# RESEARCH ARTICLE

## MICROSTRUCTURAL PROPERTIES OF BISMUTH OXIDE DOPED ZINC OXIDE RECOVERED FROM SPENT ZINC CARBON BATTERY

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| ARTICLE INFO | ABSTRACT |
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| | This study describes the preparation of ZnO based varistors by sintering a mixture of ZnO powders with small quantities of bismuth oxide at a relatively high temperature. We also investigate the influence of Bismuth oxide addition on the microstructure of zinc oxide based varistors. The ceramic microstructure was characterised by measuring density, using SEM, X-ray diffraction and EDS. Bismuth oxide doping resulted in liquid phase sintering, rapid densification and grain growth. In this study ZnO powder was prepared from zinc recovered from spent zinc carbon battery. Use of recycled zinc from waste has made the study important from both economical and environmental point of view. |

## INTRODUCTION

A varistor is a type of resistor with a significantly non-ohmic current-voltage characteristic. The most famous type of varistor is ZnO varistor. Varistors are a zinc oxide composition that has the ability to change its electrical resistance depending on the applied voltage. Varistors consists of ceramic blocks of zinc oxide that have been sintered along with small quantities of other metals such that there are defined grain boundaries between crystals. The varistor is connected from the circuit to an earth connection. If a voltage spike occurs, the varistor conducts the excess voltage to earth. Varistors were developed around 30 years ago, and still represent the most recent significant new use for zinc oxide. They have become more and more important during the past four decades due to their highly non-linear electrical characteristics and their large energy absorption capacity. Zinc Oxide intrinsically has this exceptional current-voltage characteristic but may not be able to produce varistor effect without dopants. Although commercial varistors may have as many as 15 different additive oxides making it difficult to estimate functions of each individual dopant, we can concentrate only on $Bi_2O_3$ in this discussion keeping the foregoing prerequisites for varistor functionality in mind. Zinc oxide (ZnO) and ZnO-modified semiconductor ceramics have been two of the most promissory varistor systems, due to their exceptional qualities as solid state switches (Y.G.Wang *et al.*, 2000; L.M. Levison and H.R.Philipp, 1986; R. Einzinger, 1987).

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It is well known that bismuth oxide ($Bi_2O_3$) is the key to provide ZnO ceramic with a colossal nonlinear current-voltage response (J Wong, 1980). This happens because a $Bi_2O_3$ liquid phase emerges during the sintering process, improving the densification process and enhancing the grain growth. (J Wong, 1980). However, the impact of the bismuth content in the varistor electrical response is not clear yet. It is well known that bismuth ($Bi^{3+}$) is segregated to the grain boundaries during the sintering process (Y.G.Wang, *et al.* 2000; D.R.Clarke 1999; .H.R.Philipp, 1989; J.M. Carlsson *et al.*, 2002; J.L. Baptista & P.Q. Mantas 2000) contributing to the interface state density, which originates the double Schottky barrier (G. Blatter &F.Greuter 1986; N.Yamaoka *et al.*, 1983) . Several authors have studied the $Bi_2O_3$ losses during the sintering process founding that final the bismuth content differ of the initial one, depending on sintering temperature and sintering time (J.Wong,1980; D.R.Clarke, 1999; A.C. Caballero *et al.*, 2000). The effect of Bismuth Oxide content on the sintering of ZnO was also studied by Kim et al (J. Kim *et al.*, 1989) showing that a small amount of $Bi_2O_3$ in ZnO (($\leq$0.1 mol%) retards the densification but an amount higher than 0.5mol% promotes it. The effect was attributed to the grain boundary mobility which increases by liquid formation. ZnO grains make up the bulk of the varistor. Pure ZnO was studied by Wong (J. Wong, 1975). It was found that sintering pure ZnO at 700°C for 1 hour produced a highly porous ceramic. However this high porosity pellet did not show the non-ohmic property. The grain size of ZnO grain increases with increasing sintering temperature. From the work of Asokan *et al* (T. Asokan *et al.*, 1987), the grain size increased from about 3 μm to about 20μm as the sintering temperature

increased from 900°C to 1300°C. Bi$_2$O$_3$ has the melting point at 825°C thus during sintering procedure, a liquid phase is formed. The liquid phase is accommodated by initial porosity between the ZnO grains. In this study, ZnO based varistors are formed by sintering a mixture of ZnO powders with small quantities of bismuth oxide at a relatively high temperature. Microstructural studies show that, the bismuth-rich phase can mostly be found at intergranular layers leading to the nonlinear current-voltage characteristics (K. Eda, 1978) These properties are considered to originate at the grain boundaries. Here we investigate the influence of Bismuth oxide addition on the microstructure of zinc oxide based varistors.

## EXPERIMENTAL

***Preparation of batch:*** At first the powders with right proportions were thoroughly mixed and grinded with mortar pestle to obtain a homogenous mixture powder. Then powders were mixed with 2% polyvinyl alcohol (PVA) to form a paste. Before compaction PVA solution was mixed as binder with the powder to provide some strength for subsequent handling. Then the powder was compacted into disc shaped pellets (0.8 g each) by uniaxial compaction procedure. The green compacts were then sintered at 950°C and 1000°C for 60 minutes. Two precursor oxide powder samples were prepared by mixing specific (weight %) compositions of ZnO and Bi$_2$O$_3$ : pure ZnO and (99%) ZnO + (1%) Bi$_2$O$_3$ were prepared.

***Characterization techniques:*** The samples were characterized by XRD technique using X-ray diffractometer of model: D8 ADVANCE. Identification of phases was carried out using Bruker D-8 Advance, employing CuKα radiation wavelength, λ= 1.54 A○ and a graphite monochromator with a current of 40 mA and a voltage of 40 mV was used to evaluate the composite specimen. The diffraction intensity was in the range of 12° to 45° of 2θ (Bragg angle), and the scanning speed was 2°/min. The data was collected on the 2 θ range from 20° C to 90C°.
A JSM-6490LA (JEOL) scanning electron microscope was employed for the morphological, microstructure and grain size distribution characterization. The average grain sizes were measured from the SEM images.

## RESULTS AND DISCUSSIONS

### Density

It has been observed that bulk density increases with Bi$_2$O$_3$ content. As sintering temperature increases, thus, at 950°C and 1000°C, a significant change in the rate of densification is observed. It can be argued that, during the sintering processes, temperature control is an important parameter in achieving grain growth and density compacts. This was evident in the average values calculated for each composition at these two temperatures (Table-1). Density increases rapidly from undoped ZnO to doped ZnO (1% Bi$_2$O$_3$ was added) .This fact might be associated with the presence of a Bi$_2$O$_3$ liquid phase. It is known that the enhance densification and grain growth, independently of the partial bismuth oxide volatilization (N.Yamaoka *et al*, 1983), is caused by the Bi$_2$O$_3$ melting at 835 °C (A.C. Caballero *et al*., 2000).The presence of Bismuth creates a liquid phase that allows mass transfer between the grains, leading to a more densified microstructure as the temperature is increased.

**Table 1. Average values of the densification**

| Composition | Temperature | Density before sintering (g/cm$^3$) | Density after sintering (g/cm$^3$) |
|---|---|---|---|
| ZnO (100%) | 950 °C | 2.1943 | 3.843 |
| | 1000 °C | 2.1943 | 3.899 |
| ZnO (99%) + | 950 °C | 2.6071 | 4.141 |
| Bi$_2$O$_3$ (1%) | 1000 °C | 2.1879 | 4.153 |

### XRD Analysis

ZnO materials become a varistor by addition of substitutional ions, densification by liquid-phase (i.e. sintering with a Bi$_2$O$_3$ -rich liquid phase) and segregation of large ions to the grain boundaries (Y. Ohbuchi *et al*., 2002). In many cases, this substitution result in material structural changes .The XRD patterns of super imposed form for zinc oxide which is undoped, at 950° C and 1000°C are shown in figure 1. .It shows that the structure of undoped zinc oxide is polycrystal with hexagonal wurtzite structure and all of diffraction peaks match with that of zinc oxide. . From XRD indicated that the zincite crystalline phase was successfully formed, did not indicate any other crystal phase formation. Figure 2 shows the superimposed XRD pattern form of sample containing ZnO 99% and 1% Bi$_2$O$_3$ at 950° C and 1000°C. All main peaks could be indexed as ZnO (JCPDS #75-0576) with the planes (100), (002), (101), (102), (110), (103), (200), (112) and (201).A very small peak of α-Bi$_2$O$_3$ (JCPDS #29-0236) was also detected. The major peaks belong to a zincite phase with very small traces of secondary peaks. The intensities of these minor peaks are too low to accurately determine their corresponding phases. Again from all the XRD patterns it was seen that with increasing sintering temperature, the intensity peaks become sharper i.e. crystallinity increases with increasing sintering temperature.
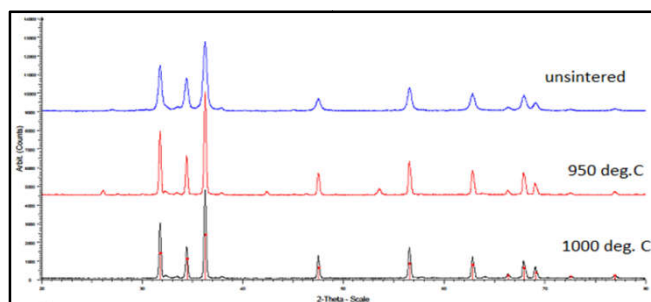


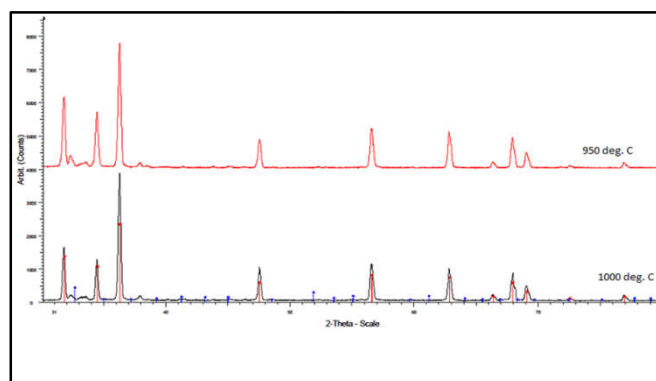**Figure 1. XRD pattern of undoped zinc oxide at different temperatures**



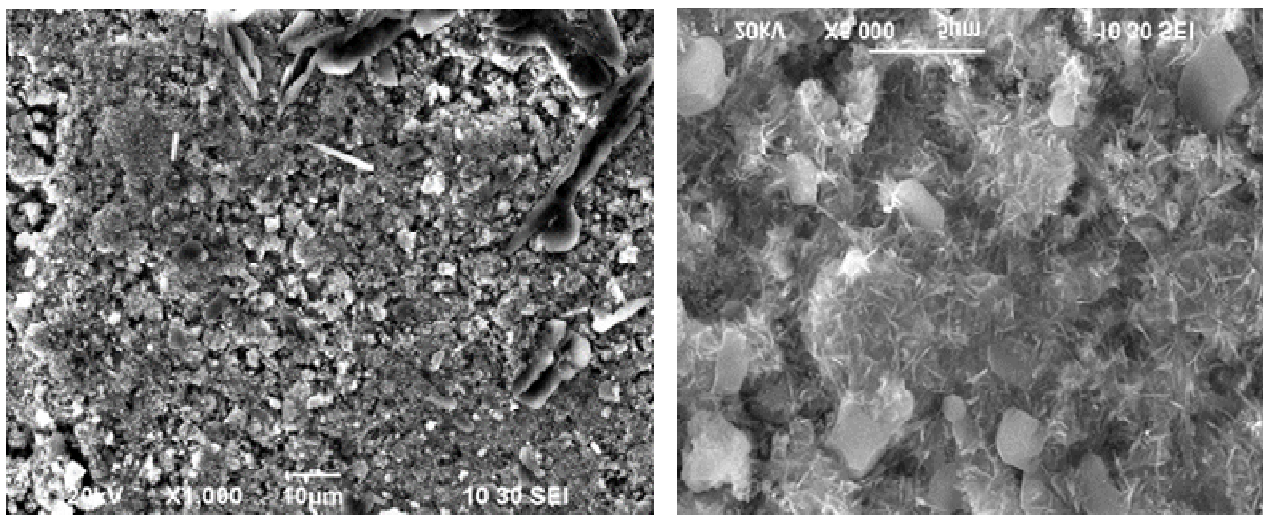**Figure 2. XRD pattern of bismuth oxide (1%) doped zinc oxide at different temperatures**

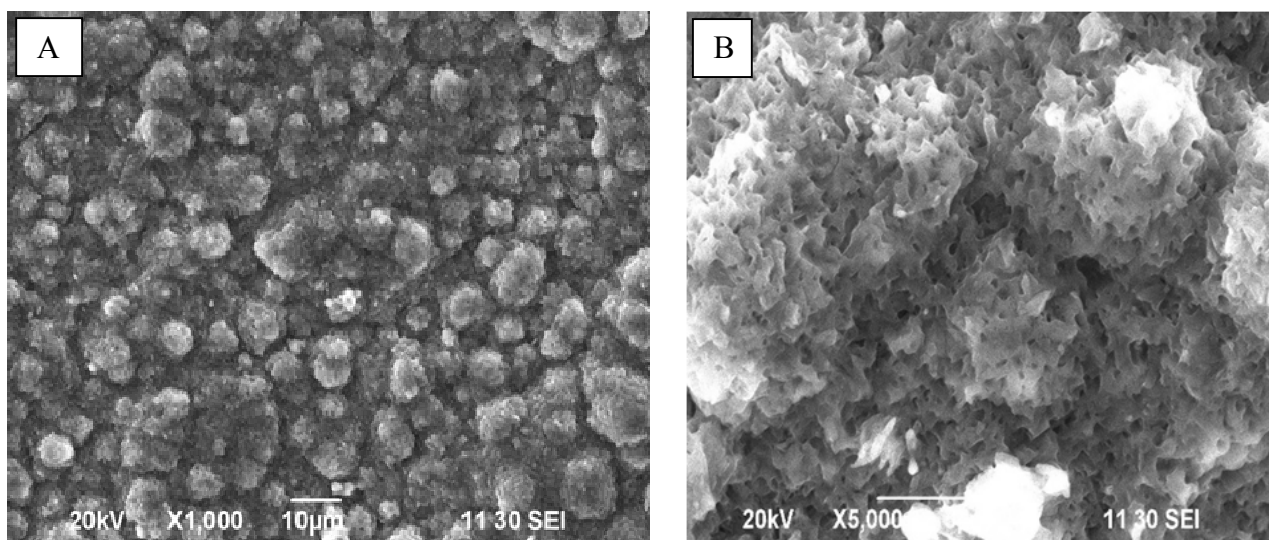**Figure 3. SEM images of unsintered zinc oxide (100%)**



**Figure 4.The SEM image of sintered zinc oxide (100%) at (A) 950°C (B) 1000°C**
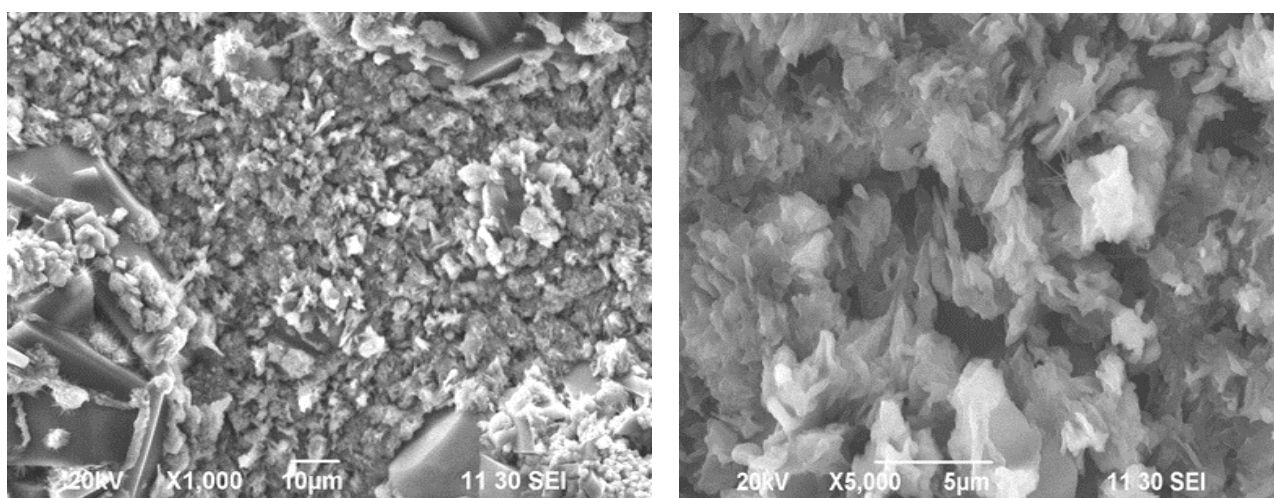


**Figure 5. The SEM image of unsintered bismuth oxide (1%) doped zinc oxide**

### *SEM Analysis*

Size and morphology of undoped and bismuth oxide doped zinc oxide were observed by SEM. Figure 3 shows the microstructure of unsintered zinc oxide.

When zinc oxide was sintered at 950°C for 1 hr. an intermediate densification stage was observed in Figure 4(a), characterized by the presence of interconnected pores. The rate of densification also increased when the temperature was increased to 1000ºC.
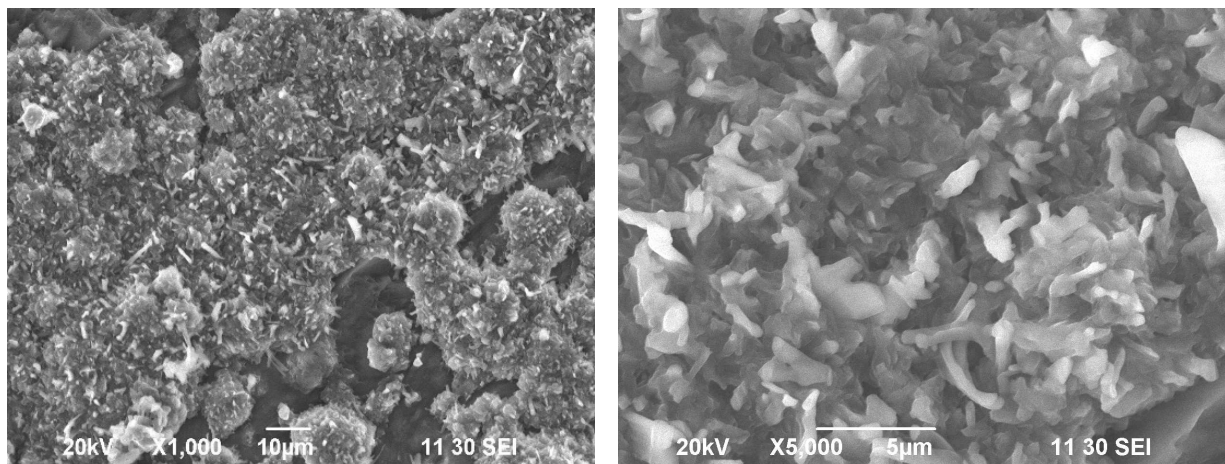
**Figure 6. The SEM image of sintered bismuth oxide (1%) doped zinc oxide at (a) 950°C (b) 1000°C**
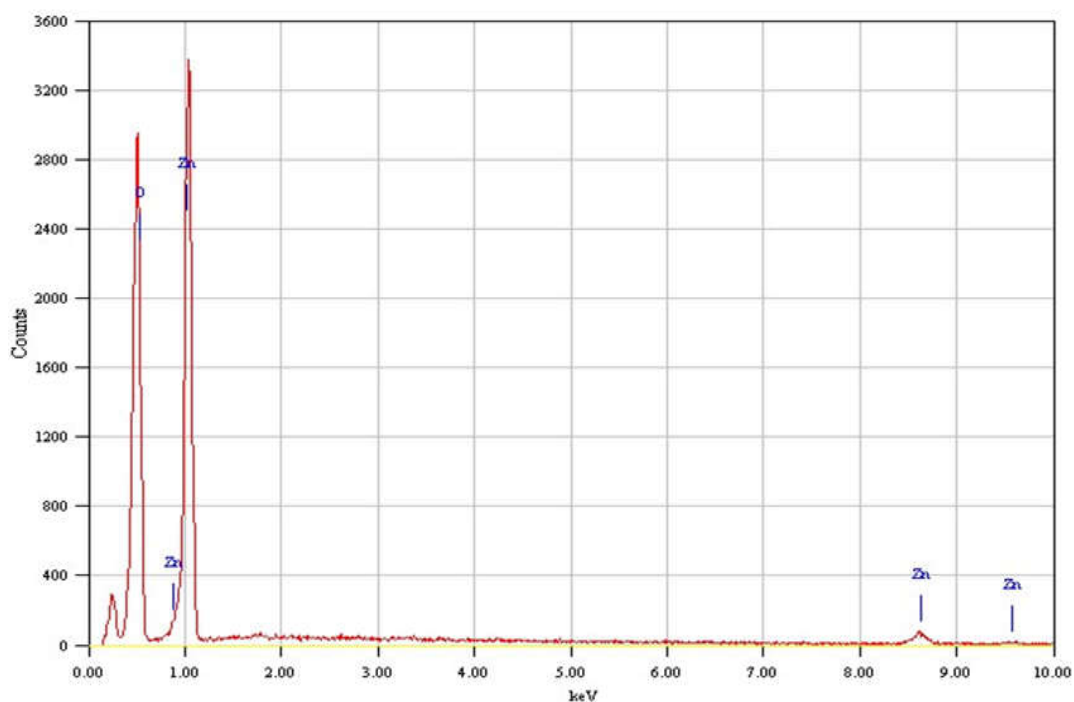


**Figure 7. The EDX spectra of zinc oxide sintered at 1000°C**

A further much densified microstructure would result if the temperature were to be raised further SEM images of undoped and Bi-doped ZnO ceramic samples are shown in Figure 4 and Figure 5. Homogeneous structure and low porosity are observed in all the samples. Grain size is also analysed, observing a grain growth as bismuth content increase. This indicates that the increase of the bismuth content in the zinc oxide samples somehow favours the cationic inter-diffusion and the mass transport processes during the sintering process. It is well known that the generality of bismuth-doped ZnO varistors have been prepared by liquid phase sintering process (J. Kim *et al.*,1989). For that reason, the microstructural changes observed in the samples could be associated with a typical ceramic liquid-phase sintering event ( J. Kim *et al.*, 1989; J. Wong 1975; T. Asokan *et al.*, 1987; K. Eda, 1978). Considering both, the eutectic point of the ZnO–Bi$_2$O$_3$ system at 835 °C and the samples sintering process at 900 ºC, it is obvious that microstructural changes (i.e., grain size improvement) are caused by the liquid phase formation process.

On the other hand, figure 5 and figure 6 show the formation of needles in the surface of the ZnO sample. This fact is associated with a superficial formation of a Bi-rich second phase, undetected by XRD but revealed by Energy Dispersive Spectroscopy (EDS) analysis.

**EDX Analysis**

The EDX spectra of zinc oxide and bismuth oxide (1%) doped zinc oxide sintered at 1000 °C were shown in Figure 7 and 8. The analysis yielded the quantitative composition of the major elements Zn and O. The EDX spectra of zinc oxide showed the elemental composition of Zn and O (Figure 7). Figure 8 shows the EDX spectra for the bismuth oxide doped zinc oxide. As expected the peaks ensures the existence of Bi. The spectrum contained three peaks, which were assigned to Zn, O, and Bi. The EDX analysis suggests that Zn, O and Bi are the main constituents in the doped zinc oxide.
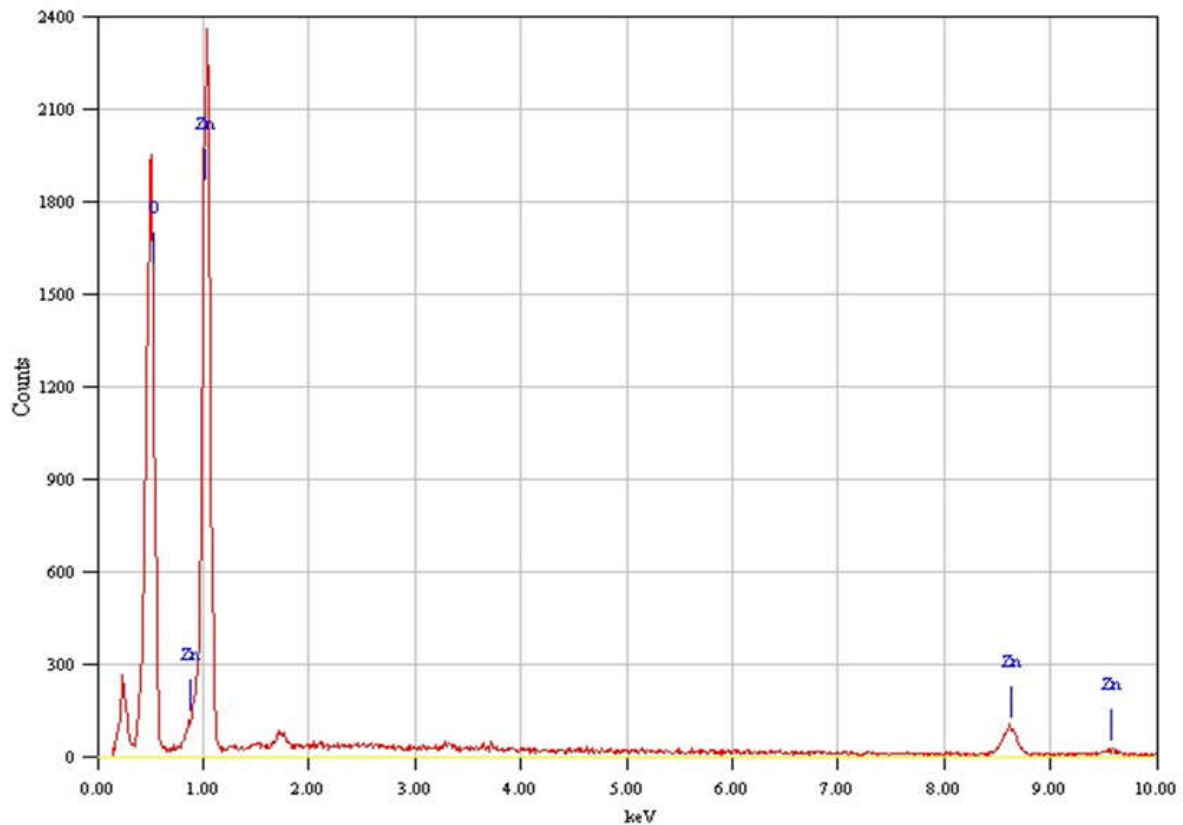
**Figure 8. The EDX spectra of bismuth oxide (1%) doped zinc oxide sintered at 1000°C**

## Conclusions

Undoped and bismuth oxide doped zinc oxide samples were prepared. Bismuth oxide was doped with zinc oxide which was recovered as zinc from spent zinc carbon battery. The influence of $Bi_2O_3$ addition on the microstructure was systematically investigated. It is observed that with increasing $Bi_2O_3$ content and sintering temperature, a significant change in the rate of densification is observed .Densification was accompanied by significant grain coarsening. The XRD result show that the phase of crystallite formed for ZnO in all the samples .The presence of $Bi_2O_3$ phase could not be detected properly by XRD measurement because of very small amount of dopant. The presence of $Bi_2O_3$ was measured using EDX. From SEM analysis homogeneous structure and low porosity are observed in all samples. All the results show that the prepared samples show similar microstructural characteristics as standard sample of bismuth oxide doped zinc oxide varistor.

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