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

Dr. Badr Al - Aaraj*

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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 $0 \leq x \leq 0.5$ 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 $d_{c-c}$ in the tetrahedral and octahedral sites.

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

*Professor, Department of Physics, Faculty of Sciences, Tishreen University, Lattakia, Syria.
دراسة معامل الشبكة البلورية للفراتي نيكل - زنك المعدلة

بإضافة تراكيز مختلفة من السليكون

الدكتور بدر الأعرج

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الملخص

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

في هذا العمل سجلت نتائج قياسات بارامتر الشبكة لمجموعة من عينات فراتي نيكل في المجال -0 ≤ x ≤ 0.5. لقد وجدنا ثابت الشبكة لكل عينة بطرقتين: أولاً قياساً متوسطة مأخوذة من طيف كل عينة وثانياً بمساعدة تابع الاستقرآء في الالعاب. وتم التأكد من الطرفي الوحيد للمشتقة السيليكاتية للعينات المدروسة باستخدام طريقة انعجار الأشعة السينية. لقد وجدنا أن ثابت الشبكة x للعينات يتناقص بزيادة تركيز السليكون.

عابرة على ذلك، حسبما المسافة الفاصلة 10c بين كاتيون - كاتيون في المواقع الرابعة والعشادية في البلورات المدروسة.

الكلمات المفتاحية: سبيت فرانيت؛ بارامتر الشبكة؛ المواقع الرابعة والعشادية؛ المسافة بين كاتيون - كاتيون.

* أستاذ - قسم الفيزياء - كلية العلوم - جامعة تشرين - اللاذقية - سورية.
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 MgAl₂O₄ and has the simple composition AB₂O₄. Normally, A is a divalent ion and B is a trivalent ion. The oxygen ions build an fcc lattice and form 46 tetrahedral - and 23 octahedral holes in one unit cell.

Usually, in a normal spinel structure the A cations occupy 8/1 of the available tetrahedral holes, i.e., 4 sites, while B cations occupy 2/1 of the octahedral holes, i.e., 6 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 4 formula of A²⁺B³⁺O²⁻ [2].

The general ferrite formula is: (A⁺ₓB²⁺)₂B₂O₄⁻

x = 1 → normal ferrite ⇒ AB₂O₄
x = 0 → inverse ferrite ⇒ B₈(A₈B₈)O₃₂
0 < x < 1 → mixed ferrite ⇒ A₈/ₓB₁₆/ₓ(A₁₆/ₓB₃₂/ₓ)O₃₂

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

![Diagram of the spinel structure showing tetrahedral and octahedral sites.](image)

Fig. 1 a,b: Structure a shows the filling of 4 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 ٩٫٩٩٪ of \(\text{Fe}_3\text{O}_4\), \(\text{NiCO}_3\) and \(\text{ZnO}\) to form the composition \(\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Si}_x\text{Fe}_{2-x}\text{O}_4\) with \(0 \leq x \leq 0.5\).

The mixed oxides were sintered in a furnace at ٠٠٠١٠°C for ٥hrs. The presintered oxides were grounded to a fine powder using a mortar made of carborundum for ٤hrs. After that, the mixture was pressed at room temperature under a pressure of ٠١ton/cm\(^2\) in order to get discs with diameter ١cm and thickness ٢mm. Finally, the discs were again sintered at ٠٠٢١٠°C for ٤hrs 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\(_\alpha\) radiation (\(\lambda_{K\alpha} = ٤٥٫١Å\)).

**Results and Discussion:**

From the X – ray diffraction patterns for the ferrite system with the composition \(\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Si}_x\text{Fe}_{2-x}\text{O}_4\), we can observe a single phase of cubic spinel ferrite. The lattice parameters \(a\) were calculated by means of two ways:

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

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

The second way bases on following diffractometer extrapolation function \( [٤] \):

\[f(\theta) = \cos \theta \cot \theta\]  \(٤\)

where \(\theta\) 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 \(\Delta a\):

\[d_{c-c} = a / \sqrt{2}\]  \(٥\)

\[d_A = \frac{3}{\sqrt{8}} d_{c-c}\]  \(٦\)

\[d_B = \frac{2}{\sqrt{8}} d_{c-c}\]

All values are listed in table ١.
Tab. 1: Contains average lattice parameter $\bar{a}$, extrapolation $a$, cation – cation distance, the tetrahedral covalent bond length and lattice parameter shift $\Delta a = a_x - a_{ref}$ (all values in Å).

<table>
<thead>
<tr>
<th>Si content %</th>
<th>$\bar{a}$/Å</th>
<th>$a$/Å</th>
<th>$\Delta a$/Å</th>
<th>$d_{c-c}$/Å</th>
<th>$d_\Lambda$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.503</td>
<td>8.400</td>
<td>0.0</td>
<td>6.787</td>
<td>7.348</td>
</tr>
<tr>
<td>10</td>
<td>8.703</td>
<td>8.603</td>
<td>0.105</td>
<td>6.787</td>
<td>7.348</td>
</tr>
<tr>
<td>20</td>
<td>8.527</td>
<td>8.421</td>
<td>0.106</td>
<td>6.787</td>
<td>7.348</td>
</tr>
<tr>
<td>30</td>
<td>8.508</td>
<td>8.405</td>
<td>0.095</td>
<td>6.787</td>
<td>7.348</td>
</tr>
<tr>
<td>40</td>
<td>8.479</td>
<td>8.386</td>
<td>0.074</td>
<td>6.787</td>
<td>7.348</td>
</tr>
<tr>
<td>50</td>
<td>8.439</td>
<td>8.363</td>
<td>0.073</td>
<td>6.787</td>
<td>7.348</td>
</tr>
</tbody>
</table>

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 $\theta = 90^\circ$. 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 $x=0.0$. 

\[ y = 0.0641x + 8.3974 \]
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 [9 – 11, 10]. When Si\textsuperscript{4+} ions are substituted by Fe\textsuperscript{3+} ions, the lattice parameter will be changed. For small amount of silicon ($x$ up to 0.7) the lattice
parameter increases and then decrease with increasing Si content [17]. This behavior may be attributed to ionic radii of the ingredient ions. The \( \text{Si}^{4+} \) ion has a smaller ionic radius \( 0.39 \, \text{Å} \) than that of \( \text{Fe}^{3+} \) ion \( 0.67 \, \text{Å} \) (see tab.2).

The ionic radii \( r_i \) of different ions and atomic weight are listed in tab.2 [17].

**Tab. 2:** contains ionic radii \( r_i \) of different ions and atomic weight.

<table>
<thead>
<tr>
<th>Ions</th>
<th>( \text{Si}^{4+} )</th>
<th>( \text{Fe}^{3+} )</th>
<th>( \text{Ni}^{2+} )</th>
<th>( \text{Zn}^{2+} )</th>
<th>( \text{Fe}^{2+} )</th>
<th>( \text{O}^{2-} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_i / \text{Å} )</td>
<td>0.39</td>
<td>0.67</td>
<td>0.74</td>
<td>0.74</td>
<td>0.77</td>
<td>1.32</td>
</tr>
<tr>
<td>( \text{M/g} )</td>
<td>28.18</td>
<td>55.85</td>
<td>58.70</td>
<td>65.38</td>
<td>55.85</td>
<td>17.08</td>
</tr>
</tbody>
</table>

Fig. 3 illustrates the behavior of \( \Delta a \) versus \( x \) – content. We notice that by increasing \( x \) the lattice parameter shift is small. This proportionality agrees with Vegard law [17]. 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 \( \text{Si}^{4+} \) and \( \text{Fe}^{3+} \) 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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