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Structural and Micro Structural Study of Zirconium (Zr^{4+}) Doped Nickel Ferrite ($NiFe_2O_4$) Nanoparticles

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Abstract: In this paper, the synthesis, structural and microstructural properties of zirconium (Zr^{4+}) doped nickel ferrite ($NiFe_2O_4$) nanocrystals prepared by sol-gel auto combustion technique have been reported. Ascorbic acid ($C_6H_8O_6$) was used as a fuel; the pH was maintained at 7 and the prepared samples were sintered at 700 ˚C for 6 h. The single phase nanocrystalline nature of the $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ was confirmed through X-ray diffraction (XRD) studies. The microstructural studies were investigated through Scanning electron microscopy (SEM) technique. The average particle size was calculated by using Debye-Scherer's formula using XRD data and is obtained to be 32 nm. The average grain size was found to be in nanometer range and found to be 52 nm obtained by using SEM images.

Keywords: Nanocrystalline, nickel ferrite, sol-gel, XRD, SEM.

I. INTRODUCTION

Ferrites are the ferrimagnetic metal-oxide materials which possess the combined properties of magnetic conductor and electrical insulator. They have been comprehensively investigated and being a subject of great interest because of their importance in many technological applications such as antenna rods, transformer cores, magnetic data storage, sensors, actuators, catalyst etc [1, 2]. These electrical and magnetic properties are affected by the type of the substituent, microstructure, chemical composition, synthesis methods and synthesis parameters [3, 4]. The ferrites are commonly prepared by ceramic technique which involves high temperature sintering and prolong heating. This method produces particles of coarse nature. The ceramic method has some inherent drawbacks and do not produce particles of small sizes of the order of nanometer. In the recent years, nanosize spinel ferrite particles received a considerable attention because of their interesting magnetic properties [5]. It is found that when the particle diameter reduce to nanometer dimension spinel ferrite particles may exhibit super paramagnetic behaviour, which is of great interest from the point of view of their applications [6].

Spinel ferrites are compounds of iron oxides and some transition metal oxides and they exhibits important electrical and magnetic properties, which made them extensively useful in technological and industrial applications such as magnetic storage in microwave devices [7, 8]. Nickel ferrite is a well known hard magnetic material with inverse spinel structure. The saturation magnetization and coercivity of nickel ferrite is higher than the other nickel, manganese spinel ferrites [9]. Nickel ferrite is the most important and abundant magnetic materials that have large magnetic anisotropy, moderate saturation magnetization, remarkable chemical stability and mechanical hardness, which make it good candidate for the recording media [10, 11]. The chemical composition method of synthesis, nature of dopant, site preference of dopants etc parameters strongly influences the structural, electrical and magnetic properties of spinel ferrites [12, 13]. Various substituents of magnetic and nonmagnetic nature like Co, Zn, Al, etc have been incorporated in nickel ferrite to modify their properties.

However, to our knowledge zirconium has not been substituted in nickel ferrite. Zirconium is a lustrous, grayish-white, soft, ductile and malleable metal which is solid at room temperature, though it becomes hard and brittle at lower purities. Zirconium is highly resistant to corrosion by alkalis, acids, salt water and other agents.

In the present study, the effect of zirconium substitution in nickel ferrite $Ni_{1+x}Zr_xFe_{2-2x}O_4$ x = 0.5, on structural and microstructural properties of nanocrystalline nickel ferrite synthesized by sol-gel auto combustion are reported. Zirconium-containing compounds are used in many biomedical applications [14].

II. EXPERIMENTAL

Preparation of $Ni_{1+x}Zr_xFe_{2-2x}O_4$ spinel ferrite nanoparticles

Materials:

The raw materials used for sol-gel auto combustion synthesis of $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ nanoparticles were nickel nitrate ($Ni(NO_3)_2.6H_2O$), zirconium nitrate ($ZrO(NO_3)_2$), ferric nitrate ($Fe(NO_3)_3.9H_2O$), ascorbic acid ($C_6H_8O_6.H_2O$). All the reagents used for the synthesis of nickel ferrite nanoparticles were analytical grade and used as received without further purification.

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Synthesis:

$Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ nanoparticles were synthesized by sol-gel auto combustion method using ascorbic acid as a fuel. The stoichiometric proportions of metal nitrates to fuel (citric acid) ratio as 1:3 were taken into separate glass beakers. These were stirred for 15-20 minutes to dissolve completely into distilled water.

After complete dissolution they were mixed together. Ammonia was added drop-wise into the solution to adjust pH value to about 7 and stabilize the nitrate-citric acid solution. Then the neutralized solution was constantly magnetically stirred and heated at 80-90 ^oC for 6 h on a hot plate. On the formation of sol-gel, very viscous gel the temperature was further raised up to 120 ^0C so that the ignition of the dried gel started and finally powder was obtained. The as prepared loose nickel ferrite powder was grinded for 30 minutes and annealed at 700 ^oC for 6 h in muffle furnace.

Characterizations

In the present work, zirconium substituted nickel ferrite samples were synthesized by sol-gel auto combustion method and characterized by X-ray diffraction technique. X-ray diffraction patterns of all the samples were recorded at room temperature by using a Regaku Miniflex-II X-ray powder difractometer operated at 40 kV and 30 mA.

The diffraction patterns were recorded in the 2θ range 20^0 to 80^0 with scanning rate of 2^0 per minute using Cu-K_α radiation of wavelength 1.5406 Å. Morphology of the prepared samples was studied using Scanning electron microscope (SEM) JEOL-JSM 840 Model.

III. RESULTS AND DISCUSSIONS

The X-ray diffraction technique was used to characterize the prepared samples of $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ system. The XRD pattern shows well defined reflections belonging to cubic spinel structure. XRD pattern of the sample 0.5 is shown in Fig.1 (a).

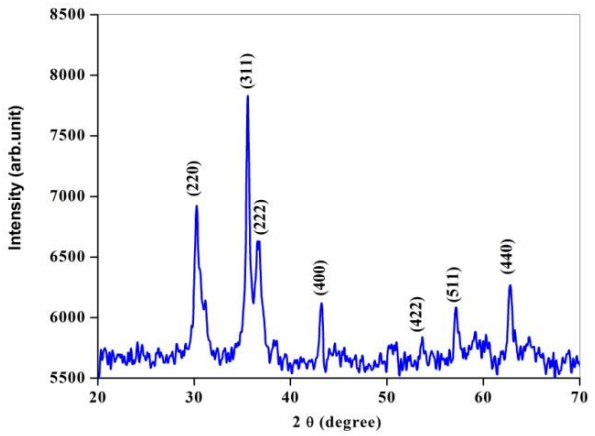

Fig.1 (a): XRD pattern of $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ system

All the peaks in the XRD pattern were indexed by using Bragg's law. The presence of planes (220), (311), (222), (400), (422), (511) and (440) in the XRD pattern reveals the formation of cubic spinel structure of all the samples. It is also evident that all the peaks are intense and sharp. No impurity peaks were observed, thus the samples are single phase in nature. It is also evident from XRD pattern that the intensity of Bragg's peak gets decreased on zirconium substitution. The peaks get broader with the substitution of Zr^{4+} ions. Similar XRD patterns have been observed for Mg doped Zn ferrites [15]. Table 1 gives the planes (hkl), corresponding Bragg's angles along with their interplanar spacing (d) values, intensity and intensity ratio of the $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$.

Table 1 : Miller indices (h k l), Bragg's angle (2θ), Interplanar spacing (d), Intensity (I) and Relative intensity ratio (I/Io) of $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ system.

h k l	2θ (degree)	d (Å)	I (a.u)	I/I_O
(220)	30.32	2.9552	825	56
(311)	35.51	2.5251	1481	100
(222)	36.46	2.4445	580	40
(400)	43.32	2.0902	242	17
(422)	53.62	1.7023	162	12
(511)	57.06	1.6130	290	20
(440)	62.61	1.4811	492	34
(533)	74.44	1.2654	164	12

It is seen from the XRD data and XRD patterns that the interplanar spacing (d) values show gradual increase with increasing Bragg's angle for all the samples. The intensity of (311) plane is more as compared to other planes like (220), (222), (400), (422), (511) and (440). The Lattice constant (a) values of the zirconium substituted nickel ferrite nanoparticles were calculated using standard relation,

$$a = d\sqrt{(h^2+k^2+l^2)} \quad Å \qquad \ldots(1)$$

where, (d) is interplanar spacing;
(h k l) is Miller Indices.

The obtained value of the lattice constant (a) is tabulated in Table 2 and it is found to be greater than that of pure nickel ferrite reported in the literature. The increase in lattice constant with zirconium content x can be interpreted on the basis of the ionic radii of the constituent ions Ni^{2+}, Zr^{4+}, Fe^{3+}. The substitution of Zr^{4+} with Ni^{2+} ions in place of two Fe^{3+} ions leads to increase in lattice constant. Similar behaviour of lattice constant was reported in the literature [16].

The particle size of the zirconium substituted nickel ferrite powders was calculated by using the most intense peak (311) and using the Debye-Scherrer relation for small and uniform sized cubic crystals mentioned below [17] and is tabulated in Table 2.

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$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{nm} \qquad \ldots(2)$$

where, λ is wavelength of the Cu-Kα radiation,
β is the full width of the half maximum
θ is Bragg's angle.

Morphology of the prepared samples was studied using Scanning electron microscope (SEM) where the secondary electron images were taken at different magnification to study the morphology. Fig. 2 represents the Scanning electron micrographs of the present system. Scanning electron micrographs indicates the formation of nano-sized grains of the $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ ferrite powder.

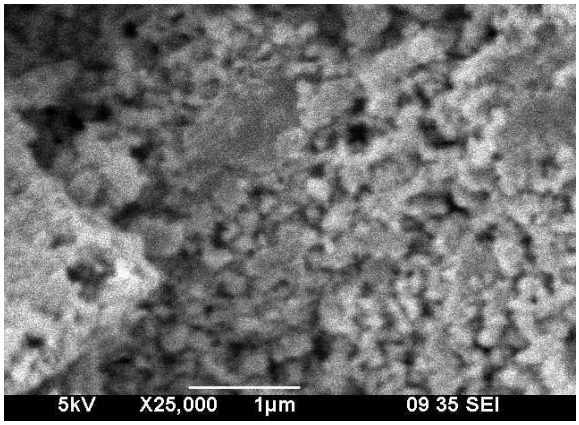

Fig.2. SEM image of $Ni_{1.5}Zr_{0.5}Fe_{1.0}O_4$ system

The grain size was determined by linear intercept method estimated using the relation:

$$D = 1.5\ L / M \cdot N \qquad \ldots(3)$$

where, L is a total test line length,
M is magnification
N is total number of the samples
The average grain size is found to be in nanometer range and of the order of 52 nm. From the SEM micrographs it is seen that the ferrite powder is an aggregation of particles. The particles observed as uniform grains confirm the crystalline nature of the ferrites. The specific surface area of all the samples using SEM images was calculated according to the relation:

$$S = \frac{6000}{D\rho} \qquad \ldots(4)$$

where, D is particle diameter in nm,
ρ is density of the particles in gm/cm^3.

The values of specific surface area are given in Table 2. The large value of specific surface area indicates the nanocrystalline nature of all the samples under investigation. The decrease in grain size increases the surface area.

Table 2: Lattice constant (a), Average Particle size (t), Grain size (G) and Specific surface area (S) of $Ni_{1+x}Zr_xFe_{2-2x}O_4$ (x = 0.5) system

'x'	a (Å)	t (nm)	G (nm)	S (m^2/g)
0.5	8.428	32	52	98.26

IV. CONCLUSION

The nanocrystalline $Ni_{1+x}Zr_xFe_{2-2x}O_4$ spinel ferrite of composition with x = 0.5, was successfully synthesized by sol-gel auto combustion technique using ascorbic acid as a fuel and AR grade metal nitrates. The X-ray diffraction results showed the formation of single phase cubic spinel structure. The crystallite size and lattice constant are in the reported range (32 nm). The substitution on Zr ions in nickel ferrite increases lattice constant. The crystallite size confirms the nanocrystalline nature of the samples. The average grain size is found to be in nanometer range and found to be 52 nm.

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