Structural characteristics and enhanced dielectric properties of neodymium substituted cobalt ferrite nanoparticles

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Abstract: A series of polycrystalline spinel ferrites with composition $CoFe_{2-x}Nd_xO_4$(x = 0.0, 0.1, 0.2, 0.3) have been synthesized by sol gel auto combustion method. The structural characterizations of the prepared samples were done using XRD and FESEM. The crystallite size shows a decrease with the increase in the neodymium content. The dielectric properties were studied at room temperature and analyzed as a function of frequency. All the samples exhibit normal dielectric behaviour which is attributed to Maxwell-Wagner interfacial polarization. The samples act as a promising candidate for high frequency recording devices. The lowering of coercivity in Nd doped system shows that it makes magnetically softer, which may find its suitability for magnetic recording devices.

1. Introduction:

In recent years, fabrication of nanomaterials and their utilization are emerging as a critical technology having applications in many industrial sectors [1, 2]. Amongst these, spinel ferrite structure of MFe_2O_4, where M represents the Ni, Mn and Zn has been expansively studied due to their unique electric, magnetic, chemical and mechanical properties [3]. Owing to these properties they are currently being used in wide application areas, such as microwave devices, memory cores, low energy inductors, transformer cores, and deflection-yokes, loading coils, choke coils, electro-magnetic interference (EMI), high-density magnetic recording and many other applications [4-9] Cobalt ferrite ($CoFe_2O_4$) is a well-known hard magnetic material with high coercivity and moderate magnetization [10]. These properties, along with their great physical and chemical stability, make $CoFe_2O_4$ nanoparticles suitable for magnetic recording applications such as audio and videotape and high-density digital recording disks, etc. [11]. The magnetic character of the particles used for recording media depends crucially on the size, shape and purity of these nanoparticles. These characteristics and applicability make cobalt ferrite as one of the highly investigated magnetic material. The versatile nature of spinel ferrite nano-particles is that their properties can be varied to suit the requirement by changing the synthesis process, precursor pH, cation substitution, annealing conditions, agglomeration etc. [12-15].

Many researchers have studied the effect of rare earth substitution on the properties of Cobalt ferrites. The review of the literature on cobalt ferrite indicates that the substitution of Fe with rare-earth enhances its dielectric and magnetic properties. Here, we are reporting the effect of rare earth metal i.e. Nd^{3+} (Neodymium) substitution for iron on the properties of spinel cobalt ferrite nanopowders prepared by sol-gel auto-combustion method.

2. Experimental

2.1 Synthesis

Polycrystalline samples of Nd substituted nanocobalt ferrites with the chemical formula $CoNd_xFe_{2-x}O_4$ (where x = 0.0, 0.1, 0.2, 0.3) were synthesized by sol-gel auto-combustion method using glycine as a fuel and nitrates ($Co(NO_3).6H_2O$), $Fe(NO_3)_3\cdot 9H_2O$ and $Nd(NO_3).6H_2O$) as oxidants. Aqueous solutions of the nitrates were prepared by dissolving stoichiometric amounts of nitrate salts in deionized water to which aqueous solution of glycine was then mixed with the help of a magnetic stirrer. The resultant solution was magnetically stirred at 150^o C till the liquid turns to a gel. The gel then automatically got converted to fluffy powders by self-ignition. Prepared powders were then sintered at 600^o C for 3 hours. As synthesized material were then ground and palletized into disc shaped using a hydraulic press and the disc shaped pellets were further sintered in a muffle furnace for further characterizations.

2.2 Characterization

X-ray diffraction (XRD) analysis was done using Rigaku Ultima- IV X-Ray Diffractometer at room temperature using Cu-K_α radiation, (λ=1.54 Å) radiation with 2θ in the range of 20^0 to 80^0. The size and morphology of the particles were estimated by Nova NanoSEM-450 Field emission scanning electron microscope (FESEM). Dielectric measurements was measured using H20KI LCR meter (IM3570) at the room temperature. The magnetic properties of the synthesized nanoparticles were measured using a vibrating sample magnetometer (VSM) at room temperature.

3. Results and Discussion

3.1. XRD analysis and Surface elucidation

The X-ray diffraction pattern (Fig.1) of the as-synthesised samples synthesized using solgel route shows that the final product is $CoFe_2O_4$ with the expected inverse spinel structure. The peaks are indexed to (111), (220), (311), (400), (422), and (511) crystal planes of $CoFe_2O_4$, respectively. With increase in Nd content, some ortho-ferrite peaks were observed marked (♣) in the figure 1. The size of the particles was determined by the Scherrer formula using the intense peak. The average sizes of the particles was found to be 50 nm which decreases to 37 nm with increase in Nd content. FESEM micrographs confirm the decrease in particle size with increase in Nd content. The particle size was found to be 40 nm which decreases to 22 nm. The prepared cobalt ferrite doped magnetic nanoparticles were highly agglomerated with homogeneous distribution. Formation of agglomerated particles arose due to less gas being released during the combustion process, which occurred in the fuel lean condition. The surface of $CoFe_2O_4$ appeared like a "platelet" type of morphology.

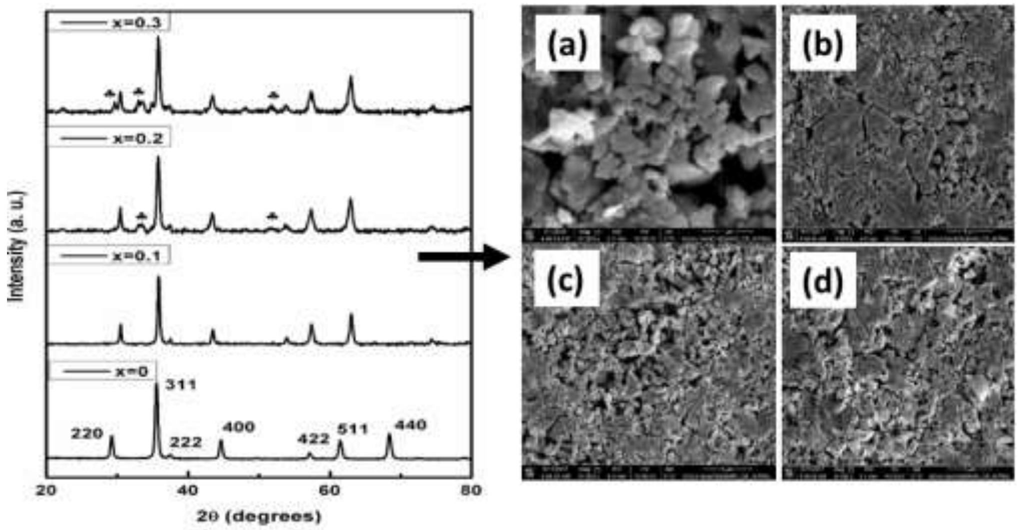

Fig. 1 XRD pattern and corresponding FESEM micrographs of $CoNd_xFe_{2-x}O_4$ (where *x* = 0.0, 0.1, 0.2, 0.3).

3.2 Dielectric analysis

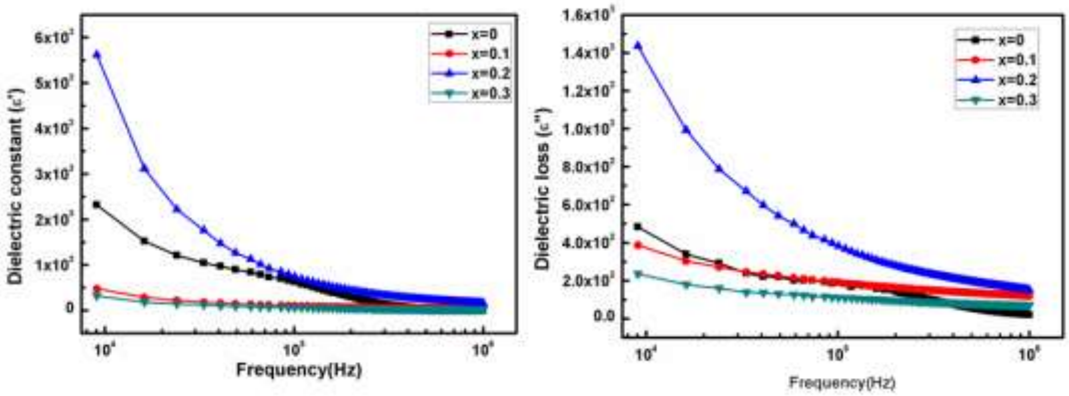

Fig. 2. Dielectric constant and dielectric loss of $CoNd_xFe_{2-x}O_4$ (where x = 0.0, 0.1, 0.2, 0.3) at room temperature.

The variation of dielectric constant with frequency is depicted in figure 2. It can be seen that dielectric constant displays an inverse frequency dependence behavior as reported for various ferrites. It decreases with frequency and remains a constant at higher frequencies. The decrease in permittivity with frequency can be explained on the basis of Koop's theory [16] which considers the dielectric structure as an inhomogeneous medium of two layers of the Maxwell-Wagner type [17]. The space charge polarization occurring at the interfaces contribute to the enhanced dielectric constant values at lower frequencies. At higher frequencies, electron exchange between Fe^{2+} and Fe^{3+} ions will not be able to follow the applied electric field thus resulting in a decrease in polarization. When Nd is doped in the system, it occupies the octahedral site in the ferrite system, decreasing the Fe^{3+} ion number responsible for polarization. Hence, the value of dielectric permittivity decreases with lower concentrations of Nd content. However, an increase in dielectric constant is noticed for higher neodymium content. Dielectric loss is also found to exhibit the same trend as dielectric constant. The dielectric constant and dielectric loss of Nd doped $CoFe_2O_4$ is relatively higher in comparison with that of $CoFe_2O_4$ nanoparticles specifying that the dopant improves the dielectric properties of the specimen. Therefore, these synthesised specimens are applicable for high frequency based devices.

The variation magnetic behaviour with different Nd concentration has been observed in figure 3. As observed the saturation magnetization M_s with x = 0.1 in the doped system shows higher value as compared to others. Similar behaviour also for coercivity is also observed. The lowering of coercivity shows that it makes magnetically softer, which may find its suitability for magnetic recording devices.

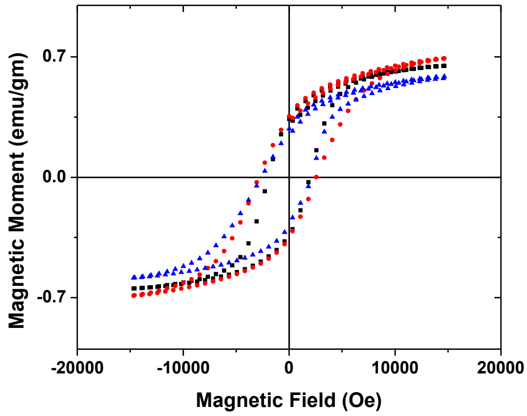

Fig. 3. MH plot for $CoNd_xFe_{2-x}O_4$ (where x = 0.0, 0.1, 0.2) at room temperature.

Conclusion:

$CoNd_xFe_{2-x}O_4$ (x = 0.0, 0.1, 0.2, 0.3) nanoferrite particles were successfully synthesized by sol-gel auto-combustion method. The variation of dielectric constant and dielectric loss for different Nd^{3+} compositions have been measured at room temperature for frequency dependence in the range of 100 Hz to 1.0 MHz using impedance analyzer. Results confirm strong dependence of the studied parameters on frequency and Nd^{3+} ion content. Increase in Nd^{3+} ion composition in the developed ferrite material increases the values of dielectric constant and dielectric loss making it suitable for high frequency based devices. The reduction in coercivity makes the material to be used as magnetic recording media.

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