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Effect of Sintering Temperature on the Microstructure and Electrical Characteristics of Low Clamping Voltage Zinc Oxide- Based Ceramic Varistor

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Abstract

Pelletized samples of polycrystalline zinc oxide ceramics doped with 2mol% MnO_2 and 3mol% PbO were prepared by the conventional method of ceramic processing. The requisite composition was obtained by the direct mixing of constituent phases (DMCP) technique. Sintering was carried out at various temperatures ranging from 650°C to 850°C. The effects of sintering on the non-linear characteristics of the doped ceramic samples were investigated. The threshold or breakdown voltages were found to decrease as sintering temperature increased.

Microstructural investigation revealed improved homogeneity and increased grain sizes with increasing sintering temperature. The random distribution of secondary phases also featured prominently. These findings were observed to correlate with the evolution of electrical characteristics while the sample sintered at 850°C exhibited the best electrical response suitable for varistor behaviour.

Keywords: ZnO varistor, sintering temperature, densification, microstructure, electrical characteristics.

1. Introduction

A number of studies have successfully proved that n- type doped zinc oxide ceramics are effective material for varistors or voltage- dependent resistors (VDR), using transition metal oxides as the dopant. The role of the individual dopants in forming potential barriers to electron flow has been reported (Clark, 1999; Haskell et al., 1999; Duran et al., 2003). Varistors have applications in the protection of electrical power transmission and electronic circuit devices against transient voltage surges (Gupta, 1990; Leach, 2005; Annas et al., 2007). Their current-voltage characteristics exhibit very high resistance at low voltages and low resistance at high voltages. The threshold voltage of transition to increased conduction, also known as clamping or breakdown voltage occur in a region of non-linearity (Matsuoka, 1991; Pillar et al., 2003). There have been reports in the literature on the basic physics of doped varistors (Levison et al., 1975; Entage, 1977), in addition to which a brief review will be pertinent here.

The microstructure of a varistor is made of thin intergranular phase separating ZnO grains which cause localized defects on the interface. These defects give rise to a schottky barrier which limits the current flow at low temperatures. When higher voltage is applied across the boundary layer, minority carriers are generated, thereby increasing conductivity significantly (Mahan et al., 1993; Pillat et al., 2003). The electronic potentials that build up at the grain boundaries arise from the charges trapped at the interface states (Fernandez- Hevia et al., 2004; Leach, 2005). Consequently, the equivalent circuit of the varistor can be represented as a parallel combination of resistors and capacitors, while the bulk varistor consists of several series and parallel combinations of micro-varistors (Kourdi et al., 1992). In this way, they are equivalent to back-to-back zener diodes, with greater current and energy handling capabilities (Peitado et al., 2007).

The mixing of two or more components to form a multicomponents system separated by distinct interfaces produce superior material properties. The behaviour of such system depends on the composition and temperature of processing and when the free energy of the system is minimum, the system remains stable (Vijaya and Rangarajan, 2003). The microstructure of the polycrystalline material largely depends on the number, size, shape and rate of formation of phases present (Barrett et al., 1973). A previous study of a ternary varistor system sintered above 800°C showed that liquid phase reactions produced functional microstructure, promoting the densification of the ceramics and the growth of ZnO grains (Leite et al., 1996). It has also been reported that mechano-chemical activation (MCA) of microstructure resulted from using the direct mixing of constituent phases (DMCP) technique with high sintering temperature. This was found to significantly reduce particles' sizes and their compactness, giving rise to more homogeneous samples with higher density and finer distribution of secondary phases (Bernik et al., 2008). This finding confirmed an earlier report by kutty (2000).

In our previous investigations (Akinnifesi et al., 2014) we studied the electrical properties of Mn^{2+}- Pb^{2+}- doped ZnO varistors and found this to be considerably influenced by the microstructure. Onreabroy et al. (2006) has also reported that the non-linear coefficient depended primarily on the sintering temperature and significantly decreased at higher temperatures. Breakdown voltages had equally been found to decrease linearly as average size of ZnO grains increased (Hozer, 1994). Interestingly, variation in microstructure and electrical properties at different sintering temperatures has been reported (Xu et al., 2009; Nahm, 2006) while homogeneity and development of interfaces have been related to sintering (Leach et al., 2000; Bernik et al., 2001). Significantly, the evolution of particle size and distribution during processing is temperature-sensitive. Consequently, the breakdown voltages can be varied by changing the grain size under sintering condition (Lee et al., 2007).

The objective of this work is therefore to investigate the effect of varying sintering temperature on the microstructure and electrical characteristics of bulk specimen of Mn^{2+}- Pb^{2+}- doped zinc oxide ceramics. This is carried out by the conventional means of electron microscopy and X-ray diffraction techniques, as well as current-voltage characterization.

2. Experimental Procedure

2.1 Sample Preparation:

Reagent grade (Sigma Aldrich) ZnO powder of 99.9% purity and mean particle size $0.28\mu m$ were doped with requisite amounts of MnO_2 and PbO powders, by direct mixing of constituent phase procedure (DMCP). This method allows the preparation of bulk-type varistors with precisely defined components. Each phase is prepared separately and the final varistor is formed by sintering the powder mixture of constituent phases (Brankovic et al., 2007). Mixing was thoroughly done in a ceramic mortar for considerable homogeneity. The mixture was then entirely scooped into the mould and pelletized with Caver Hydraulic unit with a load of 7.49MPa for about 4 minutes to enhance effective compression. The resulting pellets were disk-shaped with about 2.00mm in thickness and 10.0mm in diameter. The thickness/diameter measurements were averaged, with no substantial deviation found. The composition was 95% ZnO of 95mol% ZnO with 2mol% MnO_2 and 3mol% PbO. Specimens of these pellets were sintered at different temperatures varying from 650°C to 850°C for about 6 hours in each case. Each specimen was inserted in quartz-tube before placing in the preheated oven, to ensure there was no reaction between the furnace interior and samples, thereby avoiding any contamination. It was then inserted at the preset temperature at a heating rate of 5^oC/min and subsequently oven-cooled to about 280^oC. It was finally removed outside the oven to cool to room temperature. As the cooling to room temperature was gradual, no disc bending resulted.

2.2 Density, ρ Determination

The density of the sintered pellets were determined firstly by precise geometrical measurements of their dimension using the micrometer screw gauge. This was followed by a precise weighing of the pellet with an electronic balance of sensitivity 10^{-4}g. The mass to volume ratio of each of the samples prepared at different sintering temperatures was then evaluated to obtain the densities

2.3 Measurements of Microstructure:

To observe the microstructure of the sintered doped-ZnO ceramic samples, the fractured surface was coated with gold for examination under a Scanning Electron Microscope. The micrographs were produced by the CARL-ZEISS machine, model EVOMA10. Average grain size was determined by the linear intercept method. The crystalline phases were identified by X-ray Diffractometry. For this, a Radicon MD 10 diffractometer making use of CuKα radiation at $1.5418A^o$, in the detection range between 16^o and 72^o was employed.

2.4 Measurement of Electric Field –Current Density (E-J) Characteristics

The DC current-voltage characteristics of the sintered samples were measured by coating silver paste onto the opposite faces of the samples. The silver electrodes of 5mm in radius were formed by heating at 500^oC for about 10minutes, to establish ohmic contact. The current and voltages were obtained with a Keitheley electrometer, model 2636A and the values were expressed as current densities (in terms of the unit length of the varistor thickness respectively). Hence the breakdown voltages of the samples were obtained for different sintering temperatures.

3. Results and Discussion

3.1 Densification

The variation of the density of the varistor samples sintered at different temperatures is shown in Figure 1. An initial increase in densification with increasing temperature is revealed. This is followed by a drop in value at a temperature of 800°C. The initial increase may have arisen from the annihilation of probable voids in the microstructure, as well as from the formation of new phases and growth of ZnO grains (Han et al., 1999; Han et al., 2000). The drop is also indicative of the onset of significant loss in dopant materials at higher sintering temperature. This loss is manifested by the decrease in XRD peak intensity of PbO_2 from 0.75 at 800 °C to 0.35 at 850 °C and that of MnO_2 from 0.60 to 0.10 over the same range of temperature increase. This could serve as a guide to the choice of temperature of sintering. Densification at higher sintering temperatures can be improved by increasing the Mn doping level as this has been found to promote grain growth in the final stages of sintering (Han et al., 2002).

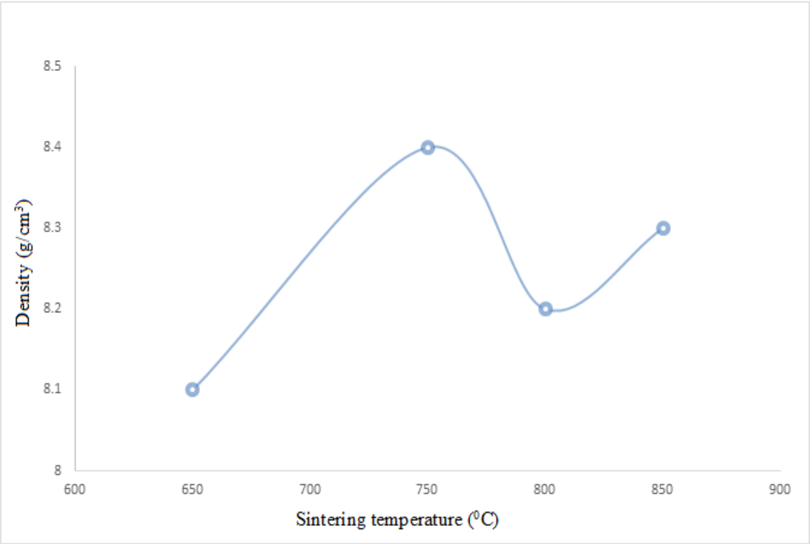


Figure 1. Variation 0f densification with sintering temperature

3.2 Microstructural Studies

Figure 2(a-d) show the scanning electron micrographs of the sintered doped ZnO ceramic samples at different temperatures of sintering. These basically consist of different phases with ZnO as the main phase. From the appearance of the phase distributions the microstructures seem identical, though with trends of improved matrix homogeneities with increasing sintering temperature. Better homogeneities have been reported to confer better varistor characteristics (Bernik et al., 2008). The variation of average grain size with sintering temperature is shown in Figure 3, in which the grain sizes increase with the sintering temperature. The emergence of the different phases with the different sintering temperatures is revealed by the x-ray diffraction spectra of the doped ceramic samples shown in Figure 4(a-d). More phases are observed to form with increasing sintering temperature, thus contributing to the creation of interface barriers to electrical conduction. The improvement in varistor behaviour would consequently be enhanced.

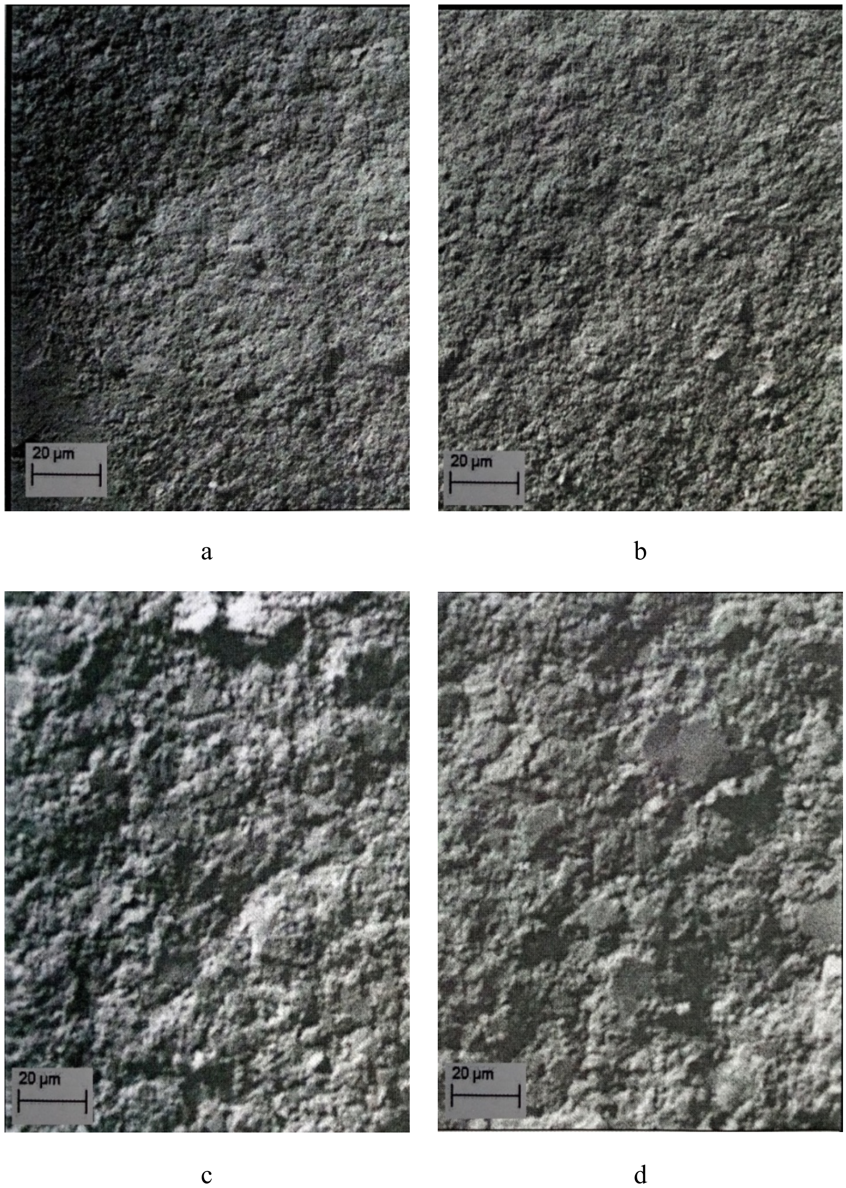


Figure 2. SEM Micrographs of samples sintered at (a) 650°C, (b) 750°C, (c) 800°C and (d) 850°C

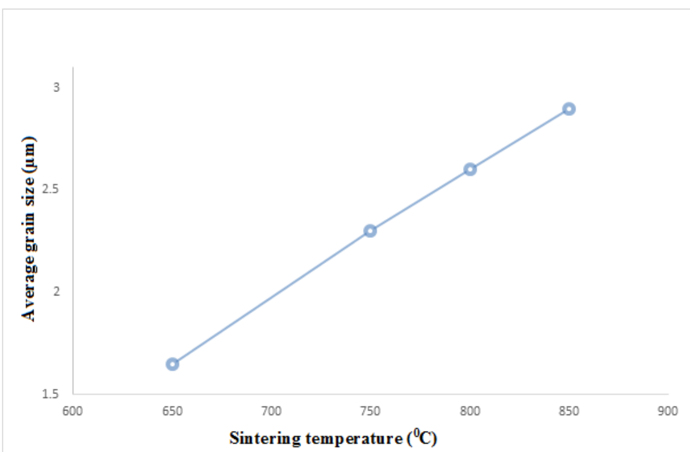
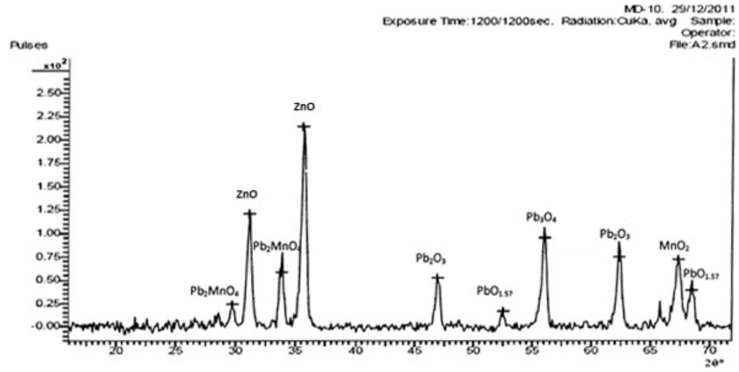
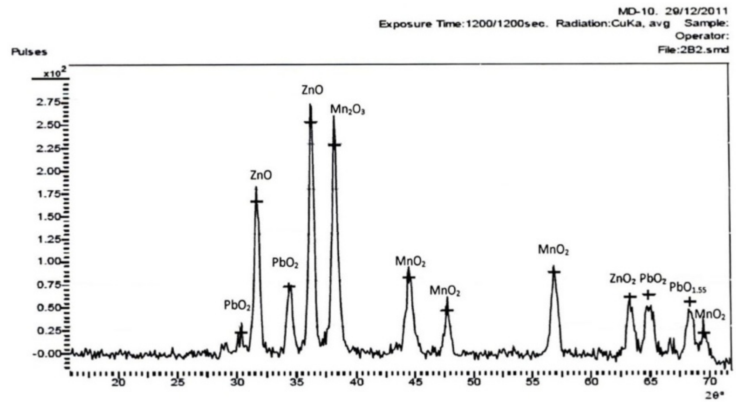


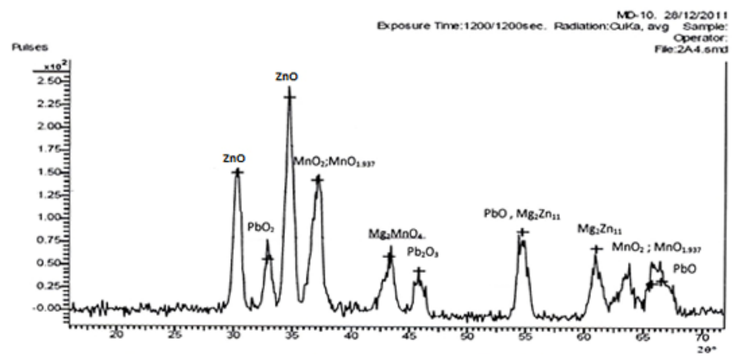
Figure 3. Variation of average grain size with sintering temperature



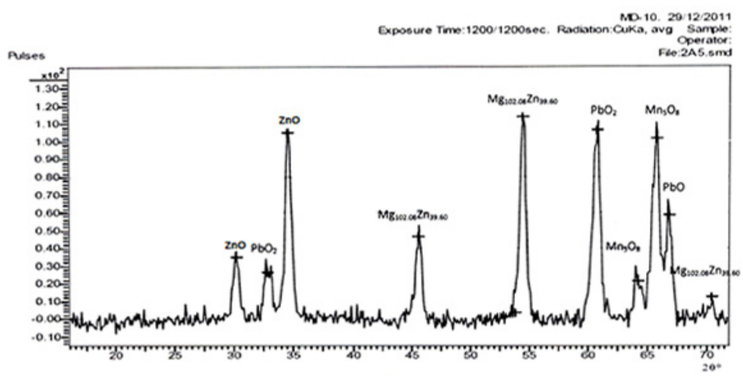
(a)



(b)



(c)



(d)

Figure 4. XRD Spectra of the sintered samples at (a) 650°C, (b) 750°C, (c) 800°C and (d) 850°C.

3.3 Electrical Characteristics

The properties of varistors are best highlighted by the electrical characteristics which result from the fabrication processes, particularly sintering. Figure 5 shows the current-voltage characteristics of the doped ZnO ceramic samples sintered at the various temperatures. These exhibit a sharp transition in the electric field from low current zones to non-linear region of higher currents. The associated threshold or breakdown voltages V_b, vary with the sintering temperatures as shown in Figure 6, where V_b decreases with increasing sintering temperatures. This variation is traceable, on one hand to the formation and consequent growth of secondary phases at the different temperatures. According to Zhang et al. (2005), the growth of secondary phases involves the dissolution of cations which makes the interphase junctions more electrically active. On the other hand, the increased average grain sizes would lead to increased conductivity and a consequent reduction in the breakdown voltage. This phenomenon was previously observed by Cheng et al. (2007). Hence, the formation of several polymorph phases and increase in grain sizes in the sample sintered at 850°C explains the occurrence of a minimum breakdown voltage at this temperature. However, it is evident from Figure 5 that the increase in breakdown voltage is accompanied by increased leakage currents. This is indicative of a deterioration tendency in the varistor microstructure. Nahm (2004), Leach et al. (2006) and Nahm (2007) have all reported a lowering of the barrier height and poorer non-linearity in the electrical response of excessively sintered varistors.

In the overall analysis, considering the knee of the non-linearity in electrical response and other important parameters, the best varistor behavior is exhibited by the sample sintered at 850 °C.

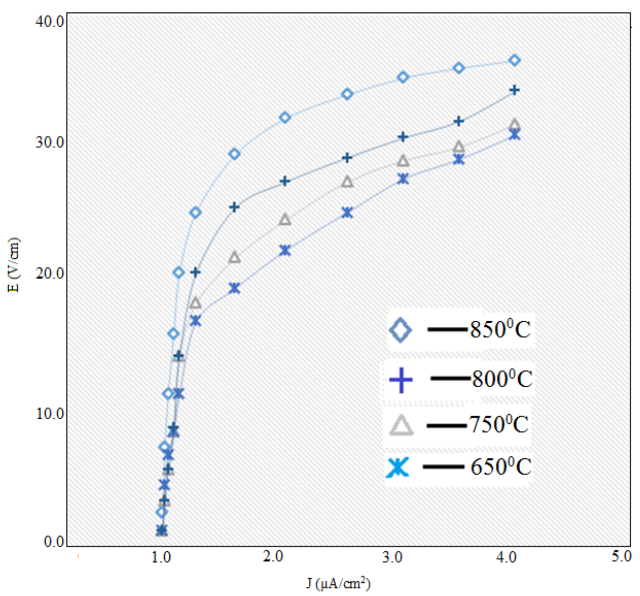


Figure 5. Current- voltage (J-E) characteristics of the sintered samples

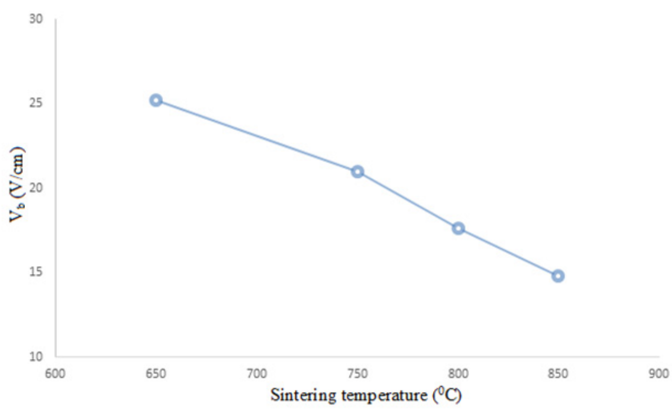


Figure 6. Variation of breakdown voltage, V_b with sintering temperature

4. Conclusion

The influence of sintering temperature on the microstructure and electrical response of MnO_2-PbO- doped ZnO varistor ceramics were investigated between 650^{o}C and 850^{o}C. The samples exhibited initial densification with increased sintering temperature.

This was followed by a reduction in densification at 800^{o}C and a subsequent improvement at a sintering temperature of 850^{o}C. SEM studies showed improved homogeneity with increasing temperature. The grain sizes also increased accordingly while XRD spectra revealed the formation of secondary polymorphic phases. The electrical characteristics exhibited sharp transitions from ohmic to non-ohmic response and the associated breakdown voltage decreased with increased sintering temperature.

The improvement in electrical response with increased sintering temperature was attributed to the improved microstructural homogeneities as indicated by more uniform phase distribution and narrower grain boundaries. The best characteristics found suitable for varistor behaviour was exhibited by the sample sintered at 850^{o}C for 6 hours. However, the duration of sintering may have been crucial to the microstructural evolutions of the ZnO-based ceramic varistor samples. As the microstructural findings correlated with the electrical characteristics, it follows that breakdown voltages can be significantly controlled by means of the sintering process.

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