ROLE OF LANTHANUM SUBSTITUTION ON THE STRUCTURAL AND MAGNETIC PROPERTIES OF NANOCRYSTALLINE NICKEL FERRITES

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ABSTRACT

Lanthanum-substituted Nickel Ferrites were prepared by the sol gel route under stoichiometric conditions. The samples obtained were investigated for their structural, morphological and magnetic properties as a function of increasing La content. Nickel ferrite being one of the important ferrites has a wide range of applications especially as microwave devices. Lanthanum, a rare earth metal is used as a dopant along with nickel ferrite and the relevant modifications in the properties are characterized accordingly. Lanthanum has an electronic configuration of $6s^2 5d^1 4f^0$ with localised f orbitals. The magnetism in the 4f band is established from the influence of the magnetism from the 5d bands as they lie close to each other. The various physical properties of the inverse spinal ferrite sample have been investigated by means of X-ray diffraction, Scanning electron microscope, and VSM analysis.

Keywords: Lanthanum, Ferrite, XRD, SEM, VSM

I. INTRODUCTION

Nanocrystalline spinal ferrites due to their varied applications are technologically very important. The most important advantage of ferrites is their very high degree of compositional variability. Spinal ferrites having a common formula of MFe_2O_4 (where M is a divalent metal ion) have a wide number of technological applications like Ferro-fluids, digital tape, high speed, rod antenna humidity sensor and multilayer chip inductor (MLCI) [1-9]. The distribution of cations over A and B sites is found to have a profound effect on the magnetic and electrical properties of inverse spinal ferrites. Factors like Madelung energy, ionic radius, lattice energy, crystal field stabilization and electronic configuration influence the metal ion distribution. The site preference energy is another factor which determines the occupancy of cations. With the knowledge of the site preference energy and other factors affecting cation distribution, the synthesis of ferrites with optimum properties in the micro regime can be manipulated accordingly. Good magnetic properties and low eddy current losses of nickel ferrites make them suitable for the core material of power transformers [4, 5]. In addition to this, Nickel ferrite nanoparticles are widely used for, targeted drug delivery, gas sensors. The Ni^{2+} ions occupy the octahedral sites and Fe^{3+} ions are equally distributed between octahedral and tetrahedral sites. However, when the particle size is in the nano range, there is a deviation in cation distribution. The desired electrical and magnetic properties of soft ferrites can be enhanced suitably by the addition of divalent, trivalent or tetravalent cations in to the spinal lattice. Substituting small amounts

of rare earth metal ions into the spinal ferrites may distort the structure due to their large ionic radius and hence induce strain and significantly modify the electrical, magnetic and micro structural properties. Rare earth ions play a significant role in determining the magneto crystalline anisotropy in the 4f-3d intermetallic compounds [6]. The properties of ferrite nanoparticles can be fine tuned by the inclusion of suitable rare earth ions due to which it has a wide range of applications.

The factors which influence the properties of nanoferrites are the composition and microstructure, which are in turn sensitive to the synthesis methodology and also to the sintering conditions. Among the available synthesis methods, the sol-gel route and the co precipitation method are two simple techniques without much complications and yield ferrite nanoparticles of high purity at low cost. The Sol-gel technique is a combination of combustion and chemical gelation process and it has the advantage of good stoichiometric control and results in ultra fine particles with a narrow grain size distribution. The rare earth nitrates are one among the most promising additives that are used for the enhancement of ferrite properties. In depth investigations have been done to study the influence of different rare earth atoms on the properties of Ni–Zn ferrite [10,11], based on which it has been accepted that the rare-earth ions have a limited solubility in the spinal lattice owing to their large ionic radii[12]. However the precise value of their solubility in the spinal lattice is still unknown. The desirable structural and physical properties of ferrites can be tuned by the suitable substitution of lanthanide ions into the spinal lattice.

II. EXPERIMENTAL

2.1 Materials

The chemicals used were all of analytical grade with purity≥ 99%. Ferric nitrate Fe $(NO_3)_2.9\ H_2O$, Citric acid $C_6H_8O_7$, Nickel nitrate Ni $(NO_3)_2.6\ H_2O$, Lanthanum nitrate La $(NO_3)_2.6\ H_2O$ were used as the starting materials.

2.2 Experimental Procedures

Lanthanum substituted nickel ferrites, $NiLaFe_20_4$ are synthesized by the sol gel route. Due to its high heat of combustion, citric acid plays the role of an organic fuel and thereby providing a platform for initiating the redox reactions between the reactants during combustion. This method is of great advantage mainly because it does not use water or any other solvent for the preparation of the precursor solutions and hence avoiding impurities caused by water completely. The metal nitrates being hygroscopic in nature tend to form a slurry mixture when they are mixed with citric acid .The mixture is completely dehydrated by heating at 70 ^{0}C .The dried mixture thus obtained is then subjected to a mechanism of closed heating, which consequently initiates a combustion process in it. Since the metal nitrates also act as oxidants, the combustion process takes place effectively by utilizing the oxygen content of the reactants themselves. The combustion process, so carried out is found to yield voluminous ash which is accompanied by fumes.

III. RESULTS AND DISCUSSIONS

3.1 Structural Studies

The X- ray diffraction patterns (XRD) of the as prepared ($NiLaFe_2O_4$) (were La=0.0, 0.025, 0.050, 0.075) nanocrystals were studied using a Phillip PW 1800 X ray diffractometer with Cu Kα radiation of wavelength 1.5405 Å .The x-ray diffraction pattern of the synthesized nickel lanthanum ferrite nanocrystals as shown in Fig: 1, shows the formation of inverse spinal cubic structure with the Fd 3m space group. The peaks obtained in the spectra closely match the data in the ICDD file card number (75-0541). For all the various dopant ratios the inverse cubic spinal structure is retained without any distortion. The absence of any additional peaks indicates that lanthanum goes as substitution into the spinal lattice .Nickel ferrite usually crystallises to form a cubic close packed structure and belongs to the inverse spinal class of ferrites with a structural formula, $Fe^{2+}[Ni^{2+}Fe^{3+}]O_4$ (Ponpandian et al 2002).The octahedral (B site) ions and the tetrahedral (A site) ions are represented by the metal ions inside and outside the square brackets respectively. The B site is occupied by half the iron ions (Fe^{3+}) along with nickel ions (Ni^{2+}) and the A site is occupied by the rest of the (Fe^{3+}) ions. Thus it can be concluded that the presence of the electrons and holes in the B site is due to the presence of Ni and Fe ions. The La^{3+} ions have a tendency of replacing the Fe^{3+} ions in the octahedral sites which can be inferred from the invariance of the lattice constant values for the various dopant ratios.

The peaks become broader as the lanthanum content increases thereby indicating a gradual decrease in the grain size which is evident from the values of crystallite sizes that are tabulated in Table 1. The Scherer's equation is used to calculate the average grain size of the particles using the full width half maximum (FWHM) values of the (311) reflection. As seen from the Table 1, it is evident that the addition of lanthanum does bring about a considerable decrease in the particle size. This particle sizes reported here are found to be much smaller than the sizes reported (R.U.Mullai et al 2012)

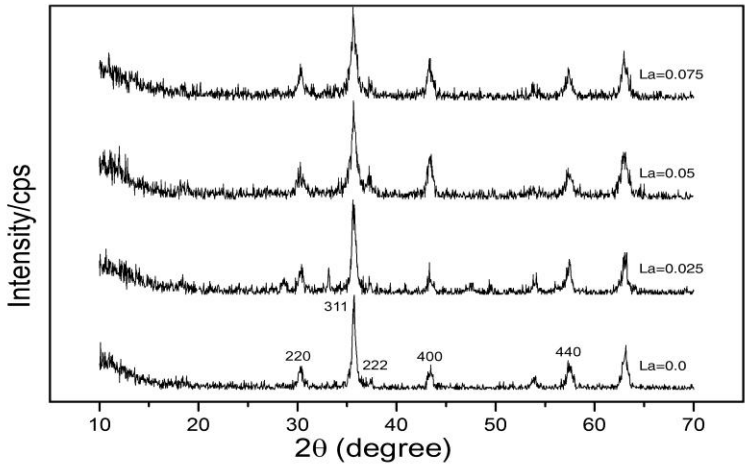

Fig:1 XRD Pattern of Nickel Lanthanum Ferrite for Various Concentration Of La

3.2 Morphological Study: (SEM)

The SEM images of nickel lanthanum ferrite nanocrystals for (La=0.0, 0.25, 0.50 and 0.75) are as shown in Fig:2. The specimens show a uniform grain distribution. The accurate grain sizes cannot be calculated using the SEM micrographs, as the distinct grain boundaries are not exactly focussed. Nevertheless it is found that the agglomeration of the particles is what leads to the constituent structure. The sizes of the agglomerations are of the order of a few nanometres. Hence using the sol-gel route of synthesis, a homogenous distribution of nano particles could be achieved. These samples are spherical with uniform crystallite size and cohesion of grains is due to the magnetic attraction. The dark portions seen in the SEM micrographs reveal the holes that are produced by the gasses that are released during the synthesis process. The composition of the elements present in the sample, measured using the energy dispersive X ray analysis is as shown in Fig: 3.As seen from the spectrum, no appreciable impurities could be detected. Also, the ratio of the elements detected in the samples was found to be in good agreement with the chemical formula for the respective compositions. Hence the sol-gel route has yielded reasonably good ferrites.

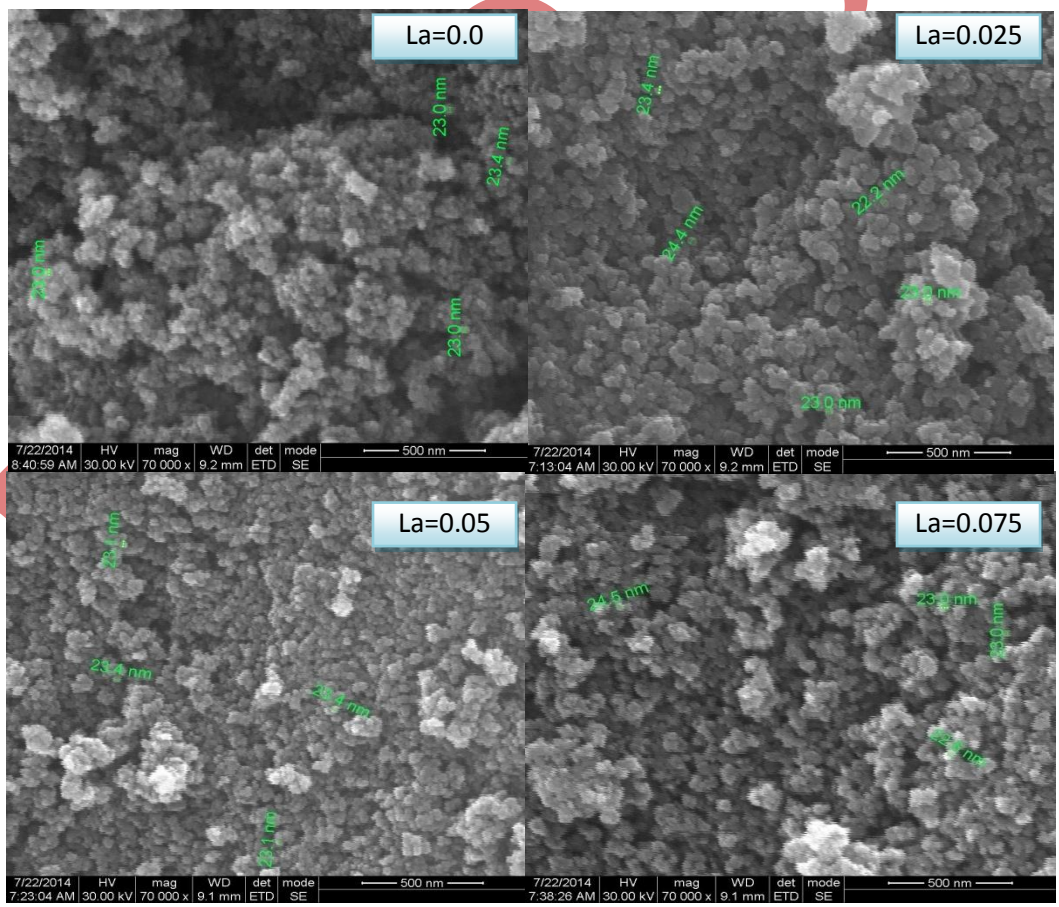

Fig:2 SEM Images of Nickel Ferrite Nanocrystals for Various Concentrations of Lanthanum.

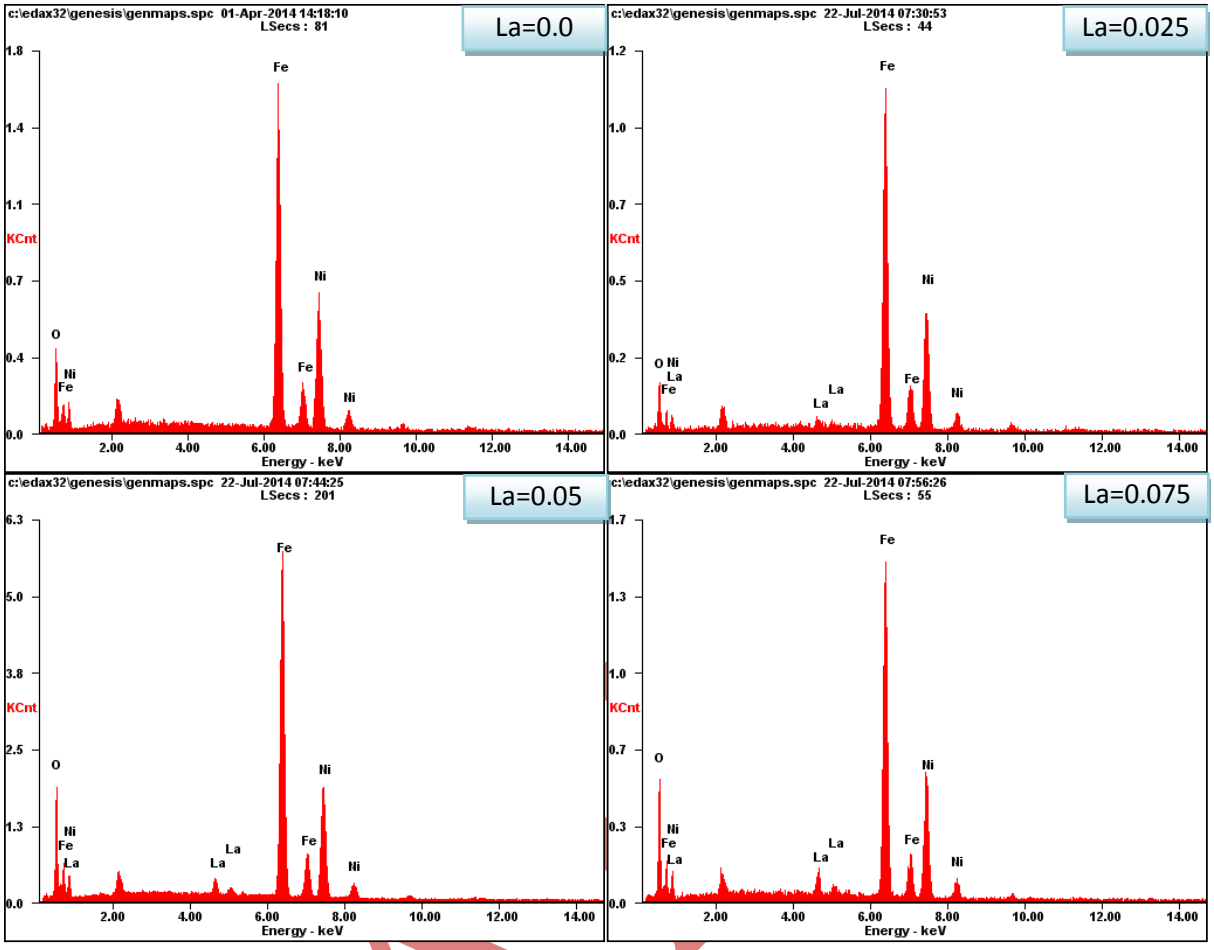

Fig: 3 EDAX Spectrum of La Doped Nickel Ferrite

3.2 Magnetic Study

The magnetic parameters of all the as prepared samples were calculated using a vibrating sample magnetometer in the range 20,000 Oe, where the samples exhibited the magnetic behaviour. The hysteresis loops were plotted from the VSM measurements, from which the saturation magnetisation values for the different compositions (La=0.0, 0.025, 0.050, 0.075) were calculated and represented graphically in Fig:4. The variation of saturation magnetisation with composition is as shown the Fig: 5. It is evident from the hysteresis loops that the sample does not saturate completely for values (x= 0.0, 0.25 and 0.05). Complete saturation occurs at La=0.075 for a field of around 15,000 Oe. The values of magnetisation for the various concentrations of lanthanum are as shown in Table: 1 from which it is evident that the saturation magnetisation decreases with the substitution of lanthanum. This decrease can be explained based on the site occupancy of the cations and also the modification in the exchange effects caused by substituting lanthanum .The Fe^{3+} ions occupying the B sites in the inverse spinal lattice are the main contributors of the magnetic properties. La^{3+} has no unpaired electrons and is paramagnetic in nature. Substituting the paramagnetic

La $^{3+}$ ions in the inverse spinal is not useful for increasing the magnetization. There is a significant decrease in the coercivity with the substitution of lanthanum. At the same time, it is worthy to recall that the XRD study too, indicated a considerable decrease in the crystallite size with increasing La content. The variation of coercivity with crystallite size was explained by Stoner –Wolfforth theory [13]. This theory states that the factors such as micro strain, magneto crystalline anisotropy, magnetic particle morphology, magnetic domain size and size distribution influence the coercivity .

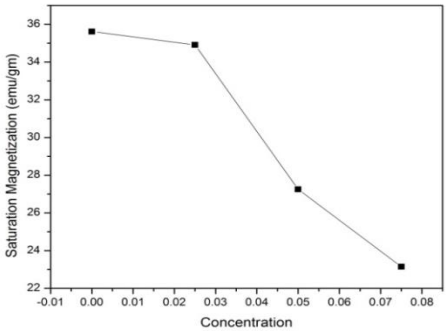

Fig: 4 Plot of Magnetization Vs Concentration

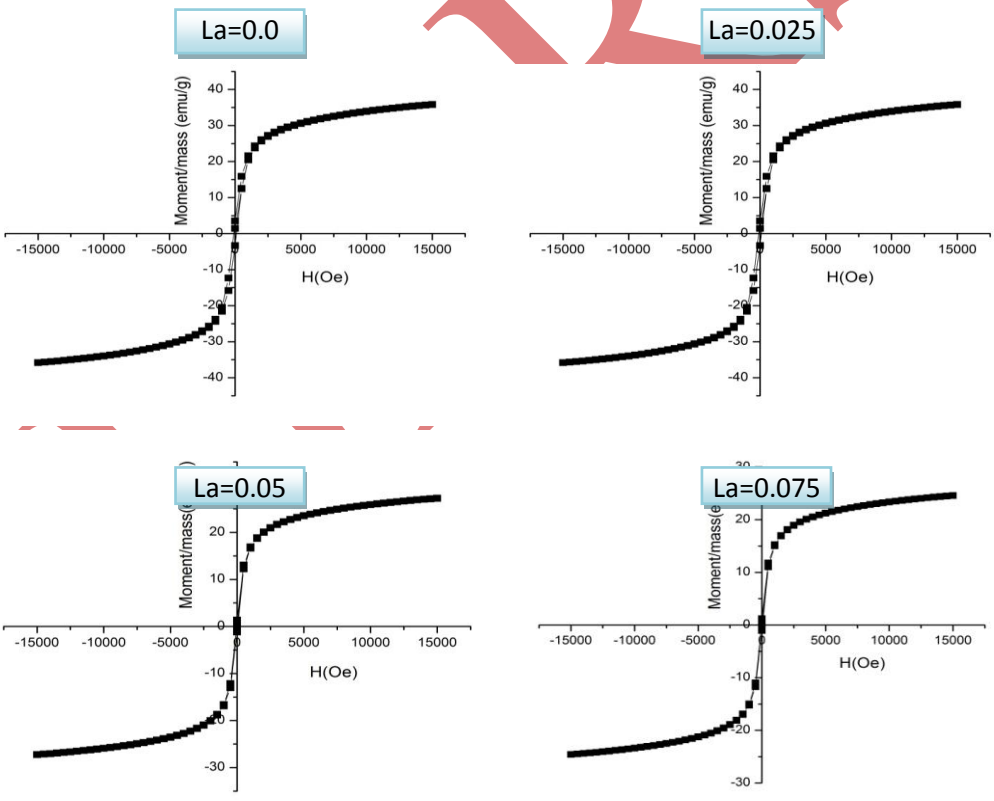

Fig:5: Hysteresis loops of nickel lanthanum ferrite for various La content

It is a well known fact that a decrease in the crystallite size brings about an increase in the grain boundary. Thus there had been no disturbance to the domain wall motion as varying size of the nano particles with different composition exist, which justifies the decrease in coercivity with increasing lanthanum content.

Table 1: Crystal and Magnetic Parameters of Nickel Lanthanum Ferrite for Various Concentrations of La

Concentration	Crystallite size (nm)	Lattice constant (Å)	Magnetization (emu/g)	Coercivity (G)	Retentivity (emu)
0.0	**17.07**	**8.26**	**35.62**	**108.21**	**47.22**
0.025	**16.50**	**8.27**	**34.91**	**83.88**	**34.33**
0.050	**15.90**	**8.27**	**27.25**	**47.45**	**30.60**
0.075	**14.13**	**8.28**	**23.15**	**32.12**	**26.60**

IV CONCLUSION

This work was intended to synthesize nanoparticles of La doped Nickel ferrites for microwave applications. Nickel Lanthanum Ferrites were successfully prepared by sol-gel process and they were sintered at 600^{o}C for 4 hours. The X-ray diffraction studies showed the formation of single phase inverse spinal structure for $NiLaFe_2O_4$. The gradual increase in the La content brought about a decrease in the crystallite size followed by a decrease in the saturation magnetisation, retentivity and coercivity. Materials with decreasing coercivity are called magnetically soft materials. Hence the lanthanum substituted nickel nano ferrites are preferential candidates as compared to normal ferrites for various applications like inductor cores, transformers, recording heads, magnetic shielding and microwave devices. The sintering temperature and sintering time plays a vital role in determining the particle size. There has been no structural distortion for the various compositions reported in the present study.

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