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Fabrication and Electrical Characterization of $Pb^{2+} - Mn^{2+}$ −Zinc oxide based varistor ceramics

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Abstract:

Varistorrs composed of ZnO, MnO_2 and PbO_2 were prepared by doping zinc oxide with the transition metal oxides in different molar quantities. The varistors were prepared by the direct mixing of constituent phases technique and sintered at $750°C$. The current-voltage characteristics of the different samples were investigated at room temperature. The undoped ZnO sample gave an ohmic behavior while the introduction of additives into the base oxide matrix was found to significantly alter the allure of the current-voltage characteristics to non-linearity. The threshold voltage of non-linearity was found to vary with the mole fraction of the dopant constituent. The mole fraction of 5% MnO_2 yielded a modest value of 65V/cm whereas a mole fraction of 5% PbO_2 gave a higher value of 85V/cm for the threshold voltage. The codoping with lead and manganese oxides gave the lowest threshold voltage value of 38V/cm, thereby making the tricomponent varistor ceramics more surge-sensitive, with a higher nonlinearity coefficient of 5.8 and the lowest leakage current of 3.2mA/cm. The elemental composition of the phases present in the varistor ceramics was ascertained by XRF analysis while the primary and secondary phases were identified with X-ray diffraction spectroscopy.

Keywords: Elemental composition, nonlinear coefficient, threshold voltage, varistor, x-ray diffraction spectra.

Introduction

Varistors are inherently polycrystalline, multijunction grain boundary devices that can absorb transient surge energy and serve to protect electronic and electrical circuit components. The voltage surges are induced by power switching and electromagnetic pulses [1]. The trend of aggressive downscaling of electronic devices into integrated low voltage application has steadily become increasingly important. This should lead to a change of paradigm in future electronic device fabrication by exploiting electron tunneling which relies on quantum mechanics rather than classical electrodynamics [2]. To this effect, metal oxide junction has the potential to receive additional attention.

Research activity in the area of zinc oxide based ceramics has been traditionally fuelled by the need for ideal candidates as intrinsic voltage regulators in the contex of circuit protection. Consequently a wide range of doped ZnO-based systems have been studies [3 - 5]. Such materials are characterized by a gradual switch in the shape of the otherwise linear current-voltage (I – V) curve of the undoped zinc oxide ceramics to a region of nonlinearity, at specific threshold voltage, V_T. The sharpness of the transition from linear to nonlinear regime is described by the nonlinear coefficient, α define by the empirical relation [6 - 7]:

$$I = kV^{\alpha} \qquad (1)$$

where k is a constant depending on the varistor material. The parameters V_T and α constitute the characteristic indices of performance for the ZnO varistor ceramics. The nonlinearity is required for the suppression of leakage current during the clamping of transient voltage. The higher the value of α, the lower the leakage current J_L and the better the varistor ceramics [8].

It is well known that the varistor is controlled essentially by the dopant additives, usually heavy transition metal oxides. The dopant ions form a thin intergranular phase separating the ZnO grains [5]. This gives rise to localized defects on the interface in the form of electron traps. The defects constitute Schottky barriers limiting current flow at low temperature while further conduction is enhanced by thermoelectric effect [9]. The role of individual dopants forming a potential barrier to electron flow in the varistor has been investigated [10 - 12]. Bernick *et al.* [13] established the improvement of the electrical characteristics of the varistor by doping with Bi_2O_3, TiO_2 , Sb_2O_3 and Cr_2O_3. Besides, a study of the influence of environmental degradation on the electrical characteristic of the device indicated a modification in structure occasioned by change in dopant ion content [14]. Excessive doping has however been found to cause a deterioration in varistor behavior [15].

Obviously, studies on compositional tailoring would serve the purpose of property improvement in varistor device fabrication. Consequently, the influence of PbO_2 and MnO_2 additives in small amounts, to the zinc oxide matrix on the electrical characteristics is the subject of this work. The study is complemented by microstructural investigation for a better understanding of the mechanisms leading to improved varistor behaviour.

Materials and Method

Pure samples of ZnO, MnO_2 and PbO_2 were obtained off the laboratory shelf. Appropriate mole fraction of each of the compounds was weighed with an electronic balance of sensitivity 10^{-4}g to obtain four samples A, B, C and D as follows: Sample A (100mol%ZnO), Sample B (95mol%ZnO, 2mol%PbO_2 and 3mol%MnO_2), Sample C (95mol%ZnO and 5mol%MnO_2) and Sample D (95mol%ZnO and 5mol%PbO_2). The conventional method of direct mixing of constituent phases (DMCP) procedure was used for the preparation of the samples [16 - 17]. Each sample was thoroughly mixed and wet-milled for several hours to obtain fine homogenous particles. The homogeneity of additives has been found to directly relate to the electrical characteristics of the varistor and also that inhomogeneity can cause local currents leading to degradation of the device when in operation [18].

To enhance electrical current-voltage characterization, at room temperature, electrode leads were carefully attached to opposite faces of the disk by means of silver paste. This was heat cured to provide ohmic contacts. A dc voltage range of 0 – 10V was applied in steps across the terminals of the samples, which gave an electrometer output current range of 20 to 100μA at room temperature. X-ray diffraction analysis was carried out on the constituent oxides as well as the tricomponent zinc oxide varistor ceramics using CuK_α radiation at 1.5468Å. A diffractometer of the type MD10 mini-diffractometer with an angle detection range between 16° and 72° was used to obtain the crystal structures of the different phases. The diffraction analysis was facilitated by the Powder Data File provided by the ICDD [19]. Analysis of the elemental composition was carried out with X-ray fluorescence technique. This gave a quantitative and qualitative analysis of the elements present in the tricomponent varistor sample.

Results and Discussion

The current per unit cross sectional area plots versus voltage per unit thickness (J – E) plots of the various varisotr ceramics are presented in Figs 1 – 4.

Figure 1 shows the ohmic behavior of the undoped ZnO samples while Figs 2 – 4 exhibit features of nonohmicity in the E – J characteristics.

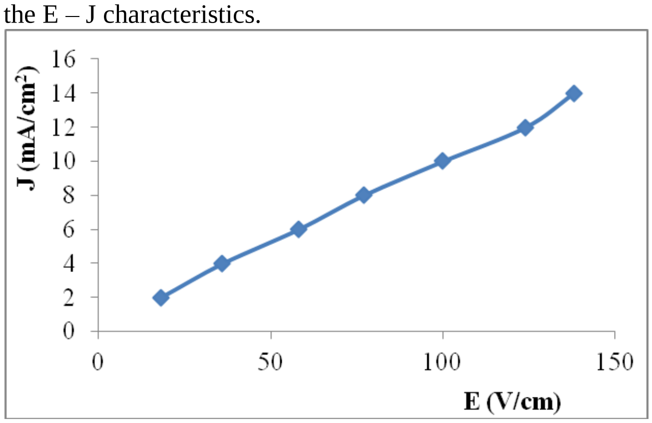

Figure 1: Current-voltage characteristics for the undoped zinc-oxide

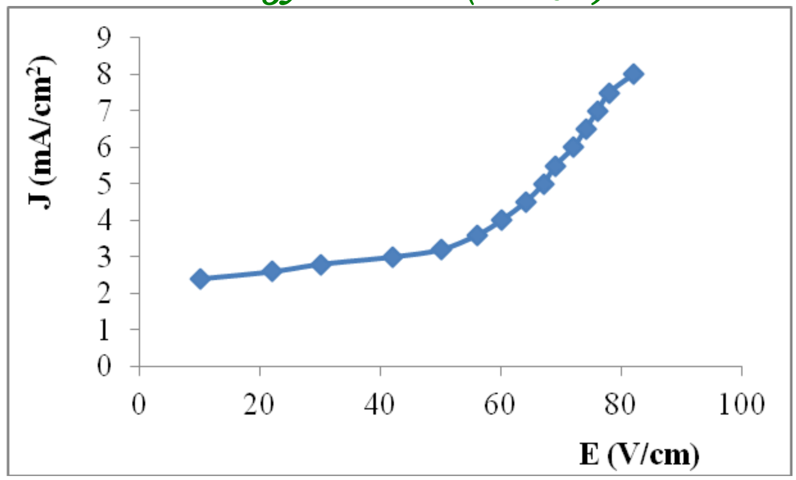

Figure 2: Current-voltage characteristics for the Pb-Mn-Zn oxide varistor

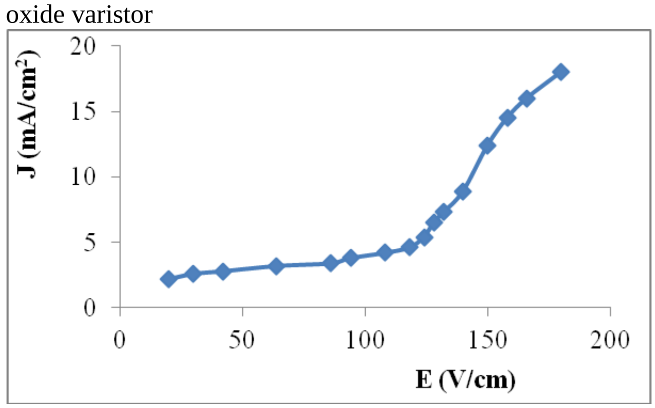

Figure 3: Current-voltage characteristics for the Mn-Zn oxide varistor

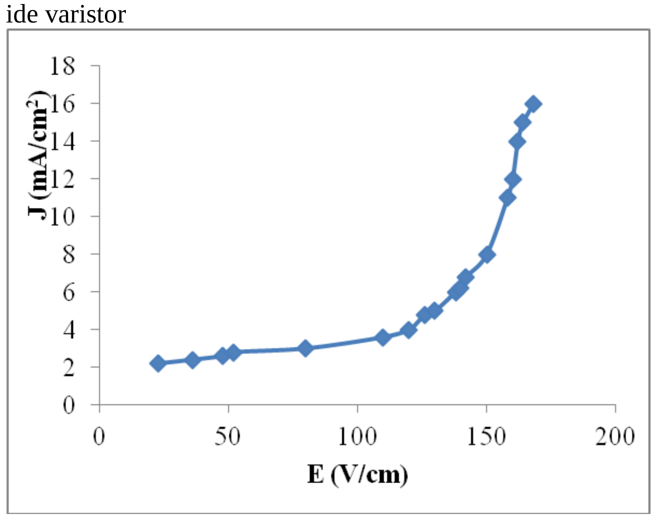

Figure 4: Current-voltage characteristics for the Pb-Zn oxide varistor

The curves consist of two regimes; the linear regime before the threshold field, which is a region of low current conduction, and the nonlinear regime preceded by the threshold voltage. The latter regime is a region of higher current conduction. The shapes of the transition edge between ohmic and nonohmic regions clearly illustrate the compositional differences and quality of the varistor samples. The nonlinear coefficient α was derived from the E – J characteristic curves by taking the natural logarithm of equation (1) i. e.

$$\alpha = \frac{d \log I}{d \log V} \qquad (2)$$

A summary of the threshold voltages, the nonlinear coefficients, α and the leakage currents, J_L for the various varistor ceramic compositions is presented in Table1.

Table 1: Characteristic parameters of the varistor ceramics

Sample	Composition	Threshold field, E_T (V/cm)	Nonlinear coefficient, α	Leakage current (mA/cm)
A	Undoped (100mol% ZnO)	-	-	-
B	95mol%ZnO, 2mol%PbO_2 3mol%MnO_2	38	5.8	3.2
C	95mol%ZnO, 5mol%MnO_2	44	4.2	4.0
D	95mol%ZnO, 5mol%PbO_2	85	3.5	4.2

The table shows that the tricomponent varistor ceramic (Sample B) has the least V_T, the highest α and the least J_L. The Mn-doped ZnO sample has a much lower V_T and higher than the Pb-doped ZnO sample. This is due to the influence of Mn which is known to suppress the leakage current in the ZnO matrix [20]. This behavior has been found to depend on the oxidation of the double ionized zinc interstitial defect at the grain boundary [21]. The presence of Pb doping on the other hand gives rise to increased threshold voltage and low α. This is probably due to an electrostatic build up at the interface resulting from trapped charges [22]. Scanning electron microscope (SEM) model ZEISS EVOMA10 was used to examine the surface morphology of the tricomponent sample and the result is shown in Figure 5 .

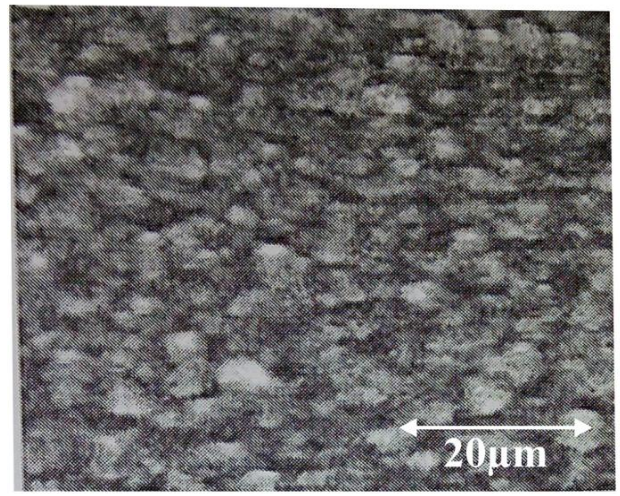

Figure 5: SEM micrograph showing the homogeneity of ticomponent sample (Sample B)

The sample has a uniform distribution of phases, suggesting that the material is homogeneous and continuous. The powdered x-ray diffraction analyses data on the individual component phases confirmed the structure of ZnO as hexagonal while those of PbO_2 and MnO_2 are orthorhombic. Figure 6 shows the diffraction pattern for the tricomponent varistor ceramic (PbO_2-MnO_2-ZnO). Sample B which reveals the formation of secondary phases such as Pb_2O_3 and ZnO_2 besides the primary phases PbO_2, MnO_2 and ZnO.

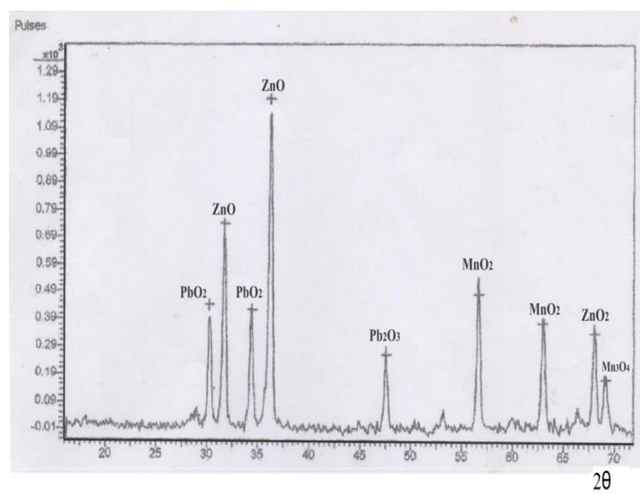

Figure 6: XRD spectra of the tricomponent sample

The relative peaks intensities of the primary phases are seen to correspond to the starting molar proportions of the constituent phases of the varistor sample. These phases must have influenced the electrical characteristics to promote the better varistor behavior [23]. Figure 7 shows the XRF spectrum of the Pb, Mn codoped sample.

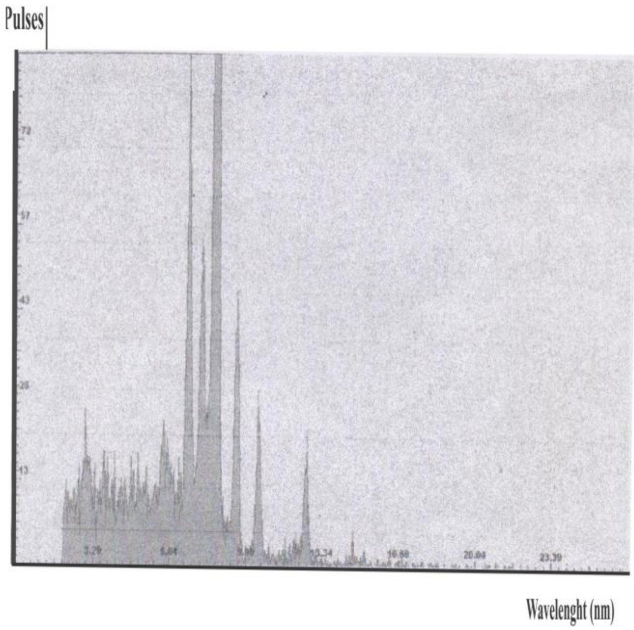

Figure 7: XRF spectrum of the tricomponent varistor (Sample B)

The relative concentrations of the elements present in the sample are summarized in Table 2.

Table 2: Relative concentrations of the elements in the Pb-Mn-ZnO varistor

Elements	K_α values (nm)	Concentration
Zn	0.1435	88%
Pb	0.1176	10.2ppm
Mn	0.2102	15ppm
Ca	0.3359	3.5ppm
Fe	0.1926	1.2ppm

The concentrations of the elements are consistent with the sample composition. The traces of Fe and Ca featuring in the analysis are considered extraneous to the sample as they were introduced into the samples in the course of device fabrication and analyses. Since they were not introduced *ab initio* as dopant oxides, they are unlikely to contribute significantly to the oxygen ion traps that give rise to the schottky interface barrier formation.

Conclution

PbO_2, MnO_2 Zinc oxide based varistor ceramics have been fabricated using the conventional DMCP technique and solid state sintering at $750°C$. The mole percentages of the metal oxide additives were thoroughly mixed into homogenous and continuous samples as confirmed by scanning electron microscopy. XRF spectrum of the tricomponent sample revealed the elemental analysis which features a consistence in the compositions of the prepared tricomponent varistor ceramics. Similarly XRD spectrum of the same sample revealed the formation of secondary phases which contributed to the electrical characteristics.

An investigation of the J-E characteristics exhibited the undoped ZnO sample as ohmic while the doped samples exhibited marked nonohmicity depending on the metal oxide inclusions in the ZnO base matrix. The different proportions of the dopant constituents gave rise to different threshold voltages, nonlinear coefficients and leakage currents. The significance of Mn doping manifested in the lowering of the threshold voltage and raising of the nonlinear coefficient whereas Pb-doping raised the threshold voltage and lowered the nonlinear coefficient. The combined effect of the two dopants produced the best characteristic varistor parameters.

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