Effect of MnO$_2$ doping and temperature treatment on optical energy band gap properties in Zn-Bi-Ti-O varistor ceramics

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Abstract. In this study, the optical band-gap energy ($E_g$) was investigated with respect to MnO$_2$ and sintering temperatures on ZnO based varistor ceramics. $E_g$ of the ceramic $(99-x)$ mol% ZnO + 0.5 mol% Bi$_2$O$_3$ + 0.5 mol% TiO$_2$ + x MnO$_2$ where $x = 0, 0.2, 0.4, 0.6$ and $0.8$ mol%, were determined using UV-Vis spectrophotometer. The samples was prepared through solid-state route and sintered at the sintering temperature from 1110, 1140 and 1170 $^\circ$C for 45 and 90 min in open air. At no doping of MnO$_2$, the values of $E_g$ are $2.991 \pm 0.001$, $2.989 \pm 0.001$ eV for 45 and 90 min sintering time; respectively. $E_g$ was decreased to $2.192 \pm 0.001$ eV at 1140 $^\circ$C at 45 min sintering time. Similar result of $E_g$ was observed at longer heat treatment. Further addition of dopant causing the $E_g$ decreases rapidly to $2.099$ and $2.106 \pm 0.001$ eV at 45 and 90 min sintering time; respectively. XRD analysis indicates that there is hexagonal ZnO and secondary phases, Zn$_2$MnO$_4$, Bi$_4$Ti$_3$O$_{12}$ and Zn$_2$Ti$_3$O$_8$. The relative density of the sintered ceramics decreased or remain constant with the increase of MnO$_2$ concentration for 45 min sintering time, however, further prolong sintering time; the relative density decreases form 90.25 to 88.35%. This indicates the pores are increasing with the increase of heat treatment. The variation of sintering temperatures to the optical band gap energy of based ZnO varistor doped with MnO$_2$ due to the formation of interface states.

1. Introduction

Zinc oxide (ZnO) is used widely in paint, sunblock in cosmetics application and textile industries as well as in electronic industries [1-4]. In electronic industries, ZnO based varistor is enormously used as an electronic component in automobile electronics and also in semiconductor electronic. They are fabricated with different types of dopants such as Bi$_2$O$_3$, Co$_3$O$_4$, MnO$_2$, Sb$_2$O$_3$, TiO$_2$ and CaMnO$_3$ [5-11]. Its unique grain boundary feature is responsible for nonlinear current-voltage ($I-V$) characteristics of the device [2, 12] and thus, is used to protect electrical surges. $I-V$ studies have been extensively investigated for ZnO based varistor by previous researchers [7, 13] and it is necessary to investigate the electronic states of ceramic ZnO and the effect of doped impurities at different processing conditions. The characterization of the absorption spectrum in semiconductors leads to the determination of the optical band-gap energy [14, 15].
In this study, the investigation regarding the optical band gap energy and relationship with X-ray diffraction (XRD) findings of ZnO-Bi$_2$O$_3$-TiO$_2$ doped MnO$_2$ with different sintering temperatures of 1110, 1140 and 1170 °C for 45 and 90 min in air.

2. Materials & Method

All oxides precursors’ of 99.9% purity (Alfa Aesar) were used. The composition consists of (98-x) mol% ZnO + 0.5 mol% Bi$_2$O$_3$ + 0.5 mol% TiO$_2$ + x MnO$_2$ where x = 0, 0.2, 0.4, 0.6 and 0.8 mol%. The powder was ball milled for 24 h in deionized water. The slurry was dried at 70 °C using hot plate and continuously magnetically stirred to avoid the sedimentation of the heavy particle and pre-sintered at 800°C for two hours in open air with heating and cooling rate of 6 °C/min$^{-1}$. The pre-sintered mixture was pulverized using an agate mortar/pestle and after 1.75 wt.% Polyvinyl Alcohol binder addition, granulated by sieving 75 micron mesh screen. The mixture was then pressed into discs of 10 mm in diameter and 1 mm in thickness, each at a pressure of 2 ton/m$^2$. Finally, the discs were sintered at 1110, 1140 and 1170 °C in open air for 45 min sintering duration at heating and cooling rate of 2.66°C min$^{-1}$. The disk from each sample was ground for optical and XRD characterizations. The crystalline phases were identified by an XRD (PANalytical X’Pert Pro PW3040/60, Philips) with CuKα radiation and the data were analyzed, using X’Pert High Score software. According to Keskenler and co-researcher [16], structural disordering can be obtained by Urbach’s Rule for the optical absorption (exponential tail) [17]. The density was measured by the geometrical method taking the average of 10 discs [18, 19]. For the microstructure analysis, each of the disk samples was thermally etched at 150 °C in a tube furnace. The microstructure morphology of sintered discs was examined by Variable Pressure Scanning Electron Microscopy (VPSEM, Leo 1455). The average grain size (d) was determined by lineal intercept method [20], given by Equation 1:

$$d = 1.56 \frac{L}{MN}$$

where \(L\) is the random line length on the micrograph, \(M\) is the magnification of the micrograph and \(N\) is the number of the grain boundaries intercepted by lines. The UV-Vis spectrophotometer was used to measure the optical band-gap energy of the ceramics. The transmission signal was measured for the wavelength from 200 to 800 nm and then converted to absorption signal for further evaluation [21]. It was assumed that the fundamental absorption edge of the ceramics is due to the direct allowed transition [22]. The optical band-gap energy is given by Equation 2 [23]:

$$(A\nu)^2 = C(h\nu-E_g)$$

where \(A\) is the optical absorption coefficient, \(C\) is the constant independent of photon energy \((h\nu)\), and \(E_g\) is the direct allowed optical band-gap energy. From the plot of \((A\nu)^2\) versus \(h\nu\), Figure 1 the value of \(E_g\) is obtained by using Origin Pro 8.0 software within the linear fitted regions at \((A\nu)^2=0\).

3. Results and Discussion

The \(E_g\) of the ceramics, Figure 1, decreases from 3.199 eV (pure ZnO) to 2.991 and 2.989 eV for the 0 mol% of MnO$_2$ at 1140 °C at 45 and 90 min sintering time, respectively. These decrements, 0.208 and 0.210 eV is due to the growth of interface states produced by combined effect of 0.5 Bi$_2$O$_3$ and 0.5 TiO$_2$. As can be seen, prolonged heat treatment make the \(E_g\) decreases slightly about 0.02 eV. The slight decrease is due to further growth of the interface states with the longer of the sintering time. When the ceramic ZnO + 0.5 Bi$_2$O$_3$ + 0.5 TiO$_2$ are doped with 0.2 MnO$_2$ then its \(E_g\) suddenly decreases to a value of 2.192 eV at 1140 °C for the 45 min sintering time. Similar result of \(E_g\) also was observed at longer sintering time. Further addition of dopant concentration causing the \(E_g\) decreases rapidly to 2.099 and 2.106 eV at 45 and 90 min sintering time. A proper interpretation regarding this
decrement is due to the growth of the interface states due to the substitution or interstitial of Mn ions in the ZnO lattice as well as in the grain boundaries.

It is observed that steepness factor $\sigma_A$, Figure 2, decreases with the doping level of MnO$_2$ indicating the increase of structural disordering in the varistor ceramics. Thus, this structural disordering introduces the growth of interface states and as a consequence, the $E_g$ value decreases [23]. The steepness factor $\sigma_B$, Figure 2, decreases with the sintering temperatures indicating the increase in thermal energy of displacement [23], hence, increases the structural disordering at all sintering temperatures with slightly decrement of $E_g$ as compared to undoped varistor ceramics.

There are two phases in XRD patterns, Figure 3, which are ZnO (ICSD code: 067454) and secondary phases, Zn$_2$MnO$_4$ (ICSD code: 039196), Bi$_4$Ti$_3$O$_{12}$ (ref. code: 00-065-2527) and Zn$_2$Ti$_3$O$_8$ (ICSD code: 083525). They were observed at all concentration except Bi$_4$Ti$_3$O$_{12}$ only seen at 0.2 mol%. Above 0.2 mol%, a few peaks of extra phase Mn$_3$O$_4$ (ref. code: 00-001-1127) were observed.
The relative density, Figure 4, of the ceramic without MnO$_2$ increases from 91.92% up to 93.69% at 1140 °C and slightly decrease or constant at 1170 °C. Relative density decreases at longer sintering time. When dopant of MnO$_2$ is added in the ceramic the relative density decreases or remains constant with the increase of doping level at 45 min sintering time. However, further prolong sintering time; the relative density decreases from 90.25 to 88.35%. This indicates the pores are increasing with the increase of sintering time. It is also observed that the overall densi ty with the doping of MnO$_2$ at all sintering condition is low indicating that the MnO$_2$ lowering the densification manner. It is found that large as well as small grains coexists and can be seen in the SEM micrographs, Figure 5. The pores are clearly observed and many of them have been seen at higher sintering temperature and time, as an additional proof with relative density, Figure 4. Some patches of additives can be seen in the ceramics. As evidence, the EDX results were conducted, Figure 6, show that the Bi is segregated in the grain boundaries at all sintering temperatures. It was found also that Mn and Ti were present near the grain boundaries; hence, this indicates that these elements are substituted in the ZnO lattice [24].

![Figure 3 XRD patterns ZnO based varistor at 1140 °C for 45 min sintering time at different MnO$_2$ dopant concentration](image)

![Figure 4 Relative densities of (a) 45 min and (b) 90 min sintering time](image)
**Figure 5** SEM micrographs of sintered varistor ceramics: from left (45 min) and right (90 min) from up to below is 0.2 mol%, 0.4 mol%, 0.6 mol% and 0.8 mol% of MnO$_2$ dopant at 1140 °C sintering temperature

**Figure 6** EDX micrographs and spectra of varistor ceramics
4. Conclusion
The lowering optical band gap energy with increment of MnO$_2$ dopant concentration had clarified through steepness factor $\sigma_A$ and $\sigma_B$. These findings are associated with EDX results that show the segregation Bi$_2$O$_3$, TiO$_2$ and MnO$_2$ at grain boundaries and possibly substitution of Ti ion with Zn ion, which creates interface states within the forbidden regime.

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