*Journal of Metals, Materials and Minerals, Vol. 32, No. 3, pp. 27-31, 2022*

# Tailoring the structural and optical properties of zinc oxide with addition of bismuth oxide prepared by two step process

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**Received date:**
22 March 2022
**Revised date**
18 June 2022
**Accepted date:**
21 June 2022

**Keywords:**
Bismuth oxide;
Linear coefficient;
Solid state;
Precipitation;
Zinc oxide

**Abstract**

This study was done to investigate the impact of bismuth oxide ($Bi_2O_3$) composites on the zinc oxide (ZnO) properties for varistor applications. ZnO-$Bi_2O_3$ samples were prepared using a two-step process, precipitation, and solid-state method. $Bi_2O_3$ was added into ZnO at various concentrations (0, 0.5, 1.0 and 1.5 mol%). All samples were characterized using X-ray diffraction (XRD), Scanning electron microscope (SEM) and UV visible spectroscopy. XRD results have shown that the crystallite size of ZnO-$Bi_2O_3$ samples became smaller when $Bi_2O_3$ was added from 0.5 mol% to 1.0 mol%. However, the crystallite size of ZnO-$Bi_2O_3$ increased over 1.0 mol% of $Bi_2O_3$ concentration. The smallest particle and grain size of ZnO-$Bi_2O_3$ appeared when composite at 1.0 mol% concentration of $Bi_2O_3$. The homogeneity and smallest grain size might be suitable to be used for varistor application. The absorbance of ZnO-$Bi_2O_3$ decreased as the $Bi_2O_3$ concentration increased. Therefore, adding $Bi_2O_3$ at various concentrations into the ZnO host material can tailor its structural and optical properties.

## 1. Introduction

A varistor is a semiconducting ceramic device that protects the electrical and electronic devices from overvoltage transients. Varistor based ZnO has been used to protect electrical circuits because of its excellent nonlinear current voltage properties [1] as well as the nonlinear coefficient, (α) [2]. The value of α shows how quickly the shift from the high resistive to the low resistive state allows the remaining current to flow through the ground. ZnO based varistors have very close current (I) and voltage (V) characteristics to that of back-to-back zener diodes [3]. From the IV curve in the linear region, the nonlinearity coefficient can be determined. The nonlinearity coefficient of ZnO exist due to electronic phenomena occurring near the grain boundaries of ZnO materials [4].

Various methods have been used to synthesize low dimensional ZnO nanocrystal for varistor applications. Recently, the solid-state method is particularly attractive due to its simple, highly reproducible, suitable for mass production for commercial applications and capability of producing nanomaterials with adjustable grain sizes and controllable morphology which will affect the varistor properties [2,5]. Precipitation process was used in this study to synthesize ZnO powder in order to obtain a pure phase of the ZnO without impurities that can be observed from the XRD patterns and well crystallized ZnO powders also can be produced via this method [6]. The electrical properties of the ZnO based varistor added with different concentrations of bismuth oxide ($Bi_2O_3$) for varistor applications via solid state method also investigated. $Bi_2O_3$ a promising oxide material was added to ZnO material to improve the properties of nonlinear electrical and its structural properties. Therefore, to the best of our knowledge, investigating the different concentrations of $Bi_2O_3$ into ZnO will influence the structural and morphological properties of ZnO varistors and might increase the performance of a varistor application. Thus, by using a little concentration of $Bi_2O_3$ as additives in ZnO could barely be sufficient to coat the grains and will produce a continuous grain boundary. The electrical properties of the varistor depend on the size of the grain and the additives distribution. The ZnO varistor added to $Bi_2O_3$ concentration exhibited good ohmic behaviors and it was the most profit oriented varistors. The major aim of this study was to determine the effect of $Bi_2O_3$ on the structural and morphological properties of ZnO for varistor applications. Various characterization techniques were employed to study and discuss the structural, morphological, and optical properties of the ZnO-$Bi_2O_3$ structure.

## 2. Experimental

### 2.1 Preparation of ZnO by precipitation process

ZnO nanoparticles were synthesized by direct precipitation method using Zn $(NO_3)_2.6H_2O$ with 0.03 mol and 150 mL 0.05 mol·$L^{-1}$ of nitric acid ($HNO_3$) to get aqueous solution of transparent $Zn^{2+}$. The polyethylene glycol (PEG4000) was added as dispersant and the solution undergoing heating process in water bath at 80°C while stirring for 30 min. After that, 250 mL 4 mol·$L^{-1}$ of NaOH aqueous solution was immediately poured into the solution. The white precipitate

was produced after intense stirring for 2 h and the as produced was filtered by using vacuum drier. The precipitate was rinsed by using deionized water and alcohol for a few times. Lastly, to get the final white ZnO powder, the white precipitate was dried under 60°C in an oven for 6 h.

### 2.2 Preparation of ZnO with $Bi_2O_3$ by solid state process

The addition of bismuth oxide is according to the empirical formula [(100-X)%ZnO)+(X% $Bi_2O_3$)] mol%. The ZnO was blended with $Bi_2O_3$ by using dry milling at different concentrations of $Bi_2O_3$ (0, 0.5, 1.0 and 1.5 mol%) of $Bi_2O_3$. The sample was grinded for 10 min to guarantee homogeneity of the sample. Adequate polyvinyl alcohol (PVA) was added as a binder to the sample in the beaker to make the mixture become viscous. The mixture underwent a heating process on a hot plate and continued the stirring process by using a magnetic stirrer to obtain the powder form from the sample. The pre-sintering process was performed in the furnace for 2 h at 800°C. This process is important to extract the PVA content and also to promote grain growth. After that, the sample was pressed into a pellet with 10 mm diameter and 1 mm thickness at the pressure of 30 tons for 5 min for each pellet by using a hydraulic press. The pellets of each sample were underwent a sintering process for the second time at a fixed temperature of 1050°C for at least 2 h. Then all samples were characterized using scanning electron microscope (SEM), x-ray diffraction (XRD) and UV-visible absorption spectroscopy.

## 3. Results and discussion

### 3.1 SEM morphology

The samples of ZnO-$Bi_2O_3$ varistor were analyzed by SEM in order to examine the structure of the sample and to discover the effect of $Bi_2O_3$ on ZnO properties when added at various concentrations. The presence of the $Bi_2O_3$ additives in ZnO may influence the grain boundaries of ZnO based varistors which can be an increase in the current–voltage behavior. It is important to apprehend the impact of certain phase changes on ZnO and ZnO-$Bi_2O_3$ samples which have been sintered at 1050°C. The condition of the sintering process and the function of additives in ZnO was the major purpose to change the materials structures that affect the properties of the varistor. The SEM images of ZnO and ZnO-$Bi_2O_3$ at different concentrations of $Bi_2O_3$ are shown in Figure 1. All of the samples had a uniform grain distribution. Figure 1(a) indicates the existing grains for pure ZnO are very large and very thin grain boundaries, respectively. However, for samples in Figure 1 (b-d), the grains have grown significantly and are well connected and the grain boundaries between them are well defined. Based on Figure 1 (b-d), it is clearly shown the liquid phase was formed when $Bi_2O_3$ composited into ZnO. Literally, the bulk of Bi based particle diffuse rapidly and homogeneously through the ZnO grain junction. The formation of the bismuth phase increased the diffusion of the grain boundary and promoted grain growth [7]. It can be noted that the presence of a greater phase of bismuth increases varistor homogeneity. The lineal intercept technique was used to calculate the average grain size of all the samples by the Equation (1),

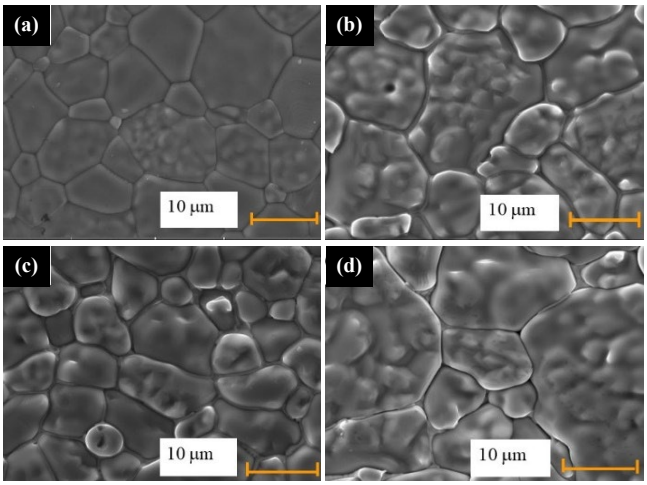


**Figure 1.** SEM images of pure ZnO and ZnO-$Bi_2O_3$ at various concentration of $Bi_2O_3$: (a) 0% $Bi_2O_3$, (b) 0.5% $Bi_2O_3$, (c) 1.0% $Bi_2O_3$, and (d) 1.5% $Bi_2O_3$ at 3.0 k magnification.

$$D = \frac{1.56\,L}{MN} \quad (1)$$

where L is the straight-line length that is randomly choosen on the SEM images, M is the magnification of SEM images and N represents the number of grain boundaries intercept by the line [8,9]. The average grain size for ZnO is 7.7 µm with standard deviation 1.5 µm. It was found that the average grain size decreased from 7.67 µm to 6.78 µm with standard from 1.4 µm to 0.8 µm when $Bi_2O_3$ was composited into ZnO from 0.5 mol% to 1.0 mol%, respectively. Further increasing of $Bi_2O_3$ concentration above 1.0 mol% resulted in the average grain size to increase again. The average grain size was reduced when $Bi_2O_3$ was composited into ZnO due to the existence of second phases at the grain boundaries that are shown in Figure 1(b) and Figure 1(c). However, compositing $Bi_2O_3$ into ZnO above 1.0 mol% concentration inhibited the grain growth and merging of grains that caused an increasing again of average grain size.

ZnO-$Bi_2O_3$ microstructures at 1.0 mol% concentration of $Bi_2O_3$ had the smallest scale of particle and grain size. Previous study shows that the decrease in grain and particle size will increase the breakdown voltage and enhance the electrical properties of the varistors [8]. Thus, the ZnO-$Bi_2O_3$ binary system enables the formation of liquid phase and grain growth which depend on the specific diffusion mechanisms of liquid phase sintering [10]. The forming of liquid phase enhanced the grain boundary diffusion resulting in wetting the grain boundary and promoted the grain growth [11]. The grain boundaries play a significant role in the development of electrical properties of a varistor [1]. The nonlinearity coefficient of ZnO is exists due to electronic phenomena occurring near the grain boundaries of ZnO materials [12,13].

### 3.2 X-ray diffraction analysis

XRD was used to determine whether the samples were in a crystalline or amorphous type structure. As shown in Figure 2, all strong peaks can be classified as the pure hexagonal phase of wurtzite-type ZnO, which has been identified with the reported data (JCPDS No.

01–075-0576) [11]. Based on the diffraction pattern of XRD result, all samples show multiple sharp peaks indicating that the ZnO-$Bi_2O_3$ varistor samples have good crystallinity [14]. The notable peaks labelled at 31.93°, 34.57°, 36.43°, 47.57°, 56.75°, 62.95°, 66.51°, 68.11°, and 69.35° correspond to the plane (100), (002), (101), (102), (110), (103), (200), (112), and (201) indicating the development of a phase of hexagonal zinc oxide [15]. Many secondary phases with small peaks were detected in the ceramics at all different concentrations of bismuth oxide and it was compared with the standard JCPDS file number 76-1730. The XRD patterns of all samples in Figure 2 show a few phases of $Bi_2O_3$ contents at 2θ were 25.55°, 27.95°, and 44.7° corresponding to (002), (120), and (223) crystal planes, respectively [16]. Figure 3 shows the peak of ZnO- $Bi_2O_3$ shifted towards larger angles with increasing of $Bi_2O_3$ concentration from 0.5 mol% to 1.5 mol%. The shift towards larger angles also reduced the ZnO phase lattice constant [17]. The size of crystallite was determined by using Scherrer formula Equation (2), and the value is represents in Table 1.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \qquad (2)$$

where D is crystallite size, λ is an X-ray wavelength which is λ=1.54 Å, $\beta$ is the broadening of the diffraction peak measured at half maximum (FWHM) in radians and $\theta$ is the angle of diffraction. It was found that the crystallite size decreased from 48.31 nm to 43.48 nm as the concentrations of $Bi_2O_3$ from 0.5 mol% to 1.0 mol%, respectively. However, the crystallite size increase when ZnO was composited with $Bi_2O_3$ at 1.5 mol% of concentrations. The crystallite size trend was matched to the average grain size obtained by using SEM micrograph. The diffraction angle of the ZnO phase increased as the $Bi_2O_3$ content increased. This implies that the interplanar spacings between the ZnO phases have shrunk [18].

## 3.2 UV-visible absorption spectroscopy

Figure 4 shows the absorbance of the samples decreases with increasing $Bi_2O_3$ content. The highest absorption peak at range 250 nm to 800 nm belongs to the ZnO microstructure without $Bi_2O_3$ content. On the other hand, ZnO microstructure with 1.0 mol% concentration of $Bi_2O_3$ content shows the smallest absorption peak at range 250 nm to 800 nm. The number, size, and morphology and surface microstructure or the effects of quantum confinement may affect the optical bandgap [19]. The sharp increase in absorption at wavelengths below 400 nm for all samples can be due to the optical bandgap absorption of ZnO [10]. The peak at wavelength above 390 nm is due to various defects in ZnO crystal structure, such as oxygen vacancies or impurities [20]. It can be observed that absorption is higher at short wavelength, and it can be assumed that energy starts to decrease when the wavelength is high. As reported by Mohammadi Aref *et al*, increase composited content into main host will make impurity level in energy gap nearly to conduction band [21]. They stated that their finding can be used as low voltage varistors with longer lifetime. Thus, increasing the concentration of $Bi_2O_3$ content to 1.0 mol% will make $Bi_2O_3$ impurity closer to conduction band in energy gap of ZnO and might be suitable to be used as a low voltage varistor with good stability.

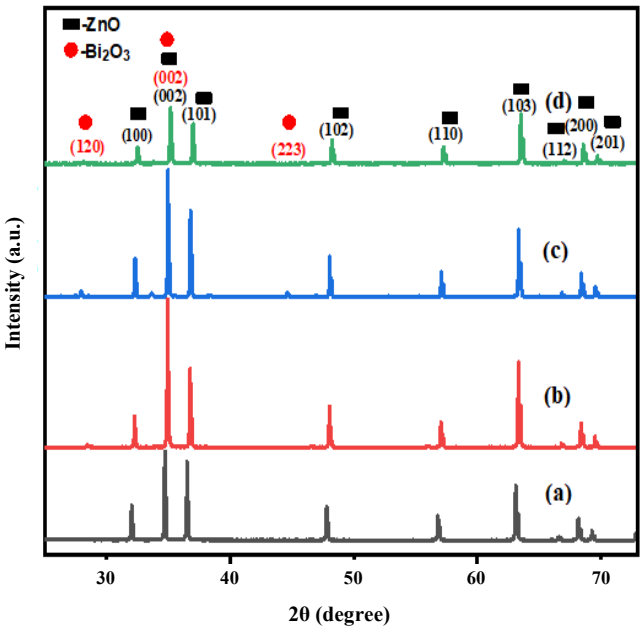


**Figure 2.** XRD patterns of pure ZnO and ZnO-$Bi_2O_3$ at various concentration of $Bi_2O_3$: (a) 0% $Bi_2O_3$, (b) 0.5% $Bi_2O_3$, (c) 1.0% $Bi_2O_3$ and (d) 1.5% $Bi_2O_3$.

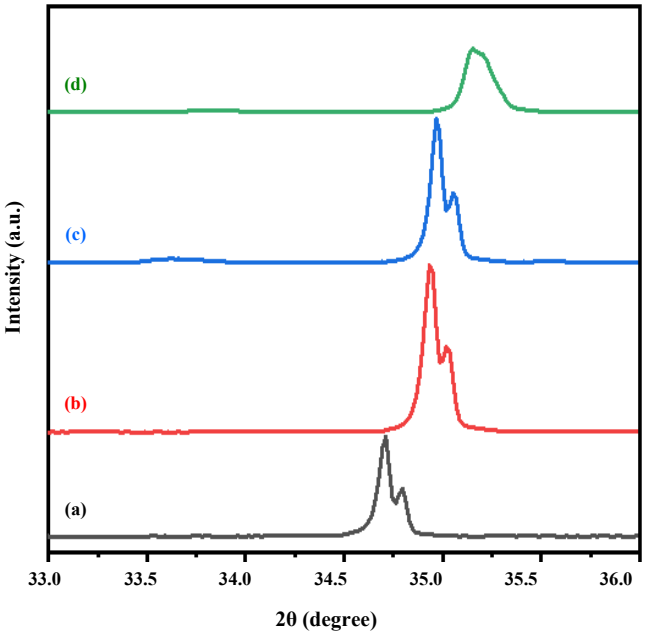


**Figure 1.** Enlarge image of diffraction peaks of ZnO and ZnO-$Bi_2O_3$ at various concentration of $Bi_2O_3$: (a) 0% $Bi_2O_3$, (b) 0.5% $Bi_2O_3$, (c) 1.0% $Bi_2O_3$, and (d) 1.5% $Bi_2O_3$ along (002) plane.

**Table 1.** The diffraction angles at (002) plane orientations, FWHM and crystallite size of ZnO-$Bi_2O_3$ structured.

| Type of sample (mol%) | 2$\theta$ (002) (°) | FWHM (°) | Crystallite size (nm) |
|---|---|---|---|
| 0.0 | 34.71 | 0.11 | 79.00 |
| 0.5 | 34.93 | 0.18 | 48.31 |
| 1.0 | 34.97 | 0.20 | 43.48 |
| 1.5 | 35.15 | 0.15 | 58.00 |

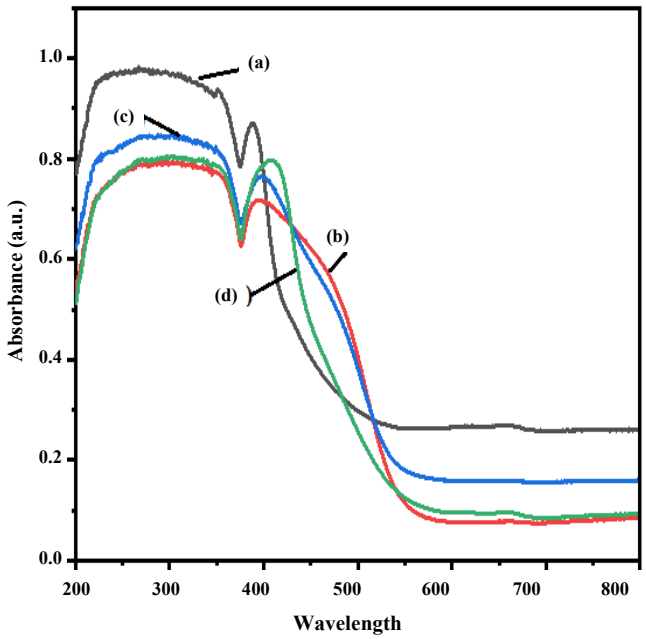


**Figure 4.** Absorbance peaks of ZnO and ZnO-$Bi_2O_3$ at various concentration of $Bi_2O_3$: (a) 0% $Bi_2O_3$, (b) 0.5% $Bi_2O_3$, (c) 1.0% $Bi_2O_3$, and (d) 1.5% $Bi_2O_3$.

## 4. Conclusions

The ZnO-$Bi_2O_3$ sample at different concentrations has been successfully prepared by two step precipitation and solid-state process. SEM image shows ZnO composited with 1.0 mol% concentration of $Bi_2O_3$ has the smallest average grain size. XRD spectrum of (002) plane shifted towards a larger angle when $Bi_2O_3$ was composited into ZnO. The smallest crystallite size is shown when 1.0 mol% concentration of $Bi_2O_3$ was composited into ZnO. UV-vis result shows the lowest absorption occurred for ZnO sample that was composited at 1.0 mol% concentration of $Bi_2O_3$ content. These findings indicate that the addition of $Bi_2O_3$ will affect the structural and optical properties of ZnO based varistors. Based on this finding it might be suitable to be used as varistor applications.

## Acknowledgements

The financial support of this project (FRGS 600-IRMI/FRGS 5/3 (264/2019) received from the Ministry of Education is highly appreciated. We would like also to express our infinite gratitude to the Research Management Institute (RMI) of UiTM and Faculty of Applied Sciences of UiTM for their support.

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