Effect of Zn Substitution on thestructural Properties of Cobalt Ferrite Nano Particles Prepared Via Sol-Gel Route

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Abstract

Zinc substituted cobalt ferrite nanoparticles ($Co_xZn_{1-x}Fe_2O_4$, with x = 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5) were prepared via sol-gel route and the effect of zinc concentration on Lattice constant and particle size and powder densitywere investigated. X-ray diffraction analysis confirms the formation of ferrites in nano phase. The Results showed that the particle size decreasing from (22) to (16) nm with increasing the concentration of zinc to the (x= 0.5). The lattice constant increased from (8.36682) to (8.40943)A^0 with increasing the concentration of zinc to (x = 0.5), while the theoretical powder density decreased from (5.3225) to (5.2237) g/cm^3 by increasing zinc ion concentration to value at (x=0.5).

Keywords: ferrite, nanoparticles, X-ray diffraction, Lattice constant.

تأثير تعويض الزنك على الخواص التركيبية لفرايت الكوبلت ذو الدقائق النانوية والمحضر بالطريقه (sol-gel).

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الخلاصة

تم في هذا البحث تحضير فيرايت الكوبالت المعوضة بايونات الزنك ذات السلسلة الفيراتية ($Co_{1-x}Zn_xFe_2O_4$, حيث تأخذ x قيم من الصفر الى 0.5) بالطريقة الكيميائية الحديثة(sol-gel auto combustion) المحضرة وأظهرت النتائج بأن حجم دقائق المسحوق يقل حجم من 22 الى 16 نانومتر مع زيادة تركيز ايونات الزنك . إن ثابت الشبيكة يزداد من 8.367 إلى 8.40943 انكستروم بزيادة تركيز ايونات الزنك إلى القيمة (x=0.5) .إما بالنسبة لكثافة المسحوق فإنها تقل من (5.3225) غم/سم^3 بزيادة تركيز ايونات الزنك وصولا إلى القيمة 5.2237غم/سم^3 عند (x= 0.5).

الكلمات المفتاحية: فيرايت - دقائق نانوية – حيود الأشعة السينية – ثابت الشبيكة

Introduction

Nanocrystalline ferrites are currently the subject of interest because of its wide application in industrial as well as research areas. They are attractive because of their importance in ferrofluids, magnetic drug delivery, hyperthermia for cancer treatment, etc.[1]. These materials are called ferrites which have general formula MFe_3O_4 where M is the divalent ion like Zn^{++}, Mn^{++}. This is the Ferrite ceramics and heterogeneous materials consist of oxides with of different iron oxide as the basic composed and the fall in this category of soft and hard Ferrite.

$CoFe_2O_4$ has inverse spinel structure with Co^{2+}ions in octahedral sites and Fe^{3+} ions equally distributed between tetrahedral and octahedral sites whereas $ZnFe_2O_4$ has a normal spinel structure with Zn^{2+}ions in tetrahedral and Fe^{3+} in octahedral sites [2]. Therefore, Zn-substitution in $CoFe_2O_4$ may have some distorted spinel structures depending upon the concentration of the precursor solutions.

The novel properties and the numerous applications of nanophase materials, especially ceramic powders, have encouraged many researchers to invent and explore the methods, both chemical and physical by which such materials can be prepared. Cobalt ferrite is synthesized by a variety methods including solid state reaction method, high energy ball milling [3], co-precipitation [4], sol-gel method [5], RF-sputtering and microemulsion method [6].

To study the crystalline structure of solids, X-ray diffraction is the most widely used and the least ambiguous method for the precise determination of the positions of atoms in all kinds of matter ranging from fluids and powders to perfect crystals. It is a non-destructive technique that provides detailed information about the materials. Through x-ray diffraction information is provided for characterization of crystalline materials represented crystal structure, phases, preferred crystal orientation and other structural parameters such as lattice parameters, crystallite size, crystallinity, strain and crystal defects.To find the crystal structure, we need to determine the lattice constant, Particle size and x-ray density.

Experimental

Materials and methods.

Ferrite powders were prepared by sol-gel auto combustion method. In this method; Cobaltnitrate, Iron nitrate, Zinc nitrate, Citric Acid and Ammonia solution were used as a starting raw materials.

Instruments used.

We have used in this work a set of devices for the purpose of testing physics that were conducted in this research and these devices are:

Mass Measurement Instrument.

We have been using the sensitive balance of a high degree of sensitivity of four decimal degrees. The type of device, DENVER Instrument, American origin.

Magnetic Stirrer.

Is a laboratory device that employs a rotating magnetic field to cause a stir bar immersed in a liquid to spin very quickl,for obtained homogenous mixer between atoms and liquid particles.

X-Ray Diffractometer (XRD).

The X-ray diffraction pattern were recorded using XRD-6000 with CuKα (λ=1.5406A°) that have an accelerating voltage of 220/50HZ which is produced by SHIMADZU company.

Preparation method.

After the weight of nitrates, appropriate amount of distilled water was added to them, according to the percentage standard stoichiometric weight: two moles of iron nitrate, one mole of nitrate (cobalt and zinc) and three moles of citric acid (the mole ratio of metal nitrates to citric acid is equal to one) to provide increased fuel to the mixture of ferrite series ($Co_{1-x}Zn_xFe_2O_4$), where x take the values (0.0 to 0.5).All these are collected in glass beaker to become a total solution and mixed well at room temperature by magnetic stirrer with high velocities and after a short period until solution becomes smooth and a slimy red-colored. Ammonia solution was slowly added in the form of drops into the mixed solution to control its pH until reach the value of (6.9 to 7) with continuous stirring.

It was subsequently raise the temperature of the solution to 60°C for a period of one hour and then increase the temperature to 80°C. After that the size of the solution in the beaker glass be less with high viscosity and after 30 minutes, the solution viscosity is very high, hence the beginning of gel formation on the surface ofthe solution.

After the completion of the solution turned to gel, the temperature drops to the room temperature and this gel becomes dry and dark brown. Then put it inside the oven at a temperature 120 ^{0}C for three hours to become dry gel. Then evaporation of some of the material at raise the temperature of the dried gel to 200 ^{0}C,After a short period we note a flame at the top of surface, so until the gel flammable in complete and becomes all the dried gel to a fine powder with a dark gray color, which marks the beginning of formation of high purity ferrite

Results and Discussion

The polycrystalline $Co_{1-x}Zn_xFe_2O_4$ ferrite have been investigated by x-ray diffraction technique are shown in Figure(1). All compositions of Co-Zn ferrites could be indexed in terms of a single phase cubic spinel structure. It can see from figures that all ferrite powders consisted of well crystalline phases. These figures also show that the x-ray spectrum showed all characteristic planes of Co-Zn spinel ferrites (220, 311, 222, 400, 422, and 511). The intensity of main diffraction peak of spinel ferrite at the (311) plane was considered as a measure of its degree of crystallinity. An increase of the concentration of zinc in the Co-Zn ferrite resulted in a measurable shift in 2θ towards the smaller angles as mechanical stress within the crystal as shown in Table (1). Also there exist residual thermal stress inside crystal due to the calcination process, thus it makes shift in 2θ towards the smaller angles.

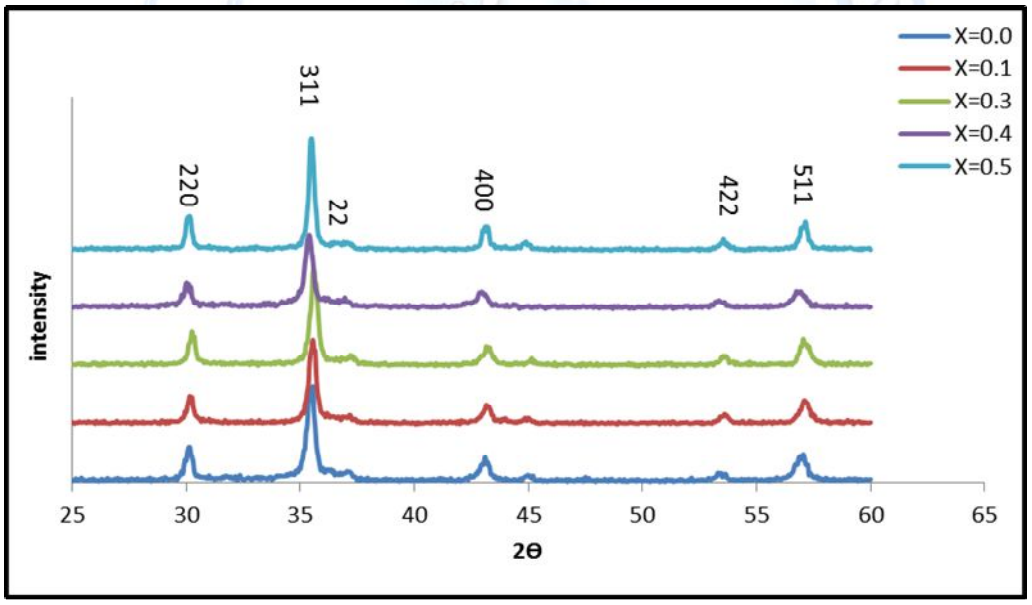

Fig. (1) XRD pattern of the x=0.0,0.1,0.3,0.4,0 And 0.5 at(200C^0 for ferrite powder).

Table (1) lattice constant, particle size, xrd density, cell volume

2θ	β	D nm	x	d	a A°	V $(a)^3$	d_x g/cm^3
35.5	0.38	21.8	0	2.52269	8.36682	585.707	5.32252
35.54	0.41	20.3	0.1	2.5266	8.37978	588.435	5.29785
35.61	0.46	18	0.3	2.5291	8.38808	590.183	5.28215
35.47	0.52	16	0.5	2.53554	8.40943	594.703	5.24201

Crystalline Size.

The Scherrer formula [7] relates the thickness of the crystallite to the widthof its diffraction peaks, and is widely used to determine particle size. The Scherrer formula is given by;

$D = k\lambda / \beta\cos\theta$ ..... (1)

where, D is the crystalline size, β is the broadening of diffraction line measured at half its max. intensity, k is the shape factor (k=0.9), λ is the wavelength of x–ray. The crystallite size of the ferrite powders was determined using the formula (1) and Table (1) show that the crystallite size decrease from 21.6 to 16 nm with increasing Zn^{+2} ion concentration as shown in figure (2). The decrease in the particle size with Zn ion content may be explained by the electronic configuration of Co^{+2} ($3d^7$), and its more tendency to interact with ligands and oxygen anions, as compared to Zn^{+2} ($3d^{10}$), which has a complete electronic configuration[8]. The lack of d-electrons is important because there are very little covalent interaction and tendency toward extension between Zn^{+2} and its ligand. Furthermore, it is reported by several researchers, that the smaller particle sizes of the ferrites doped with Zn ions are due to the lower bond energy of Zn^{+2}-O^{-2} (159 kJ/mol) as compared with that Co^{+2}–O^{-2}(384 kJ/mol).

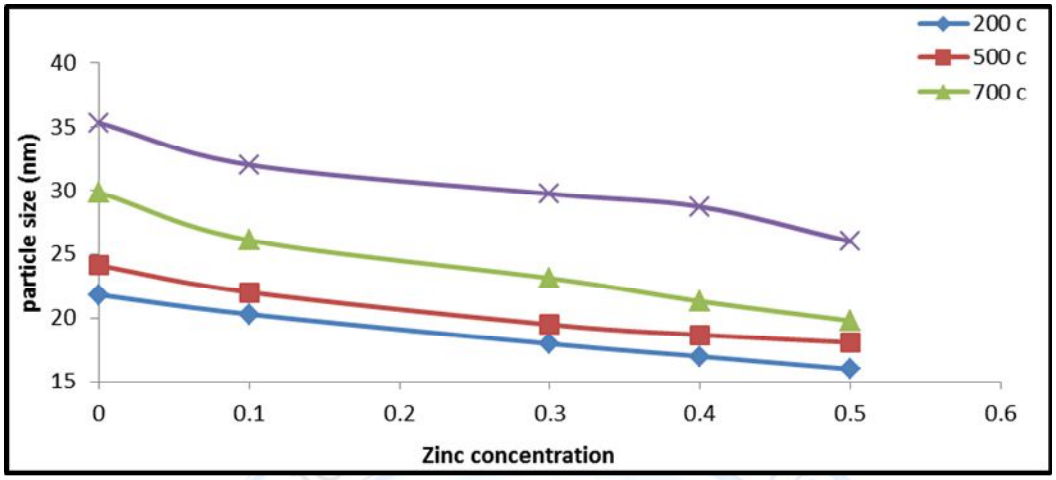

Fig (2) change in the particle size with the degree of zinc substitution in $Co_{1-x}Zn_xFe_2O_4$(X=0.0-0.5).

Lattice Constant

A parameter defining the unit cell of a crystal lattice is the length of one of the edges of the cell or an angle between edges. It is also known as lattice parameters or lattice constant. Lattice constant refers to the constant distance between the lattice points. It is calculated using of relate to the inter-planer spacing for the d_{hkl} planes in the cubic structure as:

$$a = \lambda (h^2 + k^2 + l^2)^{1/2} / 2\sin\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Bragg's condition demands that a proper combination of θ and λ is found for efficient reflection.

Lattice parameter of the ferrites was calculated using the equation (2), and table (1) show that the lattice parameter increase from 8.36682A° to 8.40943A°with Zn^{+2} ion increase. It is seen in Fig.(3) that the lattice parameter increase with Zn^{+2} ion concentration, the ionic radius of Zn^{+2} can be presented for this effect. Zinc ions have a strong tendency to be arranged at tetrahedral sites. The addition of Zn^{+2} ions into Co-ferrite structure causes migration Fe^{+3} ions from the A- site to the B- site. Zn^{+2} ions (0.82A˚) owns a larger cation, as compared to Fe^{+3}ions (0.64A˚) and Co^{+2} ions (0.78A˚), thus the lattice expands [9].

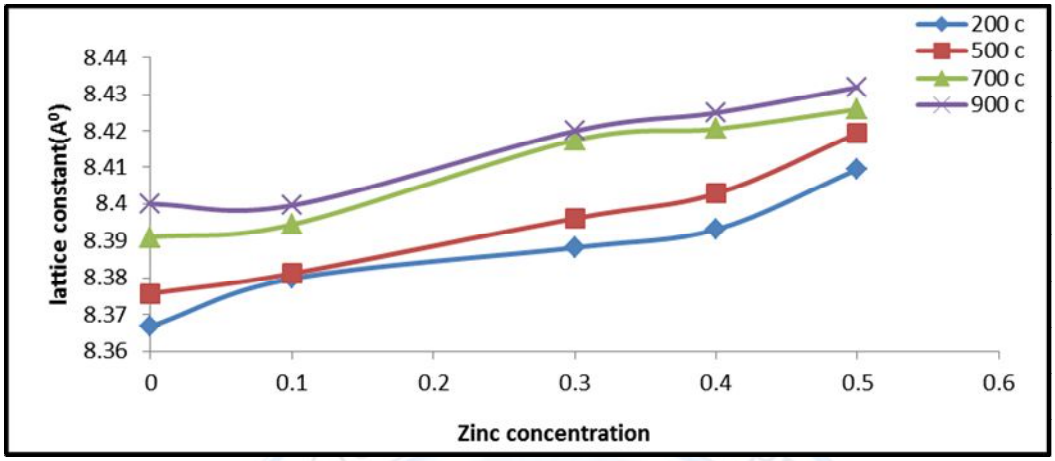

Fig.(3) change in the lattice constant with zinc substitution in Co-Zn ferrites.

X-ray density

The values of X-ray density (d_x) is calculated from the XRD data using the relation given by SmitandWijn[10];

$d_x = 8M / N_a a^3$ (g/cm^3) ……(3)

Where d_x is the x-rays density (g/cm^3) , Z is the number of molecules per formula unit ($Z = 8$ for spinel system), M is the molecular weight of the samples, N_a is the Avogadro's number, and "a" is the lattice constant.

The X-ray density (d_x) of the ferrite nanopowders was determined using the relation (3), is given in the table (1), which decreased its value from 5.422 to 5.179 g/cm^3 and their density depend upon the latticeconstant. Table (1) show that the lattice constant increase with increase in Zn ion concentration, so that the x-rays density decreased with the increase in Zn ion concentration and temperature as it shown in the figure(4)

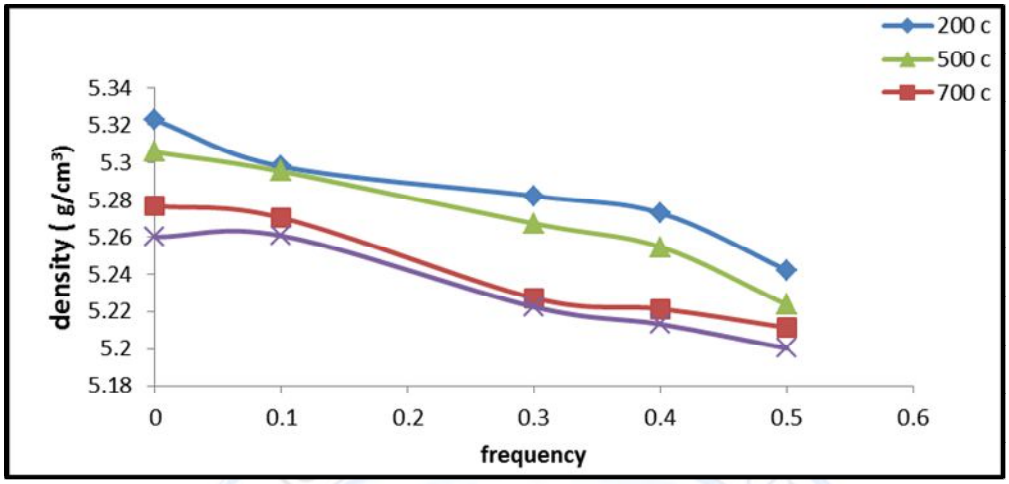

Fig.(4) change in x-ray density with the Zinc substitution in Co-Zn ferrites.

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