Crystallographic and Magnetic Properties of Al\textsuperscript{3+} co-doped NiZnFe\textsubscript{2}O\textsubscript{4} Nano-particles Prepared by Sol-gel Process

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A\textsubscript{1}O\textsubscript{1}, SUBSTITUTED nickel zinc nano-ferrite Al\textsubscript{x}Ni\textsubscript{0.5-x}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} (x = 0.0, 0.1, 0.2, 0.3) was prepared by the citrate sol-gel method using nickel, zinc, iron and aluminium nitrates and sintered at 800°C for 3 h in air. Prepared nano-sized ferrites were characterized by X-ray diffraction, High resolution transmission and scanning electron microscopy and Fourier transforms infrared spectroscopy. The estimated crystallite sizes were in the range of 24.7–32.9 nm. HR-TEM data appears that all nano-ferrite samples are composed of more or less agglomerated nanoparticles with the average particle size of nanocrystallites is ~31 nm. The impact of introducing Al ions by Ni on the magnetic properties of the prepared nano-ferrite was investigated utilizing magnetic measurements at room temperature. The changing of crystallite sizes, lattice parameter and the surface area with increasing the Al content were determined. The saturation magnetization (Ms) and coercivity (Hc) values vary from 47.894-32.314 and 70.37-60.117 G, respectively.

**Keywords:** Nano-crystalline ferrites, Nickel zinc ferrite, Sol-gel process, Spinel ferrite, Magnetic properties.

**Introduction**

Recently, soft ferrites are most versatile due to their technological applications, especially prepared by chemical methods [1]. Chemical methods as sol gel process provide high purity and homogeneity, uniform distribution of dopants ions at the molecular level and high efficiency [2]. Ni-Zn ferrites are known and have been applied in various the electrical and electronic industries, due to their interesting electrical and magnetic properties [3,4]. Nickel zinc ferrites as spinel-type structures, have a particular interest from the researchers much due to its using in various industrial electronic applications, such as communication devices (mobile phones), drug delivery, TVs, sensors, data storage, radios, microwaves, etc. [4-6]. The spinel structure name is offered due to its structure arrangement in which metal ions are distributed between (A site) tetrahedral and (B site) octahedral sites formed through the oxygen ions in a unit cell [7,8]. So, the distribution of metal ions through the A site and B site affects the magnetic properties of M-Fe\textsubscript{2}O\textsubscript{4}, which may be controlled by thermal treatment and crystallite size [9]. Nickel zinc ferrite belongs to the soft magnetic materials group, which is easily magnetized and demagnetized. Most electronic and magnetic applications require polycrystalline ferrite materials to be pressed into larger shapes, which is difficult to produce if the particles have wide-size distribution [10,11]. The variation in the starting composition of Ni–Zn-ferrite results in the rearrangement of metal ions through A and B sites, which can modify the properties of these ferrites. Thus, more investigations are still required to be done to produce Ni–Zn ferrite with narrow grain size distribution, high surface and controlled porosity leading to better structural, magnetic and electrical properties [12, 13].
properties of ferrite materials change as their nanoscale size and as the level of atoms at the surface of a material become important. The superior properties of ferrites nanoparticles are therefore largely due to the large fraction of atoms that occupies the grain boundary area [14]. The synthesis of new magnetic systems, such as iron-based, led the modification of metallic materials with a nano-crystalline structure and non-classical properties. The production process progression in the size control and characterization of these magnetic systems has entailed to numerous benefits, both in the scientific and technological fields [14,15]. Considerable interest in chemical methods for the synthesis of nano-ferrite nanoparticles has been contolled to explore better materials with controllable shape, nano-scale,and stability for multi-applications sol–gel methods [15,16].

The sol-gel method as a one of the low temperature chemical methods was used for synthesis ferrites nano materials, which allows to introduce different modifiers such as Zn, Al, Ce and Cu ions in the ferrite materials could also enhance their structural and magnetic properties [15-17].

The main idea behind using the sol-gel process is to “dissolve” the compounds in a liquid in order to bring it back as a solid in a controlled manner at nano-scale. In this study, according to the importance of $\text{Al}_2\text{O}_3$ nanoferrites, this attempt has been made to study the effect of substitution Ni ions by $\text{Al}_2\text{O}_3$ ions on the structural and magnetic properties of $\text{Al}_{1-x}\text{Ni}_{x}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanocrystalline. The nano-magnetic samples with the composition $\text{Al}_{1-x}\text{Ni}_{x}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.5, 0.8$) were prepared via citrate sol gel method and calcined at $800^\circ\text{C}$ for $3\text{h}$ in a muffle furnace with heating rate $5^\circ\text{C}/\text{min}$ in air. X-ray diffraction (XRD) patterns of the prepared sample were recorded with an X-ray diffractometer using monochromatized CuKα1 radiation of wavelength $= 1.54056$ Å. Crystallite sizes G were determined from the Scherer’s equation $(G = K\lambda / D \cos\theta)$, where $K$ is the Scherer constant (0.9), $\lambda$: is the wavelength, and $D$ is the full width (in radians) of the peak at half maximum (FWHM) intensity. The morphological features were studied using JEOL (JEM-2100) transmission electron microscope (HRTEM) and high resolution scanning electron microscope (HRSEM). Fourier Transforms Infrared, were used to determine the individual frequencies and their intensities, in the range of 400 cm$^{-1}$ to 4000 cm$^{-1}$, using the KBr pellet method. The magnetic properties were measured using a vibrating sample magnetometer (VSM Model Lakeshore).

**Results and Discussion**

**X-Ray Diffraction (XRD) Studies:**

Figure 1 represents the XRD pattern of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ doped with different concentrations of $\text{Al}_2\text{O}_3$ ions (0.1, 0.2 & 0.3) after calcination at $800^\circ\text{C}$, to analyze the formation of the crystalline phases. All the prepared samples show characteristic peaks assigned to the homogeneous cubic spinel structure (JCPDS No.08-0234) with a lattice parameter changes from 8.42 Å to 8.63 Å with introducing Alions and corresponding planes of (111), (220), (311), (222), (400), (422), (511), (531), (620), (533) and (444), representing the ferrite lattice [18,19]. From the figures the sharpness and broadening of Bragg’s peaks indicate the good and complete formation of pure and doped $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ using the citrate sol gel process. The Lattice constant, X-Ray density and the induced strain is calculated from the Williamson-Hall method [20], as shown in Table.
1. There is a small shifting of the diffraction peak towards higher (2θ); this may be due to replacement of Ni by Al ions as shown in Fig. 1. The average crystallite size of the prepared nano-ferrite samples (D) is determined from the broadening of the high intensity peak (311) using the Debye-Scherrer’s equation [20]. The crystallite size increases from 24.67 nm for the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ to 30.85 nm with increasing Al$_2$O$_3$ content. This means that the crystallite sizes are increased due to the decrease in the induced strain as shown in Table 1. The observed broadening of XRD pattern for doped nickel zinc ferrite nanocrystalline is ascribed to the crystallite size-induced or strain induced broadening. From the table it is note that the experimental lattice parameter and density decreases with increasing Al content in the spinel structure Al$_x$Ni$_{0.5-x}$Zn$_{0.5}$Fe$_2$O$_4$. This can be attributed to the change of the relative ionic radii of Ni$^{2+}$, Al$^{3+}$, and Fe$^{3+}$ ions where Ni$^{2+}$ ions have greater ionic radii (0.69 Å), than Al$^{3+}$ ions (0.67 Å) in the octahedral sites [21]. So, the partial substitution of the Ni ions by the Al ions causes little shrinkage of unit cell dimensions, thereby decreasing the lattice parameter, as shown below in Table 1.

![X-ray diffraction patterns of Al$_x$ Ni 0.5- x Zn0.5Fe$_2$O$_4$ (x=0.0, 0.1, 0.2 & 0.3) nano-crystalline calcined at 800°C for 3h.](img)

**TABLE 1. Variation of crystallite size, Lattice constant, D-spacing and X-Ray density with Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ doped with Al$_2$O$_3$ (x=0.0, 0.1, 0.2 & 0.3).**

<table>
<thead>
<tr>
<th>Al$_2$O$_3$ content (x)</th>
<th>Crystallite size (nm)</th>
<th>Theoretical Lattice constant (Å)</th>
<th>Experimental Lattice constant (Å)</th>
<th>X-Ray density (g/cm$^3$) $\times 10^{-23}$</th>
<th>d-spacing (Å)</th>
<th>Surface area (nm)</th>
<th>Strain (ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>24.67</td>
<td>8.4258</td>
<td>8.4260</td>
<td>2.02371141</td>
<td>2.54050</td>
<td>1201.80</td>
<td>0.50910</td>
</tr>
<tr>
<td>0.2</td>
<td>30.00</td>
<td>8.3950</td>
<td>8.3950</td>
<td>2.04601266</td>
<td>2.53120</td>
<td>9775.11</td>
<td>0.31301</td>
</tr>
<tr>
<td>0.5</td>
<td>32.9</td>
<td>8.360</td>
<td>8.3610</td>
<td>2.07128244</td>
<td>2.52090</td>
<td>8804.73</td>
<td>0.23730</td>
</tr>
<tr>
<td>0.8</td>
<td>30.85</td>
<td>8.360614</td>
<td>8.360</td>
<td>3.10829593</td>
<td>2.52082</td>
<td>6256.44</td>
<td>0.24905</td>
</tr>
</tbody>
</table>

**Scanning and transmission electron microscopy (HRSEM /HRTEM)**

HR-SEM images revealed that aggregate nanostructures with spherical shapes and particle sizes in nano-scales are bonded in the prepared nano-ferrites (Fig. 2a–c). From the HR-SEM images, it is clear that the surface morphology of these samples shows dense nanostructure particles assembly of fine nanoparticles and agglomerated as non-uniform sheets for the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ doped with (0.1 and 0.3) Al$_2$O$_3$ ions. Figure 2(B) appears the HR-TEM images for the prepared ferrite nano-particles, obtained at 800°C. All samples reveal that the ferrite nanoparticles of nearly spherical shape and the size about 7–29 nm are uniformly distributed. For the doped
samples with (0.1, 0.3) Al₂O₃ ions, Fig. 2 B (b, c) shows a denser distribution of nanoparticles and agglomeration. The established nanoparticles size from the HR-TEM images is agreement to the values evaluated from XRD results.

![HR-SEM and HR-TEM images](image)

Fig. 2 (A, B). HR-SEM and HR-TEM images of AlₓNi₀.₅₋ₓZn₀.₅Fe₂O₄ (x=0.0, 0.1 & 0.3) nano-crystalline calcined at 800°C for 3h.

**FTIR Analysis**

Figure 3, shows the FTIR spectra of spinel AlₓNi₀.₅₋ₓZn₀.₅Fe₂O₄ (x=0.0, 0.1, 0.2 & 0.3) nanoparticle prepared by citrate sol-gel method, in the range 400-4000 cm⁻¹. The observed FTIR peaks are at 3461 cm⁻¹ and 2357 cm⁻¹ assigned to stretching vibrations of (O-H) groups and stretching (C-H) respectively [22]. The sharp peak at 1621 cm⁻¹ and 1122 cm⁻¹ is corresponding to stretching vibration of (M-O), which confirm the formation of the metal-oxygen in ferrite-based. The absorption band at 1386 corresponding to the nitrates from which the Ni, Zn and Fe functional groups and their linkages and disappeared with introducing the Al₂O₃ ions in NiZnFe₂O₄[23]. The spectra for the prepared samples give characteristic bands at 457 cm⁻¹ and 380 cm⁻¹.
(metal ion– oxygen (M$_{\text{oct}}$–O) at octahedral-site) and 605 cm$^{-1}$ (metal ion– oxygen (M$_{\text{tet}}$–O) at tetrahedral-site), which are the significant bands of -Fe$_2$O$_4$ groups, which is due to the formation of NiZnFe$_2$O$_4$ nano-structure [24].

**Magnetic studies**

Magnetic measurements were done in room temperature of the Al$_x$Ni$_{0.5-x}$Zn$_{0.5}$Fe$_2$O$_4$ ($x = 0.0, 0.1, 0.2 & 0.3$) nano-crystalline showed typical magnetic behavior for the nano-ferrite calcined at 800°C for 3h, as observed in Fig. 4. The internal area for the M-H hysteresis loop illustrates amagnetic energy loss. This area for pure and doped NiZnFe$_2$O$_4$ is small which a particular feature for a soft ferrite. Different magnetic parameters as saturation magnetization ($M_s$), coercivity ($H_c$) and remnant magnetization ($M_r$) are specified of the room temperature hysteresis loop for various concentrations of Al$^{2+}$ ions and are evaluated in Table 2. The observed changes in values of $M_s$, $H_c$ and $M_r$ with increasing of Al concentrations can be proved to the specific basis of exchange interactions between difference ions at tetrahedral (A) and octahedral (B) sites in ferrites [25].
TABLE 2. Values of Saturation magnetization (Ms), Remnant (Mr), Coercive field, Squarness for Al$_x$Ni$_{0.5-x}$Zn$_{0.5}$Fe$_2$O$_4$ (x=0.0, 0.1, 0.2 & 0.3) nano-crystalline

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ms (emu/g)</th>
<th>Mr (emu/g)</th>
<th>Hci (G)</th>
<th>Squareness (Mr/Ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.5}$Zn$</em>{0.5}$Fe$_2$O$_4$</td>
<td>47.894</td>
<td>1.347</td>
<td>70.37</td>
<td>28.125E$^{-3}$</td>
</tr>
<tr>
<td>Ni$<em>{0.4}$Al$</em>{0.1}$Zn$_{0.5}$Fe$_2$O$_4$</td>
<td>15.194</td>
<td>1.1394</td>
<td>104.34</td>
<td>74.991E$^{-3}$</td>
</tr>
<tr>
<td>Ni$<em>{0.3}$Al$</em>{0.2}$Zn$_{0.5}$Fe$_2$O$_4$</td>
<td>24.562</td>
<td>1.2568</td>
<td>69.226</td>
<td>51.166E$^{-3}$</td>
</tr>
<tr>
<td>Ni$<em>{0.2}$Al$</em>{0.3}$Zn$_{0.5}$Fe$_2$O$_4$</td>
<td>32.314</td>
<td>1.4133</td>
<td>60.117</td>
<td>43.735E$^{-3}$</td>
</tr>
</tbody>
</table>

Where, the replacement of nonmagnetic Al$^{2+}$ ions with the magnetic Ni$^{2+}$ ions changes the magnetization behavior of the octahedral site. The effect of Al-replacement is the gradual increase in the values of Ms, Hci and Mr. Also, the decrease in the Ms and Mr in the case of doped Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ may be due to the basis of canted spin or spin of the nonmagnetic Al cation at the surface of nano-ferrites [26].

Conclusion

Al$_x$Ni$_{0.5-x}$Zn$_{0.5}$Fe$_2$O$_4$ (x = 0.0, 0.1, 0.2, 0.3) nano-crystalline were successfully prepared by the citrate sol–gel method and calcined at 800°C. The formation of single phase spinel structure was observed by X-ray diffraction powder. The obtained crystallite sizes of the prepared nano-ferrites investigated by XRD line broadening was are in the range of 24-32 nm and in good agreement with HR-TEM analysis. The FT-IR spectra confirmed the successful formation of the metal oxide bonds in the prepared nano-ferrites. The saturation magnetization (Ms) and coercivity (Hci) values vary from 47.894-32.314 and 70.37-60.117 G; respectively. The decrease of Ms and Hci values with increasing the Al$_2$O$_3$ content due to the weakening of sub-lattice interactions from the nonmagnetic Al$_2$O$_3$ with the nano-ferrites which lowers the magnetic moment of the unit cell.

Conflicts of Interest

The authors declare no conflict of interest.

References


10. Morriso A. S., Cahill L. C., Carpenter E. E., Calvin S., Swaminathan R., McHenry E. M., Harris G V., Magnetic and structural properties of nickel zinc ferrite nanoparticles synthesized at


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الخواص التركيبية والمغناطيسية للنيكل زنك فريت المطعمة جسيمات الالومنيوم النانومترية و المحضرة بطريقة السائل الجيلاتينى

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المواد المغناطيسية القائمة على النيكل زنك فريت النانومترية المطعمة بتركيزات مختلفة من الالومنيوم و المحضرة بطريقة السائل الجيلاتينى باستخدام مواد اولية في صورة نترات وليست العينات عند درجات مئوية. اختبرت الخواص التركيبية والضوئية للمواد المغناطيسية باستخدام كل من اشعة الحود السينى، الميكروسكوب الالكتروني الماسح و الميكروسكوب الضوئى، و أطيف الأشعة الحمراء. و أظهرت النتائج تكون المادة في طور المكعب للمسامى تحت تأثير زيادة ايونات النحاس. تغير الحجم الذرى من 47.894 الى 32.31 متى من 47.894 متى 32.31 نانومتراً. و ذلك يرجع إلى ان الالومنيوم نانومترى مادة غير مغناطيسية.