Structural and Morphological Properties of ZnO-SnO_2 Nanocomposite by Sol-Gel Method

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Abstract

In this work the preparation of ZnO-SnO_2 nanocomposites from ZnO and SnO_2 nanoparticles produced by Sol-Gel method. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and tin(II) chloride dehydrates ($SnCl_2.2H_2O$) have been used as precursors. The structural investigation of ZnO-SnO_2 reveal that the ZnO nanoparticle is hexagonal in structure and SnO_2 nanoparticle is tetragonal. Nanocompsites in two different molarities synthesized by Sol-Gel method. Sol-gel method is the simplest method and has the ability to control the particle size and morphology through systematic monitoring of reaction parameters. ZnO-SnO_2 composites were characterized by using XRD analysis and SEM analysis. According to XRD results, ZnO-SnO_2 (0.01/0.01), ZnO-SnO_2 (0.01/0.025) composites were obtained the average crystallite sizes were found between 45 nm to 47 nm by 500°C and 600°C. The shape of grain of ZnO-SnO_2 (0.01/0.01), ZnO-SnO_2 (0.01/0.025) were spherical feature and grain sizes were measured to be 0.990 µm, 0.886 µm at 500 °C and 0.810 µm, 0.787 µm at 600 °C.

Keywords: ZnO, SnO_2, Sol-gel, XRD, SEM

Introduction

Zinc Oxide is very suitable for sensor and transducer usage with its relatively bio-safe and biocompatible material. Besides, nanostructured metal oxide has been found to display appealing nano-morphological, functional, biocompatible, non- toxic and catalytic properties. Other applications of zinc oxide powder include electrophotography, photoprinting, capacitors, protective coatings, anti-microbial, and conductive thin-films in LCDs, solar cells, and blue laser diodes. ZnO, as semiconducting II-VI metal oxide with wide band gap 3.37 eV. ZnO possess potential material for many devices applications such as gas sensor, solar cells, optoelectronic devices and LED. SnO_2 is n-type material with the band gap 3.5-3.6 eV. SnO_2 has been applied for various applications such as solar cells, lithium ion batteries and gas sensor. SnO_2 have received attention from many researcher studied on gas sensor application for having high sensitivity and relatively low operating temperature. ZnO and SnO_2 have unique properties due to their chemical and physical properties. Mixing ZnO and SnO_2 could form various kind of composite material such as ZnO/ SnO_2, $ZnSnO_3$, $Zn2SnO_4$, Zn-doped SnO_2 and Sn-doped ZnO. Different type of ZnO/SnO_2 structured have been prepared such as nanofibers, nanorod, nanoflowers. Different method such as thermal decomposition, chemical vapor deposition, thermolysis, spray pyrolysis, condensation, hydrothermal and also available in literature to synthesize ZnO-SnO_2 nanocomposites. In this experiment, ZnO - SnO_2 nanocomposites were synthesized using sol-gel method in two different molarities as this method has several advantages such as short reaction time and easily synthesized. The aim of this project was to study the structural investigation ZnO– SnO_2 nanocomposites in two different molarities.

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Materials and Method

All the chemical were used as analytical grade without any further purification. Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), tin (II)chloride dihydrate ($SnCl_2.2H_2O$), methanol and ammonium hydroxide solution were used to prepare the ZnO-SnO_2 nanocomposites were synthesized by Sol-Gel method [5. Instruments used for synthesis are Muffle furnace, Magnetic stirrer, X-ray diffractometer and Scanning electron microscope.

Synthesis of ZnO-SnO_2 nanocomposites

Zinc acetate dehydrate and tin (II) chloride dehydrate were used as starting materials. Methanol and ammonium hydroxide solution were used as solvent and additive, respectively. All chemicals were analytical grade (AR) and used without further purification. Figure (1) shows the synthesis of ZnO-SnO_2 composite by Sol-Gel Method. The synthesis of the ZnO-SnO_2 mixed photo catalyst started by slowly adding a 0.01 M methanol into ($Zn(CH_3COO)_2.2H_2O$), previously prepared 0.01 M methanol solution into ($SnCl_2.2H_2O$ prepared in the same conditions. Typically, 0.812 g of ($Zn(CH_3COO)_2.2H_2O$) were dissolved in 37 mL of methanol and the amount of ($SnCl_2.2H_2O$)solution was opportunely dissolved in order to obtain powders with the molar ratio ZnO-SnO_2 equal to 0.01/0.01 and 0.01/0.025 respectively[5]. The obtained solutions were continuously stirred for 2h, keeping the 80 °C. Then, the NH_4OH solution was added dropwise until pH reached the value of pH 8. The solutions became gels which were dried produce xerogels. Finally, the pure oxides were synthesized in the same way by using only the corresponding precursor. The temperature of the dried precursor composites was annealed at 500℃ and 600℃ for 2 h to obtain the final product (i.e., ZnO-SnO_2 composite).

Results and Discussion

XRD Analysis

X-ray diffraction (XRD) was performed using monochromatic Cu-Kα radiation (λ = 1.54060 Å) operated at 40 kV(tube voltage) and 30 mA(tube current) was used to identify crystalline phases and to estimate the crystalline sizes. Specimen was scanned from 20° to 70° in diffraction angle 2θ and sampling pitch 0.02(deg). The XRD spectra of ZnO-SnO_2 composite annealed at 500℃ and 600℃ for 2hr were shown in figure. From figure 1(a) to figure1(d) the existence of strong and sharp diffraction peaks located at 26.2°, 34.2°, 37.52°, and 68.71° corresponding to (110), (002), (101) and (321) planes, respectively. All the peaks can be readily indexed to crystalline size of SnO2 nanocomposites (standard data of JCPDS file number of 88-0287) with tetragonal phase (a=b= 0.4737 nm and c= 0.3186 nm) and the existence of strong and sharp diffracted peaks located at 32.69°, 47.44°, 52.02° and 64.62° corresponding to (100), (102), (211) and (221) planes, respectively[5]. All the peaks can be readily indexed to crystalline size of ZnO nanocomposites (standard data of JCPDS file number of 89-7102) with hexagonal phase (a=b= 0.3249 nm and c= 0.5206 nm) and other previous works. The mean size of the ordered ZnO-SnO_2 has been estimated from full width at half maximum (FWHM) and Debye-Scherrer formula according to equation the following:

$$G = \frac{k \times \lambda}{\beta \times \cos \theta_B}$$

where β is the peak width measured at half intensity (radian), λ is the wavelength measured in Å, k is the particle shape factor or Scherrer constant (k = 0.9) and G is the diameter of the crystallites (Å)[6]. From table (1.1) to (1.8), the average crystallite sizes of the ZnO-SnO_2 composite were found to 45.4229 nm at 500 ºC, and 46.6122 nm at 600 ºC.

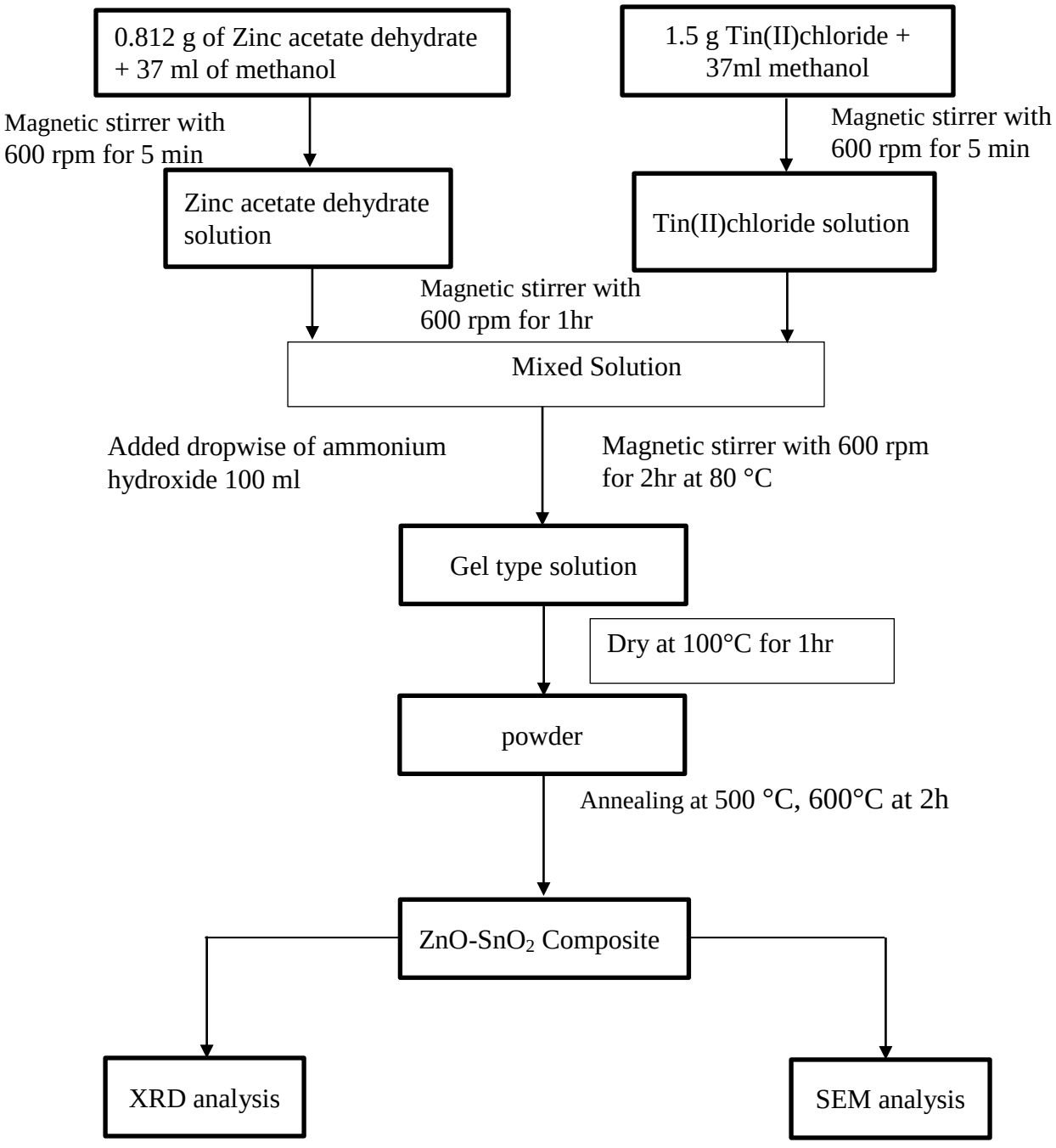


Figure 1. Block diagram of Synthesis of ZnO-SnO_2 composite by Sol-Gel Method

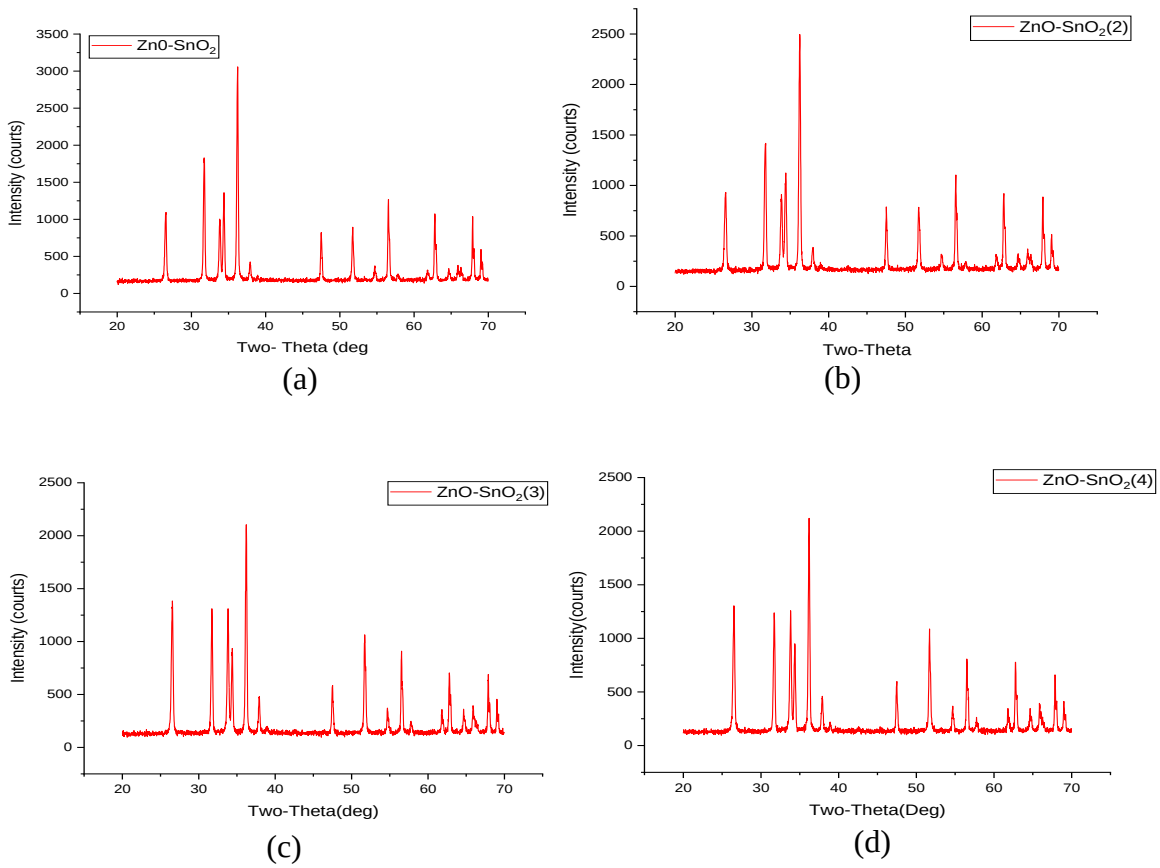


Figure 1. XRD pattern of ZnO-SnO_2 (0.01/0.01) composite at (a) 500ºC and (b) 600 ºC for 2hr, XRD pattern of ZnO-SnO_2 (0.01/0.025) composite at (c) 500ºC and (d) 600ºC for 2hr

Table 1. Diffraction angles of all Identified peak for ZnO-SnO_2(0.01/0.01) composite at 500ºC

No.	Peaks	Lattice Spacing d (A)	2θ (deg)
1	(1 0 0)	2.82009	31.7033
2	(0 0 2)	2.60816	34.3561
3	(1 0 1)	2.48039	36.1855
4	(1 0 2)	1.91395	47.4650
5	(1 1 0)	1.62693	56.5192
6	(1 0 3)	1.47887	62.7812
7	(2 0 0)	1.40859	66.3034
8	(1 1 2)	1.37982	67.8713
9	(2 0 1)	1.35983	69.0085

Table 2. Crystallite size of ZnO-SnO_2(0.01/0.01) composite at 500 ºC

No.	Peaks	FWHM (deg)	Crystallite size (nm)
1	(1 0 0)	0.2242	36.9577
2	(0 0 2)	0.2090	39.2238
3	(1 0 1)	0.2080	40.5184
4	(1 0 2)	0.1895	45.8977
5	(1 1 0)	0.1771	50.7794
6	(1 0 3)	0.1813	50.7586
7	(2 0 0)	0.1771	53.4230
8	(1 1 2)	0.1725	55.7068
9	(2 0 1)	0.1741	56.0841
Average Crystallite size			47.7055

Table 3. Diffraction angles of all Identified peak for ZnO-SnO_2(0.01/0.01) composite at 600 ºC

No.	Peaks	Lattice Spacing d (A)	2θ (deg)
1	(1 0 0)	2.81941	31.7111
2	(0 0 2)	2.60772	34.3621
3	(1 0 1)	2.47998	36.1916
4	(1 0 2)	1.91365	47.4727
5	(1 1 0)	1.62680	56.5242
6	(1 0 3)	1.47879	62.7852
7	(2 0 0)	1.40861	66.3027
8	(1 1 2)	1.37974	67.8758
9	(2 0 1)	1.35974	69.0140

Table 4. Crystallite size of for ZnO-SnO_2(0.01/0.01) composite at 600ºC

No.	Peaks	FWHM (deg)	Crystallite size (nm)
1	(1 0 0)	0.2151	37.9310
2	(0 0 2)	0.2076	40.3140
3	(1 0 1)	0.2056	40.5191
4	(1 0 2)	0.1888	45.8991
5	(1 1 0)	0.1813	49.1937
6	(1 0 3)	0.1774	52.3971
7	(2 0 0)	0.1756	53.4228
8	(1 1 2)	0.1767	53.9112
9	(2 0 1)	0.1792	54.2767
Average Crystallite size			47.5405

Table 5. Diffraction angles of all Identified peak for for ZnO-SnO_2(0.01/0.025) composite at 500 ºC

No.	Peaks	Lattice Spacing d (A)	2θ (deg)
1	(1 0 0)	2.81676	31.7417
2	(0 0 2)	2.60597	34.3859
3	(1 0 1)	2.47816	36.2192
4	(1 0 2)	1.91264	47.4995
5	(1 1 0)	1.62611	56.5504
6	(1 0 3)	1.47827	62.8097
7	(2 0 0)	1.40819	66.3249
8	(1 1 2)	1.37930	67.9005
9	(2 0 1)	1.35930	69.0395

Table 6. Crystallite size of for ZnO-SnO_2(0.01/0.025) composite at 500 ºC

No.	Peaks	FWHM (deg)	Crystallite size (nm)
1	(1 0 0)	0.2338	35.1583
2	(0 0 2)	0.2282	36.2849
3	(1 0 1)	0.2212	37.4052
4	(1 0 2)	0.1978	43.2808
5	(1 1 0)	0.1839	49.1998
6	(1 0 3)	0.1803	50.7663
7	(2 0 0)	0.1901	50.1914
8	(1 1 2)	0.1824	52.2341
9	(2 0 1)	0.1774	54.2850
Average Crystallite size			45.4229

Table 7. Diffraction angles of all Identified peak for ZnO-SnO_2(0.01/0.025) composite at 600 ºC

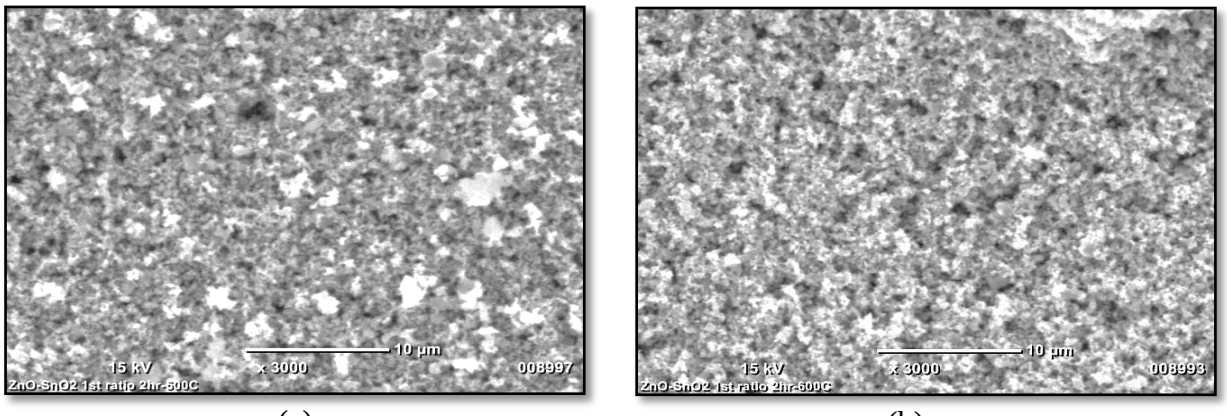
No.	Peaks	Lattice Spacing d (A)	2θ (deg)
1	(1 0 0)	2.81956	31.7094
2	(0 0 2)	2.60782	34.3608
3	(1 0 1)	2.48000	36.1914
4	(1 0 2)	1.91384	47.4677
5	(1 1 0)	1.62681	56.5238
6	(1 0 3)	1.47881	62.7842
7	(2 0 0)	1.40874	66.2955
8	(1 1 2)	1.37979	67.8729
9	(2 0 1)	1.35972	69.0151

Table 8. Crystallite size of ZnO-SnO_2(0.01/0.025) composite at 600 ºC

No.	Peaks	FWHM (deg)	Crystallite size (nm)
1	(1 0 0)	0.2285	36.0343
2	(0 0 2)	0.2150	38.1920
3	(1 0 1)	0.2089	39.4240
4	(1 0 2)	0.1878	45.8982
5	(1 1 0)	0.1834	49.1936
6	(1 0 3)	0.1783	52.3968
7	(2 0 0)	0.1886	50.1830
8	(1 1 2)	0.1780	53.9104
9	(2 0 1)	0.1775	54.2772
Average Crystallite size			46.6122

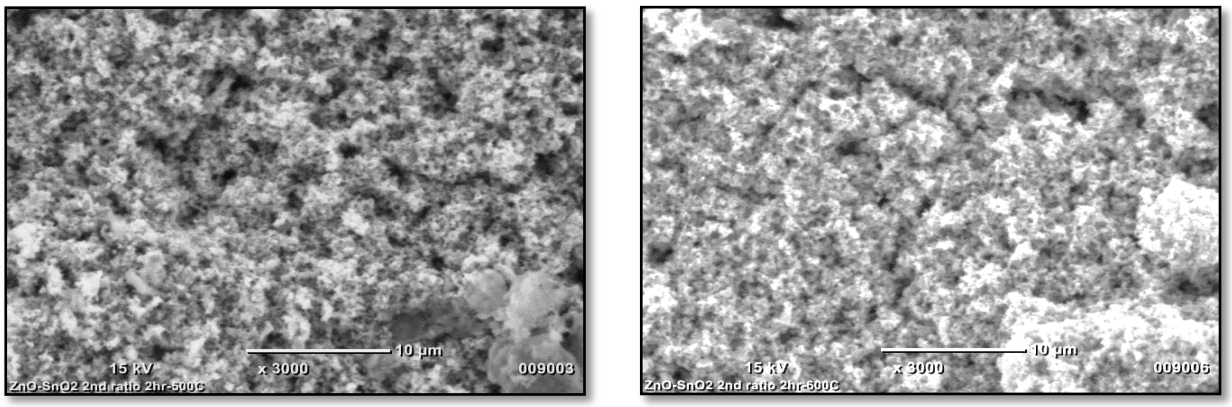
SEM Analysis

The surface morphologies of ZnO-SnO_2 composites were studied using scanning electron microscope (SEM). The SEM image of all of ZnO-SnO_2 composites were seemed to be crack-free and uniform grain distribution. Some grains were separated by holes and some were in continuity. The grain size was measured by using well known bar code system, drawing cross bars of some dimensions as provided scale and measuring number of interesting grains across them. From figure2(a) to figure3(b), the shape of grain of ZnO-SnO_2 composites was spherical feature and grain sizes of the ZnO-SnO_2 composites were measured to be 0.990 µm, 0.886 µm at 500 °C and 0.810 µm, 0.787 µm at 600°C.



(a) (b)

Figure 2. SEM image of ZnO-SnO_2(0.01/0.01) composites at (a) 500°C and (b) 600 °C



(a) (b)

Figure 3. SEM image of ZnO-SnO_2(0.01/0.025) composites at (a) 500 °C and (b) 600 °C

Conclusion

ZnO-SnO_2 composites have been successfully synthesized by simple Sol-Gel method using zinc oxide and tin oxide. The prepared ZnO-SnO_2 composites were spherical in shape and were characterized using XRD, and SEM techniques. The average crystallite sizes of the ZnO-SnO_2 composites were found to 45.4229 nm at 500ºC, and 46.6122 nm at 600ºC. According to XRD result, crystallite size well matched 45.4229 nm at 500ºC more than at 600ºC. The synthesized ZnO-SnO_2 composites obtained exhibit good crystallinity. The shape of grain of ZnO-SnO_2 composites was spherical feature and grain sizes of the ZnO-SnO_2 composites were measured to be 0.990 µm, 0.886 µm at 500 °C and 0.810 µm, 0.787 µm at 600 °C. From SEM image, it is clear that with increasing temperature the particles shape were changes to the spherical and less agglomerate.

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