



## RESEARCH ARTICLE

### EFFECT OF CALCINATION TEMPERATURES ON SYNTHESIS OF ZINC TITANATE NANO-CRYSTAL POWDERS VIA COMBUSTION TECHNIQUE

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Received 10<sup>th</sup> January, 2013; Received in Revised form; 20<sup>th</sup> February, 2013; Accepted 17<sup>th</sup> March, 2013; Published online 15<sup>th</sup> April, 2013

#### ABSTRACT

Zinc titanate ( $ZnTiO_3$ ; ZT) powders were successfully prepared by a combustion technique. The ZT powders were heated at temperature from 500 °C to 850 °C for various times 2, 4 and 6 h. Powder samples were characterized using thermogravimetric (TGA), differential thermal analysis (DTA), X-ray diffractometer (XRD), scanning electron microscopy (SEM) and laser particle size analyzer (LPSA). The second phases such as ZnO and  $TiO_2$  were detected in the powders calcined below 800 °C. A single perovskite of the ZT powders was found with calcination temperatures at 800 °C. The shape of crystalline will be changed as increasing the time of calcination temperature. The TGA-DTA results corresponded to the XRD investigation. According to SEM and LPSA analysis nano-crystal powders of ZT were obtained.

**Key words:** Combustion Technique; Calcination; Zinc titanate; Perovskite; Ultra-fine.

#### INTRODUCTION

First investigations of a binary oxide system consisting of ZnO and  $TiO_2$  introducing a phase diagram were conducted by Dulin and Race 1960, who reported that there are three compounds exist in the ZnO– $TiO_2$  system, including  $Zn_2TiO_4$  (cubic),  $ZnTiO_3$  (hexagonal) and  $Zn_2Ti_3O_8$  (cubic) (Dulin, Rase 1960; Bartram, Slepetyts 1961).  $ZnTiO_3$  was perovskite type oxide structure and could be an useful candidate for microwave resonator materials (Kim *et al.*, 1999) gas sensor (Obayashi *et al.*, 1976) (for ethanol NO, CO, etc.) catalyst (Bartram, Slepetyts 1961) and paint pigment (McCord, Saunder 1945). Yamaguchi *et al.* (1987) clarified that  $Zn_2Ti_3O_8$  is a low-temperature form of  $ZnTiO_3$ . This system still attracts the attention of researchers because of its importance in practical applications (Yamaguchi *et al.*, 1987; Chang *et al.*, 2002; Swisher *et al.*, 1995; Steinike, Wallis 1997).  $Zn_2TiO_4$  can easily be prepared by conventional solid-state reaction between 2ZnO and 1 $TiO_2$ .

But, the preparation of pure  $ZnTiO_3$  from a mixture of 1ZnO and 1 $TiO_2$  has not been successful because the compound decomposes into  $Zn_2TiO_4$  and rutile at about 945 °C. There are a lot of processing techniques for preparing ZT powders, such as the solid state reaction technique (Dulin, Rase 1960), the sol-gel method (Yamaguchi *et al.*, 1987), molten salt synthesis (Idrissi *et al.*, 1997), etc. The conventional solid state reaction method is the most widely used route. However, the ceramics which are synthesized by a solid state reaction require high temperature and the resulting powders exhibit many

undesirable characteristics: large particle size and wide particle size distribution. Wet chemical syntheses can provide homogenous nano-sized oxides of high purity at lower reaction temperatures but they have a high cost for starting materials, and are intricate and complicated. The combustion method has much interest; at present it helps to decrease the temperature in the preparation and has a small particle size. The combustion reaction method also has interesting characteristics such as its simplicity, its relatively low cost and the fact that it usually results in products with the desired structure and composition (Patil *et al.*, 1997). The applications for zinc titanates were at that time mostly paint pigments and fusion cast thermistors. Although, the first application was as a sorbent for removing sulfur from coal gasification products (Swisher *et al.*, 1995; Steinike, Wallis 1997; Idrissi *et al.*, 1997; Patil *et al.*, 1997; Hosono *et al.*, 2004). Nowadays, due to the development of microwave dielectrics, zinc-titanates can be used as dielectric resonators and filters in microwave devices (Kagata *et al.*, 1993). Thus, in this work, ultra-fine powders of  $ZnTiO_3$  successfully were obtained via the combustion method.

#### Experimental

The starting materials were commercially available ZnO (>99.5% Merck 108849) and  $TiO_2$  (>99.5% Merck 100808). The ZT powders were synthesized by the combustion route as shown in Fig 1. The powders were mixed by ball milling for 12 h with ethanol. After drying and sieving, the powders and urea were mixed and ground in an agate motor. Then, the mixed powders were calcined using various calcination temperatures, ranging from 500 to 850 °C, for 2 and 4, 6, 8, 10, 12, 14, 16, 18, 20, 24, 28, 32, 36, 40, 44, 48, 52, 56, 60, 64, 68, 72, 76, 80, 84, 88, 92, 96, 100 h.

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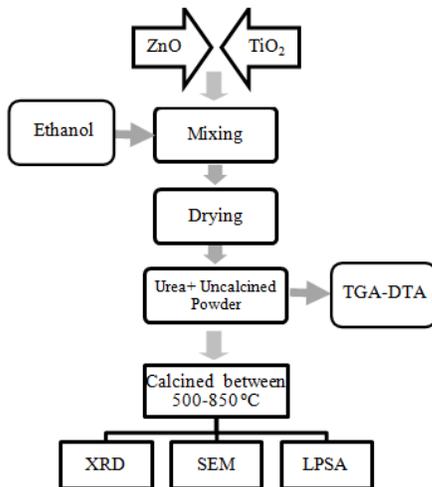


Fig. 1. Preparation route for ZT powders

The reaction of uncalcined ZT powders and urea fuel taking place during heat treatment was investigated by thermogravimetric analysis (TGA), differential thermal analysis (DTA). X-ray diffraction (XRD) was employed to identify the phase formed. The particle morphology and size were directly imaged, using scanning electron microscopy (SEM) and the particle size distribution was determined by using a laser particle size analyzer.

## RESULTS AND DISCUSSION

Fig. 2. shows the TGA and DTA curves of ZT powders prepared via the combustion route. The ZT powders demonstrated a three-stage weight loss; the first one was in the temperature range of 150 to 220 °C, the second one from 300 to 500 °C, and the last one began around 550 °C.

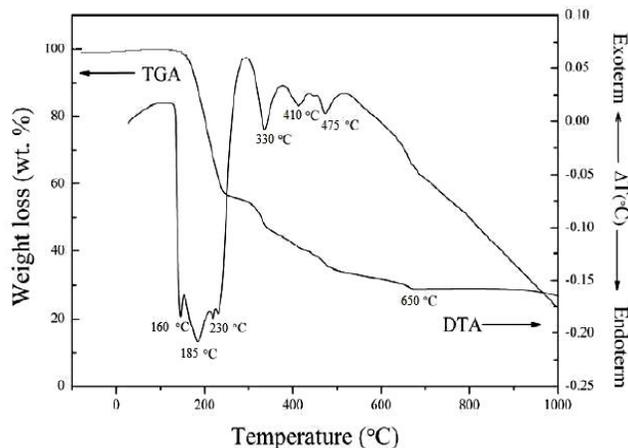


Fig. 2. DTA-TG curves of uncalcined ZT powders

The first weight loss is believed to be caused by the melting of the urea. It was related with the endothermic peaks in the DTA curves at 160, 185 and 230 °C. The second step was caused by the evaporation of water and gas. This was associated with the endothermic peak at 330, 410 and 475 °C. The last curve corresponded to a small endothermic peak at 650 °C, and represented the reaction of ZnO and TiO<sub>2</sub>. Based on the results of DTA and TGA, calcinations were carried out from

500 to 850 °C for 2 h, at a heating /cooling rate of 5 °C /min for the uncalcined ZT powders. The XRD patterns of the ZT powders, formed with different calcination temperatures, are shown in Fig 3.

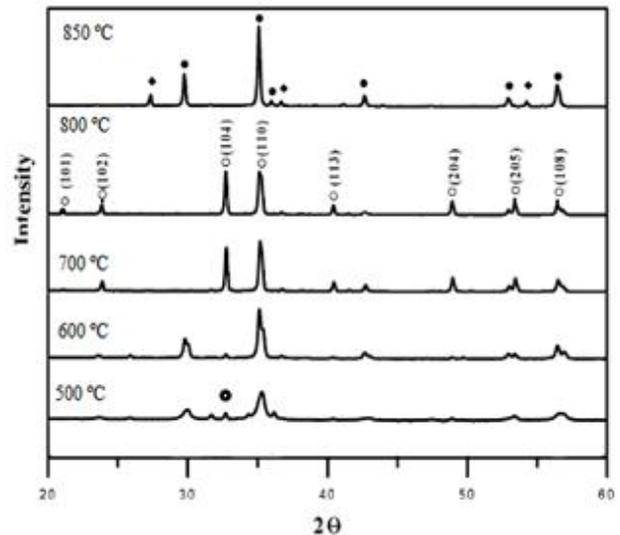


Fig. 3. XRD patterns of ZT powders with various calcination temperatures for 2 h; (○) ZnTiO<sub>3</sub>, (●) Zn<sub>2</sub>TiO<sub>4</sub> and (◆) TiO<sub>2</sub>, (◻) ZnO

After calcination from 500 to 700 °C, the precursor of ZnO and TiO<sub>2</sub> were detected. When the temperature went above 700 °C, the minor phase of ZnO remained. A high purity of the hexagonal perovskite phase was discovered in powders calcined at 800 °C, which could be matched with JCPDS file number 00-014-0033. Above 800 °C, Zn<sub>2</sub>TiO<sub>4</sub> phase formed. Results of the X-ray analysis of ZnTiO<sub>3</sub> after heat treatment at 800 °C for different times: (a) 4, (b) 6 h and are given in Fig. 4.

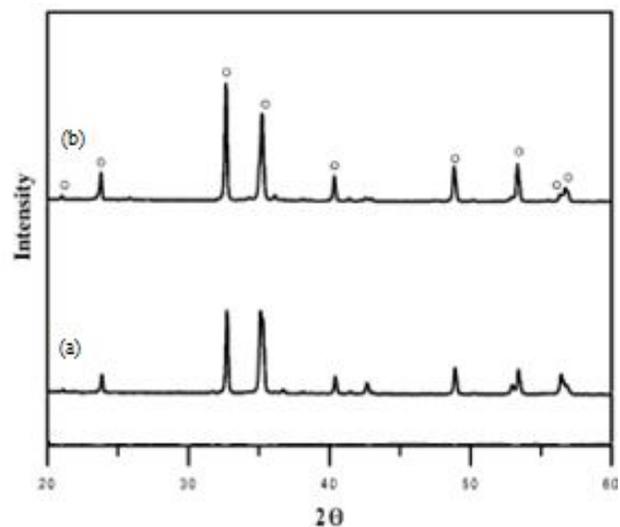


Fig. 4. XRD patterns of ZT powders after calcination at 800 °C for different times: (a) 4 and (b) 6 h; (○) ZnTiO<sub>3</sub>

The average grain sizes were determined from the XRD powder pattern according to the Scherrer's equation (14).

$$D = k\lambda / (B\cos\theta) \quad (1)$$

Where

$D$  is the size of powder,  $\lambda$  is the X-ray wavelength,  $B$  is the FWHM of diffraction peak,  $\theta$  is the diffraction angle and  $k$  is a constant equal to 0.89. The average grain sizes of powders fired at 600 °C, 700 °C, 800 °C and 850 °C were about 340, 392, 473 and 541 nm, respectively. These results are in good accordance with SEM observations which are shown in Fig 5. Heat treatment at 800 °C for different times: 4 and 6 h are given in Fig. 6 shows to enhance the atomic mobility and caused the grain growth to result in a better crystallinity. The results are in good accordance with XRD analysis.

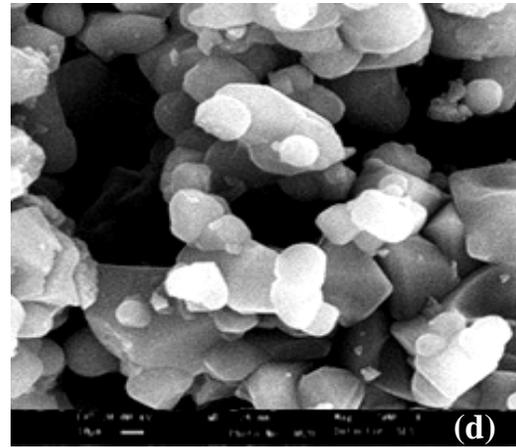
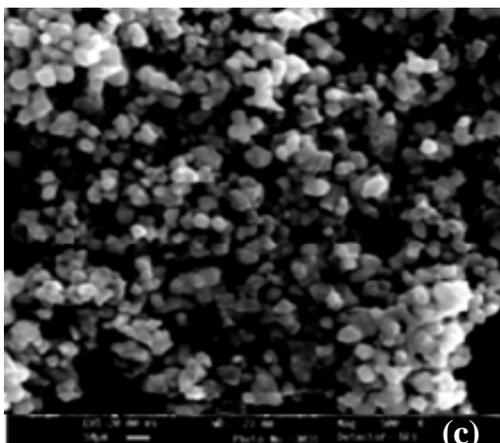
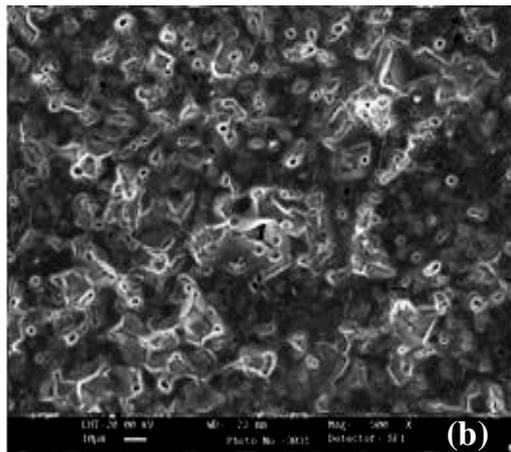
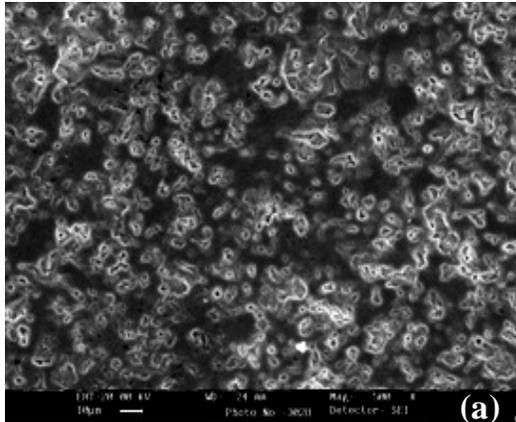


Fig. 5. SEM morphology of ZT powders calcined at (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 850 °C

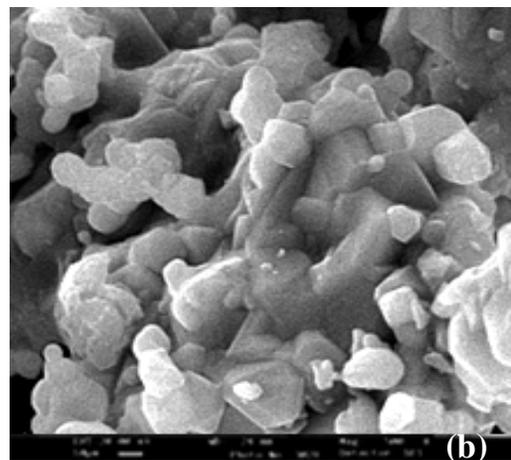
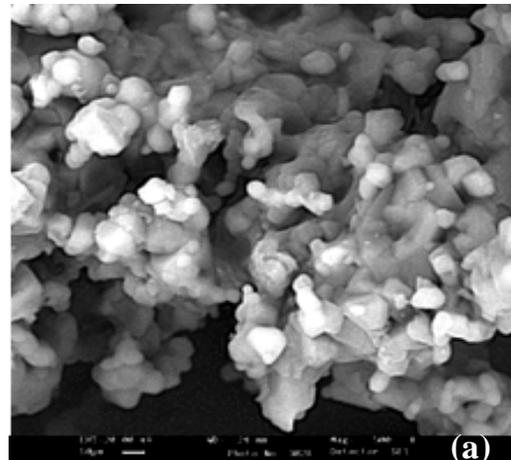


Fig. 6. SEM morphology of ZT powders after heat treatment at 800 °C for different times: (a) 4 h and (b) 6 h

SEM micrographs revealed when the temperature increased the surface morphology of the samples changes and also appears that a higher calcination temperature favors a particle with larger grain sizes. The average particle size estimated from SEM is similar with the average particle size computed by XRD data and LPSA which are shown in Fig. 7 and Table 1.

Table 1. grain size of ZT-800 °C

LPSA	ZT-800
D(10)	0.258 $\mu\text{m}$
D(50)	0.480 $\mu\text{m}$
D(90)	3.890 $\mu\text{m}$

The relative percentage in the perovskite and impurity phases were determined by measuring the major XRD peak intensities of the perovskite and impurity phases. The percentage of the perovskite phase was estimated by the following equation (15)

$$\% \text{ perovskite phase} = \left( \frac{I_{\text{Perov}}}{I_{\text{Perov}} + I_{\text{ZnO}} + I_{\text{TiO}_2} + I_{\text{Zn}_2\text{TiO}_4}} \right) \times 100 \quad (2)$$

The percent perovskite phase increased with an increase in the calcining temperature.

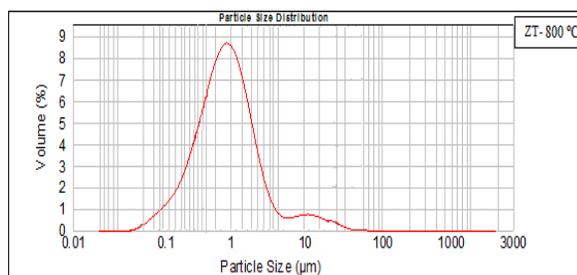


Fig. 7. Particle size distribution curve of ZT-800 °C

The percent perovskite phase increased with an increase in the calcining temperature. A hundred percent of the perovskite phase was obtained at 800 °C which are given in Fig. 8 The lattice parameter  $c$  tended to increase, while the lattice parameter  $a$  tended to decrease. Also, The  $c/a$  ratio increased with increased calcination temperatures as seen in Fig. 9.

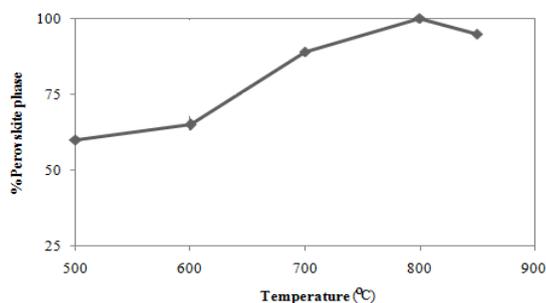
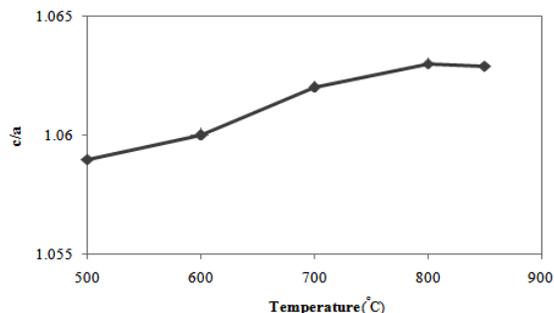


Fig. 8. The percent perovskite phase of ZT powders with various calcinations temperatures

Fig. 9. The  $c/a$  ratio of ZT powders with various calcination temperatures

## Conclusions

Perovskite  $\text{ZnTiO}_3$  powders can be successfully obtained by the combustion technique and the best conditions for calcination is 800 °C. The calcination 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-800 °C showed advantageous microstructures, with the appropriate pores/materials ratio and good candidates for application in the electronic industry as well as chemical industry as catalysts and colour pigments. Heat treatment at 800 °C for different times: 4 and 6 h enhanced the atomic mobility and caused the grain growth to result in a better crystallinity.

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