STRUCTURAL CHARACTERIZATION OF COBALT DOPED NICKEL FERRITES

Khin New Oo[1] , Moe Moe Aye[2], Min Maung Maung[3] and Khin Khin Win[4]

Abstract

Cobalt Doped Nickel Ferrites with the general formula Ni_{x-1} Co_x Fe_2 O_4 (x = 0.0, 0.1, 0.2 and 0.3) were prepared by self-combustion method and sol-gel method. Nickel II Nitrate Hexahydrate [Ni $(NO_3)_2$ 6 H_2O], Cobalt II Nitrate Hexahydrate [Co $(NO_3)_2$ $6H_2O$] and Iron (III) Nanohydrate [$Fe(NO_3)_3$ $9H_2O$] were used as the starting chemicals. The X-ray diffraction (XRD) analysis was carried out to investigate the crystalline phase formation. Microstructural properties were determined by SEM. Elemental composition characterization of prepared samples were performed by Energy Dispersive Spectroscopy(EDS).

Keyword: Cobalt Doped Nickel Ferrites, XRD,SEM and EDS.

Introduction

Nanoparticles of magnetic ferrites have attracted great research interest because of their applications in permanent magnets, drug delivery, microwave devices and high-density information storage. Cobalt ferrite has been extensively investigated because of its interesting magnetic behavior, chemical stability and mechanical hardness. Cobalt ferrite $CoFe_2O_4$, crystallizes in a partially inverse spinel structure. Nickel-ferrite is an inverse spinel magnetic material. Nickel ferrite is well known hard magnetic material with high coercivity and saturation magnetization while nickel ferrite is soft material with low coercivity and saturation magnetization. Many of these hard and soft magnetic properties make then very promising for candidates for a variety of applications. Nano size ferrites have been prepared by various techniques such as sol-gel, self-combustion, modified oxidation process, forced hydrolysis, hydrothermal process, ball milling and the micro-emulsion method[1,6]. In the present study, Nano-ferrites of the composition Ni_{1-x} Co_x Fe_2O_4 (where x = 0.0, 0.1, 0.2 and 0.3) were synthesized by citrate-gel self- combustion method and sol-gel method. Structural, microstructure properties and atomic and weight concentration of fabricated nano-ferrite were studied by X-ray diffraction (XRD), scanning electron microscopy(SEM) and Energy Dispersive Spectrometer (EDS).

Experimental

In this research spinel like ferrites belonging to the series $Ni_{1-x}Co_xFe_2O_4$, where x varies from 0.0 to 0.3 in steps of 0.1 were prepared by self-combustion method and sol-gel method. $Ni(NO_3)_2.6H_2O$, Nickel nitrate hydrate, $Fe(NO_3)_2.9H_2O$, iron nitrate hydrate and $Co(NO_3)_2.6H_2O$, cobalt nitrate hydrate were used as raw materials for $Ni_{1-x}Co_xFe_20_4$ ferrite. Before preparation of spinel like ferrites the purification of starting materials was checked by X-ray diffraction.

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Experimental Sequence for Nano-ferrites by Self-combustion Method

The self-combustion method was used for preparation because the followings two advantages.

(1) heat generated in the exothermic reaction accelerates the process and

(2) the resulting as prepared powder is fine grained with grain size smaller than that of the starting powers.

Nickel II Nitrate Hexahydrate [Ni $(NO_3)_2 \cdot 6H_2O$], cobalt II Nitrate Hexahydrate [Co $(NO_3)_2$ $6H_2O$] Iron (III) Nanohydrate [$Fe(NO_3)_3$ $9H_2O$] were weighed with desired stoichiometric compositions. The precursor solutions were prepared by dissolving the necessary powders in deionized water by molarity ratio. The mixture solution was stirred by magnetic stirrer at 80°C. Ammonium Hydroxide (NH_4OH) was added to control pH level of mixture solution. After stirring 1h, the mixture solution became viscous gel. Hard gel was obtained by continuous heating at 100°C for 2h. As the temperature increased from 100°C to 190°C, the colour of hard gel changed to black colour. Finally, self-combustion process was done at 280°C and reddish-brown powder was obtained. It was cooled down at room temperature and then ground by agate mortar. After sieved by mesh sieve, $Ni_{1-x}Co_xFe_2O_4$nano ferrite powder was obtained. Experimental sequence of Cobalt doped Nickel Ferrites using self-combustion method was shown in figure 1.

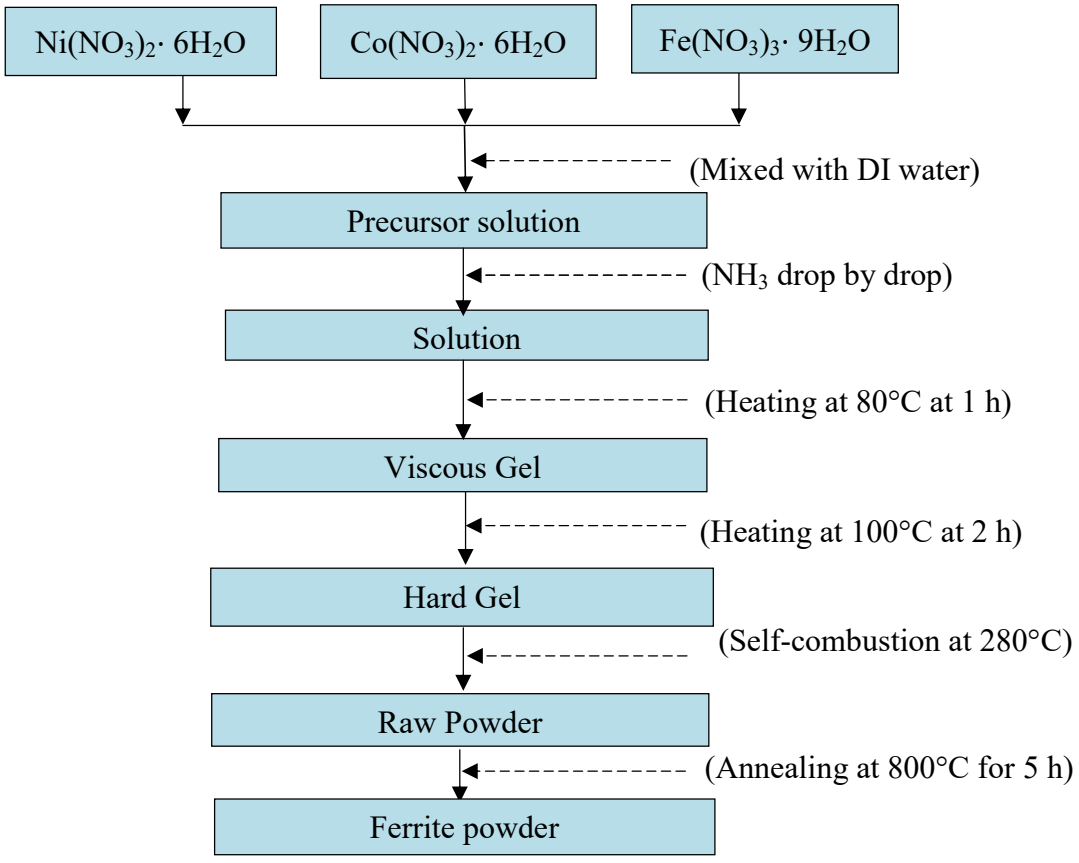


Figure 1 Experimental sequence of Cobalt Doped Nickel ferrites for Self-combustion method

Experimental Sequence for Nano-ferrites by Sol-Gel Method

Sol-gel processing, which is based on chemical engineering methods, is a technique to manufacture ceramic powders, especially oxides. The term *sol* refers to the initial solution of the chemical components for the final powder; whereas the term *gel* describes the final consolidation stage that forms the ceramic product. Sol-gel procedures have been successful in the preparation of bulk metal oxides, e.g., ceramics, glasses, films and fibers and, therefore, they have been applied for nanoparticle synthesis.

The sol-gel process consists of the following five prime steps.

(i) Preparation of a homogeneous solution either by dissolution of metal organic precursors in an organic solvent that is miscible with water, or by dissolution of inorganic salts in water. (ii) Conversion of the homogeneous solution into a sol by treatment with a suitable reagent that is generally water with or without an acid base. (iii) Aging of the solution. (iv) Shaping of the gel. (v) Thermal treatment or sintering of the final product.

Firstly, Metal precursors were prepared by using $Ni(NO_3)_2.6H_2O$, Nickel nitrate hydrate, $Fe(NO_3)2.9H_2O$, ion nitrate hydrate and $Co(NO_3)_2.6H_2O$, cobalt nitrate hydrate and deionized water. The chelating agent was prepared by dissolving the necessary powders in distilled water at 70 °C. The chelating agent solutions were maintained at 70 °C for 2 h, the solution became clear. Metal precursors were dissolved into the chelating agent solution under magnetic stirring. Ammonia (NH_3) was added drop by drop to maintain the pH at 7. The sol-gel reaction was continued for 3 h and the temperature increased to 100 °C for 10 h or until the gel dried into the form of a powder. Finally, all samples were sintered at 800 °C for 5 h and then ground and sieved, nano ferrite powder was obtained. The experimental sequence for nano ferrite powder by sol-gel method was shown in figure 2.

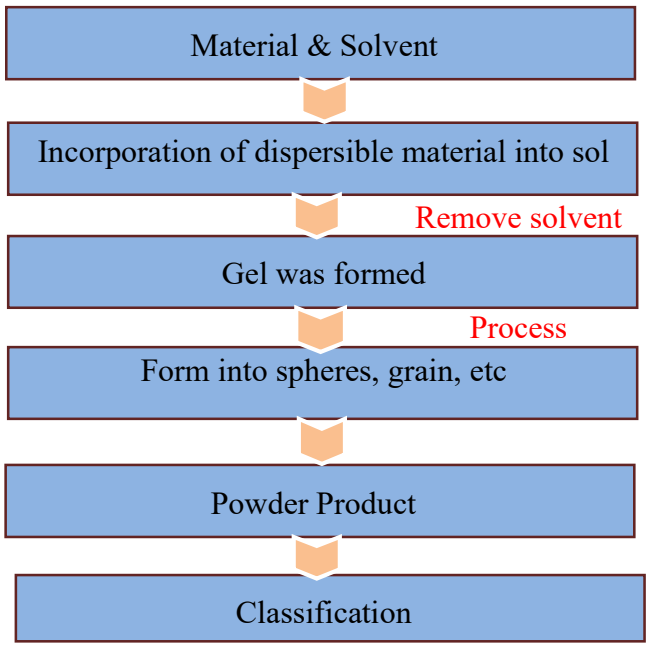


Figure 2 The production steps for sol-gel production route

Results and Discussion

Structural Investigation of Nano-ferrite

The XRD spectra of the cobalt Doped Nickel ferrites, Ni_{1-x} Co_x Fe_2 O_4 (x = 0.1, 0.1, 0.2 and 0.3)nano-ferrite were investigate by X-Ray Diffractometer. Figure 3(a-b) showed XRD profile of nano-ferrite fabricated by self-combustion method and sol-gel method with different Co concentration.

In these figures, eight diffraction patterns were clearly observed and all of these patterns were consistent with JCPDS library file No 01-077-9720.It can be seen that all the compounds thus prepared show crystallinity and the diffraction pattern is characteristic of a spinel structure. The interatomic spacing (d) values were in good conformity with that of the reported values. Moreover no other impurity lines corresponding to possible oxides of precursors used for synthesis were noticed. Thus it was ensured that the prepared compounds were single phasic in nature and they exhibit an inverse/ normal spinel structure.

In figure 3(b),all the reflections in the XRD patterns correspond to that of cobalt ferrite and no additional reflections were observed for the samples indicating the phase purity of the samples. The X-ray diffractograms clearly indicate the formation of single phase spinel structure. The XRD patterns were compared and indexed using JCPDS library file no 00-003-0875 for Ni ferrites. The reflections of the samples synthesized by sol-gel methods were shaper than that of the sample prepared by the self-combustion route, indicating the presence of larger crystallites. But their intensities were more intense than nano ferrite by self-combustion method.

The X-ray density of all the $Ni_{1-x}Co_xFe_2O_4$ ($0 \leq x \leq 0.3$) ferrites has been calculated from the molecular weight and the volume of the unit cell using the relation;

$$d_x = \frac{8M}{Na^3}.$$

The calculated values were also listed in Table1.

The average particle size of the synthesized ferrite samples was estimated from X-ray peak broadening of diffraction peaks using Scherrer formula. The calculated average crystallite sizes of these starting materials were listed in Table 2.From this results, the average crystallite size was decreased with the increasing of Co content. But at the Co content (0.3%), the average crystallite size increased again due to the material concentration. Average crystallite size of fabricated nano ferrite by sol-gel method was a little larger than that of self-combustion method. Generally the sol-gel technique yields nano size grains in the ferrite systems. But, as the sintering temperature and sintering time (800˚C for 5 h) were very high, this resulted for larger grain size in the prepared ferrite samples. Likelihood, all of fabricated nano ferrite confirmed nano meter range.

Table 1 Variation of X- ray density values for $Ni_{1-x}Co_xFe_2O_4$ nano-ferrite

$Ni_{1-x}Co_xFe_2O_4$ Nano-ferrite	X-ray density (g cm^{-3})	
	Self-combustion Method	Sol-gel Method
x =0.0	5.3530	5.3900
x =0.1	6.7244	6.7070
x = 0.2	7.2942	6.7029
x= 0.3	6.8162	6.7244

Table 2 The crystallite size of starting materials

$Ni_{1-x}Co_xFe_2O_4$ Nano-ferrite	Crystallite Size(nm)	
	Self-combustion Method	Sol-gel Method
x =0.0	45.7951	46.3617
x =0.1	43.1230	45.6355
x = 0.2	41.4354	45.1332
x= 0.3	42.5168	45.7477

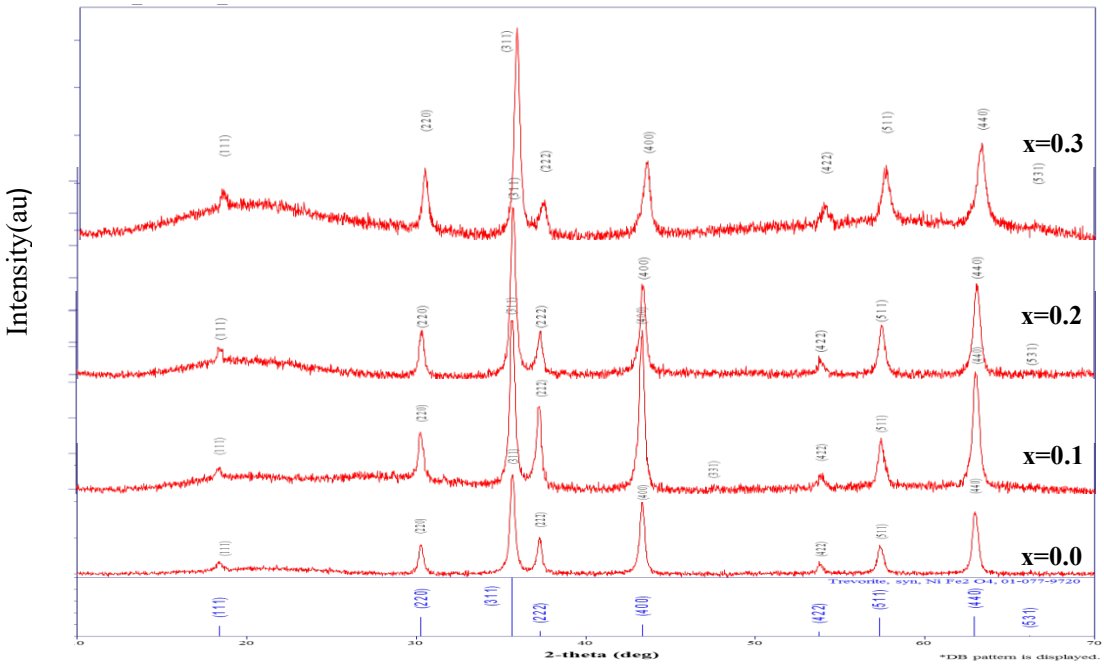


Figure 3 (a) XRD Spectrum of $Ni_{1-x}Co_xFe_2O_4$ferrites with different Co concentration by self-combustion method

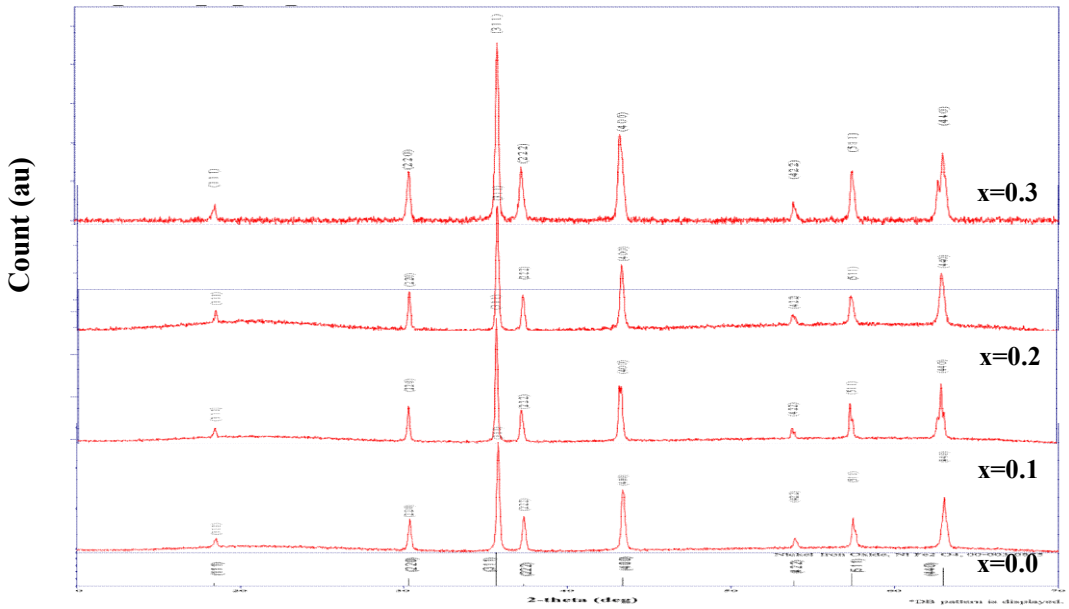
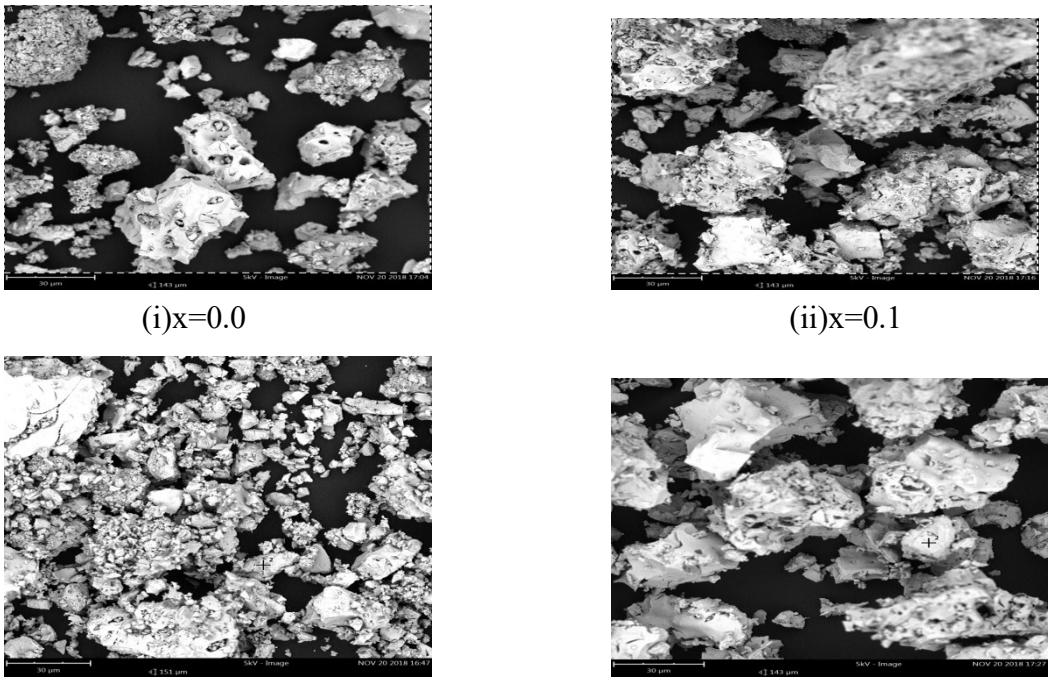


Figure 3 (b) XRD Spectrum of $Ni_{1-x}Co_xFe_2O_4$ ferrites with different Co concentration by sol-gel method

Microstructural Determination

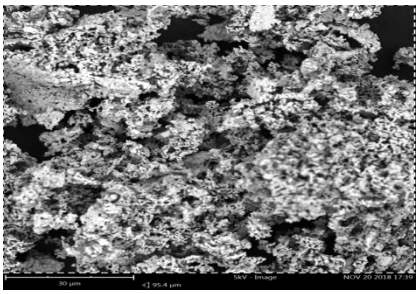
Microstructural properties of Ferrite samples were studied by Scanning Electron Microscopy(SEM). The scanning electron image of ferrite samples by self-combustion method and sol-gel method were shown in figure 4(a&b). In these figures, it can be seen that the morphology of particles for SEM micrographs of various composition is similar. They reveal largely agglomerated, well defined nano particles of the sample powder with inhomogeneous broader grain size distribution. Such broader size distribution is characteristics of mechanically activated nano sized particles.



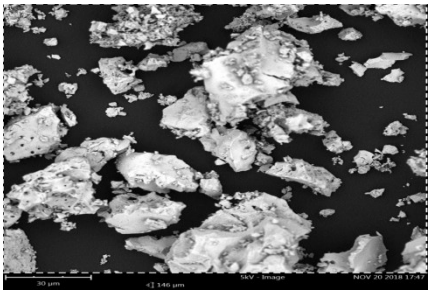
(i)x=0.0 (ii)x=0.1

(iii)x=0.2 (iv)x=0.3

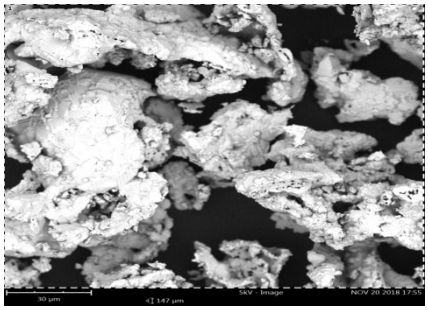
Figure 4 (a) Scanning electron images of $Ni_{1-x}Co_xFe_2O_4$ ferrites nano ferrite with different Co concentration by self-combustion method



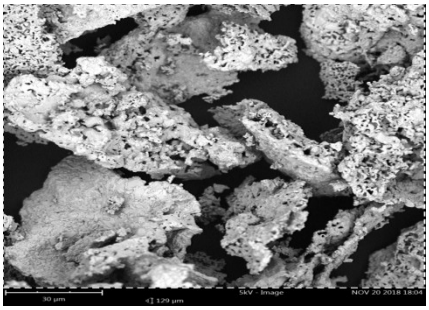
(i)x=0.0



(ii)x=0.1



(iii)x=0.2



(iv)x=0.3

Figure 4 (b) Scanning electron images of $Ni_{1-x}Co_xFe_2O_4$ nano ferrite with different Co concentration by sol-gel method

Elemental Analysis by EDS

The elemental analysis of ferrite samples with different compositions by two different methods were analyzed by Energy Dispersive Spectrometer(EDS).The EDS pattern of nanoferrites samples were shown in figure 5(a & b). In these figure, it was indicated that the elemental and atomic composition. The fabricated nanferrite showed the present of Ni, Co, Fe and O without precipitating cations. The elemental % and atomic % of different elements were shown in Table 3 and 4.

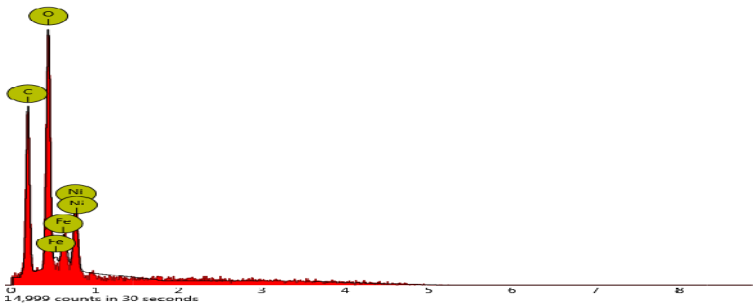


Figure 5(a)(i) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.0 concentration by self-combustion method

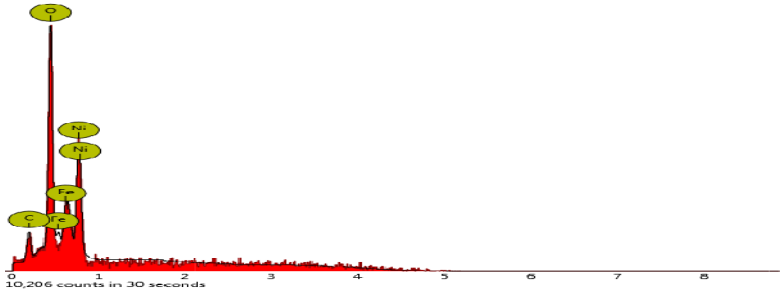


Figure 5(a)(ii) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.1 concentration by self-combustion method

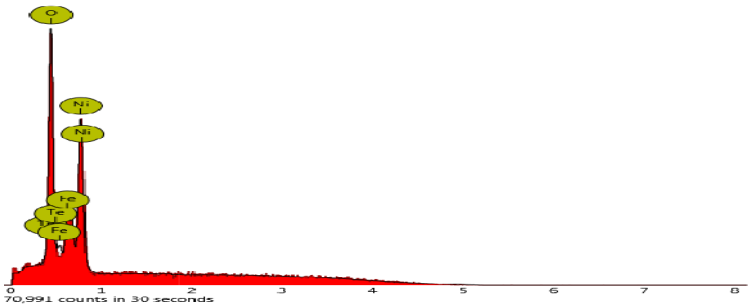


Figure 5(a)(iii) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.2 concentration by self-combustion method

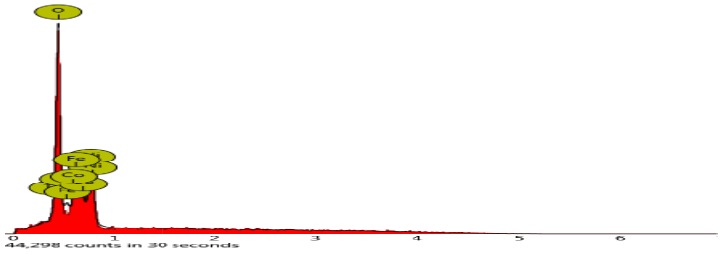


Figure 5 (a)(iv) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.3 concentration by self-combustion method

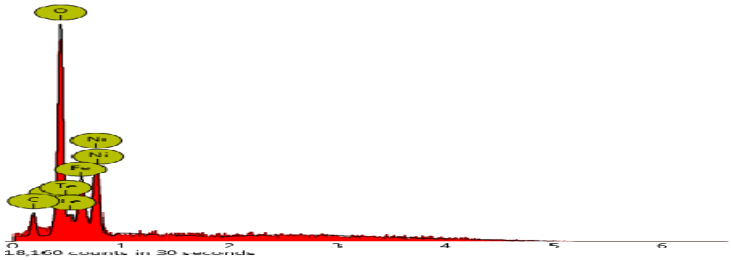


Figure 5(b)(i) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.0 concentration by sol-gel method

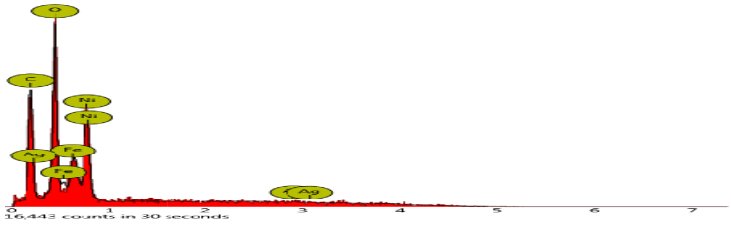


Figure 5(b)(ii) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.1 concentration by sol-gel method

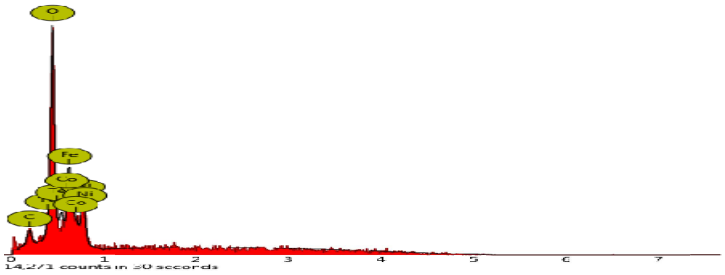


Figure 5 (b)(iii) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.2 concentration by sol-gel method

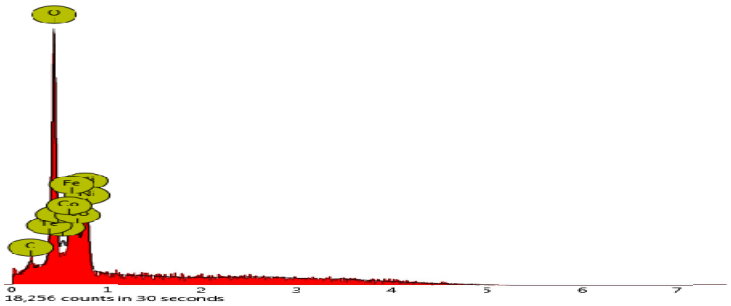


Figure 5 (b)(iv) EDS pattern of $Ni_{1-x}Co_xFe_2O_4$ nanoferrite with different Co x = 0.3 concentration by sol-gel method

Table 3 Atomic and weight concentration of nano-ferrite sample byself-combustion method

Element	Ni		Co		Fe		O	
Ferrite Composition	Atomic Conc. %	Weight Conc.%	Atomic Conc. %	Weight Conc.%	Atomic Conc. %	Weight Conc.%	Atomic Conc. %	Weight Conc.%
$NiFeO_4$	8.60	25.46			5.16	14.54	38.63	31.17
$Ni_{0.9}Co_{0.1}Fe0_4$	24.13	47.60			10.14	19.04	50.96	27.40
$Ni_{0.8}Co_{0.2}Fe0_4$	33.36	55.64			12.19	19.33	54.36	24.71
$Ni_{0.7}Co_{0.3}Fe0_4$	19.58	34.97	6.65	11.93	13.86	23.57	59.80	29.12

Table 4 Atomic and weight concentration of nano-ferrite sample by sol gel method

Element	Ni		Co		Fe		O	
Ferrite Composition	Atomic Conc. %	Weight Conc.%	Atomic Conc. %	Weight Conc.%	Atomic Conc. %	Weight Conc.%	Atomic Conc. %	Weight Conc.%
$NiFeO_4$	20.43	39.90			14.38	26.73	50.56	26.92
$Ni_{0.9}Co_{0.1}Fe0_4$	14.50	37.05			6.36	15.46	35.18	24.50
$Ni_{0.8}Co_{0.2}Fe0_4$	13.09	24.01	5.34	9.83	20.87	36.41	52.37	26.18
$Ni_{0.7}Co_{0.3}Fe0_4$	19.25	33.88	6.98	12.33	15.59	26.11	53.46	25.65

Conclusion

Nanocrystalline Cobalt Doped Nickel Ferrites, Ni_{1-x} Co_x Fe_2 O_4 (where x = 0.0, 0.1, 0.2 and 0.3) samples were successfully prepared by self-combustion method and sol-gel method. Their structural analysis was reported by using XRD. The process involved no impurity pick up and material loss. It was a very simple and economical method where no specific heating or cooling rate is required. X-ray diffraction pattern confirms the formation of cubic spinel structure in single phased without any impurity peak. The lattice parameter was not remarkablely changed

with the increase of Co substitution in Ni-Co ferrites which indicates that Co content was totally substituted in Ni. Average crystallite size of fabricated nano ferrite observed that in the range between 41 and 46 nm. SEM micrographs of various compositions indicate the morphology of particles is similar and largely agglomerated and inhomogeneous broader grain size distribution. EDS data gives the present of Ni, Co, Fe and O without precipitating cations. From the results, it is concluded that, the two fabrication methods used in this research provided improvement of crystallinity and pronounces of nano particle size.

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