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Three successful ways for k doping ZnO sol – gel synthesis

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Abstract. One of the most frequently major challenges in the recent research is controlling the doping type I will prepare $Zn_{1-x}\ k_x\ O$ once n-type and once p-type by dusting the type of reaction medium. Therefore, we transformed its preparation in three different ways or methods. In the first method, I use the strong base (KOH) that is much used in the electrical industry and managed to get n-type k doped ZnO, the second method uses halide metal salt (KCl) much used in the medical industry and managed to get p-type k doped ZnO and in the third method, I have used potassium acetate ($CH_3\ CO_2\ K$) hilly cooler use in fire extinguishing and polymer industrial purposes. All methods managed to show $Zn_{1-x}\ K_x\ O$ nanopowder. The morphology analysis studies with the x-ray spectroscopy show ZnO patterns at (100), (002), (101), (102), (110), (103), (112), and (202), the EDX spectroscopy prove doped of potassium in the zinc oxide and show peaks of Zn, K, and O with no impurity while Zn and O are major elements And the scanning electron microscope SEM show hexagonal wurtzite structure for alkali media and dray method. In the acidic media, we managed to get the unstable cube structure ZnO It is a rare formula due to its instability, as the zinc oxide crystal quickly morphs into a hexagon. We have found that it is better to use potassium hydroxide with zinc chloride for electric devise manufacturing and potassium chloride with zinc chloride for photoelectric devise manufacturing.
Keywords: ZnO nanoparticles; basal middle, acidic medium, Sol-gel method, Crystal structure.

I. Introduction

Zinc oxide is II-VI group compounded semiconductor has become a widespread use in industry for its physical properties. since it has high excitation energy (60 meV) so it excite emission near room temperature, wide direct band gap (3.37 eV) large surface area, [1-3]. In addition to its critical roles in biological function it show acceptable result and biological qualities in resisting oxidation and treating the skin undue the suitable dose (0.5 μg/mol) [4] Potassium is the third major mineral in our body related to its good transfer accrues the nerve cell and use in many industry like soap, agriculture fertilizer and planet growth [5] so potassium doping zinc oxide provide double benefit ,since we select the product related to the application we need or according to the properties we need in the result Nano powder. we try to find experimentally to get different types of K doped ZnO wurtzite, rocksalt or cubic that differ in structure and properties since wurtzite side to be n – type with strong bond between O and Zn acts as a shallow donor commonly used in the electrical conductivity: and rocksalt or cubic are p – type or acceptor impurities more suitable for optoelectronic devise [6] the morphology of $Zn_{1-x}\ K\ _X\ O$ has been experimentally studied using Rigaku Ultima IV x-ray diffractometer, the topography and

chemical compositions studies using scanning electron microscope of Thermo Fisher Scientific FE - SEM Quanta FEG 450.

2. Materials and methods

To estimate the type of the product doping nano powder semiconductor if it is p-type or n-type we use the sol-gel wet chemical method and each time we change the reaction boundary condition and the media type

2.1 Zinc oxide ZnO preparation and doping with potassium K in alkali media

Solution A prepared by dissolving zinc chloride ($ZnCl_2$) in 100 ml of ethanol at room temperature and us magnetic stirrer at 400 rpm to get a homogenous solution. (fig 1)

Solution B prepared either by dissolving potassium hydroxide (KOH) in 100 ml of ethanol to forms an acidic -base equilibrium media or by dissolving it in distilled water to form acidic media then continuously stirred at 400 rpm until homogeneous solution was obtained. Then 3 ml from solution B was added drop by drop to 97 ml from solution A to form 100 ml of mixture stirrer at 400 rpm for 10 min at room temperature to get a homogenies wight gel. Then centrifuged, washed, dray and furnace at 80 ^{o}C for 4h then grain then furnace at 450 ^{o}C for 1h and grain again. (fig 2)

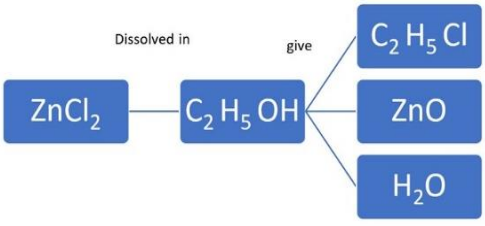

Figure 1: Zinc chloride dissolving in ethanol.

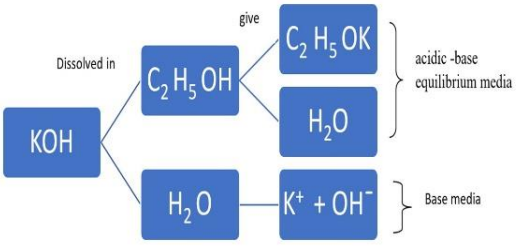

Figure 2: potassium hydroxide dissolving in water or ethanol.

2.2 Zinc oxide ZnO preparation and doping with potassium K in acidic media

Solution A prepared by dissolving zinc chloride ($ZnCl_2$) in 100 ml f ethanol at room temperature at room temperature and immediately a homogenous solution obtained.

Solution B can be prepared by dissolving potassium chloride (KCl) in 100 ml of desalted water stirred at 400 rpm until homogeneous solution was obtained. Then 3 ml from solution B was added drop by drop to 97 ml from solution A to form 100 ml of mixture stirrer at 400 rpm for 10 min at room temperature to get a transparent aqueous solution with few wight sediments at the bottom with pH =5.5 then centrifuged, washed, dray and furnace at 80 ^{o} C for 4h then grain then furnace at 450 ^{o}C for 1h and grain again. (fig3)

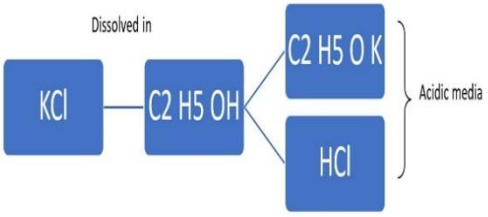

Figure 3: potassium chloride dissolving in ethanol.

2.3 preparation and doping with potassium K in dray media:

This method was invented by me, and it depends on the dismantling of micrometric materials to nanomaterial by

heating and then milling and crushing them to give a mixture of nanomaterials it is a dray method where no solutions performed we directly put 0.93 gm of $ZnCl_2$ mixed with 0.03 gm of potassium acetate ($CH_3\ CO_2\ K$) mixed and grain in a mortar, heating to 80° C for 4 hours then furnace at 450 °C for 1h and grain again.

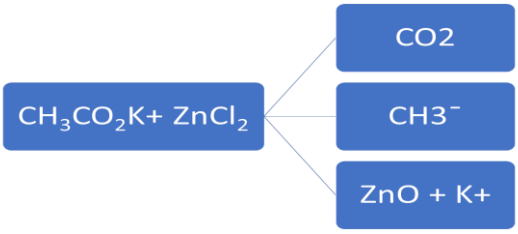

Figure4: potassium acetate furnace with zinc chloride.

3. Result:

The provided nano powder show suitable and acceptable morphology of p-type and n-type semiconductor

3.1 First method.

In alkalis medium using potassium hydroxide KOH with ZnO gave a sufficient amount of smoothie homogenise wight gel of K doped zinc oxide crystals

Because for solution A; sloping zinc oxide in ethanol will give zinc ethoxide, potassium ion and hydroxide ion

$ZnCl_2 + 2C_2H_5OH \leftrightarrow 2C_2H_5Cl + ZnO + H_2O$ (1)

for solution B; sloping potassium hydroxide in the ethanol resulted an acidic -base equilibrium solution with pH=7.7 and consist of chloroethane (C_2H_5Cl) , zinc oxide (ZnO) and water (H_2O)

$KOH + C_2H_5OH \leftrightarrow C_2H_5OK + H_2O$ (2)

Then sloping (1-x) % , in this work it is 97 %, from solution A with x% from solution B, in this work it is 3 % ,will give :

$C_2H_5Cl + ZnO + C_2H_5OK + H_2O \leftrightarrow 2C_2H_5OH + ZnO + KCl$ (3)

Then washing ones by ethanol C_2H_5OH and three times by distilled water H_2O

Also, solution B can be made by solving caustic potash KOH in distilled water to give a base solution with pH= 11 and consist of potassium ion and hydroxide ion

$KOH + H_2O \leftrightarrow K^+ + OH^-$ (4)

next equation for 97% of solution A with 3% of B will be:

$C_2H_5Cl + ZnO + H_2O + K^+ + OH^- \leftrightarrow C_2H_5OH + ZnO + KCl + H_2O$ (5)

After washing ones by ethanol and three times by distilled water the ethanol (C_2H_5OH) in equation 3 & 5, disposed of during the process of washing, potassium chloride will spread to its ions, Most of the residual consequence are ZnO and 3% K^+ definitely this contamination of potassium ions injected and merged in the lattice of ZnO in the process of burning in the oven. Then formic at 450° C to form K doped ZnO.

3.2 second method.

In acidic medium using organic smell feinol KCl with ZnO gave a transparent aqueous solution with few wight sediments at the bottom represent K doped zinc oxide so it gives a very small amount and more softer crystallin of $Zn_{0.97}\ K_{0.03}\ O$ nanopowder.

$KCl + C_2H_5OH \leftrightarrow C_2H_5OK + HCl$ (6)

$C_2H_5Cl + ZnO + H_2O + C_2H_5OK + HCl \leftrightarrow 2C_2H_5Cl + ZnO + K_2 + 2H_2O$ (7)

The ethanol (C_2H_5OH) and potassium chloride KCl disposed of during the process of washing ones by ethanol and three times by distilled water then burning in the oven. the residual consequence is Nano powder of $Zn_{1-x}K_xO$.

3.3 third method

In dray medium: gave an enough amount of $Zn_{0.97}K_{0.03}O$ nano powder, we were expecting that "since the potassium acetate ($CH_3\ CO_2\ K$) has melting point at 292° C " using thermal and mechanical disintegration methods by heating up to 450° C and grain it has been atomized into carbon dioxide (CO_2) that evaporating in heating process. The potassium methyl group

(CH_3K) at some stage breaks to methyl group ion (CH_3^-) and potassium ions (K^+) which can injected and merged into the zinc oxide (ZnO) lattice in the stage of heating up to 450 degrees Celsius to form K doped ZnO,

$CH_2CO_2K + ZnCl \leftrightarrow CO_2 + CH_3K + ZnO$ (8)

For $ZnCl_2$ mixed with potassium acetate" The x – ray spectroscopy (fig.5) show bad results for $ZnCl_2$ with potassium acetate it contain many extra peaks at low 2Theta and some peaks can note appear at high 2Theta and have very low intensity ,but when I replace the $ZnCl_2$ by ZnO, I get hexagonal wurtzite structure peaks with the highest peak (101) at $2\theta = 36.35^{\circ}$ and intensity = 14078 (au).

4. Discussions:

To study the structure morphology, the complete dissolvent of potassium in zinc oxide and see the crystal image of the resultant powder we use the flowing spectroscopy

4.1. The x-ray spectroscopy

The x-ray spectroscopy shown in (fig 1.) alkali media show hexagonal wurtzite structure i.e., the most growth on the c- axis with highest most intense peak (101) at $2\theta = 36.45^{\circ}$ and intensity =23171(au) as no extra peaks are founded that's mean the potassium completely decomposed in the ZnO. And for acidic media The x-ray spectroscopy all ZnO peaks with highest most intense peak (101) at 2θ =36.45 and intensity 29160 (au)° as no extra peaks are founded that's mean the potassium completely decomposed in the ZnO. For dray method The x – ray spectroscopy show bad results for $ZnCl_2$ with potassium acetate it contain many extra peaks at low 2 theta and some peaks can note appear at high 2theta and have very low intensity ,but when I replace the $ZnCl_2$ by ZnO, I get hexagonal wurtzite structure peaks with the highest peak (101) at $2\theta = 36.35^{\circ}$ and intensity = 14078 (au) as no extra peaks are founded that's mean the potassium completely decomposed in the ZnO.

So this method is useful only in doping a pure material.

The highest intensity was for alkali media then acidic then the dray media.

The patterns at (100), (002), (101), (102), (110), (103), (112) and (202) this agrees with others work [7] [8].

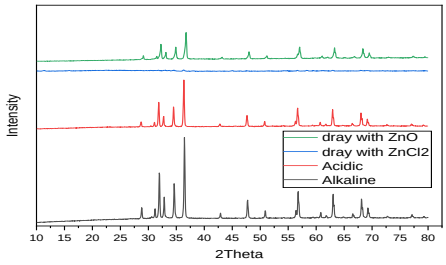

Figure5: The x – ray spectroscopy for alkaline, acidic and dray medium.

4.2 The energy dispersive x-ray spectroscopy (EDX).

The EDX images (fig .6) for the three methods show the peaks of Zn, K, and O only that prove the complete merge of potassium ions in ZnO with no impurity elements.

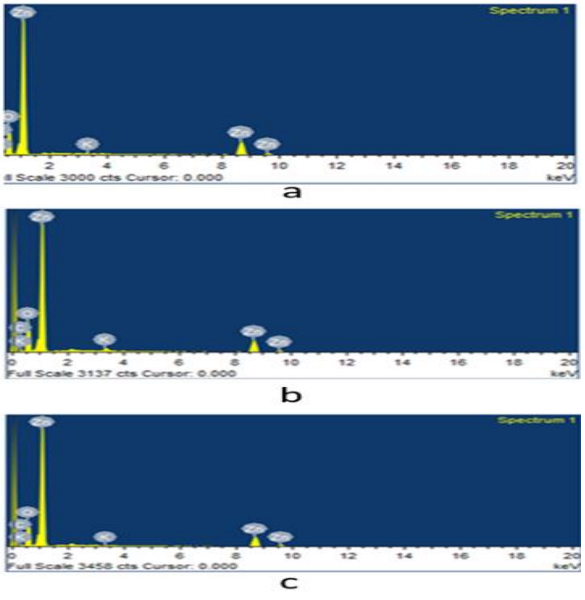

Figure 6: The energy dispersive spectroscopy (EDS) a) for alkaline medium, b) for acidic medium, and c) for dray medium

4.3 The scanning electron microscope (SEM) image

The SEM images (fig .7) show hexagonal wurtzite ZnO structure n-type for sample prepared in alkali medium and show mostly rocksalt or cubic structure p-type for sample prepared in acidic medium which is unstable and transfer to hexagonal near 550° C may be that is the reason for present of some hexagonal structure it may occur since we heat at 450° C. For dray method since we used pure hexagonal ZnO we get it.

Clusters are also found that show the importance of this work since the rocksalt has higher isothermal bulk modulus, higher constant-pressure heat capacity at the same conditions, and higher thermal expansion coefficient, [9].

Thus, we see that the difference in the reaction medium led to a difference in the characteristics of the resulting nanopowder, such as being n-type or p-type and other characteristics related to its crystal structure.

By knowing the characteristics of the product, we can determine the most appropriate way to manufacture it according to the purpose of its use

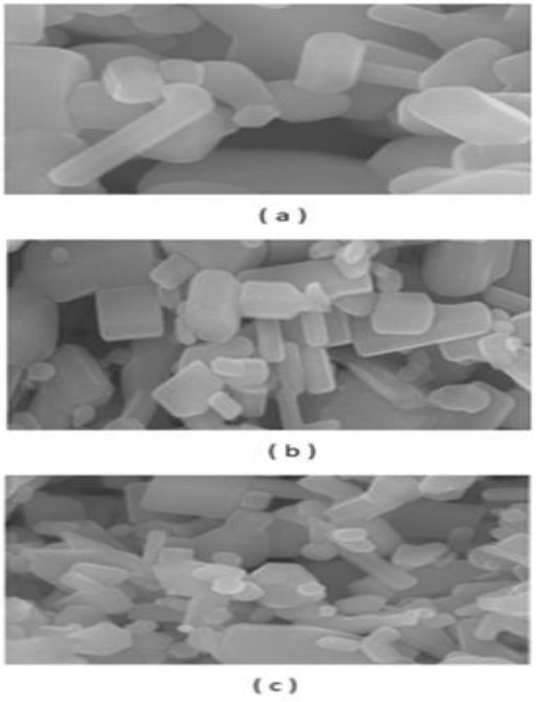

Figure 7: The scanning electron microscope (SEM) images a) for alkaline medium, b) for acidic medium, and c) for dray medium.

5. Conclusion:

Since the conductivity of n-type doped semiconductor is duple that of p-type it is better to use potassium hydroxide with zinc chloride for electric devise manufacturing and the potassium chloride with zinc chloride for photoelectric devise manufacturing. For the dray method it is peter to use pure ZnO has hexagonal wurtzite structure with potassium acetate to get $Zn_{1-x}\ k_x O$ of n-typ.

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ثلاث طرق ناجحة لتطعيم البوتاسيوم مع أكسيد الزنك بالطريقة الهلامية

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مستخلص. يعتبر التجكم في طريقة التطعيم و تحديد نوع المنتج من أهم التحديات الحديثة في صناعة المواد المتناهية الصغر ، وسوف أقدم في هذا البحث ثلاث طرق مختلفة لتحضير أكسيد الزنك المطعم بالبوتاسيوم Zn1−x kx O،كل طريقة تعطي مركب له خصائص فيزيائية مختلفة تماما عن الأخرى يترتب عليها تحديد استخداماته الصناعية .وقد حضرت ذرات بودرة متناهية الصغر من شبه الموصلات من اكيد الزنك مطعمة بالبوتاسيوم من النوع p و النوع n ، داخل بلورة واحدة من أشباه الموصلات عن طريق تغيير وسيط التفاعل . في الطريقة الأولى ، استخدمت القاعدة القوية (KOH) التي تستخدم كثيرًا في الصناعة الكهربائية وتمكنت من الحصول على ZnO من النوع n ، والطريقة الثانية استخدمت ملح معدن هاليد (KCl) الذي يستخدم كثيرًا في الصناعة الطبية وتمكنت من الحصول على ZnO من النوع p ،وفي الطريقة الثالثة استخدمت أسيتات البوتاسيوم (CH3 CO2 K) يستخدم مبرد في إطفاء الحرائق وصناعة البوليمر. تمكنت جميع الطرق من إظهار مسحوق نانوي Zn1−x Kx O. تم التأكد من نوعية المادة المنتجة و دراسات تحليل التشكل باستخدام التحليل الطيفي للأشعة السينية حيث تطابق المنتج مع أنماط ZnO في (١٠٠) ، (٠٠٢) ، (١٠١) ، (١٠٢) ، (١١٠) ، (١٠٣) ، (١١٢) و (٢٠٢) ، أثبت التحليل الطيفي EDX اندماج البوتاسيوم في أكسيد الزنك وتظهر قمم Zn و K و O بدون شوائب بينما Zn و O عناصر رئيسية ، ويظهر المجهر الإلكتروني الماسح SEM بنية wurtzite سداسية للوسائط القلوية وفي الطريقة الثالثة تم التفاعل في وسط جاف ،أما الوسط الحامضي فقد تمكنا من الحصول على ZnO بتركيب هيكل المكعب غير المستقر وهي صيغة نادر الحصول عليها لعدم استقرارها حيث سرعان ما يتحور شكل بلورة أكسيد الزنك الى السداسي.

كلمات مفتاحيه: جزيئات أكسيد الزنك متناهية الصغر، الوسط القاعدي، الوسط الحامضي، الطريقة الهلامية، تركيب الكريستال.