

Effect of Molar Ratio on Structural Properties of Nanostructure Li-Ni Ferrites Prepared by Hydrothermal Method

Sadeq H.Lafta¹, Emad K. Al-Shakarchi¹, Ali M. Musa², M.Farle³, R.Salikov³

¹Al-Nahrain University/ College of Science/ Physics Department/Baghdad, IRAQ
eks2000@hotmail.com

²Applied Science Department /University of Technology/ Baghdad, IRAQ

³AG Farle/Duisburg-Essen University/ Duisburg-Germany

Abstract: Li-Ni ferrites with chemical formula $Li_{0.5-0.5x}Ni_xFe_{2.5-0.5x}O_4$ at ($x=0, 0.1, 0.3, 0.5, 0.7, 0.9, 1$) were prepared by hydrothermal method starting from metal chlorides and sodium hydroxide as oxidant. The precipitated powder before hydrothermal stage has no response in the magnetization, whereas the product of the final powder had been magnetized. The hydrothermal treatment was done at (155°C) for (3 hr). There were many analysis such as XRD, FTIR, SEM, TEM were performed to get more details for the samples under study as a function of (x). It was found that the cubic spinel structure was obtained. Scherer method was the favor to concluded a maximum nanocrystalline size was at (0.5). Whereas the particle size distribution was recorded by SEM and TEM. It was clear that the particle size was extend to (140 nm) with maximum value around (30-50 nm). The results of XRD showed that the density of XRD-peaks was increased as a function of (x). The last one had the direct effect of partial increasing in the lattice constant with the remaining of spinel structure.

Keywords: Li-Ni ferrites, hydrothermal process, Spinel structure, FTIR spectroscopy, Scherer method .

1. INTRODUCTION

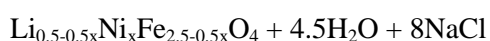
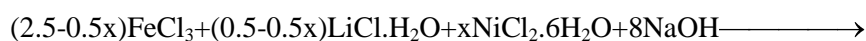
Usually spinel ferrites are important class of microwave materials because of their properties like high resistivity, very good dielectric and moderate loss behavior, and it had many technological applications over a wide range of frequencies [1, 2]. It was derived by Barriga et al. [3]. Li-ferrite and its derivative is one of a familiar ferrite used in a microwave application. There were many derivatives related to substitution of Li-ferrite by isovalent elements like Co, Zn, Cr, Mn, Ni,[4-8]. These are a promising materials for microwave applications because of their low cost, excellent temperature performance, and square of the hysteresis loops high Curie temperature, and excellent electromagnetic properties at high frequency [9,10].

Recently, the synthesis of spinel nanoparticle of ferrite powder has a great interest of the electrical and magnetic properties in a comparable with the bulk one. This reality should be enhancing their flexibility in different applications in the modern technology [8, 11]. The magnetic and dielectric properties of Li-Niferrite depend on several factors including the method of preparation, chemical composition and grain size [10]. Nanoferrites are usually prepared using various physical and chemical methods such as sol-gel precursor method [12], co-precipitation [10], traditional ceramic method [13], citrate precursor method [14], and microwave hydrothermal [11].

The aim of the present work is to investigate the effect of molar ratio on the preparation of Li-Ni ferrite as a nanopowder by hydrothermal process. The studying of physical properties for the samples produced is the main problem during the comparison with the samples prepared by other methods from the previous researches [9,13,14].

2. EXPERIMENTAL PARTS

The starting materials were $LiCl \cdot H_2O$, $NiCl_2 \cdot 6H_2O$, $FeCl_3$, $NaOH$ & Distilled deionized water due to the following chemical reaction for successful preparation at different molar ratios ($x=0, 0.1, 0.3, 0.5, 0.7, 0.9, 1$).



It is necessary to mention that NaOH quantity in above chemical equation are much less than added ones. The addition of LiCl.H₂O must be more than by 10% of the present weight in chemical equation, in order to compensate the decreasing in the weight of LiCl during the thermal reaction and the water adsorbing.

Each salts of certain amount according to stoichiometric chemical reaction were dissolved into (100ml) of distilled water. The solutions were mixed by magnetic stirrer during (5 min), producing a mixture. The solution of NaOH with (2.5M) was added as droplets until ph-value reach to 7. During that, the stirring was continued for (30 min.) in order to recognize dark brown suspension. The suspension was inserted into a homemade autoclave at (155 °C), as shown in Fig.1. It was heated by hotplate magnetic stirrer for (3 hr). The pressure was automatically controlled through temperature. Finally, the suspension was washed four times by distilled water by using centrifuge. The suspension rest was dried at (80°C) to obtain the ferrite powder which was grinded by mortar later. The block diagram of preparation method is shown in Fig.2, with the chemical amounts of starting materials as mentioned in Table 1.



Figure1. The homemade design of hydrothermal autoclave

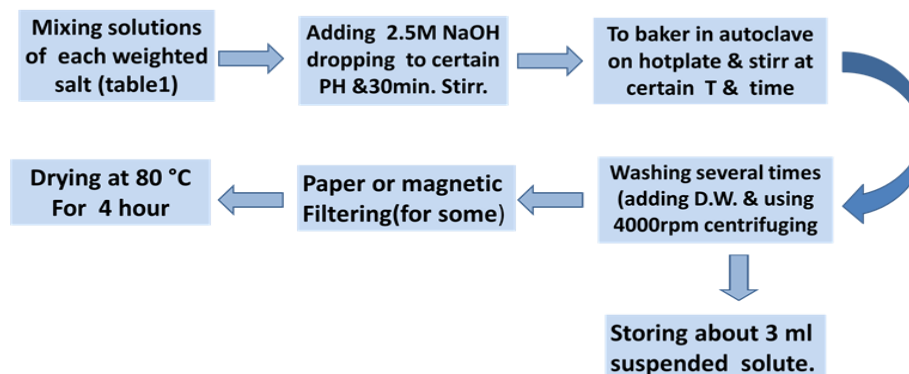


Figure2. The block diagram of the preparation process.

Table1. The molar ratio of Li-Ni ferrites with different x-value, MW: molecular weight in gm/mole, n: no. of moles.

Starting material	MW	x=0.0		x=0.1		x=0.3		x=0.5		x=0.7		x=0.9		x=1.0	
		n	W gm	n	W gm	n	W gm	n	W gm	n	W gm	n	W gm	N	W gm
FeCl ₃ In 100ml	162.21	2.5	4.06	2.45	3.974	2.35	3.812	2.25	3.65	2.15	3.488	2.05	3.325	2.0	3.244
LiCl.H ₂ O In 100ml	60.40	0.5	0.3	0.45	0.272	0.35	0.211	0.25	0.151	0.15	0.091	0.05	0.03	0	0
NiCl ₂ .6H ₂ O In 100ml	237.7	0	0	0.1	0.238	0.3	0.713	0.5	1.189	0.7	1.664	0.9	2.139	1	2.377

The analysis those were dependent represented by XRD, FTIR, SEM, and TEM. The investigation of crystalline phase has been done by using X-ray diffraction to find the crystalline phase for the samples under study. X-pert Panalytical instrument with Cu-K_α radiation at (λ=1.5418 Å) had been applied for this purpose. The analysis of their patterns was applied by using Match Impact software to find the probable crystalline phase. On the other hand, the crystalline size was determined by using Scherer formula assuming all particles have spherical shape during the following formula;

$$t = 0.9\lambda / \beta \cos\theta \tag{1}$$

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Where (t) is the particle size, (β) is the line width at half maximum, (λ) the X-ray wavelength and θ is the Bragg angle. The X-ray density (d_x) was calculated by the formula:

$$d_x = 8M/Na^3 \text{ gm/cm}^3 \quad (2)$$

(M) is molecular weight and (N) is Avogadro number [15].

FTIR spectroscopy is effective tool to detect the vibrating atoms group in a ferrite structure by tetrahedron and octahedron sites that was done by using Shimadzu FTIR 8000. Ferrites powder with different molar ratio was mixed with KBr salt powder to measure the transmission in the wave number range ($200\text{-}1000 \text{ cm}^{-1}$). The size, particle distribution, and particle shape of nanopowder samples by SEM and TEM those were done using the instruments FEILEO 1550 SEM and Philips CM 12 TEM. The elements ratio in Li-Ni ferrite and the stoichiometry was done by SEM-EDX, TEM-EDX and Atomic Absorption spectroscopy (Varian SpectraAA 110).

3. RESULT AND DISCUSSION

The analysis of XRD-patterns is shown in Fig.3, for different values of (x). It was observed that the lower value of ($x=0, 0.1$), there is a hematite phase in contradiction with previous research [16]. When molar ratio was increased to ($x \geq 0.3$) the sample had spinel ferrites phase. The simplest form of ferrite is Magnetite Fe_3O_4 which is sometime rewritten as $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, one can recognize that the valances $\text{Fe}^{+2}, \text{Fe}^{+3}$ in this formula was necessary to construct the cubic spinel phase. Hematite phase, there is no insertion of Fe^{+2} ion in the structure that is prevent the appearance of spinel structure at ($x=0, 0.1$). Whereas the increasing Ni^{+2} content as a function of (x) in the mixture. The spinel phase was started to predominant for the samples under study. We expected that Ni^{+2} takes the alternative sites with respect to Fe^{+2} completing the spinel structure. According to hydrothermal method, one can expect the formation of $\text{Fe}^{+2}, \text{Fe}^{+3}$ comparing to traditional ceramic method. That might be benefit due to a good controlling of material composition and so physical properties.

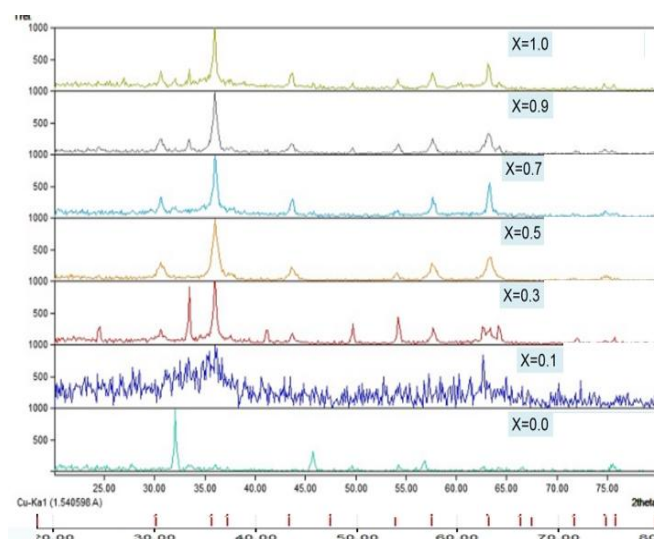


Figure3. The effect of molar ratio variation on XRD patterns.

The high intensity of the peak at ($2\theta=33.3$) at ($x=0$) for hematite phase sample was related to Fe_2O_3 and the presence of Fe^{+3} -ion in the formula is coming from FeCl_3 . The low intensity of the peak around ($2\theta=51.39$) was related to presence of NaCl in the mixture. The results of particle size by Scherer method is shown in Fig.4, it is demonstrate that the variation of molar ratio (x) on Scherer size concluded from XRD pattern. It was clear that the particle size had a minimum value (18 nm) at ($x=0.5$) and the maximum value was about (55 nm) at ($x=0$) and (37 nm) at ($x=1$). The minimum value of particle size is related to segregate of some ion in crystal boundary preventing the growth of crystallites due to the consumption of salts, quantity of NaOH , the concentration of general solution, and preparation temperature. The variation of lattice constants as a function of (x) were calculated, illustrated in Fig. 5. The range of lattice constant was agreed with previous study [9, 13]. The behavior is divide into three region, the first region at ($x=0.0\text{-}0.3$) showed a gradually increasing in lattice constants, the second region being constant around ($a=8.235 \text{ nm}$), and the last one exhibited abrupt increasing as a function of (x).

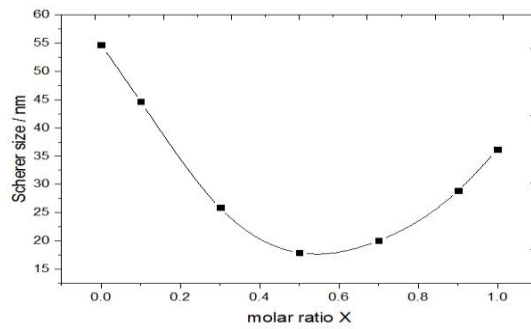


Figure4. Effect of molar ratio on Scherer particle size

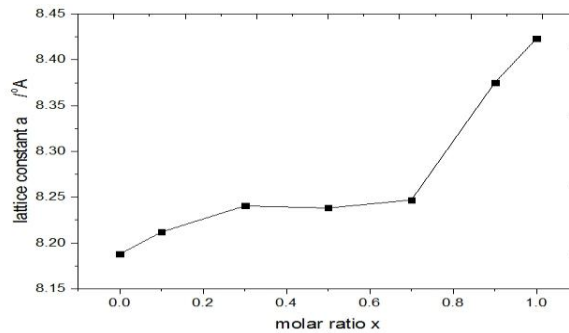
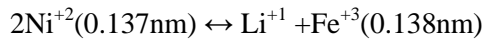


Figure5. The effect of molar ratio x on spinel lattice constant a.

The radii of Ni^{+2} , Fe^{+3} , Li^{+1} ions are (0.069, 0.064, 0.073 nm) respectively. These radii has the direct effect on increasing the lattice constant when ($x > 0.7$) because of increasing the ratio of Ni^{+2} ions in the structure and having octahedral sites rather than tetrahedron sites in the spinel structure. The fixing in the lattice constant might be attributed to a limited replacement of Fe^{+3} and Li^{+1} ion by Ni^{+2} ions [9] according to;



The difference in the lattice parameter might be attributed also to the cation migration of Ni^{+2} -ions on A-sites that exhibited a smaller ionic radius than the B-sites because of covalence effects [17]. The variation of XRD density (dx) as a function of (x) is shown in Fig. 6. It was clear that there is a linear increasing of the density (dx) with (x) ratio for all values except for ($x=0.9$), there is abrupt decreasing in (dx). The increasing in lattice volume is smaller comparing with increasing its weight due to molecular weight of Ni^{+2} are larger than Li^{+1} -ion.

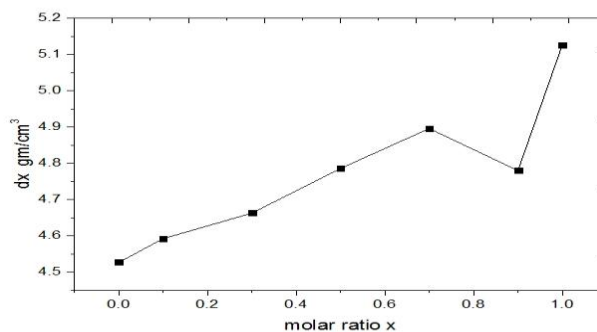


Figure6. The XRD density (dx) versus molar ratio (x)

The results of FTIR-spectrum is shown in Fig.7, there are strong major bands energies due to the absorption within the range ($400-650 \text{ cm}^{-1}$). The high frequency band (ν_1) lies in the range ($580-615 \text{ cm}^{-1}$) but the lower one was in the range ($400-480 \text{ cm}^{-1}$) [18]. IR radiation is exciting the vibrations of tetrahedral sites of spinel structure that make the stretching of metal-oxygen bond and the octahedral site is making the vibration of metal-oxygen bond later. The results of FTIR-spectrum for Li-Ni ferrites is shown in Table2, it is clear that the positions of (ν_1, ν_2) bands have no systematic distribution for each value of (x). These results have indication about the metal-oxygen bonds and their to the lattice constants. The shift in (ν_1), is return to the addition Ni^{+2} that was explained by the existence of Ni-O bond was shifted to Li-O bond, the shorter one.

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The particle shape and size distribution for ($x=0.7$) was performed by using SEM and TEM analysis, as shown in Fig.8. The results showed that the majority of particles are in range 30-40 nm and the particles with lower size are more than larger one. Whereas TEM analysis was exhibited a smaller particle size around to (35 nm) for $x=0.7$. Just for the comparison, the Scherer method was concluded a small particle size of about (21 nm).

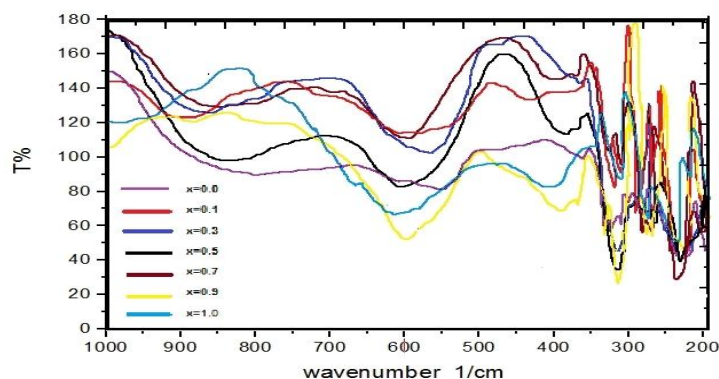


Figure7. FTIR spectrum of Li-Ni ferrites at different molar ratio (x).

Table2. the positions of IR absorption band at each molar ratio.

x	ν_1 cm-1	ν_2 cm-1
0.0	555	358
0.1	610	434
0.3	575	370
0.5	610	393
0.7	600	405
0.9	600	399
1	609	404

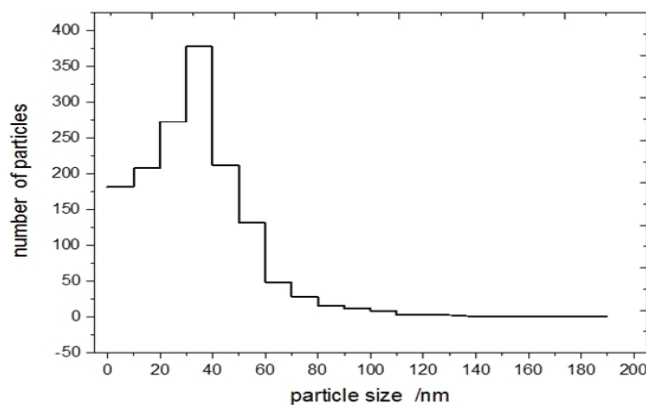
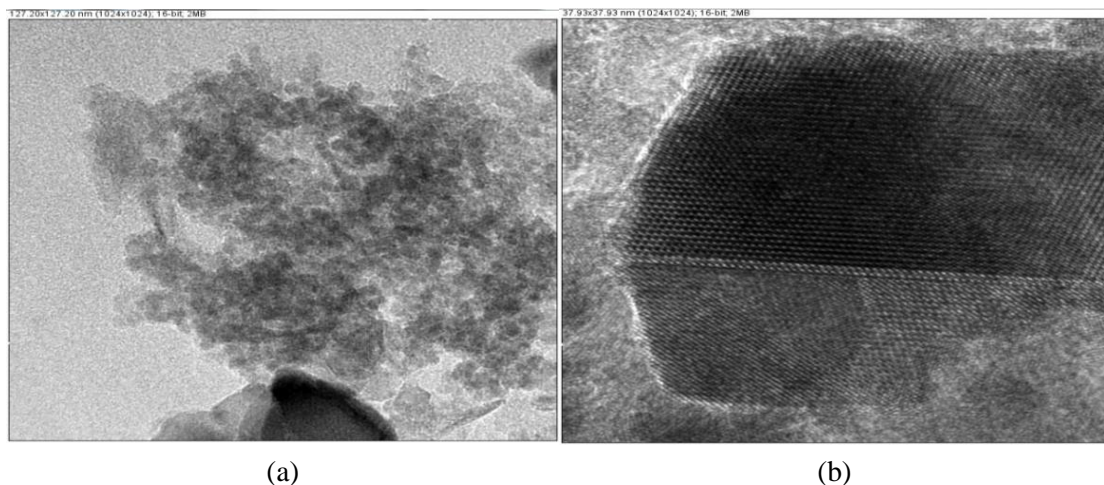


Figure8. Particles size distribution at $x=0.7$



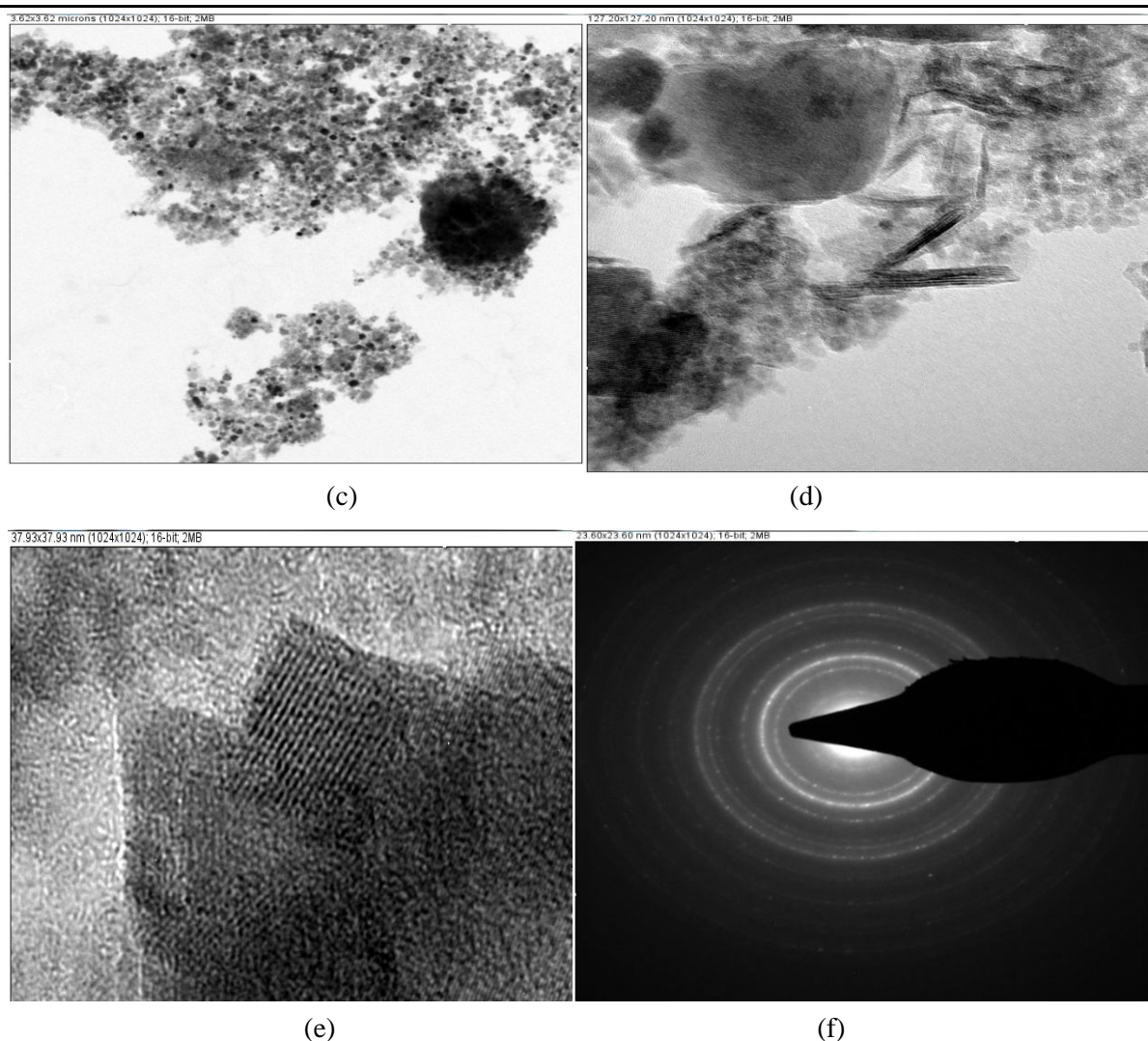


Figure 9. TEM images for $x=0.7$ are; (a) particles aggregation, (b) HRTEM of one particle, (c) another aggregation, (d) Nanorods mixed with nanoparticles, (e) HRTEM for particle contains more than one crystal, (f) Diffraction of e-beam by spinel crystal.

The particles shape and size of our samples are aggregated through the cluster formation. This accumulation is containing a different particles size and some nanorods with low ratio, as shown in Fig. 9a-f. There are particles aggregation consist of hundreds of particles by lower size of particles, as shown in Fig. 9a,c. The attraction between these particles might be return to self-magnetizing that enhances the attraction force among them. The cubic of spinel structure is clearly illustrated, in Fig. 9b. The presence of different nanostructures is appeared by TEM-photograp has shown in Fig. 9d. It contains a nanoparticles, nanosphere, nanocube and nanorods. It believed that the difference in the structures was related to the nucleation gradient and growth circumstances in autoclave besides still some different phases may exist. In fact, the most dominant particles shapes are nano sphere and the least are nanorods. The TEM-analysis that was mentioned previously, the relationship between particle size and sheerer size by consider the most of particles contain two or more crystals as shown in Fig. 9e. The electron diffraction pattern of particle for the photograp (b) represented by Fig. 9f.

The Composition Analysis was concluded from EDX-pattern during SEM and TEM analysis, as shown in Fig.10 for ($x=0.3,0.7$) respectively. There are some elements appeared in EDX analysis related to suchelements Na and C, both are related to the residual of principle compound (NaCl) and to carbon might be attributed to interference of their energy with Li-Ni ferrite elements energies. The conclusion of this analysis is represented by Fig. 11, the histogram of the elements contents in the mixture. It is clear that the Li-content decreasing with (x) increased, and increasing of Ni-content. The content of Fe-ions is nearly a constant and proportional to the weight of the sample. The concluded resultes is investigate the stoichiometric composition for all samples under study.

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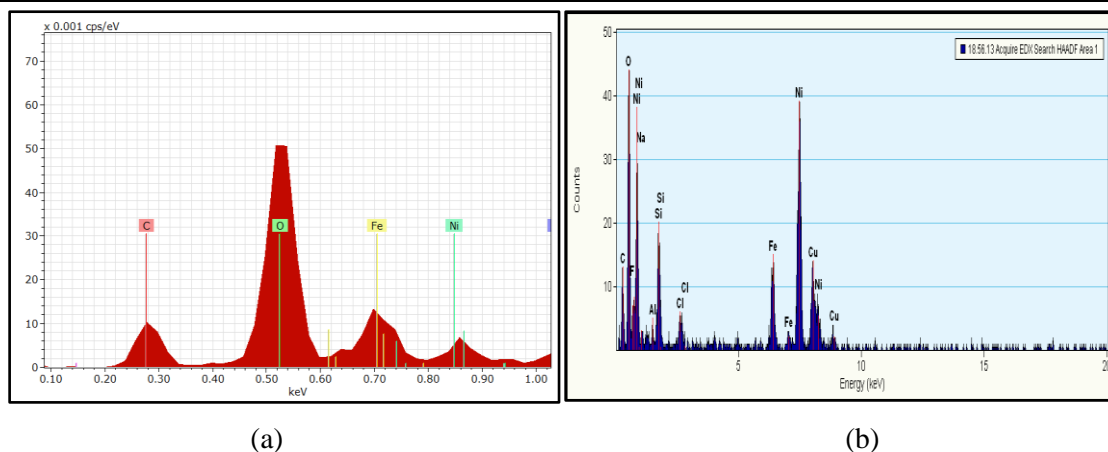


Figure10. (a) SEM-EDX analysis at $x=0.3$, (b) TEM-EDX analysis at $x=0$

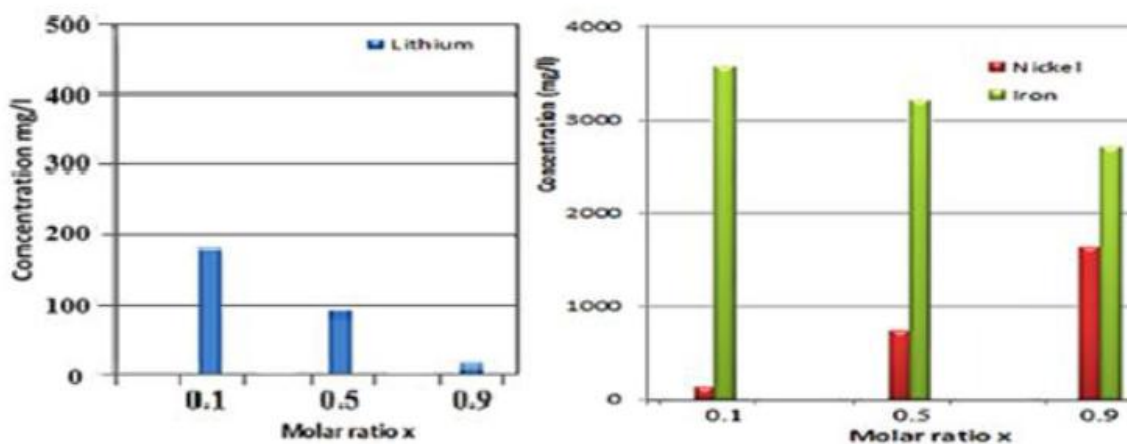


Figure11. The histogram of Atomic Absorption Analysis

4. CONCLUSIONS

Li-Ni ferrites can be prepared by hydrothermal method, and investigate the spinel structure due to the substitution of Li by Ni. Hydrothermal method showed that there is no reproducing of Fe^{+2} from Fe^{+3} . Pure Li-Ni ferrites can be obtained more clearly at molar ratio (x) more than 0.3 by chemical formula $\text{Li}_{0.5-0.5x}\text{Ni}_x\text{Fe}_{2.5-0.5x}\text{O}_4$ where ($1 > x > 0$). Increasing Ni content lead to increase the lattice constants as a function of Ni-ions those took tetrahedron sites instead of octahedron sites, in spite of Li-ion have larger radius than Ni ion. XRD density also increased with increasing Ni content due to larger mass of Ni ion with respect to Li ion.

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AUTHORS' BIOGRAPHY



Sadeq H. Lafta, Birth in Bagdad at 1972. BSc in applied physics at 1995, M.Sc. in laser physics at 1998 from University of Technology/Baghdad. From 2000 to 2009 lecturer in different Iraq and Libya Universities. From 2011 to 2015 PhD student. Five published papers in semiconductor and nanomaterials. Two years of experience in labs instruments maintenance. Email: sadeg000111@yahoo.com.



Dr. Emad Al-Shakarchi, is a Professor of Solid State Physics in Physics Department/ College of Science/ Al-Nahrain University/ Iraq. He is Member of Nanotechnology Society / Iraq and Member of American Association for Science and Technology Society, USA. The research activity is concentrated on Superconductor materials, Dielectric materials, Magnetic materials and Shape memory alloys. He was published a large number of researches in international Journals. He is the first one who is working in the superconductor material in Iraq, since 1994. He was supervised on 20 postgraduate students in different universities in Iraq, most of them in the superconductivity field. He was participated in 30 international scientific meeting during 15 years ago.



Ali M. Mousa, He was born in Baghdad in 1951. He had his B.Sc. in Physics from the University of Baghdad (Iraq) in 1973, and M.Sc. and Ph.D. degrees in Physics from University of Louis Pasteur (France) in 1980 and 1983, respectively. He had (60) published articles inside Iraq and abroad. His main field of research is semiconductor nuclear radiation detectors, laser-induced production of semiconductor structures since 1989. As well, he is heading a research group on preparation and characterization of high band gap semiconducting thin films and nanostructures by chemical bath deposition (CBD), spray pyrolysis. He is member of the Iraqi Society of Physics since 1973. and leading Iraqi Society for Alternative and Renewable Energy Sources and Techniques since 2011.