



UNIVERSITI PUTRA MALAYSIA

**CHARACTERIZATION OF ZINC OXIDE- BASED VARISTOR CERAMICS
PREPARED USING SOLID STATE ROUTE AND CO-PRECIIPITATION
PROCESSING**

MOHD SABRI BIN MOHD GHAZALI

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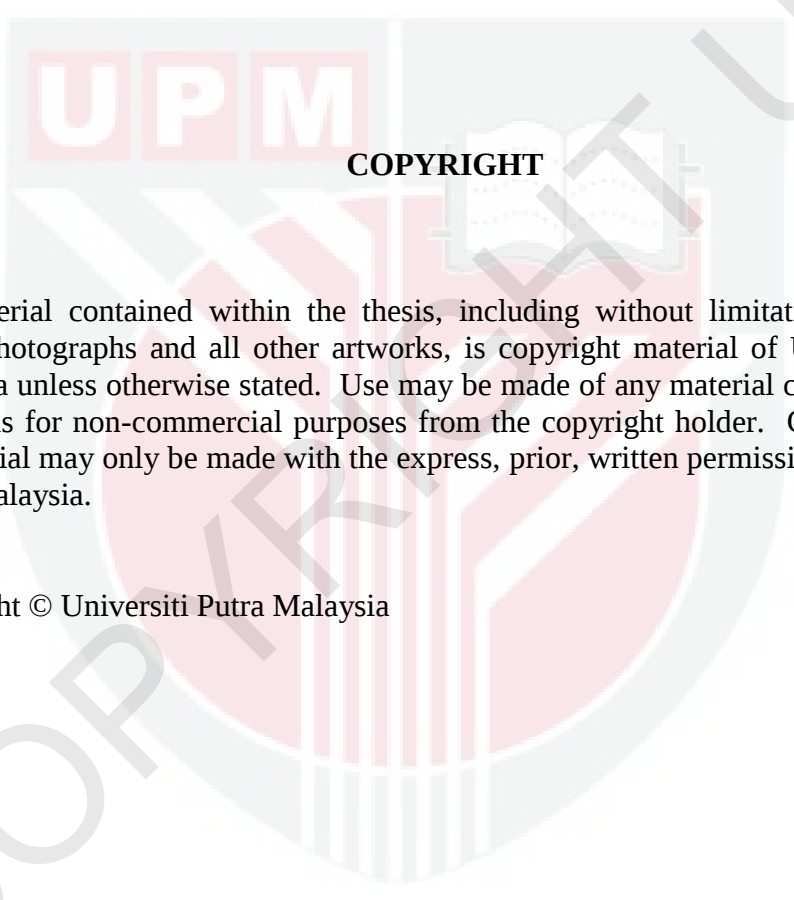
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PROCESSING**

By

MOHD SABRI BIN MOHD GHAZALI

**Thesis Submitted to the School of Graduate Studies,
Universiti Putra Malaysia, in Fulfillment of the
Requirements for the Degree of Doctor of Philosophy**

April 2013

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DEDICATION

TO MY LOVELY FAMILY

MY LATE FATHER

Mohd Ghazali bin Shamsuddin

Siti Isah binti Mansor

Maria'e binti Mohd Ghazali

Sharulazman bin Mohd Ghazali

Mohd Ridzuan bin Mohd Ghazali

Salmah binti Mohd Ghazali

Thank you for the inspiration and encouragement in everything I do

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of requirement for the degree of Doctor of Philosophy

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MOHD SABRI BIN MOHD GHAZALI

April 2013

Chairman: Professor Azmi Zakaria, PhD

Faculty: Science

There were few reports of fabrication of varistor ceramics that used as a protective device for electrical equipments from transient voltage surges, using other method than conventional solid-state. Hence, it is useful to characterize in terms of morphology, electrical non-linearity characteristics, and optical properties of it prepared by using co-precipitation processing, as this produces fine and homogenous powder, as well as conventional solid-state route. The objectives of the study are; to prepare four systems of ZnO based varistor ceramics through conventional solid-state route and co-precipitation technique to determine which factors affect most on electrical non-linearity behavior; secondly to carry out optical study of four systems of ZnO based varistor ceramics obtain from conventional solid-state route and co-precipitation technique to elucidate the structure arrangement; and thirdly to investigate the degradation behavior of one system of ZnO based varistor ceramics ($\text{ZnO-Bi}_2\text{O}_3\text{-TiO}_2$) to ascertain which preparation technique produce most stable electrical non-linearity coefficient. For the methodology, the prepared samples from

co-precipitation and solid-state route were examined with EDX microanalysis for chemical and physical examinations, SEM and FESEM for morphological examinations, XRD and optical microscopy for crystallographic examinations, UV-visible spectroscopy for optical band gap measurements and structure arrangement observation, and the *I-V* measurements for non-linearity characteristic. The selected samples were subjected simultaneously to stresses of specific temperature, and DC voltage over certain duration to study the degree of degradation.

In this study, with the use of different additives, secondary phases are developed and coexisted in the varistor ceramics that are $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Zn_2TiO_4 , and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ as a grain inhibitor and segregated at the grain boundaries and the triple point junctions. The development of these secondary phases influences the varistor ceramics performances in electrical and optical properties as well as in degradation percentage. Average density of the ceramics at all combination has the same trend where it increases with the increase of doping concentration, sintering time and temperature, as Bi_2O_3 , MnO_2 and TiO_2 are strong grain enhancers. The additive of Sb_2O_3 is a strong grain inhibitor which produces secondary phases, $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$ at low and $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ at high doping concentrations. The important findings here is that α value of solid-state route samples is optimum at 4.56, 10.36 and 5.36 at 45 min sintering time for System 2, System 3 and System 4 that used consecutive addition of Sb_2O_3 , MnO_2 and Co_3O_4 , respectively. While α is optimum at 9.59, 10.48 and 15.42 at 45 min sintering for System 2, System 3 and System 4, respectively, which fabricated by co-precipitation processing. In addition, the electrical properties of ZnO based varistor ceramic doped with different additives are investigated in conjunction with

the optical properties such as optical band-gap (E_g) and structural arrangement. Here, the E_g of the ZnO varistor ceramics and non-linearity behavior varies with the different additives and processing conditions. The E_g decreases due to the increase in the structural disordering which incorporation with the growth of interface state in the forbidden band-gap region and vice versa. Degradation has caused a decrease in varistor voltage and an increase in leakage current. After exposure to DC and heat stresses simultaneously for 12 h, the varistor ceramics experiences a slight drop in grain boundary resistances. Thus, the varistor ceramic samples exhibit high level of leakage current compared to initial state which indicates they have been degraded or deteriorate. In addition, higher leakage current signifies that samples experience greater watt loss during stress. In practice, high watt loss is unfavorable because it can increased energy consumption and increased the potential for thermal runaway. The degradation percentage was calculated in term of changes in varistor voltage before and after stresses and it shows that samples fabricated by solid-state route especially at three particular sintering temperatures of 45 min sintering time which are 1140, 1170 and 1260 °C, possess low degradation percentage as the value is 10% or below. From these criteria and as compared to I - V characteristics behavior, it is believed that the sintered samples at 1140 °C of 45 min sintering is relatively stable which does not show significant change in α , barrier height, and relative ratio of the nonlinear voltage (at 1 mA) for solid-state route samples. The percentages of the relative ratio of nonlinear voltage of all samples by co-precipitation processing exhibit low than 10%. From this result, samples fabricated by co-precipitation processing is relatively more stable that capable to withstand further stresses, low watt loss, low potential for thermal runaway and thus low energy consumption.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENCIRIAN SERAMIK VARISTOR- BERASASKAN ZINK OKSIDA YANG
DISEDIAKAN DENGAN KAEDAH KEADAAN PEPEJAL DAN PROSES
PEMENDAKAN BERTERUSAN**

Oleh

MOHD SABRI BIN MOHD GHAZALI

April 2013

Pengerusi: Profesor Azmi Zakaria, PhD

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Terdapat beberapa laporan seramik varistor, yang digunakan sebagai peranti pelindung untuk peralatan elektrik dari voltan fana mendadak, menggunakan kaedah lain selain daripada keadaan pepejal konvensional. Oleh itu, ia adalah berguna untuk mencirikan dari segi morfologi, ciri-ciri ketaklinearan elektrik, dan sifat-sifat optik yang disediakan dengan menggunakan pemprosesan pemendakan berterusan, menghasilkan serbuk halus dan sekata, selain daripada keadaan pepejal konvensional. Objektif kajian ini adalah untuk menyediakan empat sistem berasaskan seramik varistor ZnO melalui teknik keadaan pepejal konvensional dan pemendakan berterusan untuk menentukan faktor-faktor yang paling memberi kesan kepada tingkah laku ketaklinearan elektrik; kedua untuk menjalankan kajian optik empat sistem berasaskan seramik varistor ZnO diperolehi dari teknik keadaan pepejal konvensional dan pemendakan berterusan untuk menjelaskan susunan struktur; dan ketiga untuk menyiasat tingkah laku kemerosotan satu sistem berasaskan seramik varistor ZnO ($\text{ZnO-Bi}_2\text{O}_3\text{-TiO}_2$) untuk memastikan teknik penyediaan yang

menghasilkan pekali ketaklinearan elektrik yang paling stabil. Untuk metodologi, sampel yang disediakan daripada keadaan pepejal dan pemendakan berterusan telah diperiksa dengan mikroanalisis EDX untuk pemeriksaan fizikal dan kimia, SEM dan FESEM bagi pemeriksaan morfologi, XRD dan mikroskopi optik untuk pemeriksaan kristalografi, spektroskopi UV-cahaya nampak bagi pengukuran jurang jalur optik dan pemerhatian susunan struktur, dan pengukuran I - V untuk ciri-ciri ketaklinearan. Sampel yang dipilih dikenakan kepada tekanan suhu tertentu, dan voltan DC serentak sepanjang tempoh tertentu untuk mengkaji tahap kemerosotan. Dalam kajian ini, dengan penggunaan aditif yang berbeza, fasa sekunder dibangunkan dan wujud bersama dalam seramik varistor iaitu $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Zn_2TiO_4 , dan $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ sebagai perencat butir dan terasing pada sempadan butir dan persimpangan titik tiga. Pembangunan fasa sekunder ini mempengaruhi persembahan seramik varistor dalam ciri-ciri elektrik dan optik serta dalam peratusan kemerosotan. Ketumpatan purata seramik pada semua gabungan mempunyai kala yang sama di mana ia meningkat dengan peningkatan kepekatan dop, masa dan suhu pensinteran, dimana Bi_2O_3 , MnO_2 dan TiO_2 merupakan peningkat butir yang kuat. Aditif Sb_2O_3 merupakan perencat butir yang kuat yang menghasilkan fasa sekunder, $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$ pada kepekatan pendopan rendah dan $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ pada kepekatan pendopan tinggi.

Penemuan penting di sini adalah nilai α bagi sampel kaedah keadaan pepejal adalah optimum pada 4.56, 10.36 dan 5.36 pada 45 minit masa pensinteran bagi Sistem 2, Sistem 3 dan Sistem 4 yang menggunakan secara berturut-turut Sb_2O_3 , MnO_2 dan Co_3O_4 , masing-masing. α adalah optimum pada 9.59, 10.48 dan 15.42 pada 45 minit masa pensinteran bagi Sistem 2, Sistem 3 dan Sistem 4, masing-masing, yang

diperbuat secara pemprosesan pemendakan berterusan. Di samping itu, sifat-sifat elektrik berasaskan seramik varistor ZnO didopkan dengan aditif-aditif yang berbeza diasas bersama-sama dengan sifat-sifat optik seperti jurang jalur optik (E_g) dan susunan struktur. Di sini, E_g seramik varistor ZnO dan tingkah laku ketaklinearan berbeza dengan aditif yang berbeza dan keadaan pemprosesan. E_g berkurangan disebabkan oleh peningkatan dalam ketakkalaan struktur yang menyebabkan pertumbuhan keadaan antaramuka di dalam rantau jalur-tenaga larangan dan sebaliknya. Kerosotan telah menyebabkan penurunan voltan varistor dan peningkatan dalam arus bocor. Selepas pendedahan kepada tekanan DC dan haba serentak selama 12 jam, seramik varistor mengalami sedikit penurunan dalam rintangan sempadan butir. Oleh itu, sampel seramik varistor menunjukkan arus bocor tahap tinggi berbanding dengan keadaan awal yang menunjukkan ia telah alami kerosotan atau merosot. Di samping itu, arus bocor yang tinggi menandakan bahawa sampel-sampel mengalami kehilangan watt yang lebih besar semasa tekanan. Secara praktikalnya, kehilangan watt yang tinggi adalah tidak menguntungkan kerana ia boleh meningkatkan penggunaan tenaga dan meningkatkan potensi untuk pelarian haba. Peratus kerosotan dalam perubahan dalam voltan varistor sebelum dan selepas tekanan telah dikira dan ia menunjukkan bahawa sampel-sampel diperbuat menggunakan kaedah keadaan pepejal terutamanya pada tiga spesifik suhu pensinteran pada 45 minit masa pensinteran di mana 1140, 1170 dan 1260 °C, mengalami peratus kerosotan yang rendah serendah 10% atau ke bawah. Dari kriteria ini dan berbanding kepada tingkah laku ciri-ciri $I-V$, ia dipercayai bahawa sampel-sampel tersinter di 1140 °C pada 45 minit masa pensinteran adalah agak stabil yang tidak menunjukkan perubahan ketara dalam α ,

ketinggian halangan, dan nisbah relatif voltan taklinear (pada 1 mA) bagi sampel-sampel kaedah keadaan pepejal. Peratusan nisbah relatif voltan taklinear bagi semua sampel bagi pemprosesan pemendakan berterusan mempamerkan rendah daripada 10%. Daripada keputusan ini, sampel-sampel yang diperbuat melalui pemprosesan pemendakan berterusan adalah agak lebih stabil yang mampu untuk menahan tekanan lebih lanjut, kehilangan watt rendah, potensi kehilangan haba rendah dan dengan itu penggunaan tenaga rendah.

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I certify that an Examination Committee has met on 30 April 2013 to conduct the final examination of Mohd Sabri bin Mohd Ghazali on his Doctor of Philosophy thesis entitled “Characterization of Zinc Oxide- Based Varistor Ceramics Prepared Using Solid State Route and Co-precipitation Processing” in accordance with 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 candidate be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

MOHD SABRI BIN MOHD GHAZALI

Date: 30 April 2013



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