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Influence of Rare Earth (Ce^{3+}) on Electrical and Magnetic Studies of Nickel ferrite Nanoparticles

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Abstract:

Nanoparticles $NiFe_{2-x}Ce_xO_4$ ($x=0, 0.03, 0.06, 0.09, 0.12$) was prepared by solgel combustion method. The samples were characterized with VSM and Electrical measurements. Magnetic studies by Vibrating Sample Magnetometer (VSM) shows that magnetization (M_s) decreases with increase in Ce^{3+} concentration. Coercivity (H_c) first decreases for $x=0.03$, after which it increases up to $x=0.12$. Resistivity value increases as the x value increases.

Keywords: Rare earth ions, Resistivity, VSM, Magnetization, Coercivity.

1. Introduction

In the recent years, so much attention has been paid to the nanomagnetic materials that show very interesting magnetic properties. In this material, different properties and applications are appeared as compared to their bulk counterparts. The magnetic properties of nanomaterials are used in medical, electronic, and recording industries that depend on the size, shape, purity and magnetic stability of these materials. In biomedical application, one can use nano magnetic materials as drug carriers inside body where the conventional drug may not work. For this purpose, the nanosize particles should be in the super paramagnetic form with a low blocking temperature. Ferrite nanomaterials are object of intense research because of their proper magnetic properties. It has been reported that when the size of particles reduced to small size or in range of nanomaterials, some of their fundamental properties are affected. nano ferrites are simultaneously good magnetic and dielectric materials. These properties of the nano ferrites are affected by the preparation conditions, chemical composition, sintering temperature and the method of preparation . Several chemical and physical methods, such as spray pyrolysis, sol-gel, co-precipitation, combustion technique, high energy milling, etc. have been used for the fabrication of stoichiometric and chemically pure nano ferrite materials. Among the available chemical methods, the sol-gel technique is an excellent method to synthesize rare earth substituted nanoparticles with maximum purity. In spite of the development of a variety of synthesis routes, the production of nickel ferrite nanoparticles with desirable size and magnetic properties is still a challenge. This would justify any effort to produce size tuned nickel ferrite nanoparticles with rare earth substitution. In the present paper, the structural and magnetic properties of cerium substituted nickel ferrite and VSM and electrical properties were investigated.

2. Experimental

2.1. Synthesis

Nano particles of cerium substituted nickel ferrite were synthesized by the sol-gel combustion method. A stoichiometric ratio of $NiFe_{2-x}Ce_xO_4$ ($x=0.00, 0.03, 0.06, 0.09, 0.12$) was dissolved in ethylene glycol using a magnetic stirrer. The five sample solutions were then heated at $60^\circ C$ for 2 hours until a wet gel of the metal nitrates was obtained. The gel was then dried at $120^\circ C$. This resulted in the self ignition of the gel producing a highly voluminous and fluffy product. The combustion can be considered as a thermally induced redox reaction of the gel wherein ethylene glycol acts as the reducing agent and the nitrate ion acts as an oxidant. The nitrate ion provides an oxidizing environment for the decomposition of the organic component. The obtained powder of different samples $NiFe_{2-x}Ce_xO_4$ ($x=0, 0.1, 0.2, 0.3, 0.4$) was ground well collected in different packets for the measurements.

2.2. Characterization

Electrical resistivity was measured using two probe method at room temperature. Pellets (13mm diameter) of samples were used for measuring the impedance and electric modulus properties using a precision impedance analyzer (Wayne Kerr 6500B) at room temperature. Magnetic measurements were done at room temperature using a vibrating sample magnetometer (VSM) under an applied field of 10 kOe.

3. Results and Discussion

3.1. Variation of DC Electrical Resistivity

Fig.1 shows the DC electrical resistivity of $\text{NiFe}_{2-x}\text{Ce}_x\text{O}_4$ with composition ($x=0.00$ to $x=0.12$) of the dopant at room temperature. Nickel Ferrite is a highly resistant material with high activation energy. Method of synthesis, type and substitution of doped cations at A and B site, particle size and morphology and sintering temperatures largely affects the electrical properties of spinel ferrites. This can be observed from the graph that DC electrical resistivity decreases up to a concentration of $x=0.03$ but then increases with increase in Ce^{3+} concentration. There is a significant increase in the DC electrical resistivity with Ce^{3+} substitution ($x=0.12$). resistivity variations with Ce^{3+} substitution can be explained as for $x=0.03$, Ce^{3+} ions occupy A site replacing Fe^{3+} due to which number of Fe^{3+} ions at B-site increases and thus Fe^{2+} . This may happen due to lattice distortion caused by doping a concentration of $x=0.03$. A low concentration of Ce^{3+} causes a severe change in centro-symmetric FCC structure of parent crystal that causes an increase in hopping of electron and a net electric polarization.

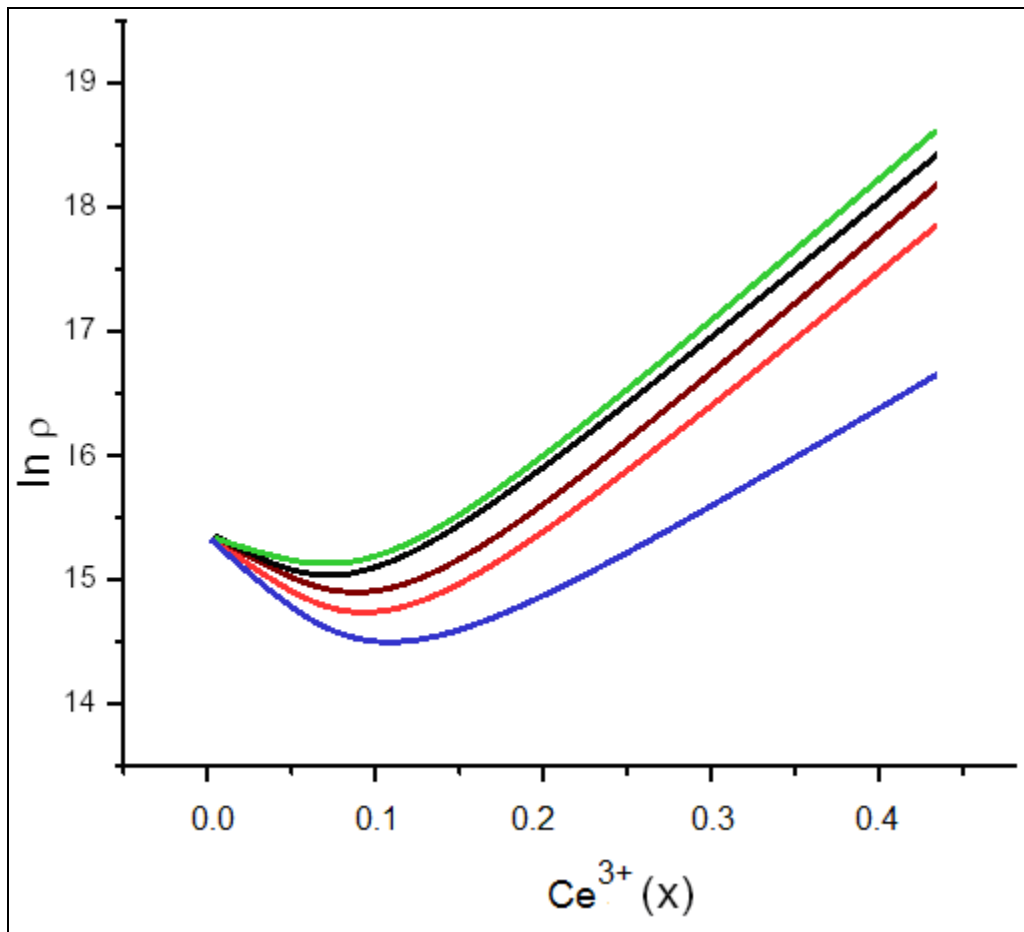


Figure 1: Variation of resistivity with concentration

3.2. Magnetic Study

To study the effects of Ce^{3+} doping on magnetization, coercivity, remanent magnetization (M_r) and magneto-crystalline anisotropy (HK) of NiFe, M-H hysteresis loops were recorded using VSM under the applied magnetic field of 10 kOe at room temperature. Fig. shows the hysteresis curves for all the samples under investigation. It is clear that all the samples show a fine s shape loops with a decrease in magnetization (M_s) and coercivity (H_c) with increase in Ce^{3+} concentration. This is due to the substitution of Ce^{3+} in place of Fe^{3+} at B-sites. Gd^{3+} ions have a higher magnetic moment ($7\mu_B$) in place of Fe^{3+} that has $5\mu_B$. The order in magnetic moments of rare earth ions is below room temperature; due to this at room temperature Ce^{3+} ion behaves as non magnetic that causes a

decrease in saturation magnetization and coercivity. This substitution causes a lattice distortion that alters the magnetic characteristics of materials. Magnetic properties of ferrite materials largely based upon the grain size, cation substitution, and A-B exchange interactions. Increase in the grain size and decrease of A-B super exchange interaction causes canting spins at the surface of nano particles that decreases the magnetic characteristics of the present samples. Spin arrangement for the Ni-Ce ferrites were analyzed by measuring the value of Bohr's magnetron by the relation

$$n_B = \frac{\sigma_s}{5585} M_w$$

Where

$$n_B = (6 + x) \cos \alpha_{Y-K} - 5(1 - x)$$

where x represents the composition of doping ion. anisotropy field (H_k) can be calculated by following equations

$$H_k = \frac{2K_1}{\mu_0 M_s}$$

where μ_0 is the permeability of the free space, M_s is saturation magnetization from the fit. It is clear from the data that cubic anisotropy decreases with increase in Cerium concentration. Pure nickel ferrite is has high anisotropy constant and field due to occupation at B-sites. It decreases due to Ce^{3+} occupation at B-sites. Cubic anisotropy constant also decreased doping gadolinium showing a decrease in coercivity for present studied samples. The anisotropy parameters (anisotropy constant and field) are not decreasing monotonically but more abruptly due to differing concentration of doping ion. This behaviour is showing a strong lattice distortion due to Ce^{3+} substitution.

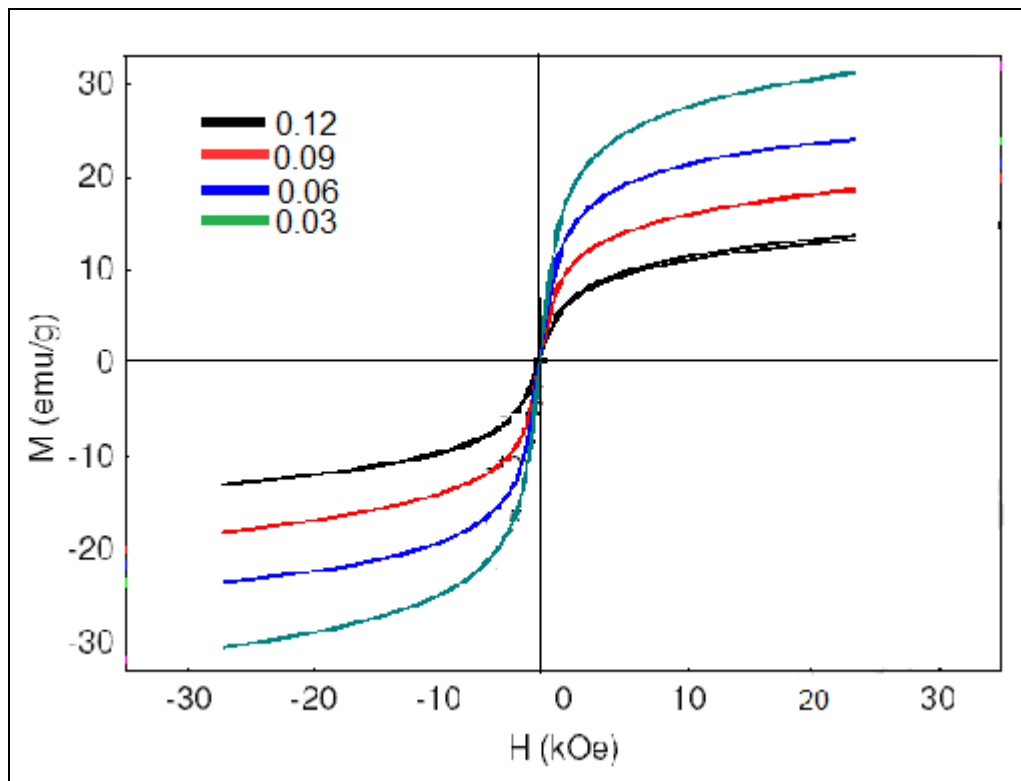


Figure 2: Hysteresis loop of $NiCe_xFe_{2-x}O_4$ at different x ($x=0.00, 0.03, 0.06, 0.09, 0.12$)

Nano spinal $NiCe_xFe_{2-x}O_4$ with x in step increment of 0.03 has been synthesized by sol-gel combustion. All the studied samples are pure cubic spinel phase ferrites without any impurity metal oxides. DC electrical resistivity increases to 9.5×10^7 with Ce^{3+} substitution except for $x=0.03$. Complex impedance reveals that the grain boundary are offering more resistance to conduction showing that smaller grains with more grain boundaries are formed for present samples. Magnetic properties of Ce^{3+} doped Ni-ferrites decrease due to influence on A-B exchange interactions and spins of electrons on nano particles surface. Saturation magnetization, coercivity and remanance all decreases with increase in dopant concentration. Magnetic anisotropy of nickel-ferrite nano particles decreases with increase in Ce^{3+} concentration (x). Thus the rare earth (Ce^{3+}) doped nickel-ferrites found an application in high frequency devices and power supply due to high resistivity and low losses.

4. Conclusions

Nano spinel $\text{NiFe}_{2-x}\text{Ce}_x\text{O}_4$ with x in step increment has been synthesized by sol-gel Combustion method. All the studied samples are pure cubic spinel phase ferrites without any impurity metal oxides. Complex impedance and Complex electric modulus plots were further studied for the complete contribution of grains and grain boundary resistances to conduction and resonance frequencies respectively. Magnetic studies by Vibrating Sample Magnetometer (VSM) shows that magnetization (M_s) decreases with increase in Ce^{3+} concentration. Coercivity (H_c) first decreases for $x=0.03$, after which it increases up to $x=0.12$.

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