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Cost Effective Methods of Zno Nano-Powder Synthesis

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Abstract: *Two different synthesis procedures: sol-gel synthesis and dry mechano-chemical processing; have been used in the present study for the synthesis of ZnO nanoparticles. The obtained ZnO nanoparticles have been structurally characterized by X-ray diffraction, indicating a wurtzite structure with high crystallinity. The UV–Visible diffuse reflectance spectrum of the ZnO nanoparticles indicates a band gap of about 3.28 eV with an onset of absorption at about 3.1 eV, showing a weak red shift compared to 3.37 eV for the bulk ZnO. The SEM images show preferred hexagonal nut shaped structures in sol-gel method. In the dry mechano-chemical process nano-sized spherical structures evolve.*

Keywords*: sol-gel, dry mechano-chemical, red shift, hexagonal nut shape, flower structure*

I. Introduction

Research on metal oxide nanopowder synthesis, has gained momentum in the recent years due to their diverse properties and hence functionalities. Of the various metal oxides, currently, ZnO nano powder has been the most researched [1], because of its vast area of applications like gas sensor [2], chemical sensor[3], bio-sensor, UV sensor[4],cosmetics[5], storage, optical and electrical devices[6], displays, solar cells[7] and as transparent conductors[8,].. ZnO is an attractive material for short-wavelength optoelectronic applications owing to its wide band gap 3.37 eV, and large exciton binding energy (60 meV) at room temperature. As a wide band gap material, ZnO is used in solid state blue to ultraviolet (UV) optoelectronics, including laser developments. In addition, due to its non-centro symmetric crystallographic phase, ZnO shows the piezoelectric property, which is highly useful for the fabrication of devices, such as electromagnetic coupled sensors and actuators [9].

The common methods to synthesis ZnO nanopowder are precipitation [10], sol–gel process, microwave assisted synthesis [11], hydrothermal synthesis and dry mechano-chemical processing[12]. In contrast to most other synthesis methods involving high temperatures or complex reaction conditions, dry mechano-chemical method is a simple and efficient method for preparing ZnO nanoparticles with high yield at low cost and low temperature.The mechanical grinding of the reactants is done at room temperature, which increases safety and reduces energy utilization. Also, scaling the method for production could be comparatively easier.

An alternative method is the sol-gel method that produces nanometric powders used initially to produce ZnO thin films[13], where an initial solution containing a zinc complex is decomposed to form zinc oxide nano powder. The mixture of a pure chemical compound (containing the zinc complex) in a second chemical causes the formation of a nanopowder.

In this paper, we study the mechano chemical and Sol-gel synthesis methods.

II. Materials and Methods

2.1. Materials

2.1.1: Dry Mechano-chemical method:

The AR-grade reactants, Zn $(CH_3COO)_2$ and $H_2C_2O_4{\cdot}2H_2O$ were from Merck . All chemicals were used as-received, without further purification.

2.1.2: Sol-gel Method:

Zinc acetate was used as a precursor, Ethanol as a solvent and PEG2000 as the surfactant. Ammonium hydroxide was added in order to vary the pH of the solution. All the chemicals used were Merck made and were used as received, without further purification.

2.2 Experimental procedure:

2.2.1. Dry Mechano-chemical method:

In a simple two step synthesis, 0.1 mol of $Zn(CH_3COO)_2$ and 0.15 mol of $H_2C_2O_4{\cdot}2H_2O$ were mixed by grinding for one hour at room temperature, forming the $ZnC_2O_4{\cdot}2H_2O$(Zinc Oxalate) nanoparticles.

Zn*(*CH3COO*)*2+H2C2O4·2H2O= ZnC2O4·2H2O+ 2CH3COOH*(*liquid, gas*)*+ H2C2O4·2H2O

ZnO nanoparticles were then obtained by thermal decomposition of the obtained $ZnC_2O_4{\cdot}2H_2O$ nanoparticles at 450 ^{0}C for one hour.

2.2.2 Sol-gel Method:

13.17gm of Zinc acetate is added to 60ml of Ethanol and mixed thoroughly using a magnetic stirrer for 2hours at room temperature. Ammonium hydroxide was added to the obtained solution until the pH of the solution turned 7.18 and the solution was stirred for another 2 hours at room temperature. A milky white solution formed is the sol. The gel was prepared by adding 5gm of PEG2000 with 100ml of distilled water. Into the prepared sol, the gel was added. The thus prepared sol-gel was allowed for 4days of ageing. The aged sol-gel was annealed at 450^0C for one hour to obtain the nano structured ZnO powder.

2.3. Characterization

The thermal decomposition of the zinc oxalate precursor is studied by thermo gravimetric analysis (TA Instruments TGA 951-2000). The powder is decomposed under a flow of dry air (100 mL/min) and at a heating rate of 10°C/min.

The crystal phase of the powders is determined using X-ray diffraction (XRD) measurements, carried out on a SEIFERT JSO DEBYEFLEX 2002 diffractometer.

The morphology of the products were studied using Quanta 200 FEG Scanning Electron Microscope.

Room temperature photoluminescence (PL) spectra between 360 and 650 nm have been recorded on a Jobin Yvon Flourolog-3-11 spectrofluorometer at SAIF, IITM, Chennai.

III. Results and Discussion

3.1 XRD Analysis:

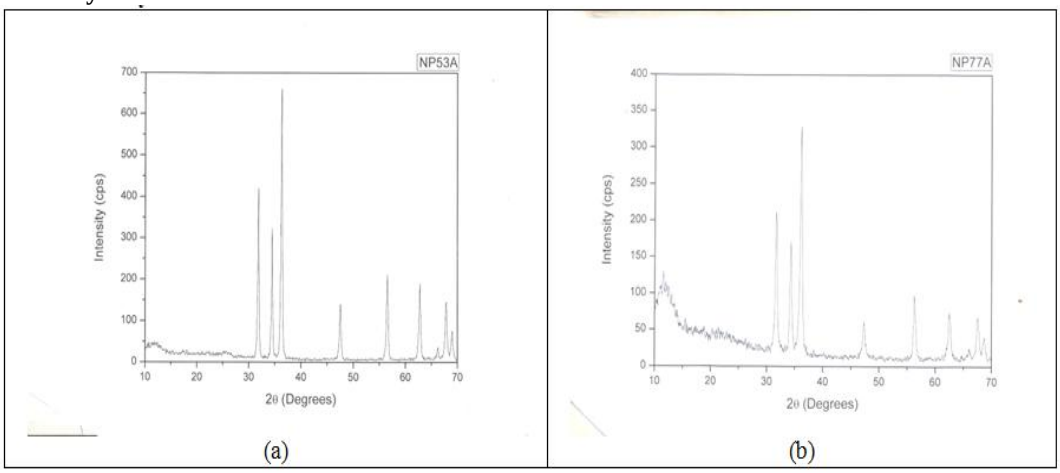

Fig:1: XRD pattern of ZnO nanopowder synthesized by Sol Gel(a) and Dry Mechano- chemical methods(b)

All the peak positions and relative peak intensities of the ZnO product through both the synthesis methods agree well with those of the standard XRD pattern and no characteristic peaks of impurities are observed, indicating that the ZnO product is of high purity. Moreover, all diffraction peaks of the product show strong peak intensities. The sharp intense peaks of ZnO confirm the good crystallinity nature of ZnO and the peaks originate from (100), (002), (101), (102), (110), (103), (200), (112) and (201). It is seen that the diffraction peaks of the samples can be indexed as the hexagonal wurtzite structure of ZnO (in JCDDS card (NO. 36-1451). This result confirms that pure ZnO was successfully synthesized by the both the methods. At ambient conditions, the thermodynamically stable phase is wurtzite.

ZnO-JCPDS file 36-1451			Sol-Gel Method			Dry Mechano-chemical Method		
hkl	2θ	Relative Intensity	*hkl*	2θ	Relative Intensity	*Hkl*	2θ	Relative Intensity
100	31.76	57	100	31.8419	63.1	100	31.6514	58
002	34.42	44	002	34.4827	48.6	002	34.2951	44
101	36.25	100	101	36.3074	100	101	36.1506	100
102	47.53	23	102	47.5534	21.4	102	47.4414	16
110	56.60	32	110	56.5534	30.6	110	56.4489	33
103	62.86	29	103	62.7956	28.2	103	62.7230	25
112	67.96	23	112	67.8442	22.3	112	67.9404	26

Table1: Comparison with JCPDS data of XRD data from ZnO synthesized by Sol gel and Dry mechano-chemical methods.

3.2 TG-DSC Analysis

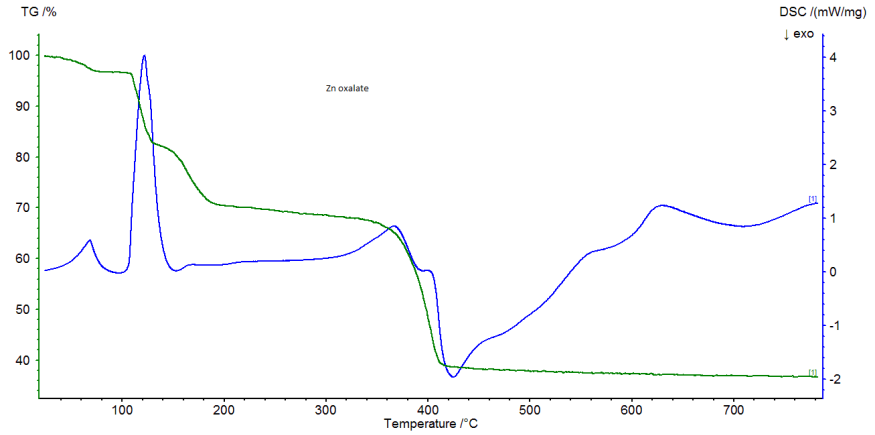

Fig2.1. TG-DSC curves of zinc oxalate

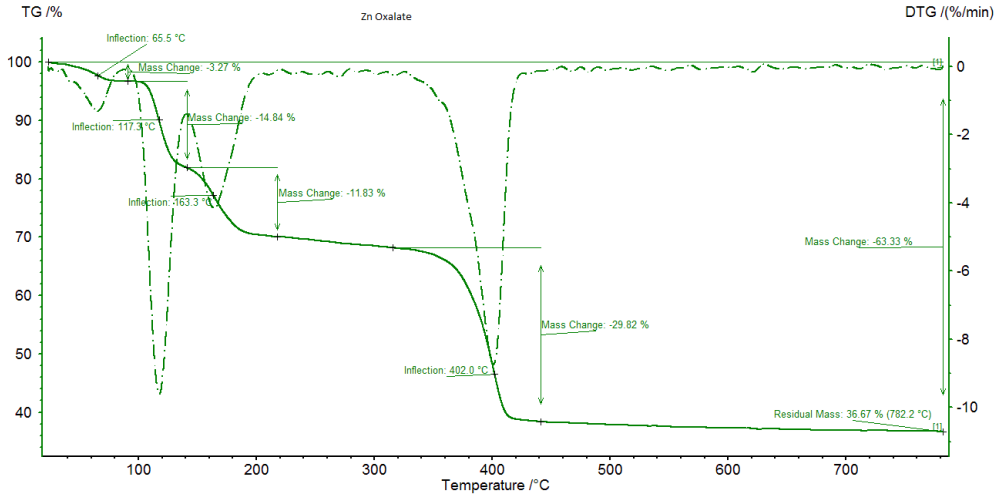

Fig2.2: TG and DTG curves of Zinc oxalate with weight loss% at various temperatures.

The thermal decomposition behavior of the powder mixture after grinding for one hour was studied by TG-DSC, and the TGA-DTA curves are shown in figure 2.1 and 2.2.
The initial small endothermic peak corresponding to 3.27% mass change indicates the release of the remaining CH3COOH product in the zinc oxalate mixture compound.

CH3COOH = CH3COOH(gas) ↑
The second endothermic peak for 14.84% mass change and centered at about 100°C, is due to the release of crystal water in $ZnC_2O_4 \cdot 2H_2O$.

ZnC2O4·2H2O = ZnC2O4 + 2H2O ↑
During the initial grinding of the reactants in the first hour, a characteristic smell of acetic acid had been sensed. The CH_3COOH has a boiling point of about 118 °C. Evidently, any CH_3COOH which remains may only be totally removed at a temperature around 120°C (above its boiling point), which is indicated by a weight loss of 11.83%.
Therefore, it is reasonable that the total 29.94% weight loss at temperatures below 300°C is larger than the theoretical crystal water content of 19.03% in pure $ZnC_2O_4 \cdot 2H_2O$.
At 320–410 °C, the exothermic peak with a total weight loss of 29.82% is attributed to the release of CO and CO_2 and the oxidation of CO during the decomposition of ZnC_2O_4 [11].
ZnC2O4·2H2O = ZnO + CO2 ↑ + CO ↑ + 2H2O ↑
CO + O2 = CO2 ↑

The chemical reactions process takes place as shown in the equations above.

The second step is a Zinc Oxalate dissociation, which is endothermic and oxidation of CO is a strong exothermic reaction. An endothermic peak due to the decomposition of ZnC_2O_4 should appear around 300–350 ºC; however, because the simultaneous oxidation of CO emits much heat, the endothermic peak is suppressed by this big exothermic peak.

DSC studies also showed two endothermic peaks corresponding to the weight losses in TG studies. The weight loss (release of water molecules, acetic acid and decomposition of zinc oxalate) was about 56.92%, which was close to the theoretical value (57.1%)[14]

3.2 Elemental Analysis by EDAX

Theoretically expected stoichiometric mass% of Zn and O in ZnO are 80.3 and 19.7 respectively and the atomic % are 50:50. The EDAX results of ZnO Nano-powders synthesized using both the methods (shown in the tabulation below), indicate a complete formation and negligible presence of any remnant byproducts.

Element	Wt%	At%
OK	20.52	51.34
ZnK	79.48	48.66
Matrix	Correction	ZAF

(a)

Element	Wt%	At%
OK	18.43	48.01
ZnK	81.57	51.99
Matrix	Correction	ZAF

(b)

Table2: EDAX data of ZnO nanopowder synthesized by Sol Gel(a) and Dry Mechano- chemical methods(b)

3.3 SEM Analysis

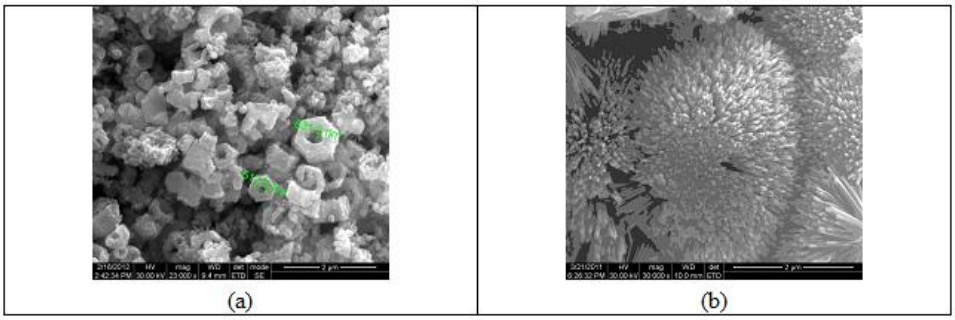

Fig3: SEM micrographs of ZnO nanopowder synthesized by Sol Gel(a) and Dry Mechano- chemical methods(b)

Figure 3 compares the SEM micrographs of the ZnO nanoparticles prepared by the sol-gel method and dry mechano-chemical method respectively. The sol-gel formation and subsequent calcination leads to mostly dense aggregates, composed of primary particles with sizes in the range of 100 to 200 nm and a considerable number of hexagon nut shaped micro crystals. In the case of dry mechano-chemical synthesis, the ZnO nanoparticles were found to be crystalized in a flower pattern with Nano tubes of length varying between 50-100nm. The reproducibility of the morphology has been confirmed in both the cases.

3.4 Optical Studies

3.4.1. Photoluminescence:

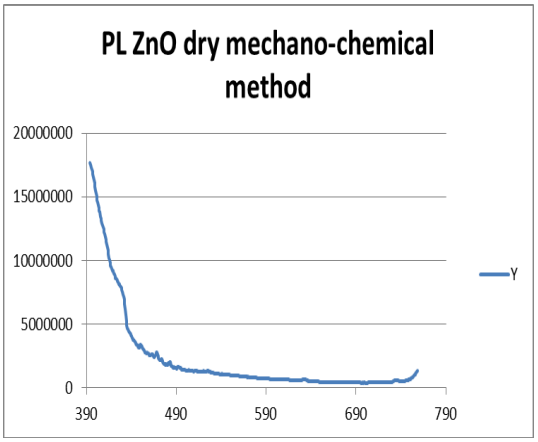

Fig4: Photoluminescence emission spectra of ZnO by Sol Gel(A) and Dry Mechano- chemical methods(B)

The synthesized ZnO particles exhibit a sharp emission peak at ~380 nm that results from the band-gap luminescence. This emission peak is clearly more intense in the case of the dry mechano-chemical synthesized product. Next to this UV luminescence, the photoluminescence spectra display in the case of sol-gel synthesis is a violet emission band (around 410nm).This may be attributed to the transition from shallow donor level to top of valence band [15]. This UV emission is more intense for the powder, obtained by a dry mechano chemical synthesis. The stronger UV luminescence and the weaker violet emission band are an indication of the better crystalline quality of the ZnO nanoparticles synthesized by means of sol-gel method.

3.4.1 UV – Visible Absorption studies:

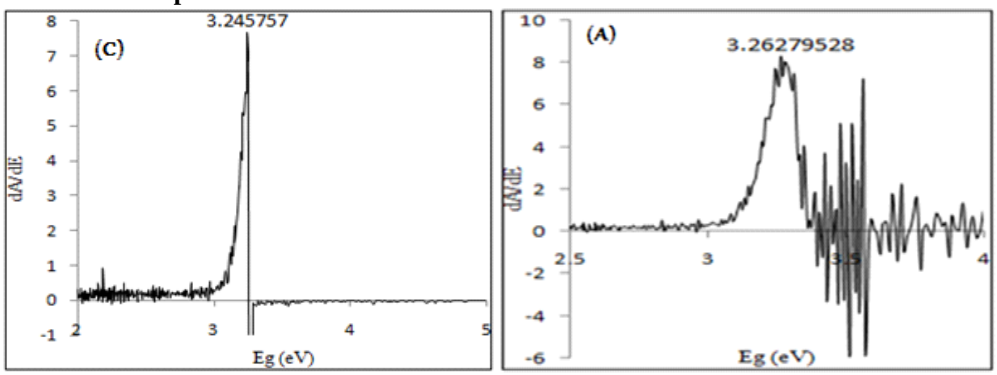

Fig 4. First derivative of UV-Vis Absorption Spectra for the ZnO samples by Sol Gel(A) and Dry Mechano-chemical methods(B)

Figure 4 shows the first derivative of the absorbance with respect to photon energy. The band gap of ~3.25 & 3.26 eV for the ZnO-NP samples shows a slight red shift compared to the band gap of 3.37 eV for bulk ZnO. This red shift of the band gap energy is due to agglomeration of the nanocrystallites into larger crystallites [16]

IV. Conclusion

Zinc oxide nanoparticles have been successfully synthesized using (a) a PEG-assisted sol-gel method and (b) by the calcination of zinc oxalate obtained from a dry mechano chemical method. Both synthesis techniques produce highly crystalline and pure ZnO Nanoparticles. While the calcined powder shows rather large, dense aggregates, the mild conditions associated with the sol-gel technique results in non-agglomerated uniform ZnO particles. This observation is supported by XRD and SEM analysis. The PL spectra of both powders show a peak at 380 nm and a broad violet emission band is observed in the case of sol-gel method. The intense UV luminescence and the weaker violet emission of the ZnO nanoparticles synthesized by means of the dry mechano chemical method indicates a better crystalline quality of these nanoparticles.

The crystallinity, purity and morphologies of the ZnO nanostructures, obtained by both the methods are found to be of good standard. The reproducibility of the nanostructures in both the cases is verified. However in contrast to most other synthesis methods involving high temperatures or complex reaction conditions, dry mechano-chemical method is a simple and efficient method for preparing ZnO nanoparticles with high yield at low cost and low temperature. The mechanical grinding of the reactants is done at room temperature, which increases safety and reduces energy utilization. Also, scaling the method for production could be comparatively easier.

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