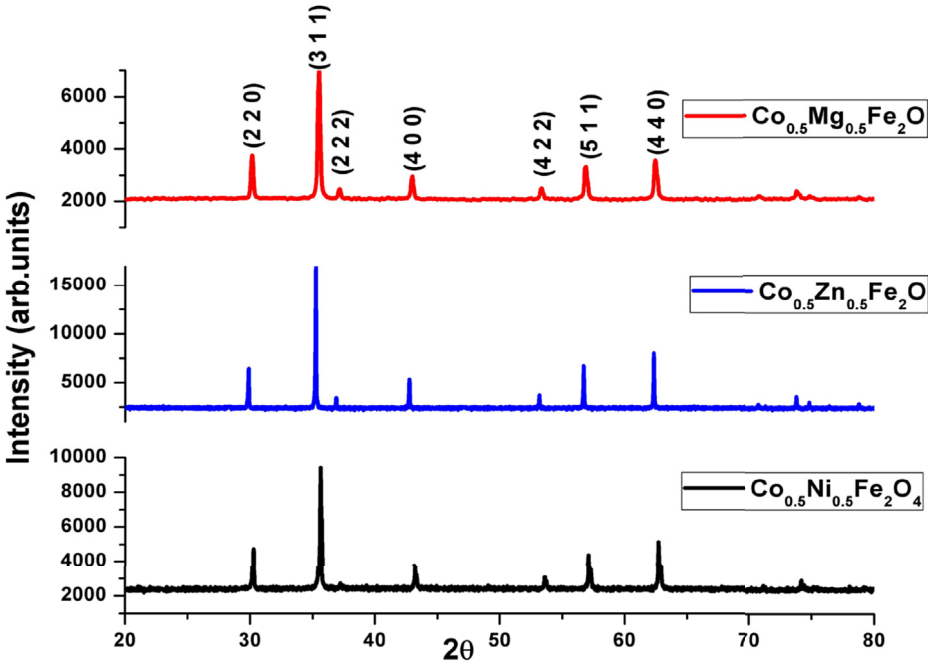

Fig. 1. Powder X-ray diffraction patterns of $Co_{0.5}M_{0.5}Fe_2O_4$ (M = Ni, Zn and Mg) ferrite nanoparticles.