Amalgamation and Characterization of NiCo Ferrite by using Sol-gel Auto Combustion Technique

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Abstract - *The effect of Nickel doped Cobalt ferrite nano particles Ni0.2CoxFe2-x04(x=0.1, 0.2, 0.3, 0.5) Created by sol-gel auto combustion technique by using citric acid as fuel. The single phase cubic structure form confirm by the XRD. The crystalline size calculated by FWHM of (311) plane using Scherer's formula. The typicalsize of the crystalline sample varies in the order of nano regime. The structural and lattice parameter were obtained by XRD data. The surface morphology of Nickel doped Cobalt ferrites was studied by Field Emission Scanning Electron Microscope (FESEM), and Scanning Electron Microscope (SEM) images. The spherical particles with the average grain size 25.62nm to 33.69nm range are observed by FESEM images. Compositional stoichiometry was confirmed by X-ray photo electron spectroscopy.*

***Keywords:** XPS, X-ray Diffraction, Auto Combustion, Surface Morphology*

I. INTRODUCTION

Due to their tremendous progress of ferrite nano particles, in last two decades researchers found remarkable applications in magnetic imaging, storage devices, magnetic Ferro fluid technology, sensors and drug delivery [1-4]. Extraordinary magnetic property of these ferrites in nanoscale plays a vital role in the in modern magnetic materials. Ferrites nanoparticles exhibit unique structural, magnetic, and chemical magnetic properties, and they have wide range of scientific applications, including recording devices, spintronics, color imaging, and biotechnology, magnetic refrigerators, and devices are having high frequency [5, 6]. Cobalt ferrite is a magnetic material with high hardness, aturation magnetization and coercive properties. For magnetic recording application, amongst the several ferrites Cobalt ferrite (CoFe2o4) is widely used due to its high mechanical hardness and chemical stability, however nickel ferrite (NiFe2o4) is a soft material with a saturation magnetization and high coercively. The properties of this mixed ferrite of hard and soft magnetic materials find remarkable application in electronic, biomedical and recording devices [7, 8]. Depending on the application, the magnetic character of nanoparticles is primarily determined by their shape; size, stability and purity [9,10]. The type of the ions, their distribution, and charges amongst the tetrahedral site and octahedral site determine the electrical and magnetic properties of spinel ferrites [11]. In medicine, ferrite nanoparticles are utilized as drug carriers in situations where traditional medication delivery techniques fail [12]. For recording devices, generally "high blocking temperature of nanoparticles is needed whereas for the applications of medicine, comparatively low blocking temperature is essential". These high and low blocking temperature often done by differing the sizes of those nanoparticles or by correcting the phases of magnetic materials concentrations of soft and hard ferrite. For this motive Ni substituted Co ferrite nanoparticles were produced by Sol-gel auto combustion

method. For synthesis of nanoparticles by Conventional techniques include co- precipitation, ball-milling, solvothermal method, micro- emulsion technique, solid- state reaction route. In fact, the size distribution and size of the nanoparticle are difficult to achieve in most types of nanoparticle synthesis using these methods. Nanometer-sized reactors are used to overcome these challenges in the formation of homogeneous nanoparticles.

II. MATERIALS AND METHOD

$Ni_{0.2}Co_xFe_{2-x}0_4$(X=0.1, 0.2, 0.3, 0.5) nanoparticles were created by the sol-gel auto-combustion method. In this method of preparation stoichiometric composition of all metal nitrates (Ni $(NO_3)_2.6H_2O$, (Co $(NO_3)_2.6H_2O$), (Fe $(NO_3)_3$. 9H2O) and chelating agent (citric acid) ($C_6H_8O_7.H_2O$) with purity 99.0% were taken then dissolved into DI water. This mixed solution of nitrates was kept on the hot plate at 60^0c, by using a magnetic stirrer the solution was stirred well continuously. Liquor ammonia was added in this mixture by drop by drop to adjust the pH level of the solution become neutral (pH=7). After 24hours the solution turn out to be dehydrated and the development of the gel is stirred and treated at 120^0c on the hot plate for 8h. During this process the process of "Auto ignition" was taken by the gel. Then the obtained floppy powder was calcinated at 800^0c for 3hours in muffle furnace. Finally, the observed sample was fine grained with the aid of pestle and mortar. The powder form of this sample is used for further characterizations.

III. RESULTS AND DISCUSSIONS

3.1 By using X-ray diffraction technique, crystalline phase and structure Analysis of $Ni_{0.2}Co_xFe_{2-x}O_4$ were analyzed. The obtained XRD diffraction pattern was shown in figure1. The diffraction planes like 220, 311, 400, 511 and 440 shows cubic spinel stage. The diffraction pattern of all Bragg peaks was indexed and matched with (JCPDS No. 08-0234) [13-15]. The lattice parameter (a) was gained by Bragg's law.

$$d = \frac{a}{\sqrt{(h^2+k^2+l^2)}}$$

Where, (h, k, l) are Miller Parameters, d is inter-planer distance.

The calculated lattice parameter values are lies in the range from 8.4226 to 8.35655 A^0, which is given in Table 1. By using Scherer equation, the average crystallite sizes were found from the maximum intensity plane (311).

$$D = 0.9\lambda/\beta \cos\theta$$

Where, D = crystallite size, λ = wavelength, β =Full width at half maximum (FWHM) and θ= Bragg angle [16].

The grain size of prepared sample lies in the nano regime. It is observed that for different composition of cobalt, the grain sizes is decreases. The X-ray density were obtained using the following equation,

$\rho_x = 8M/ Na^3$

The decreasing lattice constant values shows that different Co ions doped in the NiFe sample. The X ray densities of the prepared sample varies from 4.2039 to 4.3012 g/cm^3.

Table 1 XRD parameters of the samples $Ni_{0.2}Co_XFe_{2-X}O_4$(X=0.1, 0.2, 0.3, 0.4)

Sample	Lattice Constant	X ray density (g/cm^3)	Crystallite size(nm)
$Ni_{0.2}Co_{0.1}Fe_{1.9}O_4$	8.4226	4.2039	110.92
$Ni_{0.2}Co_{0.2}Fe_{1.8}O_4$	8.4021	4.2108	100.987
$Ni_{0.2}Co_{0.3}Fe_{1.7}O_4$	8.3594	4.2826	156.144
$Ni_{0.2}Co_{0.5}Fe_{1.5}O_4$	8.35655	4.3012	52.481

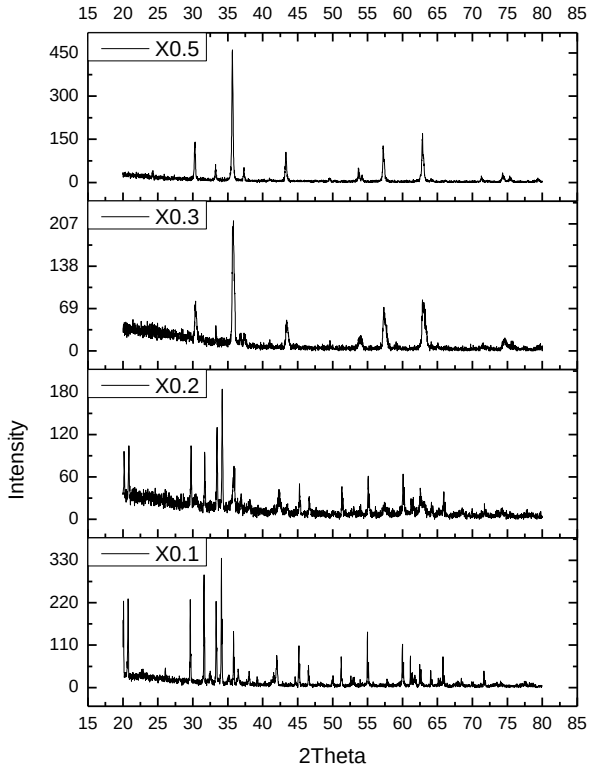

Figure 1 X-ray diffraction pattern of Ni0.2$Co_XFe_{2-X}O_4$

3.1 XPS Study

The nature of the nanoparticle surfaces, structures can be analyzed by using XPS studies. It can be used to find elemental composition, contamination presence in the nanoparticles (17). The Figure 2 shows that the valence states and elemental composition of Nickel and Cobalt present in the sample studied by using XPS. The survey spectrum of the prepared sample $Ni_{0.2}Co_{0.5}Fe_{1.5}O_4$ is shown in the Figure 2(a). This survey distinctly shows the Ni, Co, O and C elements peaks and the C element shall be used to represent air exposure. Figure2(b) shows the band of Ni2p, it was having two shakeup satellites and 2 spin-orbit doublets. There arefour identifiable features of Nickel 2p spectrum [18] are two main peaks (Ni $2p_{3/2}$ and Ni $2p_{1/2)}$) and their satellite. The corresponding value of Ni $2p_{3/2}$ are 854.775 and 856.315 eV and the corresponding peaks 873.1 and 879.22 eV are Ni $2p_{1/2}$.The two shakeup satellites of Nickel main peaks are Satellite.1 at 860.47 eV and Satellite.2 at 879.22 eV. The peak at "Local screening from lattice oxygen next to the Ni 2p core hole" [19] is

assigned to Ni 2p3/2 at 854.7 eV. Furthermore, the prevalent peak at 856.1eV suggested a greater hydroxylation of NiO in the surface of composite oxide [20], which was supported by the O 1s range. The peak of binding energies of Ni $2p_{1/2}$ is consistent with the help of $Ni2p_{3/2}$. The binding energy of Ni 2p was shown, which represents the existence of divalent oxide state of Ni was present in the sample. The Figure 2 depicts the central level spectrum of Co 2p (c). Co 2p3/2 and Co 2p1/2 have comparable peaks of 779.4 eV and 795.2 eV, respectively, and these peaks have been recorded to Co2p [21]. Shake-up peak 1 at 785 eV has a separation energy of approximately 5.2 eV with Co 2p3/2 at 779.4 eV, while shake-up peak and the level 2 has a separation energy of roughly 5.2 eV with Co 2p3/2 at 779.4 eV at an energy of 803.4 eV. The energy difference between the Co 2p main peak and the peaks, which is around 6.0 eV for Co2+ and 9–10 eV for Co3+, respectively, is linked to the oxidation states[22]. The findings verified the presence of a divalent oxide state of Cobalt. Figure 2(d) shows the decomposition of two oxygen contributions in a high resolution spectrum for the O 1s peak. The peak, which is positioned at 529.8 eV (O1), the metal–oxygen bonds (M = Ni or Co) are represented by this symbol. The surface hydroxyl groups are represented by the element O2 at 531.1 eV [23,24]. Analyzing the XPS data reveals that NiCoO2 samples comprise Ni^{2+} and Co^{2+}, as well as the atomic percentages of Nickel, Cobalt, and Oxygen, which are respectively 23.11, 23.49, and 53.4 percent. The atomic ratio of N has been computed.

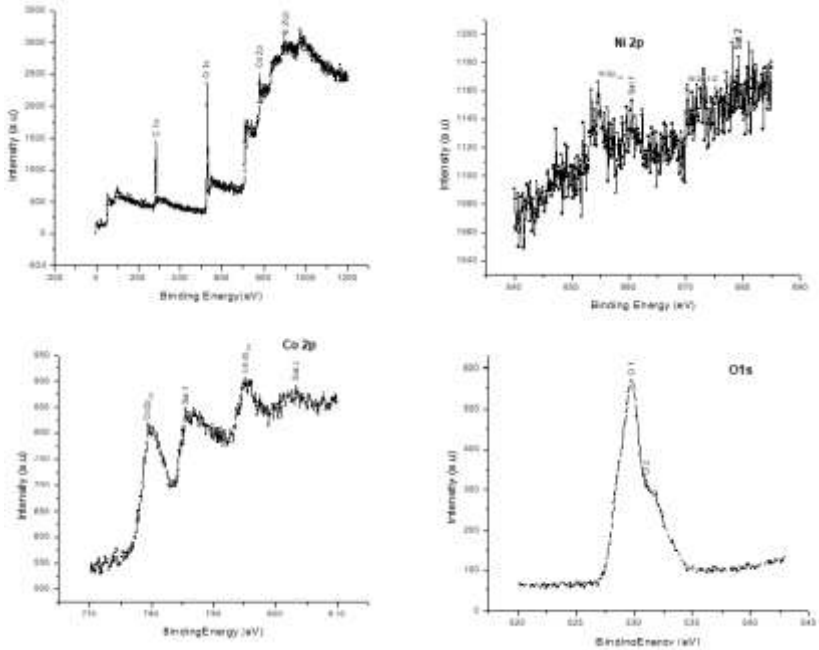

Figure 2 XPS Spectrum of [a] Survey spectrum, [b] Ni 2p spectrum, [c] co 2p spectrum [d] O1s Spectrum for the $NiCoO_2$

3.2 FESEM Study

The Figure 3 provides the pictures of FESEM of prepared sample $Ni_{0.2}Co_xFe_{2-x}o_4$ were nanoparticles. All the synthesized sample have uniform in both shape and structure. The particles obtained by this method are spherical in shape and the particles structural

morphology varied for dissimilar amount of composition. The grain size in nanoscale were confirm from XRD data was agree with FESEM micrographs. The observed image by using FESEM represents a very good homogeneity of the synthesis sample. The average grain size was obtained in the range of 25.62 - 50.88nm.

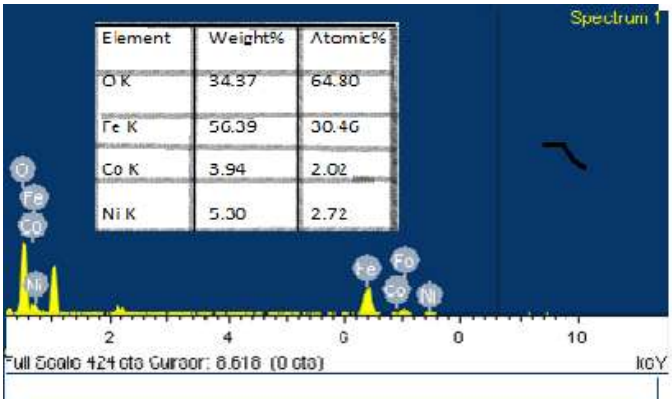

Figure 3 FESEM micrograph of $Ni_{0.2}Co_{0.3}Fe_{1.7}O_4$

IV. MICROSTRUCTURE ANALYSIS

The morphology of the synthesized $Ni_{0.2}Co_{0.1}Fe_{1.9}O_4$ ferrite nanostructures is studied through the SEM. Figure 4 shows the microstructure and surface morphology of the prepared doped samples. The SEM images of $Ni_{0.2}Co_{0.1}Fe_{1.9}O_4$ ferrite nanostructures give out remarkable variation in the porosity and nanostructures of the sample. The formation of the agglomerated nanostructures and voids are showed by the SEM images are due to large amount of gases releasing through the combustion process, the pores and voids are visible in the sample. The average particle size of $Ni_{0.2}Co_{0.1}Fe_{1.9}O_4$ ferrite is found to be 27.62, 33.69 nm from SEM images. As can be seen in SEM, the average crystallite size determined by XRD is quite tiny. SEM measurements are based on the size of secondary particles, which are made up of several crystallites generated by soft reconciliation, whereas XRD only considers the size of a single crystallite.

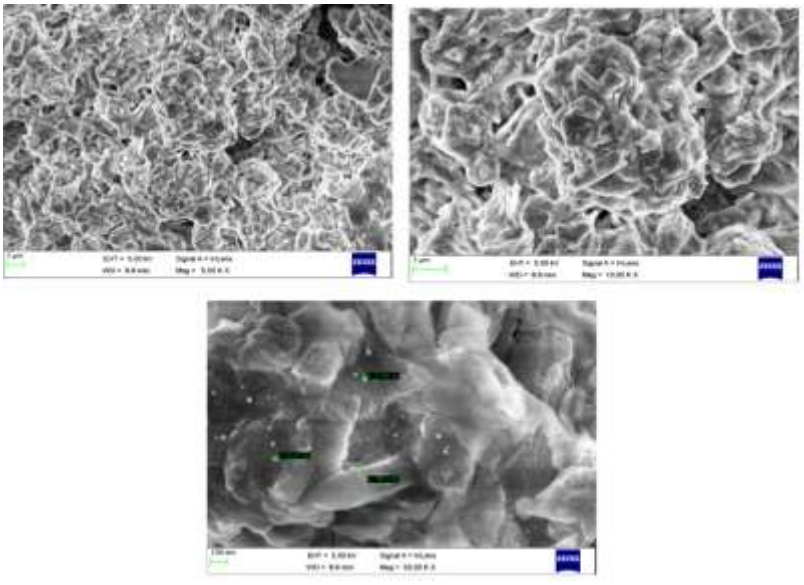

Figure 4 SEM Images of $Ni_{0.2}Co_XFe_{2-X}O_4$ (X=0.1, 0.3)

4.1 Conclusion

In this paper, citric acid was utilized as a fuel in the Sol-gel auto combustion technique to successfully synthesize spinel structured Nickel doped Cobalt ferrite nanoparticles. The structural microstructural studies of $Ni_{0.2}Co_XFe_{2-X}O_4$ (X=0.1, 0.2, 0.3, 0.5) have been investigated by XRD, XPS, SEM and FESEM. Pure formation of spinel type NiCoFe with no impurities for all the prepared samples are concluded in X-ray diffraction and XPS studies. The crystallite average size of the sample was calculated by Scherer's formula which authorizes the nano crystalline nature of the prepared samples. The average grain size calculated from FESEM technique is of the range of 26.62 - 50.88nm.The investigation results reveals that as synthesized sample are highly porous and exhibits at nanoscale size. It finds the good applications in nano-electronic devices.

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