GROWTH AND CHARACTERIZATION OF $ZnTiO_3$ PEROVSKITE FILM ON SI SUBSTRATE

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Abstract

Zinc titanate ($ZnTiO_3$; ZT) powders were successfully prepared by a solid state reaction method. ZT powder were heated at various calcination temperatures ranging from 500 °C to 850 °C for 2h. Powder samples were characterized using thermo gravimetric (TGA), differential thermal analysis (DTA), X-ray diffractrometer (XRD), scanning electron microscopy (SEM). The second phases such as ZnO and TiO_2 were detected in the powders calcined below 850 ºC. A single perovskite of the ZT powders was found with calcination temperatures at 850 ºC. The TGA-DTA results corresponded to the XRD investigation. The crystalline powders were mixed with the solvent and deposited onto the silicon substrates by using spin coating method. Annealing of the deposited films were performed at temperatures ranging from 400ºC to 800ºC for 1h. The X-ray diffraction, scanning electron microscope and UV-vis spectroscopy have been employed to characterize the deposited films. The obtained 2D materials surface were $ZnTiO_3$ with cubic structure. The absorbance spectra exhibited visible light emission and optical band gap was 3.7 eV.

Keywords: $ZnTiO_3$perovskite, solid state reaction, spin coating, optical band gap

Introduction

TiO_2 and ZnO are both wide band semiconductor with excellent properties and extensive application, and have attracted much interest on either single material or ZnO-TiO_2composites .ZnO has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics . One of the most important characteristics of ZnO is that it has a large binding energy (60 meV), which is significantly larger than other materials commonly used semiconductor for

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blue green light-emitters devices, such as ZnSe (22meV) and GaN (25 meV) . On the other hand, titanium dioxide (TiO_2) is one of the most important semiconductors with high photo catalytic activity, being non-toxic, stable in aqueous solution, and relatively inexpensive. The excellent photo catalytic property of TiO_2 is due to its wide band gap and long lifetime of photo generated holes and electrons [Dulin, F.H. et al 1960].Nowadays, due to the development of microwave dielectrics, zinc-titanates can be used as dielectric resonators and fiter in microwave devices [Kim, H.T et al 1999]. Thus, in this work, ultra-fine powders of $ZnTiO_3$ successfully were obtained via the combustion method. Perovskites are emerging as a new generation of photovoltaic materials. They are abundant in nature and have rapidly increasing power conversion efficiencies (PCE) of above 15% in common hybrid (mixed organic/inorganic)thin-film-based solar cells[Burschka, J et al 2013- Wang, Q et al 2014]. The transition metal oxide such as TiO_2, their perovskite structures $ZnTiO_3$, is widely used in optical and microelectronic applications because of their excellent mechanical, optical and insulating properties. In the past few years zinc-titanium based oxide materials (Zn–Ti–O) have been used widely because of their outstanding properties and potential scientific and technical applications[Sun,D. et al 2011].Up to now, perovskite films have been formed by film deposition approaches such as spin-coating, sequential deposition of the inorganic and organic precursor, and co-evaporation of the precursors [Burschka, J et al 2013- Liu, M et al 2013].It has a perovskite-type oxide structure and could be advantageous as a microwave resonator material [Kim, H. T et al 1999]. There are three compounds that exist in the ZnO-TiO_2 system: $ZnTiO_3$ with a hexagonal limonite structure (h-$ZnTiO_3$), Zn_2TiO_4 with a cubic spinel crystal structure, and $Zn_2Ti_3O_8$ with a cubic defect spinel structure [Bartram, S.F et al 1961]. $Zn_2Ti_3O_8$ has been observed as a low-temperature form of h- $ZnTiO_3$ that exists at T <820 °C [Steinike, U et al 1997], and is only produced based on the Zn_2TiO_4 phase [Kim, H.T et al 2001]. It is known that h- $ZnTiO_3$ decomposes into Zn_2TiO_4 and rutile TiO_2 at T >945°C [Dulin, F.H et al 1960], However, perovskite crystallizes very rapidly, so it is very challenging to form uniform, continuous, and leakage-free perovskite films by solution methods[Liu, M et al 2013] .In this study, depositions of the $ZnTiO_3$ thin films were carried out by spin coating method. In addition, the effect of structure

and microstructures and optical properties of $ZnTiO_3$ thin films were studied, where the deposited films were annealed at temperatures ranging from 400°C to 800 °C.

Experimental Procedure

In this study, ,ZnO and TiO_2 were chosen as the starting materials. Firstly ZnO and TiO_2 powder with stoichiometry (ZnO:TiO_2= 1:1molar ratio) were mixed. Ethanol was added to the mixture powders . And then the mixture solution stirred with the magnetic stirrer and milled with the ball milling machine for 12hr. Thermal behavior of the sample was performed by TG-DTA analyzer in air to investigate the calcination temperature and possible phase transformation from 500 ºC to 850 ºC for 2h at a heating/ cooling rate of 5 ºC/min. After the sample annealed at 850 ºC, $ZnTiO_3$ crystals are obtained. When the crystals were dried and sieved uniform particles obtained. X-ray diffraction (XRD) was employed to identify the phase formed. The grain size was directly imaged, using scanning electron microscopy (SEM). The flow chart of preparation of $ZnTiO_3$ powder as shown in Figure 1. $ZnTiO_3$ films was prepared using $ZnTiO_3$ powder and 2-methoxy ethanol as solvent and silicon as substrate. Firstly $ZnTiO_3$ powder was mixed with the solvent and stirred the mixture for 5h.The preparation of $ZnTiO_3$ film was shown in figure 5.And then, A few drops of zinc titanate solution were placed on a silicon substrate and spin coated. The $ZnTiO_3$ films were annealed at 400 ºC, 500 ºC, 600 ºC ,700 ºC and 800 ºCfor 1h in atmosphere. X-ray diffraction (XRD) was employed to identify the phase formed were shown in figure 6(a-e). The grain size were directly imaged, using scanning electron microscopy (SEM) were shown in figure 7(a-e).The absorption spectrum of $ZnTiO_3$was shown in figure 8(a). The optical absorbance was measured using UV-VIS spectrometer as shown in figure 8(b).

Result and discussion

Thermal analysis

These are techniques by which the thermal behavior of substances is characterized. Whatever a substrate is heated expands and the variation in the extent of expansion with increasing temperature is dependent on the bond

energy/crystal structure etc. and hence on the type of material. Thus, the changes in crystal structure, coefficient of thermal expansion and melting, can be studied with the help of Differential Thermal Analysis (DTA measures the relative expansion/ contraction between a sample and the standard with varying temperature). Thermo gravimetric analysis (TGA) measures the change in mass of the sample with varying temperature there by indicating the onset, midpoint and completion of a reaction such as oxidation, decomposition, compound formation etc. The reaction of unheated treatment ZT powders taking place during heat treatment was investigated by thermo gravimetric analysis (TGA), differential thermal analysis (DTA). X-ray diffraction (XRD) was employed to identify the phase formed. The TGA and DTA curves of ZT powders prepared by the solid state reaction method.TG-DTA curve of uncalcined powder as shown in figure 2 . The ZT powders demonstrated a three-stage weight loss; the first one was in the temperature range of 100 to 150 ºC, the second one from 150 to 280 ºC, and the last one began around 300 ºC.

XRD analysis

X-ray powder diffraction is a rapid analytical technique used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition determined. Based on the results of DTA and TGA, calcinations were carried out from 500 to 850 ºC for 2 h, at a heating /cooling rate of 5 ºC /min for the unheated ZT powders. After anneal from 500 to 700 ºC, the precursor of ZnO and TiO_2 were detected. When the temperature went above 700 ºC, the minor phase of ZnO remained. A high purity of the cubic perovskite phase was discovered in powders annealed at 850 ºC. The XRD patterns of the ZT powders, formed with different calcination temperatures for 2hr at shown in figure 3(a). The XRD patterns of ZT powders after calcination at 850 ºC as shown in Figure 3(b).The FWHM and crystalline size of $ZnTiO_3$ was listed in table 1.Grain size of ZT at various temperature shown in table 2. And then $ZntiO_3$ powder (850ºC) was heated again at various temperatures. Result of the X-ray analysis of $ZnTiO_3$powderafter heat treatment at 400ºC, 500ºC, 600ºC , 700ºC and 800ºC for 2h as shown in

in figure 6(a-e). Six diffracted peaks were formed on observed XRD profiles and well matched with those of $ZnTiO_3$ standard. The most intense peak was examined to be (311) collection. Among them, the highest peak was discovered in films annealed at 400 ºC. As the detail of the film analysis by XRD, $ZnTiO_3$ film was successfully formed on to the Si substrate at different temperatures. Table (3) showed Crystalline size of $ZnTiO_3$ film at different temperatures.

SEM analysis

The particle morphology and size were directly imaged, using scanning electron microscopy (SEM) and the particle size distribution was determined. The SEM micrographs of $ZnTiO_3$ powders annealed at different temperatures: 500ºC, 600ºC, 700ºC, 800ºC, 850ºC for 2 h in air. The sphere like particles seemed to distribute homogeneously. The grain size increase with the increase in the various temperature and caused faster grain growth, thus resulting in better crystallinity as confirmed by the X-ray diffraction analysis. The grain size of $ZnTiO_3$ powder at different temperature was shown in table 2. They were estimated to be 228.5 nm, at 500°C, 287.5 nm at 600°C, 285.7 nm at 700°C, 406.3 nm at 800°C and 400nm at 850°C. All of SEM images were separated by some porosity. As a result, it was said to be porous structure. The grain size of particle appears to increase in increasing temperature. As discussed earlier, the higher annealing temperature tends to promote phase formation and grain growth. The microstructures of the films were analyzed by using SEM . The zinc titanate films were deposited on silicon substrates at different temperatures. The SEM images of zinc titanate films from 400-800°Cwere shown in figure7(a-e). SEM images indicated the normal grain distribution and porous structures. The majority grains on SEM images were $ZnTiO_3$. The grain size of the $ZnTiO_3$ films were measured to be500 nm, 550 nm, 550nm, 568nm and 587 nm at different temperatures. The annealing temperatures were helpful in increasing gain size. Table (4) showed grain sizes of $ZnTiO_3$films at different temperatures.

UV-VIS analysis

The preparation of $ZnTiO_3$ film, zinc titanate films were characterized by UV absorbance spectra. The optical properties of $ZnTiO_3$ film are determined from absorbance measurement in the range of 263-982nm. The maximum absorbance was found at 284nm for $ZnTiO_3$ films. The absorption spectra of $ZnTiO_3$was shown in figure 4(a) .From the dependence of the absorption band edge on wavelength, the energy gap of the material can be determined. When the energy of the incident photon is greater than that of the band gap ($h\upsilon > E_g$) the absorption coefficient 'α ' is given by

$$\alpha = \frac{A}{h\upsilon} (h\upsilon - E_g)^{1/2} \text{---------- (1)}$$

where A is constant and hυ is the photon energy.

From the curve $\alpha h\upsilon^2$ versus hυ, the band gap was identified by extrapolating the linear region of the curve to the energy axis. The energy band gap value of zinc titanate film was in figure 4(b). In these results , the band gap value of Zinc titanate film was examined to be 3.7 eV.

$$\alpha = 2.3026\ A/t \text{ ……. (2)}$$

where t is thickness of the sample and A is the absorbance.

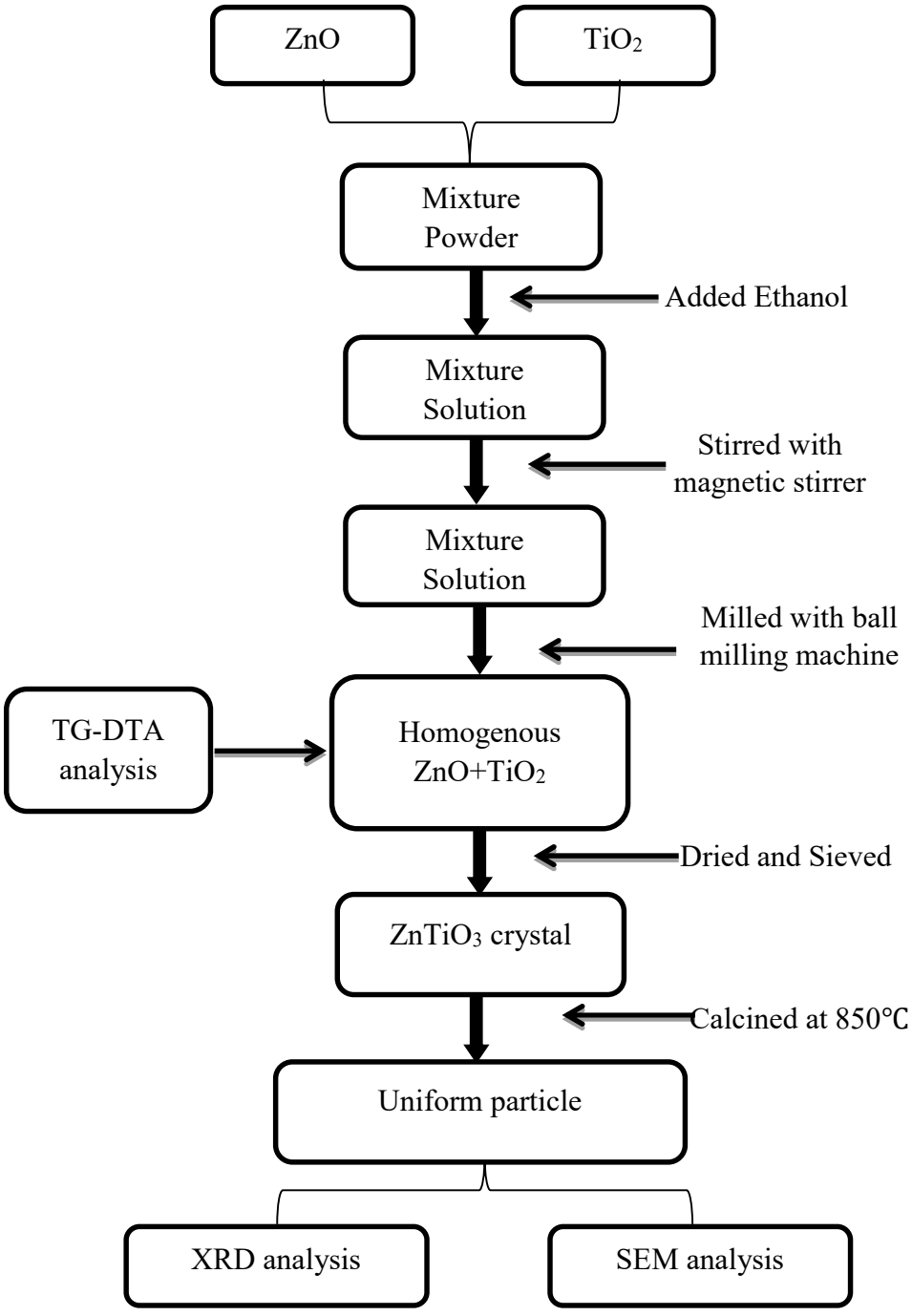

Figure 1. Flow chart for the preparation of $ZnTiO_3$ powder

Thermal Analysis

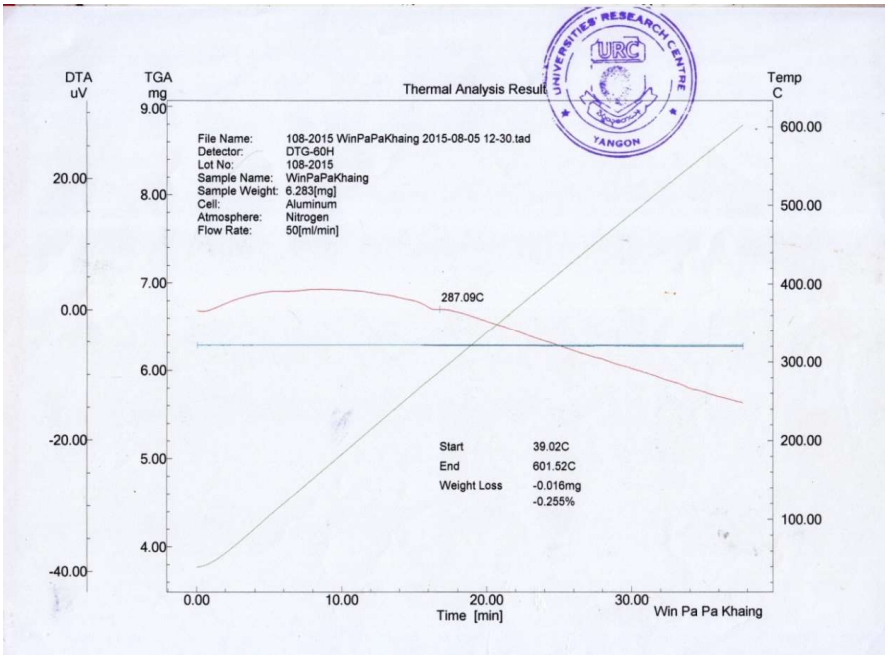

Figure 2. DTA-TG curves of uncalcined ZT powders

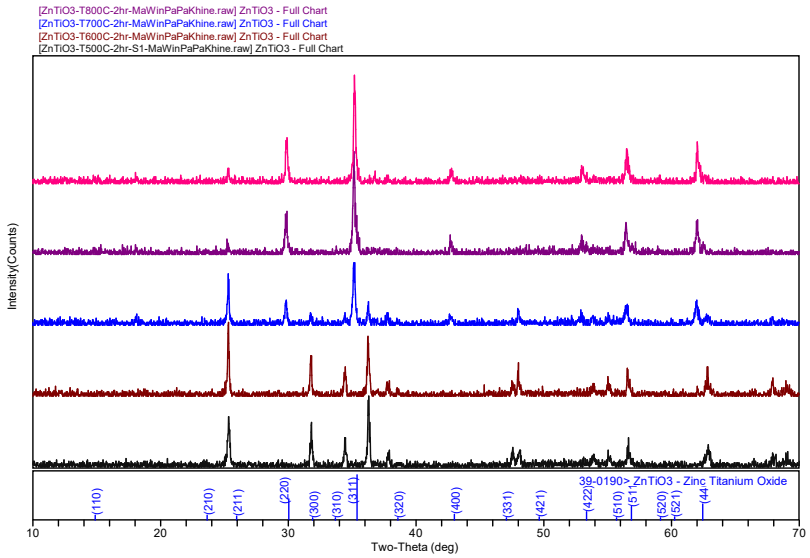

Figure 3(a). XRD patterns of ZT powders with various calcination temperatures for 2hr

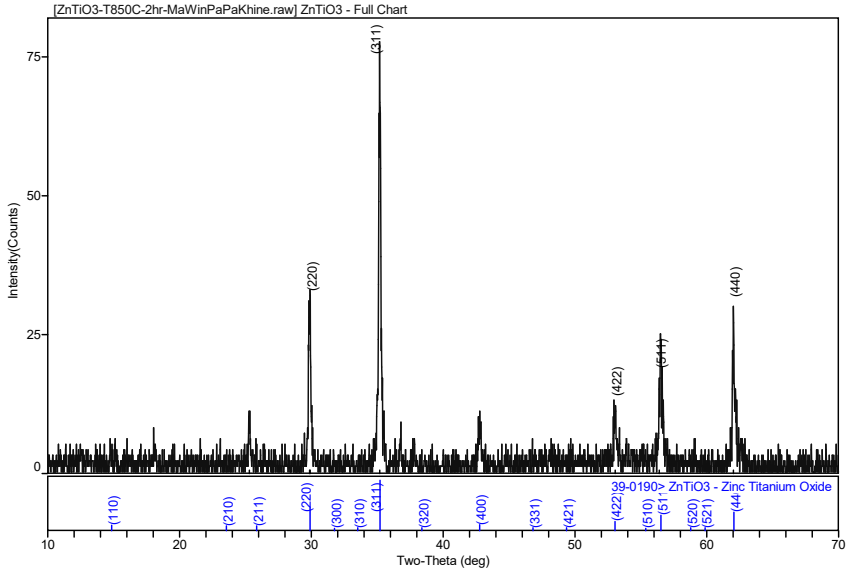

Figure 3(b) XRD patterns of ZT powders after calcination at 850 ºC

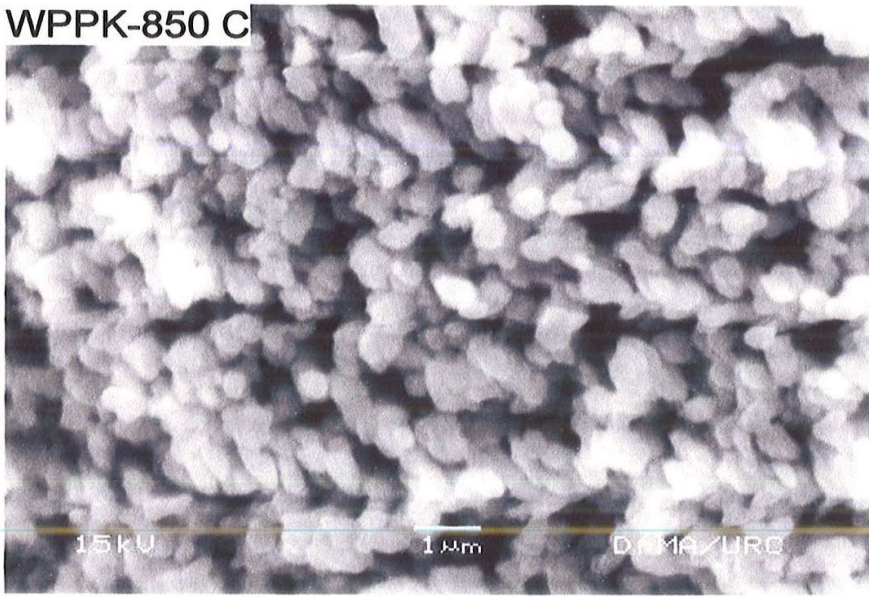

Figure 4. SEM analysis of $ZnTiO_3$ powderscalcinedat 850 ºC

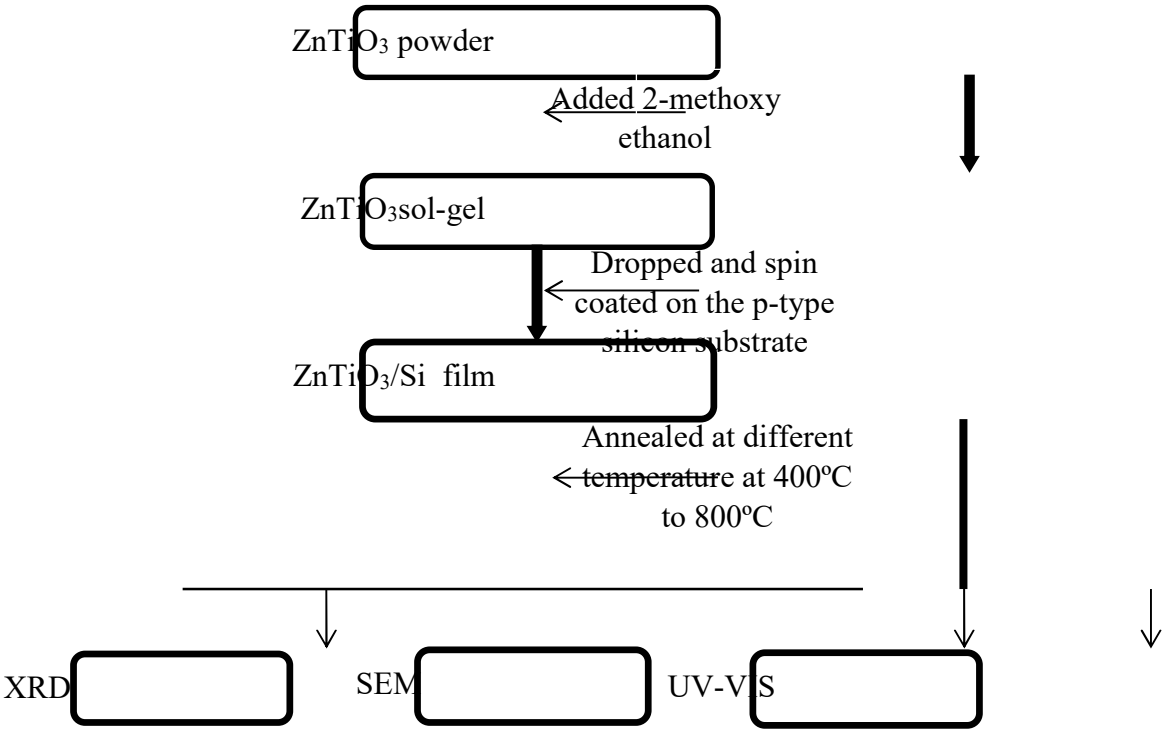

Figure 5 . Flow chart for the preparation of $ZnTiO_3$ film

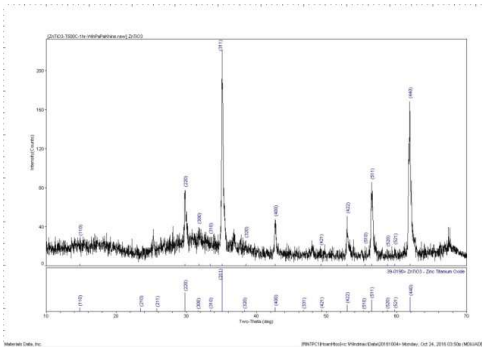

Figure 6 (a). XRD patterns of $ZnTiO_3$ film at 400 ºC

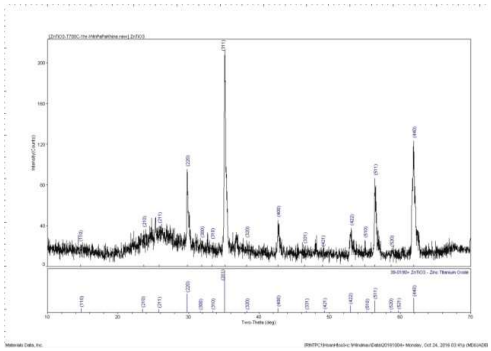

Figure 6 (b). XRD patterns of $ZnTiO_3$ film at 500 ºC

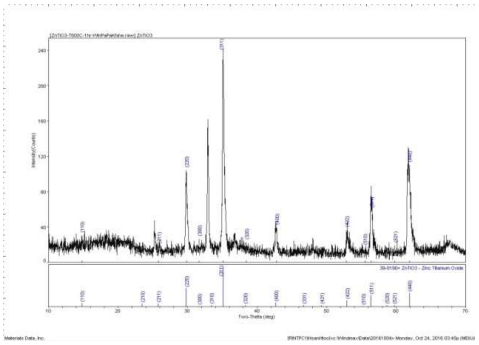

Figure 6 (c). XRD patterns of $ZnTiO_3$ film at 600 ºC

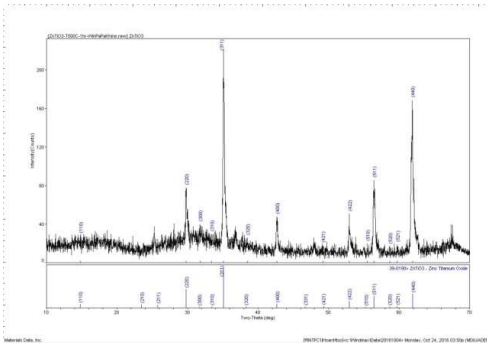

Figure 6 (d). XRD patterns of $ZnTiO_3$ film at 700 ºC

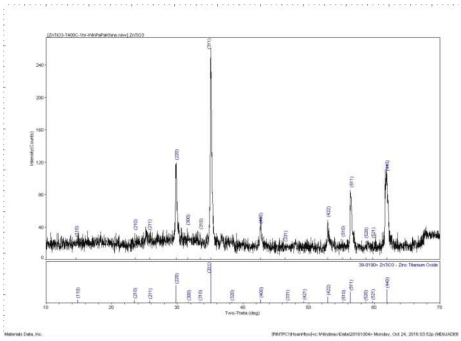

Figure 6 (e). XRD patterns of $ZnTiO_3$ film at 800 ºC

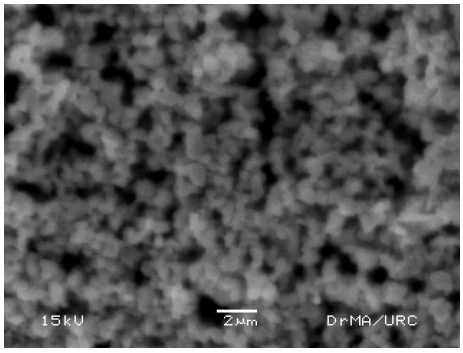

Figure 7(a). SEM analysis of ZnTiO, film at 400℃

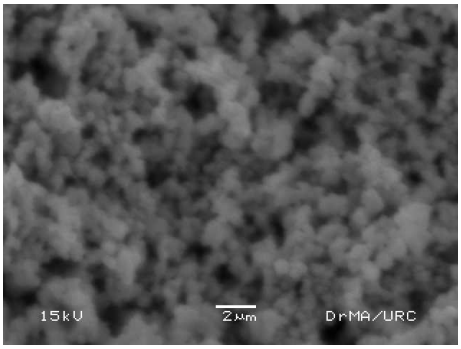

Figure 7(b). SEM analysis of ZnTiO, film at 500℃

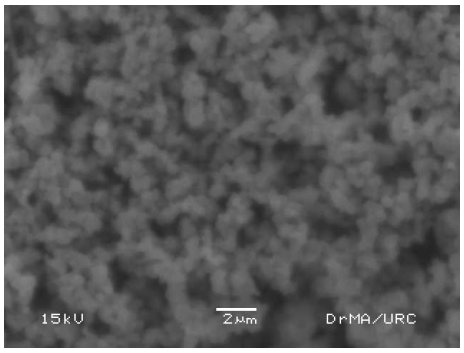

Figure 7(c). SEM analysis of ZnTiO, film at 600℃

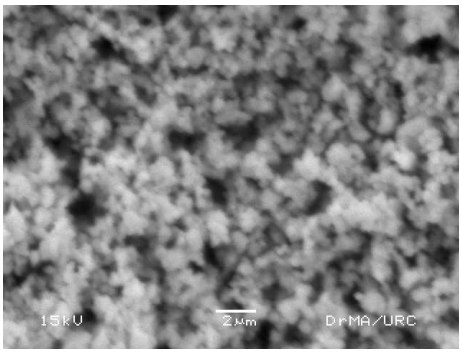

Figure 7(d). SEM analysis of ZnTiO, film at 700℃

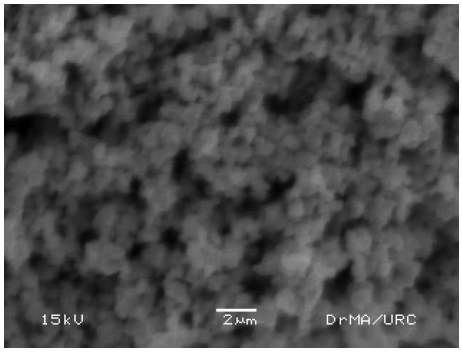

Figure 7(e). SEM analysis of ZnTiO, film at 800℃

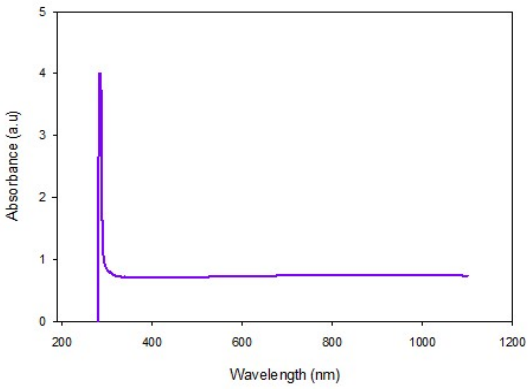

Figure 8(a) UV-VIS spectra of $ZnTiO_3$

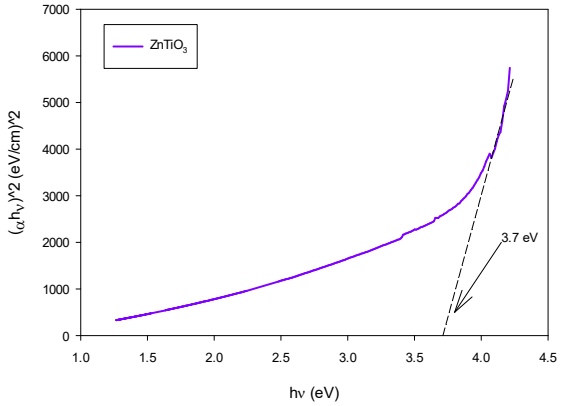

Figure 8(b). Optical energy band gap of $ZnTiO_3$

Table 1. FWHM and crystalline size of $ZnTiO_3$ at 850ºC

Peaks	FWHM (degree)	Crystallite size (Å)
(220)	0.204	40.254
(311)	0.177	71.144
(422)	0.223	39.767
(511)	0.355	25.361
(440)	0.154	60.116
Average crystalline size		**47.328**

Table 2. Grain size of ZT at various temperature

Temperature (ºC)	Grain Size (nm)
500	228.5
600	287.5
700	285.7
800	406.3
850	400.0

Table 3 . Crystalline size of $ZnTiO_3$ films at different temperatures

Temperature (°C)	Grain Size (nm)
500	228.5
600	287.5
700	285.7
800	406.3
850	400.0

Table 4 . Grain size of $ZnTiO_3$films at different temperatures

Temperature(°C)	Grain Size(nm)
400	500
500	550
600	550
700	565
800	588

Table 5. The comparison on band gaps of observed $ZnTiO_3$and others

Sr.No	Author	Journal	Band gap of $ZnTiO_3$(eV)
1	M.Vishwas et al	Nano-Research for Advanced Materials Technologies	3.15 eV
2	Kuhu Sarkar et al (2014)	Royal Society of Chemistry	4.01 eV
3	R.Hari Krishna (2014)	Asian Ceramic Societies	3.60 eV
4	Bak CHANDRU Yadav et al (2016)	Asian Ceramic Societies	4.01 eV
5	Observed Value		3.70 eV

Conclusion

Perovskite $ZnTiO_3$ powders can be successfully obtained by the solid state reaction technique and the best conditions for calcination are 850 ºC. The annealing temperatures have a strong influence on the crystal structure, percent perovskite phase and the particle size of the ZT powders. Finally, presented SEM and X-ray analyses of ZT-850ºC showed advantageous microstructures, with the appropriate pores/ materials ratio and application in the electronic industry as catalysts and color pigments. Heat treatment at 850ºC enhanced the atomic mobility and caused the grain growth to result in a better crystallinity. Growth and characterization of $ZnTiO_3$ films have been studied at different annealing temperatures. As a result of XRD,$ZnTiO_3$ was absolutely formed onto the Si-substrate at given temperatures. From the SEM results, it was found that all SEM images were porous structures. From UV-VIS spectroscopy measurement, the band gap of $ZnTiO_3$was determined to be 3.7eV and it is quite satisfactory and credible compared with others for photovoltaic applications.

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