Temperature effect on $Zn_2Ti_3O_8$ phase formation by thermal oxidation technique

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ABSTRACT

Thermal Oxidation technique has been employed for synthesis of $Zn_2Ti_3O_8$ compounds which is a stable form of ZnO-TiO_2 at low temperatures. ZnO powders mixed with 55, 60, 70, 80 and 90 mol% of anatase-TiO_2 powders were used as precursor materials. The mixed powders were ground in agate mortar for 2 h then heated in a furnace tube at temperature varied from 600˚C to 850˚C under normal atmosphere for 48 h. The influence of anatase-TiO_2 mol% and the sintering temperature on $Zn_2Ti_3O_8$ phase formation was investigated with field emission electron microscope, energy dispersive spectroscope and X-ray diffractometer. Results showed that the optimum condition for $Zn_2Ti_3O_8$ cubic defect spinel structure was 60 mol% of anatase-TiO_2 powders at sintering temperature 750˚C. $ZnTiO_3$ phase structure has been observed at sintering temperature higher than 800˚C in ZnO with 60 mol% of anatase-TiO_2 powders.

Keywords: $Zn_2Ti_3O_8$, Anatase, Thermal Oxidation Technique

INTRODUCTION

Zinc titanate has been used in a wide variety of technological applications such as sulfur capturer in coal industry, paint, microwave range dielectric, gas sensor and dye-sensitized solar cell (Swisher, 1992; Jung, 2009; Obayashi, 1976; O'regan, 1991). The ZnO-TiO_2 phase diagram were conducted and reported that there are three major forms of Zinc titanate: perovskite type $ZnTiO_3$ (hexagonal), spinel type Zn_2TiO_4 (cubic) and $Zn_2Ti_3O_8$ (cubic) by Dulin and Race in 1960 (Dulin, 1960). Yamaguchi et al. clarified that $Zn_2Ti_3O_8$ is a low-temperature form of $ZnTiO_3$ only with a cubic cell (Yamaguchi, 1987). The existence of meta stable $Zn_2Ti_3O_8$ was first reported by Bartram and Slepetys in 1961 who found that it decomposes at temperature above 700˚C (Bartram, 1961). Reddy et al. pointed out that the single phase of $Zn_2Ti_3O_8$ is produced when zinc titanyl oxalate hydrate decomposes at 650˚C for several hours (Reddy, 1984). Sheinkman *et al.* reported that with the same bulk compositions and temperature, ZnO reactions with anatase or rutile TiO_2 can form $Zn_2Ti_3O_8$ and $ZnTiO_3$, respectively (Sheinkman, 1977). There is controversy over whether $Zn_2Ti_3O_8$ is stable compound or not. Yang and Swisher proposed that $Zn_2Ti_3O_8$ is a thermodynamically stable compound and it is stable up to temperature between 750˚C and 800˚C (Yang, 1996). However, Datta reported that $Zn_2Ti_3O_8$ only forms as a metastable phase when ZnO is reacted with anatase (Datta, 1994). Budigi Lokesh et al. synthesized $ZnTiO_3$, Zn_2TiO_4 and $Zn_2Ti_3O_8$ using a simple solid-state reaction, they found that crystalline structure of TiO_2 along with calcination temperature influences the zinc titanate phase formation and the optical band gap of the compound (Budigi, 2014). Many synthesis techniques have been extensively developed to have high purity zinc titanate such as sol-gel (Chang, 2003), vapor-phase oxidation, and solid-state reaction (Dullin, 1960). In this work, the content of anatase-TiO_2 with ZnO powders and sintering temperature were varied to synthesis $Zn_2Ti_3O_8$ compound using thermal oxidation, simple and inexpensive technique. The influence of anatase-TiO_2 content and the sintering temperature on $Zn_2Ti_3O_8$ phase formation were investigated.

EXPERIMENT

$Zn_2Ti_3O_8$ compounds were prepared by thermal oxidation technique. ZnO (99.9%, Aldrich) and anatase-TiO_2 (99.8%, Univar) powders as the precursor materials were ground in agate mortar for 2 hours. The powders were mixed in various mol% of anatase-TiO_2 powders ranging from 55, 60, 70, 80 and 90 mol%. Then the mixed powders were heated in a furnace tube at different sintering temperature varied from 600˚C to 850˚C under normal atmosphere for 48 hours. The reacted powders were investigated by field emission scanning electron microscopy (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDS) (JEOL model JSM-6335F) and X-ray diffraction (XRD, Rigaku MiniFlexII) for morphology, chemical composition and phase structures, respectively.

RESULTS AND DISCUSSION

The morphology of ZnO with 60 mol% of anatase-TiO_2 powders sintered at different temperature in the range of 600˚C to 850˚C is shown in figure 1. FE-SEM micrographs revealed that the average particle size slightly increased with increasing sintering temperature. The average particle sizes of the reacted powders sintered at 600˚C, 650˚C, 700˚C, 750˚C, 800˚C, and 850˚C are about 157 nm, 169 nm, 174 nm, 240 nm, 254 nm, and 313 nm, respectively.

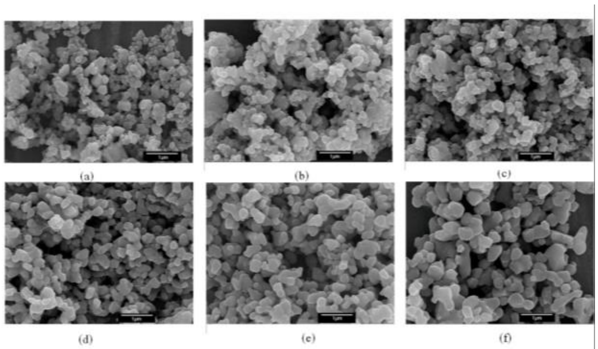

Fig. 1 FE-SEM micrographs of ZnO with 60 mol% of anatase-TiO_2 powders sintered at (a) 600˚C, (b) 650˚C, (c) 700˚C, (d) 750˚C, (e) 800˚C and (f) 850˚C

EDS spectrum of ZnO with 60 mol% of anatase-TiO_2 powders sintered at 750˚C is shown in figure 2. The spectrum was obtained by focusing electron beam on some part of the reacted powders as shown in the inset of figure 2. The result indicated that the reacted powders consisted of Zinc (Zn), Titanium (Ti) and Oxygen (O) elements. The atomic concentration of Zn, Ti and O are 11.34, 20.70 and 67.97 at.%, respectively.

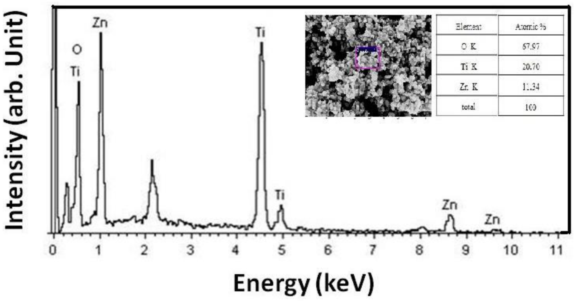

Fig. 2 EDS spectrum of ZnO with 60 mol% of anatase-TiO_2 powders sintered at 750 ˚C

Figure 3 showed X-ray diffraction pattern of ZnO mixed with various anatase-TiO_2 content (55, 60, 70, 80 and 90 mol%) sintered at 750°C. X-ray diffraction peaks are in agreement with the phase of $Zn_2Ti_3O_8$ cubic defect spinel structure. The peaks correspond to (2 1 0), (2 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (6 2 0) and (5 3 3) planes of JCPDS file number 8771781, respectively. The intensity of $Zn_2Ti_3O_8$ phase increased with the addition of anatase-TiO_2 up to 60 mol% then decreased at higher amount of anatase-TiO_2. It was shown that the optimum content of anatase-TiO_2 for $Zn_2Ti_3O_8$ cubic defect spinel structure is 60 mol%.This result is consistent with Yang and Swisher reported[Yang and Swisher , 1996].

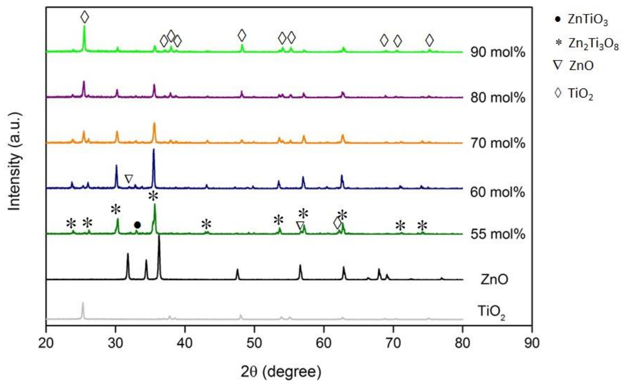

Fig.3 XRD diffraction patterns of the mixed powder of ZnO with diferrent anatase-TiO_2 content sintered at 750˚C

XRD analysis of ZnO with 60 mol% of anatase-TiO_2 powders sintered at different temperatures is shown in figure 4. The results showed that the reacted powders initially transform to $Zn_2Ti_3O_8$ cubic defect spinel structure at sintering temperature about 650˚C and the starting materials, ZnO and TiO_2, still remained when the sintering temperature was below 750˚C. The intensity of phase $Zn_2Ti_3O_8$ peaks increased with the increasing of sintering temperature indicating larger amount of the spinel phase was due to the enhancement of the atomic mobility at high sintering temperature and caused the grain growth[Chang, 2002]. $ZnTiO_3$ phase structure has been observed at sintering temperature higher than 800˚C.

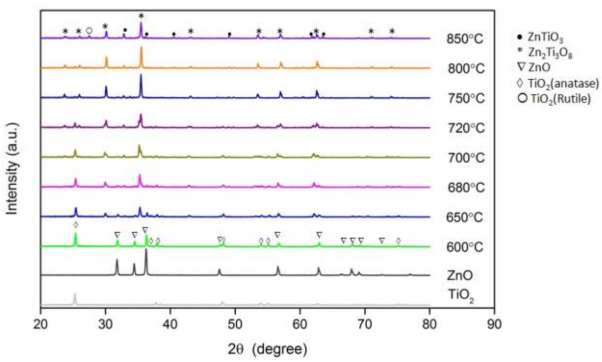

Fig. 4 XRD diffraction patterns of ZnO with 60 mol% of anatase-TiO_2 powders sintered at different temperature.

CONCLUSION

$Zn_2Ti_3O_8$ phase structure can be successfully obtained using thermal oxidation technique. It is clearly seen that both anatase-TiO_2 content and the sintering temperature played an important role on $Zn_2Ti_3O_8$ phase formation. The results showed that the average particle size slightly increased with increasing sintering temperature. The EDS result suggested that the reacted powders compose of Zn, Ti and O elements and the XRD results revealed that the optimum condition for phase formation of $Zn_2Ti_3O_8$ cubic defect spinel structure was 60 mol% of anatase-TiO_2 powders at heating temperature 750˚C and $ZnTiO_3$ phase structure has been observed at sintering temperature higher than 800°C in ZnO with 60 mol% of anatase-TiO_2 powders.

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