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Association of structural and enhanced transport properties in RE substituted cobalt nanoferrites

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ABSTRACT

Spinel ferrites belong to an important class of compounds which has variety of electrical and magnetic applications. Neodymium doped cobalt ferrites with composition $CoFe_{2-x}Nd_xO_4$ where x = 0.00, 0.05, 0.10, 0.15, 0.20 were synthesized by wet chemical route called simplified sol-gel method. Prepared samples were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) for structural analysis. All the samples were found spinel cubic belonging to Fd-3m space group. To analyze temperature effects on phase transition and to check thermal stability differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were done. Sample with x = 0.00 was found to be thermally more stable than remaining samples. Electrical analysis was done by using two probe method. DC electrical resistivity and drift mobility of sintered samples were measured as a function of temperature in the range from room temperature to 450 °C. It was observed that DC electrical resistivity has a direct dependence on dopant concentration but indirect dependence on temperature. Verwey hopping model was used to describe the results of DC electrical resistivity. Activation energy calculated from linear plots of DC resistivity for all samples was in the range of 0.532–0.594 eV. Rarely reported thermal transport properties that include thermal conductivity, thermal diffusivity and volumetric heat capacity were measured by Advantageous Transient Plane Source (ATPS) method. All the samples showed values near to that of thermal insulators. Thermal conductivity of all samples was increased up to 100–120 °C and then decreased. This behavior was thoroughly studied.

1. Introduction

Properties of nanomaterials can be exploited for different purposes and applications that include medical, electrical and optical devices. Nanoferrites are one among special types of nanomaterials which have vast number of applications in various technological fields. Ferrites with spinel structure have their own significance due to their unique electrical and magnetic properties. These properties can further be modified by various techniques such as doping of an appropriate element according to the desired applications and synthesis method to be used.

Cobalt ferrites are material of interest because they have remarkable electrical and magnetic properties. These properties are strongly dependent on cations and their distribution among tetrahedral (A) sites and octahedral (B) sites of spinel ferrites. There are different physical and chemical routes for the synthesis of ferrite nanoparticles. Among all these sol-gel method is advantageous because it gives high yield, good control over stoichiometry and high purity products [1,2]. Different properties of cobalt ferrites are tunable by adding dopants. A small amount of rare earth elements causes modification in the structural, magnetic and electrical properties of cobalt ferrites. Effect of different rare earth elements on cobalt ferrites has been studied by different researchers. These rare earth elements include Gd^{3+} [3], La^{3+} [4], Y^{3+} [5] Dy^{3+} [6], Sm^{3+}, Nd^{3+} [7] and Ho^{3+} [8]. Most of the work has been done on magnetic properties of neodymium doped cobalt ferrites [7]. Electrical and thermal transport properties of neodymium doped cobalt ferrites are scarcely found in literature. In case of thermal transport properties most of work is done on thermal conductivity of nanofluids [9,10] rather than nanoparticles.

In present study, the electrical and thermal conduction properties in Nd substituted cobalt ferrites have been analyzed. This research aims to study structural, electrical and thermal properties of cobalt ferrites by adding rare earth dopant i.e. Neodymium. Study of structural, electrical and thermal transport properties of

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cobalt ferrites with neodymium doping will allow us to find a material with suitable temperature and dopant concentration for its practical uses.

2. Experimental details

2.1. Synthesis

A nominal composition of $CoFe_{2-x}Nd_xO_4$ with x = 0.00, 0.05, 0.10, 0.15, 0.20 was prepared by using simplified sol-gel method. The stoichiometric amount of Cobalt Nitrate Hexa Hydrate ($Co(NO_3)_2.6H_2O$), Iron Nitrate Nona Hydrate ($Fe(NO_3)_3.9H_2O$), and Nd_2O_3 were taken. Then measured amount of ethylene glycol (1:14) was taken in a beaker and all precursors were added one by one with continuous magnetic stirring at room temperature. After mixing of all precursors temperature was raised to 80 °C. The solution was stirred continuously, until it became viscous and finally formed a thick gel. By increasing the temperature up to 250 °C, ignition of the gel took place. After 4 h all gel was completely burnt which resulted in powder formation. This powder was further grinded and weighed. As prepared samples were then grinded and pelletized using hydraulic press. Pellets were sintered at 550 ± 5 °C for 2 h.

2.2. Characterizations

The structural characterization of all as prepared and sintered samples was done by X-ray diffraction (XRD) technique using Cu Kα (λ = 1.5406 Å) radiations in 2θ range 20–80°. The lattice constant '*a*' was determined. Crystallite size $D_{(311)}$ was measured by using Scherrer formula [11]. The crystallite sizes were determined from line width of most intense peak that is (311). Measured density ρ_m, experimental density ρ_x and porosity P as a function of increasing Nd concentration were also determined. Fourier transform infrared spectroscopy was done in wave number range (400-800 cm^{-1}). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of all samples were also done.

DC electrical resistivity for all samples was measured by using two probe method in temperature range of 313 K–723 K. In this method constant voltage (5 V) was applied across the samples and current through the samples was measured as a function of temperature. The samples were heated within the furnace. The relationship between resistivity and temperature can be expressed by Arrhenius relation given as

$$\rho = \rho_o e^{\Delta E/k_B T} \tag{1}$$

where ρ is the DC electrical resistivity at particular temperature T, k_B is the Boltzmann constant and ΔE is the activation energy.

Drift mobility of all samples was calculated from the data of DC resistivity by using the relation given

$$\mu_d = \frac{1}{ne\rho} \tag{2}$$

In this relation e is the electronic charge in Coulomb, ρ is the DC resistivity and n is the charge carrier concentration which can be calculated by using equation [12].

$$n = \frac{N_A N_{Fe} \rho_m}{M} \tag{3}$$

Thermal transport properties that include thermal conductivity (λ), thermal diffusivity (α) and volumetric heat capacity ($\rho_t Cp$) were determined by advantageous transient plane source (ATPS) method. In this method heat flows inside the material in three dimensions. The TPS element is used as a heating source as well as temperature sensor. If all heat is transported through the material, then the thermal conductivity (λ), thermal diffusivity (α) and volumetric heat capacity ($\rho_t C_p$) can be expressed by Ref. [13].

$$\alpha = \frac{\lambda}{\rho_t C_p} \tag{4}$$

3. Results and discussions

3.1. X-ray diffraction analysis

Nano crystalline $CoFe_{2-x}Nd_xO_4$ with x = 0.00, 0.05, 0.10, 0.15, 0.20 showed a single phase cubic spinel structure as shown in Fig. 1. It was observed that lattice constant increases with increase in Nd concentration that was due to larger ionic radii of Nd^{3+} ions (0.983 Å) as compared to Fe^{3+} ions (0.645 Å). This increase in lattice constant also confirms the site occupancy of Nd^{3+} ions in exchange of Fe^{3+} ions. This increasing trend of lattice constant with doping concentration follows the Vegard's Law [14]. The crystallite size $D_{(311)}$, measured density ρ_m, X-ray density ρ_x and porosity P with increase in neodymium concentration are tabulated in Table 1. The crystallite size was within the range of 35–67 nm.

3.2. FTIR analysis

In the wave number range 400–900 cm^{-1} of infra-red spectra there were two prominent absorption bands as shown in Fig. 2. The absorption band (υ_1) was observed in the range of 400–450 cm^{-1}. According to Xavier et al. [15] this corresponds to octahedral-metal stretching and absorption band (υ_2) in the range of 550–600 cm^{-1} represents the intrinsic stretching vibrations of the metal at the tetrahedral site. This confirmed the formation of cubic spinel structure in prepared samples. These bands slightly shifted to lower frequency when Nd is added this may be due to expansion of unit cells due to substitution of neodymium with larger ionic radii compared to that of iron.

3.3. TGA/DSC

TGA curves for $CoFe_{2-x}Nd_xO_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20) are shown in Fig. 3. They showed three distinct steps at which weight

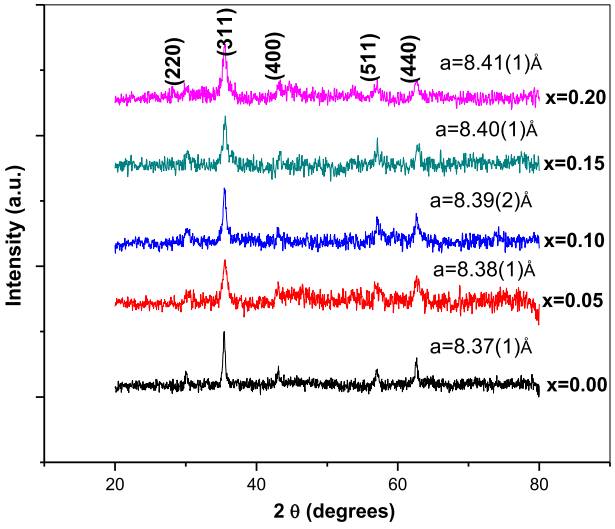

Fig. 1. XRD pattern of $CoFe_{2-x}Nd_xO_4$ (x = 0.00, 0.05, 0.10, 0.15, 0.20).