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Effect of Sintering Time on the Structural and Optical Properties of $Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$ Nano Spinel Ferrite

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Abstract :

Spinel ferrite with the chemical formula ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$) was synthesized using chemical precipitation method at $600C^0$ with different sintering times (2hr, 4hr, 6hr). The effect of sintering time on the structural and spectral properties was studied using X-ray diffraction(XRD) and spectroscopy techniques(UV-visible), The XRD results showed that all samples have a single-phase cubic spinel crystal structure, and both the lattice constant (a) and the grain size(D_t) increase with increasing sintering time, which is accompanied by a decrease in porosity (P%). As for the optical properties, the results showed that all samples behave normally as semiconductor materials within the wavelength range (200nm - 1100nm). The values of the direct optical energy gap allowed for the samples were calculated, where we notice a decrease in the energy gap value, which is (3.80ev,3.76ev,3.68ev) with increasing sintering time

Keywords: Ni – Al nano Ferrite , Sintering Time ,Structural Properties .

تأثير زمن التلبيد على الخواص التركيبية والبصرية لفرايت النانو سبينل ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$)

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مستخلص:

تم تحضير فرايت الأسبينل ذو الصيغة الكيميائية ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$) بطريقة الترسيب الكيميائي. عند درجة حرارة 600°C . وبأزمان تلبيد مختلفة (2 , 4, 6 hour). أذ تم دراسة تأثير زمن التلبيد على الخواص التركيبية والطيفية . بأستخدام تقنيات حيود الأشعة السينية XRD ومطياف للأشعة المرئية وفوق البنفسجية (UV- visible)، أذ تبين من خلال نتائج حيود الأشعة السينية XRD أن جميع العينات ذات تكوين بلوري مكعبي مغزلي أحادي الطور ،وزيادة كل من ثابت الشبيكة (a) والحجم الحبيبي مع زيادة زمن التلبيد ويقابلها نقصان في المسامية (P%) . أما الخواص البصرية أظهرت النتائج أن جميع العينات تسلك السلوك الطبيعي للمواد شبه الموصلة ضمن مدى الطول الموجي (200nm – 1100nm). أذ تم حساب قيم فجوة الطاقة البصرية المباشرة المسموحة للعينات حيث نلاحظ أنخفاض قيمة فجوة الطاقة وهي (3.80ev ,3.76ev ,3.68ev) مع زيادة زمن التلبيد .

الكلمات المفتاحية : فرايت نانوي(Ni – Al) ،الخواص التركيبية ، زمن التلبيد ، الخواص البصرية .

Introduction

Ferrite compounds are among the most important magnetic ceramic materials that are characterized by their unique properties, such as high electrical resistance and excellent magnetic properties [1-3].Due to these properties, ferrites have become an essential component in various applications, including magnetic storage devices, electrical transformers, electronics, drug delivery systems, sensors, and catalysts[4-6] It is divided according to its crystal structure into three types: garnet ferrite, hexagonal ferrite, and spin ferrite [7], which is the subject of our interest in this research, as the formations of nanocrystalline spinel ferrite play an important role in determining its physical properties at the nano and sub-nano levels. Usually, nanocrystalline spinel ferrite is represented by the general formula (MFe2O4), where M is usually a divalent metal ion (for example, Ni^{+2}, Zn^{+2}, Cu^{+2}, Co^{+2}, Mn^{+2}, etc.) [8] Chemical precipitation is one of the most prominent techniques for preparing ferrites, due to its simplicity and efficiency in controlling the crystal size and structural properties, This method is Distinguished by the fact that it does not require high temperatures and long sintering time, so it is an effective method for preparing homogeneous, smooth and repeatable ferrite at relatively low temperatures. Moreover. It is environmentally friendly, and thus provides a suitable method for producing high-quality nano-ferrite powder [9-10] Ferrite compounds containing multiple ions. Such as ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$), are of particular interest due to the possibility of tuning their structural and spectral properties by controlling the preparation conditions. Among these conditions, sintering time is one of the main factors that greatly affect the crystal size, crystal shape and spectral absorption properties. This research aims to study the effect of sintering time on the structural and spectral properties of ferrite compound ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$) prepared using chemical precipitation method The research aims to study the effect of sintering time on the crystal structure and crystal size using X-ray diffraction (XRD) techniques, And to explore the spectral properties using a spectrometer(UV-visible) by evaluating the effect of sintering time on the spectral behav-

ior. including absorption and electronic transitions using spectral analysis techniques. It is expected that the results of this research will contribute to improving the understanding of the effect of sintering time on the properties of ferrites Which enables the design of more efficient materials for advanced industrial and technological applications,.

Experimental techniques

Materials

Selection of high-purity raw materials used in preparation of nano-ferrite compound ($Ni_{0.25}Zn_{0.25}$ $Al_{0.5}Fe_2O_4$) as shown in **Table (1)**

Table (1): Raw materials used in the preparation of ferrite compound

Material	Chemical Formula	Molar Mass(g/mole)	Origin	(%)Purity
Iron Nitrate	Fe(NO3)3.9H2O	404g/mol	HIMEDIA/INDIA	98%
Aluminum Nitrate	Al(NO3)3.9H2O	375.13g/mol	HIMEDIA/INDIA	99%
Nickel Nitrate	Ni(NO3)2.6H2O	290.795g/mol	HIMEDIA/INDIA	99%
Zinc nitrate	Zn(NO3)2	189.39g/mol	HIMEDIA/INDIA	99%

Sodium hydroxide (NaOH) was prepared as a precipitation auxiliary agent and polyvinyl alcohol (PVA) as a binding material. Laboratory tools were also prepared for the chemical precipitation method and a quantity of distilled water.

Sample preparation

Preparation of raw materials used in the preparation of nano-ferrite . compound. Each substance is dissolved separately by dissolving it in (200 ml) of distilled water at a temperature of $60C^0$ with continuous stirring using a (Magnetic Stirrer) for half an hour until we ensure that the substance is completely and homogeneously dissolved in the water. By following the same previous steps, nickel nitrate, aluminum nitrate, iron nitrate and zinc nitrate are dissolved. After preparing the solutions, we mix all of these solutions in a glass flask at a temperature of ($60C^0$) for half an hour with continuous stirring using a (Magnetic Stirrer) and we check the homogeneity and mixing of the materials and that the mixing temperature affects the elemental union of the prepared compound, then we prepare a solution of sodium hydroxide (NaOH) and its benefit as a

precipitating agent is that we add 40 gm of sodium hydroxide to (400 ml) of distilled water at (60 C^0) with continuous stirring for (15) minutes . we distill the mixture of iron, aluminum, nickel and zinc nitrate solutions using a distillation tube on the sodium hydroxide solution also at a temperature of (60C^0) with continuous magnetic stirring until the iron, aluminum, nickel and zinc nitrate solutions are completely distilled on the sodium hydroxide solution. After measuring the (pH) of the solution, we notice that the solution (pH≈12) Then we wash the resulting solution several times until we get a neutral solution with (pH=7) for all the prepared models, where scales were used to measure (pH) and temperature, as the precipitation temperature and the (pH) factor affect the elemental union of ferrite, as the auxiliary factors such as temperature and pH values are factors for improving the resulting material, as these factors affect the solubility and elemental union after obtaining a neutral solution, it is filtered with filter papers to get rid of the water. Then, we place the material in a drying oven at a temperature of (100C^0) in order to obtain a dry compound free of moisture.

3- Grinding

Grind the resulting powder in an agate ceramic mortar for (30) minutes to obtain a homogeneous powder. After that, we add (3) drops of the binding material polyvinyl alcohol (PVA) and mix it well until it is homogeneous

4-Pressing

Use a hydraulic press to form the samples by pressing with a metal mold with a diameter of (10mm) and a pressing force of (5 tons) for three minutes

5- Sintering

The electric furnace in the laboratory of the Department of Physics, College of Science, Tikrit University, with a range of (1300C^0) was used. The sintering temperature (600C^0) was used with different sintering times (2h, 4h, 6h), where the model was placed in a ceramic (alumina) flask with a tight lid that can withstand a temperature of 1800°C . The models are covered with a powder of the same compound and left until the temperature reaches room temperature. In the sintering process, there is an internal diffusion of adjacent particles where they have the opportunity to concentrate and distribute

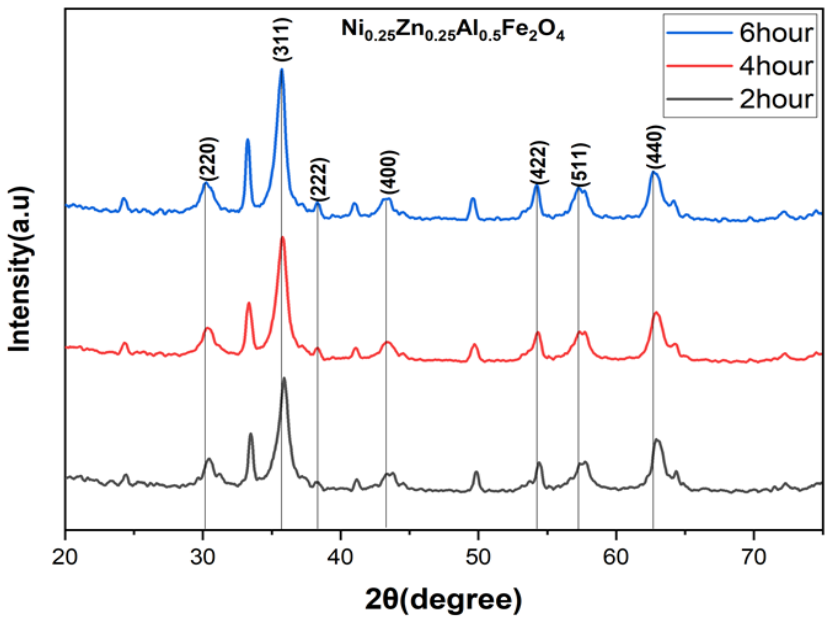
in their places as they stick together, reducing the pores due to the spread of voids on the surface of the sample, where we get a solid and less brittle ceramic model, but its surface is not smooth, as we notice that increasing the sintering temperature reduces the porosity and thus increases the grain size.

Results and discussion:

X-ray diffraction

Figure (1) shows the X-ray diffraction patterns of the ferrite compound with the chemical formula ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$) prepared by the chemical precipitation method at different sintering times (2hr, 4hr, 6hr). The figure shows several diffraction values at Braak angles (2θ). They match the known crystal planes of ferrite and are consistent with the standard card (JCPDS 00-008-0234). The characteristic peaks at (220), (311), (222), (400), (422), (511), (440) are consistent with the cubic crystal structure of spinel ferrite, which indicates good crystallization of the prepared material. With increasing sintering time, we find a decrease in the width of the middle of the peak and an increase in the interspaces. This leads to an increase in the growth of the grain size and an increase in the lattice constant(a). This is what we notice from the improvement of the crystal structure, which is consistent with what the researcher has reached[11].

FIGURE 1. XRD graph of samples at different sintering time



1-The crystal lattice constant for the cubic spinel crystal structure, the interlayer distance (d), the lattice constant (a) and the Miller coefficients (hkl) corresponding to each plane in the sample are related by the following mathematical equation (1) [12].

$$d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

2- the grain size of the samples (Dt) was calculated using Equation (2)(Debye-Sherrer Equation)[13]

$$D_t = \frac{k\lambda}{\beta cos\theta} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

Where:

: K is the formal constant and its value is (0.9)

λ: the wavelength and its value is (1.54060Å)

Θ: Braak angle after multiplying it by (π/180) converted from ((Degree to Radian))

β: the width of the peak at mid-intensity (FWHM)

3-Porosity

For ferrite compounds, the X-ray intensity is calculated by the following relationship (3) [14]:

$$\rho_{x_1} = \frac{8M}{Na^3} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Where

M: molecular weight in gm.

N: Avogadro's number, $6.023X10^{23}mol^{-1}$.

a: is the lattice constant

As for measuring the physical density of all samples, it was done using [the following relationship (4) [15

$$:\rho_b = \frac{m}{v} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

Knowing the values of X-ray intensity and bulk density, the porosity of the samples was calculated using the following relationship (5)[16]

$$P = \frac{\rho_x - \rho_b}{\rho_x} 100\% \dots\dots\dots\dots\dots\dots\dots\dots (5)$$

Where: ρ_x: represents the density in terms of X-ray diffraction

ρ_b : represents the bulk density

Table (2) shows the values of the lattice constant (a), grain size (Dt), true density (ρx), and porosity (P%) at the highest peak of XRD (311). The bulk density (ρb) of the ferrite compound ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$) was also calculated.

Sintering time	2hr	4hr	6hr
2θ(degree)	36.13	35.85	35.62
d-spacing[A^0](d)	2.50333	2.52011	2.53205
FWHM(rad)	0.8710	0.7172	0.5632
Crystallite size(D_t)	9.6nm	11.6nm	14.8nm
Lattice constand(a)	8.30	8.35	8.39
X-ray density(ρ_x)(gm/cm^3)	5.12 g/cm^3	5.05 g/cm^3	4.95 g/cm^3
Bulk density(ρ_b)(gm/cm^3)	2.21g/cm^3	2.28g/cm^3	2.41g/cm^3
Porosity(P%)	56.83	54.58	51.31

Figure (2) shows the relationship between the bulk density and porosity of the ferrite compound at different sintering times. Increasing the sintering time leads to an increase in the bulk density (ρb) and a decrease in the porosity value (P%), as shown in Figure (2). This is consistent with what researchers have concluded[17-18]

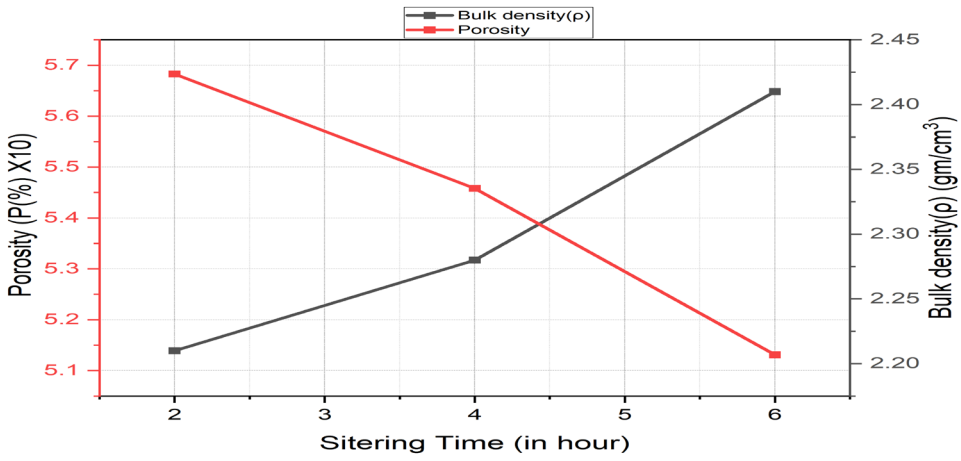


FIGURE 2. The effect of sintering time on both bulk density(ρ_b) and porosity (P)

Spectral characteristics results

Results of spectral properties of the nano-ferrite compound with the chemical formula ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$) prepared by chemical precipitation method at a temperature of 600C0 and

with different sintering times (2hr, 4hr, 6hr). Using a spectrometer(UV-visible). Figures (3) (4) show a decrease in absorbance and absorption coefficient, respectively, with increasing wavelength from 200nm to 1200nm for all samples at all sintering times.This is a common property of semiconductors, where we notice in the wavelength range between (200nm-1200nm), that the sample absorbs photons more at short wavelengths. Then the absorption begins to decrease with increasing wavelength. Figure (5) shows the calculation of the energy gap from the relationship 2(αhυ) versus (hυ) using the (Tauc Plot) diagram, and according to the relationship (6) [19]

$$\alpha h\upsilon = B(h\upsilon - Eg)^{x} \quad \ldots\ldots\ldots \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The linear part was extrapolated to determine the energy gap, where the results showed a decrease in the energy gap values (3.80ev, 3.76ev, 3.68ev) with increasing sintering time. This is due to the growth of the grains and the reduction of porosity, which affects the electronic structure and leads to a reduction in the energy gap. This is consistent with the researcher [20,21]. These results indicate that controlling the sintering time can be an effective tool for controlling the optical properties of the material. This may be useful in optics and electronics applications.

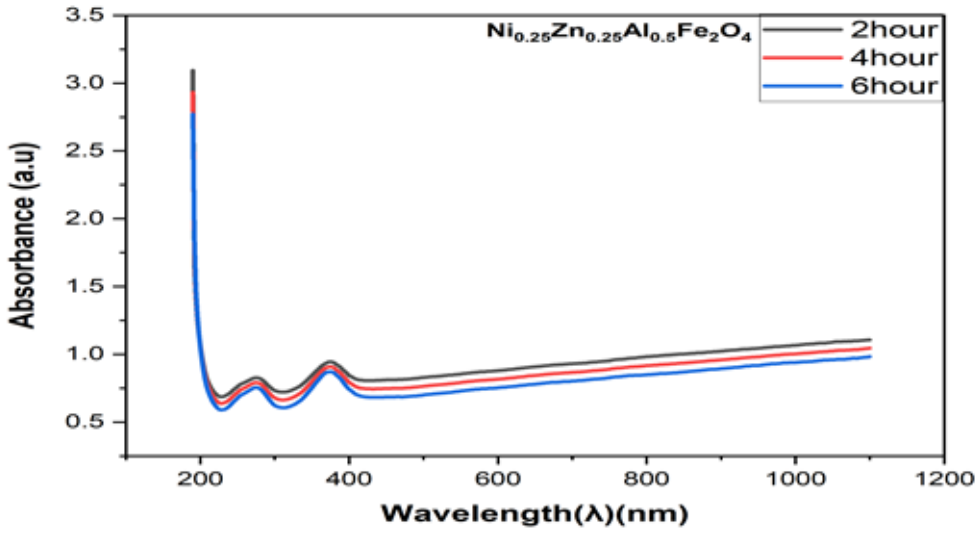


FIGURE 3. Change of absorbance with photon wavelength

FIGURE 4. Change of absorbance coefficient(α) with photon wavelength

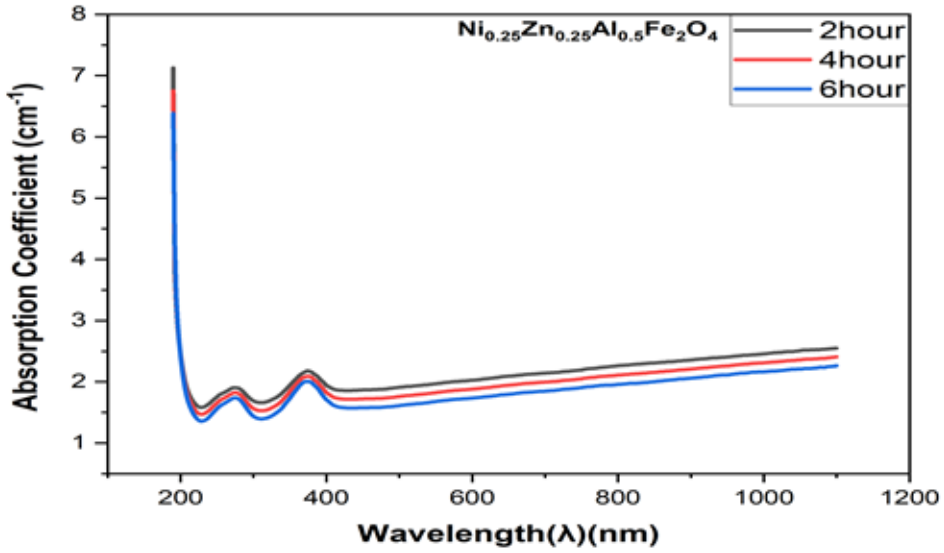
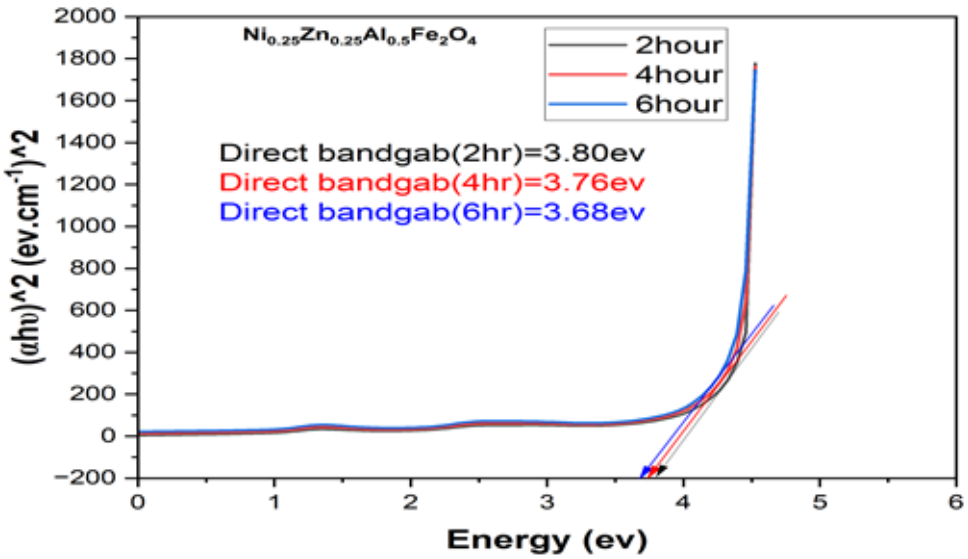


FIGURE 5. The amount of energy gap at different sintering time



Conclusion

In this research, the effect of sintering time on the synthetic and optical properties of Ferrite nanocomposites was studied by chemical formula ($Ni_{0.25}Zn_{0.25}Al_{0.5}Fe_2O_4$) prepared by chemical precipitation method was studied. The results showed that increasing the sintering time leads to fundamental changes in the structure and optical properties of the material, where an increase in the grain size was observed, reflecting the growth of crystalline grains as a result of thermal sintering .This also led to a decrease in porosity, indicating an improvement in

crystalline compactness and a reduction in gaps between grains. Spectrally, the energy gap was calculated using (Tauc plot). It was found that the energy gap decreases with increasing sintering time, which can be explained by the increase in grain size and the decrease in boundary dispersion between grains, which affects the electronic structure of the material.. This study confirms that the setting of the sintering time is a crucial factor in controlling the synthetic and optical properties of ferrite nanocomposites, which opens the way for their use in various applications such as electronic devices, sensor materials, and magnetic applications. The study recommends further research on the influence of other factors such as sintering temperature or the addition of new elements to explore further possible improvements in the properties of these materials.

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