

MORPHOLOGICAL AND MAGNETIC BEHAVIOR OF NEODYMIUM DOPED $\text{LiNi}_{0.5}\text{Fe}_2\text{O}_4$ NANOCRYSTALLINE FERRITES PREPARED VIA MICRO-EMULSION TECHNIQUE

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Neodymium substituted nanoferrite $\text{LiNi}_{0.5}\text{Fe}_2\text{O}_4$ with different concentrations were fabricated by micro-emulsion method. Scanning electron spectroscopy (SEM) and magnetic properties are employed to study the effect of substitution of the neodymium on surface morphology and magnetic parameters. The particles size estimated by SEM was found (50–120 nm) on addition of Nd contents. The VSM was employed for magnetic studies between -10000Oe and 10000Oe range. An improved 'Ms' saturation magnetization (40.52 emu/g) and 'Hc' coercivity values (668Oe) have been obtained. The value of Hc is low, so synthesized $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ferrites is suitable for low core losses on transformers.

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1. Introduction

Research in nanotechnology is becoming one of the vital and fast growing areas, especially the nano sized ferrites are being investigated to optimize the structural and electrical properties in order to make them suitable for high frequency appliances and other advanced technological applications [1]. These nanoferrites are also being used for the medical application such as MRI. Surface coating of these nano ferrites make them more suitable for MRI contrast agent [2]. There are also some other applications of these versatile particles in microwave devices, filters, antennas, read/write heads for digital tapes and transformer cores [3]. The structure, surface properties and electric properties and magnetic properties depends on the composition of ferrites [4, 5]. Lithium ferrites with improve properties are prepared by different techniques like solid state method, chemical method, sintering method and microemulsion method [6]. Dopant having larger ionic radii change significantly structure, electric and magnetic properties [7, 8]. Studies showed that various rare earth ion doping changes different behavior of spinel ferrite [4]. Moreover rare earth elements doping could enhanced electrical conductivity and optical behavior in materials. A lot of work have been done and properties of ferrites has been modified by doping of rare earth cations in these ferrites [6].

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2. Experimental details

Nd-doped $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.0, 0.035, 0.070, 0.105, 0.140, 0.175$) spinel ferrites were synthesized by micro-emulsion method [9, 10]. The details of chemicals used is as follow: $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (Merk-Germany, 99 %), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (BDH, 99%), Cetyltrimethylammonium bromide (CTAB) (Bio Basic-Canada, 99%), $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, 99.9%) and aqueous NH_3 (BDH 35%). Solution of Li, Ni, and Nd were prepared with concentration of 0.1M were prepared. Whereas 0.2M solution of Fe was prepared. CTAB was prepared with concentration 0.3M. All solution was prepared in distilled water. Solutions were mixed according to calculated volume and stirred on thermostat controlled hotplate using a magnetic stirrer. Achieving temperature to 55°C , CTAB was mixed and pH was raised to 10 and maintained between 9 and 10 using aqueous ammonia. The mixture of cation is further stirred for 5 hr. Iron oxide in form of precipitate settled down. These precipitates were washed, dried and grinded. The samples in powder form were annealed at 950°C . The annealed material in powder form was characterized by various techniques.

3. Results

The Dy substituted $\text{LiNi}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrites were prepared by micro-emulsion route and were characterized by thermogravimetric analysis, X-ray diffraction, scanning electron microscopy etc. The synthesis and characterization of $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ nanoferrites has been described in detail in our previous communication (doi:10.1016/j.physe.2015.06.001), where crystalline size was in nano range [11].

3.1 SEM

The SEM analysis of $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ nanoferrites was performed using Jeol JSM-6490A electron microscope. The theme of the SEM analysis is to study the surface and morphology of ferrite. SEM images also employed to compare the particle size with available XRD data. Typical SEM images of $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ nanocrystalline are shown Fig. 1. Where micrographs indicate the existence of agglomerated grainy structure along with the bunch of fine particles on the surface. The surface also depicts uniformity in the morphology. Moreover shapes of the particles are cubical to nearly spherical and almost regular. Such morphology of the samples indicates that nature of particles is fine and nano sized crystals; hence having large surface area. These large values of surface to volume ratio indicate possible use of these nanoferrites for efficient micro wave devices [12]. There are also pores and voids on the surface of the ferrites sample that could be cause of gases liberated during annealing process. These pores also indicate the combustion of samples in powder form having tiny water molecule. These water molecules are trapped between the cations during the synthesis by microemulsion method [13, 14]. Moreover all samples are crack free and size of particle increase with the increase of Nd contents up to $x=0.7$. Although there are some agglomerates, these agglomerates are due to chemical process [15, 16]. When more Nd content is added in lithium ferrites there is decrease in particle size that is attributed due the production of second phase in the form of NdFeO_3 , this is in agreement with available data [17]. These kind of metal oxides particles aggregation has also been reported earlier [18, 19]. The estimated particles size from SEM image is 30–120 nm, that is in agreement with crystallite size determined by XRD data (25–80) [11]. Fig. 1 shows the SEM images of the $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ferrites having different concentration of Nd and annealed at same temperature. It is observed that the particle size increases with increase the dopant concentration, but decrease when more dopant cannot incorporate in ferrite; hence producing orthophase that is reported in XRD data [1, 20].

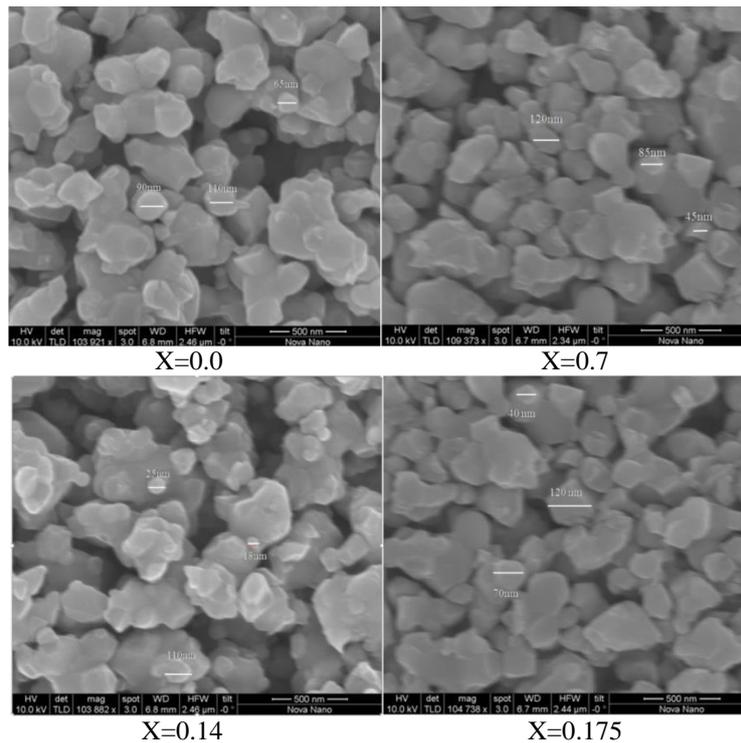


Fig. 1: The scanning electron micrographs of $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ferrite samples

3.2 Magnetic measurement

Magnetic parameters were investigated by using a vibrating sample magnetometer (VSM) Lakeshore-74071 at 298 K. Magnetic hysteresis loop of ferrite series $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.00, 0.035, 0.07, 0.105, 0.140, 0.175$) at room temperature was described as shown in figure 2, which exhibit a perfect S-shape. The replacement of Nd^{3+} ions in the lithium Ni-ferrite with iron content was also affected the magnetic properties significantly. Table 1 reflects the different magnetic parameters such as the saturation magnetization (M_s), remnant magnetization (M_r), anisotropic constant and coercive force (H_c) with increasing neodymium contents [21]. This M-H loop evident the coercivity value of these ferrites samples were in the range of soft ferrites [22, 23].

Table 1: Various magnetic parameters for " $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ " spinel ferrites ($x=0.0$ to 0.175)

| Magnetic Parameters In | $x=0$ | $x=0.035$ | $x=0.070$ | $x=0.105$ | $x=0.140$ | $x=0.175$ |
|---------------------------------|------------|------------|-------------|------------|------------|------------|
| Coercivity (H_c)/Oe | 161.53 | 143.2 | 150.1 | 178.7 | 181.3 | 137.71 |
| Magnetization (M_s) (emu/g) | 27.52 | 31.11 | 19.59 | 34.1 | 20.5 | 18.75 |
| Retentivity (M_r) (emu/g) | 6.4 | 6.8 | 4.7 | 7.5 | 4.6 | 4.1 |
| Squareness Ratio (M_r/M_s) | 0.232558 | 0.218579 | 0.239918 | 0.219941 | 0.22439 | 0.218667 |
| Magnetic moment $\eta_B(\mu_B)$ | 1.02248749 | 1.17310504 | 0.749557421 | 1.32363241 | 0.80708812 | 0.74857696 |
| Anisotropy constant (J/m^3) | 0.00279307 | 0.00279913 | 0.001847545 | 0.00382877 | 0.00233524 | 0.00162236 |

The variation in M_s , M_r and H_c values as function Nd content is shown in Fig.2. The M_r was in small range and increased inhomogenously similarly M_s value increased inhomogenously

with increased of Nd content in LiNi-ferrite but the value of M_s and M_r was maximum when $x=0.105$. These small values of M_r in ferrite samples in small ranges were due to presence of Nickel cation on A and B sub-lattices in $\text{LiNi}_{0.5}\text{Fe}_2\text{O}_4$ [24, 25].

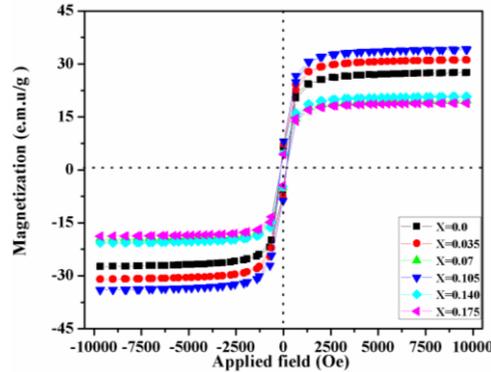


Fig.2: Hysteresis loop for “ $\text{LiCo}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ” spinel ferrites ($x=0.0$ to 0.175).

More over Li^{1+} do not contribute to the magnetization of sub-lattices being nonmagnetic, So net magnetization is due to the contributions of Fe^{3+} and Ni^{2+} at B-sites [26]. As Neodymium was substituted in ferrites, the Nd cation settled on octahedral sites and couple the magnetization of Fe^{3+} on the B-sites, this increase was the cause of the net magnetization of the B-sublattice and resulting an increase in the saturation magnetization [27, 28]. This increasing M_s with increasing content Nd was explained on the basis of Neel’s two sub-lattice model. Therefore, M_s was expected to further increase with Nd content in $\text{LiNi}_{0.5}\text{Fe}_2\text{O}_4$ [29]. On the further substitution of Nd saturation magnetization decreases, this decrease was due the formation of secondary orthophase (NdFeO_3) [30]. The evaluation of secondary phase respond this decrease in M_s value was in agreement with the reported literature [31].

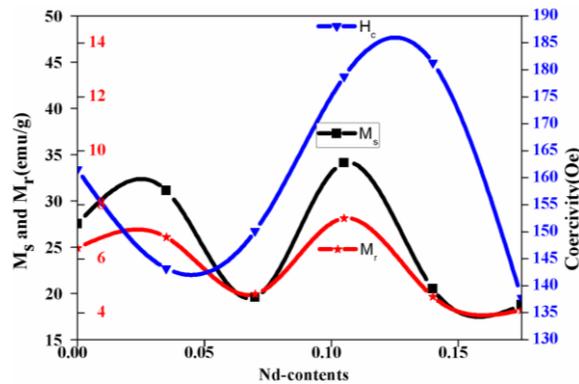


Fig.3. The variation in M_s , M_r and H_c values as function Nd content in “ $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ” spinel ferrites

Whereas coercivity values increase on substitution of neodymium content and get saturated at $x=0.140$, so higher value of coercivity was observed. Similar magnetic behavior of nanoferrites has been reported in literature [32]. On the other side the value of coercivity remain in small range that exhibits soft magnetic nature of ferrites. In ferrites, the coercive force obtained by reversal of the directions of the wall movement and that of domain rotation on reversing the direction of the applied magnetic field [33]. Generally, the effective pinning for domain wall causes the coercivity; it was known that the larger grain size decreases H_c . In the present investigation, the coercive values were increasing with increasing Nd contents; hence probability

of domain rotation was also observed high [34]. In this current work, an improved 'Ms' saturation magnetization (40.52 emu/g) and 'Hc' coercivity values (668Oe) have been obtained. The value of Hc is low, so synthesized $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ferrites is suitable for low core losses on transformers.

4. Conclusions

Nd substituted lithium ferrites were successfully prepared by facile microemulsion method. The particle size estimated by SEM was 50-120nm. Magnetic parameters were also observed on applying the external magnetic field. Saturation magnetization was 18.75 to 31.11 emu/g for $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ferrites. This decrease in saturation magnetization value was due to the appearance of secondary phase in form of NdFeO_3 .

The retentivity values of these ferrites are 4.1 to 7.5 emu/g for $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ferrites. One of the important magnetic features is coercivity; its value was 137.71 to 181.30 Oe for $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ ferrite system. Moreover anisotropic constant was very small for this ferrites, hence showed isotropic nature of the ferrite system. On the basis of magnetic data, it can be concluded that ferrite systems $\text{LiNi}_{0.5}\text{Nd}_x\text{Fe}_{2-x}\text{O}_4$ can be used for iron core of transformer.

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