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Influence of Cr $^{3+}$ substitution on structural and Magnetic properties of Ni-Zn Nanoferrites by Chemical Route.

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Abstract:

Cr $^{3+}$ substitution in Ni-Zn (NZCr) ferrite as chemical formula $Ni_{0.5}$-$Zn_{0.5}$ Cr_x fe_{2-x} O4(x= 0.2, 0.4, 0.6) ferrite were synthesized by chemical route at low temperatures. The Synthesized samples were characterized by X-ray diffraction (XRD), VSM and FT-IR and analysis to obtained the results. The structural and strain obtain by XRD are single pahse spinel structure. The average grain size obtains by XRD pattern is nanostructure in the range of 35- 23 nm. FT-IR studies confirmed the spinel structure of compounds formed by this method. The FTIR characterization shows frequency bands near 560 cm-1conferem the formation of ferrite. The lattice parameter is decreeing with increases Cr 3+ concentration as well as particle size also decreases. The magnetic properties studied by hysteresis loop the nature of material is soft magnetic material.

Keywords: Ni-Zn ferrites, Cr $^{3+}$ doping, sol –gel method, XRD, FTIR and VSM

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Introduction:

Spinel ferrites have been extensively investigated in the past two decades for their useful electrical and magnetic properties [1, 2]. They have different applications in information of magnetite has a great significance in large number of fields: magnetic recording media such as audio and video tape, high-density digital recording disks, magnetic fluids, data storage, in the areas of medical care such as drug delivery systems (DDS), medical applications, including radiofrequency hyperthermia, photo magnetics, and medical diagnostics, microwave devices, magneto-optics devices, sensors, high frequency applications, catalysis and magnetic sensing [3-6].

Ferrites exhibit various properties in technological and scientific applications. The majority of ferrites contain iron oxides as their major constituents (7-10). Ferrites exhibit

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various properties, including magnetic, electrical, Electrochemical, magneto-electronic and optoelectronics (11-12). There are several criteria to obtain high-quality ferrites that are preparation techniques, chemical composition, sintering duration and sintering temperature (13-14). Significant variations are seen in the properties of bulk and nanoferrites synthesized by various techniques (15-16). The Researchers are reported the results of Fe^{3+} spinel ferrites substituted with trivalent rare earth ions (17-20]. Nanoferrite for enhanced their properties (21-22). The dielectric and structural properties were studied and reported the Ni-Zn ferrite(23).

In this preswnt work we are studied the structural and magnetic properties of Ni-Zn ferrite substituted CXe3+ in details by chemical route method such as $Ni_{0.5}$-$Zn_{0.5}$ Cr_x fe_{2-x} O4(x= 0.2, 0.4, 0.6) and characterized by X-ray diffraction (XRD) , Fourier Transform Infra-Red (FTIR) spectroscopy and VSM.

2. Experimental methods and materials:

The synthesis of NZCr ferrite are used basic chemical formula is Ni $_{0.}5Zn$ $_{0.5}Cr_xFe_{2-x}$ O_4 (where x = 0.2, 0.4, 0.6) are high purity AR grade ferric nitrate (Fe_2 $(NO_3)_3$.9H2O), Nickel nitrate (Ni (No3)3.6H2O), Zinc nitrate (Zn (NO3)3.6H2O), Chromium nitrate (Cr (NO3)3·6H2O), citric acid (C6H8O7) and ammonium hydroxide solution (NH4-OH) of 30%. All nitrates and citric acid using stoichiometric proportion all materials dissolved into 100 ml distilled water for the formation of homogeneous solution. The chemical reaction is as given.

$$Ni(No_3)6H_2O + Zn(NO_3)_2.6H_2O + Cr(NO_3)_{2.}3H_2O + Fe(NO_3)_3.9H_2O + 3C_6H_8O_7 \xrightarrow[100^0C \text{ for } 5hrs]{\triangle} NiZnCrFe_2O_4$$

The solution was then slowly heated at about 30 °C and stirred using a hot plate magnetic stirrer. Then ammonia solution was added to the solution drop by drop to maintain its pH 7. The solution was evaporated with the heating on a hot plate. Continuous stirring forms a continuous till to become a gel formation, after 4 to 5 hrs auto combustion takes place. Then fine powder was sintered in furnace at 600 ° C for 5 hrs for removing any impurity from the synthesized sample. The prepared nanoferrite NZCr ferrite samples were characterized by different techniques like XRD, FTIR and VSM..

3. Results:

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3.1 X-ray characterization (XRD):-

The X-ray diffraction (XRD) patterns of NZCr ferrite i.e. $Ni_{0.5}Zn_{0.5}Cr_xFe_{2-x}O_4$ (where x = 0.2, 0.4, 0.6) were recorded with the X-ray diffractometer was shown in figure 2. XRD of all samples were recorded in 2θ range of 10-80^o by scanning rate 5^0 / minute with cu-kα radiation (λ=1.54178 A^o) at room temperature. All peaks were identified by comparing the "2θ" i.e. diffraction angle with that of the JCPDS data in order to confirm the present crystalline phase. Crystallite size (t) was determined by using Scherrer formula which is given as (2θ).

$$t = \frac{0.9\,\lambda}{\beta \cos\theta} \quad \text{----------(1)}$$

Where, t is the crystallite size (nm), β is a full width at half maxima of diffraction peak,λ= 0.154A^0 is the wavelength of X-ray and θ is the diffraction angle.

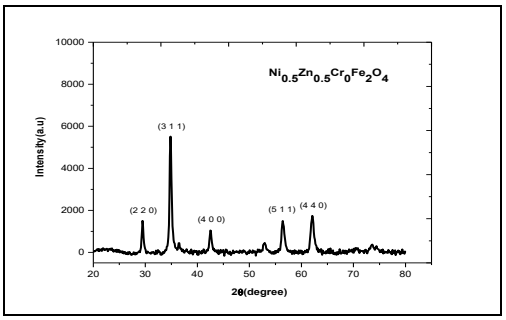

Figure 1 (a) XRD of $NiZnCr_{(x)}Fe_{(2-x)}O_4$ where x=0

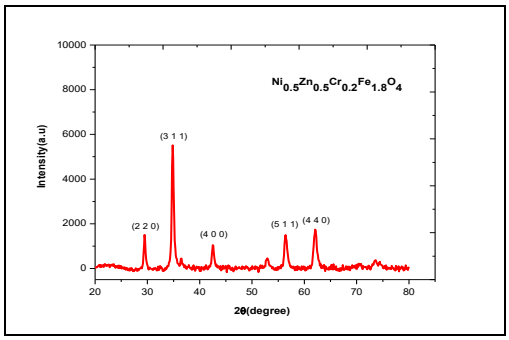

Figure 1 (b) XRD of $NiZnCr_{(x)}Fe_{(2-x)}O_4$ where x=0.2

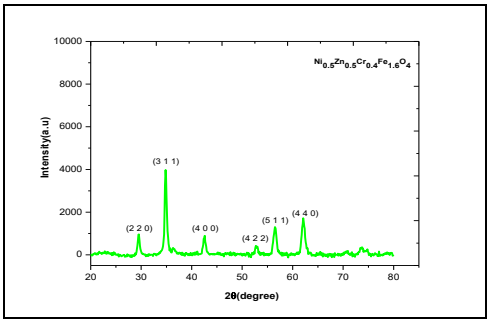

Figure 1 (c) XRD of $NiZnCr_{(x)}Fe_{(2-x)}O_4$ where x=0.4

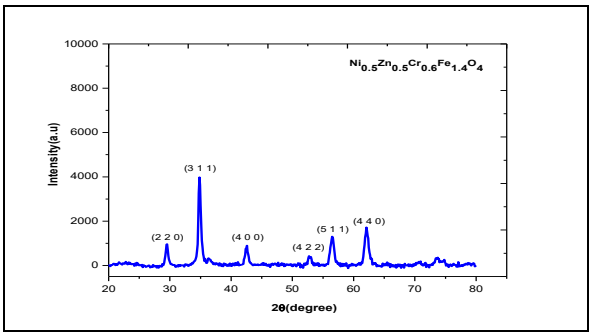

Figure 1 (d) XRD of $NiZnCr_{(x)}Fe_{(2-x)}O_4$ where x=0.6

Figure 1. 'a' , 'b' 'c' and 'd' shows that the XRD patterns of NZCr nanoferrite

The XRD pattern of the NZCr nanferrite shows that the plane reflection of peaks (220) , (311), (222), (400), (422), (333) and (440) all these planes are cubic spinel structure. All peaks of diffraction correspond well to those mentioned in the literature (24) . From the XRD peak there is no any extra peaks are observed it means the pure sample was synthesized. The

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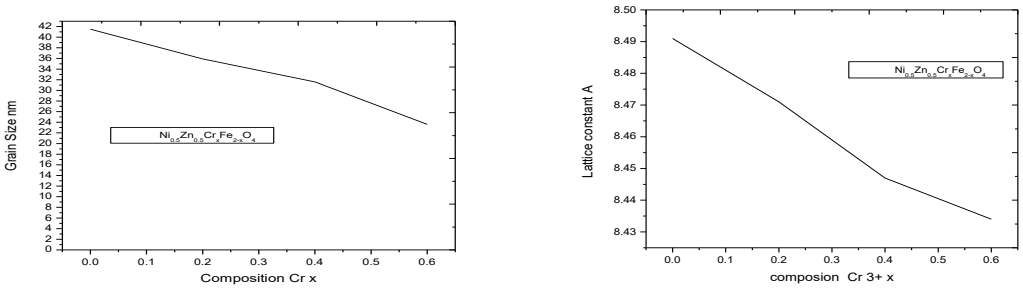
substitution of Cr^{3+} in Ni-Zn nano ferrites reveals that the average crystallite size decrease with increasing Cr^{3} composition is shown in Table 1.

Table 1: Lattice constant (A), Crystallite Size (t), , dislocation density (**δ**), hopping length A site d_A and B- Site d_B of $Ni_{0.5}Zn_{0.5}Cr_xFe_{2-x}O_4$ nanoferrite.

Composition Cr^{3+} x	Lattice Constant A(A^0)	GRAIN SIZE (nm) Scherer's formula	Dislocation Density δ (Δlines/m^2) E^{+14}	Hoping length	
				tetrahedral A site (d_A)	octahedral B site(d_B)
0	8.491	41.5	5.806	3.6766	2.9973
0.2	8.471	35.9	7.759	3.6679	2.9902
0.4	8.447	31.6	10.014	3.6575	2.9817
0.6	8.434	23.6	17.954	3.6519	2.9772

The average crystallite size of the $Ni_{0.5}Zn_{0.5}Cr_xFe_{2-x}O_4$ was between 35 nm and 23 nm. The particle size decreases with increasing Cr^{3} concentration as well as lattice parameter also decreasing with respective x shown in figure 3 and results are tabulated in table 1.



(a) (b)

Figure 2: (a) shows the crystallite sizes with Cr^{3+} content by Scherrer's formula and (b) lattice constant .

The XRD data were used to calculate the lattice parameter for each sample using the following formula,

$$a = d \times \sqrt{h^2 + k^2 + l^2} \quad \text{----------(2)}$$

Where, a is lattice constant, d is the inter planer spacing and hkl are the miller indices of planes. The values of lattice constant are listed in table 1. The lattice constant decreased with

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increasing the x concentration is in the range 8.491Å to 8.434Å. The decrease of lattice constant 'a' and particle size with the Cr^{3+} concentration increase this may be due Cr^{3+} ions replacing to Fe 3+ ions is shown in figure 2.

The dislocation density was calculated from crystallite size using the following relation.

$$\delta = \frac{1}{t^2} \quad \text{-------(3)}$$

Dislocation density varies from 5.806 E^{+14} to 17.954 E^{+14} Δlines /m^2 with Cr $^{3+}$ ion concentration.

The hoping length between cations on the A-sites (L_A) and cations on the B-site (L_B) can be determined using the lattice parameter of the NZnCr ferrite sample by using the following equations.

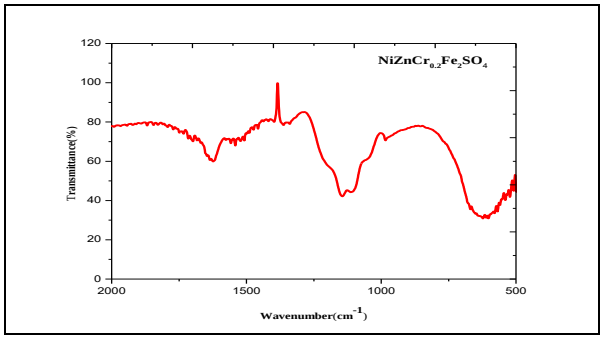
$$L_A = \frac{a*\sqrt{3}}{4} \quad \text{-------(4.i)}$$

$$L_B = \frac{a*\sqrt{2}}{4} \text{-------(4.ii)}$$

$Ni_{0.5}\ Zn_{0.5}\ Cr_xFe_{2-xO4}$ nanoparticles hoping length was measured at tetrahedral and octahedral sites and shown in Table 1. The hoping length at both tetrahedral and octahedral sites decreases.. It is because the hopping length of the sites was directly proportional to the s lattice parameters. This can be interpreted by the replace in ionic radii of Cr^{3+t} to ionic radii of Fe^{3+}.

3.2. Fourier transforms infrared spectroscopic FTIR:

FTIR spectra of $Ni_{0.5}Zn_{0.5}Cr_xFe_{2-x}O_4$ nanoferrite NZCr Samples were recorded in the wave number range of 400–2000 cm^{-1} . The absorption frequency observed two peaks values υ_1 and υ_2 are 604.57 cm^{-1} and 1107.90 cm^{-1} of x= 0.2 and 661.42 cm^{-1} and 1146.47 cm^{-1}. FTIR spectra display two main absorption bands corresponding to ferrite metal oxide (M-O) vibration modes. The higher frequency band in the range of 1107-1146 cm^{-1} is attributed to the tetrahedral-cluster-stretching mode, while the lower frequency band in the range of 604-646 cm^{-1} is attributed to the octahedral cluster stretching mode.



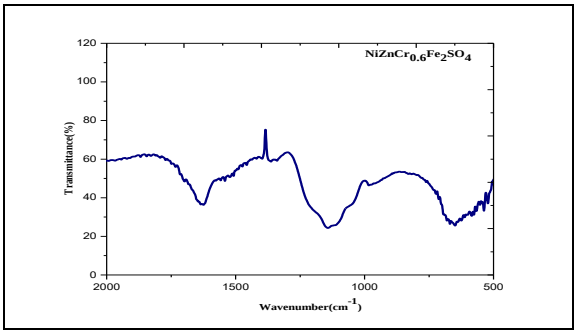


Figure 3 : (a) FT-IR of $NiZnCrFe_2O_4$ at x=0.6 **Figure3: FT-IR of $NiZnCrFe_2O_4$ at x=0.6**

The absorption frequency υ_1 and υ_2 was slightly shifted to higher frequencies with increasing x Cr^{3+} content. This shift in υ_1 and υ_2 can be caused by the substitution of Cr chromium iron at octahedral sites because its atomic weight is less than iron, affecting distances of $Fe^{3+} - O^{2-}$ at octahedral sites.

3.3 VSM Hysteresis Loop Analysis:

The figure 3 shows that magnetic properties of NZCr ferrite synthesized samples from the hysteresis graph revealed that the synthesized material is soft nature these magnetic propertiy recorded at room temperature. The results are tabulated in Table 2 it was found that with increasing concentration of Cr^{2+} coercivity (H_c) goes on decreasing also Ms magnetic saturation.

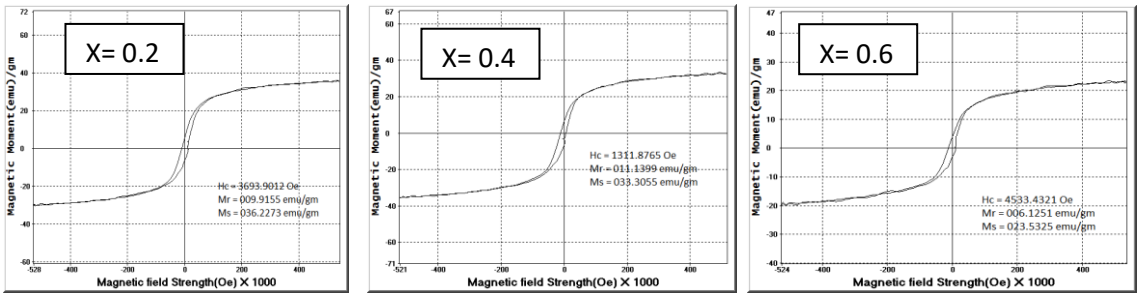


Figure : 3 Hysteresis (VSM) of NiZnCr (NZCr) ferrite at X=0.2, 0.4 and 0.6

Table 2 : The Magnetic properties of of $Ni_{0.5}Zn_{0.5}Cr_xFe_{2-x}O_4$ nanoferrite.

x	M_s (emu/gm)	M_r (emu/gm)	(M_r/M_s)	H_c (Oe)
0.2	36.227	9.915	0.27369	3693.901
0.4	33.305	11.139	0.33445	1311.876
0.6	23.532	6.125	0.26028	4533.432

The change in coercivity (H_c) with Cr^{2+} concentration is shown in Figure 3. The values of saturation magnetization Ms, and coercivity Hc, are recorded and given in the tabulated form. The magnetic saturation of the NZCR ferrite goes to decreases with increasing x chromium composition.

4. Conclusion:

Cr^{3+} substituted in Ni-Zn ferrite NZCr were successfully synthesized by chemical route at low temperature. The X-ray diffraction showed sample phase purity and provided evidence of single phase spinel cubic structure. The crystallite size of synthesized nanomaterial was

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determined by Scherrer's formula within 41.5 -23.6 nm. The FTIR spectroscopy the peak observed in the range of 604 to 646 to confirm the synthesized NZCr sample ferrite material. It observed that the bond shifted to words higher side due to the Cr^{3+} ions replace by $Fe3^{+}$ ions. Magnetic property from hysteresis graph shows that the NZCr ferrite is soft materials. The magnetic saturation decreases with increasing the Chromium concentration. This soft material may use in modern technological various applications.

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