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Study of the structural and magnetic properties of ($Ni_{1-x}Co_xFe_2o_4$) prepared by the chemical co- precipitation thermal method

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Received: 6 August 2022 **Accepted: 20 September 2022**

DOI: https://doi.org/10.24237/ASJ.01.03.657C

Abstract

Cobalt-doped nickel ferrites nanoparticles with chemical formula $Ni_{1-x}Co_xFe_2O_4$ for the x values, (x= 0.0, 0.1, 0.3, 0.5, and 0.7) were synthesized at temperature (700 ºC) and pH=11 using chemical co-precipitation thermal method. The powder XRD pattern confirms single-phase cubic structure and the average particle size calculated by Scherrer equation ranged between (16-29 nm) based on X-ray diffraction. The results of studying magnetic properties for the prepared compound showed, that the values of the ratio between Mr/Ms are less than 0.5, and some ratios showed the hysteresis loop in the form of a line indicating the transformation of the material to a state of superparamagnetic.

Keywords: doping; chemical co-precipitation thermal, XRD, VSM

دراسة الخواص التركيبية والمغناطيسية لمركب (Ni1-xCoxFe2o4) المحضر بالطريقة الحرارية الكيميائية للترسيب المشترك

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الخلاصة

تم تصنيع جسيمات فريتات النيكل المشوب بالكوبلت النانوية بالصيغة الكيميائية $Ni_{1-x}Co_xFe_2O_4$ لقيم (x=0.0,0.1,0.3,0.5,0.7) عند درجة حرارة (700 ºC) ودرجة حموضة = 11 باستخدام الطريقة الحرارية الكيميائية للترسيب المشترك. تؤكد بيانات حيود الاشعة السينية التركيب المكعب أحادي الطور ومنها تم حساب متوسط حجوم الجسيمات بواسطة معادلة شيرر ووجد ان قيمها كانت ضمن المدى (16-29 nm). أظهرت نتائج دراسة الخواص المغناطيسية للمركب المحضر أن قيم النسبة بين Mr / Ms أقل من 0.5، وأظهرت بعض النسب ان حلقة الهسترة لها على شكل خط وهنا دلالة على تحول المادة إلى حالة البارا مغناطيسية الفائقة.

الكلمات المفتاحية: التشويب، طريقة الترسيب المشترك، مقياس حيود الاشعة السينية، مقياس الخواص المغناطيسية.

Introduction

Newly, the magnetic materials can be used in many products such as electronic apparatuses, data processing apparatuses, and communication instruments. According to the work of George J. Orenchak, soft ferrite is a magnetic material used primarily as the core of high-frequency inductors and transformers. The first name for magnetite ferrite comes from this region. Magnetic materials lead us to better results for obtaining high-frequency materials called Ferrites [1]. Therefore, ferrite has been used in various electronic applications, energy applications, and magnetic interference. So far, ferrite materials have been synthesized by various techniques, standards, and conditions, in the forms of nano-crystals and thin films and in the study of structural, magnetic, ferrite has a high magnetic permeability that enables it to store a magnetic field stronger than iron. Ferrite magnets have good anti-corrosion performance so there is no need for surface treatment. [2]. The magnetic properties of ferrite materials allow them to be used in many applications, such as micro-wave components, high-frequency devices, and magnetic memory storage. Ferrites are mostly ionic and have very stable crystal structures. Iron oxides of the type of spinel have the general formula AB_2O_4, where A is divalent transition metal cations such as (Co^{2+}). And B is Fe^{3+} having an ionic radius that approximately lies between 0.6 and 1 Å which belongs to Fd-3m space group and (O) indicates the oxygen ion site. The general chemical formula for spinel ferrite is $A^{+2}Fe^{+3}{}_2O_4$. There are two types of ferrites soft ferrite, and hard ferrite. Soft ferrite does not retain much magnetism while Hard ferrite is permanent [3-4]. In recent years, a number of chemical synthesis methods have been developed to prepare single-dispersion super magnetic nanoparticles depending on the size, composition, surface chemistry, and aggregation state. In particular, the practical synthesis methods were chemical co- precipitation thermal, ceramics, sol-gel, and hydrothermal synthesis ect [5]. In the present work, the chemical co-precipitation thermal method is chosen for the fact that it is a simple and cost-effective method. It gives nanoparticles of good homogeneity, fair particle size distribution, and high purity. Ferrite is an inexpensive material and its properties depend on the shape and size of nanoparticles, sintering temperature, method of preparation, and the type and quantity of ferrite-forming elements [6]. In 1909, Hilpert describes the chemical composition and magnetic properties of different ferrites [7]. Spinal ferrites are prepared such as Ni, Mg, and Co. After almost 20 years, Hilpert, and Forestier prepared many ferrites and magnetization [8].The present work is concerned with the synthesis of cobalt substituted nickel ferrite nanoparticles with the chemical formula $Ni_{1-x}Co_xFe_2O_4$ via the chemical co-precipitation thermal method .The use of this method can produce a single-phase structure of ferrite nanoparticles. The structural and magnetic properties of the ferrite nanoparticles can studied by using XRD and VSM analyses.

Materials and methods

Synthesis of cobalt doped nickel ferrites

Ferrite nanoparticles of $Ni_{1-x}Co_xFe_2O_4$ with x ranging from (0.0, 0.1, 0.3, 0.5 and 0.7) were prepared by chemical co-precipitating thermal method. aqueous solutions of [$NiCl_2$.6 (H_2O)], [$CoCl_2$.6 (H_2O)], and iron chloride [$FeCl_3$]. The molarity of the co-precipitation agent (NaOH) used was 3 M L^{-1}. According to the stoichiometric percentage, two moles of iron chloride, and one mole of chlorides (Cobalt, nickel). In their stoichiometry (25 ml of 0.9M $NiCl_2$.6(H_2O), (25 ml of 0.1M $CoCl_2$.6(H_2O) and 50 ml of 2M $FeCl_3$ in the case of ($Ni_{0.9}Co_{0.1}Fe_2O_4$). Likewise, they were dissolved in distilled water while being constantly stirred for the other values of x. Analytical grade chemicals were used throughout. With distilled water, the precipitates were carefully washed until the wash was devoid of sodium and chloride ions. To remove the water content, the product was dried in an electric oven at 50 °C for the entire night. In an agate mortar and pestle, the dried powder was thoroughly blended for 20 minutes. After the stage of obtaining the powder, the process of calcination of the powder begins, which is a heat treatment of the material under normal atmospheric pressure. The heating system of the furnace is controlled by a controller, we put the powder (Ni-$CoFe_2O_4$) at a temperature of (700 °C) for an three hour, and the temperature is set according to the point of the melting of the material and leaving the powder inside the oven until the next day to cool down that the purpose of the calcination process is to obtain the stage of ferrite growth as well as to get rid of some oxides. After the heat treatment stage, the samples are prepared, the shape of the sample depends on the type of examination required.

Results and Discussion

XRD measurement

The basis of the work of the XRD technique is to consider the surfaces of materials as mirrors, so that the laws of reflection of radiation can be applied, $\theta_{incidence} = \theta_{reflection}$, therefore the angle of incidence is equal to the angle of reflection. The concept of constructive and destructive interference also applied to understand the intensity of absorption, that is, the interference criteria of Bragg's law are applied (radiations in the same phase swells, the radiations in the opposite phase subsides). The X-Ray Diffraction (XRD) analysis of prepared compounds exhibits high intensities peaks as shown in Figures 1 to 5, the high-intensity peaks due to the constructive interference achieve Bragg's law. The miler indexes of nano-crystals were calculated according to Bragg`s law, also the nano-particles sizes were calculated by Scherrer equations as shown in Table 1. All samples showed the main peaks of the prepared ferrites with high crystallinity but there are some slight shifts and widening in the peaks [9-16]. The ferrites $NiFe_2O_4$ and $Ni_{(1-x)}Co_{(X)}Fe_2O_4$ are identical to JCPDS cards NO-54-0964 and JCPDS cards 44–1485 or 22–1086 attributable to single-phase cubic structure [9-18].

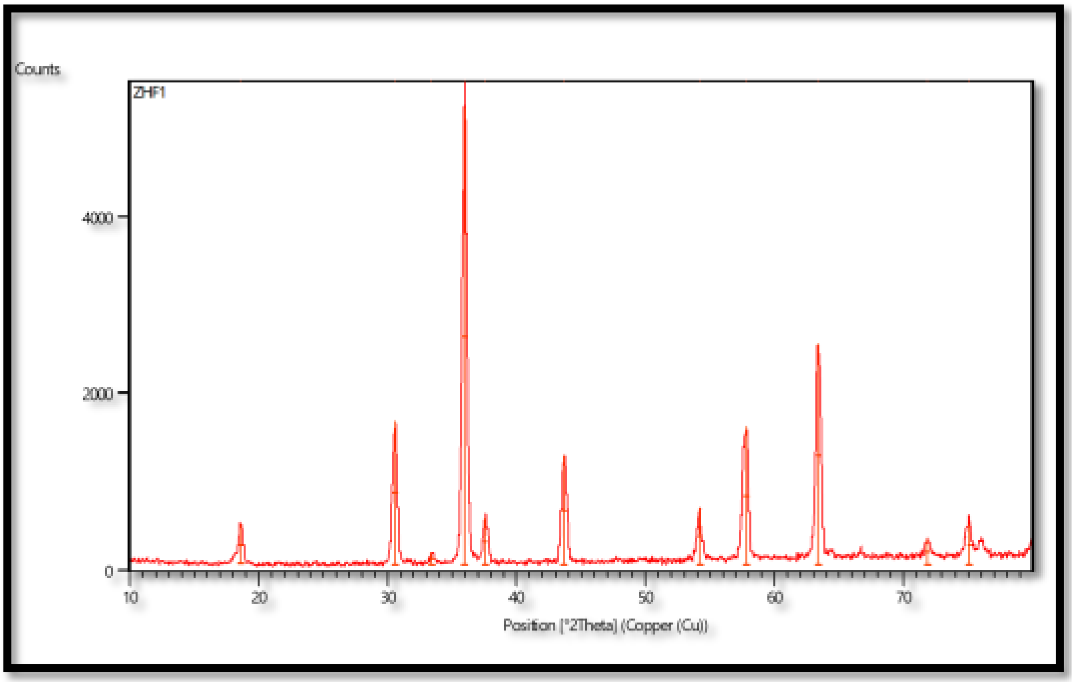

Figure 1: XRD of $NiFe_2O_4$

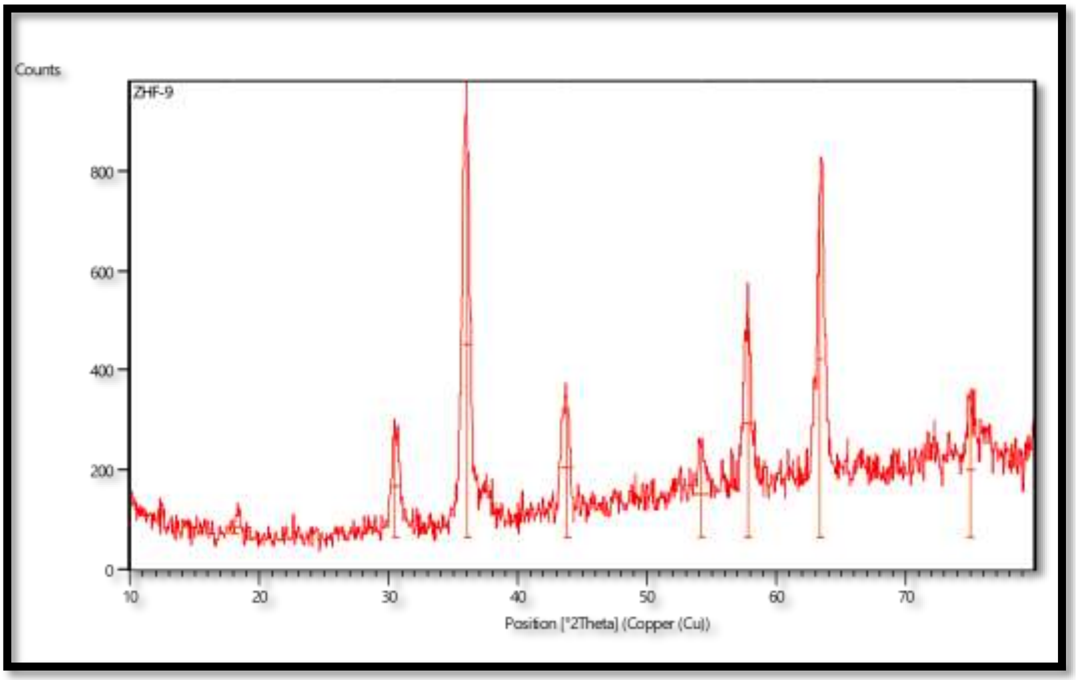

Figure 2: XRD of $Ni_{0.9}Co_{0.1}Fe_2O_4$

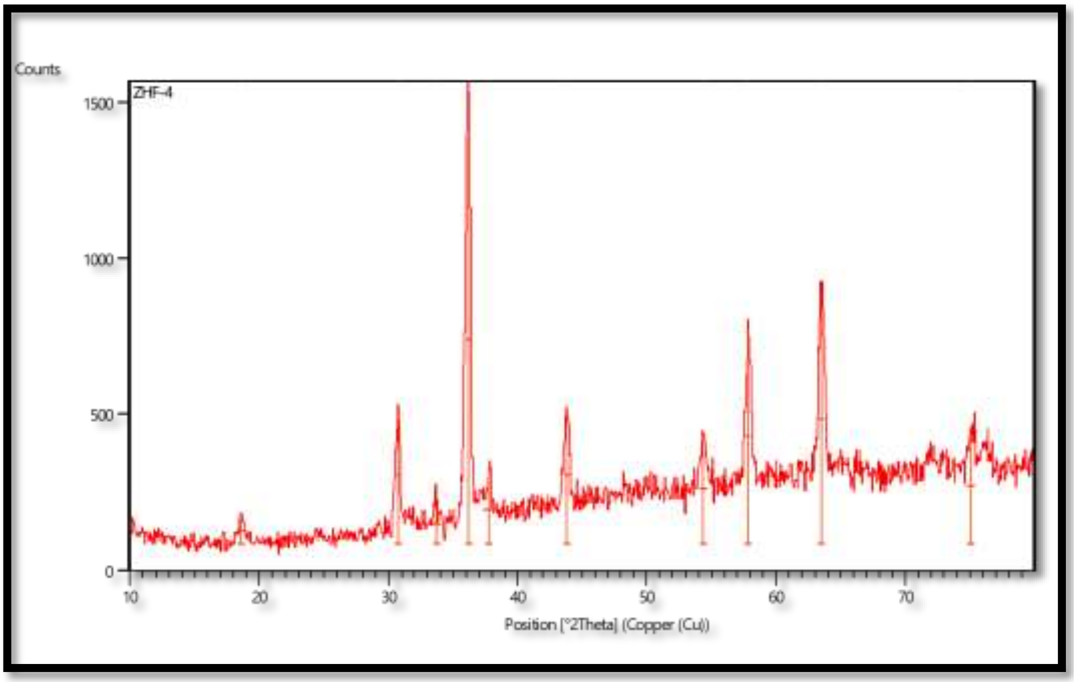

Figure 3: XRD of $Ni_{0.7}Co_{0.3}Fe_2O_4$

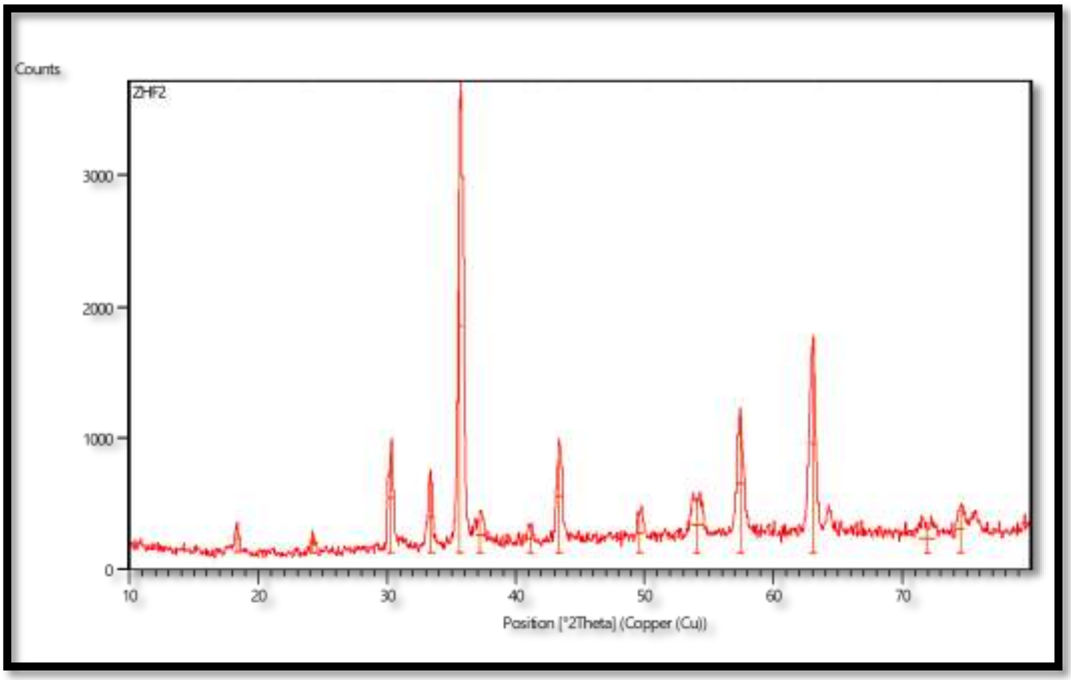

Figure 4: XRD of $Ni_{0.5}Co_{0.5}Fe_2O_4$

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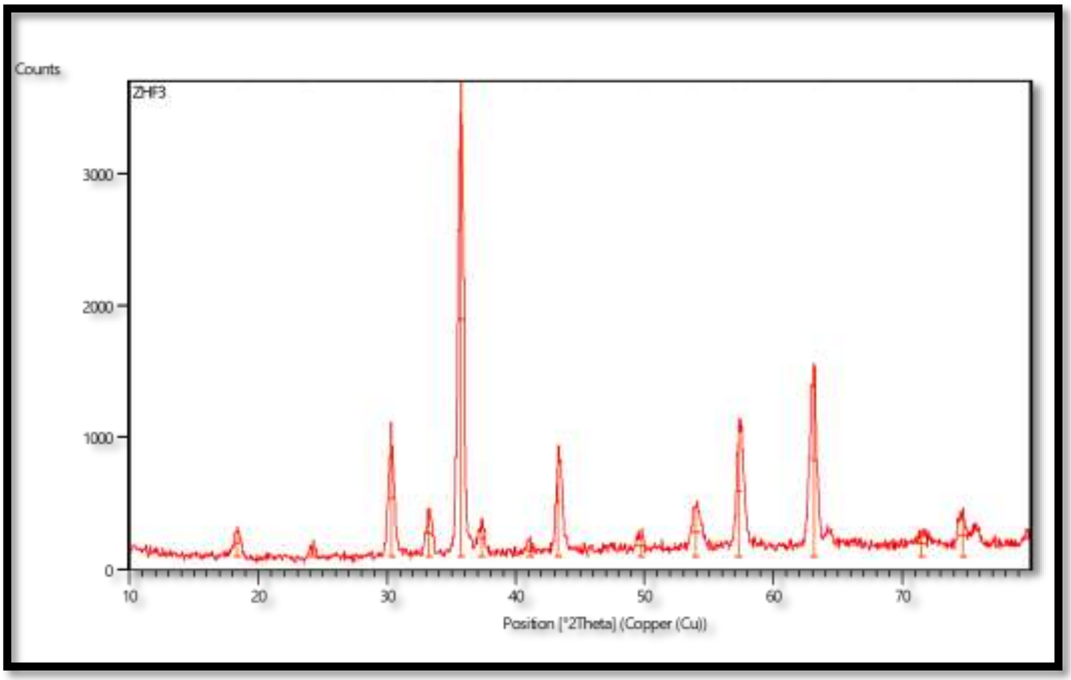

Figure 5: XRD of $Ni_{0.3}Co_{0.7}Fe_2O_4$

Table 1: XRD information with Miller indices and average particle size of prepared compounds

material	2θ	Intensity	FWHM	d spacing	h,k,l	D(nm)	Avg. D(nm)
$NiFe_2O_4$	18.5927	434.48	0.2460	4.77240	111	34.18691	29.53936
	30.5426	1612.94	0.3444	2.92698	220	24.98058	
	33.3755	119.88	0.3936	2.68473	221	22.0133	
	35.9191	5141.32	0.3444	2.50024	311	25.33286	
	37.5427	513.00	0.2460	2.39576	222	35.63322	
	43.6396	1223.55	0.3936	2.07415	400	22.71343	
	54.1831	627.10	0.1968	1.69283	422	47.36979	
	57.8152	1549.53	0.3936	1.59483	511	24.08748	
	63.3627	2474.85	0.2952	1.46791	440	33.0382	
$Ni_{0.9}Co_{0.1}Fe_2O_4$	18.0957	24.47	1.1808	4.90234	111	7.117287	16.31286
	30.5184	206.66	0.5904	2.92925	220	14.57116	
	36.0869	775.52	0.5412	2.48900	222	16.12858	
	43.8109	279.93	0.7872	2.06644	410	11.36353	
	54.1715	173.38	1.1808	1.69316	500	7.894556	
	63.4011	712.55	0.2460	1.46711	661	39.65404	
$Ni_{0.7}Co_{0.3}Fe_2O_4$	18.5732	79.76	0.5904	4.77735	111	14.24415	22.62181
	30.7351	439.3	0.1968	2.90909	220	43.73613	
	33.6793	126.14	0.5904	2.66121	310	14.68726	
	36.2043	1305.69	0.3936	2.48119	311	22.18421	
	37.7341	214.54	0.7872	2.38404	222	11.14172	
	43.8233	439.28	0.492	2.06588	400	18.18244	

	54.3837	351.42	0.492	1.68706	422	18.96493	
	57.8095	685.11	0.2952	1.59497	511	32.11575	
	63.5019	797.11	0.3444	1.46502	440	28.33972	
$Ni_{0.5}Co_{0.5}Fe_2O_4$	18.336	211.2	0.2952	4.83863	111	28.47872	20.70982
	30.2787	847.56	0.4428	2.95189	220	19.41718	
	33.3778	540.29	0.3936	2.68455	310	22.01343	
	35.6035	3463.76	0.3936	2.52167	311	22.14656	
	43.3566	867.67	0.4428	2.08703	400	20.16984	
	49.6463	306.25	0.492	1.83636	421	18.58616	
	54.045	417.72	0.984	1.69683	422	9.468127	
	57.425	1054.72	0.4428	1.60473	511	21.37103	
	63.0516	1661.46	0.3936	1.4744	440	24.73729	
$Ni_{0.3}Co_{0.7}Fe_2O_4$	18.3607	201.42	0.492	4.83216	111	17.08783	23.73566
	30.3103	889.45	0.246	2.94888	220	34.95353	
	33.2105	353.75	0.492	2.6977	310	17.60306	
	35.7009	3644.31	0.4428	2.51502	311	19.69121	
	37.3314	287.6	0.3936	2.40883	222	22.25685	
	43.2825	844.05	0.246	2.09043	400	36.29639	
	53.9272	376.98	0.6888	1.70026	422	13.51882	
	57.2992	988.61	0.3444	1.60796	511	27.46054	
	63.1676	1462.63	0.3936	1.47197	440	24.75267	

Finally, the particle size values computed via the Scherrer equation based on X-ray diffraction data.

Magnetic properties

An apparatus is known as a Vibrating-Sample Magnetometer (VSM), also known as a Foner magnetometer, which measures magnetic properties in accordance with Faraday's Law of Induction. If the sample is magnetic, it will align its magnetization with the external field after being first placed in a steady magnetic field. The sample's magnetic dipole moment generates a magnetic field that varies over time as the sample is raised and lowered. Typically, a piezoelectric substance is used to do this. In the pickup coils of the VSM, the alternating magnetic field produces an electric field. The samples magnetization and current are proportional; the bigger the generated current, the stronger the magnetization. The resulting hysteresis curve is often recorded, and from there we can infer the samples magnetic characteristics. The results of studying magnetic properties for the prepared compounds showed, that the values of the ratio between Mr/Ms are less than 0.5, which indicates that the magnetic moments that include two directions have been organized in their direction, meaning that the non-directing moments have been also organized. With the prevailing trends as the values reach their peak at the ratio of 0.3 and the ratio of 0.5 and then decreases, as shown in Table 2 and Figures 6 -10. However, these values are in agreement with the values obtained in previous studies [19-22].

Table 2: It shows the values of saturation magnetization (Ms) and remanent magnetization (Mr) of prepared compounds

Material	Molur ratio	Ms (emu/g)	Mr (emu/g)	S=Mr/Ms
$NiFe_2O_4$	0.0	8.169	3.523	0.43
$Ni_{0.9}Co_{0.1}Fe_2O_4$	0.1	36.066	18.012	0.49
$Ni_{0.7}Co_{0.3}Fe_2O_4$	0.3	0.362	0.143	0.39
$Ni_{0.5}Co_{0.5}Fe_2O_4$	0.5	33.748	16.120	0.47
$Ni_{0.3}Co_{0.7}Fe_2O_4$	0.7	4.485	1.951	0.43

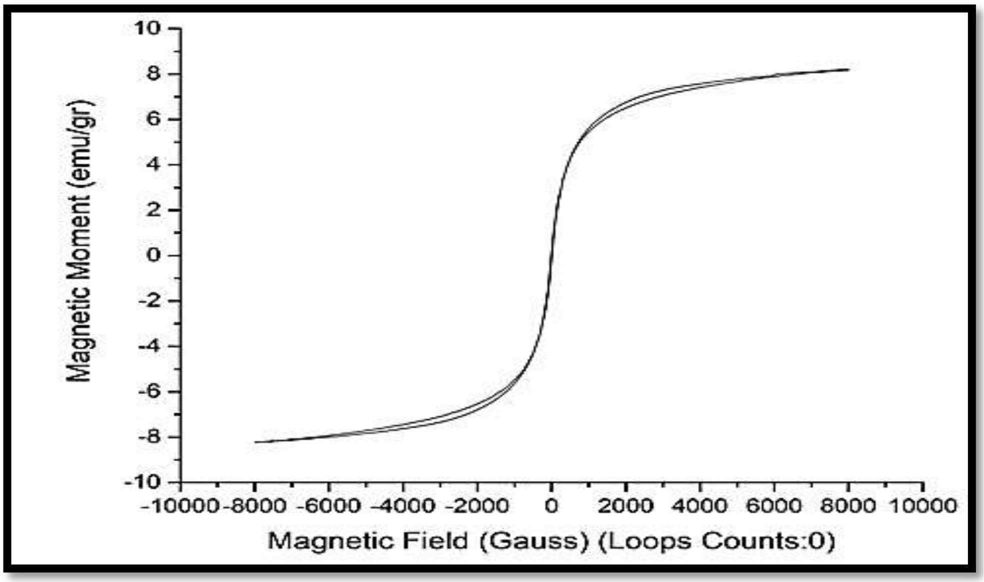

Figure 6: VSM diagram of $NiFe_2O_4$

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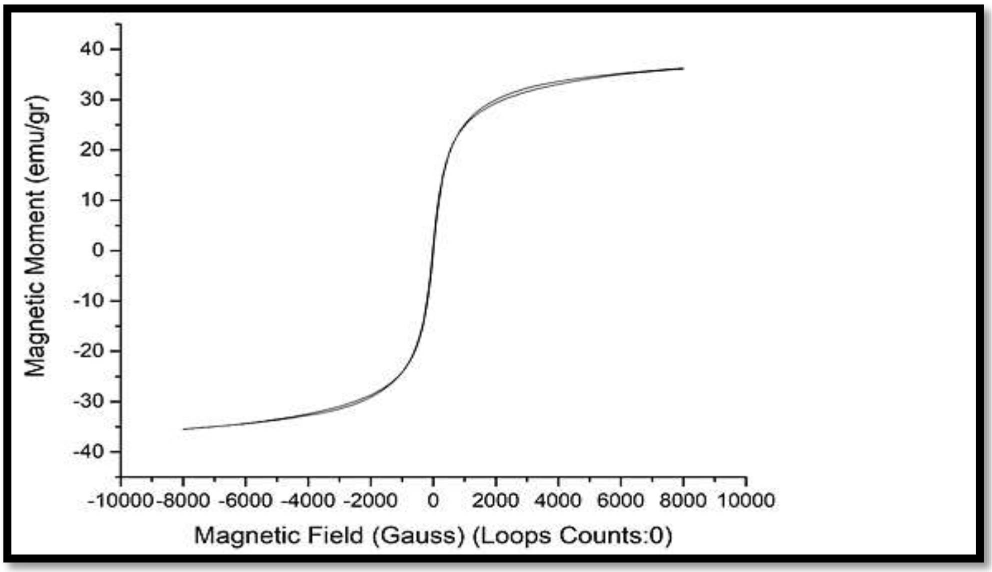

Figure 7: VSM diagram of $Ni_{0.9}Co_{0.1}Fe_2O_4$

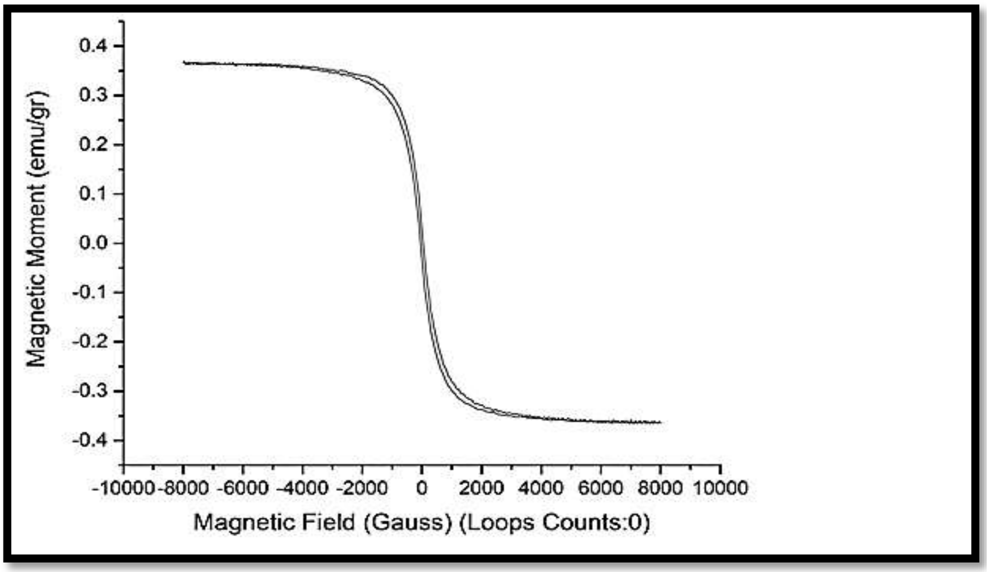

Figure 8: VSM diagram of $Ni_{0.7}Co_{0.3}Fe_2O_4$

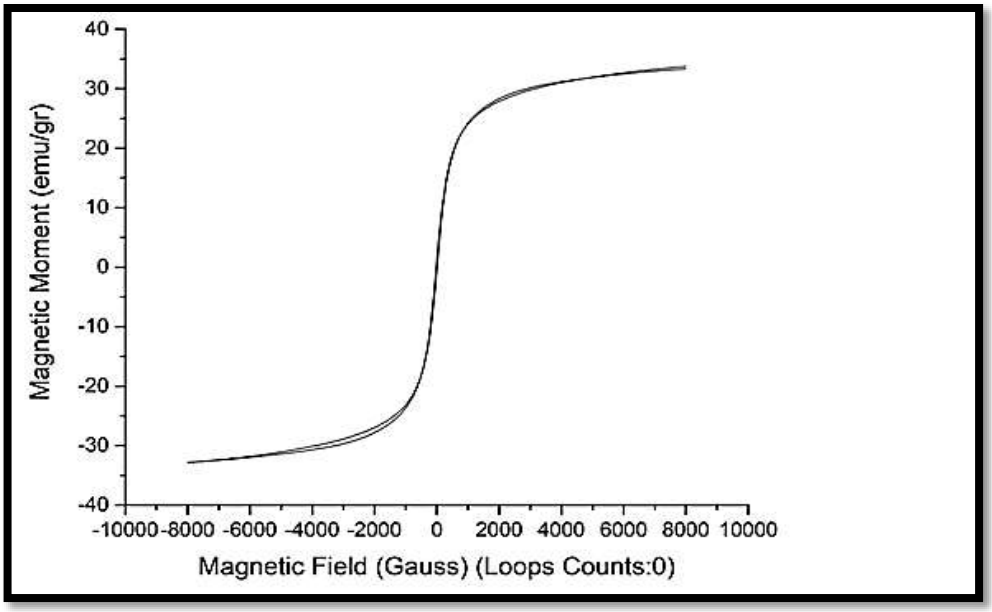

Figure 9: VSM diagram of $Ni_{0.5}Co_{0.5}Fe_2O_4$

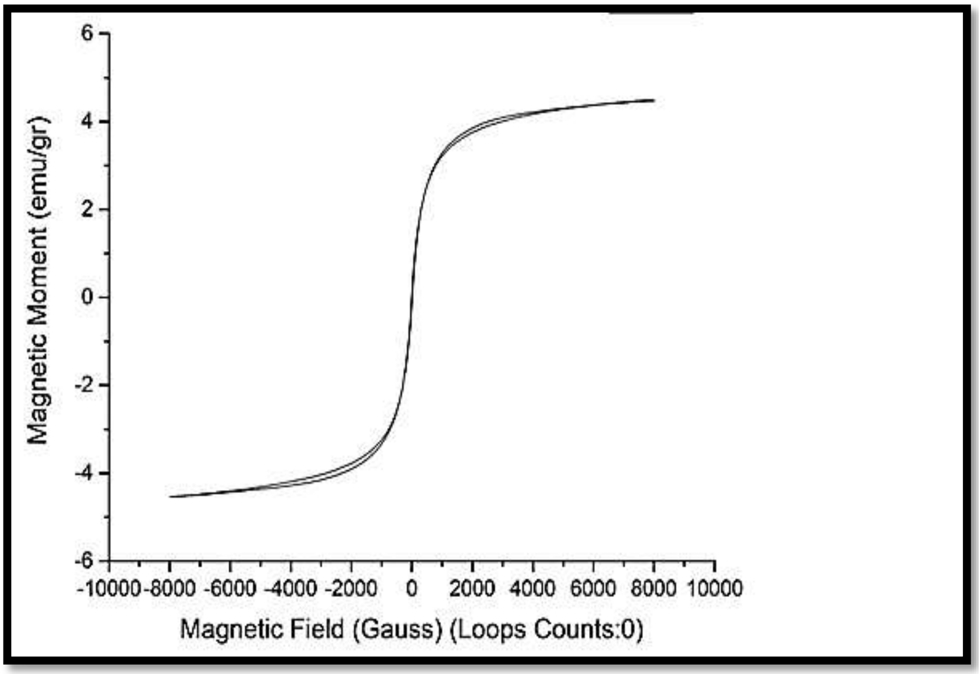

Figure 10: VSM diagram of $Ni_{0.3}Co_{0.7}Fe_2O_4$

We note that the addition of cobalt to the $NiFe_2O_4$ with aforementioned optimum ratios improved the magnetic properties of the main ferrite with a good to high ratio from through the narrowness of the hysteria loop gives the characteristics of soft ferrite, and some ratios showed the hysteresis loop in the form of a line indicating the transformation of the material to a state of super paramagnetic, and this confirms the lack of high energy consumption. Finally, we conclude from the above, there was a noticeable impact of chemical structure on magnetic behavior on Magnetization-Magnetic Field curves as well as its derivative curves. It is noted from Table 2 that the values of saturated magnetization vary with the addition of cobalt. The magnetic moment of the A-site sublattice (M_A) decreases or increases while that of the B-site sublattice (M_B) increases or decreases. As a result, the value of M, which equals M_B-M_A, the net magnetic moment, will alter [23, 24].

Conclusions

1. In the present study, the mixed ferrites $Ni_{1-x}Co_xFe_2O_4$ have been successfully synthesized by chemical co-precipitation thermal method.

2. The powder XRD pattern confirms single-phase cubic structure and the average particle size calculated via Scherer equation ranged between (16-29 nm) based on X-ray diffraction.

3. The results of studying magnetic properties for the prepared compound showed, the hysteresis loop in the form of a line indicating the transformation of the material to a state of super paramagnetic and this confirms the lack of high energy consumption.

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