

Structural characterization of sol gel-synthesized ZnO nano powders with different sources of Al doping

F. Mahcene^{*}, A. Chari, O. Hioual, N. Belabed and S. Kazout

Physics Chemistry of Semi Conductor Laboratory, Physics Department, Exact sciences faculty, Constantine University, Constantine 25000, Algeria

^{*}Corresponding author, email: fatima.mahcene@gmail.com

Received date: March 18, 2019 ; accepted date: Apr. 21, 2019

Abstract

Nanocrystalline zinc oxide powders with atomic Aluminum to Zinc ratio varying between 0.1% and 20% were synthesized using a simple solgel method and annealed at different temperatures. The samples were characterized by X ray diffraction, Raman spectroscopy and SEM imaging. It is found that Aluminum doping induces a monotonous decrease in ZnO grain size for annealing temperatures of 700°C and beyond. No such effect was observed below 500°C. furthermore, peaks associated with the ZnAl₂O₄ spinel phase were observed at high doping concentrations on both the X ray and infrared spectral.

Keywords: ZnO; Al₂O₃; DRX; Infra Red; Sol-gel; SEM; ZnAl₂O₄; nano composite ZnO/PMMA.

1. Inoduction

For several decades, nanometric scale transition metal oxides have been of a particular interest to researchers working on semi-conducting materials. Zinc oxide is the most studied material of this type. In its pure state, it is a n-type conductivity is induced by the existence within it of point defects such as oxygen vacancies and zinc interstitial [1]. It possesses a wide direct band gap of 3.37 eV which is associated with a large exciton binding energy of 60 meV [2]. This material's properties make it suitable for non linear optic applications [3, 4] as a gas detector [5, 6] and photocatalyst [7, 8]. In optoelectronics it serves as a filter, rectifier or resonator [9]. and it is a good transparent window in solar cells [10]. Enhancement of ZnO conductivity is obtained by dopants incorporation, the most common of which being Aluminum. This is well known to cause undesirable modifications of the structural properties of the ZnO film it is incorporated within. It has been reported that aluminum doping retards material densification [11] and decreases grain size [12].

In a previous work we reported the existence of a spinel phase type as ZnAl₂O₄ for Al content between 5% and 7%, incorporated by mixing a pure ZnO sample with alumina and annealing at temperatures higher than 500°C. This new phase was observed using Fourier transform infrared spectroscopy but not in the X-ray diffractogram [9, 13].

In this work we are pushing this study further by exploring the effect of higher aluminum doping (10% ≤ [Al] ≤ 20%) obtained using both Al₂O₃ mixing with gel ZnO and AlCl₃ incorporation in substrate solution on the structural properties of ZnO nano powder.

2. Experimental details

2.1. Preparation of pure ZnO nano crystalline powders

Nano crystalline ZnO powders were prepared using a sol-gel method described elsewhere [14]. 25.05g of zinc

acetate dihydrate precursor is dissolved in 120ml of distilled water to prepare a first solution. A second solution is prepared by dissolving 1g of glacial citric acid in 120ml of pure ethanol. The first solution is heated to a temperature of 50°C under continuous magnetic stirring, to which the second solution is slowly added. a white precipitate is immediately formed which is mainly and amorphous ZnO powder. This precipitate is dried at 80°C during one hour. It is then subjected to crystallization annealing between 450°C and 900°C for one hour in order to obtain the pure ZnO powder

2.2. Aluminum doped ZnO nano crystalline powders

Aluminum doping of ZnO nano particles was obtained via the two routes described below:

a- Gel doping

The white precipitate of pure ZnO dried at 80°C for one hour has been mixed with an Al₂O₃ nano crystalline commercial powder in the atomic ratios of 0.1, 0.5, 0.75, 1%, 10, 15 and 20% of aluminum relatively to zinc. Mixtures were annealed afterwards at 450 and 750°C for one hour in order to incorporate aluminum into ZnO and crystallize the doped samples.

b-Solution doping

AlCl₃ was added to the second citric acid/ethanol solution and fully dissolved before mixing with the Zinc Acetate solution. Atomic aluminum is thus directly incorporated into the Zn-based gel. Using this doping method, Al/Zn ratio was varied between 1% and 20%. After drying, the °C.

3. Results

3.1. X rays diffraction

3.1.1 Pure ZnO nano powder

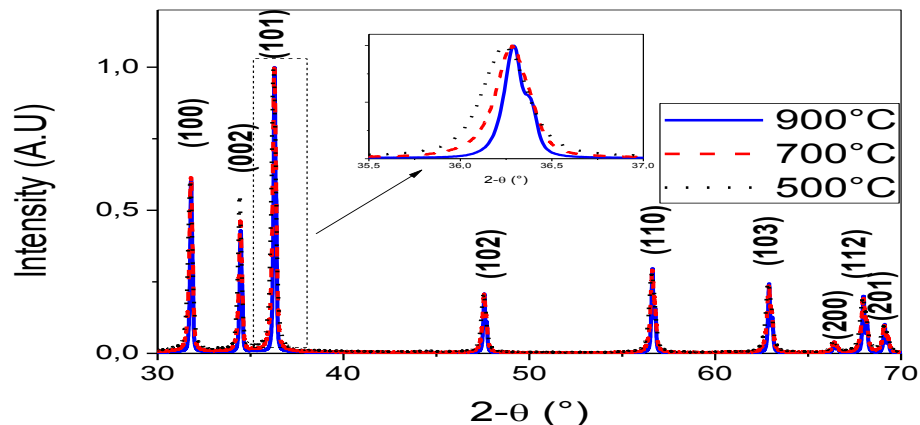


Figure 1. XRD diffractograms for pure ZnO samples annealed at different temperatures. The insert shows a zoom-in on the (101) peak.

When the crystallization temperature increases the X-Ray peak is refined showing an increase in crystallite size. Grain size inferred from the FWHM of the (101) peak

rises steadily from 29 nm to 50 nm as the annealing temperature rises from 500°C to 900°C, as shown in figure 2.

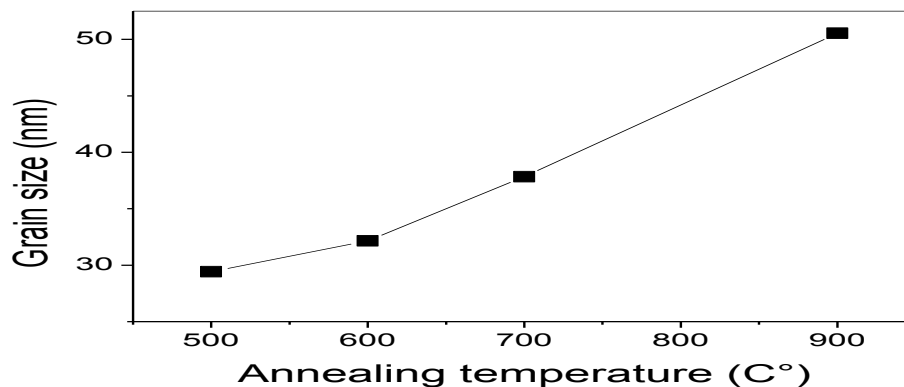


Figure 2. Grain size of undoped ZnO samples annealed at different temperatures

3.1.2. Aluminum doped ZnO nano powders

The figures 3 shows the X-ray diffraction diagram of Al doped ZnO nano powders doped with AlCl_3 at different Al concentration after annealing at 500°C and 900°C. No

significant change in grain size is seen for the samples annealed at 500°C while the ZnAl_2O_4 is detected at high doping (10 and 20%) after annealing at 700°C and above.

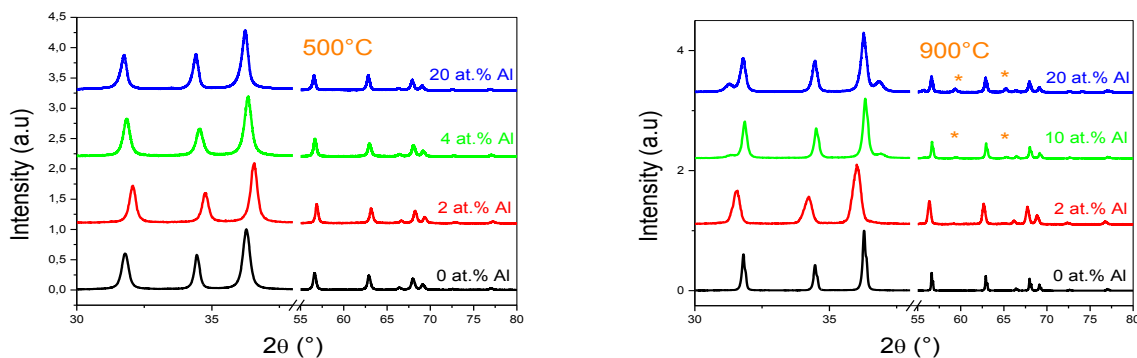


Figure 3. XRD patterns for ZnO samples doped with AlCl_3 and annealed at 500°C and 900°C. ZnAl_2O_4 peaks are highlighted with asterisks.

Figure 4 shows normalized particles grain size inferred from XRD data for both ZnO samples doped at different temperatures and using both aluminum sources. The trend is very similar for both sets of samples. No significant change in particles size is observed for either method of doping when the samples are annealed at 500°C or below.

When the samples are annealed at 700°C or above, we see a sharp decrease in particles for an aluminum concentration of up to 2% approximately. Above that concentration, particles size is constant at about 70% of that of undoped samples.

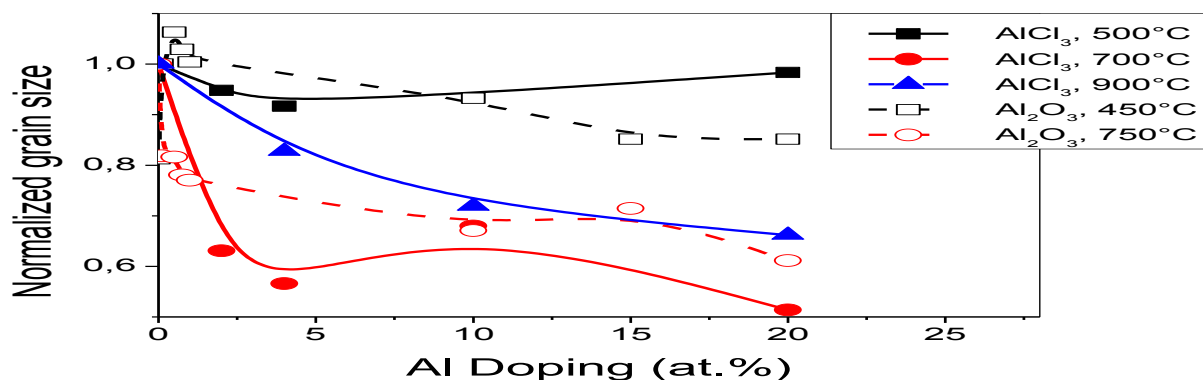


Figure 4. Evolution of ZnO particles grain size as a function of Aluminum doping using Al₂O₃ or AlCl₃ doping, and annealing at different temperatures.

3.1. Scanning electron microscopy

Figure 5 shows SEM images for undoped ZnO samples annealed at 500°C, 700°C and 900°C respectively. One clearly sees mainly spherical particles for all annealing temperatures. An increase in grain size is observed

between 500°C and 700°C. Between 700°C and 900°C, we observe the formation of large monolithic structures associated with the sintering of ZnO particles (see the top right corner of figure (c)).

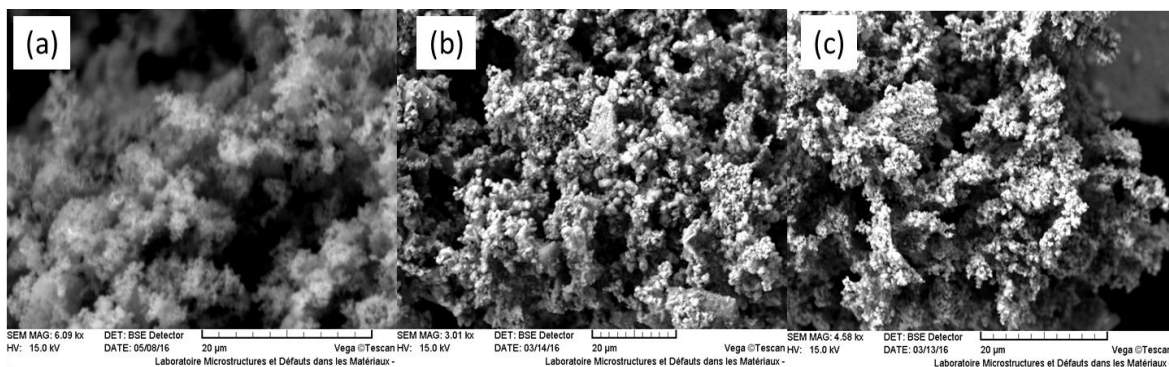


Figure 5. SEM images of undoped ZnO samples annealed at 500°C (a), 700°C (b) and 900°C (c) respectively. See the larger structure on the top right corner of figure (c)

Figure 6 shows the effect of Al doping through Al₂O₃ solid phase addition, followed by an annealing at 750°C on the structure of ZnO nanoparticles. One can observe that

doped ZnO particles are still spherical in shape and their size decreases when Al doping is increased from 0.1at.% to 1at.%.

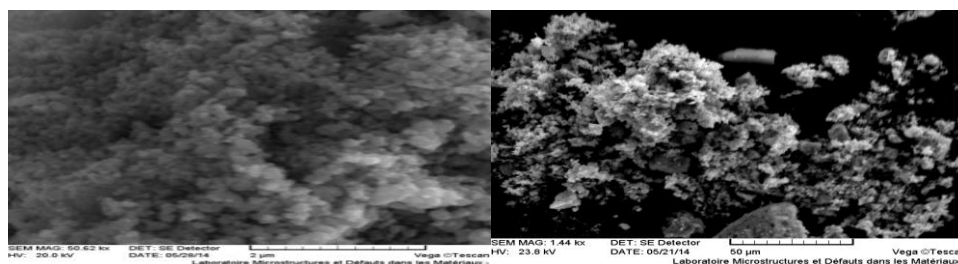


Figure 6. SEM images for ZnO samples doped with 0.1% and 1% Aluminum and annealed at 750°C

3.2. UV-Visible transmission measurement

Figure 7 shows the optical band gap extracted from transmission measurements for samples annealed at 750°C with different concentrations of solid phase Al doping. We first see a sharp increase in band gap, between 0 and 1% Al at.%, the band gap then stabilizes and starts decreasing for concentrations above 7 Al at.%, which coincides with the apparition of the AlZn_2O_4

spinel phase on XRD diffractogram. No such trend is observed when annealing the samples at 450°C.

The increase in band gap is easily explained by confinement effects induced by the reduction in grain size associated with Al doping. The following sharp decrease in band gap is attributed to the formation of the mixed $\text{ZnO}/\text{ZnAl}_2\text{O}_4$. These results correlate very well with XRD results shown above. The gap value observed in literature; i. e. 3.8 eV[15] is comparable with the gap domain found experimentally.

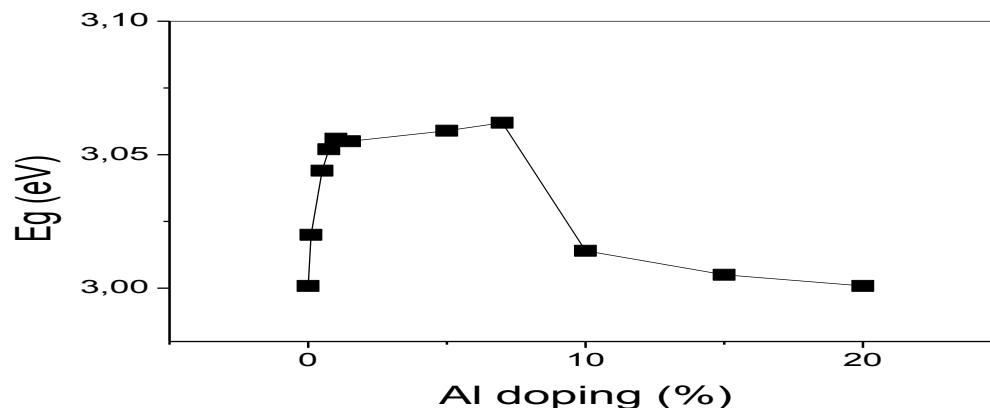


Figure 7. Optical band gap for ZnO samples annealed at 750°C and doped using Al_2O_3 .

3.3. FTIR measurements

FTIR measurements were performed on ZnO samples doped with both methods and annealed at various temperatures.

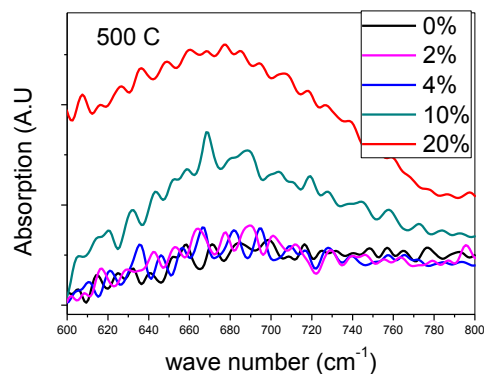
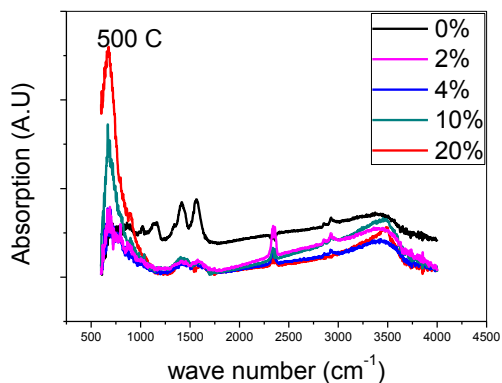
Figure 8 shows the absorption spectra for the samples doped using AlCl_3 . Similar results were obtained when doping with Al_2O_3 .

For samples annealed at 500°C on which no spinel phase was observed, we see the apparition of a broad Gaussian peak centered at around 680 cm^{-1} , when Al is introduced into the sample. This peak increases

monotonically with Aluminum concentration. This peak is thus associated with an intermediary phase in the ZnO matrix. [16]

When annealing at 900°C, an identical peak is also seen. When doping at 10 Al. at% and above, we also see a much narrower peak located at about 650 cm^{-1} which is not seen for samples annealed at 500°C.

Based on XRD results this second peak is unambiguously associated with the ZnAl_2O_4 phase.



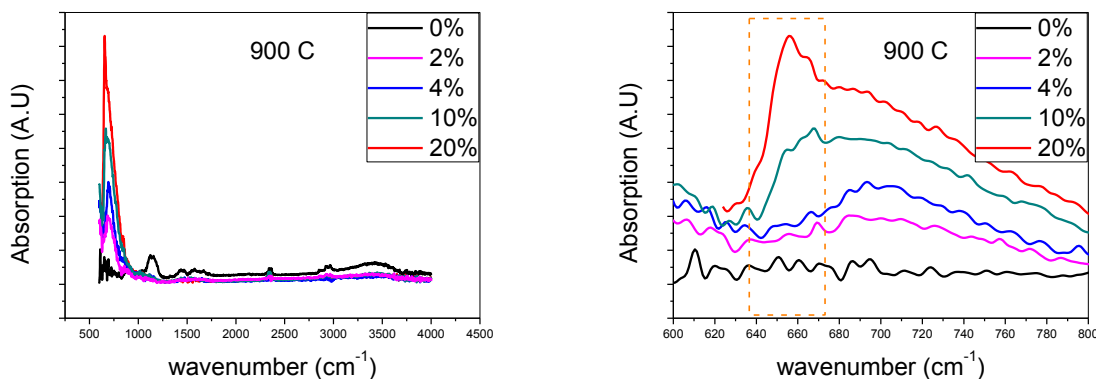


Figure 8. FTIR spectra for ZnO samples doped using AlCl₃. Results for samples annealed at 500°C (above) show a broad peak at 680 cm⁻¹. An additional peak at 650 cm⁻¹ is observed with an annealing at 900°C for Al concentrations at 10% and above.

4. Discussion

The evolution of particles size as a function of annealing temperature and Al doping could easily be understood in terms of Zn long range diffusion during annealing followed by crystallization around Al₂O₃ particles. Al₂O₃ particles are either directly introduced by doping, or formed from AlCl₃/H₂O in the solution. Results are hence very similar regardless of the method with which Al is introduced. The increase in aluminum content leads to a higher density of crystallization sites and thus an overall decrease in ZnO particles size. Zn diffusion is thermally activated and hence is much lower at 500°C. This explains why we do not observe a significant grain size reduction when annealing at 500°C and below.

Other works have shown that Aluminum can also diffuse into ZnO. In our case, however, when using solid phase doping ZnO is not yet formed and when Al₂O₃ is introduced into a loosely bonded gel matrix, Zn diffusion should therefore be easier.

At temperatures of 700°C and above, Al₂O₃ amalgamates with the ZnO matrix inducing doping of ZnO crystals. If Al local concentration exceeds the solubility limit of 3.7%, we have formation of the ZnAl₂O₄ spinel phase.

5. Conclusion

In this paper we have studied the effect of Aluminum incorporation into ZnO. We have observed that identical results are observed regardless of the doping source. Aluminum doping is believed to involve long range Zn diffusion towards Al₂O₃ particles followed by an amalgamation at sufficiently high temperatures, leading to the formation of the ZnAl₂O₄ spinel phase when Al concentration exceeds the solubility limit. XRD results are in excellent

agreement with both SEM and optical band gap trends. Comparison with

FTIR measurements allowed to associate the 650 cm⁻¹ peak with the spinel phase.

Acknowledgments

The authors would like to thank M^{cm} Kirouche , Prof. M . Zaabat , M A. Boudjada and M Boultif for measurement.

References

- [1] A.F. Kohan, G. Ceder, D. Morgan , C. D. Van, first principles of point defects in ZnO, Phys. Rev. B, 61, (2000)15019-15027.
- [2] W. Y. Liang and A.D. Yoff, Transmission spectra of ZnO single crystal, Phys. Rev. Lett. 20, (1968) 59-62.
- [3] W. Li, D. Mao, F. Zhong, X. Wang, X.Liu, S. Zou and Q. Li and J. Xu, Characteristics of ZnO: Zn phosphor thin films by post deposition annealing, Nucl. Instrum. Methods. Phys. Res.; B-Beam interaction with materials and atoms, 69, (2000) 59-63.
- [4] P. Fons., K. Iwata, S. Niki, A. Yamada and K. Matsubara, Growth of higher quality epitaxial ZnO on *α*-Al₂O₃, J. Cryst. Growth 201-202, (1999) 627- 632.
- [5] J. M. Davidson, C. H. Lawrie and K. Sohail; Kinetic of the absorption of hydrogen sulfide by high purity and doped high surface area zinc oxide., Ind. Eng. Chem. Res., 34, (1995) 2981-2989.
- [6] G. Goraillo and C. Calderon, Effect of Gas Chemisorption on the Electrical Conductivity of ZnO Thin Films, Advances in Materials Science and Technology, Vol 1, N° 1, (1996) 01-05.
- [7] M. C. Markham, M. C. Hannan and S. W; Evans, Factor Influencing the Oxidation of Phenols

- Catalyzed by Zinc Oxide and Light, *J. Am. Chem. Soc.*, 76(3), (1954) 820-823.
- [8] H. Yoshiki, K. Hashimoto and A. Fujishima, Reaction Mechanism of Electrodes Metal Deposition using ZnO Thin Films(1): Process of Catalyst Formation. *J. of The Electrochem. Soc.* Vol 142, Issue 2, (1995) 428-432.
- [9] C. R. Gorla, N. w. Emanetoglou, S. Lang, W. E. Mayo, Y. Lu, M. Wraback and H. Shen, *J. Appl. Phys.*, 85, (1999) 25595.
- [10] A. Chari, A. Chaieb, F. Mahcene and M. Malik, Pure and Al Doped ZnO Nano Powders, X-Ray and Infra red Analysis, ICCMREA 18-22 January 2014, Sousse Tunisia.
- [11] G.K. Williamson and W. H. Hall; X-ray line broadening from filed aluminum and wolfram, *Acta Metall.*;1, (1953) 22.
- [12] C.M. Fong, C. K. Loong and G. A. de Wijs. Phonon spectrum of Zn₂O₄ spinel from inelastic neutron scattering and first principles inelastic neutron scattering and first principles calculations. *Phys. Rev. B*, 66(14), (2002) 14431.
- [13] Y.S. Kim and W-P.Tai, Electrical and optical properties of Al-doped ZnO thin films by sol-gel process, *Applied Surface Science* 253, (2007) 4911-4916.
- [14] M. Ohyama, H. Kozuka and T. Yoko, Sol-gel preparation of transparent and conductive aluminum-doped zinc oxide films with highly preferential crystal orientation, *J. Am. Ceram. Soc.* 81, (1998) 1622-1632.
- [15] C.Wan, H. Tan, SheJin, H Yang. M. Tang and J. He Highly conductive Al-doped tetra-needle-like ZnO whiskers prepared by a solid state method, *Materials Science and Engineering B* 150, (2008) 203-207.
- [16] R. Chandramohan, V. Dhanasekran, R. Arumugam, K. Sundaram, Thirumalai and T. Mahalingam, Physical properties evaluation of annealed ZnAl₂O₄ alloy thin film,. *D. J. of Nanomaterials and Biostructures* 7, 3, July - September (2012) 1315 - 1325