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ELECTRICAL CHARACTERISATION AND MICROSTRUCTURE OF METAL OXIDE-DOPED ZnO VARISTORS

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ABSTRACT

Zinc oxide ceramic varistors were realized by doping ZnO with small quantities of MnO_2 and PbO. The preparation technique of Direct Mixing of Constituent Phases (DMCP) was used. The samples were pelletized at a pressure of $1.24 X 10^3$ N/cm^2 and sintered in ambient atmosphere at a temperature of 850°C for a period of 36hours. They were characterized by measuring the current-voltage response to evaluate the non-ohmic behaviour. Breakdown threshold voltages of $2.02 X 10^3$ V/m and $4.80 X 10^3$ V/cm were recorded at currents 1.05 μA/cm^2 and 1.20μA/cm^2 respectively. Microstructural analyses were carried out using x-ray diffraction and scanning electron microscopy techniques. The XRD spectra revealed the formation of structures and polymorphs of the additives in the sample while the SEM micrographs revealed the sizes, types and distribution of grains in the matrix. The grain sizes for the respective sample types were obtained as 1.621 μm and 1.020 μm. The microstructural analysis gave good correlation with the electrical response of the varistor samples.

Keywords: *Ceramic varistors, electrical characteristics, threshold voltage, SEM micrographs, x-ray diffraction spectra.*

1.0 INTRODUCTION

The miniaturization of electronic devices (Yin-Pin *et al.*, 1996) occasion their operation on low power consumption which makes them sensitive to the inconsistencies and fluctuations associated with power sources. The switching of circuits during normal operation or maintenance gives rise to surges which are generally unavoidable. Also power transient in the form of dips or spikes often occurring in ac power lines may arise from component failure or induction from neighbouring electrical devices.

To safeguard against the foregoing, several methods of protection are applicable but a more reliable and efficient way is by the use of zinc oxide ceramic varistors. These are polycrystalline materials comprising of zinc oxide grains and oxides of other metals, exhibiting outstanding non-linearity in their current-voltage characteristics (Clarke, 1999) .The varistors significantly control the appearance of spikes and function as surge absorbers and arresters, thereby offering protection to electronic devices by limiting the applied voltages to that which is not harmful to the protected circuit, at the characteristic threshold of breakdown. The Figures 1(a) and 1(b) illustrate the normal and varistor-protected states of the circuit while Figure 1(c) represents the equivalent circuit representation of a varistor. The energy absorption capacity, accompanied by no significant rise in temperature is another striking stability characteristic of Zinc oxide varistors which make them more widely used (Levinsky and Phillip, 1986).

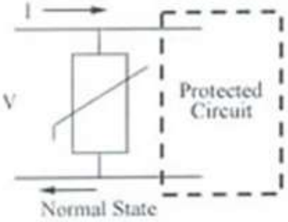

Figure 1a

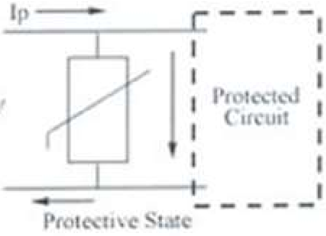

Figure 1b

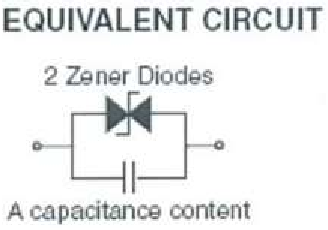

Figure 1c

The high non-linearity at ohmic breakdown has been reported to be due to a back to back Schottky barrier across the grain boundary (Levine 1975). Shengtao (*et al.*, 2002) showed that the inter-granular layers at the grain boundary constitutes the double schottky barriers along the grain boundary with native defects in zinc ZnO forming localized defect states. This was corroborated by Nahm (2009). Mahan *et al.* (1979) also proposed that the high nonlinearity in the breakdown region was generated by majority carrier creation in the schottky barrier region. Consequently small grains would enhance high breakdown strength. The bonds between sintered ZnO particles at the interfaces are highly resistive while the resistivity is lower in the grains than at the boundary layers. Conductivity thus increases significantly as the threshold voltage is exceeded, giving rise to the breakdown or non-linear characteristics.

ZnO varistors are fabricated by sintering ZnO powder (a ceramic material) containing various minor additives. By virtue of their ceramic nature they can be fabricated into a variety of sizes and systems. The additives are generally of two classes - the varistor forming oxides such as the oxides of cobalt and Bismuth (Matsuoka, 1971; Greuter and Blatter, 1990), and the 3d transition metal oxides which significantly improve the non-ohmic behavior. However, high volatility and reactivity of bismuth oxide at high sintering temperatures coupled with the requirement of many additives to obtain high non-linearity and electrical stability constitute major drawbacks.

We then investigate in this work, the performance of tri-component varistors with just two additives, MnO_2 and PbO, by studying their microstructural features, which determine their microscopic electrical behaviour. This is with a view to enhancing microstructural control for the optimization of the varistor behavior.

2.0 MATERIALS AND METHODS

Few techniques are possible for the realization of varistors, including diffusion (Bi-Shiou, Chiout *et al.*, 1989), Sol-gel method (Reddy *et al.,* 1999), direct mixing of constituent phases (DMP) (Brankovi *et al.*, 2007) and Ball-bill method (Peiteado *et al.*, 2007). Of these the DMCP technique is most suitable for the preparation of bulk-type varistors with precisely defined structures. Each phase is prepared separately and the final varistor is formed by sintering the powder mixture of constituent phases. The sintering process largely determines the varistor characteristics as it provides the mechanism for the formation of barriers against electrical conduction at the ZnO/ZnO interfaces.

2.1 Sample preparation

For this work, pure samples of zinc oxide were weighed, using a digital balance of sensitivity 0.0001 g in the relative proportions indicated as follows:

Samples type A: 95% wt ZnO, 3% wt MnO_2, 2% wt PbO
Sample Type B: 95% wt ZnO, 2% wt MnO_2, 3% wt PbO

The phases were prepared such that the proportion of one of the dopants is higher than the other in each sample type.

The respective constituents for each sample type were thoroughly ground and mixed in a mortar to ensure homogeneity. Each mixture was entirely scooped into a mould and pelletized using carver hydraulic unit with a load of 6 tonnes applied for about three minutes to allow proper compression. They were subsequently sintered for 36 hours at a temperature of 850°C using an open ended furnace which was preheated to 180°C before inserting the samples. The oven delivered heat at the rate of 5°C/min and was later left to cool to about 50°C.

2.2 Sample Characterization

The Samples were first characterized by measuring the current-voltage response at room temperature. For this purpose samples A1 and B1 were provided with electrical leads by attaching conductors on both faces of the pelletized discs using silver paste and were allowed to dry in ambient atmosphere and tested for ohmic contact. A Keithley 2636A multimeter within a Guassian cage was used.

For Samples A2 and B2, Xray diffraction analysis was carried out using a K_α - line at 1.5418A from a Radicon MD10 diffract meter in the detection angle range between 16°C and 72°C for the crystal phase detection.

Scanning electron microscopy (SEM) was used to obtain highly magnified images from samples A3 and B3 with a CARL ZEISS SEM machine, model EVO MA10

3.0 RESULTS AND DISCUSSION

The current - voltage (E - J) characteristics for samples A and B are presented in Figures 2a and 2b. The shapes of the curves indicate a sharp degree of non-linearity and the sharper the change in slope of the curve, the better the varistor behaviour.

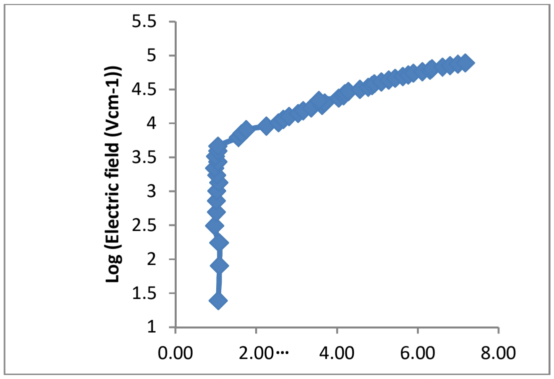

Figure 2a: current-voltage characteristics for 95% ZnO, 3% MnO_2, 2% PbO varistor.

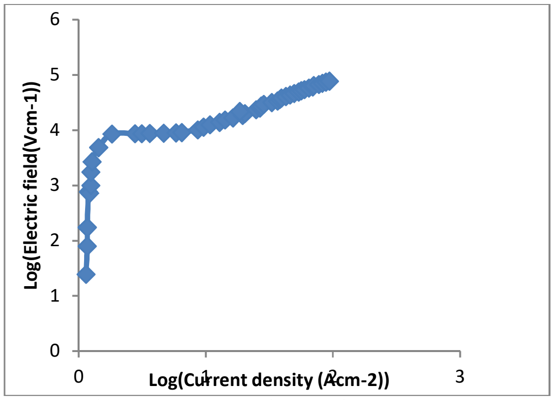

Figure 2b: Current – voltage characteristics for 95% ZnO, 2% MnO_2, 3% PbO varistor.

The curves exhibit a remarkable transition from ohmic behaviour at low voltages to non-ohmic behaviour at the breakdown region. Here conductivity is grain-controlled and is more marked in sample A (Figure 2a) with a higher % MnO_2. This is consistent with the finding of Han *et. al.* (2002) that the presence of Mn induces the oxidation of zinc ion interstitials at the grain boundary causing the better non- linear behaviour. The threshold voltages of non-linearity for Samples A and B are found as 2.02×10^3 V/m at current 1.05 $\mu A/cm^2$ and 4.80×10^3

V/m at current 1.20 μA/cm^2 from figures 2a and 2b respectively. A final regime of high current ohmic region is reached where conductivity is grain boundary controlled. A better varistor behaviour is obtained with the higher concentration of MnO_2.

Figures 3a and 3b present the x-ray diffraction spectra of samples A2 and B2 respectively. These feature the phases present in the sample .The different phases correspond to the diffraction peaks as indicated in the XRD spectra. In Figure 3a, the spectum shows that the higher concentration of MnO_2 give rise to more prominence in the crystal phases, which would have enhanced the better varistor behaviour is obtained in sample A with a higher % MnO_2 as indicated by the current-voltage characteristics.

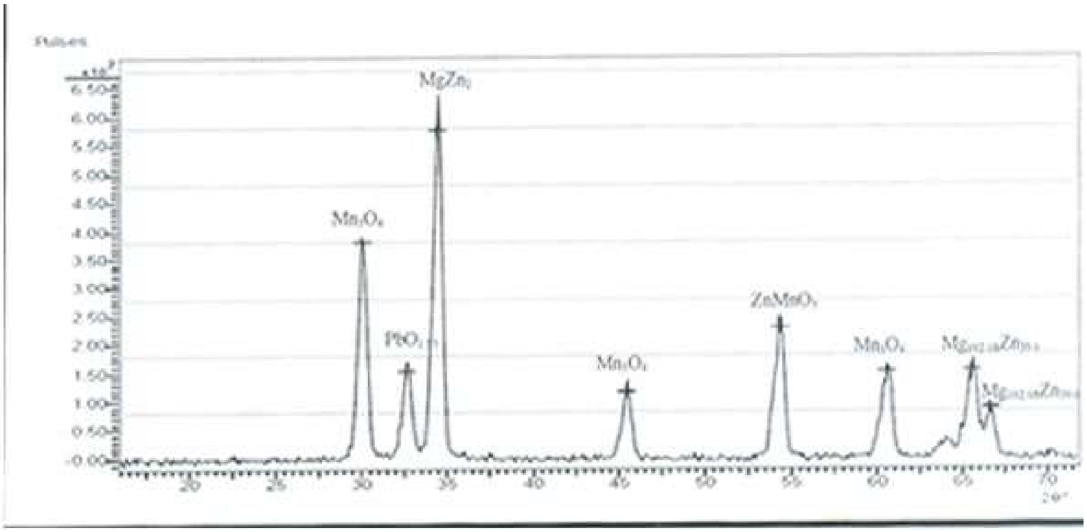

Figure 3a: XRD Spectrum of Sample A

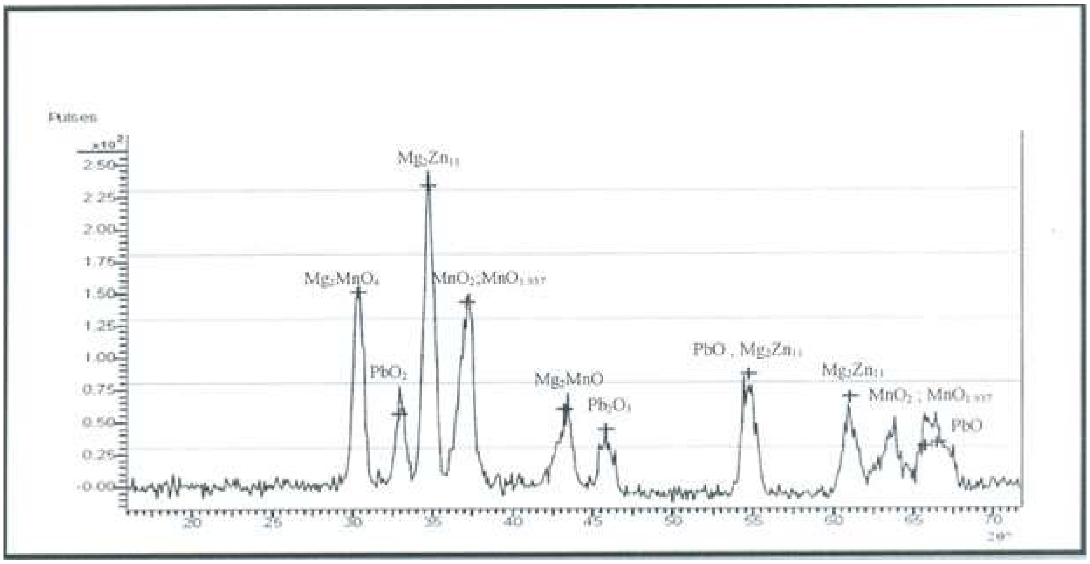

Figure 3b: XRD Spectrum of Sample B

This is consistent with the finding of Han *et al* (2002) that the presence of Mn induces the oxidation of Zn ion interstitials at the grain boundary causing the better non-linear behaviour. The formation of polymorphs of the additives such as Mn_3O_4 and $PbO_{1.55}$ and other secondary phases are also indicated. Figure 3b which has a higher proportion of PbO additive also features the polymorphs Pb_2O_3 (monoclinic) and PbO_2. The Presence of magnesium as secondary phases (Mg_2MnO_4, (cubic) and Mg_2Zn_{11} (cubic) in the samples got introduced inadvertently in the course of fabrication. These could have prevented grain growth.

Figure 4a represents the micrograph of sample A showing a large number of grains and different crystal phases with an average particle size of 1.621 μm while figure 4b for sample B shows smaller grains with average particle size of 1.02 μm and pores homogeneously distributed in the sample.

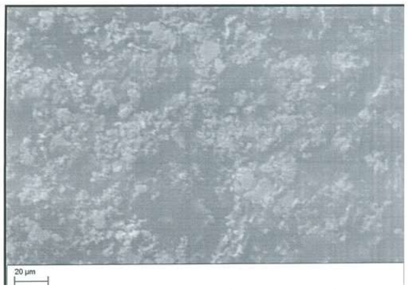

Figure 4a: SEM micrograph of Sample A (500x)

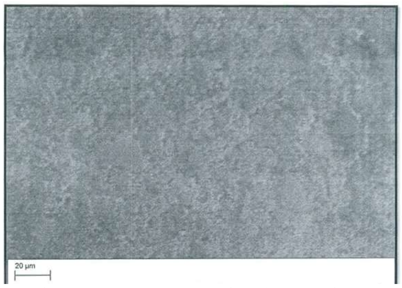

Figure 4b: SEM micrograph of Sample B (500x)

Few slightly larger grains are randomly distributed in the matrix and this can inhibit grain growth by pinning down the movement of grain boundaries (Peiteado *et al.*, 2005).The higher grain size in figure 4a decreases breakdown field due to increased donor concentration (Nahm, 2012) The pores influence the characteristic breakdown voltage by increasing its value and gives rise to low densification, which can decrease the number of conduction paths leading to electrical instability. A post-sintering annealing of the sample at a slightly higher temperature could improve the varistor behavior.

4.0 CONCLUSION

The microstructural and electrical characterization of ZnO - PbO - MnO_2 ceramic varistors were investigated at different %wt composition of PbO_2 and MnO_2 in two different sample types. The samples were pelletized and sintered at a temperature of 850°C for a period of 36hours. The current-voltage response was measured for each sample type while microstructural analyses were carried out by measuring the X-ray diffraction spectra and obtaining the Scanning electron micrographs of each sample type. Threshold voltages of non-linearity or breakdown regime were obtained as 2.02×10^3 V/m at current 1.05 $\mu A/cm^2$ for the Sample with the higher proportion of MnO_2 (Sample A) and 4.80×10^3 V/m at current 1.20 $\mu A/cm^2$ for the Sample with a higher proportion of PbO (Sample B). Both Sample types exhibited good varistor behaviour with a tendency for better behaviour when MnO_2 fraction is higher.

The different phases formed during the sintering process in each sample type were revealed by the XRD spectra while the particle sizes of 1.621 μm for sample A and 1.020 μm for sample B, as well as distribution of grains were revealed by the SEM micrographs. Since the size and grain types determine the varistor behaviour, proper mechanism for the control of microstructure need to be established through further investigation of sintering parameters.

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