

Structural Properties of Zinc Aluminate $ZnAl_2O_4$ Compound

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ABSTRACT

Zinc Aluminate, $ZnAl_2O_4$ is prepared using the double sintering heating which is known as the ceramic method at high temperatures 1000 C° . The structural properties are studied using the X-ray and Infrared techniques at room temperature. It was found that the compound has the spinel face centered cubic structure by showing the diffractions from the main crystalline planes of the spinel structured. The infrared spectrum shows the main absorption bands for the tetrahedral and octahedral sites. The lattice constant, " a_{hkl} ", is calculated using Bragg's equation and found to be equal to (8.0573Å) . The force constants, the average crystallite size, densities and the porosity are calculated using the X-ray and Infrared results.

Keywords: Spinel structure, Sintering heating, X-ray, Infrared.

الخصائص التركيبية لمركب ألومينات الخارصين $ZnAl_2O_3$

المخلص

تم تحضير مركب ألومينات الخارصين بطريقة المعالجة الحرارية المزدوجة المعروفة بالطريقة السيراميكية عند درجات حرارية عالية 1000 C° . تم دراسة الخصائص التركيبية لمركب ألومينات الخارصين باستخدام تقنية الأشعة السينية والأشعة تحت الحمراء في درجة حرارة الغرفة. أوضحت نتائج الدراسة امتلاك المركب الناتج لتركيب السبينل المكعب متمركز الأوجه. حيث ظهرت انعكاسات المستويات البلورية الرئيسية في طيف حيود الأشعة السينية الدالة على هذا التركيب. كما ظهرت حزمًا امتصاص الأشعة تحت الحمراء الرئيسيتين الدالتان على مواقع رباعي السطوح ومواقع ثماني السطوح في تركيب السبينل. تم حساب ثابت الشبكة البلورية باستخدام معادلة براك ووجد بأنها مساوية إلى (8.0573 Å) . كذلك تم توظيف نتائج طيف الأشعة تحت الحمراء في حساب ثوابت القوة في المواقع البلورية المختلفة مواقع رباعي السطوح ومواقع ثماني السطوح. كما تم حساب حجم البلورات الصغيرة والكثافة النظرية والعملية وحساب المسامية.

الكلمات الدالة: تركيب السبينل، المعالجة الحرارية، الأشعة السينية، الأشعة تحت الحمراء.

INTRODUCTION

Recent decades have witnessed a wide interest and very active search for spinel compounds (Ferrites, Aluminate and others). This is due to the fact that these materials have excellent synthetic, electrical and magnetic properties. They can be used in industrial applications such as permanent magnets, magnetic recording devices, electronics, communications and by Core transformers (Snelling, 1988) (Sugimoto, 1999).

Another advantage of this material is the ability to control these properties by changing the elements involved in the installation of these materials. The general chemical formula of these materials can be represented as AB_2X_4 . ($A^{2+} = \text{Co, Ni, Cu, Mg, Zn, ...}$), while **B** represents a trivalent metal such as iron, nickel, chrome, aluminum, manganese and others ($B^{3+} = \text{Fe, Cr, Al, ...}$).

Ni, Mn,...). And X is a bivalent metal, such as oxygen, sulfur, selenium, tellurium and others ($O^{2-} = O, S, Se, Te, \dots$).

The normal spinel cell unit contains 32 Oxygen ions O^{2-} in a face center cubic lattice. Oxygen is penetrated by 32 cations in octahedral locations and there are 64 sites in tetrahedral locations. While 1/8 binary sites occupied tetrahedral positions, and the trivalent cations occupied 1/2 sites of the eight octahedral or octahedral positions (Snelling, 1988).

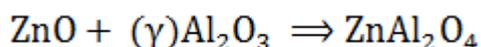
The compound under this study zinc aluminate $ZnAl_2O_4$ is found in nature and is known as Gahnite metal (Mineralogy Database, 2001-2005). This compound is one of the wide-band gap semiconductors which are used in metal and alloy reinforcement industry to provide durability against most reactions. It has also become technically important because of its optical properties, as it has an optical band gap equal to (3.8-3.9) eV, Making it very suitable in the hardware industry of photo-electronic devices operating in ultraviolet frequency range. It was also used in the manufacture of ceramics and electrodes due to its high mechanical and chemical properties (Martin, 2010). The electronic composition of this compound and the calculation of the energy gap of the spinel compounds were studied and found to be equal to 4.11 eV (Sampath, 1999).

Most studies have shown that zinc ions prefer to be found in tetrahedral locations and that aluminum ions prefer to be present at eight surface locations. The distribution of different cations in different locations depends greatly on the conditions such as methods of heat treatment, temperature, duration of heating, concentration of these cations and others. It has been demonstrated practically and theoretically that the $ZnAl_2O_4$ compound favors normal spinel synthesis. The structure of this compound will be treated as a (Normal Spinel) structure. The divalent zinc ions occupy the four-tetrahedral positions and the trivalent aluminum ions act as the octahedral sites. This is supported by most studies on the composition of the substance (Hill, 1979) (Standley, 1962).

As this study using X-Ray Diffraction (XRD) and Infrared (IR) spectroscopy are important scientific research methods in investigating the structure properties of materials. Through using of X-Ray Diffraction technology, the crystalline structure can be determined by calculating lattice constants of materials and by calculating the small size of these materials (Crystallites). Besides Infrared Absorption Technique clearly shows numbers and types of frequencies at which the absorption of the radiation occurs between the chemical bonds of atoms. By using these frequencies we can calculate force constants between ions with different chemical equivalents such as zinc, aluminum and oxygen ions in this compound.

EXPERIMENTAL PART

Zinc aluminate samples were prepared by using (Ceramic double sintering method). By taking the appropriate weights from the primary oxides of zinc oxide ZnO and aluminum oxide Al_2O_3 in the ratio of 1:1 and then grinding and mixing ingredients well so as to increase the degree of homogeneity. The mixture then placed in a ceramic crucible in the furnace at $1000\text{ }^\circ\text{C}$ for 24 hours and then gradually cooled to room temperature. Repeat the grinding and mixing process again. At this stage a quantity of material is taken and a disc is brought with a piston and under high pressure. This disc will be used later in calculating the practical density for comparison with the theoretical density and then calculating the porosity. The heating is returned at a relatively higher temperature of $1100\text{ }^\circ\text{C}$ for 24 hours, Gradually cooled to room temperature. The chemical reaction between ZnO and aluminum oxide Al_2O_3 expected as following:



Quantities of the resulting material are taken for the purpose of studying the (X-Ray diffraction) spectra and Infrared Spectrum. X-Ray sample was prepared by placing a quantity of powder on a glass slide placed in the X-Ray diffraction by type Phillips PW1820 diffract meter with ray source $\text{CuK}\alpha$ and the wavelength ($\lambda = 1.5404 \text{ \AA}$) in the range of angles 5° to 70° . And by mixing a small amount of powder with a quantity of KBr powder and mix well and then be compressed into a disk with a thickness of up to 1mm placed in infrared device type PERKIN-ELMER-1430.

RESULTS AND DISCUSSION

The X-Ray diffraction spectrum of ZnAl_2O_4 shown in Fig. (1), of the main reflections of the crystal levels known for spinel compounds in the range of reflection angles ($5^\circ - 70^\circ$). Table (1) illustrates these levels and reflection angles 2θ , intensity, the value of crystal lattice, and the mid width reflection (Full width at half maximum, FWHM).

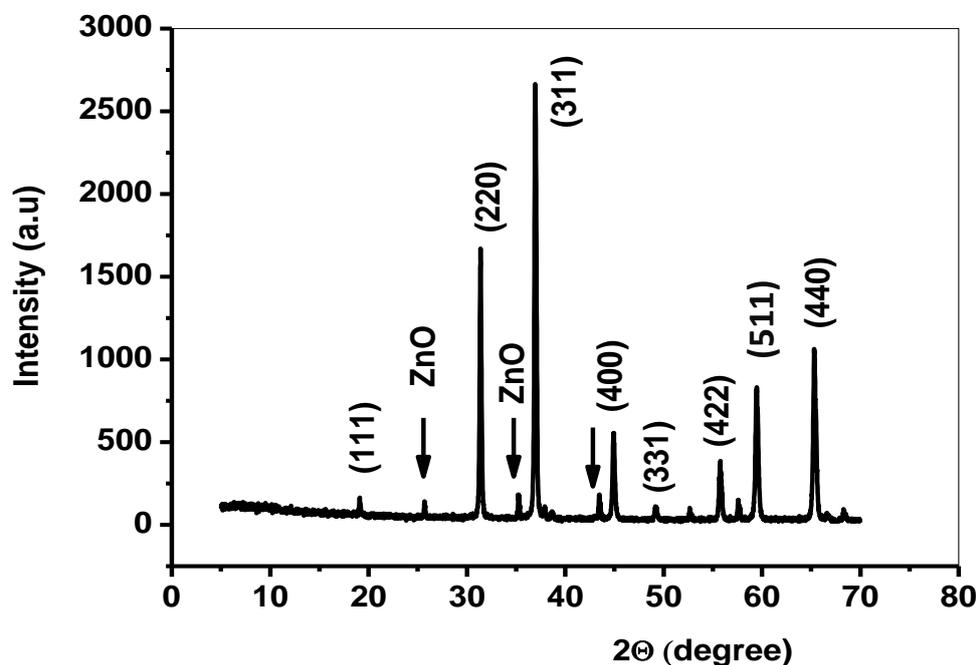


Fig. 1: X- Ray diffraction spectrum of ZnAl_2O_4 sample

The analysis of (X-Ray diffraction) explain that the main grains orientations of spinel formation found as (111), (220), (311), (400), (331), (422), (511) and (440) planes at 2θ values equal to 19.1° , 31.4° , 36.9° , 44.9° , 49.2° , 55.8° , 59.4° and 65.5° respectively. It also shows that there are traces and low percentages of zinc oxide ZnO . These results are consistent with the results of other studies on the same article (Martin, 2010) (Ciupina, 2004).

The value of lattice constant (a_{hkl}), a is calculated using Bragg's equation in the diffraction per peak of the spectrum (Cullity, 1978):

$$a_{(hkl)} = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta_{(hkl)}}$$

Table (1) shows that the values of (a_{hkl}) for each set of detraction crystalline levels of X-rays. The average of these values is equal to 8.0573 \AA . This value is very similar to other values obtained by other researchers and are equivalent to 8.086 \AA and 8.066 \AA (Gama, 2009). When

compared with its counterpart in the natural spinel compound, Zinc Ferrite $ZnFe_2O_4$, which is equivalent to 8.4041 Å (Suman, 2007) it is found to be less due to the difference between the radius of the iron ion (0.67 Å) and the radius of the aluminum ion (0.54 Å).

Table 1: The values of (a_{hkl}) for each set of Diffraction crystalline planes of X-Rays

2θ	(hkl)	Intensity	Sin θ	a_{hkl} (Å)
19.1057	111	165	0.16587	8.0357
31.3884	220	1669	0.27037	8.0507
36.9366	311	2666	0.31663	8.0612
44.9413	400	557	0.38320	8.0579
49.1860	331	112	0.41597	8.0644
55.7702	422	388	0.46748	8.0651
59.4467	511	815	0.49558	8.0693
65.4794	440	689	0.54058	8.0537
			Average	8.0573

The study also examined the measurement of Infrared spectrum of Zinc aluminate, $ZnAl_2O_4$ in the frequency range (400-1000 cm^{-1}). Fig. (2) and (Table 2) show the infrared spectrum of the Zinc Aluminate $ZnAl_2O_4$ and shows that there are four frequencies with a clear Infrared absorption. They are at (668, 559, 508, 463) cm^{-1} wave number [First frequency ν_1 at (668 cm^{-1}), second frequency ν_2 at (559 cm^{-1}), third frequency ν_3 at (508 cm^{-1}) and the fourth frequency ν_4 at (463 cm^{-1})]. (But the frequency ν_0 at higher value than the other frequencies (850 cm^{-1}) is due to the effects of the presence of traces the compound ZnO) (Mineralogy Database, 2001-2005).

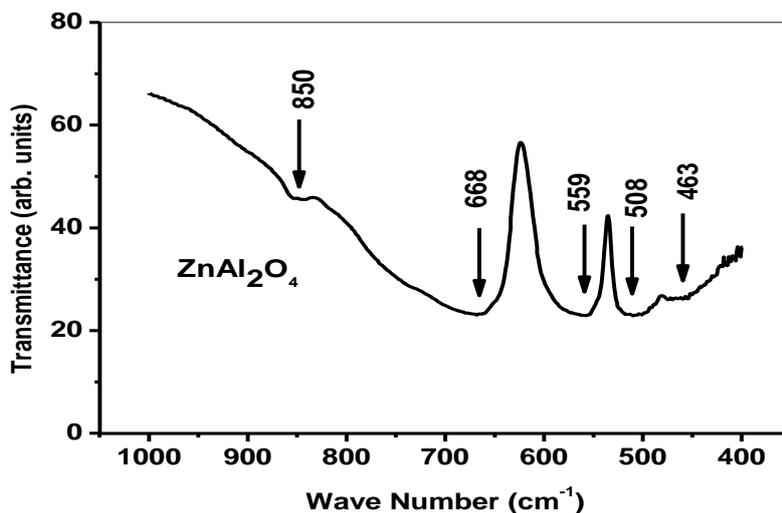


Fig. 2: IR spectrum of $ZnAl_2O_4$

Table 2: Values of the absorption frequencies of the Infrared the sample $ZnAl_2O_4$

Absorption Band	Y_0	Y_1	Y_2	Y_3	Y_4
Wave Number (cm^{-1})	850	668	559	508	463

Many studies on the spectrum of infrared absorption in spinel compounds have shown that they are due to:

First frequency ν_1 : This frequency is primary and is due to the vibration of the divalent ion bonds (or triangular) with oxygen in the tetrahedral locations. Second frequency ν_2 : This frequency is also major and is due to the vibration of three - valence bonds (or binary) with oxygen in octagonal locations. The third frequency ν_3 is due to bi-metal vibrations with oxygen at eight-surface locations. The fourth frequency ν_4 depends on the mass of the divalent ion vibration in the tetrahedral location (Modi, 2006).

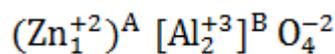
The appearance of the first and second main frequencies is often cited as one of the main and important evidence of the complete spinel composition, the formation of the four-tiered subsystem and the eight-branch subsystem in the structure of the cell unit. The values of the first beam are higher than the values of the second beam, indicating that the bonds between the oxygen ions and the metal ions in the tetrahedral locations are shorter than those of the eight surfaces.

The main absorption frequency values can be used to calculate the average stress values of K_t and K_o between the ions in the tetrahedral and octahedral locations using the following relationships (Modi, 2006):

$$K_t = 7.62 M_1 \nu_1^2 \cdot 10^{-3} \text{ (dyne/cm)}$$

$$K_o = 5.31 M_2 \nu_2^2 \cdot 10^{-3} \text{ (dyne/cm)}$$

Where ν_1 , ν_2 , M_1 and M_2 represent the absorption frequencies and the molecular mass rate in the tetrahedral and octahedral locations, respectively. The values of the molecular masses were calculated according to the distribution of ions between the sites mentioned on the basis that the aluminate of zinc is a natural spinel, that is, the distribution of cations takes the following formula:



The brackets ()^A and []^B represent the positions of the tetrahedral and eight surfaces, respectively. The values of M_1 , M_2 , K_t and K_o were equals to **65.926 g/mol**, **53.963 g/mol**, **2.155×10^5 dyne/cm** and **0.8954×10^5 dyne/cm**, respectively.

The information available from the X-ray reflection can be used to calculate D_{hkl} the average size of the small crystalline space between plane of the compound using following equation (Cullity, 1978):

$$D_{hkl} = \frac{K \lambda}{\beta_{hkl} \cos \theta_{hkl}}$$

Where K represents a fixed quantity and is often taken as equal to (0.9) and λ represent the wavelength of X-ray used equal to (1.5405 Å), and β_{hkl} , represents the maximum reflection width at maximum half values (FWHM; Full width at half maximum) at the angle, θ_{hkl} and the rate of display of small crystals D_{hkl} . Using the main reflection of the X-ray diffraction spectrum (311) at the angle 2θ is equal to (36.937°) as shown in Fig. (3), we found the value of D_{hkl} is equal to about (41 nm). A smaller size was obtained equal to (34 nm), (11 nm) (Ciupina, 2004) and (20 nm) (Gama, 2009) from samples prepared using different methods. It is known that the method of heat treatment in the preparation of samples often results in the size particles relatively large when compared with other preparation methods, because these samples show an increasing tendency for Zn to order into A sites to form a big normal spinels. (Henderson, 2007).

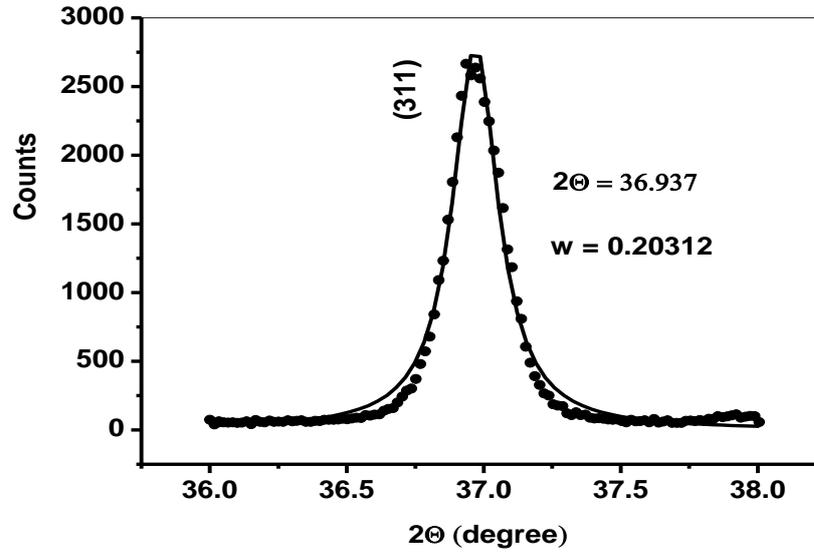


Fig. 3: The greatest diffraction of X-Ray in (311) direction

Beside the physical density can also be calculated the density XRD by using the following relation (Cullity, 1978):

$$\rho_{\text{XRD}} = \frac{8M}{N_A a}$$

Where M represents the molecular weight of the sample (**181.3403 g/mol**), N_A represents Avogadro's number (6.02×10^{23}) and $a_{(hkl)}$ is the measured lattice constant using X-Ray Diffraction data (8.0307 Å). It was found that the theoretical density value equal to **4.653 g/cm³**.

The experimental density of material been used was calculated by finding a circular disk mass, the radius r and thickness t then applying the following equations:

$$V = \pi r^2 t$$

$$\rho_{\text{EXP}} = \frac{m}{V}$$

It was found that the density value is equal to 1.876 g/cm³. When comparing the densities, the theoretical density is higher than the practical density. This is due to the fact that the sample prepared in practice contains internal pores. Theoretically observed that band gap increase with the increase in the concentration of Zn suggests that the structural change occurring in the composite is responsible for such a variation (Joshi, 2003).

The porosity value, P_o can be calculated by applying the following equation (Cullity, 1978):

$$P_o = \left(\frac{\rho_{\text{XRD}} - \rho_{\text{EXP}}}{\rho_{\text{XRD}}} \right) 100 \%$$

It was found that the porosity value is equal to 60%. This means that this sample contains component defects and it is porous as is the case with other type of components ferrite.

CONCLUSIONS

The main findings of this study can be summarized as follows:

1. Zinc aluminate $\text{Zn Al}_2\text{O}_4$ was prepared using dual heat treatment method and high temperature. X-Ray measurements have shown that the quadrilateral spinel structure is positioned by the

appearance of crystalline reflections on the structure. The cubic chain constant was calculated and found to be equal to 8.0573 Å.

2. The IR spectrum also showed the two main absorption bands, ν_1 and ν_2 . The functions on the composition of the tetrahedral structure and the eight-brightness installation in the complete spinel structure. The value of ν_1 equal to 685 cm^{-1} , which was due to vibrations of the Zn^{2+} - O^{2-} bonds in the tetrahedral locations. While the value of ν_2 equal to 569 cm^{-1} was attributed to the vibrations of the Al^{3+} - O^{2-} bonds in octagonal locations. As well as other absorption frequencies.
3. The force parameters were calculated in the tetrahedral and octagonal sites using IR results and found to correspond to their values for this type of compound (10^5 dyne/cm).
4. The size of the small crystals in this compound was calculated by using the results of dental rays and found to be equal (41 nm). This value is considered a nature in this type of compounds and heat treatments.
5. The theoretical and practical densities of the sample and the porosity were calculated. These calculations showed that the sample contains structural defects and that it is porous with a large scale and about 60% as well as this type of compound.

REFERENCES

- Ciupina, V.; Carazeeanu, I.; Prodan, G. (2004). Characterization of ZnAl_2O_4 nanocrystals prepared by coprecipitation and microemulsion techniques. *J. Optoelect. Advanc. Mater.*, **6**, 1317-1322.
- Cullity, B.D. (1978). Elements of X-ray Diffraction. *Addison Wesley*.
- Gama, L.; Ribeiro, M.A.; Barros, B.S.; Kiminami, R.H.A.; Weber, I.T.; Costa, A.C.F.M. (2009). Synthesis and characterization of the NiAl_2O_4 , CoAl_2O_4 and ZnAl_2O_4 spinels by the polymeric precursors method. *J. Alloy. Comp.* **483**, 453 – 455.
- Henderson, C.M.B.; Charnock, J.M.; Plant, D.A. (2007). Cation occupancies in Mg, Co, Ni, Zn, Al Ferrite spinels: a multi-element EXAFS study. *J. Phys. Condense. Matter.*, **19** (076214), 25.
- Hill, R.J.; Craig, J.R.; Gibbs, G.V. (1979). Systematic of the spinel structure type. *Phys. Chem. Miner.* **4**, 317–339.
- Joshi, G.P.; Saxena, N.S.; Mangal, R.; Mishra, A.; Sharma, T.P. (2003). Band gap determination of Ni–Zn ferrites. *Bull. Mater. Sci.*, **26**(4), 387–389.
- Martin, R.F.; Serra, O.A. (2010). Thin film of ZnAl_2O_4 : Eu^{3+} synthesized by a non-alkoxide precursor sol-gel method. *J. Braz. Chem. Soc.*, **21**, 1395-1398.
- Mineralogy Database, Mineral Data Publishing, version 1, (2001-2005).
- Modi, K.B.; Trivedi, U.N.; Sharma, P.U.; Lakhani, V.K.; Chhantbar, M.C. (2006). Study of elastic properties of fine particles Copper-Zinc ferrites. *Ind. J. Pure. Appl. Phys.* **44**, 165-168.
- Sampath, S.K.; Kanhere, D.G.; Pandey, R. (1999). Electronic structure of spinel oxides: Zinc Aluminates and Zinc Gallate. *J. Phys.: Condens. Matter.*, **11**, 3635-3644.
- Snelling, E.C. (1988). "Soft Ferrites: Properties and Applications". 2nd ed. Butterworth-Heinemann.
- Standley, K.J. (1962). "Oxide Magnetic Materials". Clarendon Press, Oxford.
- Sugimoto, M.; Ceram, J. A. (1999). The past, present and future of ferrites. *J. Phys. Condens. Matter.*, **82**, 269-280.
- Suman, R.L.; Sharma, N.D.; Taneja, S.P.; Reddy, V.R. (2007). Structural and magnetic properties of Zinc Ferrite Aluminates. *Ind. J. Pure Appl. Phys.*, **45**, 231-237.