



UNIVERSITI PUTRA MALAYSIA

***EFFECT OF V₂O₅ AND Sb₂O₃ DOPING ON THE MICROSTRUCTURE,
ELECTRICAL PROPERTIES AND DC DEGRADATION BEHAVIOR OF
ZnO-Bi₂O₃-MnO₂ LOW VOLTAGE VARISTOR CERAMICS***

DAHIRU UMAR

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By

DAHIRU UMAR

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
fulfillment of the Requirements for the Degree of Master of Science**

May 2016

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

EFFECT OF V_2O_5 AND Sb_2O_3 DOPING ON THE MICROSTRUCTURE, ELECTRICAL PROPERTIES AND DC DEGRADATION BEHAVIOR OF $ZnO-Bi_2O_3-MnO_2$ LOW VOLTAGE VARISTOR CERAMICS

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May 2016

Chairman : Professor Azmi Bin Zakaria, PhD
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There is a need to enhance the nonlinear coefficient (α) of low varistor ceramic by substituting V_2O_5 instead of the usual Bi_2O_3 as a liquid sintering aid and improve the stability against DC-thermal stress. Therefore in this study, the first aim to study the effect of small intervals of sintering temperatures on the microstructure and electrical properties of V_2O_5 doped $ZnO-Bi_2O_3-Sb_2O_3-MnO_2$ varistor ceramics and secondly, to evaluate the stability of $ZnO-Bi_2O_3-MnO_2$ varistor ceramics doped with V_2O_5 and Sb_2O_3 against DC-thermal stress. To achieve these objectives the materials were divided into three systems System 1 ($98.3 - x$) ZnO , xV_2O_5 , $0.7Bi_2O_3$, $0.3Sb_2O_3$, $0.7MnO_2$; for $x = 0$ mol%, system 2 ($98.3 - x$) ZnO , xV_2O_5 , $0.7Bi_2O_3$, $0.3Sb_2O_3$, $0.7MnO_2$; for $x = 0.08$ to 0.4 mol%, and system 3 ($98.4 - y$) ZnO , $0.2V_2O_5$, ySb_2O_3 , $0.7Bi_2O_3$, $0.7MnO_2$; for $y = 0$ to 1 mol%. The constituent raw powders were weighed according to their weight proportion and then process via solid state reaction technique. The J-E characteristics of the sintered ceramics were measured at a room temperature by means of a source measure unit. The morphology of varistor ceramic samples was investigated via XRD SEM and EDX. The stability was investigated by subjecting the samples at $120^\circ C$ and DC thermal stress for a period of 18 hours.

The XRD analysis shows the presence of two main phases of ZnO and MnO_2 in system 1 and 2, another phase, including spinel and polymorphs secondary phase is related to V, Bi, Sb and Mn species. The SEM and EDX results show the microstructure and the presence of all the elements used. It was found that V_2O_5 improved the varistor ceramic microstructure through densification and grain boundary enhancement. In system 1, the density decreased with the increase in sintering temperature (from 1200 to $1300^\circ C$) for ZBSM varistor ceramics. When doping 0.2 mol% V_2O_5 the varistor ceramic had the optimum α and the grain boundary enhances (system 2). However, at a fixed $0.2 V_2O_5$ and varying Sb_2O_3 on ZVBM varistor ceramics. The average grain size increase with the increase in sintering temperature, this was also observed for samples containing an x mol % Sb_2O_3 (system 3).

In DC and thermal stress experiment (system 3), the undoped ceramics sintered between 1200-1300 °C are found to have low stability with Kt value $8.82 \times 10^{-6} \text{ mAh}^{-1/2}$ and α decreases after the stress test. Subsequently, the stability of the doped samples containing Sb_2O_3 improves to Kt value of $5.8 \times 10^{-7} \text{ mAh}^{-1/2}$ for sample with 0.6 mol% Sb_2O_3 . The Kt improves further to $2.02 \times 10^{-7} \text{ mAh}^{-1/2}$ with the increase of Sb_2O_3 content up to 1 mol% which shows a high stability. Thus, in this study the V_2O_5 doping improved the varistor ceramic α which proves the hypothesis. However, 1 mol% of Sb_2O_3 content shows that after the DC and thermal stress varistor ceramic stability can be improved.



Abstrak tesis ini dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

KESAN PENDOPAN V_2O_5 DAN Sb_2O_3 KEATAS MIKROSTUKTUR, CIRI-CIRI ELECTRIC DAN SIFAT DEGRADASI DC PADA SERAMIK VARISTOR BERVOLTAN RENDAH $ZnO-Bi_2O_3-MnO_2$

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Terdapat keperluan untuk menambahbaik pekali ketaklinearan (α) seramik varistor dengan menggantikan Bi_2O_3 dengan V_2O_5 sebagai pensinter cecair semasa fabrikasi telah diperbaiki menggunakan Sb_2O_3 . Objektif kajian ini adalah pertamanya untuk mengkaji kesan sela kecil suhu pensinteran terhadap sifat-sifat keelektrikan dan mikrostruktur seramik varistor berasaskan $ZnO-Bi_2O_3-Sb_2O_3-MnO_2$ yang didopkan dengan V_2O_5 , dan keduanya untuk menilai kestabilan seramik varistor berasaskan $ZnO-Bi_2O_3-MnO_2$ yang didopkan dengan V_2O_5 dan Sb_2O_3 terhadap tegasan AT dan terma. Untuk mencapai sasaran ini, bahan-bahan dibahagikan kepada 3. Sistem 1 ($98.3 - x$) ZnO , xV_2O_5 , $0.7Bi_2O_3$, $0.3Sb_2O_3$, $0.7MnO_2$; for $x = 0$ mol%, sistem 2 ($98.3 - x$) ZnO , xV_2O_5 , $0.7Bi_2O_3$, $0.3Sb_2O_3$, $0.7MnO_2$; for $x = 0.08$ to 0.4 mol%, dan sistem 3 ($98.4 - y$) ZnO , $0.2V_2O_5$, ySb_2O_3 , $0.7Bi_2O_3$, $0.7MnO_2$; for $y = 0$ to 1 mol%. Bahan serbuk mentah ditimbang berdasarkan bahagian jisim, kemudian melalui teknik tindak-balas keadaan pepejal. Ciri-ciri J-E bagi seramik yang disinter diukur pada suhu bilik menggunakan unit ukur punca. Kestabilan diselidiki dengan mendedahkan sampel pada suhu $120^\circ C$ dan tegasan terma AT selama 18 jam. Fasa dan mikrostruktur seramik varistor disiasat menggunakan XRD, SEM dan EDX.

Analisis XRD menunjukkan kewujudan dua fasa utama ZnO dan MnO_2 bagi bahan dalam sistem 2 dan sistem 3, manakala fasa-fasa sekunder lain yang berkaitan dengan V, Bi, Sb dan Mn juga dikesan. Keputusan SEM dan EDX menunjukkan mikrostruktur dan kehadiran semua unsur-unsur yang diguna dalam sistem ini. Adalah didapati bahawa V_2O_5 memperbaiki struktur seramik varistor menerusi pensinteran fasa cecair. Dalam sistem 1, secara umumnya ketumpatan menurun dengan peningkatan suhu pensinteran (dari 1200 hingga $1300^\circ C$) untuk varistor seramik ZBSM apabila didop dengan 0.2 mol% V_2O_5 adalah didapati bahawa seramik varistor mempunyai nilai α yang optimum dan mempunyai pembaikan sempadan butiran (sistem 2). Dalam sistem 3, dengan $0.2 V_2O_5$ tetap, dan dengan mengubah kandungan pendop Sb_2O_3 dalam seramik varistor ZBSM dalam seramik varistor, pembesaran butiran ditunjukkan apabila suhu pensinteran bertambah.

Dalam eksperimen kestabilan AT dan tegasan terma (sistem 3), bagi sampel tidak didop disinter pada suhu diantara 1200-1300 °C, didapati mempunyai nilai kestabilan rendah dengan nilai K_t $8.82 \times 10^{-6} \text{ mAh}^{-1/2}$ dan nilai α menurun selepas ujian tegasan. Seterusnya bagi sampel yang mengandungi Sb_2O_3 didapati bertambah baik kepada nilai K_t $5.8 \times 10^{-7} \text{ mAh}^{-1/2}$ bagi sampel yang didop dengan 0.6 mol% Sb_2O_3 . K_t terus bertambah baik kepada $2.02 \times 10^{-7} \text{ mAh}^{-1/2}$ dengan pertambahan kandungan Sb_2O_3 sehingga 1 mol% yang menunjukkan kestabilan yang tinggi. Seterusnya, dalam kajian ini didapati bahawa pendop V_2O_5 meningkatkan nilai α seramik varistor yang membuktikan hipotesis. Walau bagaimanapun, kestabilan bagi kandungan 1 mol% Sb_2O_3 menunjukkan selepas tegasan AT dan terma bagi seramik varistor boleh diperbaiki.

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LIST OF ABBREVIATIONS

I-V	Current-voltage
J-E	Current density-electric field
DC	Direct current
AC	Alternating current
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray spectroscopy
XRD	X-ray diffractometer
DSB	Double Schottky barrier
D	Average grain size
a	constant of J-E fitting
ZBSM	ZnO Bi ₂ O ₃ Sb ₂ O ₃ MnO ₂
ZVBM	ZnO V ₂ O ₃ Bi ₂ O ₃ Sb ₂ O ₃ MnO ₂

LIST OF SYMBOLS

θ (°)	Diffraction angle
A	Nonlinear coefficient
J_L (mA/cm ²)	Leakage current density
E_b (eV)	Breakdown voltage
ω (m)	Depletion width
T (°C)	Absolute temperature
A (A/cm ² K ²)	Richardson's constant
K	Thermal conductivity of the sample
ϕ_B (eV)	Potential barrier height
A (mm)	Area of the metal contact parallel to the depletion layer region in semiconductor
$\% \Delta \alpha$ (%)	Percentage change in nonlinear variation
$\% \Delta E_B$ (%)	Percentage change in breakdown voltage
$\% \Delta J_L$ (%)	Percentage change in leakage current
$\% \Delta \phi_b$	Percentage change in barrier height
$\rho_{\text{theoretical}}$ (g/cm ³)	Theoretical density
E (V/mm)	Electric field
λ (nm)	X-ray wavelength
K_T (mA/h ^{1/2})	Degradation rate coefficient
Zn_i	Zinc interstitial
O_i	Oxygen interstitial
V_{Zn}	Zinc vacancy
$t^{1/2}$ (min ^{1/2})	Stressing time
d-spacing (Å)	Dimension spacing

CHAPTER 1

INTRODUCTION

1.1 Research Background

The development of an alternative way for improving the electrical and microstructural properties of ZnO low voltage varistor ceramics in regards to the experimental conditions has been the main focus of this thesis. The ZnO varistor ceramics fabrication is relatively challenging especially for the appropriate selection of sintering temperature and additives to be use as doping material for varistor ceramic improvement. Due to these challenges there is need for small amounts of metal oxides, such as V_2O_5 , Sb_2O_3 , to be added in ZnO, Bi_2O_3 , MnO_2 , and to ascertain if varistor performance will improve in terms of electrical nonlinear coefficient (α) and microstructure properties of the varistor ceramics. It is difficult to control the formation of Bi_2O_3 due to the multiplicity of different polymorphic phases which varies strongly with the sintering conditions and the type of formulation. Also V_2O_5 is enhancing the varistor ceramic sintering aid through liquid phase sintering compared to Bi_2O_3 . However, addition of V_2O_5 on ZnO varistor ceramic can improved the densification even at a lower sintering temperature which is parallel to the Bi_2O_3 -doped ZnO materials (Izoulet et al., 2014). The addition of V_2O_5 -species in this work will modify the varistor ceramics through liquid phase sintering and improving the nonlinear behavior. Furthermore, ZnO varistor ceramics are bounded to electrical deterioration caused by various factors after subjecting the varistor ceramics to DC thermal stress, this depend on the sintering temperature and the quantity of Sb_2O_3 added. The material (Sb_2O_3) is extensively used as ZnO varistors stabilizer with positive effect. The conventional technique as a way of mixing V_2O_5 , Sb_2O_3 doped ZnO - Bi_2O_3 - MnO_2 was chosen for investigating the effect of sintering temperature, composition and varistor DC thermal degradation.

1.2 Zinc oxide varistor

Zinc oxide (ZnO) is a white inorganic compound that exists in hexagonal crystals. The compound has been identified for a long period of time, due to its unique properties, as a semiconductor material. (Leon, 1960). However, in line with a deep research, it was found that ZnO material has an excellent wide band gap around (3.37.eV) and allows electron mobility with applied thermal energy. ZnO is soluble in acids and alkalis with a density of 5.61 g/cm³ and melting point of 1975 °C. Furthermore, ZnO is found to be in the groups II – VI semiconductor of the periodic table (Nahm, 2011). Pure ZnO without any impurities or dopants is a non-stoichiometry n-type semiconductor which originates from oxygen vacancies or zinc interstitials. Therefore, the material can be used for varistor ceramic fabrication. The popularly known ZnO varistors are called by many names, such as independent resistors, surge suppressors, quick transient responders, voltage limiters or stabilizers, nonlinear resistors etc. ZnO varistor ceramics have found acceptance for many years because they can protect the excess incoming high voltage pulse transmitted into electrical system. The transmitted surge is absorbed by the varistor to prevent damage of the electrical system. The first ZnO

varistor was invented by Matsuoka and co-workers at Matsushita Electric (Japan) in 1968, and has been available in the market since 1972. Since then a number of efforts have been made in an attempt to fully understand the influence of metal oxides on the microstructure and nonlinear electrical properties of ZnO-based varistor ceramics (Peiteado, et. al., 2005). The role of the metal oxide additives was discovered and the processing conditions were optimized over the years ago. The microstructures and the physical properties of the grain boundaries were gradually identified, and found a rapid applications in protecting electrical circuits and electronic components, such as transistors and ICs, against voltage surges (Wong, 1980). The sintered polycrystalline ceramics are excellent in exhibiting nonlinear current-voltage (I-V) characteristics and having the capability of energy absorption. Semiconductor devices were protected against transient voltage a surge, which was achieved by using ZnO varistors, for example, electronic equipment such as ovens, television sets etc. ZnO varistors were later extensively used as surge absorbers in industrial heavy machines, lately, the technological development of ZnO varistors have become the most important fields of competition. Since it is a useful to protect electrical devices against the dangerous of voltage transient. Similar to that of the Zener diode, their current-voltage (I-V) characteristic is nonlinear. Varistors are capable of limiting overvoltage equally in both polarities, which cannot be accomplished in a diode, thus this gives rise to the I-V characteristic which is analogous to a back-to-back diode. ZnO varistors are useful in the field of; (1) direct or alternating currents, (2) voltage range, from a few volts to maximum volts and (3) currents range from microamperes (μA) to miliamperes (mA). Currently, their functions make them to become valuable in both the scientific and technological research (Hove, 2006; Eda, 1989). The protection offered by the varistors is not only to guard the expensive and voltage sensitive equipment from physical damage but also to improve the functional reliability of the components that can encounter temporary upset due to transient voltages of lower amplitudes.

The development of an alternative way for improving the electrical and microstructural properties of ZnO low voltage varistor ceramics in regards to the experimental conditions has been the main focus of this thesis. The ZnO varistor ceramics fabrication is relatively challenging especially for the appropriate selection of sintering temperature and additives to be used as doping material for varistor ceramic improvement. Due to these challenges there is need for small amounts of metal oxides, such as V_2O_5 , Sb_2O_3 , to be added in ZnO, Bi_2O_3 , MnO_2 , and to ascertain if varistor performance will improve in terms of electrical nonlinear coefficient (α) and microstructure properties of the varistor ceramics. It is difficult to control the formation of Bi_2O_3 due to the multiplicity of different polymorphic phases which varies strongly with the sintering conditions and the type of formulation. Also V_2O_5 is enhancing the varistor ceramic sintering aid through liquid phase sintering compared to Bi_2O_3 . However, addition of V_2O_5 on ZnO varistor ceramic can improved the densification even at a lower sintering temperature which is parallel to the Bi_2O_3 -doped ZnO materials (Izoulet et al., 2014). The addition of V_2O_5 -species in this work will modify the varistor ceramics through liquid phase sintering and improving the nonlinear behavior. Furthermore, ZnO varistor ceramics are bounded to electrical deterioration caused by various factors after subjecting the varistor ceramics to DC thermal stress, this depend on the sintering temperature and the quantity of Sb_2O_3 added. The material (Sb_2O_3) is extensively used as ZnO varistors stabilizer with positive effect. The conventional technique as a way of mixing V_2O_5 , Sb_2O_3 doped ZnO - Bi_2O_3 - MnO_2

was chosen for investigating the effect of sintering temperature, composition and varistor DC thermal degradation.

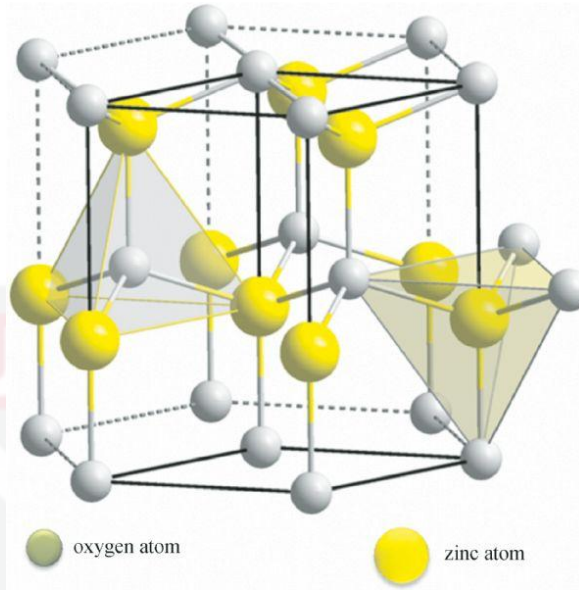


Figure 1.1. Schematic image of ZnO wurtzite crystal structure (Elf wing & Olsson, 2002)

1.3 ZnO Varistor Characteristics (I-V)

The region between the threshold voltage and a current of 100 Acm^{-2} is considered as the most important part of the varistor action. The region where the varistor voltage remains approximately constant for a large change in current is its switching curve. The varistor characteristics of this region can be described by the equation (1.1) (Jinliang et al., 2004).

$$I = KV^\alpha \quad 1.1$$

where I is a current which flows through the varistor. V is the voltage of both varistor terminals with a constant K and α is the degree of nonlinearity and it is the significant parameter for the varistor action. The α calculated from the formula:

$$\alpha = \frac{(\log J_2 - \log J_1)}{(\log E_2 - \log E_1)} \quad 1.2$$

where, E_1 and E_2 are the electric field correspond to the current density J_1 and J_2 (Aguilar et al., 2013).

The I-V characteristics of the ZnO varistor can be observed in three regions: the leakage region is considered to be the low current curve at which the I-V approaches the ohmic region, and the varistor resistance is high in this region which behaves like an open circuit (Figure 1.2). In the middle or non-ohmicity region, the varistor characteristics obey equation 1.1 above. The Final varistor curve departs from the nonlinear region and approaches the material bulk resistance. This region is called an upturn at which the varistor becomes nearly a short circuit (“GE Transient Voltage Suppression Manual, 1976.pdf,” 1976)

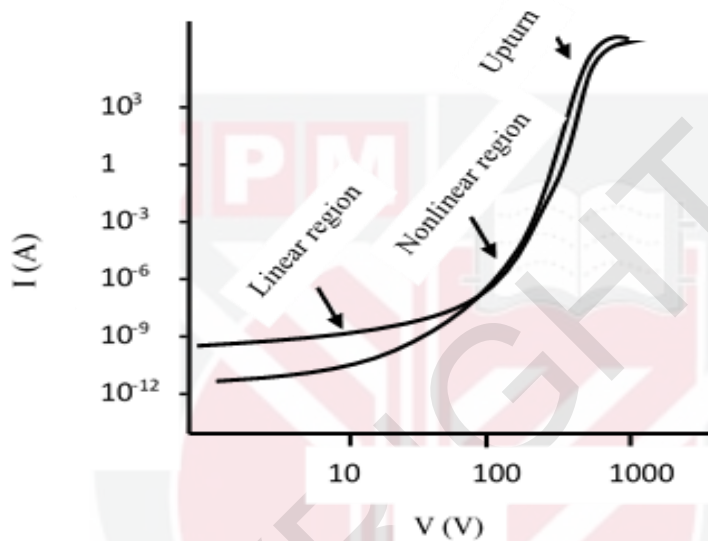


Figure 1.2. Typical I-V characteristics of ZnO varistors ceramic (Newnham, 1989)

1.4 Low Voltage Varistor

Low voltage varistor is a varistor whose exhibit high nonlinear-current voltage characteristics below it nominal voltage (Wang et al., 2008). Low voltage varistors can be achieved by increasing the size of ZnO grains, since the varistor breakdown voltage is proportional to the number of ZnO grains in series between the electrodes (Yao and Zhang, 2008). Therefore, in this work low voltage varistors can be achieved by introducing an important additive of V_2O_5 and Sb_2O_3 differently to on ZnO- Bi_2O_3 - MnO_2 which are greatly improves the ZnO grain growth. Accordingly, the current-voltage nonlinear (I-V) behavior of the varistor ceramics' response is related to thin insulating layers around the ZnO grains. Generally, the microstructure of the thin insulating layers around the ZnO grains are related to a bismuth-rich phase along the grain boundary of ZnO homojunctions (Xu et al., 2009). In the present days, electrical devices require varistors for a better functions with a relatively low breakdown electrical field intensity. There are three classes of dopants (Ahmad et al., 2012);

- (1) Those that contribute to the formation microstructure of the ZnO varistors; Bi_2O_3 is one such dopants
- (2) Those used in certifying the non-linearity of the varistor ceramic stimulate the creation of deep charge carrier traps (Co_3O_4 and MnO) and are the root of the surface potential formation of the grains
- (3) Those used as stabilizers, e.g. Sb_2O_3 , the dopant that stabilizes the ZnO varistor inter-granular layers under electrical stress and external factors, such as temperature and humidity, this raises the stability of the electrical characteristics and reliability of the varistors.

To achieve these, new varistor materials, such as Bi_2O_3 , CO_2O_3 , SrTiO_3 , TiO_3 , Sb_2O_3 , SnO_2 , V_2O_5 , etc., were required. The SrTiO_3 -based varistor ceramic is capable of high energy-absorption (Gao et al., 2008). TiO_2 is a spinel-forming dopant which is commonly used as a grain growth enhancing additive in the production of low-voltage ZnO-based varistor ceramics (Dorraj et al., 2014). It is commonly used as an enhancing additive in Bi_2O_3 -doped ZnO varistors. However, its addition causes a large spread in grain size with grain boundary voltage greater than that of Bi_2O_3 -doped ZnO varistors, V_2O_5 -doped ZnO varistors are potentially useful for the manufacture of low-voltage varistors (Hng and Knowles, 2000). In short, each of the dopants and sintering temperatures plays an important role in ZnO varistor ceramic microstructure. When subjecting the mixture via conventional method, the ceramic forms a good microstructures with several grain-boundaries as the root cause of nonlinear I-V characteristic's behavior (Nahm, 2011). Moreover, a growing attention to ZnO varistors has resulted from the fact that their nonlinear characteristic provides circuit protection; this enables them to replace "SiC- based devices", the most popular nonlinear resistor prior to the advent of the ZnO varistor (Eda 1989a).

At low currents and voltages, varistors have a high resistance; but, at higher voltages and currents, the resistance drops dramatically (Jiang et al., 2013). ZnO grains form diodes with the surrounding matrix, creating a complex array of parallel and anti-parallel diodes. At low voltage, each miniature diode between the grain boundaries has a very low voltage across it and very little current flows. The resistance drops dramatically at higher voltage and the varistor become highly conductive. Other factors such as grain size, the nature of the matrix material between the grains and the thickness of the ceramic (disk) determine the properties of the varistor.

To obtain a low voltage "turn on" and improve conductivity, most metal oxide varistors (MOV) are made as a multi-layer structure. MOVs are always bidirectional devices but are manufactured with a very wide range of current and voltage capacities for applications ranging from surge protection for high voltage transmission lines to small surface mounted devices. Therefore, varistors have a limited application in the protection of high speed signal lines against electrostatic discharge (ESD) threat (Atsumi, 2010).

1.5 Microstructure of ZnO Varistor

ZnO varistors are polycrystalline ceramics composed of semiconducting ZnO grains with the presence of grain boundaries and have a resistivity of 0.1 to 1 Ω -cm. ZnO grain boundaries are highly resistive with a non-ohmic property. The breakdown voltage of the sintered varistor is proportional to the number of grain boundaries between the two electrodes. Meaning, the breakdown voltage is proportional to the inverse of the ZnO grain size. However, material composition, sintering time, sintering temperature, and heating/cooling rates usually determine the sizes of the ZnO grains. Addition of Sb_2O_3 in ZnO varistor ceramics forms $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ spinel-phase near the grain boundaries (Eda, 1989a). The precipitation of $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ at the grain boundaries contribute to the ion migration. This suppresses the ZnO grain growth. Large breakdown voltage usually results from small grain sizes. During sintering, Bi_2O_3 acts as a liquid phase sintered and it changes to α - or β - phase. When cooling, the Bi_2O_3 rich intergranular layers (Figure 1.3). Silicon dioxide also suppresses grain growth. On the other hand, higher temperatures and longer sintering times are also attributed to large ZnO grains. This indicates significantly that the ZnO grain size depends on two parameters, sintering temperature and the sintering time; any increase in these two parameters will contribute well to an increase in grain size and fewer grain boundaries. In the same manner, some average grain sizes are obviously larger and this is mostly observed from the samples sintered at higher temperatures and for a longer time (Houabes et al., 2005). There is also a report on Ti/Sb oxide with a ratio of the two on ZnO where the average grain size was found to be 20 μm (Zhang et al., 2002). Some ZnO grains have a single twin, which is characterized by one straight line grain boundary. Secondary phases are seen mostly distributed near the grain-boundary. Gupta 1992 reported five phenomena related to grain boundaries:

- (1) The grain boundary is a muddled layer like a dislocated core, existing between two crystalline grains. The grain boundary has an open structure and can be given a distinctive width for easier accommodation of external atoms due to zinc vacancy and for the relaxation of the structure upon doping.
- (2) The grain boundary offers a rapid diffusion path, particularly for the anions. This arises from the need to transport both ionic species during the processing of ceramics, such as sintering. Secondly, many post sintering treatments, such as annealing in the varistor and the heat treatment in magnetic spinel ferrite, are known to require rapid diffusion of oxygen through the grain boundary.
- (3) The ability of the grain boundary is to segregate charges during the process of cooling by the ceramic. An appropriate segregation of charges will allow formation of a potential at the grain boundary to provide a barrier to the majority carrier flow.
- (4) The grain boundary can act as an infinite source and sink for neutral vacancies. This arises from the need to conserve mass and to make defect reactions occur at the grain boundary, as is shown for the annealing of the ZnO varistor. Note that, only the neutral vacancies can be generated or annihilated at the grain boundary at will.
- (5) The ease of vacancies and interstitials formation is larger and they have faster migrations within the grain boundaries than in the grain. The ease of formation of vacancies and interstitials is greater and their migrations are faster in the grain boundary than in the grain. Tsai and Wu (1996) reported three different features related to V_2O_5 doped specimens:

- (1) Presence of large grains dispersed in a matrix composed of small grains
- (2) There is a faster growth for large grains than small grains
- (3) The large grains contain an oblong shape

Therefore, ZnO grain growth is typically used to determine the behavior of ZnO varistor ceramics performance. It generally happens when the normal grain is enhanced by the presence of a secondary phase during sintering (see Figure 1.3). The ZnO microstructure contains the basic compounds that include spinel, pyrochlore and several Bismuth rich phases. This usually occurs from the reaction of the ZnO and the additives during the sintering process, forming pyrochlore and spinel phases as an intermediate compound. Meanwhile, the pyrochlore phase forms at a low temperature; while, the spinel phase is due to a high temperature. Furthermore, a commercial ZnO varistor has a typical grain size between 15-20 μm (Karim, 1996). The ZnO grains act as doped semiconductors. Moreover, the grain boundary regions provide barriers to electrical conduction, and Bi-rich phases are predominantly localized at triple junctions and form a continuous network throughout the varistors. ZnO varistors typically include two conduction paths. Firstly, a combination of ZnO grains and grain boundary related barriers are responsible for the varistor effect. Secondly, Bi-rich phases form at the triple junctions of ZnO grains and along the microstructure. Although, the varistor's microstructure exhibits a considerable variation depending on the nature of the fabrication, they all exhibit the characteristics of a typical ceramic prepared by liquid-phase sintering, comprising big grains with a varistor former-rich secondary phase at the nodal points (triple junctions) and intergranular layer regions (Figure 1.4).

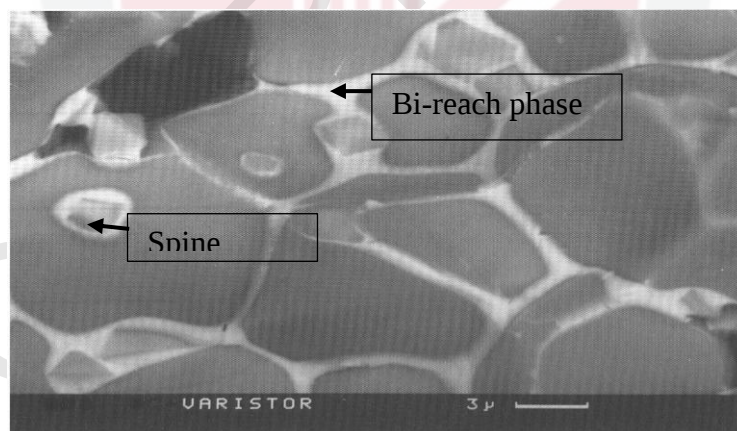


Figure 1.3. Microstructure of multiphase ZBS showing spinel phase surrounded by Bismuth (Greuter, 1995)

In the present day, the growing demand for ZnO varistor have received wide acceptance to meet the present day transient voltage suppression on electrical systems.

1.6 Application of the ZnO Varistor

ZnO varistor can be used for the purpose of:

- (1) Voltage stabilization in TV sets,
- (2) Telephone and other communication lines,
- (3) Electronic equipment protection,
- (4) Radio communication equipment,
- (5) Power supply protection, etc.

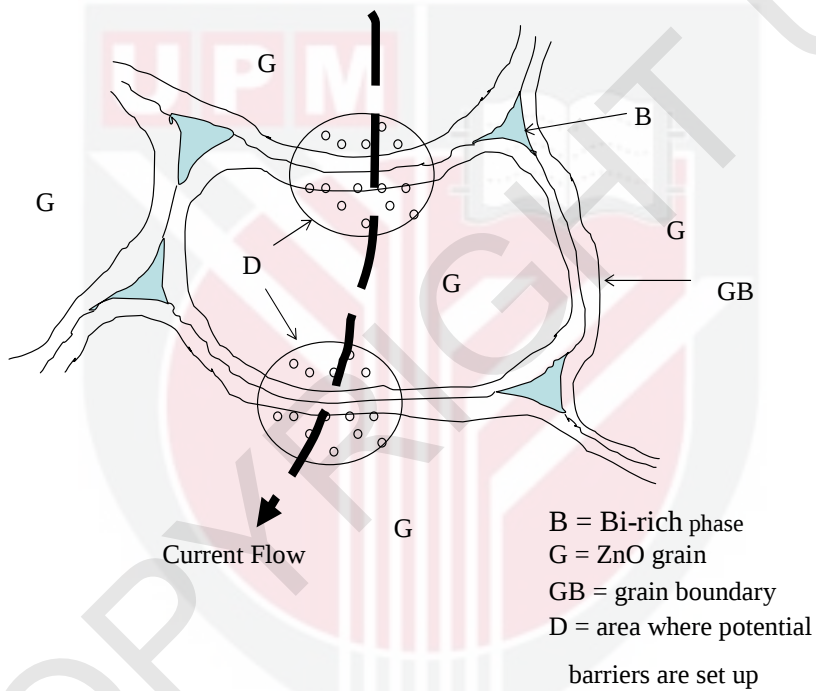


Figure 1.4. ZnO-based varistor microstructure formation (Hove, 2006)

1.7 Problem Statement

The interest of using vanadium oxide (V_2O_5) addition, instead of the usual bismuth oxide Bi_2O_3 in fabrication of low voltage ZnO based varistor arises due to its many advantages. The V_2O_5 act as a varistor former and improves the densification in the form of liquid sintering process similar but liquefied at a lower temperature than that of Bi_2O_3 . Secondly, it is expected that a good varistor ceramics stability would be provided by using antimony oxide (Sb_2O_3) compared to previous praseodymium oxide (Pr_6O_{11}) in the ZnO based varistor ceramics which was reported to have low stability and thermal runaway (Nahm, 2013). The varistor ceramic stability could be studied under the influence of DC and thermal stress simultaneously and observe the direct changes in the electrical properties. Therefore, by varying the V_2O_5 , and Sb_2O_3 contents at various sintering temperature, it is expected that the optimum microstructure that contribute to reasonably high nonlinear electrical properties as well as improving the stability could be obtained.

1.8 Objectives

The objectives of this work were essentially based on the efforts made to improve the capability of ZnO low voltage varistor ceramics. Much of this work was devoted to probe the effects of sintering temperature and the dopants. Some other related processing characteristics were also calculated to identify the donating factors that affect the performance of the ZnO varistor.

The objectives of this work were as follows:

- (1) To study the effect of a small interval sintering temperature on the electrical and microstructural properties of V_2O_5 doped ZnO- Bi_2O_3 - Sb_2O_3 - MnO_2 low voltage varistor ceramics.
- (2) To evaluate the stability of V_2O_5 and Sb_2O_3 on ZnO- Bi_2O_3 - MnO_2 low voltage varistor ceramics against DC and thermal stresses and compare which of the dopant contribute a good stability of the varistor ceramics.

1.9 Significance of the Study

This research was required because the J-E characteristic of a ZnO-based varistor advances substantially due to the type of material oxide used as dopants and also the sintering temperature. However, this work will contribute to the deviation of the microstructure, which determines the electrical behavior, typically, the J-E characteristic of ZnO low voltage varistor ceramics. The J-E characteristic deviation is in three areas: the ohmic region, the nonlinear region and the up-turn region (see Figure 1.2). Deviation in the leakage area of the J-E characteristic means that when the ZnO-based varistor has a higher leakage current it may eventually lead to the degradation of the J-E characteristic.

In the breakdown region, the responsible feature for the uncertainty in the active region is largely thermal in nature with a finite gradient of the J-E characteristic of this region. Thermal-based breakdown also supports degradation of the J-E characteristic of varistor ceramics.

The Upturn region of the J-E characteristic indicates that if the current flow is greater than the eventual, the varistor no longer compromises the required protection since the varistor switches from highly conductive to highly resistive, which is not desirable.

1.10 Scope of the Study

This research work has been limited to the preparation of $\text{ZnO-Bi}_2\text{O}_3\text{-MnO}_2$ varistor ceramics by doping two different ionic oxides (V_2O_5 and Sb_2O_3) via a conventional technique. The effect doping and sintering temperature on microstructure, electrical properties and DC degradation behavior were investigated.

1.11 Hypothesis

The hypothesis used in this experiment is to fine the relations between sintering temperature and doping. The hypothesis of this research include the following:

- (1) Through optimizing the sintering temperature and composition of V_2O_5 the nonlinear electrical properties would improve.
- (2) Varistor would have good stability after subjecting the ceramics to DC electrical and thermal stresses.

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