

STRUCTURAL AND DIELECTRIC STUDIES OF TERBIUM SUBSTITUTED NICKEL FERRITE NANOPARTICLES

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Abstract- Nanoparticles $\text{NiFe}_{2-x}\text{Tb}_x\text{O}_4$ ($x=0.00, 0.04, 0.08, 0.12$) ferrite was prepared by sol-gel combustion method. The samples were characterized with X-ray diffraction and TEM measurements. The effect of Tb^{3+} cations substitution on structure of prepared nanoparticles was investigated. From the analysis, the system was found to be inverse spinel cubic structure. The lattice parameter (a) changes increases with Tb doping content. Room temperature DC electrical resistivity decreases. Dielectric properties have been studied in the frequency range of 1 kHz to 5 MHz. Permittivity and tangent loss ($\tan\delta$) decreases with the substitution of Tb^{3+} in parent crystal structure.

Keywords: Rare earth ions, XRD, Dielectric properties, Permittivity.

I. 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 terbium substituted nickel ferrite and XRD, SEM, TEM and electrical properties were investigated.

II. EXPERIMENTAL

A. Synthesis

Nano particles of terbium substituted nickel ferrite were synthesized by the sol-gel combustion method. A

stoichiometric ratio of $\text{NiFe}_{2-x}\text{Tb}_x\text{O}_4$ ($x=0.00, 0.04, 0.08, 0.12$) were dissolved in ethylene glycol using a magnetic stirrer. The five sample solutions was then heated at 60°C for 2 hours until a wet gel of the metal nitrates was obtained. The gel was then dried at 120°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 $\text{NiFe}_{2-x}\text{Tb}_x\text{O}_4$ ($x=0.00, 0.04, 0.08, 0.12, 0.16$) was ground well collected in different packets for the measurements.

B. Characterization

The nickel ferrite samples were characterized by an X-ray powder diffract meter (XRD, Bruker AXS D8 Advance) using radiation ($wavelength= 1.5406 \text{ \AA}$) at 40 kV and 35 mA. Lattice parameter was calculated. The crystal structure, crystallite size and X-ray density were determined. Particle morphology was studied using Transmission Electron Microscope (Philips- CM200) operating at 20-200 kV with resolution 2.4 \AA . Electrical studies conducted using RF material analyser (AGILENT E4991A)

III. RESULTS AND DISCUSSION

A. Structural Analysis

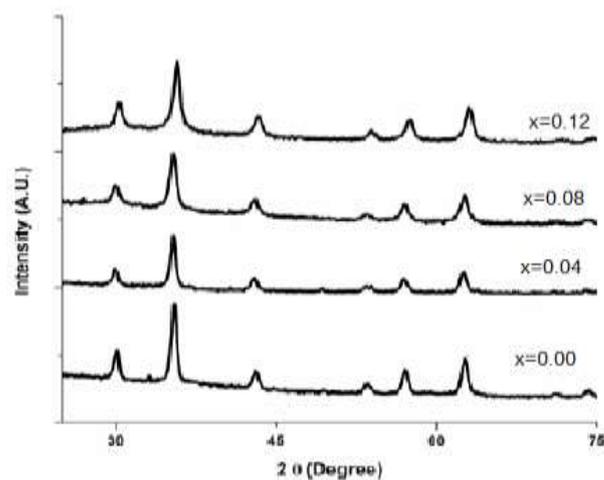


Fig.1. XRD patterns of $\text{NiFe}_{2-x}\text{Tb}_x\text{O}_4$ ($x=0.00, 0.04, 0.08, 0.12$)

The XRD patterns of $\text{NiFe}_{2-x}\text{Tb}_x\text{O}_4$ ($x=0.00, 0.04, 0.08, 0.12$) nanoparticles are depicted in Fig. 2 and are typical of spinel structure. Comparing the XRD pattern with the standard data, the sample with terbium concentration zero shows highest peak and concentration 0.12 shows lowest. The diffraction peaks are broad because of the nanometer size of the crystallite. The crystallite size 'D' of the samples

has been estimated from the broadening of XRD peaks using the Scherrer equation.

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

Lattice parameter 'a' for all the samples has been calculated by interplanar spacing (dhkl) and 2-theta values using the standard relation,

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$$

Value of lattice constant for x=0.0 comes out to be 8.3865Å, well in agreement with reported value. Lattice constant has increased monotonically with increment in Tb³⁺ concentration. This increase can be easily explained due to substitution of large ionic radii of Tb³⁺ (0.94Å) in place of smaller Fe³⁺ (0.67 Å) ions. Also rare earth ions are usually present at grain boundaries that cause hindrance in the grain growth, therefore crystal size and unit cell parameters increases.

The crystallite size was observed to increase with the increase of terbium concentration. It has been reported that the doping process generally decreases lattice defects and strain, but this technique can cause the coalescence of smaller grains, resulting in an increased average grain size for the nanoparticles. Calculated values of lattice parameter of terbium substituted nickel ferrite samples were in close agreement with standard data.

B. TEM Analysis

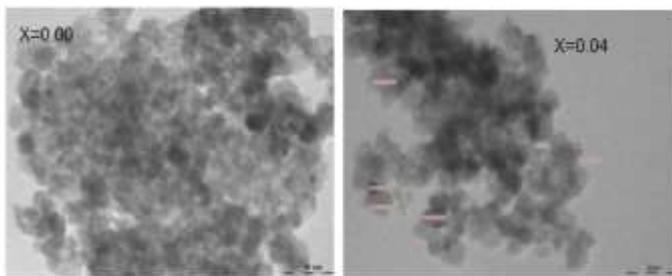


Fig.2. TEM Image of NiFe_{2-x}Tb_xO₄ at x= (0.00, 0.04)

The particle size was estimated using TEM analysis. The reduction in particle size with rare earth doping is evident from TEM images. figure 2 shows the images of NiFe_{2-x}Tb_xO₄ at x=0.00 and 0.04. Most of the nano-particles are spherical in shape and are agglomerated. Agglomeration of nano-crystals may be due to the tendency of nano particles to aggregate to achieve a low free energy state by reducing the specific superficial area by lessening the interfaces with other particles. Average particle size calculated from the TEM images Values are almost comparable with the crystallite size obtained from XRD.

C. Dielectric study

Dielectric behavior of nano spinel ferrites mainly depends upon the nature and distribution of metal cations on A-sites and B-sites in the spinel lattice. Spinel nickel ferrites are considered good dielectric materials and the high frequency dielectric behavior is mainly dependent upon the

particle size and method of synthesis of nano particles. Different studies have been provided relating the dielectric parameters of Tb³⁺ doped ferrites. Dielectric parameters (real and imaginary parts of relative permittivity, dielectric loss tangent) for the prepared series of NiTb_xFe_{2-x}O₄ (x=0.0 to x=0.12) have been studied in the frequency range 1 MHz to 1GHz at room temperature. Figs.3 shows the variation of relative permittivity with frequency at room temperature. It can be observed from the figure that relative permittivity for all the samples decreases with increase in frequency and ultimately becomes constant at higher frequencies. This decrease in permittivity is more rapid in the low frequency region and becomes sluggish as the applied frequency increases. This behaviour is subjected to dielectric polarization under the application of AC field.

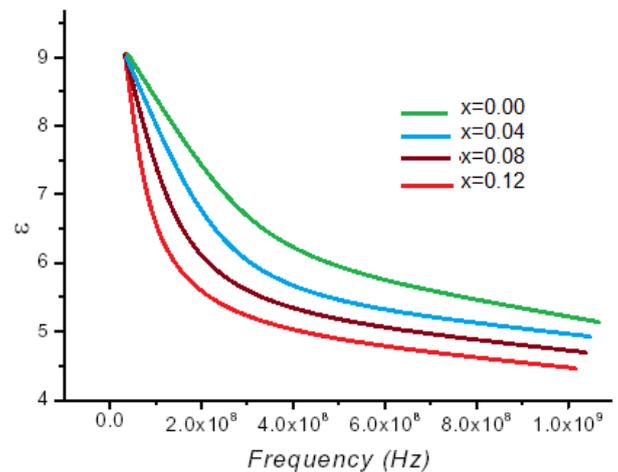
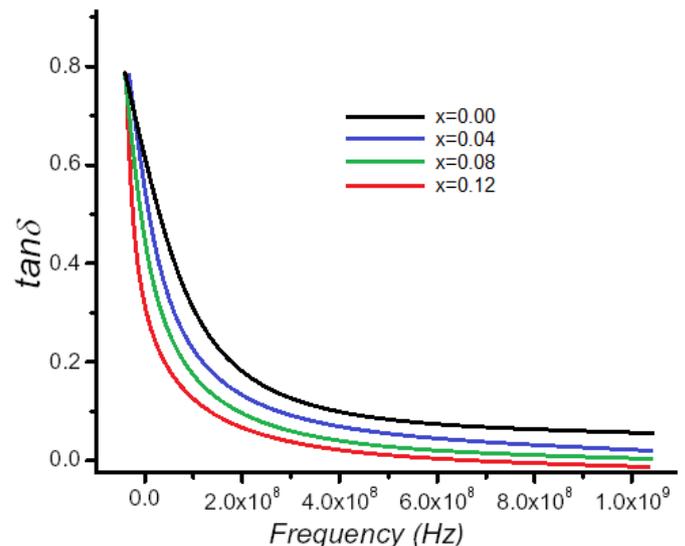


Fig.3. Variation of permittivity as a function of frequency

It can be seen that dielectric loss tangent has the same trend as permittivity losses. It decreases with increase in frequency and becomes constant up to 1GHz due to decreased polarization at high AC fields. At x=0.12 shows a low loss dielectric behaviour which allows its use in high frequency data reading/writing in electronic structures.



IV. CONCLUSIONS

Nano spinel NiFe_{2-x}Tb_xO₄ 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. Lattice constant and crystallite size increases with increase in Tb^{3+} concentration, due to increase ionic radii and atomic weight of gadolinium as compared to Fe^{3+} . Substitution of Tb^{3+} ion in parent crystal causes a lattice distortion that can be observed by increased lattice strain in W-H plots. Dielectric constant and loss tangent decreases to 4.92 and 0.016 respectively with increase in the dopant concentration showing that the material with $x=0.12$ is a low loss dielectric.

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