# β- structure properties of Zn-Phthalocyanine organic semi-conductor

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## Abstract:-

The x-ray fluorescence (XRF) of Znpc molecule with (flow of Ar) and Znpc molecule with (grow in $N_2$) showed two peaks at (8.5and 9.5 Kv) referring to orbital transition ($K_\alpha$-shell & $K_\beta$-shell) respectively.

The study of x-ray diffraction (XRD) where it was observed good growth of the crystal structure as a needle by the sublimation technique with a β-phase of (monoclinic structure ) . Using Bragg equation the value of the interdistance of the crystalline plane (d-value) were calculated. We noticed good similarity with like once in the American Standards for Testing Material (ASTM) .Powder Diffraction File (PDF) Program was used to ensure the information obtained from (ASTM) . The output of (PDF) was compared with celn program, where the value of angle(2θ) , crystal axis (a,b,c) and axial angles (α,β,γ) were calculated.

The partical grain size of $H_2PC$ was between (27-35)nm, while for ZnPC was between (17-50)nm by applying of Schreer equation. The results are in a good agreement with c-size program.

The morphology was distinguished by optical microscope of (200X) magnification for a tini-fiber like a (whisker needle type) with blue color, porous nature and short term structure. The diameter of the fiber $H_2PC$ and ZnPC were (20 and 16μm) respectively.


## Introduction

Phthalocyanines are widely used as charge generation materials in solid-state devices such as solar cells and electro-photographic copiers and printers as well as a gas sensor.(1)

As most organic compounds have an appreciable vaopur pressure below their melting point, it is possible to purity and crystallize these compounds by the vapour transport method. (2,3)

Linsted and Lowe(4), Heilmeier and Harrison (5) and Hamann (6) have used the vaopur transport method for growth of the most stable.

β- modification of phthalocyanine, their methods included the transportation of the subliming phthalocyanine molecule by an inert gas (such as Ar, $N_2$, $Co_2$) from the heating furnace to the growth zone, where the vaopur is condensed as single crystals. The process of sublimed material in the presence of flowing gas is named entainer sublimation.

The sublimation technique takes advantage of a special characteristic at phthalocyanine compounds, namely that is proceeds directly from that vapour phase to the solid phase when it crystallizes(7&8). An additional advantage of the sublimation technique is that impurities are removed if the impurities have vaopur pressures different from those of phthalocyaniine compounds.

## Experimental

Phthalocynine metal free (95% dye content) and zinc phthalocynine (97% dye content) were obtained from Aldrich

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chemical company and were used as received.

XR.Fluorescence Oxford instrument model MSOO5. VI was used to find the concentration of the zinc metal in phthalocynine and any other impurity. X-ray diffraction instrument from philps company was also used to find the crystal plane (hkl).

Finally Nikon-Eclipse ME600 optical-microscope was also used to study the morphology of the whisker needle type of (phthlocynine & zinc-phthalocynine crystal with 200X magnification.

## Results and Discussion

X-ray diffraction (XRD) of phthalocynine metal free show a good growth of the crystal structure as a needle by the sublimation technique with a β-phase of monoclinic structure as shown in Fig. (1).

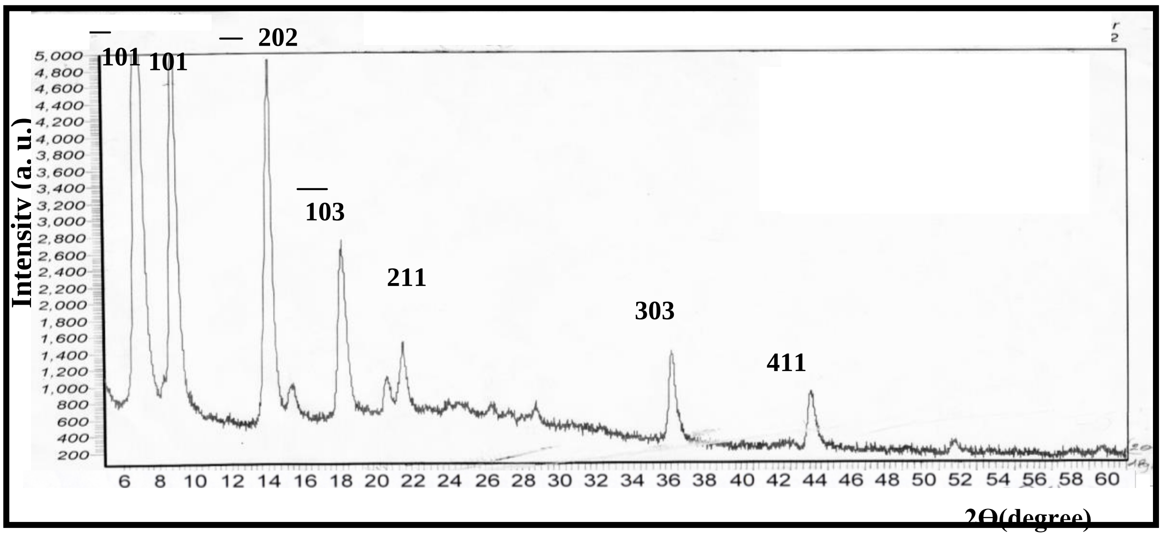
The experimental results of the (XRD) of phthalocyanine metal free parameters (hkl, 2θ,d) are in a good agreement with the theoretical study as calculated by using (Celen, PDF) program as shown in table (1,2) respectively.

Fig. (2) shows the X-ray fluorescence (XRF) of zinc in ZnPc molecule with (flow of Ar) and zinc in ZnPc molecule with (grow in $N_2$) showed two peaks of zinc metal at (8.5 and 9.5 Kv) referring to orbital transition ($K_\alpha$ -shell & $K_\beta$ -shell) respectively.

Fig. (3) shown the X-ray diffraction of zinc-phthalocyanine were it was observed good growth of the crystal structure as a needle by the sublimation technique with a β-phase of monoclinic structure. From calculation the value of the interdistance of the crystalline plane (d-value) using Bragg equation, we noticed good similarity with like once in the American Standard for testing material (ASTM) powder diffraction file (PDF) program was use to ensure the information obtained from (ASTM). The output of (PDF) was calibrated with celen program as shown in table (3 & 4) respectively.

The partical grain size of $H_2Pc$ was between (27-35)nm, and for ZnPc was between (17-50)nm by applying of Schreer equation as shown in Fig. 4a-1 and Fig. 4b-3 respectively. The result are in good agreement with c-size program.

The morphology was distinguished by optical microscope of (200X) magnification like a (Whisker needle type) with blue color, porous nature and short term structure as shown in Fig. 4b-5. The diameter of the needle $H_2Pc$ and ZnPc were (20 and 16μm) as shown in Fig 4a-2 & Fig. 4b.4 respectively.



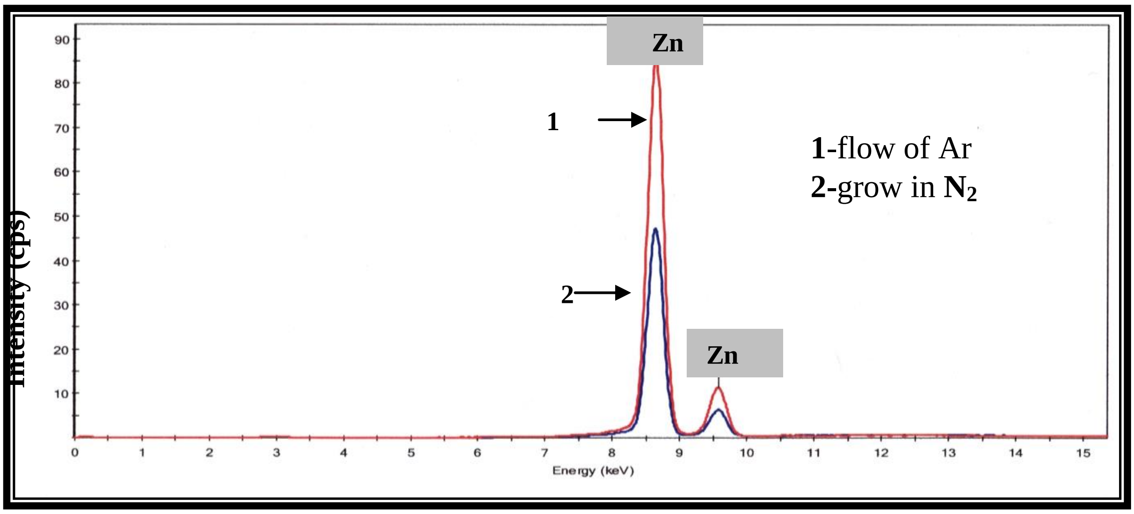

**Fig(1)X-ray diffraction of pthalocyanine metal free**

**Table(1)X-ray diffraction of pthalocyanine metal free parameters**

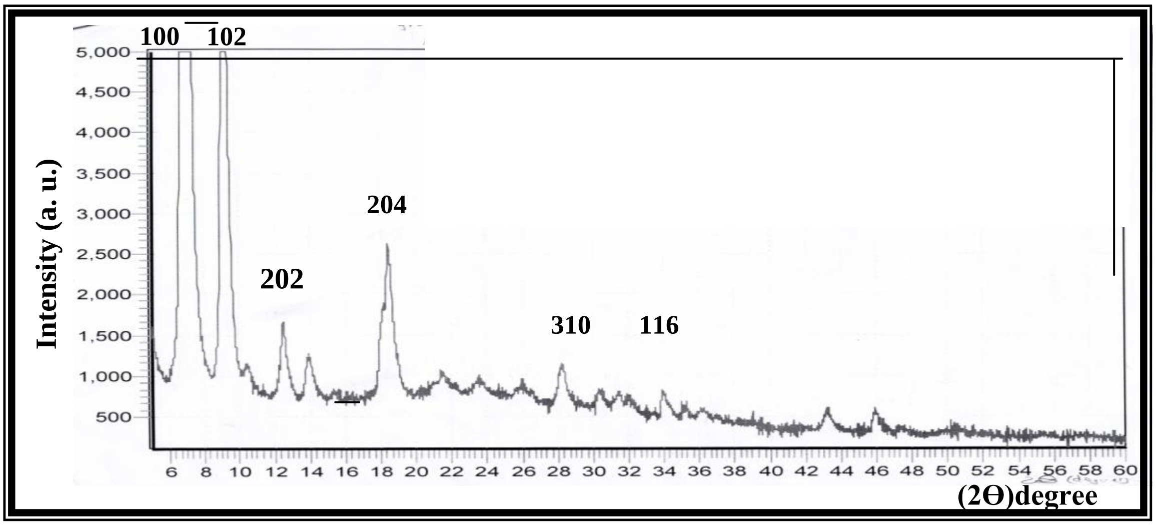
| 2Θ (degree) | h k L | Intensity (a.u.) | d(A°) | d(A°) ASTM | Error percentage between d(A°)& d(A°) ASTM |
|---|---|---|---|---|---|
| 7 | (101) | 5.000 | 13.01 | 12.8 | 0.016 |
| 8.74 | (101) | 5.000 | 10.10 | 9.64 | 0.045 |
| 14 | (202) | 4.900 | 6.351 | 6.35 | 0.00015 |
| 18 | ( 103) | 2.700 | 4.961 | 4.95 | 0.0022 |
| 21 | (211) | 1.500 | 3.763 | 3.83 | 0.017 |
| 35.85 | (303) | 1.400 | 3.153 | 3.25 | 0.030 |
| 43 | (411) | 1.000 | 2.521 | 2.98 | 0.18 |

**Table (2) Shown the value of the Miller indices, angles (2θ) and the error percentage for the pthalocyanine metal free molecule**

| Miller indices hkl | 2θ by (PDF) | 2θ by (Celn) | 2θ by (XRD) | Error percentage XRD & Celn | Error percentage XRD & PDF |
|---|---|---|---|---|---|
| (101) | 9.166 | 9.200 | 8.74 | 0.46 | 0.426 |
| (201) | 13.047 | 13.520 | 13.9 | 0.38 | 0.853 |
| (300) | 15.985 | 15.977 | 15.1 | 0.877 | 0.885 |
| (103) | 20.446 | 20.888 | 20.3 | 0.588 | 0.146 |
| (211) | 23.205 | 23.219 | 23.6 | 0.381 | 0.395 |
| (004) | 25.135 | 25.352 | 25.9 | 0.548 | 0.765 |
| (402) | 27.165 | 27.166 | 27.9 | 0.734 | 0.735 |
| (303) | 27.420 | 27.43 | 28.2 | 0.77 | 0.78 |
| (411) | 29.960 | 29.951 | 29.1 | 0.851 | 0.86 |
| (403) | 31.589 | 31.581 | 31.9 | 0.319 | 0.311 |




**Fig(2)XRF of zinc phthalocyanine with 1-flow of Ar & 2-grow in $N_2$**




**Fig(3)X-ray diffraction of Zinc-pthalocyanine**

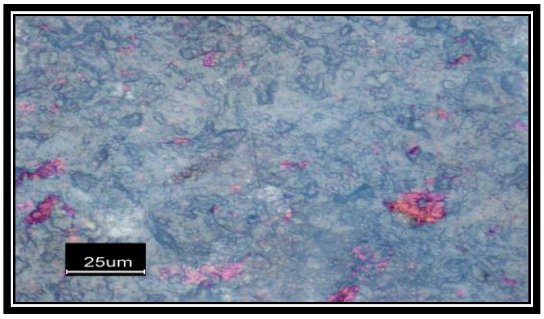
**Table(3)X-ray diffraction of zinc-phthalocyanine parameter**

| 2Θ(degree) | h k L | Intensity (a.u.) | d(A°) | d(A°) ASTM | Error percentage between d(A°)& d(A°) ASTM |
|---|---|---|---|---|---|
| 6.8 | (100) | 5.000 | 12.9 | 12.6 | 0.023 |
| 9.0 | (102) | 5.000 | 9.720 | 9.49 | 0.023 |
| 12.51 | (202) | 1.600 | 7.084 | 7.02 | 0.0090 |
| 18.74 | (204) | 2.600 | 4.810 | 4.73 | 0.016 |
| 28.01 | (310) | 1.100 | 3.16 | 3.18 | 0.006 |
| 34.5 | (116) | 900 | 2.552 | 2.59 | 0.014 |

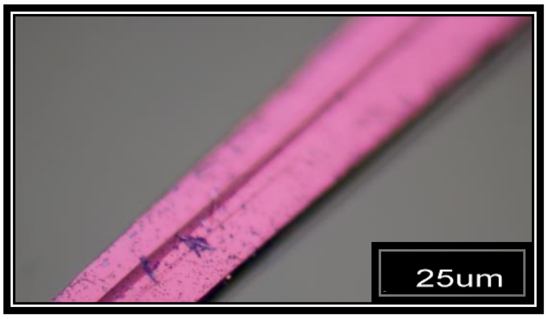
**Table(4)Shown the value of the Miller indices, angles (2θ) and the error percentage for the Zinc- pthalocyanine molecule**

| Miller indices hkl | 2θ by (PDF) | 2θ by (Celn) | 2θ by (XRD) | Error percentage XRD & Celn | Error percentage XRD & PDF |
|---|---|---|---|---|---|
| (100) | 7.010 | 7.000 | 6.8 | 0.2 | 0.21 |
| (002) | 10.650 | 10.601 | 10.3 | 0.301 | 0.35 |
| (200) | 14.068 | 14.005 | 13.9 | 0.105 | 0.168 |
| (102) | 15.451 | 15.423 | 15.3 | 0.123 | 0.151 |
| (012) | 21.136 | 21.120 | 21.4 | 0.28 | 0.264 |
| (013) | 24.299 | 24.100 | 24.6 | 0.5 | 0.301 |
| (400) | 28.036 | 28.020 | 28.1 | 0.08 | 0.064 |
| (311) | 30.591 | 30.441 | 30.3 | 0.141 | 0.291 |
| (204) | 31.249 | 31.223 | 31.4 | 0.177 | 0.151 |
| (006) | 32.172 | 32.160 | 31.8 | 0.36 | 0.372 |
| (015) | 32.533 | 32.521 | 32.1 | 0.421 | 0.433 |

(a)

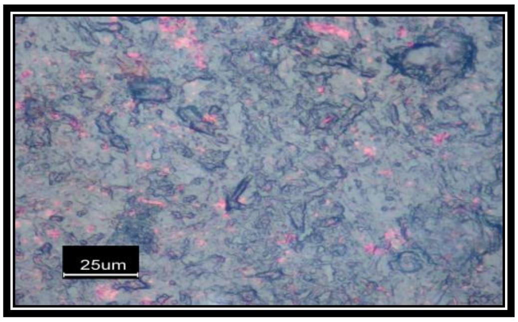



1. $H_2Pc$ with KBr

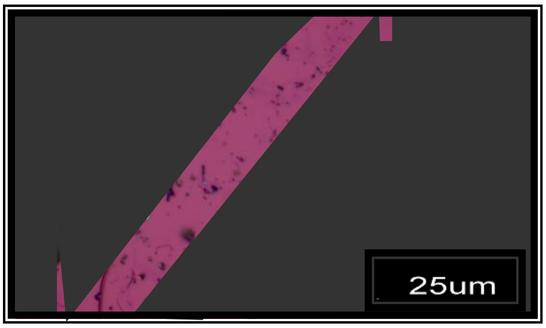



2. 20µm with (200X) magnification

(b)




3. ZnPc with KBr




4. 16µm with (200X) magnification

5. (ZnPc) as whisker needle type

**Fig (4): Shown the optical microscope of**

**a-1.$H_2PC$ with KBr as a disc,2.$H_2PC$ as tini fiber of(200X) magnification**
**b-3.ZnPC with KBr as a disc,4.ZnPC as tini fiber of(200X)magnification**
**5.Phthalocyanine with Zinc(Znpc)as whisker needle type**

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# دراسة الخواص التركيبية للفثالوسيانين -خارصين كشبه موصل عضوي

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**الخلاصة**

تم قياس طيف فلورة الاشعة السينية(XRF) للنموذج(Znpc) المعامل بالاركون (Flow of Ar) والذي يوضح قمتين مختلفتين الشدة وعند طاقتين بحدود(8.5،9.5 كيلوفولت) والمتمثلة بالانتقال المداري ($K_\alpha$-shell) و ($K_\beta$-shell) على التوالي. ومثلها بالنسبة للنموذج المعامل بالنتروجين (Grow-in $N_2$).

كذلك تم دراسة الخواص التركيبية من خلال دراسة حيود الاشعة السينية (XRD) لجزيئة الفثالوسيانين المعوض بالخارصين، حيث لوحظ نمواً جيداً للتركيب البلوري الابري من خلال عملية التقنية بالتسامي (Sublimation) وظهور طور β احادي الميل (Monoclinic Structure) . وتم حساب قيم المسافات البينية (d- value) باستخدام معادلة براك والتي تتطابق مع مثيلاتها في بطاقة المؤسسة الامريكية لفحص المواد (ASTM) (American Standards for Testing Material) وبالاستعانة ببرنامج (PDF) (Powder Diffraction File) للتاكد من المعلمات التي تم الحصول عليها من (ASTM) لكلا الجزيئتين ومعايرته مع برنامج Celn، تم حساب قيم الزوايا (2θ) وقيم المحاور البلورية (a,b,c) والزوايا المحورية (α,β,γ)، كذلك تم حساب حجم الحبيبة (Grain size) لجزئية الفثالوسيانين بدون معدن والفثالوسيانين – خارصين بتطبيق مباشر لمعادلة شيرر وكانت قيمها بحدود (27-35) نانومتر و (17-50) نانومتر على التوالي، ومقارنتها مع برنامج (c-size) فاعطى نتائج مطابقة.

كذلك تم فحص الشكل البلوري (Morphology) بواسطة المجهر الضوئي وبقوة تكبير (200X) لليف الفثالوسيانين بدون معدن وليف الفثالوسيانين-خارصين حيث يكون الليف شبيه بشعرة القط (Whisker needle type) ذو اللون الازرق وطبيعة مسامية وانتظام بلوري قصير وان قطر الليف للفثالوسيانين بدون معدن بحدود (20µm) و الفثالوسيانين –خارصين بحدود (16µm).