International Journal of Latest Research in Engineering and Technology (IJLRET)
ISSN: 2454-5031
www.ijlret.com || Volume 04 - Issue 04 || April 2018 || PP. 45-51

Low Hydrothermal Temperature Synthesis and Characterization of ZnO Nanoparticles

F. M. El – Hossary[1], A. M. Abd El-Rahman[1], M. AbdelhamidShahat[2], A. A. Ebnalwaled[3,4]

[1](*Physics Department, Faculty of Science/ Sohag University, Sohag, Egypt)*
[2](*High Institute of Engineering and Technology, El-tod, Luxor, Egypt)*
[3](*Electronics & Nano Devices Lab, Physics Department, Faculty of Science/ South Valley University, Qena, 83523 Egypt)*
[4](*Egypt Nanotechnology Center (EGNC)/ Cairo University Sheikh Zayed Campus, 12588 Giza, Egypt)*

Abstract: Simplistic, effective, and surfactant-free hydrothermal method was developed and employed for the synthesis of ZnO nanoparticles. In this work, hydrothermal method was used to prepare ZnO nanoparticles at 4h hydrothermal reaction time. The morphology, microstructure and optical properties of the prepared ZnO nanoparticles were investigated. XRD, TEM, HRTEM, SEM, FT-IR and UV-VIS photometry measurements were employed as a characterization analysis. XRD and FT-IR results confirm obtaining ZnO nanoparticles with hexagonal structure. XRD showed that the crystallite size of ZnO is 11.9 nm. The obtained ZnO has relatively high absorption coefficient in the visible region with direct energy gap of 3.11 eV, which indicates that this material can be used in photovoltaic applications.

Keywords: ZnO nanoparticles, hydrothermal method, optical band gap

I. INTRODUCTION

Semiconductors with dimensions in the nanometer realm are significant ~~because~~ owing to their electrical, optical and chemical properties can be adjusted by changing the size of the constituent particles. Optical properties are of great interest for application in optoelectronics, photovoltaics and biological sensing. Various chemical synthetic methods have been developed to prepare such nanoparticles [1].

Zinc Oxide (ZnO) is a unique material with a direct band gap of 3.37eV and large excitation binding energy of 60meV [2, 3]. ZnO and ZnO-related materials have attracted more and more attention over the past few years because of its applications in various fields, such as filtering materials for ultraviolet (UV) light-emitters, catalysts, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensor, field emission display and solar cells, etc. [4-6]. However, so as to attain ZnO powders with suitable chemical and physical properties definite for their intended applications, the purity and particle size during their synthesizing process can be considered as important factors. Different methods such as precipitation [7-9], spray pyrolysis [10], thermal decomposition [11] and hydrothermal process [12-16] have been employed for preparing ZnO powders. The hydrothermal synthetic method [17, 18] has advantages to attain high-crystallized powders with fine grain size-distribution and high purity without the costly precursors, sophisticated equipment and heat treatment at high temperature [18-22].

Many researchers prepared ZnO using hydrothermal method at relatively high reaction temperature 120 °C and 24 h as reaction time [23, 24]. In this paper, the main aim is to study the possibility synthesize of ZnO nanoparticles by simplistic, effective, and surfactant-free hydrothermal method at low reaction temperature 75 °C and short processing time 4h. The structure and the optical properties of the prepared nanoparticles will be investigated.

2. Experimental

2.1 Materials

Analytical grade zinc nitrate hexahydrate (Zn $(NO_3)_2.6H_2O$, 98%) and sodium hydroxide (NaOH, 97%) were purchased from Sigma-Aldrichand used as received without any purification process.

2.2 ZnO nanoparticles preparation

Zinc Oxide (ZnO) nanoparticles were obtained by hydrothermal method at different reaction times (4, 8, 12, and 18 h) and the preparation technique is shown in Fig. (1). An amount of 2.97 g from Zinc nitrate hexahydrate (Zn $(No_3)_2$ $.6H_2O$) was dissolved in 2 ml of distilled water. Then, a solution of sodium hydroxide NaOH(s) was prepared by dissolving 4.0 g of sodium hydroxide in 20 ml distilled water. An aqueous solution of 5 mol/L of Zn $(NO_3)_2.6H_2O$ was mixed with 5 mol/L NaOH solution under magnetic continuous stirring for 1h at 900 rpm. The reaction mixture was sonicated for about 10 minutes in a glass veil; the mixture

was transferred to a Teflon lined stainless steel autoclave and heat-treated at 75 ^{o}C for 4 h. Then, the autoclave was allowed to cool to room temperature naturally for 24h. The precipitation was filtered out, washed several times with ethanol and distilled water, and then dried at 100 ^{o}C for 3h.

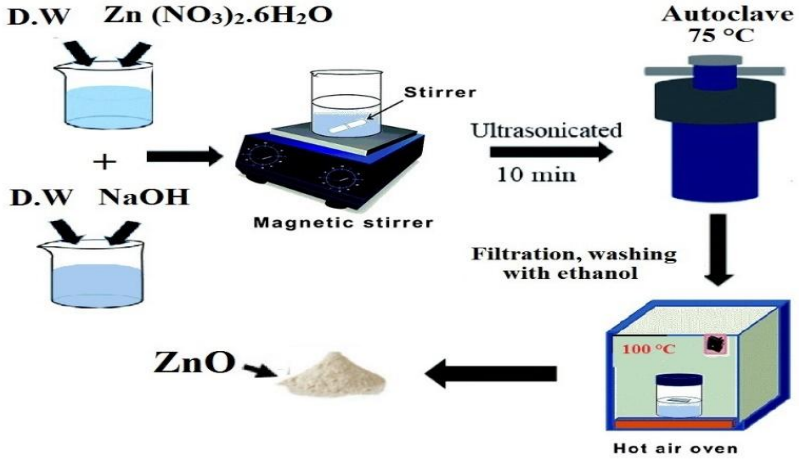

Fig (1): Preparation procedure of ZnO nanoparticles by hydrothermal method

3. Characterization

The phase purity and structure of the prepared samples were characterized by X-ray powder diffraction (XRD), using PANalytical diffractometer with a Cu target and a graphite monochromator (λ=1.54056 Å). The morphology of the obtained ZnO nanoparticles was characterized with high resolution scanning electron microscope (SEM) (JOUL SEM model JSM – 5500 - Japan), with accelerated voltage 10 KV. The features and shapes of the particles were also imaged by high resolution transmission electron microscope (HRTEM), model JEOL, JEM- A 2100 – Japan, performed at an accelerating voltage of 200 kV. Moreover, the functional groups in the prepared samples were evaluated using Fourier transform infra-red (FT-IR) spectra (Jasco Model 4100_Japan) from 4000 to 400cm^{-1} with a resolution of 4cm^{-1} at room temperature.
The optical properties of the prepared ZnO nanoparticles were performed by means of a computerized SPECORD 200 PLUS spectrophotometer with 1 nm step, at normal incidence at room temperature in the wavelength range 190 – 1100 nm.

4. Results

4.1 X-Ray analysis

The XRD patterns of the prepared ZnO nanoparticles are shown in Fig. (2). The figure demonstrates that the plans of ZnO nanoparticles (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) with hexagonal structure [25]. Moreover, the preferred orientations are (100), (002) and (110).

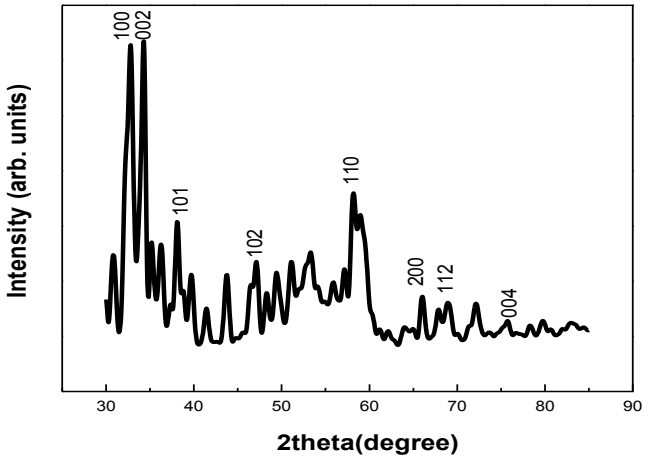

Fig. (2): XRD spectra of ZnO nanoparticles

Table 1 presents a comparison between d_{hkl} for the obtained ZnO nanoparticles and d_{hkl} for the standard hexagonal ZnO crystals [25]. From the table one can find that, the XRD data of the prepared ZnO nanoparticles are in close agreement with the standard hexagonal ZnO crystals.

Table 1: Comparison between d_{hkl} for the obtained ZnO nanoparticles and d_{hkl} for the standard hexagonal ZnO crystals

hkl	d_{hkl} (Å) calculated	d_{hkl} (Å) for standard hexagonal ZnO[26]
100	2.78	2.81
002	2.61	2.60
101	2.48	2.48
102	1.93	1.91
110	1.61	1.62
200	1.42	1.41
112	1.38	1.38
201	1.36	1.36
004	1.31	1.30

3.2 Morphology and FT-IR spectra

Scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM) were employed to obtain the shape and the size of the prepared ZnO nanoparticles. It is known that HRTEM uses both the transmitted and the scattered beams to create the image. As shown from Fig. (4), the uniform size and shape distribution of ZnO obtained at low hydrothermal reaction time and temperature. From the HRTEM the nano size of the obtained ZnO is confirmed.

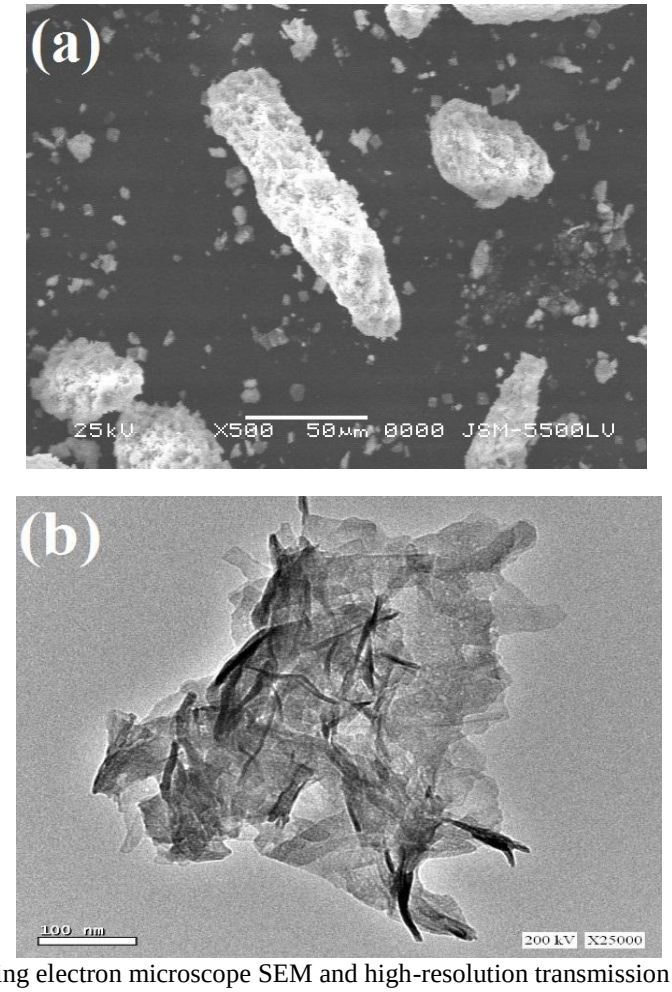

Fig. (4): (a, b) The scanning electron microscope SEM and high-resolution transmission electron microscope HRTEM respectively, for ZnO nanoparticles

The Fourier-transform infrared spectroscopy (FT-IR) was obtained as transmission spectra of the KBr sample pellets as shown in fig. (5) in order to characterize the bond structures of ZnO nanoparticles.

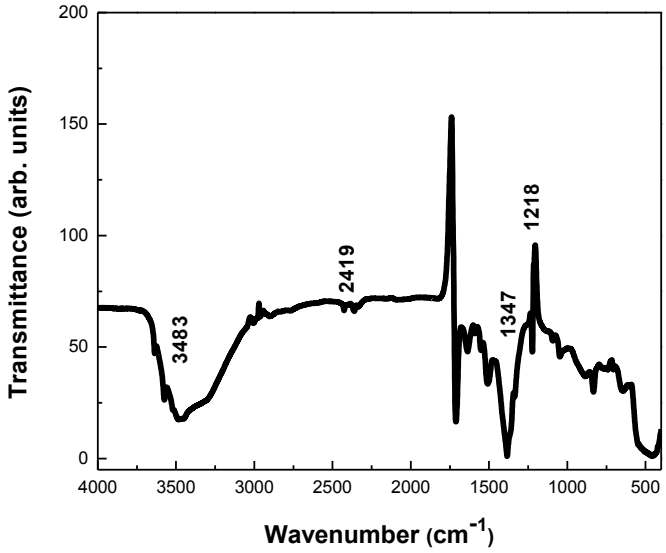

Fig. (5): FT-IR spectra for ZnO nanoparticles

Fig. (5) shows the FT-IR of the ZnO-NPs prepared by hydrothermal method in the range of 4000–400 cm^{-1}. A broad band between 450-500 indicates the presence Zn–O vibration mode. It is also observed that, there is a small peak shift to a lower wavenumber as the reaction time increases, which leading to the improvement of the optical band gab. This shift can be related to the change in the lattice parameters of the ZnO-NPs. Further, there are two absorption bands observed at 2419 and 3483 cm^{-1}. These absorption bands are expected to the stretching vibrations bonds of C=O and O–H, respectively.

3.3 Crystallite size and microstrain

The crystallite size (D) and microstrain(ε) of the obtained nanoparticles can be calculated from the peak broadening in the XRD patterns using Williamson-Hall analysis. As illustrated from eq.(2) [26], the total line broadening considers two physical factors; the first one is responsible about the crystallite size (D), while the second one reflects the strain (ε) effects:

$$\boldsymbol{\beta = \beta_D + \beta_\varepsilon} \quad (1)$$

The Williamson-Hall equation can be written as in the following:

$$\boldsymbol{\Gamma cos\theta = \frac{0.94\lambda}{D} + 4\varepsilon sin\theta} \quad (2)$$

The size broadening (β_D) is proportional to $cos^{-1}\theta$ and the strain broadening (β_ε) is proportional to $tan\theta$.
In order to calculate the crystallite size and microstrain of the ZnO nanoparticles, a relationship between $\boldsymbol{\Gamma cos\theta}$ and sinθ is drawn for prepared sample and is shown in fig (6). the average crystallite size 11.99 nm, while its microstrain value is about 0.039.

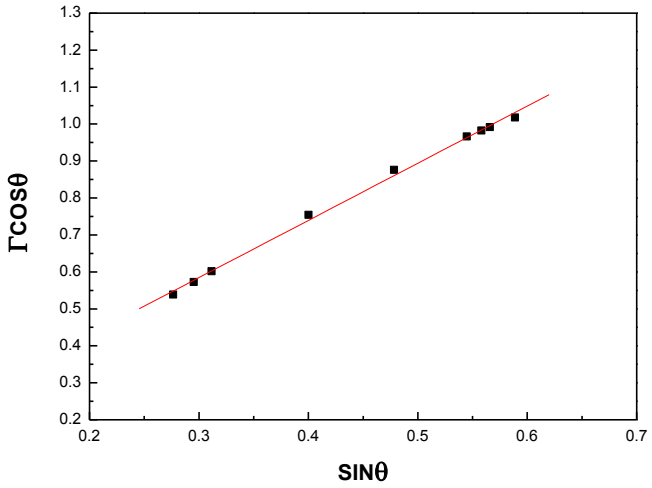

Fig. (6): Williamson-Hall plot for ZnO nanoparticles

3.4 Optical properties

Optical property of nanoparticles gives specific information about size, shape, concentration, agglomeration state, etc., near the surface of the nanoparticles. These nanoparticles interact with the incident light and show a maximum absorption at a specific wavelength. Fig. (7, 8) show the absorbance and transmittance spectra of ZnO nanoparticles over a spectral ranging between 200–900 nm. Absorption spectrum was recorded through a suspending nanopowder in distilled water at room temperature using UV-visible spectroscopy. Various absorption peaks are observed in spectra due to the relatively large binding energy of the excitation (60 mV).

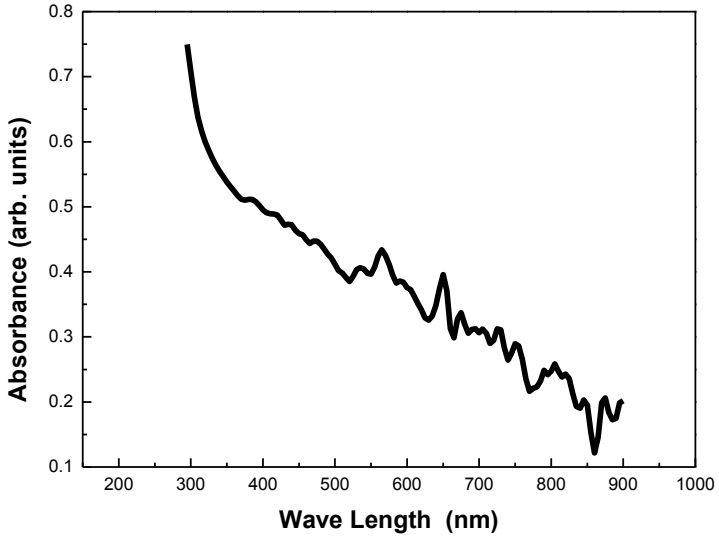

Fig. (7) The absorption spectra for ZnO nanoparticles

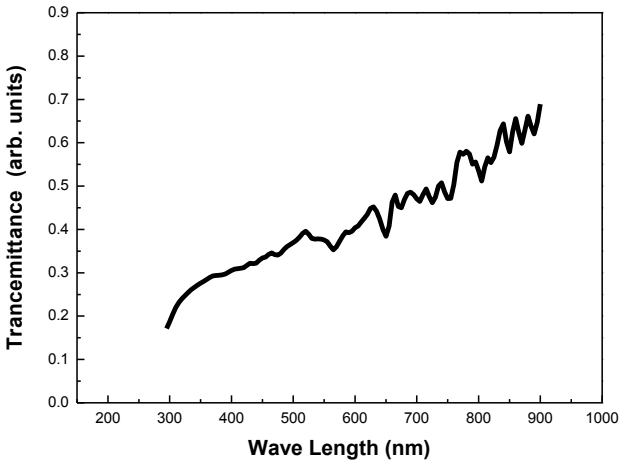

Fig. (8): The transmission spectra for ZnO nanoparticles

The optical band gap with direct transition can be calculated from the following Tauc relationship [27].

$$\alpha h\nu = B\left(h\nu - E_g\right)^n \qquad (3)$$

Where hν is a photon energy, *B* is a parameter which depends on the transition probability, α is the absorption coefficient, Eg is the optical band gap and n is a number characterizing the transition process which may take values of 1/2 and 3/2 for direct allowed and forbidden transitions, respectively [28].
Fig. (9) shows plots of $(\alpha h\nu)^2$ vs hν. The values of the optical band gap E_g of ZnO nanoparticles sample was determined to be 3.11 eV.

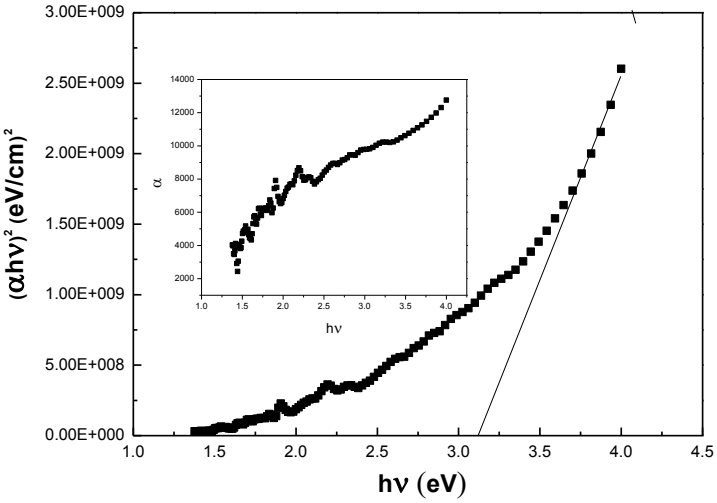

Fig. (9) The relation between $(\alpha h\nu)^2$ and hν for obtained ZnO nanoparticles

4. Conclusion

ZnO nanoparticles were synthesized at low hydrothermal temperature (75^0C) for short reaction time (4h). XRD and FT-IR results confirm obtaining ZnO nanoparticles with hexagonal structure. The obtained ZnO nanoparticles reveal that the prepared nanoparticles have relatively high absorption coefficient in the visible region, which indicates that this material can be used in photovoltaic applications.

References

[1] P. M. Aneesh, K. A.Vanaja, M. K. Jayaraj, "Synthesis of ZnO nanoparticles by hydrothermal method",Nanophotonic Materials IV, Vol. 6639, 66390J, (2007);DOI: 10.1117/12.730364.
[2] Gyu-Chul Y, Chunrui W. and Won Il P. "ZnOnanorods: synthesis, characterization and applications" Semicond. Sci. Technol, 20, S22, 2005
[3] Qiuxiang Z, Ke Y, Wei B, Qingyan W, Feng X, Ziqiang Z, Ning D, Yan S, "Synthesis, optical and field emission properties of three different ZnO nanostructures", Materials Letters, 61, 3890, 2007.
[4] Chen D, Jiao X and Cheng G. "Hydrothermal synthesis of zinc oxide powders with different morphologies". Solid State Commun 2000; 113: 363-66.
[5] Peaton SJ, Norton DP, Ip K, Hero YW and Steiner T. Recent progress in processing and properties of ZnO. SuperlatticeMicrost 2003; 34: 3-32.
[6] Hu J.Q, Ma X.L, Xie Z.Y, Wong N.B, Lee C.S, and Lee S.T. Characterization of zinc oxide crystal whiskers grown by thermal evaporation. Chem. Phys. Lett 2000; 344: 97-100.
[7] Haile S.M, Johnson D.W, Wiseman G.H, and bowenH.K.. J. Am. Ceram. Soc 1989; 72: 2004-8.
[8] Costa M.E.V, Baptista J.L. Characterization of zinc oxide powder precipitated in the presence of alcohols and amines. J. Eur. Ceram. Soc 1993; 11: 275-81.
[9] Trindade T, Pedrosa de Jesus J.D. and O'Brien P. "Preparation of zinc oxide and zinc sulfide powders by controlled precipitation from aqueous solution". J. Mater.Chem 1994; 4: 1611-17.
[10] Liu T.Q, Sakurai O, Mizutani N, and Kato M. Preparation of spherical fine ZnO particle by the spray pyrolysis methodusing ultrasonic atomization techniques. J. Mater. Sci 1986; 21: 3698-702.
[11] Andres-Verges M, Matinez-Gallego M. Spherical and rod-like zinc oxide microcrystals: morphological characterization and microstructural evolution with temperature. J. Mater. Sci 1992; 27: 3756-62.
[12] Chen Q, Qian Y, Chen Z, Zhou G. and Zhang Y. Hydrothermal Preparation of highly oriented polycrystalline ZnO thin films. Mater Lett 1995; 22: 93-95.
[13] Andeen D, Loeffler L, Padture N, and Lange FF. Crystal chemistry of epitaxial ZnO on (111) MgAl2O4 producted by hydrothermal synthesis. J. Cryst. Growth 2003; 259: 103-109.
[14] Sue K, Kimura K, Yamamoto M, and Arai K. Rapid hydrothermal synthesis of ZnOnanorods without organics. Mater Lett 2004; 58: 3350-52.
[15] Sue K, Kimura K. and Arai K. Hydrothermal synthesis of ZnOnanocrystals using microreactor. Mater Lett 2004; 58: 3229-31.
[16] Ohshima E, Ogino H, Niikura I, Maeda K, Sato M, Ito M. and Fukuda T. Growth of the 2-in-size bulk ZnO single crystals by the hydrothermal method. J. Cryst. Growth 2004; 260: 166-70.
[17] Yoshimura M. Importance of soft solution processing for advanced inorganic materials. J. Mater. Res 1998; 13: 796-802.
[18] Byrappa K, Yoshimura M. Handbook of Hydrothermal Technology: A technology for Crystal Growth and MaterialsProcessing, William Andrew Publishing, LLC Norwich, New York; 2001.
[19] Komarneni S, Li Q, Stefansson KM, and Roy R. Microwave-hydrothermal processing for synthesis of electroceramic powders. J. Mater. Res 1993; 8: 3138-76.
[20] Lencka MM, Oledzka M. and Riman RE. Hydrothermal synthesis of sodium and potassium bismuth titanates. Chem. Mater 2000; 12: 1323-30.
[21] Nishizawa H, Tani T, and Matsuoka K. Crystal growth of ZnO by hydrothermal decomposition of Zn-EDTA. J. Am Ceram Soc 1984; 67: c-98-c-100.
[22] Chittofrati A, Matijevic E. Uniform particles of zinc oxide of different morphologies. Colloid Surface 1990; 48: 65-78.
[23] Lai, Youlei, et al. "Photoluminescence and photocatalysis of the flower-like nano-ZnOphotocatalysts prepared by a facile hydrothermal method with or without ultrasonic assistance." Applied Catalysis B: Environmental 105.3-4 (2011): 335-345.
[24] Baruah, Sunandan, and JoydeepDutta. "Hydrothermal growth of ZnO nanostructures." Science and Technology of Advanced Materials 10.1 (2009): 013001.
[25] Reported File Card No: 00-003-0888, United Steel Companies, Sheffield, England, UK., *Private Communication.*
[26] G. K. Williamson and W. H. Hall, X-ray line broadening from filed Aluminum and wolfram, Acta Met. 1 (1953) 22 – 31.
[27] J. Tauc, R. Grigorovici, A. Vancu, Phys. Status Solidi 15 627 (1966).
[28] Mark Fox, "optical properties of solid", Oxford University Press. (2001).