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Green Mediated Synthesis and Characterization of ZnO Using Euphorbia Milli Latex as Fuel

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Abstract: ***In this paper, a simple green route combustion method of synthesis was adopted for the synthesis of Zinc oxide nano particles using Euphorbia milli latex as fuel. As prepared product was characterized by Powder X Ray Diffractometer (PXRD), Fourier Transform Infra-Red spectroscopy (FTIR), UV-Visible spectroscopy, Rietveld refinement, Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS) and Transmission Electron Microscopy (TEM). The concentration of plant extract plays an important role in controlling the size of the particle and its morphology. PXRD graphs showed that the particles were well crystallised. The average particle size was calculated using Scherrer equation and advanced WH plots. The average particle size is around 50nm. This result was also supported by SEM and TEM analysis. FTIR shows the characteristic peak of ZnO at 435 cm^{-1}. SEM and TEM micro graphs show that the particles are spherical in nature. EDS of SEM analysis confirmed that the elements are only Zn and O. No other impurity elements were found in the sample. Crystal parameters were determined using Rietveld refinement. From UV-Visible spectra band gap energy was found to be 3.44 eV. This method is fast, eco friendly and convenient for the synthesis of ZnO nano particles (NPs).***

Keywords: ZnO NPs, Euphorbia milli latex, SEM with EDS, Rietveld refinement

1. Introduction

Nano crystalline metal oxides have attracted wide attention due to their unique properties, which are technologically very useful in nano device fabrications . In recent years, nanomaterials have been widely studied compared to their bulk materials due to their interesting chemical and physical properties [1]. Among them, Zinc oxide is a unique and very important inorganic material. This is because of its distinct characteristic features and novel applications in wide areas of technology and science. ZnO has typical properties such as transparency in the visible range, direct band gap, high electrochemical stability, toxic absorbance and plenty of availability in nature [2]. The III–V and II–VI based dilute magnetic semiconductors (DMS) are very encouraging materials for spintronics applications because DMS show ferromagnetic nature at room temperature [3]. ZnO has a high excitation binding energy of 60 meV and wide semiconductor band gap of ~3.37 eV [4,5]. It is one of the hardest materials in the II to VI group of elements. As a result of this ZnO devices do not suffer from dislocation degradation during working [6–8]. ZnO has gained much importance as it can be applied in many applications such as for gas sensing, catalyst, for semiconductors, UV-shielding materials, nano generators, an antibacterial agent, cosmetics as well as medicinal applications [9-13]. In recent days controllable synthesis of ZnO nanomaterials of desired size and shapes has been the subject of investigation by researchers because it has been found that most of the properties of ZnO nanoparticles are size and morphology dependent. Several methods have been developed to synthesize ZnO nanoparticles such as precipitation, hydrothermal, combustion, sono chemicals, chemical vapor deposition, spray pyrolysis, sol gel [14-20]. Among various methods developed, combustion synthesis is a simple, convenient, fast and efficient method which involves the redox reaction between an oxidizing reagent usually desired metal salts and a reducing agent forming highly pure products [21,22].

Euphorbia milli is a species of flowering plant in the spurge family, Euphorbia, native to Madagascar. The sap is moderately poisonous and causes irritation on contact with skin or eyes. This plant has gained the Royal Horticultural Society's Award of Garden Merit. *Euphorbia milli* serves as a potted ornamental in many different countries. Tropical residents also use it for hedges. *Euphorbia milli* plays a role in folk medicine. The Chinese use it as a cure for cancer, and some Brazilians believe that it can cure warts. Milin, an extract of *Euphorbia milli* latex, is a glycosylated serine protease (an enzyme that breaks down protein and has a sugar attached to it). Because it is more stable than most proteases, it will be useful to food processers and makers of detergents who have been using proteases in their operations. Milin will also be useful to research scientists who use serine proteases to get rid of unwanted proteins so that they can obtain the ones they want in pure form.

Green mediated synthesis was largely unexploited compared to other synthesis routes. Chandrasekhar et al. [23] reported the synthesis of ZnO:Eu3+ nano phosphor using E-tirucalli plant latex. The phosphors synthesized by this method showed very good chromaticity coordinates in the white light region which was highly useful for white light emitting diodes. D. Kavyashree et al synthesised ZnO using Guizotia abyssinica seed extract and reported that the prepared samples can be used for the display device applications[24]. D. Suresh et al. studied Photo degradative, antimicrobial and

antioxidant activities of ZnO nano powders and reported that ZnO can be a good photo degradative [25].

2. Experimental

In the present report, the milky latex of *Euphorbia milli* was used as a reducing agent for the synthesis of Zinc oxide (ZnO) nano particles. Hydrated Zinc Nitrate was procured from Sigma-Aldrich and used as starting materials without further purification. Latex of *Euphorbia milli* was used as fuel for synthesis of ZnO nano particles. In a typical synthesis 2ml, 4ml and 6ml of crude latex were dissolved in 8ml-10 ml of double distilled water. To each 1g of Zinc Nitrate was added and mixed well using magnetic stirrer for approximately 5-10 min and then placed in a preheated muffle furnace maintained at 450 ± 10° C. The reaction mixture boils froths and thermally dehydrates forming foam. The entire process was completed in less than 30 min. Further, the final white powder was kept for calcination at a temperature of 750 ^{0}C for two hr in the muffle furnace.

3. Results and Discussion

Fig.1 shows the PXRD pattern of ZnO NPs prepared using different volumes of *E.milli* latex (2ml, 4ml, 6ml) fuel via solution combustion method. All the diffraction peaks were indexed to hexagonal wurtzite structure of ZnO NPs with lattice constants a = 3.2595 Å , c = 5.221 Å.

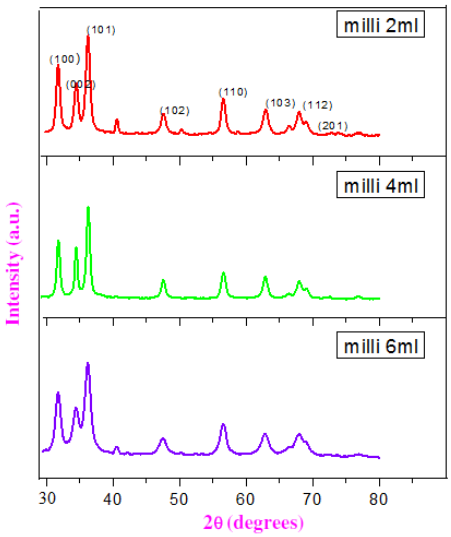

Figure 1: PXRD patterns of ZnO prepared using latex of *Euphorbia milli* as fuel (2ml, 4ml and 6ml).

The crystallite size of the ZnO NPs with different *E.milli* latex was calculated using Scherrer's equation D = kλ/β cosθ where D is the crystal size, k is the shape constant (~0.9), λ is the X ray wavelength, θ is the Bragg's angle and β is the line broadening at half the maximum intensity (FWHM) in radians. The crystallite size was found to be in the range of 3–11 nm. Further dislocation density (δ) and micro strain (ϵ) was estimated by the relation $\delta = 1/D^2$ where D is the crystal size in nm and micro strain ε = β cosθ/4. The micro strain is found to increase with increase in fuel concentration. The average dislocation density for 6ml,4ml and 2ml *E.milli* was found to be 104.49X10^{15}, 59.53X10^{15} and 24.38X10^{15} as shown in Table1.The small δ for ZnO NPs indicates higher crystallization of the sample. Thus 6ml shows high level of surface defects and deteriorates crystal quality. But 4ml and 2ml ZnO NPs shows the low level of surface defects.

Table 1: Crystallite size, strain, Dislocation density and stress of ZnO nano particles prepared by various concentration of *E. milli* plant milky latex

Sample ZnO (ml)	*Scherrer Equation D(nm)*	*Strain ε x 10^{-3}*	*Dislocation density δ=1/D^2 x10^{15}*	*Stress ζ=εYx 10^{6}Nm^{-2}*
2	11	4.68	24.338	0.609
4	5	7.77	59.536	1.01
6	3	10.94	104.494	1.422

The crystallite size was also estimated for the powder from the full width half maximum of the diffraction peaks using William Hall modified form strain, Uniform Deformation Model (UDM), Uniform Stress Deformation Model (USDM), Uniform Deformation Energy-Density Model (UDEDM). Depending on different θ positions the separation of size and strain broadening analysis was done using William and Hall plots. The following results are the addition of the Scherrer equation and ε ≈ βs/tanθ. Therefore β_{hkl} = (kλ/β cosθ) + 4ϵ tanθ. Rearranging this equation we get β cosθ = kλ/D + 4ε sinθ .This equation stands for Uniform Deformation Model (UDM), where it is assumed that strain is uniform in all crystallographic directions. From the lattice parameters calculations it was observed that this strain might be due to the lattice shrinkage. Figure 2 shows W-H plot (UDM) of ZnO nanoparticles using *E.milli*i latex as fuel.

Using the intercept and slope, particle size and micro strain were calculated.UDM analysis is shown in Table2.From the Hooke's Law maintaining linear proportionality between stress and strain, $\zeta = Y\varepsilon$, where ζ is the stress and Y is the Young's modulus. USDM was a plot of β cosθ versus 4 sinθ /Y (where Y= 130x10^9 Nm^{-2}) The USDM plot was shown in figure 3.

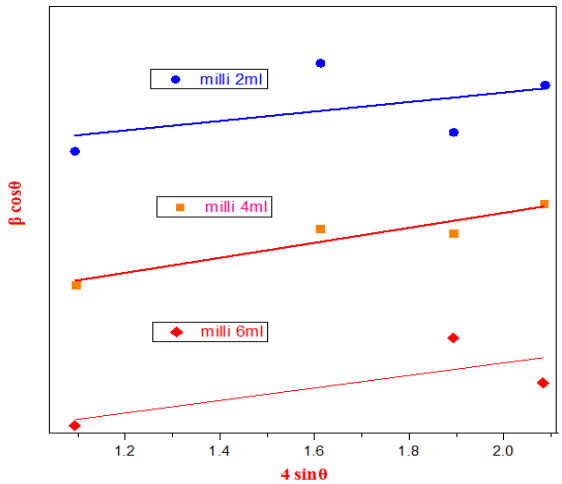

Figure 2: The W-H analysis (UDM plot) of ZnO nanoparticles using *Euphorbia milli* as fuel

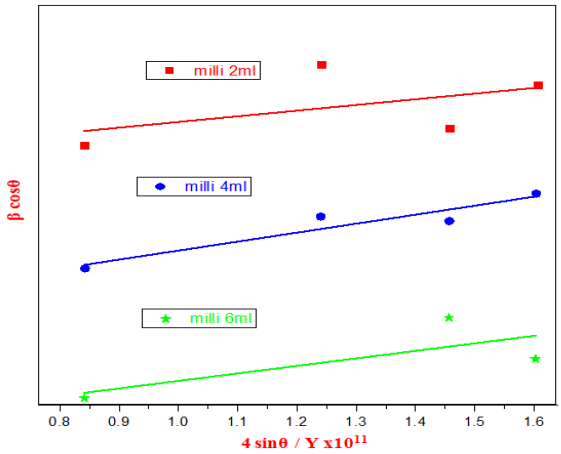

Figure 3: The W-H analysis (USDM plot) of ZnO nanoparticles using *Euphorbia milli* as fuel

The graph of β cosθ versus 4 sinθ /$(Y/2)^{1/2}$ (where Y= 130x10^9 Nm^{-2}) was plotted. The plot obtained is shown in Figure 4. Using the intercept and slope particle size and energy density were calculated. micro strain ε = $(2u / Y)^{1/2}$ and stress ζ = εY were also calculated. UDEDM analysis results are shown in Table 2. From the table2 we can conclude that as the particle size decreases, strain increases and energy density increases.

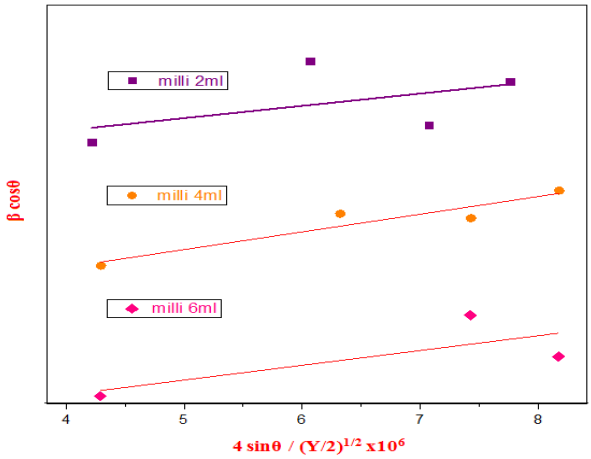

Figure 4: The W-H analysis (UDEDM plot) of ZnO nanoparticles using *Euphorbia milli* as fuel

Figure.5 shows the FTIR spectra of ZnO NPs taken in the range (400-4500 cm^{-1}). The FTIR peak at 3436cm^{-1} represented O-H group stretching of O-H, H-bonded single bridge. The broad peak in the range of 3900 to 3800 cm^{-1} is attributed to water molecule present in thin films. The transmittance band at 435 cm^{-1} correspond to the ZnO bonding and confirm the formation of ZnO particles.

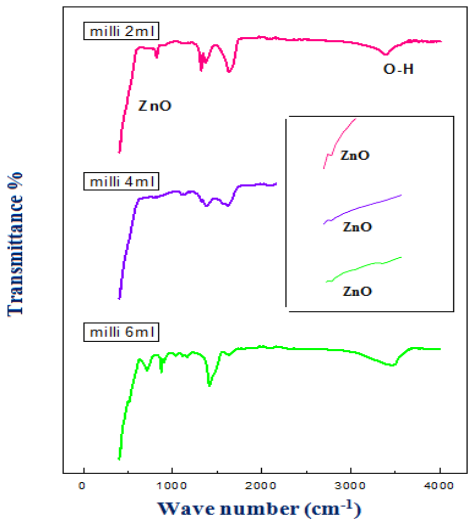

Figure 5: FTIR of ZnO with *E. milli* as latex

Fig 6 shows the optical absorption spectrum of ZnO NPs synthesized by using latex of *E.milli*. The sample has a clear and strongly observed absorption peak below at 400 nm. The band gap energy corresponds to the absorption limit can be roughly evaluated by the relation $E_g = hC/\lambda$ Where E_g : band gap energy (eV), h: Planck's constant (6.625X10^{-34} J s), C:velocity of light and λ: wavelength (nm) correspond to maximum absorption. From Fig 6 the absorption edge are positioned at 360 nm which corresponds to the band gap value of 3.44 eV.

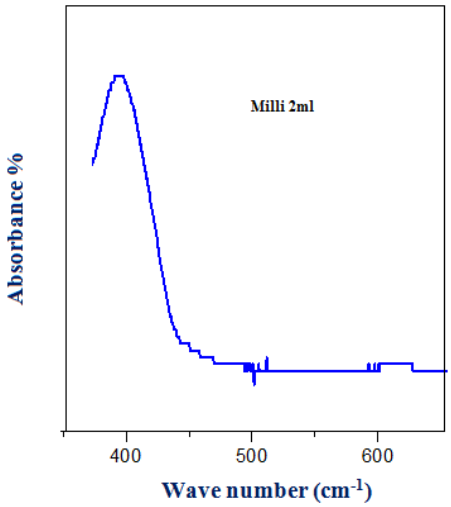

Figure 6: UV Visible spectra of ZnO using *E.milli* latex as fuel

Fig 7 shows the SEM micro graphs of as prepared ZnO NPs. It is observed that the particles were almost spherical in nature. Further, the particles are agglomerated to form foam like bunch of particles. The agglomeration could be induced by densification resulting in the narrow space between particles. When gas is escaping with high pressure, pores are formed with the simultaneous formation of small particles. The morphology of the powders reflects the inherent nature of the combustion process. The observations of the SEM studies crystallite size determination calculations were supported by TEM analysis.EDS and the table shows weight and atomicity of Zn and O in ZnO sample.

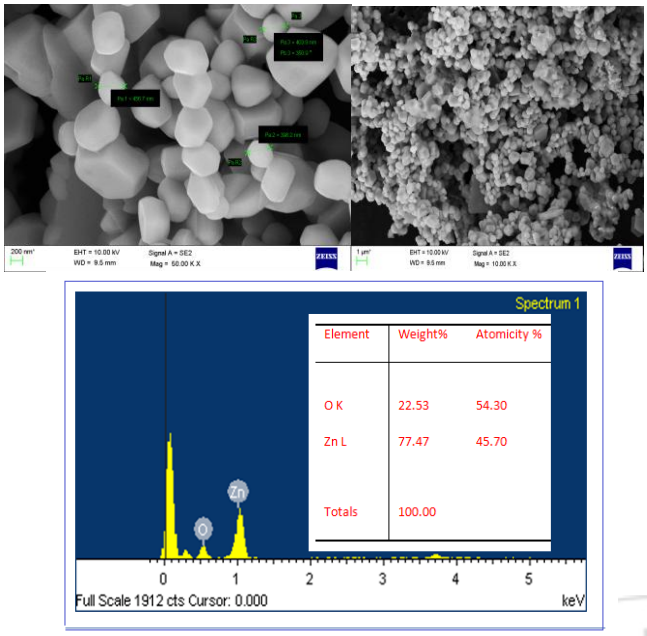

Figure 7: SEM images and EDS of ZnO nanoparticles.

The TEM images of ZnO are shown in Fig.8 respectively. The TEM study was carried out to understand the crystalline characteristics and size of the nanoparticles. The images TEM of ZnO confirm that the particles are almost spherical with non uniform thickness. The average particle size by histogram was found to be 50 nm to 200nm. This image reveals that most of the ZnO NPs are quasi-spherical and their diameter is about 50 nm. The SAED pattern revealed that the diffraction rings of the synthesized ZnO exhibited Debye–Scherrer rings assigned (100), (002), (101),(102), (110), (103), (200), (112), (201), (004) and (202) respectively. Lattice planes of the face centered cubic (fcc) ZnO, indicating that the biogenic NPs seen in the TEM images are nano-crystalline in nature as shown in Fig 8c. The HRTEM shows the planes with inter-planar spacing of 3.128Å. The particle size determined from TEM analysis is in good agreement with XRD analysis.

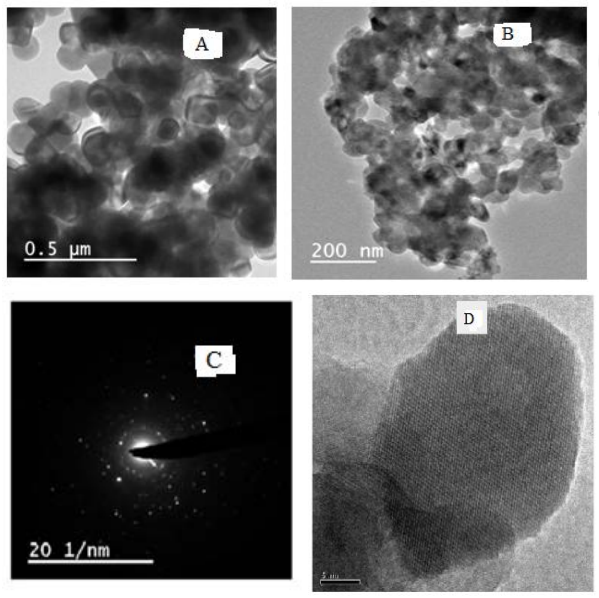

Figure 8: TEM images of ZnO NPs (A & B), SAED pattern(C) and HRTEM (D) of ZnO .

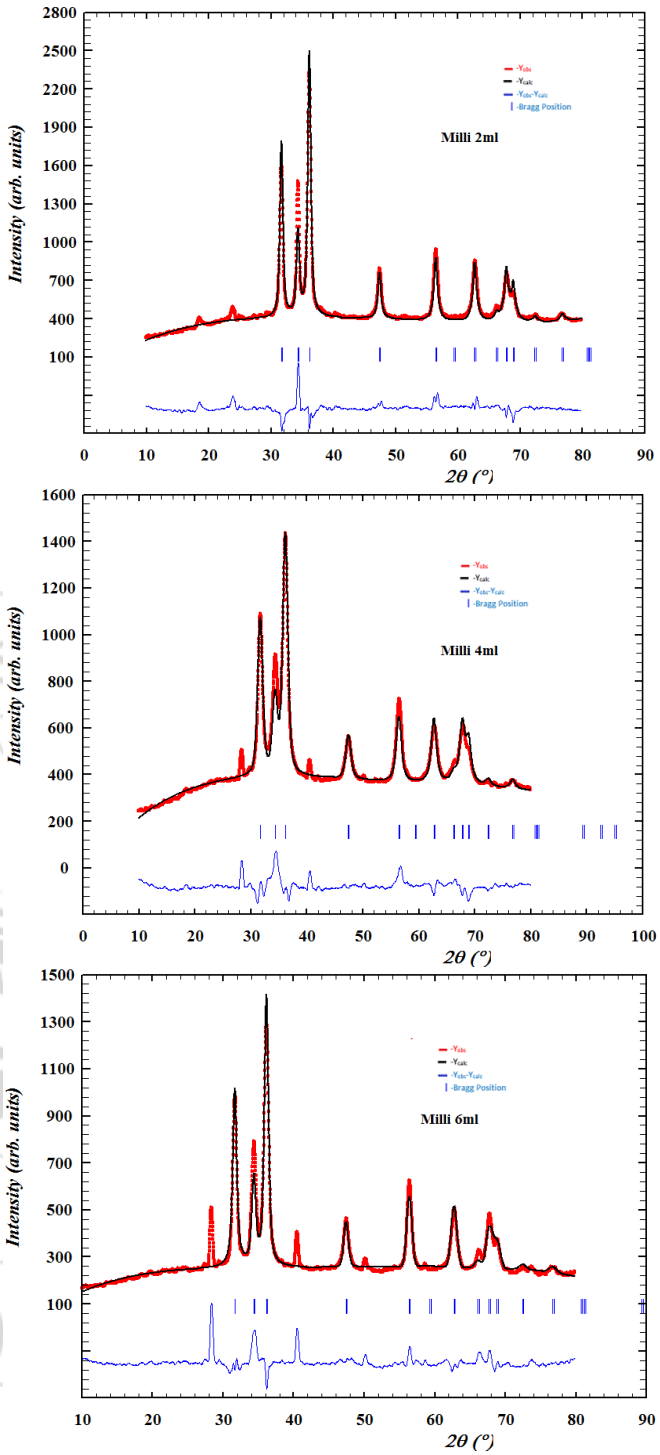

Figure 10: Rietveld refinement of ZnO

Rietveld refinement was done using FullProf software. Pseudo–Voigt function was used in order to fit the several parameters to the data point. The refined parameters such as occupancy, atomic functional positions for ZnO NPs at 2ml, 4 ml and 6ml latex of *E.milli* were summarized in Table 3. A good agreement was obtained between the experimental relative intensity (observed XRD intensities) and simulated intensity (calculated XRD intensities). Cell parameters and cell volume confirms hexagonal wurtzite structure of ZnO.

4. Conclusions

ZnO NPs were synthesized by combustion method using *E.milli* latex as reducing agent. From XRD, particle size were 11nm, 5nm and 3nm. This result was also supported by SEM and TEM results. FTIR spectra showed characteristic spectra of ZnO at 435 cm^{-1}. From UV Visible spectra energy gap was found to be 3.44 eV. SEM and TEM micro graphs shows that the particles are spherical in shape. The HRTEM of this method shows the planes with inter-planar spacing of 3.128 A°. GOF (goodness of fit) by Rietveld refinement is ~ 1.2, which shows good agreement between theoretical and experimental values. Advantages of this method is that it is eco friendly, fast , convenient and ZnO can be used for suitable applications like gas sensing, catalyst, for semiconductors, UV-shielding materials, nano generators, an antibacterial agent, cosmetics as well as medicinal applications.

References

[1] C.R. Martin, Science 266 (1994) 1961–1966.
[2] V. R. Shinde, T. P. Gujar, C. D. Lokhande, R. S. Mane, and S. H. Han, *Mater. Chem. Phys*. Vol 96, 2006, pp 326-330.
[3] S. Y. Yang, A. B. Pakhomov, S. T. Hund, and C. Y. Wong, *IEEE Trans. Magn.* Vol 38, 2002, pp 2877 – 2879.
[4] Y.I. Alivov, E.V. Kalinina, A.E. Cherenkov, D.C. Look, B.M. Ataev, A.K. Omaev,M.V. Chuki Chev, D.M. Bagnall, Appl. Phys. Lett. 83 (2003) 4719–4721.
[5] D. Calestani, M.Z. Zha, R. Mosca, A. Zappettini, M.C. Carotta, V. Di Natale, L.Zanotti, Sens. Actuat. B Chem. 144 (2010) 472–478.
[6] L.L. Xia, T.Q. Xin, S.C. Lu, L.Y. Chun, Chin. Phys. Let. 22 (2005) 998–1001.
[7] C. Suresh, J.M. Kelly, R. Ramesh, D.E. Mc, J. Mater. Chem. C 1 (2013) 3268–3281.
[8] Z.L. Wang, J. Phys. Condens. Matter 16 (2004) R829–R858.
[9] A. Yu, J. Qian, H. Pan, Y. Cui, M. Xu, L. Tu, Q. Chai, X. Zhou,Sensors Actuators B Chem. 158 (2011) 9-16.
[10] R. Li, S. Yabe, M. Yamashita, S. Momose, S. Yoshida, S. Yin,T. Sato, Solid State Ionics 151 (2002) 35-241.
[11] M.P. Lu, J. Song, M.Y. Lu, M.T. Chen, Y. Gao, L.J. Chen,Z.L. Wang, Nano Lett. 9 (2009) 1223-1227.
[12] Ling Chuo Ann, Shahrom Mahmud, Siti Khadijah Mohd Bakhori, Amna Sirelkhatim, Dasmawati Mohamad, Habsah Hasan, Azman Seeni, Rosliza Abdul Rahman, Ceram. Int. 40 (2014) 2993-3001.
[13] R. Salehi, M. Arami, N.M. Mahmoodi, H. Bahrami, S. Khorramfar, Colloids Surfaces B 80 (2010) 86-93.
[14] Davood Raoufi, Renew. Energy 50 (2013) 932e937.
[15] J. Ma, J. Liu, Y. Bao, Z. Zhu, X. Wang, J. Zhang, Ceram. Int.39 (2013) 2803-2810.
[16] K.S. Sumana, B.M. Nagabhushana, C. Shivakumara, M. Krishna, Chandrasekhara Murthy, N. Raghavendra, Int. J. Sci. Res. 1 (2012) 83-86.
[17] S. Suwanboon, Structural and optical properties of nanocrystalline ZnO powder from sol-gel method, Sci. Asia 34(2008) 31-34.
[18] L.V. Podrezora, S. Porro, V. Cauda, M. Fontana, G. Cicero, Comparison between ZnO nanowires grown between chemical vapor deposition and hydrothermal synthesis, App. Phys. A 113(2013) 623-632.
[19] R. Ayouchi, F. Martin, D. Leinen, J.R. Ramos-Morrado, Growth of pure ZnO thin films prepared by chemical spray pyrolysis on silicon, J. Cryst. Growth 247 (2013) 497-504.
[20] A. Khorsand Zak, W.H. Abd Majid, H.Z. Wang, Ramin Yousefi, A. Moradi Golsheikh, Z.F. Ren, Sonochemical synthesis of hierarchical ZnO nanostructures, Ultrason. Sonochem 2 (2013) 395-400.
[21] K.C. Patil, S.C. Aruna, M. Mimani, Combustion synthesis: an update, Curr. Opin. Solid State Mater. Sci. 6 (2002) 507-512.
[22] K.C. Patil, M.S. Hegde, Tanu Rattan, S.T. Aruna, Chemistry of Nanocrystalline Oxide Materials, World Scientific, New Jersey,2008.
[23] M. Chandrasekhar, H. Nagabhushana, S.C. Sharma, K.H. Sudheer Kumar, N. Dhananjaya, D.V. Sunitha, C. Shivakumara, B.M. Nagabhushana, J. Alloy. Compd. 584 (2014) 417
[24] D. Kavyashree , R.AnandaKumari , H.Nagabhushana , S.C.Sharma , Y.S.Vidya , K.S. Anantharajuf, B.DarukaPrasad , S.C.Prashantha , K.Lingarajuh, H.Rajanaik Journal ofLuminescence167(2015)91–100
[25] D. Suresh , Udayabhanu , P.C. Nethravathi , K. Lingaraju , H. Rajanaika , S.C. Sharma ,H. Nagabhushana, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 1467–1474

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Table 2: Crystallite size, strain, stress and energy density of ZnO by WH plots.

sample	*UDM*		*USDM*			*UDEDM*			
	D (nm)	$\epsilon X 10^{-3}$	*D (nm)*	$\epsilon X 10^{-3}$	ζ *(M Pa)*	*D (nm)*	$\epsilon X 10^{-3}$	ζ *(M Pa)*	*U* (kJm^{-3})
2ml	11	14.03	11	14.07	1830	11	14.04	1825.2	12816
4ml	7.4	18.57	7.4	18.79	2443	7.4	18.55	2441.4	22944
6ml	5	18.79	5	18.56	2414	5	18.55	2411.5	22372

Table 3 Crystal parameters of ZnO by Rietveld refinement

	Milli 2ml	*Milli 4ml*	*Milli 6ml*
Crystal system	Hexagonal	Hexagonal	Hexagonal
Laue class	6/m	6/m	6/m
Point group	6	6	6
Bravis lattice	P	P	P
Lattice symbol	hP	hP	hP
Cell parameters			
a=b	3.2595	3.2595	3.2617
c	5.221	5.221	5.216076
$\alpha=\beta$	90	90	90
γ	120	120	120
Direct cell volume(A°)^3	48.041	48.041	48.0594
Atomic coordinates			
Zn			
x	0.3333	0.3333	0.3333
y	0.6666	0.6666	0.6666
Z	0.0362	0.0362	0.0362
B	2.32496	2.32492	11.91064
Occupancy	0.80144	0.80144	0.53234
O			
x	0.3333	0.3333	0.3333
y	0.6666	0.6666	0.6666
Z	0.3838	0.3838	0.3838
B	23.78005	23.78005	22.4229
Occupancy	2.46826	2.4682	1.14675
R_p	21	20.5	29.2
R_{wp}	19.1	18.5	26.2
R_{exp}	15.42	18.32	19.79
R_{brag}	4.01	3.37	4.68
R_F	5.74	4.88	7.73
χ^2	1.54	1.02	1.75
GOF index	1.2	1	1.3
Density of compound (g/cc)	7.926	7.926	6.9