Journal of Kerbala University , Vol. 13 No.3 Scientific . 2015

Determine the Structural and Optical Properties of ZnO Nanoparticles Prepared by Hydrothermal Method

تحديد الخواص التركيبية والبصرية لجسيمات اوكسيد الزنك النانوية المحضرة باستخدام طريقة *Solvothermal*

.[1] Dunia K. M. Al – Nasrawy, .[2]Mohammed H.K.AL-Mamoori,.[3]Ahmed.K.Kodeary i
.[1]Dept. Of physics, college of science ,Baghdad university,Baghdad,Iraq.
..[2,3]Dept. Of physics, college of science for women ,Babylon university ,hilla,babil

البحث مستل

Abstract

In this work ,zinc oxide nanoparticles(powder) with diameter 12.1 nm was prepared using *Solvothermal Method*. The structural and optical properties of ZnO nanoparticles was studied by X-ray diffraction, atomic force microscopy AFM, EDS, FTIR, UV-Visible absorption spectroscopy and Flourometer spectrum. X-ray diffraction reveal the formation the purity of prepared phase of ZnO particles with hexagonal wurtzite structure . The energy dispersion scattering (EDS) examination explains the ZnO nanoparticle is purity. The Atomic Force Microscopy (AFM) shows the spherical shape of nanoparticles with diameter around 60 nm. The optical absorption spectral study identified the blue shift of the sample in comparison to bulk ZnO in three dimensions . fluorescence spectrum at room temperature confirms the strong UV emission around 397 nm and its indicate that the zinc oxide nanoparticles is a purity and don't contain on a defects.

Key ward: Solvothermal technique, ZnO nanoparticles, structural and optical properties

الخلاصة:

في هذا البحث ،جسيمات اوكسيد الزنك (باودر) بقطر 12.1 نانومتر حضرت باستخدام طريقة Solvothermal . الخواص التركيبية والبصرية لجسيمات اوكسيد الزنك النانوية المحضرة درست بواسطة حيود الاشعة السينية X-ray Diffraction، ومطياف القوة الذرية AFM، EDS، FTIR، UV-Visible absorption spectrophotometer وجهاز قياس طيف الفلورة Fluorescence Flourometer .حيود الاشعة السينية اظهرت ان جسيمات اوكسيد الزنك النانوية المحضرة تكون نقية و ذات تركيب (wurtzite) السداسي .فحص energy dispersion scattering (EDS) اظهر ان جسيمات اوكسيد الزنك النانوية هي نقية ايضا وخالية من الشوائب .كذلك قياس Atomic Force Microscopy (AFM) بين ان جسيمات اوكسيد الزنك النانوية ذات شكل كروي بقطر 60 نانومتر .دراسة طيف الامتصاص البصري للجسيمات النانوية بينت وجود ازاحة زرقاء blue shift بالمقارنة مع اوكسيد الزنك الاساسي في ثلاث ابعاد (bulk zinc oxide).طيف الفلورة عند درجة حرارة الغرفة اظهر انبعاث قوي عند المنطقة فوق البنفسجية (UV-region) حول 397 نانومتروهذا يشير الى ان جسيمات اوكسيد الزنك النانوية المحضرة هي نقية وغير محتوية على شوائب.

1-Introducton:

Zinc oxide, is an important semiconducting and piezoelectric material with a direct Bandgap of 3.37 eV and a large excitation binding energy 60 meV and exhibits near UV-emission and transparent conductivity [1,2]. ZnO nanostructure is an emerging optoelectronic material in large area electronic application [3].several methods are available for growing ZnO nanostructures some of them are Sol-Gel method[4,5] , simple solution route (by reaction zinc acetate dehydrate with sodium hydroxide and polyethylene glycol-2000 (PEG2000) at 180 C^0 for 4 h in solution) [6] , a simple wet chemical method [7], metal-organic chemical –vapor deposition [8], ultrasonic synthesis [9] , citric acid assisted microwave solution combustion method [10], precipitation method from zinc nitrate[11],micromulsion rout[12],electrochemical deposition technique [13],microwave irradiation [14],spray Pyrolysis [15],vapor-phase transport using the mixture of ZnO and graphite powder in air [16],chemical path deposition [17],pulse laser deposition [18],the Pyrosol method [19],hydrothermal technique [20,21],solvothermal technique[22,23,24].a variety of zinc oxide nanostructures such as Nanowires ,nanospheres,nanorodes ,flower –like ,tubules and

tetrapods[25],nanoparticles[26]. ZnO is widely used in a number of application like solar cell application [27], with light emitting diodes were fabricated by combining n-ZnO Nanorods and hollow Nanotube with different p-type material to form hetrojunction [28] , Photocatalyst [29],UV-absorbers[30] , development of gas sensors[31] and nanolaser materials[32].

In this work Solvothermal technique was used to produce ZnO nanoparticles because it have several advantages :large surface area, high crystallinity and high thermal stability [22].power with nanometer-size can be obtained by this method, the reaction is carried out under moderate condition ,power obtained with different morphology by adjusting the reaction condition and the prepared powder have different properties, and the prepared ZnO nanoparticles can be used as active medium when it deposition on a substrate .

2-Experimental Method:

2-1:Preparation of ZnO Nanostructures*:*

Solvothermal technique were used to synthesis ZnO nanoparticles using tree stages(stage one and stage two make at the same time):

Stage one: 5 g of Zinc Acetate Dehydrate $Zn(CH_3COO)_2.2H_2O$ (SCR-INDIAN) is used as a source of zinc was added slowly to 100 ml of distilled water under stirring for 1.5 h at 60 C^0 at this interval time 2ml of concentrated hydrochloric acid was added slowly in this mixture.

Stage tow: 2 g of Oxalic Acid $(COOH)_2 2H_2O$ (DIDACTIC , Panr. -ESPANA) dissolved in 100 ml of distilled water under stirring for 1.5 h at 60 C^0

Stage three: the mixture of the stage tow added slowly to mixture of the stage one under stirring for 3 min. , then the final mixture was transferred into Teflon lined sealed stainless steel autoclave and maintained in oven at temperature 150 C^0 for 24 h. then it was allowed to cool naturally to room temperature .The resulting product was washed several times with distilled water and dried at 50- 60 C^0 for overnight.

2-2:Characterization :

The resulting products were analyzed by X-Ray diffraction (XRD) using Cu Kα radiation (λ=1.5417 A) at scanning angle (10-80) deg. and scanning speed of 8 deg/min over 2θ range (Shimadzo XRD-6000-Japan) . the morphology of the obtained ZnO nanostructure was observed by atomic force microscopy (AFM).Energy Dispersive Spectroscopy (EDS)(Angstrom advanced Inc. USA) ,it was characterized the element composition of the sample .UV-Visible absorption spectroscopy (CECIL ,CE7200,Korea) in the range from (200-1100)nm is widely being used technique to examine the optical properties of nanosized particles .the quality and composition of the synthesized ZnO nanostructure were characterized by the Fourier transform infrared spectroscopy (FTIR-8400S-SHIMADZU) in the range of$(400-4000cm^{-1})$. The photoluminescence study was done using fluorescence spectrophotometer (F96pro-Chaina)

3-Results and Discussion :

3-1-X-Ray Diffraction :

Fig.(1) represents the x-ray diffraction pattern of ZnO nanoparticles . A definite line broadening of the XRD peaks give an indicates that the prepared material consist of particles in Nanoscale range . From XRD patterns analysis , peak intensity , position and width (full width at half maximum) (FWHM) data can be determined. the diffraction peaks located at 2ɵ: 31.82 , 34.44 , 36.28 , 47.58 , 56.63 , 62.86 , 66.38 , 67.99,69.04,72.51 and 77.00 corresponding to the following lattice planes (100), (002),(101) , (102), (110) ,(103),(200),(112), (201),(004) and (202) respectively ,Keenly indexed as a hexagonal wurtzite phase of ZnO as reported in many research works[33,34]and agreeing with reported in ASTM file card.inexistence of any peaks related to the impurities indicate high purity of the grown ZnO nanostructure .the sharp peaks indicate that the

product was good crystallinity [35]. the intense (101) diffraction peak indicate that the preferential orientation is along c –axis because it is stronger and narrower than the other peaks . Scherer's formula has been used to calculate the particle size of ZnO nanoparticles [36].

$$D = \frac{K\lambda}{\beta \cos\theta} \dots\dots\dots\dots\dots\dots\dots (1)$$

Where D is the particle size ,K is a constant (0.9), λ is the X-Ray wavelength used , (θ) is the Bragg angle and (β) is the full width at half maximum of diffraction peaks (expressed in radian).the value of particle size which calculated using the above formula is 12.1 nm).

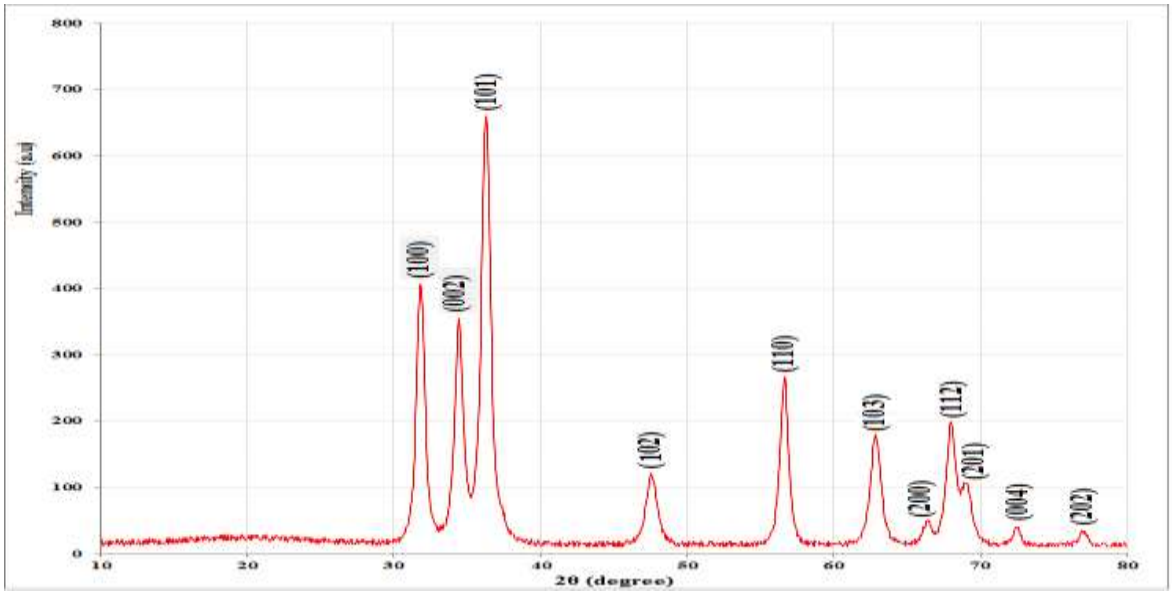


Fig.1:X-ray diffraction of ZnO nanoparticles

The lattice parameters (a) and (c) estimated using braggs law [37]:

$$a = \sqrt{\frac{1}{3}}\ \frac{\lambda}{\sin\theta} \dots\dots\dots\dots\dots\dots\dots\dots (2)$$

$$c = \frac{\lambda}{sin\theta} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (3)$$

Where (λ) is the X-ray wavelength of the incident Cu Kα radiation (0.154056nm) .the values obtained for the unit cell of the ZnO is a=b=2.85863 A^0 and $c = 4.95130A^0$. these values exhibit a good agreement with the bulk ZnO ($a = b = 3.23877A^0$) and $c = 5.20987\ A^0$[38] with error percentage 11.73% for($a = b$) and 4.96% for (c)these simple mistake can be attributed to the increase in temperature decreases the lattice constant of ZnO[38].

The Dislocation Density (δ) which represent the amount of defects in the crystal ,is estimated from the following equ.[37]

$$\delta = \frac{1}{D^2} \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

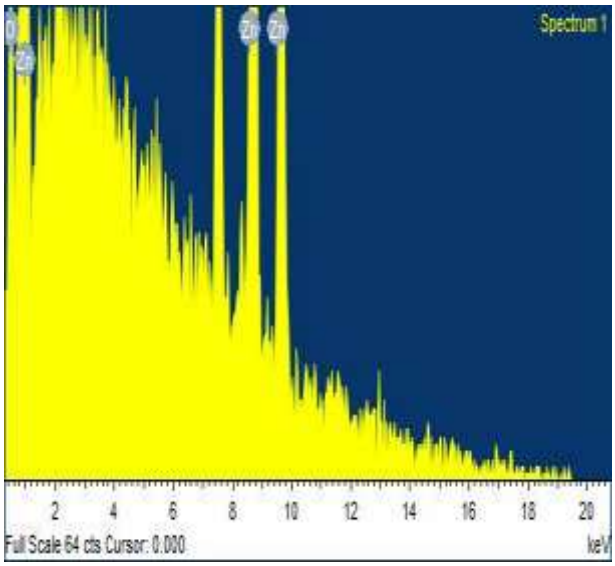
The dislocation density for the ZnO nanoparticles synthesis by Solvothermal is equal to 0.0076 nm^{-2} . The strain induced in powder due to crystal imperfection and distortion was calculated using the formula[39]:

$$£ = \frac{\beta}{4\ tan\theta} \dots\dots\dots\dots\dots\dots\dots\dots (5)$$

The calculated strain was to be 0.09545

3-2-EDS Examination:

Fig (2) show the energy dispersion scattering of ZnO nanoparticles .the pattern indicates that No evidence of other impurities was found and the prepared ZnO nanostructure has high purity and exhibit a good agreement with X-ray diffraction .



Element	Weight%	Atomic%
O K	67.88	89.62
Zn K	32.12	10.38
Totals	100.00	

Fig.(2):EDS Of the ZnO nanostructure

3-**3-Surface Morphology (Atomic Force Microscopy) (AFM)**

Fig.(3) illustrated the topography of the ZnO nanostructure in 3D Dimensions .the AFM analysis exhibit a growing of grain particle in a specific direction (to the top).the particle size of the prepared sample was 60 nm.

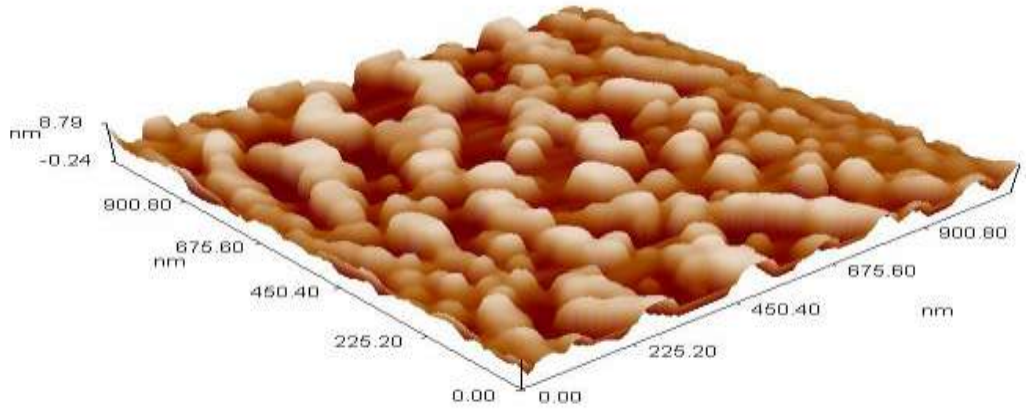


Fig.(3): :the AFM of the prepared ZnO nanoparticles

4-FTIR Spectroscopy: 3-

FTIR measurement was performed in order to verify the bond structure for ZnO nanostructure using optimized parameters. fig.(4) shows the infrared absorption spectra of ZnO nanostructure in the 4000-400cm^{-1} $wavenumber\ rang$.

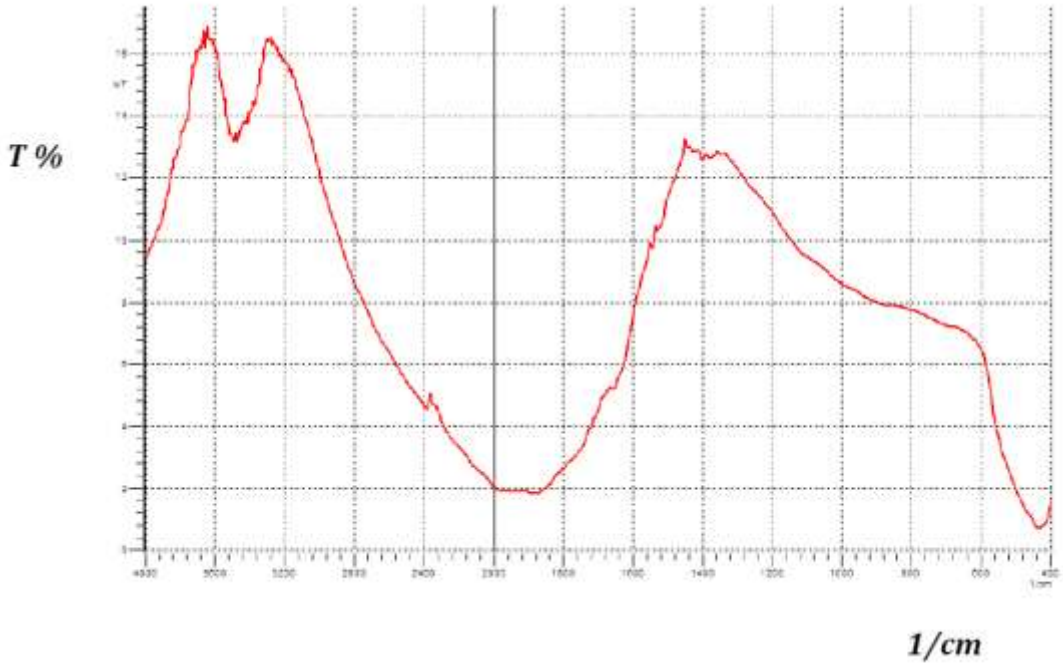
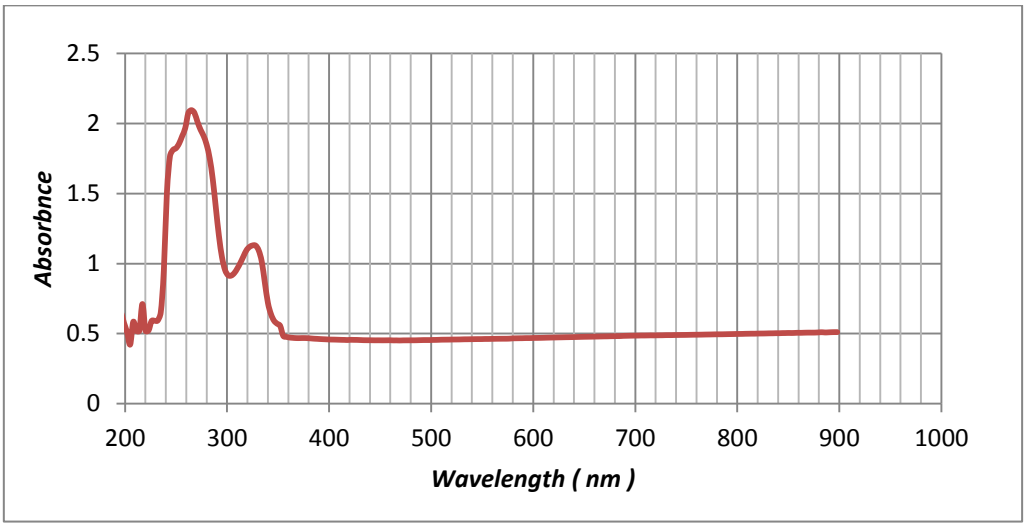


Fig.4:FTIR of ZnO nanoparticles

Fig.(4) shows that the band located at 460-560 cm^{-1} is correlated to the stretching mode of Zn-O this indicate the presence of ZnO nanoparticles in calcined compound [39] . the absorption peak in the range of 3200-3600 cm^{-1} corresponding to the stretching vibration of intermolecular hydrogen bond (O-H) existing between the adsorbed water molecular and indicates the higher amount of hydroxyl group[40] .

3-5-UV-Visibile Spectrum of ZnO Nanoparticles:

Fig.(5) depicts a UV- visible spectrum of the ZnO Nanoparticles ,which was obtained by dispersing of ZnO powders in a chloroform alcohol and using chloroform alcohol as reference . an excitonic absorption peak is found at about 262 nm, due to the ZnO nanoparticles which lie much below the band gap wavelength of 322 nm (strong absorption band) and its corresponding the energy gap $E_g = 3.85\ ev$ .A clear shift towards blue light wavelength compared with that of bulk because of the quantum confinements[11]



Fig(5):UV-visible absorption spectrum of ZnO Nanoparticles.

the blue shift indicate the synthesis of ZnO nanoparticles in Nanoscale. The energy gap can be calculated too by tauc plots as shown in fig.(6) and its equal to $\sim 3.80\ ev$

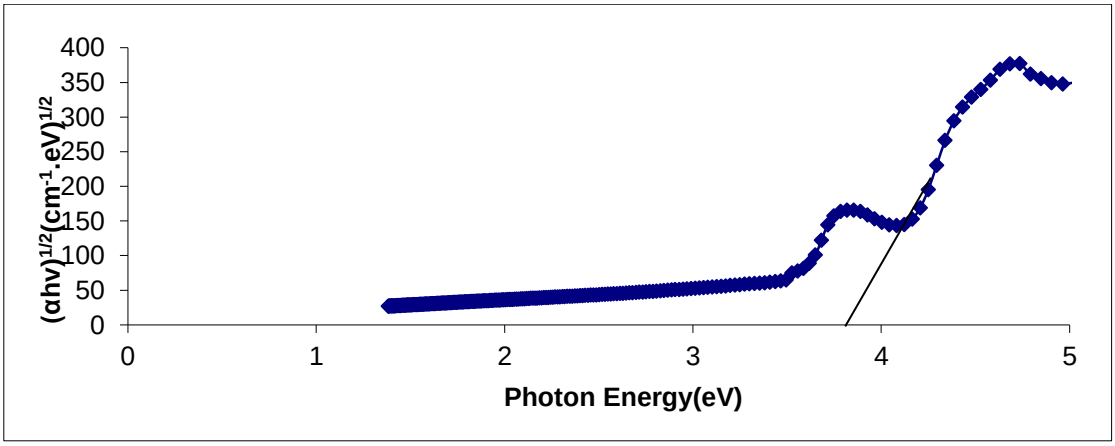


Fig.(6):determine the energy gap of ZnO nanoparticles by using tauc plots

3-6-Flouresence Spectrum of ZnO Nanoparticles :

The study of photoluminescence spectrum is an effective way for investigating the defect structures of ZnO nanoparticales,fig(7)shows the fluorescence spectrum obtained for the sample with excitation wavelength 400 nm with high emission band centered around 397 nm in the UV-region .the UV emission peak is strong as well as sharp, this strong luminescence is an indicator of good quality of the ZnO nanoparticles .the UV emission of the sample can be attributed to the Near Band-Edge Emission (NBEE), coming from radioactive recombination of electrons in the conduction band and holes in the valance band [41]

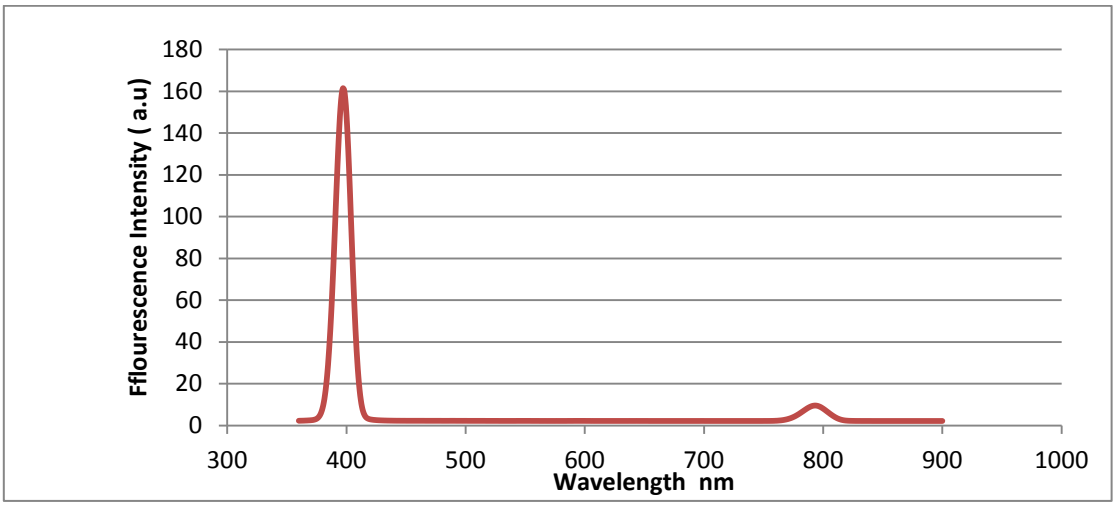


Fig.(7):fluorescence intensity as a function of wavelengths of ZnO nanoparticles

4- Conclusion

ZnO nanoparticles with wurtzite shape was successfully prepared by solvothermal method with diameter 12.1 nm.this process is a simple, low cost ,friendly environment and lead to high crystalline particles(high purity) with controllable morphology. the blue and energy gap shift occur because of the quantum confinement and it indicate that the prepared ZnO Nanoparticles in Nanoscale and low defect .

References

1- Z.L.Wang, X.Y.Kong,Y.Ding,P.Gao,W.L.Hunhes,R.Yangand Y.Zhang,"Semiconducting and Piezoelectric Oxide Nanostructures Induced by Polar Surface ",Adv.Funct.Mater.Vol.14,No.10,October ,2004.

2-S.Samuel M,L.Bose and G.KC,"Optical Properties of ZnO Nanoparticles ",Academic Review ,Vol.XVI:No.1 and 2SB,pp.57-65,2009.

3-S.A.Kamaruddin , M.Z.Shadan ,Kah-Yoong Chan , M.Rusop, H.Saim, "Synthesis and Characterization of Zinc Oxide Nanostructures ",Informacije MIDEM 40,1,Ljubljana,2010 .

4-W.Q.Peng ,S.C.QU,G.W.Cong ,Z.G.Wng ,"Structure and Visible Luminescence of ZnO Nanoparticles",Material Science in Semiconductor Processing ,Vol.9,pp.156-159,2006.

5-T.V.Kolekar ,H.M.Yadav,S.S.Bandgar and P.Y.Deshmukh,"Synthesis by Sol-Gel Method and Characterization of ZnO Nanoparticales",Indian Streams Research Journal ,Vol.1,Issue -1,Feb-2011.

6-J.Wang ,S.He,S.Zhang,Z.Li,P.Yang,X.Jing ,M.Zhang,Z.Jiang,"Controllable Synthesis of ZnO Nanostructures by a Simple Solution Route", Materials Science –Poland ,Vol.27,No.2,2009.

7-P.K.Samanta ,S.K.Patra,A.Ghosh and P.R.Chaundhuri,"Visible Emission from ZnO Nanorods Synthesis by a Simple Wet Chemical Method", International Journal of Nanoscince and Nanotechnology ,Vol.1,No.1-2,pp.81-90,2009.

8-S.T.Tan ,B.J.Chen ,X.W.Sun and W.j.Fan ," Blue Shift of optical Bandgap in ZnO Thin Films Grown by Metal –Organic Chemical-Vapor Deposition ",Journal of Applied Physics ,Vol.98, No.013505,2005.

9-N.Morales-Flores ,R.Galeazzi, E.Rosendo,T.Diaz,S.Velumani and U.Pal,"Morphlogy Control and Optical Properties of ZnO Nanostructures Grown by Ultrasonic Synthesis ",Advances in Nano Research ,Vol.1,No.1,PP.59-70,2013.

10-L.C.Nehru and C.Sanjeeviraja ,"ZnO Nanoparticles by Citric Acid Assisted Microwave Solution Combustation Method", Journal of Ceramic Processing Research ,Vol.14,No.6,pp.712-716, 2013.

11-S.Talam ,S.R.Karumuri and N.Gunnam ,"Synthesis ,Characterization an Spectroscopic Properties of ZnO Nanoparticles ",International Scholarly Research Network ,Vol.2012,Article ID 372505,6 pages.

12-H.Kumar ,R.Rani,"Structural and Optical Characterization of ZnO Nanoparticles Synthesized by Micromulsion Route ",International Letters of Chemistry ,Physics and Astronomy ,Vol.14,pp.26-36,2013

13- N.K.Hassan , M.R.Hashim , Y.Al-Douri and K.Al-Heuseen , "Current Dependence of ZnO Nanostructures by Electrochemical Deposition Technique "Int.J.Electrochem.Sci.Vol.7,pp.4625-4635,2012 .

14-N.F.Hamedani and F.Farzanhe,"Synthesis of ZnO Nanocrystals With Hexagonal (Wurtzite) Structure in Water Using Microwave Irradiation ",Journal of Science ,Islamic Republic of Iran ,Vol.17,No.3,pp.231-234,2006.

15-F.Yakuphanoglu,S.Ilican ,M.Caglar ,Y.Calar,"The Determination of the Optical Band and Optical Constants of Non-Crystalline and Crystalline ZnO Thin Films Deposited by Spray Pyrolysis ",Journal of Optoelectronics and Advanced Materials ,Vol.9.No.7,July.pp.2180-2185,2007.

16-C.X.Xu,G.P.Zhu,X.Li,Y.Yang ,S.T.Tan,X.W.Sun ,C.Lincoln and T.A.Smith ,"Growth and Spectral Analysis of ZnO Nanotubes",Journal of Applied Physics ,Vol.103,No.094303,2008 .

17-G.Jia,Y.Wang and J.yao ,"Growth Mechanical of ZnO Nano-structure Using Chemical Path Deposition "Journal of Ovonic Research ,Vol.6,pp.303- 307,November-December 2010

18-E Deposada,L Moreira,J Perez De La Cruz,M Arronte ,L V Ponce ,T Flores and J G Lunney ,"Oxidation of ZnO Thin Films During Pulse Laser Deposition Process",Bull.Mater.Sci.Vol.36.No.3,pp.385-388,June 2013.

19-Otilia-Ruxandra Vasile ,Ecaterina Andronescu,C.Ghitulica ,B.S.Vasile ,O.Opera ,E.Vasile and R.Trusca ,"Synthesis and Characterization of Nanostructured ZnO Oxide Particles Synthesized by Pyrosol Method ",Journal Nanopart Res ,Vol.14,No.1269,2012 .

20-Di Liu ,Y.Liu ,R.Zong ,X.Bai and Y.Zhu ,"Controlled Synthesis of 1D Nanostructured Via Hydrothermal Process "Materials Research Bulletin ,Vol.49,pp.665-671,2014 .

21-D.Polsongkram ,P.Chamninok ,S.Pukird ,L.Chow ,O.Lupan ,"Effect of Synthesis Condition on the Grouth of ZnO Nanorods Via Hydrothermal Methode",Physics B ,Vol.403.,pp.3713-3717,2008 .

22-D.Yiamsawas ,K.Boonpavanitchakul and W.Kangwansupamonkon ,"Preparation of ZnO Nanostructures by Solvothermal Method ,"Journal of Microscopy Society of Thailand,Vol.23,No.1,pp.75-78,2009. .

23-M.Segovia ,C.Sotomayor ,G.Gonzales and E.Benavente ,"Zinc Oxide Nanostructure By Solvothermal Synthesis ,"Mol.Cryst.Liq.Crys.,Vol.555,pp.40-50,2012.

24-W.Zhang ,X.Chen ,N.XU,R.Xiang ,Y.Zhu and Z.Tang,"Morphology and Optical Property of ZnO Nanostructures Grown by Solvothermal Method :Effect of the Solution Pretreatment "Journal of Nonmaterial ,Vol.2013,Article ID 986157,4pages ,2013.

25-A.Khan ,"Raman Spectroscopy Study of the ZnO Nanostructures ",Journal Pak Mater Soc.,Vol.4,No.1.2010.

26-R.Razali,A.K.Zak ,W.H.Abed.Majid,M.Darroudi,"Solvothermal Synthesis of Microsphere ZnO Nanostructures in DEA Media ",Ceramics International ,Vol.37.pp.3657-3663,2011.

27-H-Ming Cheng ,Wei-Hao Chiu ,Chia-Hua Lee ,Song-Yeu Tsai and Wen-Feng Hsieh,"Formation of Branched ZnO Nanowires From Solvothermal Method and Dye-Sensitized Solar Cell Application ",J.Phys.Chem.C,Vol.112,pp.16359-16364,2008.

28-M.Willander ,O.Nur,J.Rana Sadaf ,M.I. Qadiar,S.Zaman,A.Zainelabdin,N.Bano and I.Hussain ,"Luminescence from Zinc Oxide Nanostructures and Polymers and their Hybrid Devices",Materials ,Vol.3,pp.2643-2667,2010.

29-M.Soltaninezhad and A.Amini far ,"Study Nanostructures of Semiconductor Zinc Oxide (ZnO) As a Photocatalyst for the Degradation of Organic Pollutants", International Journal of Nano Dimension ,Vol.2,No.2,pp.137-145,Autum 2011.

30-A.Becheri,M.Durr,P.L.Nostro and P.Baglioni ,"Synthesis and Characterization of Zinc Oxide Nanoparticles: Application to Textiles as UV-Absorber ",Journal Nanopart. Res,Vol.10,pp.679-689,2008.

31-S.K.Gupta,A.Joshi and M.Kaur ,"Development of Gas Sensors Using ZnO Nanostructures", Journal .Chem.Sci.Vol.1,pp.57-62,January 2010.

32-C.Zhang ,F.Zhang ,T.Xia,N.Kumar ,Jong-In Hahm ,J.Liu,Z.L.Wang and J.Xu ,"Low –Threshold Tow –Photon Pumped ZnO Nanowire Laser "Optics Express ,Vol.17,No.10,May 2009.

33-A.Singh,R.Kumar ,N.Malhotra and Suman ,"Preparation of ZnO Nanoparticles by Solvothermal Process "International Journal For Science and Emerging Technologies With Latest Trend ,Vol.4,No.1,pp.49-53,2012.

34-S.Bhat,Shrisha B.V. and K.G.Naika,"Synthesis of ZnO Nanostructure By Solvothermal Method "Arch.Phy.Res.,Vol.4,No.2,pp.61-70,2013.

35-N.Elamin and A.Elsanousi,"Synthesis of ZnO Nanostructures and Their Photo catalytic Activity ",Journal of Appl.and Industrial Sciences,Vol.1,No.1,April 2013.

36-N.Saraswathi ,N.N.Pillai,C.K.Mahadevan,"Optical and Magnetic Studies on ZnO Nanocrystals Both Pure and Doped Prepared by Microwave Assisted Solvothermal Method", International Journal of Engineering Research and Application ,Vol.3,pp.2468-2473,Issue 4,Jul.Aug.2013.

37-M.Saleem,L.Fang ,A.Wakeel,M.Rashad and C.Y.Kong ,"Simple Preparation and Characterization of Nano-Crystalline Zinc Oxide Thin Films by Sol-Gel Method on Glass Substrate ",World Journal of Condensed Matter Physics ,Vol.2,pp.10-15,2012.

38-K.L.Foo,U.Hashim ,K.Muhammad and C.H.Voon,"Sol-Gel Synthesized Zinc Oxide Nanorods and Their Structural and Optical Investigation for Optoelectronic Application ",Nanoscale Research Letters ,Vol.9,No,429,2014.

39-D.J.Sornalath,P.Murugakoothan ,"Room Temperature Synthesis of ZnO Nanostructure Using CTAB Assisted Sol-Gel Method for Application in Solar Cell ",International Journal of Emerging Technology and Advanced Engineering ,Vol.3,Issue 9,Semptember 2013.

40-S.Bagheri,C.K.G and S.B.Abd Hamid ,"Facile Synthesis Nano-Sized ZnO by Direct Precipitation Method "Der Pharma Chemica ,Vol.5,No.3,pp.256-270,2013.

41-N.S.N.Jothi,R.Gunaseelan and P.Sagayaraj,"Investigation on the Synthesis ,Structural and Optical Properteis of ZnO Nanorods Prepared Under CTAB Assisted Hydrothermal Conditions"Archives of Applied Scinse Research ,Vol.4,No.4,pp.1698-1704,2012.