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LOW TEMPERATURE SYNTHESIS AND CHARACTERIZATION OF $ZnTiO_3$ BY SOL-GEL METHOD

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$ZnTiO_3$ nanoparticles were prepared by a modified sol-gel method at the low sintering temperature of 550 ц*C. Titanium tetra isopropoxide and Zinc acetate dihydrate ($C_4H_{10}O_6Zn(H_2O)_2$) materials were used as a source of titanium and zinc, respectively. The prepared nanopowders were characterized by means of X-ray diffraction (XRD), thermal gravimetric analysis (TGA), field emission Scanning electron microscope (FE-SEM) and Raman spectroscopy. The XRD patterns and Raman spectra revealed that in the temperature range of* 550 *to* 800 °C*, $ZnTiO_3$ is the only zinc titanate compound exists in the samples.*

Keywords: *ZINC TITANATE, $ZnTiO_3$, SOL-GEL METHOD, SEMICONDUCTOR, DIELECTRIC PROPERTIES.*

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1. INTRODUCTION

Dulin and Rase [1] and Bartram and Slepetys [2] reported that there are three compounds exist in the ZnO-TiO_2 system, namely, $Zn_2Ti_3O_8$ (cubic), $ZnTiO_3$ (hexagonal) and Zn_2TiO_4 (cubic). $Zn_2Ti_3O_8$ is a low temperature form of $ZnTiO_3$ existing below 820 °C [3]. At the temperature about 945 °C, $ZnTiO_3$ was reported to decompose into Zn_2TiO_4 (zinc orthotitanate) and TiO_2 [1]. Zn_2TiO_4 is stable up to its liquid temperature (1418 °C).

Zinc titanate ($ZnTiO_3$), a perovskite type oxide structure, has a promising material as a gas sensor [4] (for ethanol, NO, CO, etc.), paint pigment [5], catalyst [6] and etc. Also $ZnTiO_3$ has been reported as a material with an excellent electrical properties which could be a useful candidate as microwave resonator [7]. This material has a dielectric constant of 19, quality values of 30.0 GHz and the temperature coefficients of the resonant frequency of - 55 ppm/°C [8].

The structures of titanium dioxide (TiO_2), Zn_2 Ti_3O_8, $ZnTiO_3$ and Zn_2 TiO_4 comprised of TiO_6 octahedra. In rutile and in $ZnTiO_3$, the connection of the TiO_6 octahedra results chains and/or layers. As a result of this similarity, $ZnTiO_3$ is formed only in the presence of rutile [9].

Different methods have been reported to prepare $ZnTiO_3$ powder in the literatures, including conventional solid-state reaction [1], sol gel route [10], molten salt method [11]. The solid state reaction method has some disadvantages such as high firing temperature and difficulties to control the size of particles.

In this paper we prepared $ZnTiO_3$ nano crystalline powder at relatively low temperature by a modified sol-gel method.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

All reagents were of analytical grade and used as received. Titanium tetra isopropoxide (TTIP) with a normal purity of 97 % and Ethanol (C_2H_5OH) were purchased from Sigma Aldrich. Zinc acetate dihydrate ($C_4H_{10}O_6Zn(H_2O)_2$) and Ethanolamine (C_2H_7NO) were obtained from Merck Chemicals, and 18 MΩ deionized water (H_2O) was used to prepare the solutions.

2.2 Preparation of Zinc Titanate powder

The Zinc titanate nano crystalline powders were prepared by a modified sol-gel method. The experimental procedures are as follows: 3.28 ml Ethanolamine (ETA) were dissolved in ethanol (50 ml). The solution was stirred for 10 min at room temperature following by addition of 7.8 ml TTIP. The solution was successively stirred at room temperature for 15 min (solution A). Meanwhile, 5.62 gr of Zinc acetate was dissolved in ethanol (20 ml) and sonicated for 15 min to prepare solution B. Solution B was subsequently added to solution A under vigorous stirring. The solution was subsequently stirred for further 30 min (solution C). 3.41 ml ETA and 1.86 ml deionized water were dissolved in ethanol (45 ml) under vigorous stirring for 15 min to prepare solution D. Subsequently, solution D added dropwise to solution C under stirring. The obtained sol was stirred for further 2 h and aged for 48 h at room temperature. As-prepared zinc titanate gel were dried at 80 °C for 24 h. The obtained solids were ground ant finally calcined at 550 and 800 °C for 2 h. (heating rate = 5 °C/min)

3. CHARACTERIZATION

The X-ray diffraction (XRD) patterns were obtained using an Inel diffractometer (XRG 3000, France), $\lambda = 1.78897$ Å. Structural characteristics of as-prepared powders were observed using field emission transmission electron microscopy (FE-SEM, CARL – ZEISS – Ultra tm 55). The structural evolution of samples was characterized by Raman spectroscopy (LabRAM HR, using a wavelength of 633 nm laser).

4. RESULTS AND DISCUSSION

4.1 Thermal analysis

TGA/DTA analysis was used to understanding the synthesis process. Fig. 1 shows TGA/DTA curves of dried gel powder heated in air at 50 °C/min α-alumina was used as the reference sample. By the fig. 1, the weight loss of dried gel takes place at four distinctly separable levels. During the first level, a small endothermic peak appeared at about 80 °C as shown in DTA curve, which indicated the loss of water and ethanol in the composite sol (9.5 % weight loss). Decomposition of the organic components and

Ethanolamine takes place in the second level. The total weight loss in this level is about 26.6 %. The exothermic peak at 310 °C seems to be corresponded to the detachments of surface-modifier [12]. The third level following by 7 % weight loss in the range of 415 - 495 °C results from the dehydroxylation of Ti-OH into rutile – TiO_2, as corroborated by an exothermic peak at 425 °C. A dramatically peak at 540 °C with the weight loss about 13 % between 495 and 597 °C ascribed to the direct crystallization of $ZnTiO_3$ from an amorphous component. In the temperature range of about 600 to 800 °C there is no significant change in the weight of sample. The phase stability of ($ZnTiO_3$ composition) in the range of 600 to 800 °C confirmed by XRD patterns.

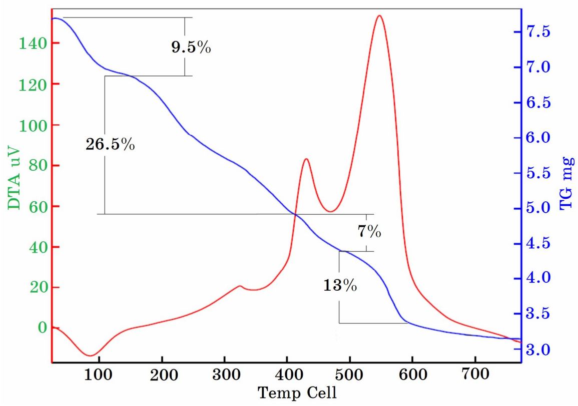


Fig. 1 *– The TGA/DTA curves of* $ZnTiO_3$ *gel*

4.2 XRD analysis

Powder X-ray diffraction (XRD) patterns of powders were recorded with an Inel diffractometer (XRG 3000, France), $\lambda = 1.78897$ Å using CoK_α radiation. As shown in fig. 2, the 2θ peaks appearing at 27.8, 38.2, 41.2, 47.3, 57.5, 62.9, 73.2 and 75.2 in the synthesized samples are attributed to the reflections from (110), (121), (110), (120), (220), (231), (130) and (211) plans of $ZnTiO_3$, respectively (JCPDS no. 850547). The rutile phase was detected by peak at $2\theta = 32.1$ (110), 42.3 (101), 48.5 (110), 64.4 (211) and 67.3 (67.3) (JCPDS no. 881172).

The crystallite size of $ZnTiO_3$ is determined by means of the Debye-Scherrer equation [13] (eq. 1) expressed as follows:

$$d = \frac{0,9\lambda}{\beta \cos\theta} \qquad (1)$$

where d is the crystallite size, λ is the X-ray wavelength (1.78897 Å), β is the full width at the half maximum of the diffraction peak and θ is the Bragg diffraction angle. The crystallite sizes are about 41 and 61.8 nm for calcined samples at 550 and 800 °C, respectively.

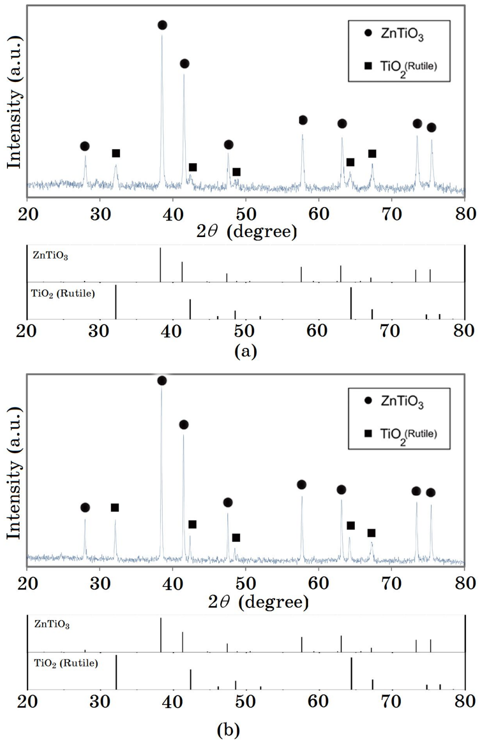
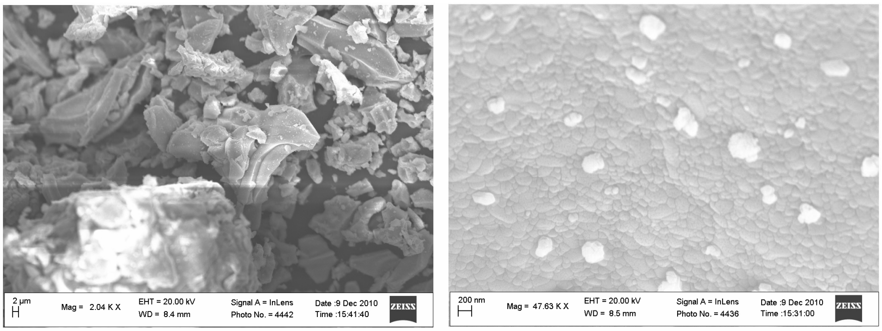


Fig. 2 – *XRD patterns of powders calcined at* 550 °C *(a) and* 800 °C *(b)*

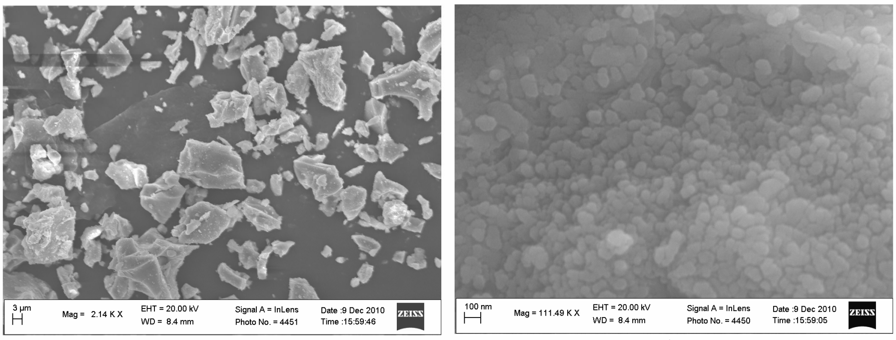
4.3 SEM micrographs of $ZnTiO_3$ powders

Morphologies of the prepared powders were characterized by FE-SEM. Fig. 3a and 4a show the low magnification surface of prepared $ZnTiO_3$ and fig. 3b and 4b give the SEM micrographs of $ZnTiO_3$ powders after heat treatment at (3b) 550 and (4b) 800 °C for 2 h. Fig. 3b and 4b clearly show that a higher calcination temperature is an increase in grain size. These results are in good agreement with the grain sizes calculated by Debye-Scherrer equation.



(a) (b)

Fig. 3 – *Surface morphology of the powder calcined at* 550 °C



(a) (b)

Fig. 4 *– Surface morphology of the powder calcined at* 800 *°C*

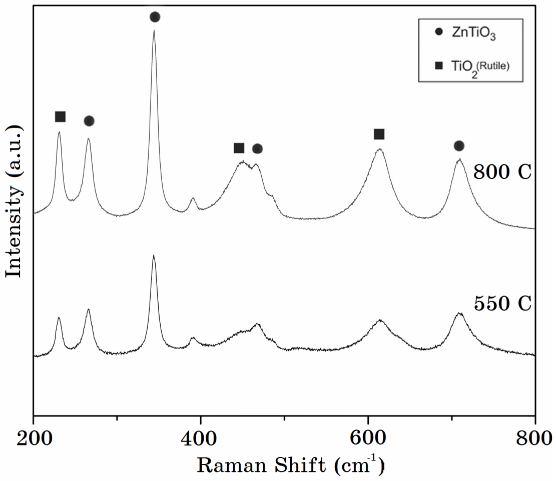


Fig. 5 *– Raman spectra of powders calcined at* 550 *°C and* 800 *°C*

4.4 Raman spectroscopy

To further investigate the synthesized powders, the Raman spectra were collected with 633 nm laser as excitation. Fig. 5 shows Raman spectra of calcined powders at 550 and 800 °C. The Raman spectroscopy results are in good agreement with XRD patterns. The peaks are located at about 264, 343, 462 and 705 cm^{-1} are ascribe to hexagonal ZnTiO$_3$. The peaks are located at about 229, 445 and 610 cm^{-1} related to existence of rutile in the samples [10].

5. CONCLUSION

ZnTiO$_3$ composite materials with nanocrystalline structure have been obtained using sol-gel method at relatively low temperature of 550 °C. Titanium tetra isopropoxide were used as titanium and zinc precursors. The obtained gel calcined under air at 550 and 800 °C. The grain sizes of ZnTiO$_3$ increase when calcination temperature increased.

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