UNIVERSITI PUTRA MALAYSIA

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

DAHIRU UMAR

FS 2016 34

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

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

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

By

DAHIRU UMAR

May 2016

Chairman : Professor Azmi Bin Zakaria, PhD
Faculty : Science

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, $0.7Bi_2O_3$, $0.3Sb_2O_3$, 0.7 MnO_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 °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°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 8.82×10^{-6} $mAh^{-1/2}$ and α decreases after the stress test. Subsequently, the stability of the doped samples containing Sb_2O_3 improves to Kt value of 5.8×10^{-7} $mAh^{-1/2}$ for sample with 0.6 mol% Sb_2O_3. The Kt improves further to 2.02×10^{-7} $mAh^{-1/2}$ 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 DEGRADACI DC PADA SERAMIK VARISTOR BERVOLTAN RENDAH ZNO-BI_2O_3-MNO_2

Oleh

DAHIRU UMAR

Mei 2016

Pengerusi : Profesor Azmi Bin Zakaria, PhD
Fakulti : Sains

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, 0.7 MnO_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 °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 °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 ditunjukan 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 Kt 8.82×10^{-6} $mAh^{-1/2}$ dan nilai α menurun selepas ujian tegasan Seterusnya bagi sampel yang mengandungi Sb_2O_3 didapati bartambah baik kepada nilai Kt 5.8×10^{-7} $mAh^{-1/2}$ bagi sampel yang didop dengan 0.6 mol% Sb_2O_3. Kt terus bertambah baik kepada 2.02×10^{-7} $mAh^{-1/2}$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.

ACKNOWLEDGEMENTS

All praise be to Allah the beneficent and the merciful for his blessing and the strength upon prosperous achievement of this research work. I would like to use this medium to express my deepest appreciation to my supervisor, Professor Dr. Azmi Zakaria for his patience, diligent supervision, suggestions and guidance that he has given me through the research period. His support and encouragement has leaded me to the success of my master's study. I am highly impressed to his immense effort in introducing me to the field of material science. His competence in this field has really motivated me to pursue my future academic carrier in this unique field. This research would not have been ended perfectly without his guidance, constructive criticism and cordial supervision.

Together with him, I would like to express profound gratitude to my co-supervisor Dr. Che Azurahanim Che Abdullah. I also thank to Dr. Yadollah Abdollah, Dr. Wan Rafiza binti Wan Abdullah for their assistance and advice given me to during my lab work. I also expressed word of thankfulness to my lab mates in persons of Rosno Kinsu, Mohammed Abdulazeez Nareeman, Masoumeh Dorraj, Ismail Ibrahim Lakin. Raheleh Mohammadi and Dr. Munir Noroozi.

I wish to express my profound gratitude to my father Alhaji Umaru Kyari, my mother Habiba, brothers and sisters for their immense prayers and contribution throughout this study. My gratitude goes to my wife, Salma Nura Sallau and daughters, Khadija Dahiru Umaru, Tsaharatu Dahiru Umaru, Mohammad Dahiru Umaru and Hafsat Dahiru Umaru for their patience and prayers.

I certify that a Thesis Examination Committee has met on 10 May 2016 to conduct the final examination of Dahiru Umar on his thesis entitled "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" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

Halimah bt Mohamed Kamari, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Chen Soo Kien, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Mat Johar Abdullah, PhD
Professor
School of Physics
Universiti Sains Malaysia
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 28 June 2016

This thesis was submitted to the senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory committee were as follows:

Azmi bin Zakaria, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Che Azurahanim Che Abdullah, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- This thesis is my original work
- Quotations, illustrations and citations have been duly referenced
- The thesis has not been submitted previously or concurrently for any other degree at any institutions
- Intellectual property form the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the University Putra Malaysia (Research) Rules 2012
- Written permission must be owned from supervisor and deputy vice – chancellor (Research and innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, models, proceedings, popular writing, seminar paper, manuscripts, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- There is no plagiarism or data falsification/ fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software

Signature: ____________________ Date: ____________________

Name and matric No.: Dahiru Umar, GS 39972

Declaration by Members of Supervisory Committee

This is to confirm that:

- The research conducted and the writing of this thesis was under our supervision;
- Supervision responsibility as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) were adhered to.

Signature ______________________________
Name of Chairman of Supervisory Committee: Professor Dr. Azmi bin Zakaria

Signature ______________________________
Name of Member of Supervisory Committee: Dr. Che Azurahanim Che Abdullah

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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_2O_3 Sb_2O_3 MnO_2
ZVBM	ZnO V_2O_3 Bi_2O_3 Sb_2O_3 MnO_2

LIST OF SYMBOLS

θ (°)	Diffraction angle
A	Nonlinear coefficient
J_L (mA/cm2)	Leakage current density
E_b (eV)	Breakdown voltage
ω (m)	Depletion width
T (°C)	Absolute temperature
A (A/cm^2K^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
$\rho_{theoretical}$ (g/cm^3)	Theoretical density
E (V/mm)	Electric field
λ (nm)	X-ray wavelength
K_T ($mA/h^{½}$)	Degradation rate coefficient
Zn_i	Zinc interstitial
O_i	Oxygen interstitial
V_{Zn}	Zinc vacancy
$t^{½}$ ($min^{½}$)	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/cm^3 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.

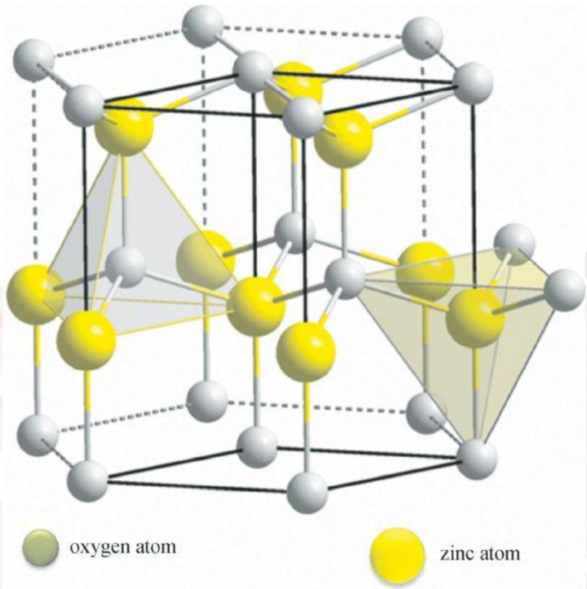

Figure 1.1. Schematic image of ZnO wurtzite crystal structure (Elf wing & Olsson, 2002)

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 it switching curve. The varistor characteristics of this region can be described by the equation (1.1) (Jinliang et al., 2004).

$$I\ KV^{\alpha} \qquad 1.1$$

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:

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

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)

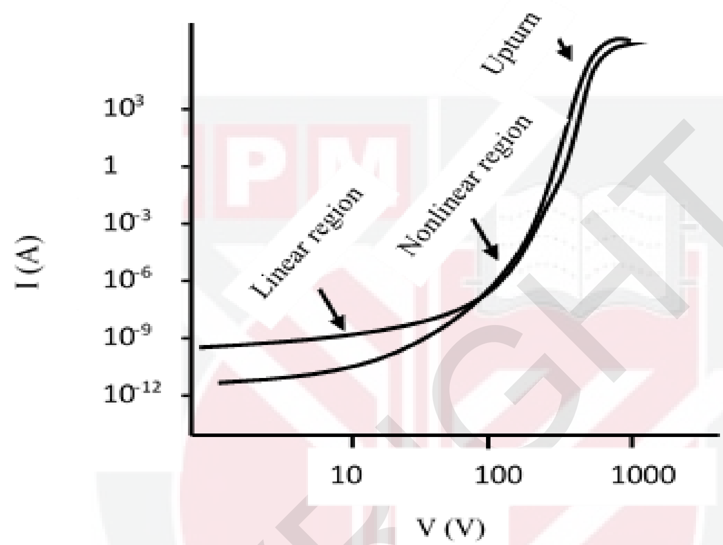

Figure 1.2. Typical I-V characteristics of ZnO varistors ceramic (Newnham, 1989)

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 $Zn_7Sb_2O_{12}$ spinel-phase near the grain boundaries (Eda, 1989a). The precipitation of $Zn_7Sb_2O_{12}$ 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).

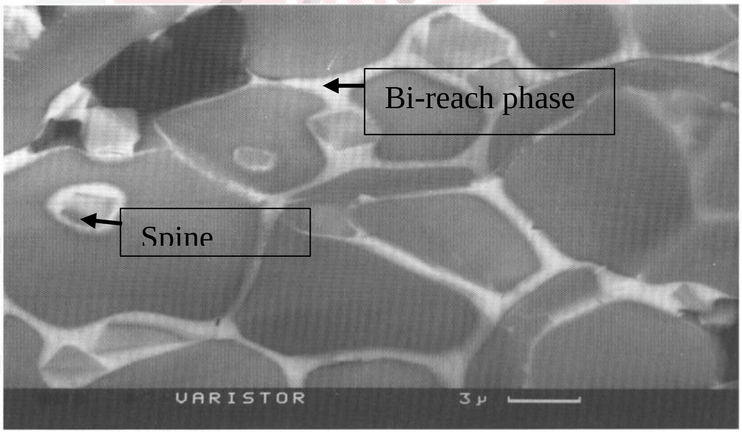

Figure 1.3. Microstructure of multiphase ZBS showing spinel phase surrounded by Bismuth (Greuter, 1995)

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.

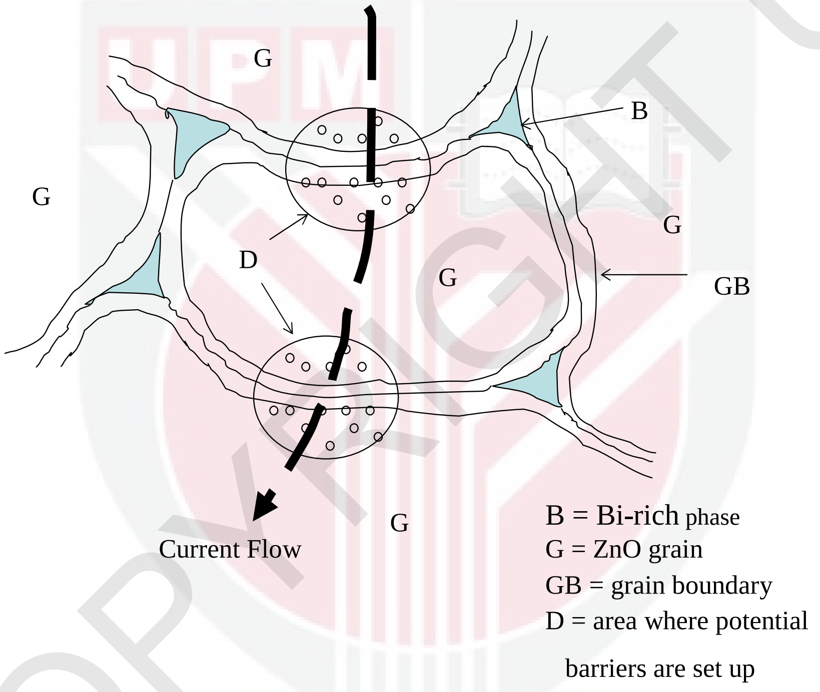

Figure 1.4. ZnO-based varistor microstructure formation (Hove, 2006)

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 runway (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 form 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 ZnO-Bi_2O_3-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.

REFERENCES

Abdullah, W.R.W., Zakaria, A. and Ghazali, M.S.M. (2012). Synthesis mechanism of low-voltage praseodymium oxide doped zinc oxide varistor ceramics prepared through modified citrate gel coating. *International Journal of Molecular Sciences*. *13*(4): 5278–5289.

Aguilar-Martínez, J. A, Pech Canul, M. I., Hernández, M. B., Glot,A B., Rodríguez, E. and García Ortiz, L. (2013). Effect of sintering temperature on the electric properties and microstructure of SnO_2–Co_3O_4–Sb_2O_5–Cr_2O_3 varistor ceramic. *Ceramics International*. *39*(4): 4407–4412.

Ahmad, M. Bin, Fatehi, A., Zakaria, A., Mahmud, S. & Mohammadi, S. A. (2012). Fabrication of an electrically-resistive, varistor-polymer composite. *International Journal of Molecular Sciences*. *13*(12): 15640–15652.

Akinnifesi, J. O.; Erinfolami, F. B. and Akinwunmi, O. O. (2014). Influence of microstructure on the non-ohmic behavior of zinc oxide varistor ceramics prepared by direct mixing of constituent phases. *Ife Journal of Science*. *16*(1): 91–98.

Alles, A. B. and Burdick, V. L. (1991). The effect of liquid-phase sintering on the properties of Pr_6O_{11}-based ZnO varistors. *Journal of Applied Physics*. *70*(11): 6883.

Asokan, T. and Freer, R. (1994). Dependence of ZnO varistor grain boundary resistance on sintering temperature. *Journal of Materials Science Letters*. *13*(13): 925–926.

Asokan, T., Iyengar, G. N. K. and Nagabhushana, G. R. (1987). Studies on microstructure and density of sintered ZnO-based non-linear resistors. *Journal of Materials Science*. *22*(6): 2229–2236.

Atsumi, T. (2010). Measurement of switching voltage of zinc oxide varistors between pre-breakdown and breakdown regions. *Journal of the Ceramic Society of Japan*. *118*(1374): 161–163.

Bai, S. and Tseng, T. (1995). Degradation Phenomena Due to Impulse-Current in Zinc Oxide Varistors. *Journal of the American Ceramic Society*. *78*(10): 2685–2689.

Bernik, S., Branković, G., Rustja, S., Žunić, M., Podlogar, M. and Branković, Z. (2008). Microstructural and compositional aspects of ZnO-based varistor ceramics prepared by direct mixing of the constituent phases and high-energy milling. *Ceramics International*. *34*(6): 1495–1502.

Bernik, S., Daneu, N. and Rečnik, A. (2004). Inversion boundary induced grain growth in TiO_2 or Sb_2O_3 doped ZnO-based varistor ceramics. *Journal of the European Ceramic Society*. *24*(15-16): 3703–3708.

Bernik, S., Maček, S. and Ai, B. (2001). Microstructural and electrical characteristics of Y_2O_3-doped ZnO–Bi_2O_3-based varistor ceramics. *Journal of the European Ceramic Society*. *21*(10-11): 1875–1878.

Bernik, S., Podlogar, M., Daneu, N. and Rečnik, A. (2008). Tailoring the microstructure of ZnO-based ceramics. *Materiali in Tehnologije*. *42*(2): 69–77.

Bradt, R. C. and Burkett, S. L. (1998). Microstructural control of zinc oxide varistor ceramics. In *Ceramic Microstructures. New York*. Springer.

Calestani, G., Marghignani, L., Montenero, A. and Bettinelli, M. (1986). DC conductivity of ZnO-V_2O_5 glasses. *Journal of Non-Crystalline Solids*. *86*(3): 285–292.

Chen, C. S. (2003). Effect of dopant valence state of Mn-ions on the microstructures and nonlinear properties of microwave sintered ZnO-V_2O_5 varistors. *Journal of Materials Science*. *38*(5): 1033–1038.

Chen, G., Li, J., Chen, X., Kang, X. and Yuan, C. (2015). Sintering temperature dependence of varistor properties and impedance spectroscopy behavior in ZnO based varistor ceramics. *Journal of Materials Science: Materials in Electronics*. *26*(4): 2389–2396.

Chen, Y. C., Shen, C. Y., Chen, H. Z., Wei, Y. F. and Wu, L. (1991). Grain growth and electrical properties in ZnO varistors with various valence states of additions. *Japanese Journal of Applied Physics*. *30*(1): 84–90.

Chiang, Y.-M. (1982). Compositional changes adjacent to grain boundaries during electrical degradation of a ZnO varistor. *Journal of Applied Physics*. *53*(3): 1765.

Cho, S., Lee, H. and Kim, H. (1997). Effect of chromium on the phase evolution and microstructure of ZnO doped with bismuth and antimony. *Journal of Materials Science*. *32*(16): 4283–4287.

Choi, J. S. and Yo, C. H. (1976). Study of the nonstoichiometric composition op zinc oxide. *Journal of Physics and Chemistry of Solids*. *37*(12): 1149–1151.

Clarke, D. R. (2004). Varistor Ceramics. *Journal of the American Ceramic Society*. *82*(3): 485–502.

Cordaro, J. F., Shim, Y. and May, J. E. (1986). Bulk electron traps in zinc oxide varistors. *Journal of Applied Physics*. *60*(12): 4186–4190.

D'Amico, N. R., Cantele, G. and Ninno, D. (2012). First-principles calculations of clean and defected ZnO surfaces. *The Journal of Physical Chemistry C*. *116*(40): 21391–21400.

Daneu, N. and Rec, A. (2003). Grain Growth Control in SbO -Doped Zinc Oxide. *Journal of the American Ceramic Society*. *86*(8): 1379–1384.

Daneu, N., Rečnik, A. and Bernik, S. (2003). Grain Growth Control in Sb_2O_3-Doped Zinc Oxide. *Journal of the American Ceramic Society*. *86*(8): 1379–1384.

de la Rubia, M. A., Peiteado, M., Fernandez, J. F. and Caballero, A. C. (2004). Compact shape as a relevant parameter for sintering ZnO–Bi_2O_3 based varistors. *Journal of the European Ceramic Society*. *24*(6): 1209–1212.

Dorraj, M., Zakaria, A., Abdollahi, Y., Hashim, M. and Moosavi, S. (2014). Optimization of Bi_2O_3 , TiO_2 , and Sb_2O_3 Doped ZnO-Based Low-Voltage Varistor Ceramic to Maximize Nonlinear Electrical Properties. Scientfic world journal. (10): 1155.

Durán, P., Capel, F., Tartaj, J. and Moure, C. (2002). A strategic two-stage low-temperature thermal processing leading to fully dense and fine-grained doped-ZnO varistors. *Advanced Materials*. *14*(2): 137–141.

Zhigang Z. F.. (2010). Sintering of Advance Materials Fundamentals and Processes. New Delhi. Woodhead Publishing

Eda, K. (1978). Conduction mechanism of non-Ohmic zinc oxide ceramics. *Journal of Applied Physics*. *49*(5): 2964.

Eda, K. (1989a). Zinc oxide varistors. *IEEE Electrical Insulation Magazine*. *5*(6): 28–32.

Eda, K. (1989b). Zinc oxide varistors. *IEEE Electrical Insulation Magazine*. *5*(6): 28–30.

Eda, K., Iga, A. and Matsuoka, M. (1980). Degradation mechanism of non-Ohmic zinc oxide ceramics. *Journal of Applied Physics*. *51*(5): 2678.

Einzinger, R. (1978). Metal oxide varistor action -a homojunction breakdown mechanism. *Applications of Surface Science*. *1*(3): 329–340.

Ezhilvalavan, S. and Kutty, T. R. N. (1996). Dependence of non-linearity coefficients on transition metal oxide concentration in simplified compositions of ZnO+Bi_2O_3+MO varistor ceramics (M=Co or Mn). *Journal of Materials Science: Materials in Electronics*. *7*(2): 11–14.

Greuter and Blatter. (1990). Contact us My IOPscience Electrical properties of grain boundaries in polycrystalline compound semiconductors. *IOP Science*. 5(2): *111*.

Fan, J. and Freer, R. (1994). Deep level transient spectroscopy of zinc oxide varistors doped with aluminum oxide and/or silver oxide. *Journal of the American Ceramic Society*. *77*(10): 2663–2668.

Fayat, J. and Castro, M. S. (2003). Defect profile and microstructural development in SnO_2-based varistors. *Journal of the European Ceramic Society*. *23*(10): 1585–1591.

Feng, H., Peng, Z., Fu, X., Fu, Z., Wang, C., Qi, L. and Miao, H. (2010). Effect of TiO_2 doping on microstructural and electrical properties of ZnO–Pr_6O_{11}-based varistor ceramics. *Journal of Alloys and Compounds*. *497*(1): 304–307.

Gambino, J. P., Kingery, W. D., Pike, G. E., Levinson, L. M. and Philipp, H. R. (1989). Effect of Heat Treatments on the Wetting Behavior of Bismuth-Rich Intergranular Phases in ZnO:Bi:Co Varistors. *Journal of the American Ceramic Society*. *72*(4): 642–645.

Gao, H., Zhang, Z., Lai, Y., Li, J. and Liu, Y. (2008). Structure characterization and electrochemical properties of new lithium salt Lio Dfd for electrolyte of lithium ion batteries. *J. Cent. South Univ. Technol. (Engl. Ed.)*. *15*(6): 830–834.

GE Transient Voltage Suppression Manual 1976.pdf. *(Electronic Park, Syracuse, New york 13201).*

Greuter, F. (1995a). Electrically active interfaces in ZnO varistors. *Solid State Ionics*. *75*: 67–78.

Greuter, F. (1995b). Electrically active interfaces in ZnO varistors. *Solid State Ionics*, *75*(94), 67–78.

Guo, R., Fang, L., Zhou, H., Chen, X., Chu, D., Chan, B. and Qin, Y. (2013). $SbVO_4$ doped ZnO–V_2O_5-based varistor ceramics: microstructure, electrical properties and conductive mechanism. *Journal of Materials Science: Materials in Electronics*. *24*(8): 2721–2726.

Gupta, T. K. (1971). Inhibition of Grain Growth in ZnO. *Journal of the American Ceramic Society*. *54*(8): 413–414.

Gupta, T. K. (1981). Current instability phenomena in ZnO varistors under a continuous ac stress. *Journal of Applied Physics*. *52*(6): 4104.

Gupta, T. K. (1990). Application of Zinc Oxide Varistors. *Journal of the American Ceramic Society*. *73*(7): 1817–1840.

Gupta, T. K. (1992). Microstructural engineering through donor and acceptor doping in the grain and grain boundary of a polycrystalline semiconducting ceramic. *Journal of Materials Research*. *7*(12): 3280–3295.

Gupta, T. K. and Carlson, W. G. (1982). Barrier voltage and its effect on stability of ZnO varistor. *Journal of Applied Physics*. *53*(11): 7401–7409.

Gupta, T. K. and Carlson, W. G. (1985). A Grain-Boundary Defect Model For Instability Stability of a ZnO Varistor. *Journal Of Materials Science*. *20*(10): 3487–3500.

Gupta, T. K. and Coble, R. L. (1968). Sintering of ZnO: II, Density Decrease and Pore Growth During the Final Stage of the Process. *Journal of the American Ceramic Society*. *51*(9): 525–528.

He, J., Hu, J. and Lin, Y. (2008). ZnO varistors with high voltage gradient and low leakage current by doping rare-earth oxide. *Science in China, Series E: Technological Sciences*. *51*(6): 693–701.

He, J., Zeng, R., Chen, Q., Chen, S., Guan, Z., Han, S. W. and Cho, H. G. (2004). Nonuniformity of Electrical Characteristics in Microstructures of ZnO Surge Varistors. *IEEE Transactions on Power Delivery*. *19*(1): 138–144.

Hng, H. H. and Chan, P. L. (2002). Effects of MnO_2 doping in V_2O_5-doped ZnO varistor system. *Materials Chemistry and Physics*. *75*(1-3): 61–66.

Hng, H. H. and Chan, P. L. (2004). Microstructure and current–voltage characteristics of ZnO–V_2O_5–MnO_2 varistor system. *Ceramics International*. *30*(7): 1647–1653.

Hng, H. H. and Halim, L. (2003a). Grain growth in sintered ZnO – 1 mol % V_2O_5 ceramics. *Materials Letters*. *57*(8): 1411–1416.

Hng, H. H. and Halim, L. (2003b). Grain growth in sintered ZnO–1 mol% V_2O_5 ceramics. *Materials Letters*. *57*(8): 1411–1416.

Hng, H. H. and Knowles, K. M. (1999). Characterisation of $Zn_3(VO_4)_2$ Phases in V_2O_5 -doped ZnO Varistors. Journal of the European Ceramic Society. *19*(7): 721–726.

Hng, H. H. and Knowles, K. M. (2000). Microstructure and Current–Voltage Characteristics of Multicomponent Vanadium-Doped Zinc Oxide Varistors. *Journal of the American Ceramic Society*. *83*(10): 2455–2462.

Hng, H. H. and Tse, K. Y. (2003). Grain growth of ZnO in binary ZnO-V_2O_5 ceramics. *Journal of Materials Science*. *38*(11): 2367–2372.

Hng, H. H. and Tse, K. Y. (2003). Grain growth of ZnO in binary ZnO-V_2O_5 ceramics. *Journal of Materials Science*. *38*(11): 2367–2372.

Houabes, M., Bernik, S., Talhi, C. and Bui, A. (2005). The effect of aluminium oxide on the residual voltage of ZnO varistors. *Ceramics International*. *31*(6): 783–789.

Houabes, M. and Metz, R. (2007). Rare earth oxides effects on both the threshold voltage and energy absorption capability of ZnO varistors. *Ceramics International*. *33*(7): 1191–1197.

Hove, M. (2006). Improvement of the V-I Characteristic of Zinc oxide (ZnO) Based Metal oxide varistors (MOVs) Using Silicon Telluride (SiTe 2) and Lanthanum. http://hdl.hndle.net/10539/7047

Hozer, L. (1994). *Semiconductor ceramics: grain boundary effects*. Prentice Hall. London.

Huang, J.-L. and Li, K.-B. (2011). The effects of heat treatment on B_2O_3-contained ZnO varistor. *Journal of Materials Research*. *9*(06): 1526–1532.

Hwang, J.-H., Mason, T. O. and Dravid, V. P. (1994). Microanalytical Determination of ZnO Solidus and Liquidus Boundaries in the ZnO-Bi_2O_3 System. *Journal of the American Ceramic Society*. *77*(6): 1499–1504.

Ik, H., Jin, O. and Kim, H. (2006). Effect of Sb_2O_3 addition on the varistor characteristics of ZnO-Bi_2O_3 -ZrO_2 -MtrO (M tr = Mn , Co). *J Electroceram*. *17:* 1083–1086.

Inada, M. (1978). Crystal Phases of Nonohmic Zinc Oxide Ceramics. *Japanese Journal of Applied Physics*. *17*(1): 1.

Inada, M. (1980). Formation Mechanism of Nonohmic Zinc Oxide Ceramics. *Japanese Journal of Applied Physics*. *19*(3): 409.

Izoulet, A., Guillemet-Fritsch, S., Estournès, C. and Morel, J. (2014). Microstructure control to reduce leakage current of medium and high voltage ceramic varistors based on doped ZnO. *Journal of the European Ceramic Society*. *34*(15): 3707–3714.

Jiang, F., Peng, Z., Zang, Y. and Fu, X. (2013). Progress on rare-earth doped ZnO-based varistor materials. *Journal of Advanced Ceramics*. *2*(3): 201–212.

Jinliang, H., Jun, H. and Qingheng, C. (2005). Influence of Rare-Earth Oxide Additives on Electrical Performance of ZnO Varistor. *Rare Metal Materials and Engineering*. *34*(2): 1129.

Johnson, J. L. (2010). *Sintering of Advanced Materials*. Woodhead Publishing Limited, Abington Hall Granta Park, Great Abington, Cambriedge CB21 6AH, UK.

Ju, J. H., Wang, H. and Xu, J. W. (2011). Grain Boundary Characteristics of 0.01 mol%V_2O_5-Doped ZnO-Bi_2O_3-Based Varistor Ceramics. *Advanced Materials Research*. *320*: 240–243.

Ju, J., Wang, H. and Xu, J. (2011). Microstructures and electrical properties of V_2O_5-doped ZnO–Bi_2O_3–Co_2O_3–$MnCO_3$–TiO_2 low-voltage varistor ceramics. *Journal of the Chinese Ceramic Society*. *39*(11): 1813–1818.

Karim, A N. M. (1996). Effect of Compaction Parameters and Sintering C onfigurations on the Performance of ZnO Varistor. Advance Methods in Material Processing Defects. 143–153

Ke, L. E. I., Yuan, Y. and Zhao, H. U. A. (2013). Influence of Rare-Earth Doping on the Electrical. *Ceramics,Silikáty*. *57*(1): 53–57.

Khafagy, A. H., El-Rabaie, S. M., Dawoud, M. T. and Attia, M. T. (2014). Microhardness , microstructure and electrical properties of ZVM ceramics. *Journal of Advanced Ceramics*. *3*(4): 287–296.

Kharchouche, F., Belkhiat, D. E. C. and Belkhiat, S. (2013). Non-linear coefficient of $BaTiO_3$-doped ZnO varistor. *IET Science, Measurement & Technology*. *7*(6): 326–333.

Kim, C.-H. and Kim, J.-H. (2004). Microstructure and electrical properties of ZnO–ZrO_2–Bi_2O_3–M_3O_4 (Co, Mn) varistors. *Journal of the European Ceramic Society*. *24*(8): 2537–2546.

Kim, J., Kimura, T. and Yamaguchi, T. (1989). Sintering of Sb_2O_3-doped ZnO. *Journal of Materials Science*. *24*(1): 213–219.

Kim, M. S., Kim, H. T., Chi, S. S., Kim, T. E., Shin, H. T., Kang, K. W. Kim, D. M. (2003). Distribution of Interface States in MOS Systems Extracted by the Subthreshold Current in Mosfets under Optical Illumination. Journal of the Korean Physical Society. *43*(5): 873–878.

Kingery, W.D. and Francois, B. (1968). The sintering of crystalline oxides. I. Interactions between grain boundaries and pores. In *pp 471-98 of Sintering and Related Phenomena. Proceedings of the International Conference, Univ. of Notre Dame. Kuczynski, GC Hooton, NA Gibbon, CF (eds.). New York, Gordon and Breach*. Massachusetts Inst. of Tech., Cambridge.

Kobayashi, K. I., Wada, O., Kobayashi, M. and Takada, Y. (1998). Continuous existence of bismuth at grain boundaries of zinc oxide varistor without intergranular phase. *Journal of the American Ceramic Society*. *81*(8): 2071–2076.

Kramer, S. (1995). A novel titanate-based oxygen ion conductor: $Gd_2Ti_2O_7$. *Solid State Ionics*. *82*(1-2): 15–23.

Kuo, C., Chen, C. and Lin, I. (1998). Microstructure and Nonlinear Properties of Microwave-Sintered ZnO – V_2O_5 Varistors : I , Effect of V_2O_5 Doping. *Journal of the American Ceramic Society*. *81(11)*: 2942–2948.

Lanfredi, S., Nobre, M. A D. L. and Sp, S. C. (2003). Dielectric Dispersion in Bi 3 $Zn_2Sb_3O_{14}$ Ceramic : a Pyrochlore Type Phase. Material Research. *6*(2): 157–161.

Lao, Y. W., Kuo, S. T. and Tuan, W. H. (2007). Effect of Bi_2O_3 and Sb_2O_3 on the grain size distribution of ZnO. *Journal of Electroceramics*. *19*(2-3): 187–194.

Leach, C., Ling, Z. and Freer, R. (2000a). The effect of sintering temperature variations on the development of electrically active interfaces in zinc oxide based varistors. *Journal of the European Ceramic Society*. *20*(16): 2759–2765.

Leach, C., Ling, Z. and Freer, R. (2000b). The effect of sintering temperature variations on the development of electrically active interfaces in zinc oxide based varistors. *Journal of the European Ceramic Society*. *20*(16): 2759–2765.

Lee, W. S., Chen, W. T., Lee, Y. C., Yang, T., Su, C. Y. and Hu, C. L. (2007). Influence of sintering on microstructure and electrical properties of ZnO-based multilayer varistor (MLV). *Ceramics International*. *33*(6): 1001–1005.

Lee, Y. S., Liao, K. S. and Tseng, T. Y. (1996). Microstructure and Crystal Phases of Praseodymium Oxides in Zinc Oxide Varistor Ceramics. *Journal of the American Ceramic Society*. *79*(9): 2379–2384.

Leite, E. R., Nobre, M. A. L., Longo, E. and Varela, J. a. (1996). Microstructural development of ZnO varistor during reactive liquid phase sintering. *Journal of Materials Science*. *31*(20): 5391–5398.

Levinson, L. M. and Philipp, H. R. (1975). The physics of metal oxide varistors. *Journal of Applied Physics*. *46*(3): 1332.

Levinson, L. and Philipp, H. (1977). ZnO Varistors for Transient Protection. *IEEE Transactions on Parts, Hybrids, and Packaging*. *13*(4): 338–343.

Li, H. F., Xu, Y. C., Wang, S. L. and Wang, L. Q. (1995). Electrical characteristics and pulse degradation of ZnO varistors with Nb_2O_5 dopant. *Journal of Materials Science*. *30*(20): 5161–5165.

Lionel, L. M. and Philipp, H. R. (1986). Zinc oxide varistors-a review. *Ceram. Bull*. *65*(4): 639–646.

Liu, H., Ma, X., Jiang, D. and Shi, W. (2007). Microstructure and electrical properties of Y_2O_3-doped ZnO-based varistor ceramics prepared by high-energy ball milling. *Journal of University of Science and Technology Beijing, Mineral, Metallurgy, Material*. *14*(3): 266–270.

Liu, J., He, J. L., Hu, J. and Long, W. C. (2011). The dependence of sintering temperature on Schottky barrier and bulk electron traps of ZnO varistors. *Science China Technological Sciences*. *54*(2): 375–378.

Lu, C. H., Chyi, N., Wong, H. W. and Hwang, W. J. (2000). Effects of additives and secondary phases on the sintering behavior of zinc oxide-based varistors. *Materials Chemistry and Physics*. *62*(2): 164–168. 2

Mahan, G. D., Levinson, L. M. and Philipp, H. R. (1979). Theory of conduction in ZnO varistors. *Journal of Applied Physics*. *50*(4): 2799.

Matsuoka, M. (1971). Nonohmic Properties of Zinc Oxide Ceramics. *Japanese Journal of Applied Physics*. *10*(6): 736–746.

Mikrostruktur, S. and Zno, T. S. (2013). Microstructural and Nonlinear Electrical Properties of ZnO Ceramics with Small Amount of MnO_2 Dopant. *Sains Malaysia*, *42*(8), 1139–1144.

Mirzayi, M. and Hekmatshoar, M. H. (2013). Effect of V_2O_5 on electrical and microstructural properties of ZnOceramics. *Physica B: Condensed Matter*. *414*: 50–55.

Molak,a, Paluch, M., Pawlus, S., Klimontko, J., Ujma, Z. and Gruszka, I. (2005).Ceramics. *Journal of Physics D: Applied Physics*. *38*(9): 1450–1460.

Moon, P. K. and Tuller, H. L. (1988). Ionic conduction in the $Gd_2Ti_2O_7$−$Gd_2Zr_2O_7$ system. *Solid State Ionics*. (*28)30*: 470–474.

Nahm, C. (2001). The nonlinear properties and stability of, (January), 182–187.

Nahm, C. W. (2008). Improvement of electrical properties of V_2O_5 modified ZnO ceramics by Mn-doping for varistor applications. *Journal of Materials Science: Materials in Electronics*. *19*(10): 1023–1029.

Nahm, C. W. (2009). Effect of MnO_2 addition on microstructure and electrical properties of ZnO-V_2O_5-based varistor ceramics. *Ceramics International*. *35*(2): 541–546.

Nahm, C. W. (2010). Effect of dopant (Al, Nb, Bi, La) on varistor properties of ZnO-V_2O_5-MnO_2-Co_3O_4-Dy_2O_3 ceramics. *Ceramics International*. *36*(3): 1109–1115.

Nahm, C. W. (2015). Effect of small changes in sintering temperature on varistor properties and degradation behavior of V–Mn–Nb–Gd co-doped zinc oxide ceramics. *Transactions of Nonferrous Metals Society of China*. *25*(4): 1176–1184.

Nahm, C. W. (2007). Microstructure and varistor properties of ZnO–V_2O_5–MnO_2-based ceramics. *Journal of Materials Science*. *42*(19): 8370–8373.

Nahm, C. W. (2011). Microstructure, electrical properties, and aging behavior of ZnO–Pr_6O_{11}–CoO–Cr_2O_3–Y_2O_3–Er_2O_3 varistor ceramics. *Ceramics International*. *37*(8): 3049–3054.

Nahm, C. W. (2012). Effect of sintering process on electrical properties and ageing behavior of ZnO–V_2O_5–MnO_2–Nb_2O_5 varistor ceramics. *Journal of Materials Science: Materials in Electronics*. *23*(2): 457–463.

Nahm, C. W. (2013). Characteristics of ZnO- V_2O_5- MnO_2- Nb_2O_5- Er_2O_3 semiconducting varistors with sintering processing. *Materials Science in Semiconductor Processing*. *16*(3): 778–785.

Nahm, C. W. (2013). Low-temperature sintering effect on varistor properties of ZnO–V_2O_5–MnO_2–Nb_2O_5–Bi_2O_3 ceramics. *Ceramics International*. *39*(2): 2117–2121.

Nahm, C. W., Park, J. A., Shin, B. C. and Kim, I. S. (2004). Electrical properties and DC-Ceram. Int. 30, 1009 (2004). *Ceramics International*. *30*(6): 1009–1016.

Nahm, C.-W., Shin, B. C. and Min, B. H. (2003). Microstructure and electrical properties of Y_2O_3-doped ZnO–Pr_6O_{11}-based varistor ceramics. *Materials Chemistry and Physics*. *82*(1): 157–164.

Neamen, D. A. (2003). *Semiconductor physics and devices*. McGraw-Hill Higher Education. Homewood, IL 60430 Boston, MA 02116.

Newnham, R. E. (1989). Electroceramics. *Reports on Progress in Physics*. *52*(2): 123.

Olsson, E. and Dunlop, G. L. (1989). The effect of Bi_2O_3 content on the microstructure and electrical properties of ZnO varistor materials. *Journal of Applied Physics*. *66*(9): 4317.

Olsson, E., Dunlop, G. and Österlund, R. (1993). Development of functional microstructure during sintering of a ZnO varistor material. *Journal of the American Ceramic Society*. *76*(1): 65–71.

Oskokovic. Science of Sintering, 48 Metal Powder Report 139–449 (1993).

Ott, J., Lorenz, A., Harrer, M., Preissner, E. A., Hesse, C., Feltz, A., Schreiber, M. (2001). The influence of Bi_2O_3 and Sb_2O_3 on the electrical properties of ZnO-based varistors. *Journal of Electroceramics*. *6*(2): 135–146.

Park, J. S., Han, Y. H. and Choi, K. H. (2005). Effects of Y_2O_3 on the microstructure and electrical properties of Pr–ZnO varistors. *Journal of Materials Science: Materials in Electronics*. *16*(4): 215–219.

Peiteado, M., Rubia, M. A., Velasco, M. J., Valle, F. J. and Caballero, A. C. (2005). Bi_2O_3 vaporization from ZnO-based varistors. *Journal of the European Ceramic Society*. *25*(9): 1675–1680.

Pfeiffer, H. and Knowles, K. M. (2004). Effects of vanadium and manganese concentrations on the composition, structure and electrical properties of ZnO-rich MnO_2–V_2O_5–ZnO varistors. *Journal of the European Ceramic Society*. *24*(6): 1199–1203.

Philipp, H. R. and Levinson, L. M. (1982). Degradation phenomena in zinc oxide varistors: a review. In *Additives and Interfaces in Electronic Ceramics. Proc. Special Conf. held at Cincinnati 4-5 May 1982. Advances in Ceramics*. 7: 1.

Phillp, H. R. and Levinson, L. M. (1977). Zinc Oxide Varistors for Transient protection. IEEE Transaction on Parts, Hybrits, and Parkaging. 13(4): 338–343.

Roberts, J. P. and Hutchings, J. (1959). Non-stoichiometry of zinc oxide and its relation to sintering. Part 2.—Sintering of zinc oxide in controlled atmospheres. *Transactions of the Faraday Society*. *55*: 1394–1399.

Sabri, M. G. M., Azmi, B. Z., Rizwan, Z., Halimah, M. K., Hashim, M., Sidek, H. A A. and Serdang, U. P. M. (2009). Application of Direct Current and Temperature Stresses of Low-Voltage ZnO Based Varistor Ceramics Department of Physics , Faculty of Science , Alternative and Renewable Energy Laboratory , Institute of Advanced Technology , National Textile University , S. *American Journal of Applied Sciences*. *6*(8): 1591–1595.

Safronov, G. M., Batog, V. N., Stepanyuk, T. V. and Fedorov, P. M. (1971). Equilibrium diagram of the bismuth oxide–zinc oxide system. *Russ. J. Inorg. Chem*. *16*(3): 460–461.

Science-poland, M. (2009). The effect of aluminium additive on the electrical properties of ZnO varistors. *Material Science-Poland*. *27*(4): 1208–1218.

Sedky, A. and El-Suheel, E. (2010). A Comparative Study between the Effects of Magnetic and Nonmagnetic Dopants on the Properties of ZnO Varistors. *Physics Research International*. 1–9.

Leon S. (1960). *Solid State Physics: Advances in Research and Applications (Vol. 10). Journal of the Amirican Chemistry Society. 82(23): 6210–6211.*

Seitz, M. A., Verma, A. K. and Hirthe, R. W. (1989). AC electrical behavior of individual MOV grain boundaries. *Ceramic Transactions. 3: 135*.

Senda, T. and Bradt, R. C. (1990). Grain growth in sintered ZnO and ZnO-Bi_2O_3 ceramics. *Journal of the American Ceramic Society*. *73*(1): 106–114.

Senda, T. and Bradt, R. C. (1991). Grain Growth of Zinc Oxide During the Sintering of Zinc Oxide-Antimony Oxide Ceramics. *Journal of the American Ceramic Society*. *74*(6): 1296–1302.

Society-discussions, T. A. C. (1970). Grain Fully ZnO, (January). 61–62.

Solorzano, I. G., Sande, J. B. Vander, Baek, K. K. and Tuller, H. L. (2011). Compositional Analysis and High Resolution Imaging of Grain Boundaries in Pr-doped ZnO Ceramics. *MRS Proceedings*. *29:* 189.

Song, X., Liu, F. and Zhang, H. (1996). Study on the Developing Process of Grains in ZnO Ceramics. *Journal-Xian Jiaotong University*. *30*: 1–7.

Tomsia, A. P. and Glaeser, A. M. (1998). Procedings of the NATO Advanced Research Workshop on Interfacial Scince *Ceramic Joining. Springer*.

Tsai, J. K. and Wu, T. B. (1996). Microstructure and nonohmic properties of binary ZnO-V_2O_5 ceramics sintered at 900 °C. *Materials Letters*. *26*(3): 199–203.

Tsai, J.-K. and Wu, T.-B. (1995). Microstructure and Nonohmic Properties of Z n O - V_2O_5 Ceramics. *Japanese Journal of Applied Physics*. *34*(12R): 6452.

Tsai, J.-K. and Wu, T.-B. (1996). Microstructure and nonohmic properties of binary ZnO-V_2O_5 ceramics sintered at 900°C. *Materials Letters*. *26*(3): 199–203.

Tu, Y., Wang, Q., He, J., Li, X. and Ding, L. (2013). TSC characteristics of AC aged ZnO varistors. *Science China Technological Sciences*. *56*(3): 677–682.

Chien-chen D. C., Chien, S., Yang, C., Chan, H., Chen, Y. and Chung, H. (2008). The Nonlinear Characteristics of Different Additives Added. Key Engineering materials 368-372: 493-496.

Wang, H. and Chiang, Y. (1998). Thermodynamic Stability of Intergranular Amorphous Films in Bismuth-Doped Zinc Oxide. *Journal of the American Ceramic Society*. *81*(1): 89–96.

Wang, M. H., Yao, C. and Zhang, N. F. (2008). Degradation characteristics of low-voltage ZnO varistor manufactured by chemical coprecipitation processing. *Journal of Materials Processing Technology*. *202*: 406–411.

Wang, M., Tang, Q. and Yao, C. (2010). Electrical properties and AC degradation characteristics of low voltage ZnO varistors doped with Nd_2O_3. *Ceramics International*. *36*(3): 1095–1099.

Wang, M., Yao, C. and Zhang, N. (2008). Degradation characteristics of low-voltage ZnO varistor manufactured by chemical coprecipitation processing. *Journal of Materials Processing Technology*. *202*(1-3): 406–411.

Wang, Q., Qin, Y., Xu, G. J., Chen, L., Li, Y., Duan, L., Cui, P. (2008). Low-voltage ZnO varistor fabricated by the solution-coating method. *Ceramics International*. *34*(7): 1697–1701.

Waser, R. (1995). Electronic properties of grain boundaries in $SrTiO_3$ and $BaTiO_3$ ceramics. *Solid State Ionics*, *75*, 89–99. http://doi.org/10.1016/0167-2738(94)00152-I

Wei, K., Guo, W., Du, C., Zhao, N. and Li, X. (2009). Preparation of Pr x Zn 1−x nanopowder with UV–visible light response. *Materials Letters*. *63*(21): 1781–1784.

Werner, J. and Peisl, M. (1985). Exponential band tails in polycrystalline semiconductor films. *Physical Review B*. *31*(10): 6881.

Wong, J. (1980). Sintering and varistor Characteristics of ZnO-Bi_2O_3 ceramics. *Journal of Applied Physics*,.*51*(8): 4453–4459.

Xia, C. Q., Liu, Q. Bin. and He, M. (2012). Effect of Sintering Temperature on Electrical Properties of ZnO Varistor Ceramics. *Advanced Materials Research*. *442*: 31–34.

Xiaolan, S., Fuyi, L. and Shengtao, L. (1995). Effects of Sub-grainboundaries on the Characteristics of ZnO varistor ceramics. *Journal of XI'AN Jiaotong University*. *3: 123*.

Xu, D., Shi, L., Wu, Z., Zhong, Q. and Wu, X. (2009). Microstructure and electrical properties of ZnO-Bi_2O_3-based varistor ceramics by different sintering processes. *Journal of the European Ceramic Society*. *29*(9): 1789–1794.

Zhang, C., Hu, Y., Lu, W., Cao, M. and Zhou, D. (2002). Influence of TiO_2/Sb_2O_3 ratio on ZnO varistor ceramics. *Journal of the European Ceramic Society*. *22*(1): 61–65.

Zhu, J. F., Gao, J. Q., Wang, F. and Chen, P. (2008). Influence of Pr_6O_{11} on the Characteristics and Microstructure of Zinc Varistors. *Key Engineering Materials*. *368-372*: 500–502.

(www.diva-portal.org/smash/get/diva2:544479/Fulltext 01.pdf)