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A Study of Lattice Parameter of Ni – Zn Ferrite Modified by Addition of Silicon

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□ ABSTRACT □

The purpose of this study is to provide precise quantitative data for the lattice parameter as a function of silicon concentration, which can be used as a means of determining composition of samples. The results of lattice parameter measurements on the series $Ni_{0.65}Zn_{0.35}Si_xFe_{2-x}O_4$ ferrite over the range $0 \le x \le 0.5$ are reported. The lattice constants were calculated by two ways: first, as average and second, in terms of diffractometer extrapolation function. The single phase spinel structure of the sample was confirmed by X – ray diffraction technique. We found that the lattice constant decreases as x increasing. In addition, we calculated the cation – cation distance $d_{c\text{-}c}$ in the tetrahedral and octahedral sites.

Keywords: Spinel ferrite; lattice parameter; tetrahedral – and octahedral sites; cation – cation distance.

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دراسة معامل الشبكة البلورية للفرايت نيكل – زنك المعدلة بإضافة تراكيز مختلفة من السليكون

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□ الملخّص □

تهدف هذه الدراسة إلى تقديم بيانات كمية دقيقة عن بارامتر الشبكة بتابعية تركيز السليكون والتي يمكن أن تستخدم كوسيلة لتحديد تركيب العينات المدروسة.

في هذا العمل سجّلت نتائج قياسات بارامتر الشبكة لسلسلة من عينات فرايتية $Ni_{0.65}Zn_{0.35}Si_xFe_{2-x}O_4$ في المجال $0 \le x \le 0.5$. لقد وجدنا ثابت الشبكة لكل عينة بطريقتين : أولا،كقيمة متوسطة مأخوذة من طيف كل عينة ،وثانياً بمساعدة تابع الاستقراء في الانعراج. وتم التأكد من الطور الوحيد للبنية السبينلية للعينات المدروسة باستخدام طريقة انعراج الأشعة السينية. لقد وجدنا أن ثابت الشبكة a للعينات يتناقص بزيادة تركيز السليكون x. علاوةً على ذلك، حسبنا المسافة الفاصلة d_{c-c} بين كاتيون – كاتيون في المواقع الرباعية والثمانية في البلورات المدروسة .

الكلمات المفتاحية: سبينل فرايت؛ بارامتر الشبكة؛ المواقع الرباعية والثمانية؛ المسافة بين كاتيون – كاتيون.

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Introduction:

Precise determination of lattice constants plays an important role in determining thermal expansion coefficient, real density and porosity for these samples. Ferrite materials crystallize in three forms: cubic, garnet and hexagonal and display interesting electrical and magnetic properties. The spinel structure is named after the mineral $MgAl_2O_4$ and has the simple composition AB_2O_4. Normally, A is a divalent ion and B is a trivalent ion. The oxygen ions build an fcc lattice and form 64 tetrahedral - and 32 octahedral holes in one unit cell.

Usually, in a normal spinel structure the A cations occupy 1/8 of the available tetrahedral holes, i.e., 8 sites, while B cations occupy 1/2 of the octahedral holes, i.e., 16 sites. In the case of an inverse spinel the B cations distribute in half between A and B sites while the A cations occupy the other remaining half of the octahedral sites [1].

On the other hand, the A and B cations can be mixed.

Thus, the unit cell contains 8 formula of $A^{2+}B_2^{3+}O_4^{2-}$ [2].

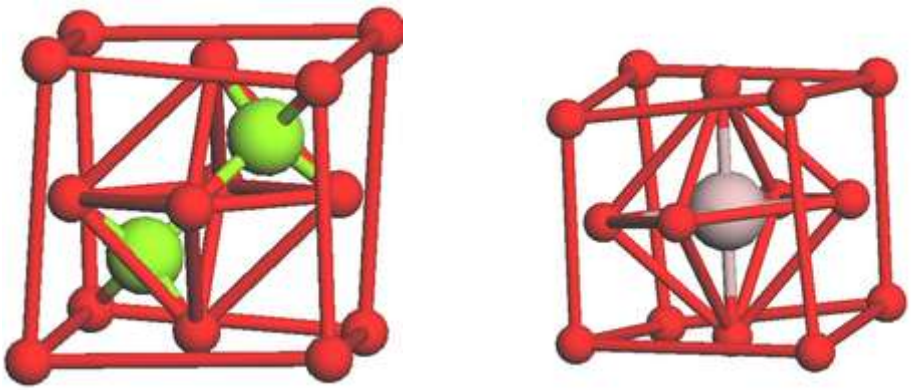
The general ferrite formula is: $(A_x^{2+}B_{1-x}^{3+})[A_{1-x}^{2+}B_{1+x}^{3+}]O_4^{2-}$:

$x = 1 \rightarrow$ normal ferrite $\Rightarrow AB_2O_4$

$x = 0 \rightarrow$ inverse ferrite $\Rightarrow B_8(A_8B_8)O_{32}$

$0 < x < 1 \rightarrow$ mixed ferrite $\Rightarrow A_{8/3}B_{16/3}(A_{16/3}B_{32/3})O_{32}$

The above mentioned sites are surrounded by 4 and 6 oxygen ions, respectively as shown in fig.1–a,b [3].



(a) (b)

Fig. 1 – a ,b : Structure a shows the filling of 2 tetrahedral sites (A is in green and O is in red) and structure b also shows a filled octahedral sites (B is in gray and O is in red).

Aim of the research:

The purpose of this study is to provide precise quantitative data for the lattice parameter as a function of silicon concentration, which can be used as means of determining composition of samples, thermal expansion coefficient, porosity and real density $D_{X-ray} = \frac{8M}{N_a a^3}$ where M is molecular weight and N_a the Avogadro's number.

The electrical, thermal and magnetic properties of ferrites depend on the chemical composition, cation distribution and method of preparation. Therefore, the study of

structure is very important to understand the behavior of the physical properties. From the application side Ni – Zn ferrite represents the most important types where it is used in many ferrite devices such as: inductor cores, converters, magnetic heads, etc.

Ni – Zn ferrites have high resistivity, low dielectric loss and high Curie temperature.

Material and Method:

The samples were prepared from stoichiometric amounts of

pure oxides 99.9% of Fe_2O_3 , $NiCO_3$ and ZnO to form the composition $Ni_{0.65}Zn_{0.35}Si_xFe_{2-x}O_4$ with $0 \le x \le 0.5$.

The mixed oxides were sintered in a furnace at 1000 ^{0}C for 5hrs. The presintered oxides were grounded to a fine powder using a mortar made of carborundum for 4 hrs. After that, the mixture was pressed at room temperature under a pressure of 10 ton/ cm^2 in order to get discs with diameter 1cm and thickness 2 mm. Finally, the discs were again sintered at 1200 ^{0}C for 4 hrs and then slowly cooled to RT by turning off the furnace.

The disc of each composition was powdered to make it suitable for X – ray diffraction. The X – ray diffraction pattern for each sample was recorded by using a Shimadzu X – ray diffractometer working with Cu K_α radiation ($\lambda_{k\alpha}$ = 1.54 Å).

Results and Discussion:

From the X – ray diffraction patterns for the ferrite system with the composition $Ni_{0.65}Zn_{0.35}Si_xFe_{2-x}O_4$, we can observe a single phase of cubic spinel ferrite. The lattice parameters **a** were calculated by means of two ways:

First, we calculated $\bar{a}$ as the slope of $\sqrt{h^2+k^2+l^2} = f(1/d_{hkl})$ for each sample using the following relation:

$$a = d_{hkl}\sqrt{h^2+k^2+l^2} \qquad (1)$$

The second way bases on following diffractometer extrapolation function [4] :

$$f(\theta) = \cos\theta\cot\theta \qquad (2)$$

where θ is the diffraction angle.

It is meaningful to consider the following parameters: cation – cation distance d_{c-c} , tetrahedral- , octahedral covalent bond length d_A and d_B , lattice parameter shift Δa :

$$d_{c-c} = a/\sqrt{2} \qquad (3)$$

$$d_A = \sqrt{\frac{3}{8}}\, d_{c\text{-}c}$$

$$d_B = \sqrt{\frac{2}{8}}\, d_{c-c} \qquad (4)$$

All values are listed in table 1 .

Tab. 1: Contains average lattice parameter $\bar{a}$, extrapolation a, cation – cation distance ,the tetrahedral covalent bond length and lattice parameter shift $\Delta a = a_x - a_{x=0.0}$ (all values in Å).

Si content %	$\bar{a}$ /Å	a / Å	Δa/ Å	d_{c-c} /Å	d_A /Å
0	8.553	8.400	0.0	6.047884	3.703558
10	8.605	8.505	0.105	6.084654	3.726074
20	8.567	8.494	0.094	6.057784	3.70962
30	8.508	8.475	0.075	6.016064	3.684072
40	8.479	8.464	0.064	5.995558	3.671515
50	8.469	8.463	0.063	5.988487	3.667185

The lattice constant **a** was determined by means of diffractometer extrapolation function for all sample as shown in

figures (1 – a,b,c,d,e,f). In this case, extrapolation means that $f(\theta) = 0$ when $\theta = 90^0$ then we get the values of **a** as an intersection between drawn line with ordinate axis in each graph. From the fig.(1,f), we notice that the scattering values indicate to the not perfect preparation of this sample.

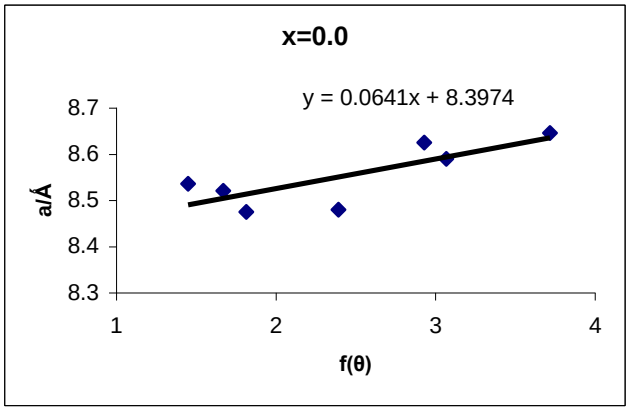


Fig.(1,a): represents the relation between a and diffractometer extrapolation function for x=0.0

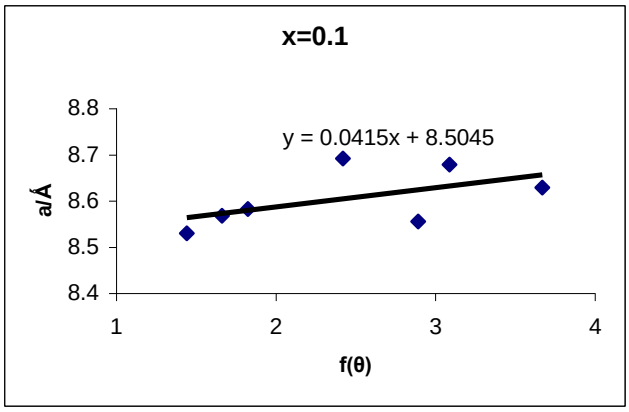


Fig.(1,b): represents the relation between a and diffractometer extrapolation function for x=0.1.

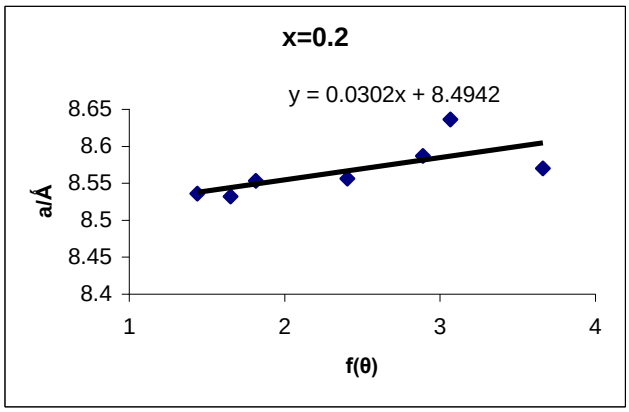


Fig.(1,c): represents the relation between a and diffractometer extrapolation function for x=0.2.

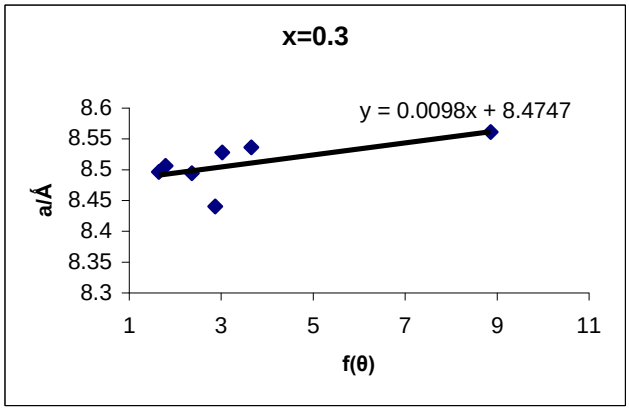


Fig.(1,d): represents the relation between a and diffractometer extrapolation function for x=0.3.

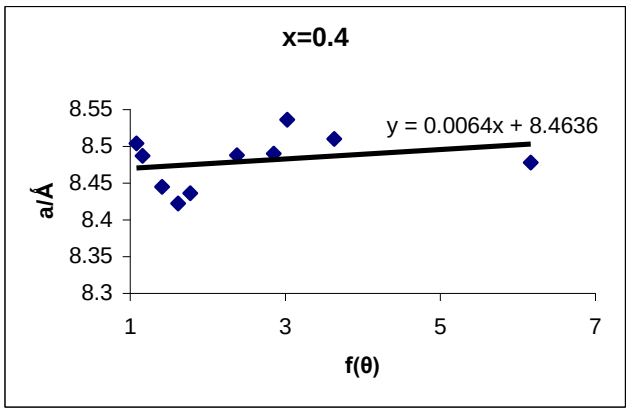


Fig.(1,e): represents the relation between a and diffractometer extrapolation function for x=0.4.

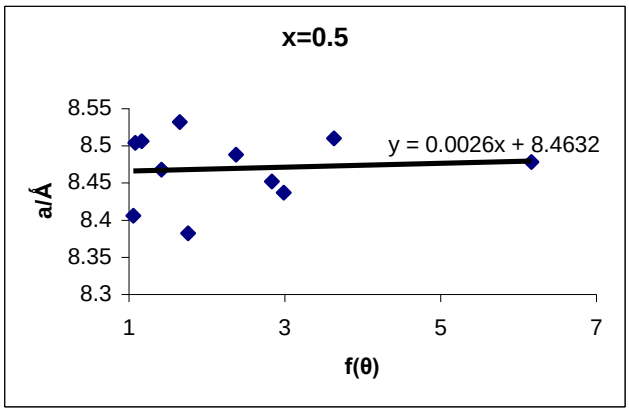


Fig.(1,f): represents the relation between a and diffractometer extrapolation function for x=0.5.

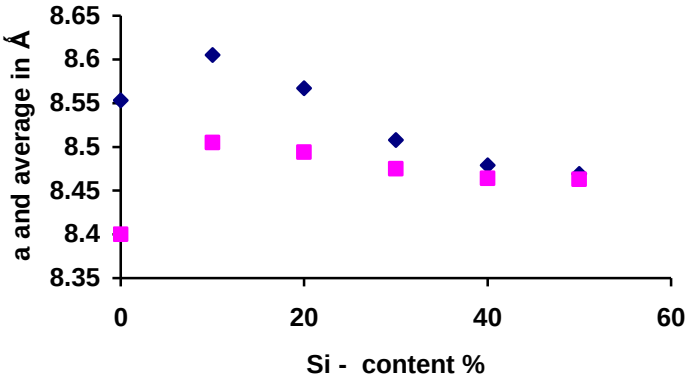


Fig. 2 : shows the effect of composition on lattice parameter a measured by two ways .

We notice from fig.2 that the variations of a and $\bar{a}$ with Si concentration for all investigated samples have the same direction. Our results have the same direction as mentioned in references [5 – 8, 10,11]. When Si^{4+} ions are substituted by Fe^{3+} ions , the lattice parameter will be changed. For small amount of silicon (x up to 10%) the lattice parameter increases and then decrease with increasing Si content [12]. This behavior may be attributed to ionic radii of the ingredient ions. The Si^{4+} ion has a smaller ionic radius 0.39 Å than that of Fe^{3+} ion 0.67 Å (sea tab.2) .

The ionic radii r_i of different ions and atomic weight are listed in tab.2 [12] .

Tab. 2: contains ionic radii r_i of different ions and atomic weight.

Ions	Si^{4+}	Fe^{3+}	Ni^{2+}	Zn^{2+}	Fe^{2+}	O^{2-}
$r_{i\ /\ Å}$	0.39	0.64	0.74	0.74	0.76	1.32
M/g	28.086	55.85	58.70	65.38	55.85	16.00

Fig. 3 illustrates the behavior of Δa versus x – content. We notice that by increasing x the lattice parameter shift is small. This proportionality agrees with Vegard law [13]. The sample for x=0.0 is taken as a reference sample for shifts.

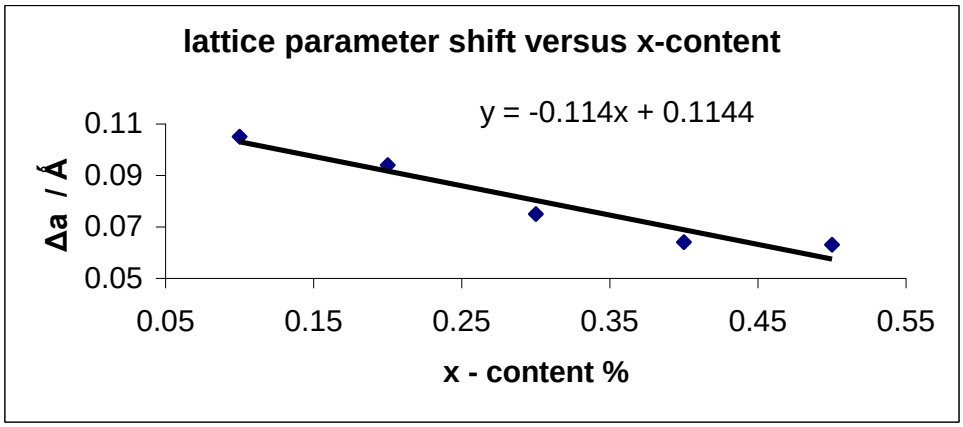


Fig.3: the lattice parameter shift as a function of x – content without x=0.0.

Conclusion:

The single phase spinel structure of the studied sample was confirmed by X – ray diffraction technique. The lattice parameter **a** decreases by addition some silicon concentration which is related to the difference in the ionic radii of Si^{4+} and Fe^{3+} ions, i.e., the average cation - cation distance also decreases. After knowing the lattice constant, we could determine thermal expansion coefficients, real density, porosity and composition for each sample. A further study in the future is needed for higher concentrations of silicon. Furthermore, we could continue this work on studying the electrical and magnetic properties.

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