

## **DETERMINATION OF THE ENERGY BAND-GAP OF THE CERAMIC ZnO -xTiO<sub>2</sub> USING PHOTOPYROELECTRIC SPECTROSCOPY**

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### **ABSTRACT**

Photopyroelectric (PPE) spectroscopy is a useful tool for examining optical properties in semiconductor materials. The ceramic (ZnO - xTiO<sub>2</sub>) was sintered at 1270 °C for 1 and 3 hours to investigate the variations of energy band-gap with respect to mol % of dopant TiO<sub>2</sub>. The X-ray diffractometry shows that the crystal structure of ZnO doped at low level remains to be of hexagonal type but has developed second phase, Zn<sub>2</sub>TiO<sub>4</sub>, at high level. Microstructure and compositional analysis of the selected areas are analyzed using SEM and EDAX. The maximum grain size obtained were 26.8, 52.4 μm at 0.4 mol % of TiO<sub>2</sub> for 1 and 3 hours sintering time, respectively. The band-gap determined from the photopyroelectric spectrum has the value of 2.82 ± 0.01 eV for samples sintered for 1 and 3 hours at the doping level of 0.4 mol % of TiO<sub>2</sub> and decreases with the increase of TiO<sub>2</sub>.

### **INTRODUCTION**

A white polycrystalline ZnO is a n-type semiconductor with a wide energy band-gap of 3.2 eV [1]. It crystallizes into a wurtzite structure, and is a complete hexagonal closed-packed (hcp) lattice. It is widely used in the manufacturing of paints, rubber products, cosmetics, pharmaceuticals, floor covering, plastics, textiles, ointments, inks, soap, batteries, and also in electrical components such as gas sensors, phosphors, piezoelectric transducers and varistors (voltage dependant resistor) [2, 3]. The lattice constants of ZnO vary depending on how great is the unavoidable deviation from stoichiometry towards an excess of the metal (Zn<sub>1+x</sub>O). The fact that the bonds in ZnO are 50 - 60% ionic [4] gives no indications to the type of defects. The measurements of the electron density [5] have shown that dominant defects are interstitial zinc ions [6,7]. Other investigators, however, suggest that it is oxygen vacancies V<sub>o</sub> that predominates and this hypothesis never been refuted. The value of x in Zn<sub>1+x</sub>O ranges from 0 to 0.7 depending on the temperature and oxygen partial pressure [8].

Varistors are extensively used as protective devices to regulate transient voltage surges of unwanted magnitudes [9]. The exact role of many additives in the electronic structure of ZnO varistors is uncertain. ZnO based varistor is formed with other metal oxides of small amounts such as Bi<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO, Sb<sub>2</sub>O<sub>3</sub> etc. These additives are the main tools that are used to improve the non-linear response and the stability of ZnO varistor [10]. Varistor effect (highly nonohmic behavior in the *I-V* characteristics),

which can be explained by mechanism involving the grain boundaries and the associated defect concentration gradients [11]. The distribution of vacancies and impurities as well as their behavior during annealing treatments appear as one of the factors that determine the electrical properties of ceramic ZnO.

PPE spectroscopy a powerful technique is a non-radiative tool [12] to study optical properties of the materials. The method is based on photothermal effect where the pyroelectric (PE) film transducer is used to detect the temperature variation from the light-induced periodic heating in the sample. When there is absorption of incident light, the non-radiative de-excitation processes within the solid will cause the sample temperature to fluctuate, through heat diffusion to the surrounding PE film. Due to this temperature change, a PE voltage is observed in the PE film.

Much work has been done in *I-V* studies on ZnO based varistor by previous workers [10, 13]. It is necessary to get information on optical absorption of ceramic ZnO doped with different metal oxides for the investigation on electronic states of ceramic ZnO and doped impurities during sintering process and in this paper we discuss the effect of TiO<sub>2</sub> on the energy band-gap variation of ZnO ceramic.

## EXPERIMENT DETAILS

ZnO (99.9% purity) was doped with xTiO<sub>2</sub> (99.9 % purity) ( $x = 0.4, 0.6, 1.0, 1.7, 2.5$  mol %). All samples were prepared using solid state route. Samples pre-sintered at temperatures 700 °C for 2 hours in air. Then each sample was ground and polyvinyl alcohol (1.4 wt %) was mixed as a binder. The dried powder was pressed under a force of 1000 kg cm<sup>-1</sup> to form a disk of 10 mm diameter with 0.7 mm thickness. Finally the pellets were sintered at 1270 °C for 1 and 3 hour in air at heating and cooling rate of 6 °C min<sup>-1</sup>. Density was measured by geometrical method [14]. The mirror like polished samples was thermally etched for the microstructure analysis by SEM and the average grain size was determined by the grain boundary-crossing method. The disks of each sample were ground to make a fine powder for the photopyroelectric (PPE) spectroscopy and XRD analysis. Cu K<sub>α</sub> radiation with PANalytical (Philips) X'Pert Pro PW1830 was used for X-ray diffraction, and the XRD data were analyzed by using X'Pert High Score software for the identification of the crystalline phases.

Prior the PPE measurement, the fine powder sample was ground in deionised water and then a few drops of each mixture were dropped on the 1.5 cm<sup>2</sup> aluminium foil and dried in air to form a thin sample layer on the foil. The foil was placed in contact to polyvinylidene difluoride PE film sensor [15] using a very thin silver conductive grease. The measurement of PPE signal amplitude using the PPE spectrometer system to produce a PPE spectrum has been described elsewhere [16]. In the system, a light beam from 1 kW Xenon arc lamp (Oriel 6921) was mechanically chopped at 9 Hz for scanning wavelengths range of 300 to 800 nm. The true sample spectrum was obtained by normalisation with respect to the carbon black PPE spectrum. In determining the energy band-gap ( $E_g$ ), it was assumed that the fundamental absorption edge of doped ZnO is

due to the direct allowed transition. The optical absorption coefficient  $\beta$  varies with the excitation light energy  $h\nu$  [17] and is given by the expression,  $(\beta h\nu)^2 = C (h\nu - E_g)$  near the band-gap, where  $h\nu$  is the photon energy,  $C$  is the constant independent of photon energy, and  $E_g$  is the direct allowed band-gap. The PPE signal intensity  $\rho$  is directly proportional to  $\beta$ , hence  $(\rho h\nu)^2$  is related to  $h\nu$  linearly. From the plot of  $(\rho h\nu)^2$  versus  $h\nu$ , the value of  $E_g$  is obtained by extrapolating the linear fitted region that crosses photon energy axis.

## RESULTS AND DISCUSSION

Figure 1 shows all the samples have two phases, i.e. ZnO grains and intergranular layers. The intergranular layers are composed of TiO<sub>2</sub> (ref. code 01-089-4203) and appears as a very small peaks in the XRD pattern. A secondary phase spinel (Zn<sub>2</sub>TiO<sub>4</sub>, ref. code 01-073-0578) are very clear at higher TiO<sub>2</sub> doping level for the both sintering times. [18]

The density of the ceramics, Figure 2 (a), decreases from 94.3 and 93.0 % to 87.2 and 92.2 % of the theoretical density for 3 and 1 hour of sintering time, respectively. The decrease in the density for 1 hour sintering time is slow as compared with the 3 hour sintering time. This explains the ceramic density is not much affected with the increase of TiO<sub>2</sub> for 1 hour sintering time. It is much affected with the 3 hour sintering time at 1.7 mol %. This indicates that the pores are developed in the TiO<sub>2</sub> doped ceramic with high doping level and sintered at longer sintering time.

Grain size analysis, Figure 2 (b), shows that the grain size increases with the increase of sintering time from 1 to 3 hours. The grain size is about constant at 26.8, 52.4  $\mu\text{m}$  up to 1 mol % of TiO<sub>2</sub> and then decreases to 13.1, 31.4  $\mu\text{m}$  with the increase of the TiO<sub>2</sub> mol % for 1 and 3 hours of sintering time, respectively. The decrease in the grain size is due to the development of the sufficient amount of secondary phase Zn<sub>2</sub>TiO<sub>4</sub> (spinel) which inhibits the grain growth mechanism [18]. SEM micrographs, Figure 3, show that the grain boundaries and triple point junctions are well defined and are very clear. SEM micrographs show that the grains are elongated at lower doping of TiO<sub>2</sub> mol % of for 1 hour sintering time. At higher doping level of TiO<sub>2</sub> mol %, grains are more uniform but some small grains have been seen along with the big grains. EDAX analysis at the grain boundaries and at the surfaces of the grain shows the absence of titanium ions but some patches of titanium have been seen on the surface of the grains.

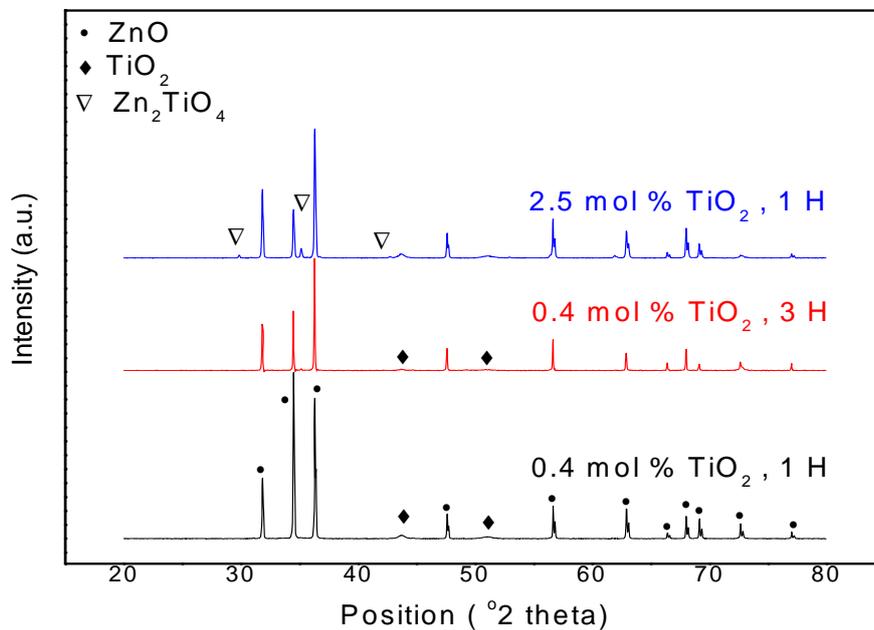
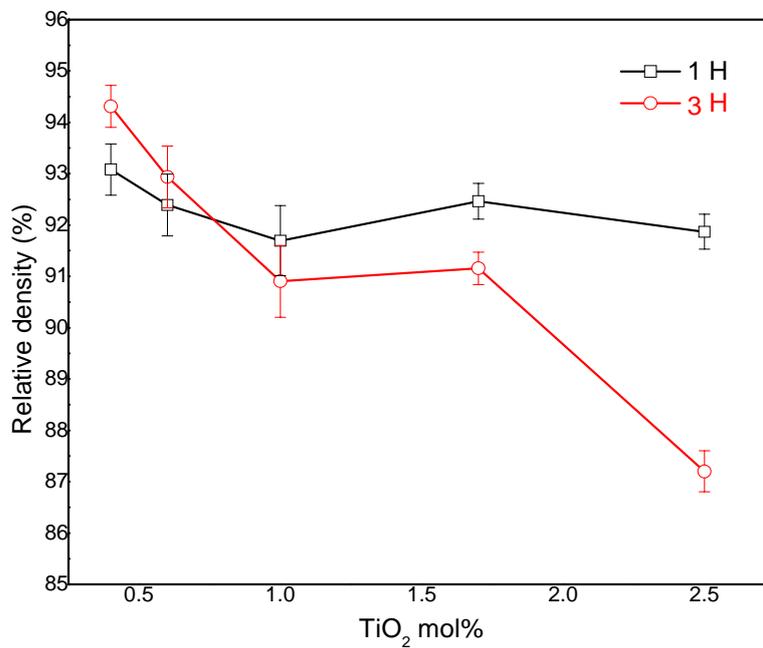
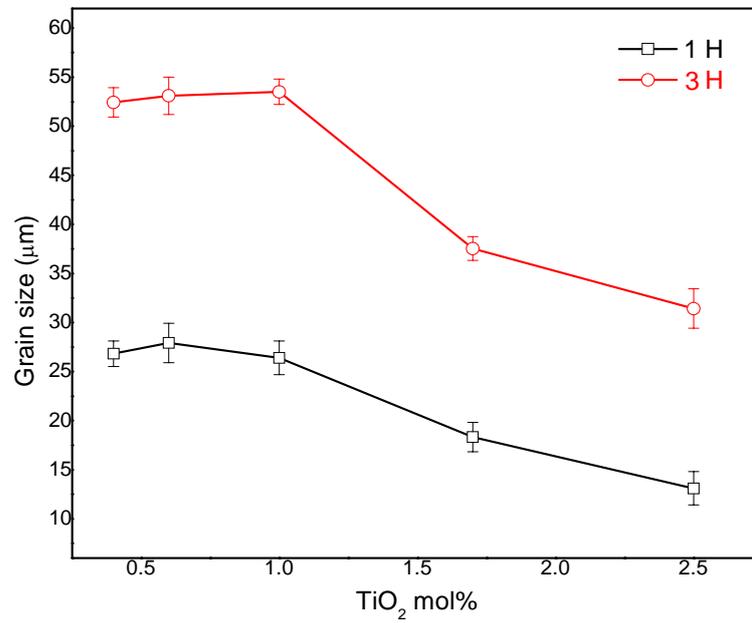


Figure 1: XRD analysis of TiO<sub>2</sub> doped ZnO for 1 and 3 hour sintering time.

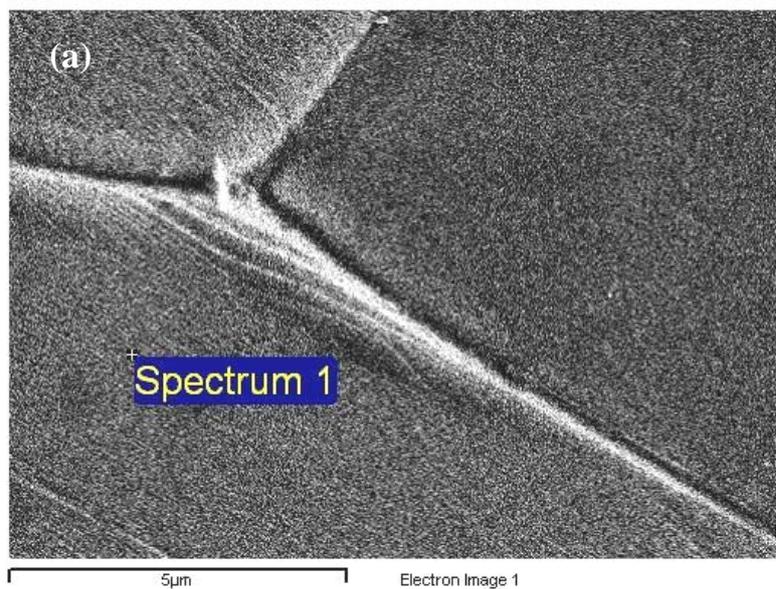


(a)



(b)

Figure 2: Density (a) and grain size (b) dependence on TiO<sub>2</sub> mol %, for 1 and 3 hour of sintering time.



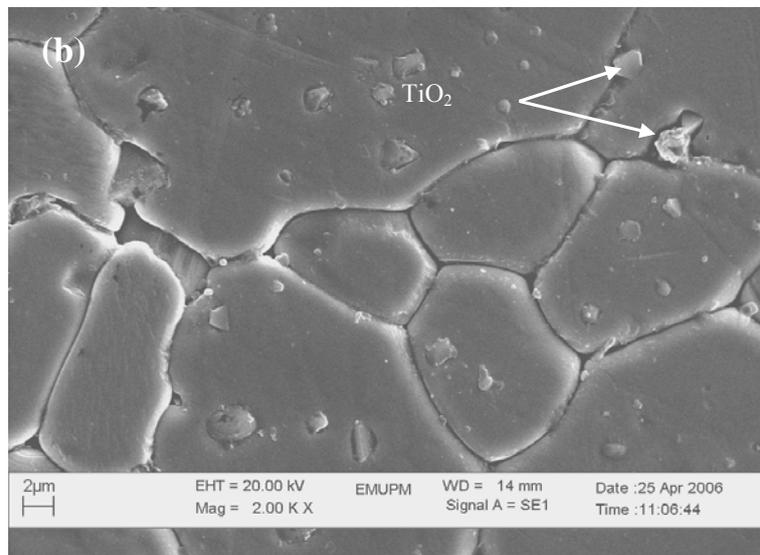
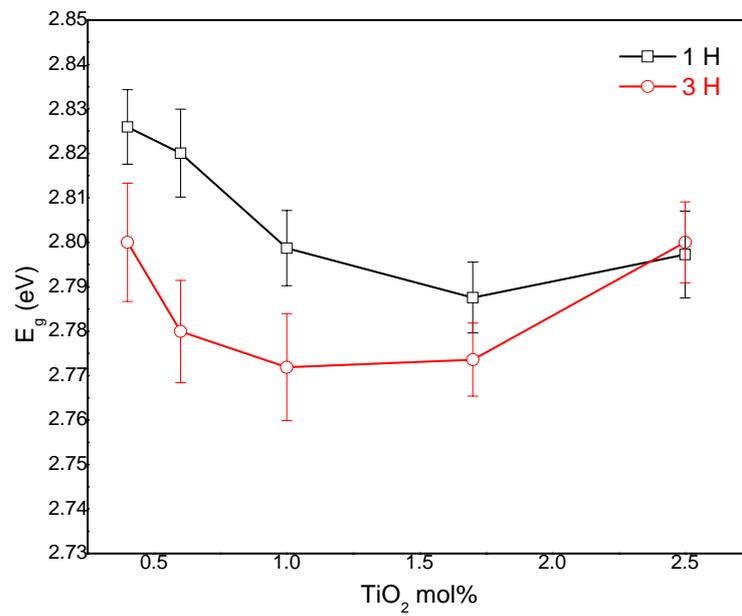
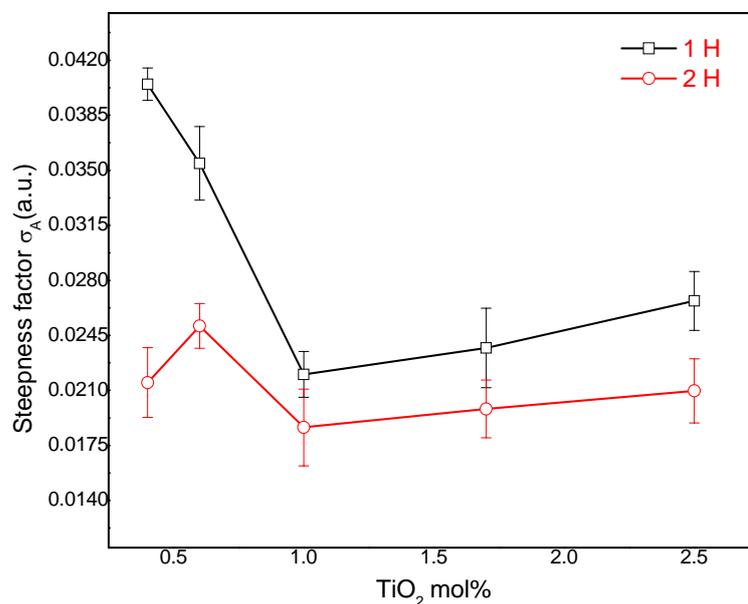


Figure 3: SEM micrograph at 1.7 mol% TiO<sub>2</sub> for 3 hour sintering time.



(a)



(b)

Figure 4:  $E_g$  dependence on TiO<sub>2</sub> mol % (left); Dependence of the steepness factor  $\sigma_A$  on TiO<sub>2</sub> mol % (right).

Energy band-gap dependence on the TiO<sub>2</sub> mol % is shown in Figure 4.  $E_g$  decreases from 3.2 eV (pure ZnO) 2.83 eV doping level 0.4 mol %, and further increase of TiO<sub>2</sub>, the value of  $E_g$  is decreased to 2.79 eV for 1 hour sintering time.  $E_g$  is decreased to 2.8 eV at 0.4 mol % TiO<sub>2</sub> and is further decreased to 2.77 eV at 1.7 mol % of TiO<sub>2</sub>. The decrease in  $E_g$  due to the doping of TiO<sub>2</sub> is about 0.04 eV. The value of  $E_g$  is lower for longer sintering time. This explains that the growth of interface states is higher for the longer sintering time. The steepness factor  $\sigma_A$  (in A-region), Figure 4, which characterizes the slop of exponential optical absorption, sharply decreases from 0.041 to a minimum value 0.022 with the increase of TiO<sub>2</sub> mol % for 1 hour sintering time. A slow decrease in  $\sigma_A$  from 0.021 to 0.020 is observed for 3 hour sintering time which indicates the increase in the PPE signal intensity. This means the structural disordering is increasing and the interface states are slightly increasing, hence correspondingly the value of  $E_g$  is slightly decreasing as shown in Figure 4.

## CONCLUSION

Doping of TiO<sub>2</sub> and sintering times are correlated with the PPE spectroscopy. A small decrease of about 0.04 eV is observed due to the growth of interface states. It was found that the band-gap is not much affected with the increase of TiO<sub>2</sub> mol %. EDAX

analysis shows that there is no segregation of TiO<sub>2</sub> at the grain boundaries and the substitution of titanium ions in the ZnO lattice is expected. Extra phase Zn<sub>2</sub>TiO<sub>4</sub> was found in the XRD analysis due to the TiO<sub>2</sub> which is responsible for the decrease of grain size especially after the 1 mol % of TiO<sub>2</sub>

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### REFERENCES

- [1]. T.K. Gupta, (1990); *J. Am. Ceram. Soc.* **73**(7), 1817-40.
- [2]. H.M. Lin, S.J. Tzeng, P.J. Hsiau, W.L. Tsai, (1998); *Nanostruct. Mater.* **12**, 465-77.
- [3]. D.C. Look, (2001); *Materials Science and Engineering B* **80**, 383-387.
- [4]. G. Neumann. (1981); Non-stoichiometry and defect structure, E. Kaldis, (ed) *Currents Topics in Material Science, Vol.7 (Zinc Oxide)*, North Holland, Amsterdam, 153.
- [5]. G.P. Mohanty and L.V. Azaroff, (1961); *J. Chem. Phys.* **35**(4), 1268.
- [6]. K.I. Hagemark and L.C. Chacka.(1975); *J. Solid State Chem.* **15**(3), 261.
- [7]. P.W. Li and K.I. Hagemark, (1975); *J. Solid state Chem.* **12** (3/4), 371.
- [8]. Jae Shi Choi and Chul Hyun Yo, (1976); *J. Phys. Chem. Solids*, **37**(12), 1149.
- [9]. David R. Clarke, (1999); *J. Am. Ceram. Soc.* **8**, 485-501.
- [10]. K. Eda, (1989); *IEEE Elect. Insul. Mag.* **5**, 28-41.
- [11]. R. Einzinger, (1979); *Appl. Surf. Sci.* **3**, 390-408.
- [12]. A. Minamide, M. Shimaguchi, Y. Tokunaga, (1998); *Jpn. J. Appl Phys.* **37**, 3144-47.
- [13]. Choon-Woo Nahm, (2003); *J. Eu. Ceram. Soc.* **23**, 1345-53.
- [14]. J.F. Wang, Wen-Bin Su, Hong-Cun Chen, Wen-Xin Wang, and Guo-Zhong Zang, (2005); *J. Am. Ceram. Soc.* **88**(2), 331-34.
- [15]. A.C. Tam and H. Coufal, (1983), *Appl. Phys. Lett.* **42**, 33-35.
- [16]. A. Mandelis, (1984); *Chem. Phys. Lett.* **108**, 388-92.
- [17]. T. Toyoda, H. Nakanishi, S. Endo, T. Irie, (1985); *J. Phys. D Appl. Phys.* **18**, 747-51.
- [18]. S. Bernik, N. Danue, A. Recnic, (2004); *J. Eu. Ceram. Soc.* **24**, 3703-8.