

## Preparation and Characterization of Zinc Titanate Nanostructures by Oxidation Reaction Technique

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### ABSTRACT

*Zinc titanate nanostructures were prepared by oxidation reaction technique. Zinc and titanium oxide powder were mixed and screened on alumina substrate. Then, it was sintered in the furnace for 6 hours under normal atmosphere. The sintering temperature was varied from 500-800°C. The obtained products were investigated by field emission scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, and Raman spectroscopy. The belt-like nanostructures were observed outward from micro particles for all sintering temperatures. The diameter and length of nanostructures were in the range of 100-400 nm and 1-6 μm, respectively. These nanostructures exhibited zinc titanate phase as well. These results as a function of sintering time will be discussed.*

**Key words:** Zinc titanate, Nanostructures, Oxidation reaction

### INTRODUCTION

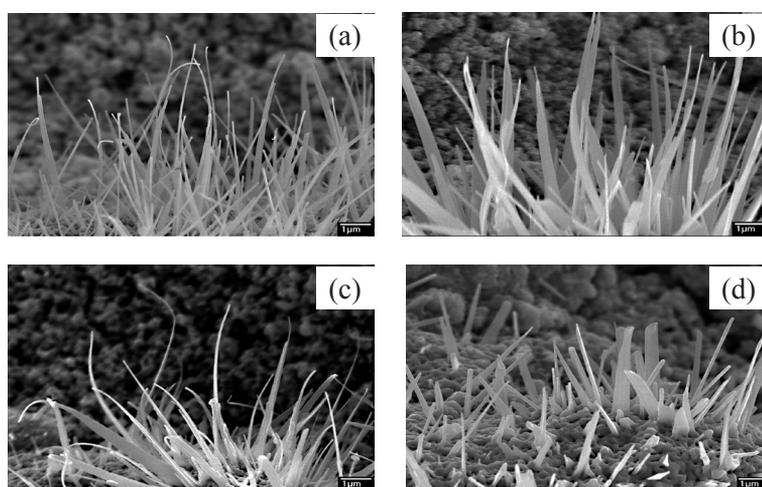
Spinel type zinc titanate  $Zn_2TiO_4$ , a mixed metal oxide typically prepared by combining zinc oxide (ZnO) and titanium oxide ( $TiO_2$ ), is currently of interest due to its wide range properties. This material is used in many applications such as photoelectrochemical cells, microwave dielectrics and gas sensors. Several phases, including  $Zn_2TiO_4$  (cubic),  $ZnTiO_3$  (hexagonal) and  $Zn_2Ti_3O_8$  (cubic) existed according to a phase diagram for the ZnO- $TiO_2$  system recently reported (Yang et al., 2004). Several techniques could be used to prepare these compounds. The spinel-type  $Zn_2TiO_4$  could be prepared by solid-state reaction of ZnO and  $TiO_2$  in the molar ratio of 3:2 at 1350°C (Li et al., 2000). The compound could also be prepared by vapor-phase oxidation of ZnO nanoparticles and  $TiO_2$  in various ratios (Zhu et al., 2004). In the present work, zinc titanate nanostructures were prepared by oxidation reaction of Zn and  $TiO_2$  powders.

## MATERIALS AND METHODS

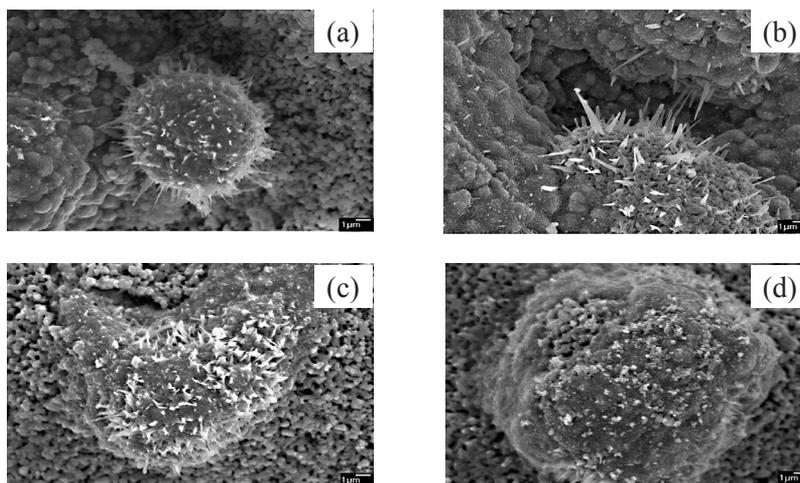
Zinc titanate nanostructures were prepared by oxidation reaction technique. Zn and TiO<sub>2</sub> powders (supplied by Aldrich and Univar, respectively) with diameter 50 μm were hand-ground in agate mortar and used as starting materials. The powders were mixed in various TiO<sub>2</sub> amount of ranging from 20, 40, 60 and 80 mole percent with polyvinyl alcohol (PVA). The mixed powders were screened on alumina substrate and sintered under normal atmosphere. The sintering temperature was varied from 500-800°C and sintering time was 6 hours. The reacted powders were investigated by Field Emission Scanning Electron Microscopy (FE-SEM) for morphology, by X-ray diffraction (XRD) for phase structures and energy dispersive spectroscopy (EDS) and Raman spectroscopy for chemical composition.

## RESULTS AND DISCUSSION

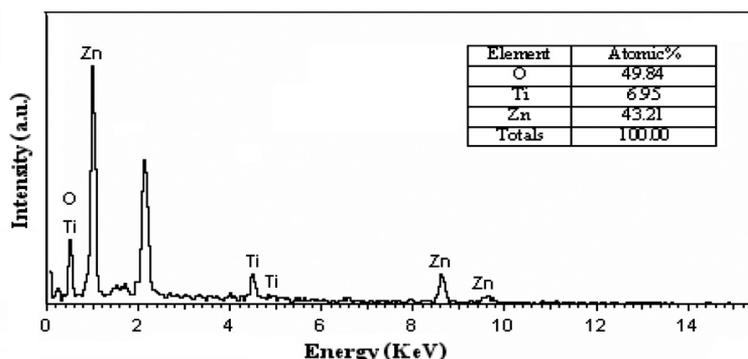
Morphology of zinc titanate nanostructures is shown in Figure 1 for Zn-20% TiO<sub>2</sub> sample. The belt-like nanostructures were observed as growing outward from micro particles for all sintering temperature. The diameter and length of zinc titanate nanostructures were in the range of 100-350 nm and 2-5.5 μm at 20% TiO<sub>2</sub>, respectively. At sintering temperature of 600°C, the diameter was largest and the length was longest. The amount of belt-like nanostructures was formed to decrease at higher amount of TiO<sub>2</sub> as shown in Figure 2 for all sintering temperature.



**Figure 1.** FE-SEM images of zinc with 20% titanium oxide sintered at (a) 500°C, (b) 600°C, (c) 700°C, and (d) 800°C.



**Figure 2.** FE-SEM images of zinc with various titanium oxide content (a) 20%, (b) 40%, (c) 60%, and (d) 80% sintered at 800°C.

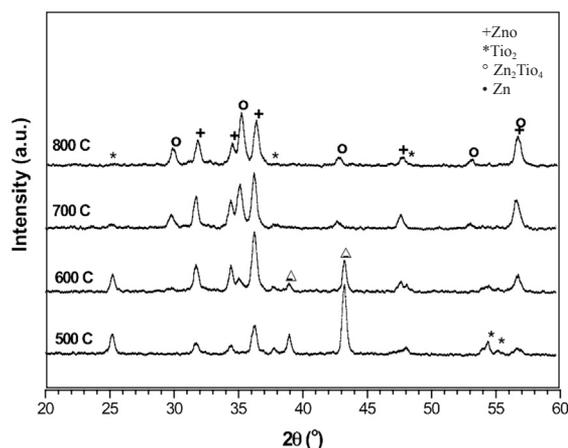


**Figure 3.** EDS spectrum of zinc with 20% titanium oxide sintered at 700°C.

Figure 3 showed EDS spectrum of zinc with 20% titanium oxide sintered at 700°C. The spectrum was obtained by focusing electron beam in a middle of a belt-like nanostructure. The spectrum was shown Zn, Ti, O, and Au signals, Au was coated before investigation. According to phase diagram (Yang et al., 2004), zinc titanate has three stable phases ( $\text{Zn}_2\text{TiO}_4$ ,  $\text{ZnTiO}_3$ , and  $\text{Zn}_2\text{Ti}_3\text{O}_8$ ) and at low mole percent of  $\text{TiO}_2$  (0-33%) the compounds are  $\text{Zn}_2\text{TiO}_4$  and ZnO phase. At higher  $\text{TiO}_2$  content (over 50 mole percent), phase diagram show that  $\text{Zn}_2\text{TiO}_4$  decompose to  $\text{ZnTiO}_3$  but it still remains  $\text{Zn}_2\text{TiO}_4$ . Thus, zinc titanate nanostructure in this work is probably the  $\text{Zn}_2\text{TiO}_4$  phase.

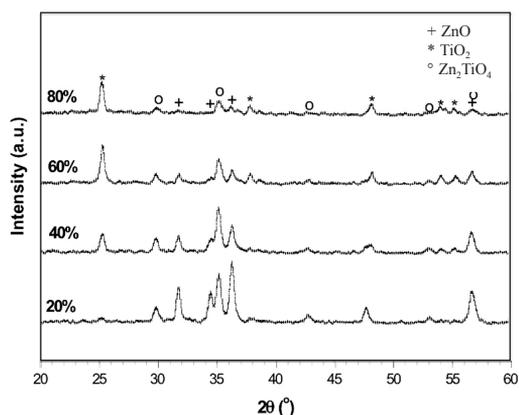
XRD analysis of mixed powder with 20% titanium oxide sintered at different temperatures is shown in Figure 4. The starting material, Zn, still remained when the sintering temperature was below 700°C and some Zn partially transformed to ZnO. But  $\text{TiO}_2$  (anatase phase) was formed at all temperatures. Mixed powder began to transform to spinel  $\text{Zn}_2\text{TiO}_4$  structure at sintering temperature of 600°C regardless of  $\text{TiO}_2$  concentration but the amount was small. With increasing

sintering temperature, the intensity of spinel phase increased indicating the larger amount of spinel phase was due to the enhancement of the atomic mobility at high temperature and caused the grain growth (Chang et al., 2003).

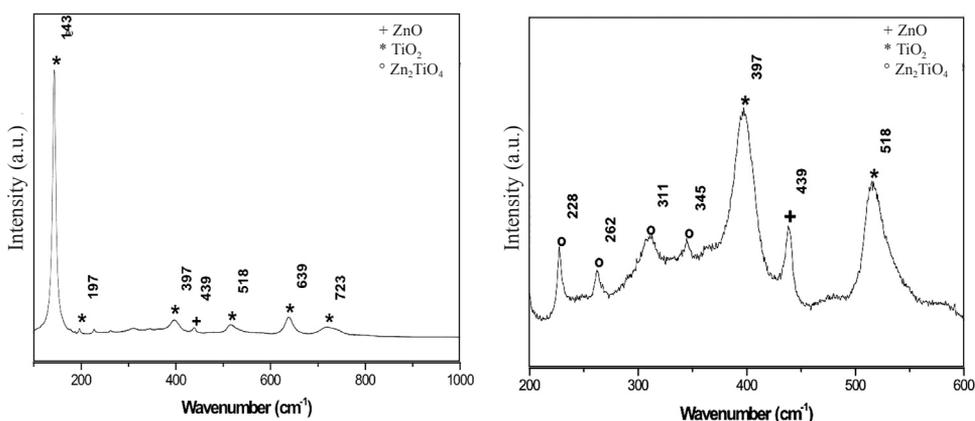


**Figure 4.** XRD diffraction patterns of the mixed powder with 20% TiO<sub>2</sub> content sintered at different temperature.

Figure 5 shows X-ray diffraction patterns of Zn mixed with various TiO<sub>2</sub> concentration (20, 40, 60 and 80%) sintered at 700°C. The intensity of Zn<sub>2</sub>TiO<sub>4</sub> increased with the addition of TiO<sub>2</sub> up to 40 % (20 and 40% are nearly the same) then decreased at higher amount of TiO<sub>2</sub>. This result is consistent with Zhu et al. They found that when ZnO was mixed with TiO<sub>2</sub> lower than 10 wt% (1, 5 and 10 wt %) the intensity of Zn<sub>2</sub>TiO<sub>4</sub> increased with increasing amount of TiO<sub>2</sub>. Because the equilibrium TiO<sub>2</sub> content mixed with Zn is approximately 33% according to the following reaction:



**Figure 5.** XRD diffraction patterns of the mixed powder with different TiO<sub>2</sub> content sintered at 700°C.



**Figure 6.** Raman spectrum of zinc with 20% TiO<sub>2</sub> sintered at 700°C (a) at wavenumber up to 1000 cm<sup>-1</sup> (b) at wavenumber up to 600 cm<sup>-1</sup>

Raman spectrum exhibited mixed phases as shown in Figure 6 (a) that included TiO<sub>2</sub>, ZnO and the spinel Zn<sub>2</sub>TiO<sub>4</sub>. The intense peaks at 143, 197, 397, 518, 639 and 723 cm<sup>-1</sup> can be assigned to TiO<sub>2</sub> (anatase phase). They corresponded to the Raman active normal modes of representations A<sub>1g</sub>, 2B<sub>1g</sub>, 3E<sub>g</sub> of the space group (Pineda et al., 1997) and the peak at 439 cm<sup>-1</sup> corresponds to E<sub>2</sub> (high) of ZnO bulk (Alim et al., 2005). The weak peaks at 228, 262, 311 and 345 cm<sup>-1</sup> as shown in Figure 5 (b) were assigned to the spinel-structure, Zn<sub>2</sub>TiO<sub>4</sub>, corresponding to the normal modes of representations F<sup>3</sup><sub>2g</sub>, E<sub>g</sub>, F<sup>2</sup><sub>2g</sub> and F<sup>1</sup><sub>2g</sub> of the space group (Pineda et al., 1997).

## CONCLUSION

We have successfully synthesized zinc titanate from mixed powder of Zn with various mole percent of TiO<sub>2</sub> by oxidation reaction technique. The diameter and length of zinc titanate nanostructures were in the range of 100-400 nm and 1-6 μm, respectively. From XRD analysis, it was found that zinc titanate exhibited spinel structure Zn<sub>2</sub>TiO<sub>4</sub>. The results of Raman also confirmed the formation of the spinel phase.

## ACKNOWLEDGEMENTS

This work was supported by Nanoscience and Nanotechnology Center, Faculty of Science, Chiang Mai University. Surat Sedpho would like to acknowledge the Graduate School, Chiang Mai University for financial support.

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