

# *Properties and transformation phases of ZnO–Bi<sub>2</sub>O<sub>3</sub> binary varistors based on nanometric powders*

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**Abstract**— Because of its wide range of interesting applications including varistor devices, zinc oxide (ZnO) has been extensively studied by several researchers. Pure and 1%mol bismuth doped ZnO nanopowders have been synthesized by sol-gel method to study the effect of sintering temperature of phases  $\alpha$ ,  $\beta$  and  $\delta$  on the electrical varistors behavior. The used temperatures were: 650 °C, 730 °C, 800 °C and 900 °C. The investigations were made by XRD and SEM to determine the structural properties and the Bi intergranular phases. To connect these results to varistor effect, eclectic characteristics J (E) were plotted. Generally, a reasonable amount of Bi<sub>2</sub>O<sub>3</sub> is sufficient to improve the non-ohmic behavior of ZnO-Bi<sub>2</sub>O<sub>3</sub> binary varistors.

**Keywords**—Semiconductors, ZnO-Bi<sub>2</sub>O<sub>3</sub>,  $\alpha$ ,  $\beta$  -Bi phases, ZnO varistors.

## I. Introduction

Several varistors have been manufactured based on semiconductor materials [1], ZnO is one among the bests. Zinc oxide devices have good non-linear current-voltage characteristics and are therefore very suitable for the manufacture of good varistors [2]. The varistors, in general, are polycrystalline ceramics semiconductor devices, having a particular microstructure and composition [3]. Various additives have been incorporated to ZnO varistors, such as manganese, aluminium, Bismuth and cobalt [4-7] in order to improve the electrical behavior of the devices. Bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) has been widely used in this field [8]. M.H Oh et al. [9] reported that the introduction of bismuth oxide even in small amounts in ZnO improves varistor effect; the increase of the concentration of Bi leads to an increase of the threshold voltage. In addition, microstructural studies of Bi<sub>2</sub>O<sub>3</sub> doped ZnO sintering have shown that Bi<sub>2</sub>O<sub>3</sub> exists as a liquid phase. The presence of this liquid phase during the sintering of the varistors is important because it wets the grains of ZnO and thus improves the sintering [10]. Thus it is very important to study each phase appearing in this process, especially as a function of sintering temperature. C Nan et al [11] studied the different phases of binary system ZnO-Bi<sub>2</sub>O<sub>3</sub> varistor. They note that the monoclinic phase  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> is stable from ambient temperature up to 730°C, where it is transformed into  $\delta$ -Bi<sub>2</sub>O<sub>3</sub> according to the cooling process,  $\beta$ -Bi<sub>2</sub>O<sub>3</sub> liquid phase is obtained during cooling from phase  $\delta$ . This metastable phase can be theoretically observed in a temperature range of 650 °C to 330 °C [12]. The  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> phase is also obtained during the cooling of the  $\delta$  phase.  $\gamma$  is known as metastable polymorphs, resulting from the cooling from high sintering temperature and is then transferred to  $\alpha$  -Bi<sub>2</sub>O<sub>3</sub> at 500 °C. The role of Bi<sub>2</sub>O<sub>3</sub> is primarily to provide a medium for liquid phase sintering and improve the growth of ZnO grains [13]. Most Bi-doped ZnO varistors are generally prepared by liquid phase sintering of

ZnO powder or doped with other dopants according to the desired use [14].

The objective of this study is to synthesize ZnO nanopowders for varistor application doped by 1% mol Bi and sintered at different temperature by sol gel technique .

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## II. Materials and methods

Pure and 1mol% Bi doped ZnO were synthesized by soft chemistry method, the Sol-Gel route. First, zinc acetate Zn (CH<sub>3</sub>COO)<sub>2</sub>.2H<sub>2</sub>O and citric acid are dissolved in ethylene glycol in a molar ratio of 0.06. Then, calculated amounts of bismuth chloride using BiCl<sub>3</sub> are added to the solution to obtain the desired concentration (1mol% Bi). After that, some drops of monoethanolamine were added to stabilize the reaction mixture. The solution is then stirred at 130°C for 2 hours. The final solution is transparent and homogeneous. Finally, a very fine gray powder is obtained after a calcination in air at 500 °C with a rise and fall speed of 6 °C / min.

The compaction of the obtained powders of pure and Bi<sub>2</sub>O<sub>3</sub> doped ZnO was carried out using a hydrostatic mechanical

press. The obtained pellets have a cylindrical shape of dimensions: 13 mm in diameter and 2 mm in thickness. The sintering process is carried out in a tubular furnace at different temperature: 650 °C, 730 °C, 800 °C and 900 °C for 15 minutes. After sintering, the pellets change the color, and a great densification has been obtained. After this step, metallization electrode gold is deposited on both sides of the sintered pellets in order to do the electrical measurements tests.

### III. Results and Discussion

#### A. Structural properties

Figure 1 shows the XRD spectra of pure ZnO and 1% mol Bi varistors sintered at : 650°C, 730°C, 800°C and 900°C for 2θ ranging from 20° to 160°. These temperatures were chosen from the transformation phases diagram [16] as it is shown in (Tab.1). The spectra exhibit the presence of the würtzite structure for all samples. In addition, different phases were appeared for each sintering temperature, we note: ZnO phase, β-Bi<sub>2</sub>O<sub>3</sub> liquid phase, α-Bi<sub>2</sub>O<sub>3</sub>, and δ-Bi<sub>2</sub>O<sub>3</sub>.

To explain these observations, we can say that: the β-Bi<sub>2</sub>O<sub>3</sub> phase is formed by sintering the pellets at 650 °C for 15 min, whereas a phase transformation of the bismuth oxide occurs between the β phase and the α phase for annealing at 730 °C. Then, at a higher temperature, a cubic phase of the bismuth is formed; the β-Bi<sub>2</sub>O<sub>3</sub> phase is transformed into δ phase. The appearance of the β -Bi<sub>2</sub>O<sub>3</sub> phase in the ZnO-Bi<sub>2</sub>O<sub>3</sub> system again just after 900 °C is due to the cooling mode of the pellets out of equilibrium, or that Bi<sub>2</sub>O<sub>3</sub> forms a solid solution linked to a higher temperature treatment to stabilize the structure of β-Bi<sub>2</sub>O<sub>3</sub>. However, a difference in peak intensity was recorded, indicating that the sintered samples have a lower crystalline quality than pure one.

To calculate the grain size the Debye-Scherrer equation is used. It is valid up to 100 nm, above this value, the equation is not valid because of the internal line width of the diffractometer. As our powders are nanometric, the average crystalline size was calculated using this equation [17]:

$$D = K\lambda / \beta \cos\theta \quad (1)$$

Where D is the grain size, λ the X-ray wave length (λ=1.541838Å), β the full width at half-maximum (FWHM), θ is the Bragg angle and K is a constant (K = 0.9 for these ceramics).

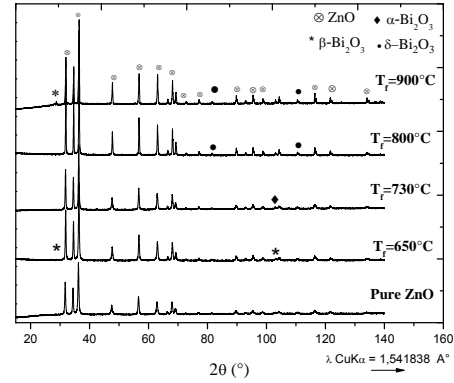


Figure 1. XRD patterns of pure and doped 1% mol Bi varistors sintered at different temperatures.

TABLE I. XRD AND SEM DATA OF DIFFERENT SINTERING TEMPERATURE ZNO VARISTORS PREPARED WITH 1% MOL BI NANOPOWDERS.

T (°C)	XRD analysis		
	Transformation phases	Grain size (nm)	Location (SEM)
650	β-Bi <sub>2</sub> O <sub>3</sub>	56.92	Grain
730	α-Bi <sub>2</sub> O <sub>3</sub>	58.92	Triple point
800	β-Bi <sub>2</sub> O <sub>3</sub>	75.20	Liquid phase
900	δ-Bi <sub>2</sub> O <sub>3</sub>	63.75	Grain

Figure 2 shows the variation of grain size as a function of temperature, which indicated that all the obtained varistors are nanometric. It can be said also that the grain size increases when the sintering temperature increases, it reaches a maximum value of 75.2 nm at 800 °C and then decreases for the higher temperatures . It should be noted that this size keeps always the nanometric dimension.

In our opinion, the only parameter that can explain this phenomenon is that the onset of the δ-Bi<sub>2</sub>O<sub>3</sub> phase begins just after 800 °C, which is responsible for the decrease in grain size. We can see that when we know that this phase is incorporated in the boundaries of the grains, causing the compression of these grains, or that the appearance of this phase slows the germination and consequently the growth of grains and by the same their size.

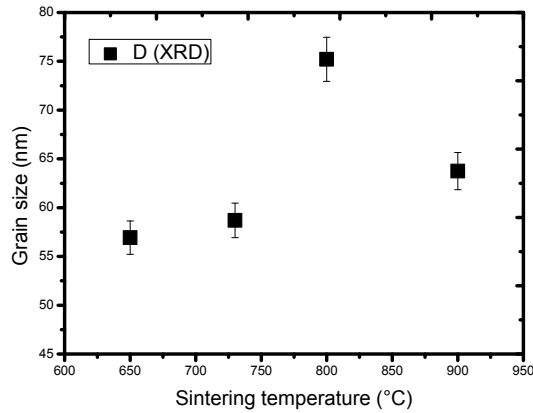


Figure 2. Variation of the grain size of Zn-1mol% Bi-O varistors synthesized from nanopowders annealed at different temperature.

### B. Microstructural properties

The microstructure of the sintered pellets was observed by scanning electron microscopy (SEM). The figure 3 shows SEM images of Bi<sub>2</sub>O<sub>3</sub> doped ZnO varistors sintered at different temperatures for 15 min. First of all, the images show that the particles are uniformly distributed and keep the same structure. Moreover, we confirm that the Bi-rich phase is responsible for an enhanced densification in the initial stage of sintering [18, 19, 20].

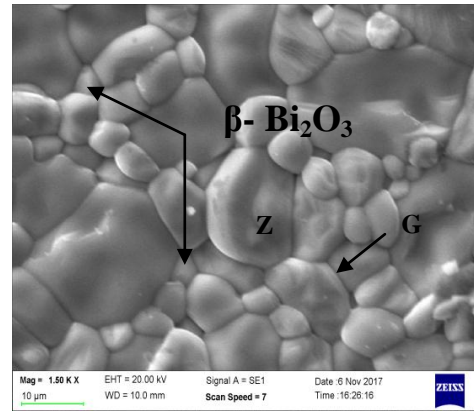
For each temperature many phases were observed in the microstructure of the sintered binary varistors Zn%1mol Bi-O obtained from nanopowders (Fig.3a, 3b, 3c and 3d). The rapid growth of the particles of these phases during the sintering and the cooling process at grain boundaries, as it is shown, has a desirable effect on the characteristics of the Schottky double barrier [21]. However, W. Onreabroy et al [22] had reported the formation of triple points between the ZnO matrix grains contained crystallites that could be identified to tetragonal β-Bi<sub>2</sub>O<sub>3</sub>, cubic γ-Bi<sub>2</sub>O<sub>3</sub> and δ-Bi<sub>2</sub>O<sub>3</sub>. We observe the same behavior in Fig.3.

The images in Fig. 3 also show us that the growth of ZnO grains is favored by Bi<sub>2</sub>O<sub>3</sub> doping. The distribution of different phases is well indicated in Fig. 4.

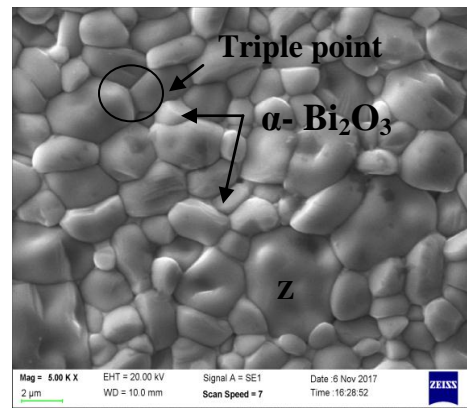
The relationship between the phase's transformation during the sintering of the varistors and the grain size is recommended in this study. It can be seen from Fig.3 that the appeared phases are uniformly distributed throughout the varistor for each temperature. From Fig. 4 we recorded the average particle size of the phases during the pellets sintering: 123 nm for the sample of 1%Bi sintered at 650 °C, 53 nm for 1% Bi sintered at 730 °C, 800 nm for 1%Bi sintered at 900 °C respectively.

By comparing Figs. 3 and 4 it is possible to deduce the effect of the phase transformation, due to the increase of the sintering temperature, on the grain size of the pellets: It is clearly visible that the small size of α- Bi<sub>2</sub>O<sub>3</sub> and β- Bi<sub>2</sub>O<sub>3</sub> are at the origin of the increase in the size of the grains and that,

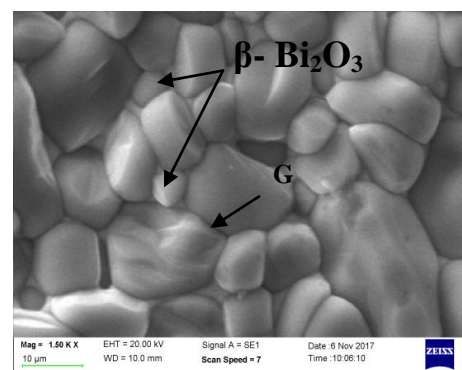
on the other hand, the phase β- Bi<sub>2</sub>O<sub>3</sub> at the temperature of 650 °C and the phase δ-Bi<sub>2</sub>O<sub>3</sub> at 900°C reduce the size, this confirms the explanation given previously, which stipulates that the phase larger size placed in the grain boundaries press these and reduce their size.



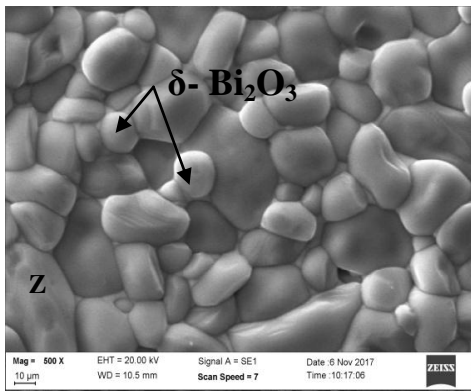
(a)



(b)



(c)



(d)

Figure 3. Phases identification SEM images of the sintered Zn%BiO varistors, (a) Pellet 1 sintered at 650 °C, (b) Pellet 2 sintered at 730 °C (c) Pellet 3 sintered at 800 °C and (d) Pellet 4 sintered at 900 °C (G: grain boundaries, Z: ZnO grain)

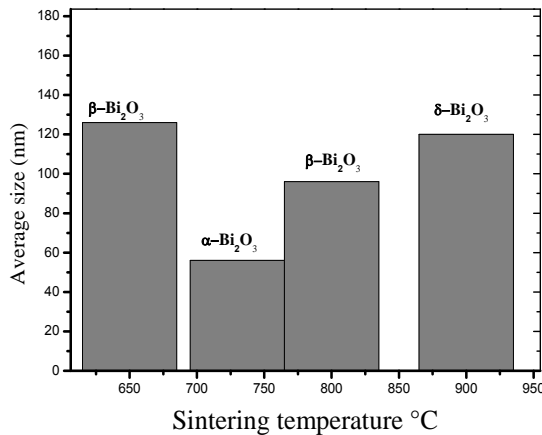


Figure 4. Phases distribution size of Bi<sub>2</sub>O<sub>3</sub> doped ZnO varistors as a function of sintering temperature.

### C. Optical properties

UV-visible absorption spectroscopy has been used to determine the band optical gap of Zn1% mol Bi-O sintered varistors in the range of 200-1000 nm. Usually the optical gap is determined by drawing the tangent to the absorption edge and take the value of its intersection with the energy axis.

This method leads to make errors because of imprecision in tracing the tangent, which can vary from author to another [23]. There is however a more precise method, it is the second derivative of the absorbance [24], where the peak is well indicated and giving the exact value of the optical gap. The spectra of the second derivatives of the absorbance are shown in Fig 5. So we can accurately determine the optical gap of each varistors, the values are listed in tab.2.

TABLE II OPTICAL GAP OF THE SINTERED VARISTORS

T (°C)	Optical Gap (eV)
650	3.35
730	4.33
800	4.36
900	4.36

The variation of the energy of the bandgap (E<sub>g</sub>) as a function of sintering temperature is shown in Fig 6, where, it is noted that E<sub>g</sub> exhibits a value close to pure ZnO at room temperature for the sintered varistor at 650 °C, then increases abruptly at 730 °C and gives a value of E<sub>g</sub> equal nearly to 4.33 eV and remain constant for the other temperatures.

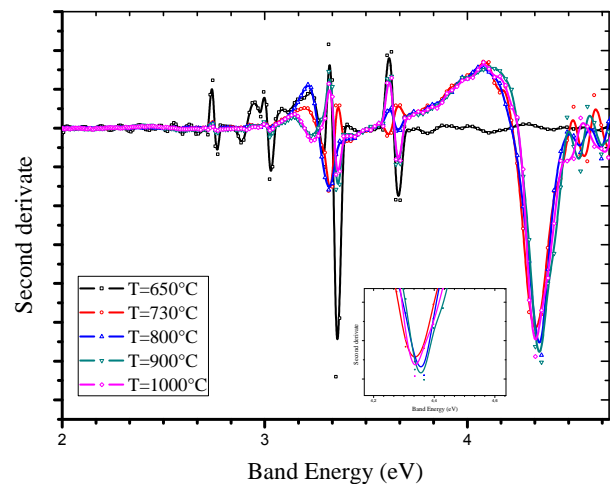


Figure 5. Second derivative of the absorbance of ZnO doped at 1% Bi<sub>2</sub>O<sub>3</sub> annealed at different sintering temperatures

It is therefore noted that the material becomes more insulating for the highest sintering temperatures that is to say that the material acquires a ceramic character, and more suitable for the manufacture of varistors. It is therefore recommended to choose sintering temperatures higher than 730 °C for the manufacture of better quality varistors.



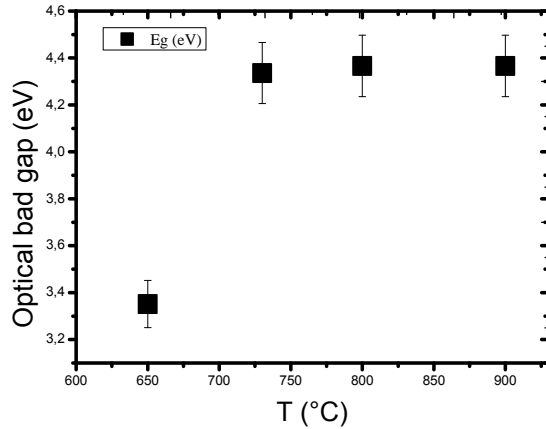


Figure 6. Variation of the band gap as a function of sintering temperature

#### D. Electrical measurements

The E-J curves of the sintered Bi<sub>2</sub>O<sub>3</sub>-ZnO varistors at different temperatures are presented in Fig.7. As we can see, all the sintered varistors show the non-linear electrical behavior. The current-voltage relation of a varistor is given by the following formula [22, 23]:

$$J = (E/C)^\alpha \quad (2)$$

Where J is the current density, E is the applied electric field; C is a constant corresponding to the resistance of ohmic resistor (nonlinear resistance),  $\alpha$  represents the nonlinear coefficient of the varistor. We plotted the current-voltage curves on a log-log scale from which the slope of the curve gives the exact value of  $\alpha$  [24]. The results of different electrical parameters of the samples in terms of the presence of ZnO grain boundaries are presented in Table 3. Since Schottky type grain boundary barriers exist in the sintered samples, the current density in the ohmic region of varistor is related to the electric field by the following equation [23]:

$$V_B = V_{gb}/D \quad (3)$$

The different values of the threshold voltage ( $V_B$ ) were deduced from the plotted curves of J (E). They allowed us to calculate the breakdown voltage per grain boundary ( $V_{gb}$ ), given by the equation above and listed in Tables 3, with D the average of grain sizes. An average value of 21 mV  $\pm$  0.3 mV is obtained. The leakage current density ( $J_L$ ) was determined as the current density at 0.75 percentage of breakdown voltage based on the E-J characteristics. The results obtained showed that the non-linearity coefficient increases with increasing sintering temperature from 1.63 for 650 °C to 12.5 for 730°C. On the other hand, the values of the threshold voltage varied between 360 V/cm and 701 V/cm. An investigation of the effects of microstructure and different types of grain interface on the measured values of  $V_B$  and  $\alpha$  has been reported by R. Einzinger [26].

According to the grain potential barriers  $V_{gb}$ , the values increase with increasing sintering temperature, they vary between 0.0114 V to 0.0218 V (Tab 3). However, it is important to note that the decrease in  $V_{gb}$  with the threshold voltage favors the use of the powders in nanoscale for the manufacture of varistors to protect devices against over voltages.

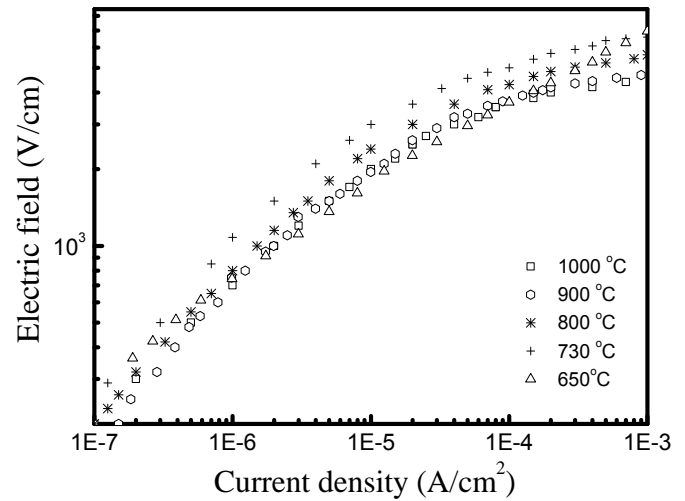


Figure 7. J (E) characteristics of ZnO-Bi<sub>2</sub>O<sub>3</sub> varistors as a function of sintering temperature.

TABLE III ELECTRICAL CHARACTERISTICS OF THE SINTERED VARISTORS

T (°C)	I(V) characteristics		
	Threshold Voltage V/cm	Nonlinearity coefficient	Leakage current A/cm <sup>2</sup>
650	360	1.63	0.25
730	701	12.5	0.30
800	580	10.25	0.52
900	450	10.02	0.6

#### Conclusion

Different sintering temperatures of pure and 1mol% Bi doped ZnO were synthesized successfully to manufacture varistor device by sol-gel route. XRD spectra confirm the wurtzite structure and the presence of many phases for each temperature with grain size varying from 56.92 to 75.20 nm. SEM images confirm the existence of nanoparticles with different shapes and structure. On the other hand the UV-visible spectra show that the material becomes more insulating for the highest temperature.

The eclectic characteristics J (E) of these varistors indicate a good non-ohmic behavior for all samples; threshold voltage  $V_B$  ranges between 360 to 701 V/Cm and the coefficient of non-linearity between 1.63 to 12.5 .

Bismuth oxide incorporation was found to be necessary in order to obtain good quality of varistor performance.

As it has been successfully reported in our work, microstructural evolution phases of the sintered samples can be efficiently control the electrical parameters on one hand and nano-sized pure and Bi-doped ZnO sintered binary varistors on the other hand.

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