Some of Physical Properties of Nanostructured ($Mg_{1-x}Co_xFe_2O_4$) Ferrites Prepared by Sol-Gel Method

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Abstract:

Sol-gel auto combustion technique was used to prepare nanoparticles of magnesium-cobalt ferrites with the chemical formula $Mg_{1-x}Co_xFe_2O_4$ for (x=0, 0.2, 0.4, 0.6, 0.8, 1), where x added as weight percentages, and sintering at temperature (1100 ^oC). The X-ray patterns of prepared powder has confirmed the structure of cubic spinel structure (fcc). The prepared samples were composed of nearly spherical nano particles .An average particle size of magnesium-cobalt ferrite were calculated using Debye Scherer's relation is equal 53.12 nm. The surface structure of the samples was investigated by Scanning Electron Microscope(SEM). The electromagnetic properties for prepared samples were investigated using Vector Network Analyzer (VNA) in X-band microwave region.
Keywords: Sol-gel auto combustion, magnesium -Cobalt Ferrites, Spinel Ferrite.

الخلاصة :

استخدمت تقنية سول– جل ذات الاحتراق الذاتي لتحضير جسيمات نانوية من فرايت مغنيسيوم – كوبلت ذات الصيغة الكيميائية $Mg_{1-x}Co_xFe_2O_4$ حيث قيم (x=0, 0.2, 0.4, 0.6, 0.8, 1)حيث x المضافة نسب وزنية وتلبد عند درجة حرارة (1100 ^oC). انماط حيود الاشعة السينية للباودر المحضر اكدت ان تركيب الفرايت هو سبينيل مكعبي متمركز الأوجه . النماذج المحضرة تتألف من جسيمات نانوية كروية تقريبا . معدل حجم جسيمات لفرايت مغنيسيوم – كوبلت تم حسابه باستخدام علاقة ديباي – شيرر هو٥٣,١٢ نانو متر. التركيب سطح للنماذج درست بواسطة الماسح الالكتروني . الخواص الكهرومغناطيسية للنماذج المحضرة درست باستخدام محلل الشبكي الاتجاهي او الناقل.
الكلمات المفتاحية : سول – جل ذات الاحتراق الذاتي، مغنيسيوم – كوبلت فرايت، سبينيل فرايت .

Introduction:

Ferrites have a chemical formula of AFe_2O_4 where A refers to any of various metal cations. They are classified as ferrimagnetic materials so that they are electrically nonconductive material. [Carter, & Norton, 2013].They are two types of ferrites classified according to their magnetic coercivity and demagnetized resistance. The first has high coercivity and it is called hard ferrite, it is difficult to demagnetize, and it is used to make magnets. While the second type is soft ferrites, it has low coercivity, and it is used to make ferrite cores for inductors and transformers, and in microwave components.[Okamoto, 2009]. Spinel ferrites have a closed packed cubic structure[Ozgüri *et al*., 2009], they have been widely studied by the researchers to investigate their structural, electrical and magnetic properties [Partha *et al*., 2013]. These ferrites are appropriate for magnetic sensors, microwave applications, and catalytic materials due to their dielectric constant, magnetic permeability, high Curie temperature and low tangent loss, also to chemical stability at low frequencies and mechanical strength.[Ahmed *et al*., 2003; Binu *et al*., 2011]. Nickel ferrite is a soft magnetic material [Maaz *et al*., 2009], which has several applications in electronic devices, such as inductors and transformator cores [Van Uitert, 1956]. While Cobalt ferrite is recognized as hard ferrite compound with a temperate magnetization and a high coercivity. These features along with its large physical and chemical stabilities

make Cobalt ferrite attractive for many practical applications such as digital recording disks, audio and video tapes, etc.[Pallai & Shah, 1996 ;Katalin *et al*., 2012].

Experimental Method and Materials

To prepare a one mole of $Mg_{1-x}Co_xF\square_2O_4$, for (x=0, 0.2, 0.4, 0.6, 0.8, 1), they have been taken the calculated weights of the metal nitrates and mixed them with ferric nitrate, then dissolved in (100 ml) of distilled water in a glass beaker. The stirring process was carried out for the solution using magnetic hot plat-stirrers model (LMS-1003) to obtain a homogenized solution with complete dissolution for the raw materials. After that, ammonia solution was added to the homogenized solution to raise the pH of the solution to be (~7) .

The temperature of hot plat- stirrer had been increased gradually to reach (50 ^oC), then it had been kept at this temperature for (15 min). The temperature had been increased to (60 ºC) for (2 hr), then to (70 ºC) for (10 min), then to (80 ºC) for (3 hr), the sol was initially transformed into gel. The temperature had been increased gradually to (90 ºC) for (15 min), then to (100 ºC), the gel had been dried at this temperature. The temperature had been increased gradually to (110 ºC) for (10 min), then it had been increased gradually to (120 ºC) and up to, then the dried gel was burnt in a self-propagating combustion manner until all gels were completely burnt out to form a fluffy loose structure.

The fluffy material was ground to get ferrite powder using the electric grinder for 10 minutes. The as-burnt ash was calcined at (600 °C) for rate 5 ºC per min, then trying to fix the temperature at (600 °C) for one hour, after that the oven had been leaved to cool gradually, to get better crystallization and homogeneous of the spinel crystallite. Powder had been mixed with glycerin material 6 wt% with purity of 88% as a binder. The powder was pressed at (40 kN) by the electrical piston to obtain samples as parallelogram of (2.4×1.2×1.2) cm in dimensions. Attended six samples for each value of x. The samples were sintered for 6 hr at (1100 ºC) sintering temperature with the rate of heating (3 ºC per min), with staying at this temperature for (3 hr), then the temperature decreased gradually, it were left to be spontaneously cooling inside the furnace. Refine the samples to make its dimensions (7.5×21.5×9.5) mm.

Theoretical Background:

I. Structural properties:

The structural properties that include the interplane distance (d) and lattice constant (a) which can be calculated using Bragg's law equation (1) and equation (2) which is standard relation for the cubic system [Kittle, 2005]

$$n\lambda = 2d \sin\theta \quad \text{..... (1)}$$

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

where (hkl) is the miller indices, λ is the wavelength of X-ray radiation and θ is the Bragg angle.

The crystallite size (C.S) is calculated using Scherrer's formula equation (3) : [Arabi and Ganjali, 2013].

$$C.S = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad (3)$$

where β is the FWHM (full width at the half maxima) of the peak at angle θ (deg).

The percentage porosity (p) is calculated depending on values of X-ray density (ρ_{x-ray}) and bulk density (ρ_{bulk}) using the following equation[Cullity,1956]:

$$p = \left(1 - \frac{\rho_{bulk}}{\rho_{x-ray}}\right)\% \qquad (4)$$

II. Electromagnetic properties:

According to Nicolson-Ross-Weir method for a sample with a thickness d with scattering parameters S_{11} and S_{21} varied with current frequency (ω). The relation that govern the reflection coefficient (Γ) and transmission coefficient (T) are begin with the functions V_1 and V_2, and these are:

$$V_1 = S_{21} + S_{11} \qquad (5)$$

$$V_2 = S_{21} - S_{11} \qquad (6)$$

these functions submit a new function which is:[Mohamed *et al.*, 2013].

$$X = \frac{1 - V_1 V_2}{V_1 - V_2} \qquad (7)$$

then

$$\Gamma = X \pm \sqrt{X^2 - 1} \qquad (8)$$

$$T = \frac{V_1 - \Gamma}{1 - V_1 \Gamma} \qquad (9)$$

and the appropriate sign is chosen so that $|\Gamma| < 1$.

the relative permittivity(ϵ_r) and permeability(μ_r)are given by: [Nicolson & Ross, 1970]

$$\mu_r = \sqrt{c_1 c_2} \qquad (10)$$

$$\epsilon_r = \sqrt{\frac{c_2}{c_1}} \qquad (11)$$

where

$$c_1 = \frac{\mu_r}{\epsilon_r} = \left(\frac{1 + \Gamma}{1 - \Gamma}\right)^2 \qquad (12)$$

and

$$c_2 = \mu_r \epsilon_r = -\left[\frac{c}{\omega d} ln\left(\frac{1}{T}\right)\right]^2 \qquad (13)$$

where c is light speed, ω is the angular frequency,$c_1$and c_2 are parameters, and d is the sample thickness.

Keep in mind that because the s-parameters are complex number then all other properties calculated from s- parameters are complex. Such as complex permeability and permittivity are thus obtained from measurement of the transmission and reflection scattering coefficients of a slab of the material. [Nicolson & Ross, 1970; Kooti and Afshari, 2012].

Results and Discusion:

I. Structural properties:

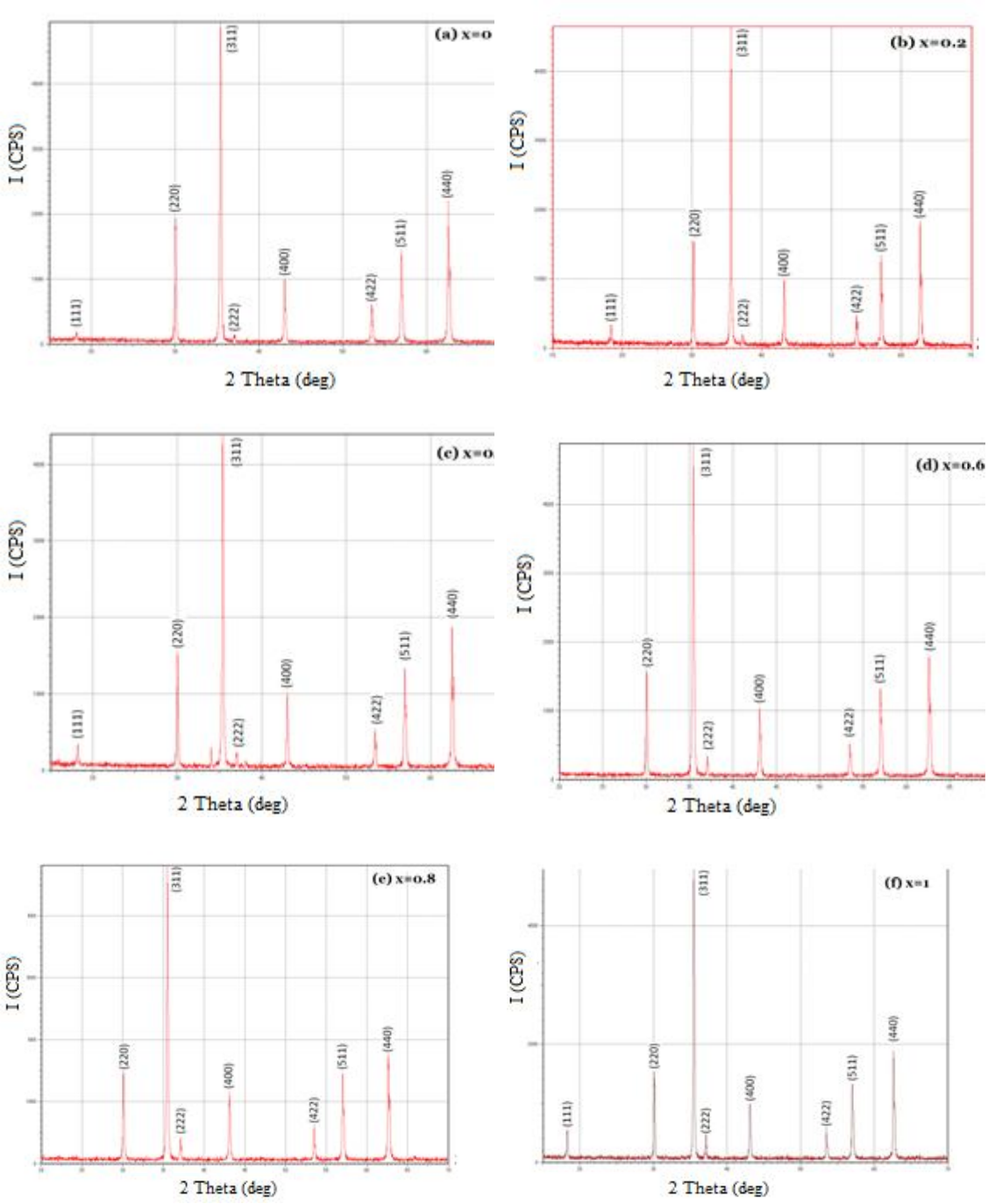
(a). XRD characterization:

Figure 1 shows the X-ray diffraction (XRD) patterns of the samples of $Mg_{1-x}Co_xFe_2O_4$ where (x=0, 0.2, 0.4, 0.6, 0.8, 1). The XRD patterns show well developed diffraction line assigned to pure cubic spinel phase. The measured XRD peaks match well with the standard patterns of inverse spinel ferrite. The crystallite size (C.S) for the prepared samples was found in the range of ($\sim 50 - \sim 55$) nm. The percentage porosity (p) was found in the range of ($\sim 48\% - \sim 55\%$).

Table (1) contain the values of structural parameters. The intensity, and width of the Bragg's peak conforming, ideal crystallinity, and nano particle size.

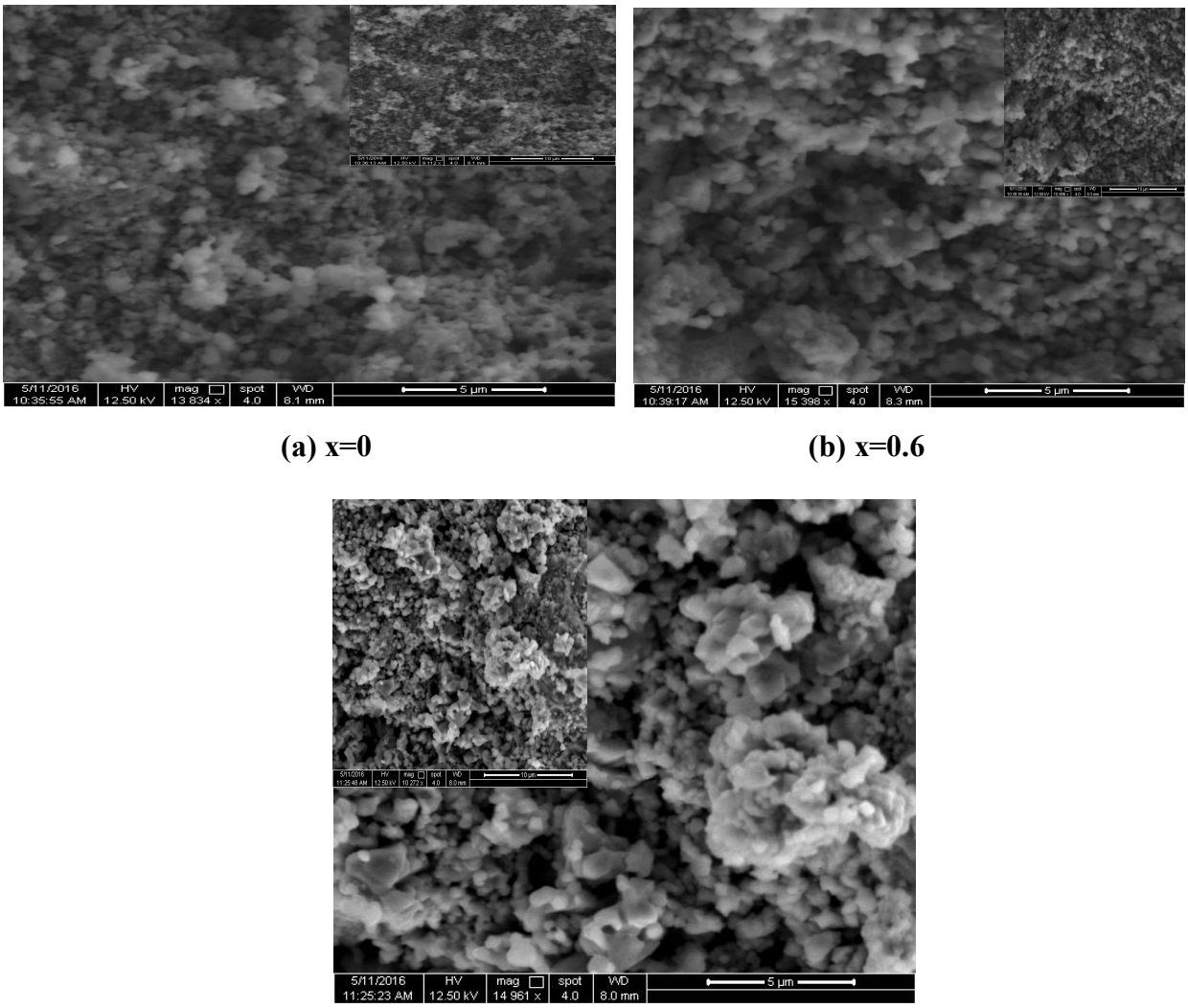
Table (1):Structural parameters of $Mg_{1-x}Co_xFe_2O_4$ Ferrite.

x	Lattice constant (a) nm	Crystal size (C.S) nm	Interplane Distance(d) nm	Porosity %
0	0.8382	52.42	0.2454	47.77
0.2	0.8369	54.56	0.2451	49.88
0.4	0.8394	53.41	0.2460	48.77
0.6	0.8377	54.87	0.2452	48.05
0.8	0.8372	49.91	0.2451	52.89
1	0.8374	53.53	0.2453	54.49



(b). Scanning Electron Microscope:

The morphological patterns of $Mg_{1-x}Co_xFe_2O_4$ samples are shown in figure (2) which taken by scanning electron microscope (SEM). SEM images confirmed the formation of Nano size crystallites. The average grain size was found to be in range of (400-600) nm using linear intercept method. Clearly, from the figure (2) the presence of clusters of particles due to the presence of cobalt cation and it depends on the radius of the cation added (Co^{+2}), and characteristics of(Mg ; Co) cations .



(a) x=0 **(b) x=0.6**

(c) x=1

Fig. (2): SEM images for $Mg_{1-x}Co_x Fe_2O_4$ ferrite at magnification (5µm).

II. Electromagnetic properties:

It was utilized, a sample of flat faces with 7.5 mm in thickness. The scattering parameters were measured by Anritsu vector network analyzer at X-band microwave region. The relative dielectric constant and relative permeability were taken as a function of cobalt content as shown in figures (3,4) respectively. It was shown the relative dielectric constant increase with cobalt content, in general. As well relative permeability increase with cobalt content. Because of the cation cobalt is ferromagnetic material .

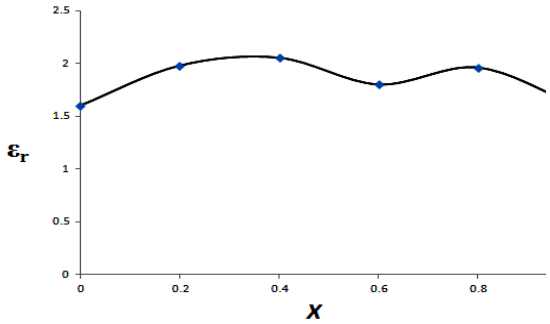


Figure (3): relative dielectric constant of $Mg_{1-x}Co_xFe_2O_4$ ferrite as a function of Co content

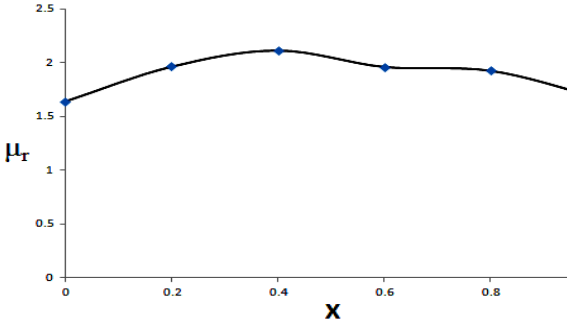


Figure (4): relative permeability of $Mg_{1-x}Co_xFe_2O_4$ ferrite as a function of Co content

The reflection(Γ) and transmission(T) coefficients for the ferrite samples were taken as a function of cobalt content as shown in figures (5) and (6) respectively, these behaviors of reflection coefficient and transmission coefficient with cobalt content due to the increasing in electron density with increasing of cobalt content.

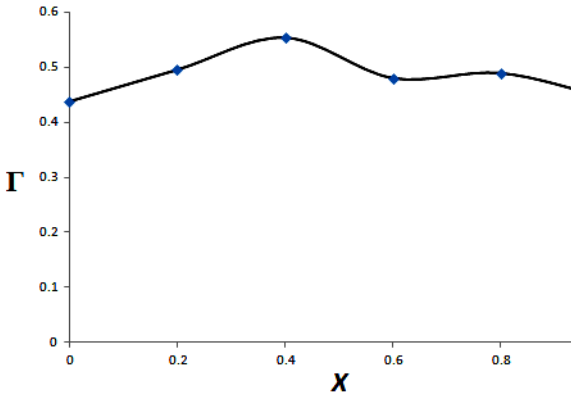


Figure (5): reflection coefficient of $Mg_{1-x}Co_xFe_2O_4$ ferrite as a function of Co content

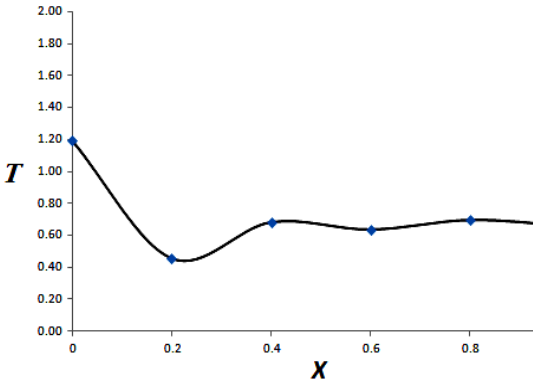


Figure (6): transmission coefficient of $Mg_{1-x}Co_xFe_2O_4$ ferrite as a function of Co content

The other quantities had been investigated are return loss, attenuation (insertion loos)and loss tangent which shown in figures (7, 8, 9), respectively each one of them is plotted as a function of cobalt content.

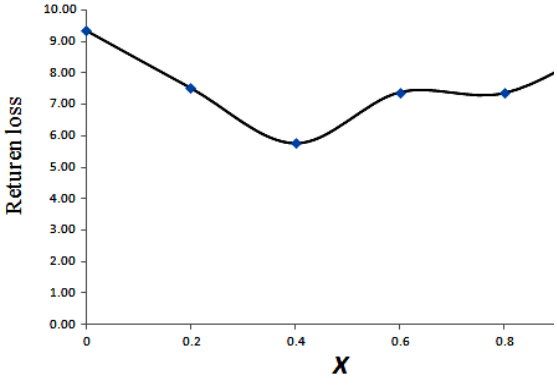


Figure (7): return loss of $Mg_{1-x}Co_xFe_2O_4$ ferrite as a function of Co content

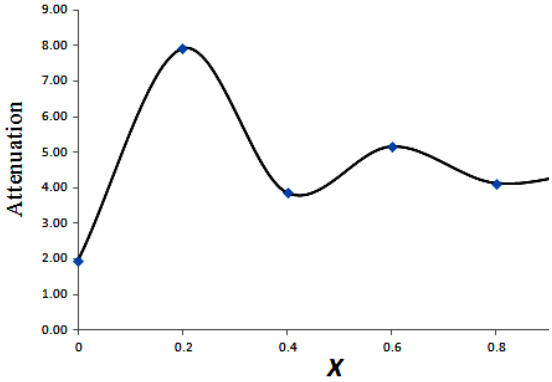


Figure (8): attenuation(insertion loos) of $Mg_{1-x}Co_xFe_2O_4$ ferrite as a function of Co content

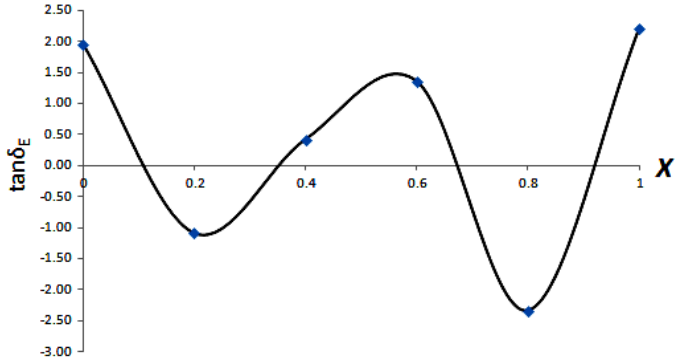


Figure (9): loss tangent of $Mg_{1-x}Co_xFe_2O_4$ as function of Co content

It was noticed return loos decrease with x, and less value when (x=0.4), while attention (insertion loos) increase with x, max value when (x=0.2). The range values of loss tangent of $Mg_{1-x}Co_xFe_2O_4$ ferrite as function of Co content and between positive values, and negative values because of the properties electric and magnetic for (Mg ;Co) cations .

Conclusions:

The $Mg_{1-x}Co_xFe_2O_4$ (where x=0, 0.2, 0.4, 0.6, 0.8, 1), nano size were prepared using sol-gel technique. The change in the Co^{2+} content gives the significant effects in electrical and magnetic properties of the material. The X-ray diffraction dates shown the crystallite size is obtained 50 to 55 nm, and X-ray diffraction results showed the presence of all characteristic reflections (111), (220), (311), (222), (400), (422), (511), (440) which confirmed the structure of cubic spinel ferrite. The lattice parameter increase with increasing Co^{2+} content .As well as porosity increase with increasing Co^{2+} content.

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