UNIVERSITI PUTRA MALAYSIA

FABRICATION AND EFFECT OF APPLIED FIELD STRESSES ON STABILITY OF ZnO CERAMICS WITH $CaMnO_3$ AS ADDITIVE FOR VARISTOR APPLICATION

ISMAIL IBRAHIM LAKIN

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By

ISMAIL IBRAHIM LAKIN

Thesis Submitted to the school of Graduate Studies, Universiti Putra Malaysia,
in Fulfillment of the Requirements for the Degree of Master of Science.

February 2014

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DEDICATION

I hereby dedicate this thesis to the Almighty Allah who has been my help, sustainer, provider, guide, encouragement, keeper and my all in all throughout the course of my studies and also to my parents (Late Alhaji Ibrahim Lakin and Maimuna (Kande) Pate), whose prayers and support has kept me going. Finally to my brothers and sisters who are always by my side.

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

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Chairman: Professor Azmi Zakaria, PhD

Faculty: Science

The major challenge in the continuing development of varistor has been to reduce the energy loss which is due to temperature and applied field stresses and to attain a good stability. The aims of this study are; to study the effect of $CaMnO_3$ (CMO) contents on nonlinearity coefficient (α) enhancement of ZnO based varistor ceramics; and secondly to study the nonlinear stability of this ceramic against DC electrical field and thermal stresses as function of CMO contents. The first aim has been carried out by synthesis of ZnO + xCMO ceramics by citrate gel coating technique, where x ranging from 3 – 7 mol% and sintered at various sintering times from 1 – 3 hrs. The prepared samples were characterized by using TG/DTA, EDX, SEM, XRD, and I-V measurements. The second aim was carried out by choosing the samples with best electrical properties subjecting them simultaneously to stresses of specific temperature and DC voltage over a certain period of time to study the degree of degradation. XRD analysis shows that the main phase in the material systems was ZnO while CMO as the secondary phase increase gradually with the increase of mol%, x. The TG/DTA analysis shows that, good quality of ZnO-CMO can be achieved at calcination temperature above 650 °C. Average density of the ceramics in all systems has the same trend where it decreases with the increase of doping level and sintering time. The maximum grain size was found to be 23.4 µm at the highest sintering time at 3 hrs at 7 mol% CMO doping level, as Mn is a strong grain enhancer. The SEM and EDX results verified that Ca and Mn were distributed within the grain as well as in the grain boundaries and triple point junctions. The value of α was found to increase with amount of CMO up to 5 mol% concentration. An optimum sintering time of 3 hrs for 5 mol% doping level gave the best α, attaining a value of 42.3 which represent a high protective function of ZnO varistor. The DC stress has caused a decrease in varistor voltage, α, and also an increase in leakage current. After exposure to DC and heat stresses for 18 hours, the varistor ceramics experienced a slight drop in nonlinearity. Thus, the varistor ceramic samples exhibited a high level of leakage current compared to samples before degradation which indicated they have been degraded or deteriorated. The degradation percentage was calculated in terms of changes in varistor parameters before and after stress. It showed that sample with 3 mol% CMO possess lowest degradation percentage. From this result, it was found that samples fabricated at 3 hrs sintering time have the best microstructure and electrical properties.

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

FABRIKASI DAN DEGRADASI ZnO + CaMnO$_3$ SERAMIK VARISTOR BERVOLTAN RENDAH

Oleh

ISMAIL IBRAHIM LAKIN

Februari 2015

Pengerusi: Professor Azmi Zakaria, PhD

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Cabaran utama dalam pembangunan berterusan varistor adalah merendahkan kehilangan tenaga yang mana bersabit dengan tegasan-tegasan suhu dan medan gunaan, dan untuk mendapatkan kestabilan tinggi. Tujuan kajian ini adalah; mengkaji kesan kandungan CaMnO$_3$ (CMO) keatas peningkatan pekali tak-linear (α) seramik varistor berdasarkan ZnO; dan keduanya mengkaji kestabilan tak-linear seramik ini terhadap tegasan-tegasan medan elektrik DC dan terma sebagai fungsi kepada kandungan CMO. Objektif pertama telah dilakukan dengan mensintesis seramik ZnO + xCMO menerusi teknik salutan gel sitrat, yang mana x mencangkup dari 3 – 7 mol% dan disinter pada pelbagai masa sinteran dari 1 – 3 jam. Sampel tersedia dicirikan dengan menggunakan TG/DTA, EDX, SEM, XRD, and pengukuran I-V. Manakala untuk objektif kedua, sampel dari sistem dengan ciri-ciri elektrikal terbaik di kenakan secara serentak tegasan-tegasan suhu dan voltan DC spesifik menerusi satu kala masa untuk mengkaji darjah degradasi. Analisis XRD menunjukkan bahawa fasa utama dalam sistem bahan adalah ZnO manakala CMO sebagai fasa sekunder bertambah secara perlahan dengan pertambahan mol% x. Analisis TG/DTA menunjukkan bahawa, kualiti baik dari ZnO-CMO boleh dicapai pada suhu pengkalsinan melebehi 650^{o}C. Ketumpatan purata dari seramik dalam semua sistem mempunyai trend yang sama dimana ia mengecil dengan bertambahan paras pendopan dan masa pensinteran. Saiz butir maksimum yang didapati adalah 23.4 µm pada masa pensinteran tertinggi pada 3 jam dan pada paras pendopan 7 mol% CMO, kerana Mn adalah penumbuh butiran. Hasil-hasil SEM dan EDX membuktikan bahawa Ca dan Mn adalah tertabur didalam butiran juga didalam sempadan butiran dan simpang titik tiga. Nilai α didapati bertambah dengan amaun CMO sehingga ke kepekatan 5 mol%. Masa persinteran optimum adalah 3 jam untuk paras pendopan 5 mol% memberikan α terbaik, mencapai nilai 42.3 yang mana mewakili fungsi perlindungan tinggi dari seramik varistor ZnO. Tegasan DC menyebabkan penurunan pada voltan varistor, α, dan juga pertambahan dalam arus bocor. Selepas pendedahan kepada tegasan DC dan suhu untuk selama 18 jam, seramik varistor mengalami penurunan kecil dalam ketak-linearan. Jadinya, sampel varistor seramik menunjukkan paras tinggi arus bocor berbanding dengan sampel sebelum degradasi yang mana menunjukkan mereka telah terdegradasi atau merosot. Peratus degradasi dikira dalam sebutan dari perubahan dalam parameter varistor sebelum dan selepas tegasan. Ia menunjukkan bahawa sampel dengan 3 mol% CMO mempunyai peratusan degradasi terendah. Daripada hasil ini, adalah didapati bahawa sampel difabrikasi pada masa sinteran 3 jam mempunyai mikrostruktur dan sifat-sifat elektrik terbaik.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirements for the degree of Master of Science.
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LIST OF ABBREVIATIONS

I	Current
V	Voltage
α	Nonlinear coefficient
K	Material constant
°C	Degree celcius
$\alpha=b=c$	Lattice constant of ZnO wurtzite structure
Å	Angstrom
ρ	Resistivity
x	Doping level of dopant (mol %)
d	Spacing between the lattice planes in the crystals
Z	Atomic number
J_L	Leakage current density
I_L	Leakage current
V_{on}	Varistor Voltage
E_b	Breakdown voltage
V_T	Threshold voltage
θ	Angle of diffraction
λ	Wavelength of the X-ray (0.154nm for CuKα)
ρ	Density
ρ_{water}	Density of water (1 gcm^{-3})
W_{air}	Weight of pellet in air
W_{water}	Weight of pellet in water
I_1	1 mA
1_2	10 mA
V_1	Voltage corresponding to I_1
V_2	Voltage corresponding to I_2
$\rho_{theoretical}$	Theoretical density of ZnO

ΔE_b	Variation rate of breakdown voltage
$\Delta \alpha$	Variation rate of nonlinear coefficient
ΔI_L	Variation rate of leakage current
K_T	Degradation rate coefficient
Zn_n	Zinc

CHAPTER 1

INTRODUCTION

1.1 Introduction

In this chapter, Zinc Oxide (ZnO) varistor ceramic is being introduced and discussed in detail. This includes the application of ZnO and what makes them to be highly demanded and become the focus of interest of many researchers in the field of solid state semiconductor ceramic devices. The basic operation of ZnO varistor concern of how it works as electronic device in the field of circuit over voltage protection has been discussed. Lastly, research problems, scope of research and objectives of this present research work have been outlined in this section. This work focuses on effect of Calcium Manganite ($CaMnO_3$) as dopant on nonlinear coefficient (alpha), electrical properties, degradation and stability of ZnO varistor.

1.2 Varistor: Low Voltage varistor

A varistor is a device that exhibit non-ohmic behaviour with resistivity values dependent on the applied voltage. It is used as a protective device to regulate transient voltage surges of unwanted magnitudes by shunting them to the ground. The unwanted magnitudes refer to over voltage transients that damage the operating voltage of the equipment being protected. These transients are generated due to the phenomena internal to the equipment, or of atmospheric origin. Therefore, the transients are inherent in the electrical system (Das, 2010).

These excess energy and over voltage are hazardous to electrical appliances and electrical circuits. It can cause power system failures which can result in huge losses of product output. These transients occurs a few thousand times a year for a typical household and office premises. Nowadays, ZnO varistor plays a major role in preventing these power surges from causing power failures.

The varistor works in similar way as a back-to-back Zener diode and usually placed in parallel with circuits to protect them from voltage surges. A good protector would contain at least three varistors, two connected to the live wire and the other is connected to the neutral wire. The second varistor component can continue the protection service if the first varistor fails after many years of service. This is why several varistors are arranged in parallel to each other, so that it can survive for more than half a century under normal condition. Normally, varistors are usually connected close to the protected device and located at the incoming power lines before the power supply reaches the circuitry being protected for optimum protective performance. For offices and households, the normal power supply is 240 volts (rms). If a transient over voltage of 300 volts (rms) is transmitted through the household socket, the varistor will perform its action. The varistor will immediately detect the presence of the transients in nanoseconds speed, it will absorb most of the power voltage transients voltage energy and redirect (or shunt) the remaining transient energy to the ground.

A varistor is not a perfect conductor but when energy is absorbed by a varistor, the varistor becomes more conductive and therefore, its life expectancy increases exponentially as varistor rating is increased. The normal ratings of the varistor components are either 25 volts (rms) for low voltage varistor or 300 volts (rms) for high voltage varistor. A varistor failure can be avoided by significantly increasing varistor energy ratings by using a varistor of higher joules or by connecting more varistor devices in parallel. Discrete component varistor have rather high breakdown voltage (≈50 V), well above the safe applied voltage levels for silicon devices. For the past decades, the usual methods for producing low-voltage varistors involved either grinding down a conventional disk varistor or promoting large grains in the sintered material. Use of titanium dioxide (TiO_2) as additive to promote secondary recrystallization has been employed, but suffers from limited control over final grain size (Trontelj et al., 1986). The second method employs a pre-sintered pure ZnO substrate material into which varistor additives are diffused. This may either be from screen printed paste of the additives (Schwing and Hoffmann, 1981) or solid dopant layer sandwiched between two ZnO substrates (Selim et al., 1980). Both methods produce workable device but with small active area that limit the current capabilities.

To achieve lower voltage reliability, a method of producing thin varistor layers had been devised. Shohata et al., (1981) successfully fabricated multilayer varistor by tape casting or laminating process used to produce multilayer capacitors. This technique enable the production of extremely thin resistor layer of the order of 20 μm compared to the 0.5 mm achieved through die pressing. By reducing the number of grains between the electrodes, the varistor's breakdown voltage can be reduced to a lower limit of approximately 4 V. Meanwhile increasing the area of the varistor potentials increases current handling capabilities.

1.3 Zinc Oxide Based Varistor

ZnO based varistor is one of the success phenomena of solid state semiconductor ceramic devices and become the preferred approach technology predominantly in the field of circuit overvoltage protection. Varistor are defined as voltage dependent Resistor (VDR). The resistivity of ZnO varistor depends upon the applied voltages, where the resistivity is very high below the breakdown voltage (V_b) but becomes very low at voltages above V_b (Nahm, 2004). Therefore, the varistor is so-called voltage dependent resistor. V_b is the minimum voltages that cause a set of insulator to become conductor. ZnO varistors are widely used as valve electronic devices of lightning arrestors for protecting electrical power lines or as surges absorbers to protect electronic components against voltage surges. In summary, ZnO varistor is a ceramic semiconductor used to protect electrical and electronic systems against dangerous overvoltage surges, switching surges, electromagnetic transient surges, and electrostatic discharges (Nahm, 2005).

A varistor function is to conduct significantly increased current when voltage is excessive. Before the invention of the ZnO varistor, silicon carbide is widely used in protection system (SIMOES et al., 2006). Then, ZnO become commercial and attract more attention due to excellent nonlinear current – voltage (I-V) characteristics and their high energy withstanding capabilities. In less than 30 years of its discovery, the varistor now become widespread in the application of varistor as voltage surge protectors in the electrical circuits (Bai et al., 1995). More than two billion of this kind of varistors have been manufactured by now and their popularity is rapidly increasing due to their low cost, high amazing versatility and ability to absorb large amount of energy (Bernik and Daneu, 2007). Moreover, due to their superior electrical properties, increasing number of ZnO varistors is now being used in automobiles.

This Metal Oxide Varistor (MOV) contains metal oxides such as small amount of bismuth, cobalt, manganese e.t.c that can affect the varistor properties in matrix with ZnO grains. ZnO ceramic alone cannot exhibit a nonlinear behaviour without doping the heavy elements with large ionic radii such as Ba, Pr, Bi etc (Nahm and Park, 2000). Currently, these ceramics are produced with minor addition of typically Bi_2O_3, Sb_2O3, CoO, MnO_2, $CaMnO_3$, and Cr_2O_3.

The characteristics of varistor ceramics are closely related to the microstructure (Bernik and Daneu, 2007) where each dopant plays an important role to improve the non-ohmic properties of ZnO varistor. ZnO varistor exhibit high nonlinearity and stability with many additives (Nahm, 2003). In addition to nonlinearity, the electrical stability is technologically very important characteristics of ZnO varistors.
The relationship between the voltage across the terminals, V, and the current in the device, I, is typically expressed by

$$I = KV^{\alpha}. \tag{1.1}$$

where

K = constant
α = nonlinearity coefficient

The nonlinear I-V characteristics of ZnO varistors are attributed to a double Schottky barrier formed to the grain boundaries, which are essentially formed by the segregation of varistor forming oxides towards the ZnO grain boundaries.
The main properties of ZnO varistors are;

a. High energy absorption capability ranging from a few joules for smaller models and up to thousands of kilojoules for larger models.
b. ZnO can sense and clamp transients repeatedly, in thousands of times without being destroyed.
c. ZnO varistor have superfast response to over voltage transients whereby they can sense and clamp transients in nanoseconds speed.
d. High nonlinear coefficient values ranging from tenths to hundreds.
e. Small size with various geometries and design.
f. Low power loss of only 10 – 100 W/cm^3.
g. Long life span of more than 10 years.
h. Highly versatile, it is applicable both in low voltage and mega voltage.

Regarding to the unique properties of ZnO listed above, lots of attention has been shifted to these ZnO varistors. Moreover, the collaboration between ZnO varistor and dopants are incredible phenomena in device civilization for industrial applications. A lot of work has been done on the ZnO varistor system and further investigations are still going on in order to enhance the varistor performances.

1.4 Zinc Oxide

Zinc Oxide (ZnO) is a polycrystalline solid material and it is widely used in the manufacturing of paints, plastics, glass, cement, rubber products, cosmetics, textiles, inks, soaps, pharmaceuticals, floor covering, batteries, adhesive and many other products. It is also used in the fields of UV devices, chemical and gas sensor, piezoelectric transducers, light emitting diodes, lasers (Eda, 1978) and varistors.

ZnO occurs as a white powder with a common name zinc white. ZnO is nearly insoluble in water but soluble in acids and alkalis. ZnO would change colour from white to yellow when it is heated. ZnO has a density of 5.606g/cm3 and with a melting point of 1975 ^{0}C. The resistivity of ZnO ranges from 1 to 100 Ωm, which corresponds to the electron concentration of the order of 10^{21}-10^{23} m^{-3}. ZnO has several other favourable properties such as good transparency, high electron mobility, wide band gap and strong room temperature luminescence where those properties already used in heat protecting windows and electronic applications as thin film transistors and light emitting diodes.

ZnO is a group II -VI semiconducting compound because Zinc and Oxygen belongs to 2nd and 6th groups of the periodic table respectively. ZnO Oxide becomes a great interest for electronic and photonic devices it is also studied for a variety of applications. ZnO has a wide band gap of 3.37 eV at room temperature and large excitation binding energy of 60 MeV that are technologically important in the application for short wavelength optical devices such as ultraviolet, violet, blue light, emitting diodes and laser diodes. It is also important in the development of electronic and optoelectronic devices (Srinivasan and Kumar, 2008).

The advantages of wide band is higher breakdown voltage, ability to sustain large electric field, lower electronic noise and power operation that make ZnO as one of the most promising material for electronic applications. Pure ZnO is an n-type intrinsic semiconductor where the intricity is due to Zinc interstitial and oxygen deficiency. In commercial varistor, ZnO has to be doped with elements such as Co, Sb, Mn, Ni, Mg and Bi.

ZnO has a wurtzite structure as shown in Figure 1.1. The physical properties of ZnO are as follows;

i) Perfect ZnO crystals exist in the hexagonal wurtzite structure,

ii) The ZnO lattice type is hexagonally close packed in which oxygen atoms are arranged and half of the tetrahedral sites filled up by zinc atoms,

iii) Zinc and oxygen atoms are tetrahedrally coordinated giving rise to equal positioning to each other,

iv) The mean lattice constant of the wurtzite structure are a = b = 3.257Å and c = 5.213Å which gives a unit cell of volume 47.9Å.

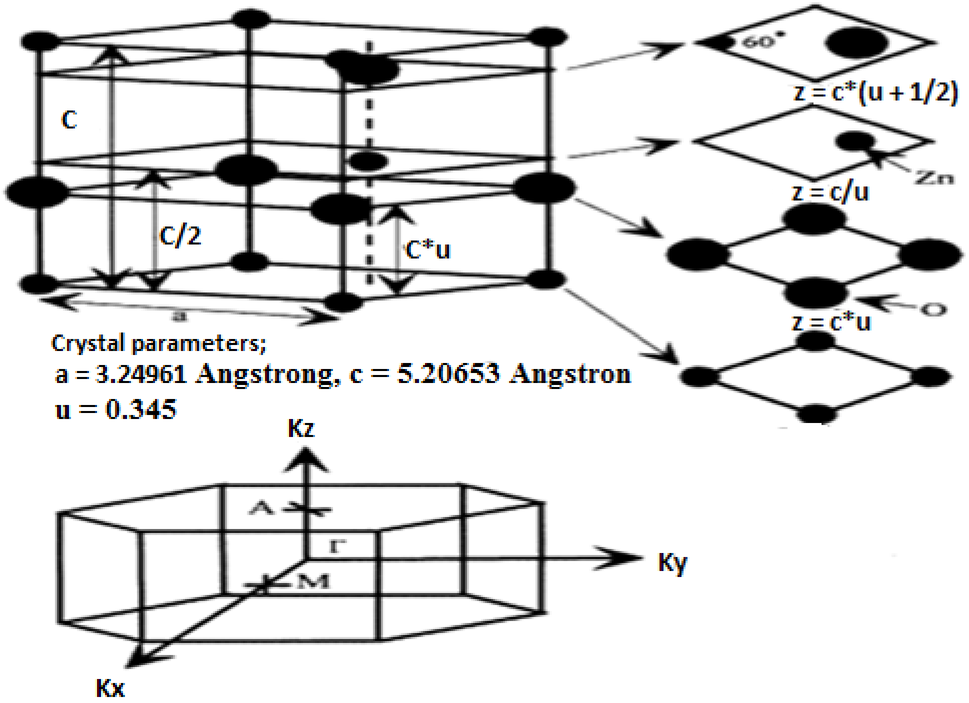

Figure 1.1: Wurtzite structure of ZnO (Oshikiri et al., 2001)

The ZnO structure is relatively open, all of the octahedral and half of the tetrahedral sites are empty. So, external dopants easily incorporate into the ZnO lattice (Mahan, 1983). Therefore dopants such as manganese (Mn) can easily occupy these empty sites and improve the nonlinear current – voltage characteristics in ZnO varistor by affecting the defect chemistry at the grain boundary (Han et al., 2002). There are different opinions about the dominant intrinsic defect that occur in the ZnO and have long been a subject of controversial discussion in the literature. The electron density measurements have shown that dominant defects are interstitial zinc ions. However, other investigations suggest that it is oxygen vacancies that predominate in pure ZnO.

1.5 Calcium Manganite

Calcium manganite (CMO) Transition metal oxides with perovskite-type structure are attractive materials for thermoelectric applications. The properties of these materials originate from strong interactions between the d-state electrons of the transition metal atoms (Alfaruq et al., 2012). Perovskite type manganates are well known for their high magnetoresistance which can be explained by double-exchange model. CMO is an antiferromagnetic insulator that was extensively studied in recent years, the mixed valence of Mn^{3+} and Mn^{4+} as function of the elemental composition strongly govern the physical properties (e.g thermoelectric properties) of manganates. An alternative way to modify the physical properties is by changing the morphology of the samples, e.g., by creating low dimensional structures or nanostructures (Wiebe et al., 2001).

Early neutron diffraction experiments performed on stoichiometric CMO indicate an orthorhombic perovskite structure ($a = \sqrt{2}_c$, $b = 2a_c$, $c = \sqrt{2}a_c$ where a_c = cell constant of cubic perovskite). And it is antiferromagnetic insulator with a Neel temperature (T_N) of 120K. CMO also exhibit a ferromagnetism below Neel temperature (Macchesney et al., 1967).

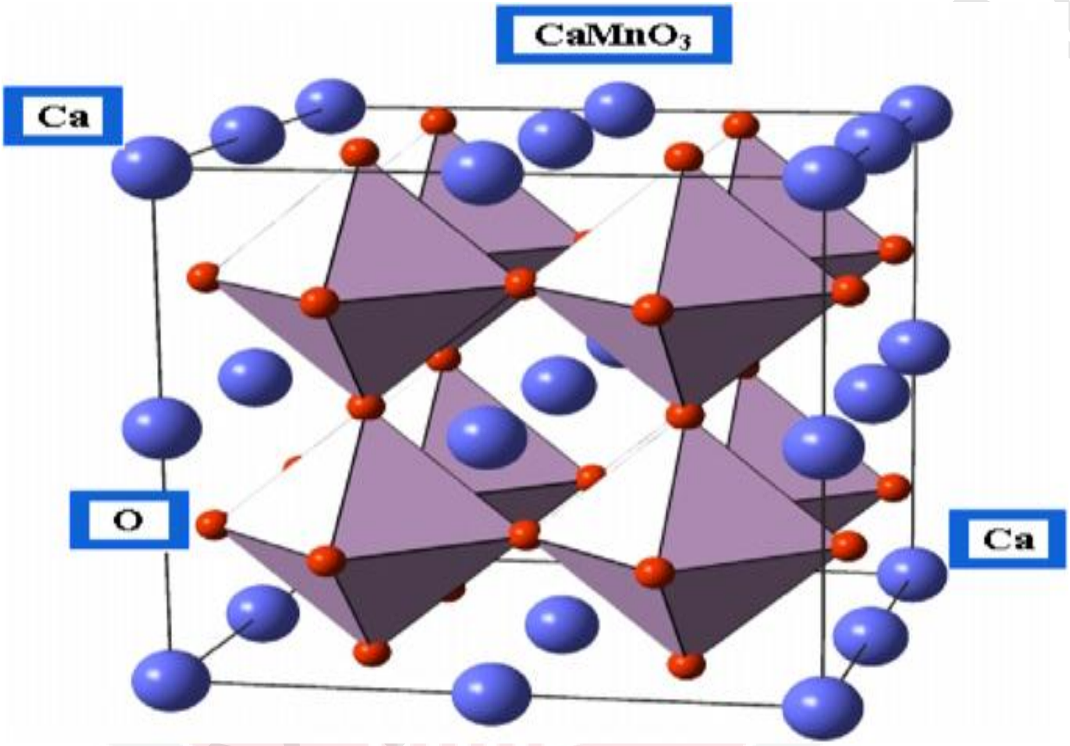

Figure 1.2: Ideal cubic perovskite crystalline structure formula (Hamdad and Bouhafs, 2010)

1.6 Sintering

Sintering is a method for making objects from powder, by heating the material until its particle adheres to each other. In other words it refers to powder compacting process by applying thermal treatment. Sintering is also a processing technique used to produce density-controlled materials and components from metals and ceramic powders by the use of thermal energy.

Sintering originated in the era of firing pottery. Since 1940’s, sintering was studied fundamentally, scientifically and then, a remarkable in sintering science have been made. In the sintering step, there are various techniques and processing variables which can produce variations in the micro structure and results of the sintered body. In general, the aim of sintering is to produce sintered parts with reproducible and, if possible, designed microstructure through control of sintering variables.

Microstructure control including the control of grain size, sintered density, pores and also size and distribution of other phases. In most cases, the final aim of sintering is to control both densification and grain growth process (Figure 1.3).

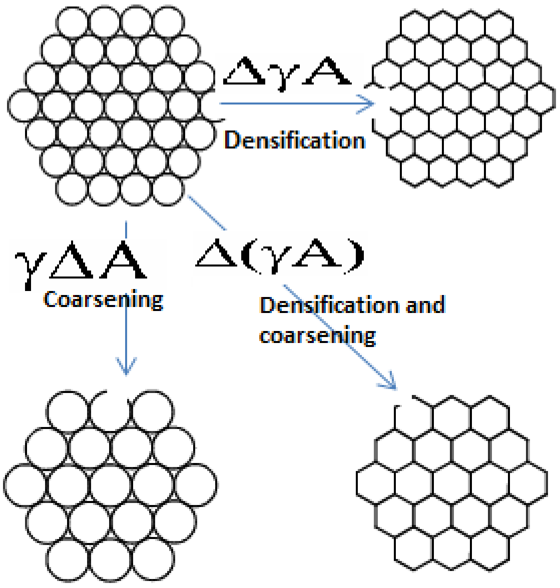

Figure 1.3: Basic phenomena occurring during sintering under the driving force for sintering, Δ(γA) http://v5.books.elsevier.com/bookscat/samples/9780750663854/4355-Kang-01.pd

Densification is the act of reducing porosity in a sample thereby making it dense. Grain growth is the process of grain boundary motion; hence increase the average grain size. A great change in microstructure properties is technologically important in order to produce a better varistor performance. Liquid phase sintering is a consolidation technique of powder compacts containing more than one component at the temperature above the solidus of the components in the presence of liquid. It is essential to have an amount of liquid phase that is large in size, a near complete solubility of the solid in the liquid, and wetting of the solid by the liquid for densification to occur. Densifications usually occur in the solid state during heating of powder mixture compact. Densification is derived from capillary pressure of the liquid phase located between the fine solid particles. A capillary pressure is developed when the liquid wets the solid particle and each space between the particles becomes a capillary. Liquid flows in to fine capillaries due to the capillaries pressure difference between the fine and coarse channels between solid particles and the solid particles can be redistributed by this liquid flow.

In final sintering stage, pores are present at grain boundary and particularly at triple junction and inhibit grain growth. During liquid phase sintering, most of the sites of particles melted and become pores because of liquid flow into fine capillary between solid particles. As sintering proceeds, elimination of pores and grain growth occur in the liquid matrix (Figure 1.5). The capillary pressure exerts on a particle hence, the solubility of the atoms in the particles increases in the matrix. When particles of different size are dispersed in liquid, material transport occurs from small to large grains because of the difference in the solubility between the grains. The small grains dissolve and large grains grow further and therefore the average grain size increases (Figure 1.6).

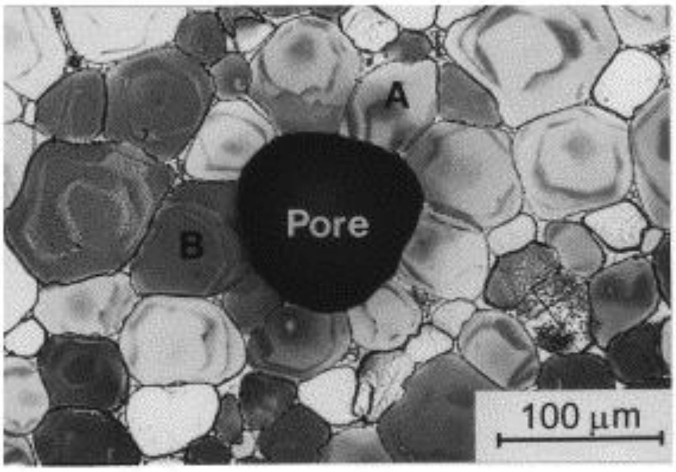

Figure 1.4: Large pore during sintering, where A and B are grains

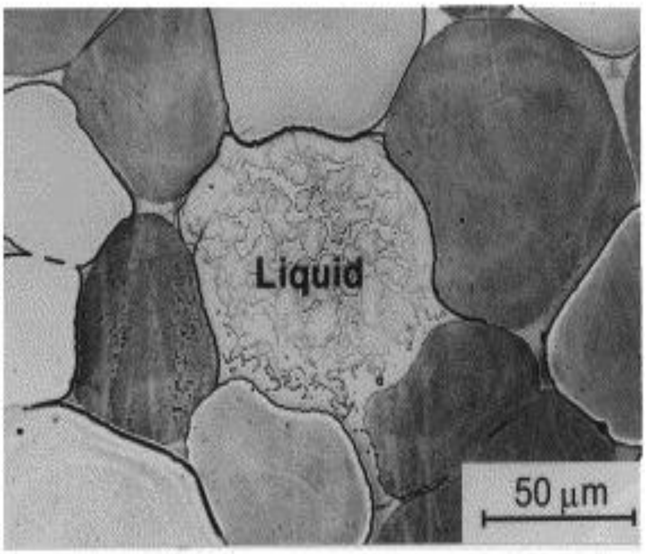

Figure 1.5: Elimination of pores by instantaneous filling with liquid

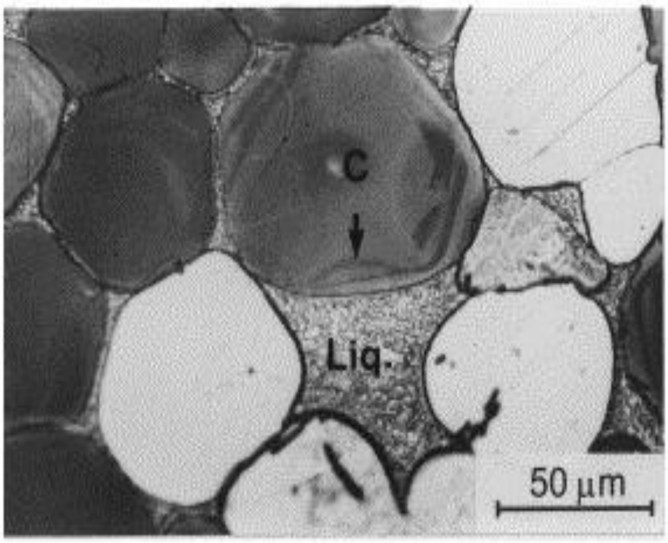

Figure 1.6: Elimination of the liquid pocket by grains growth toward the liquid pocket center upon prolong sintering. (Lee and Kang, 1998)

Grains growth happens due to the motion of the atoms across a grain boundary. Grain growth is divided into two parts, normal and abnormal grain growth. Normal grain growth is a simple and invariable distribution of relative grain size. Abnormal grain growth occurs by the formation of some exceptionally large grains in a matrix of fine grains and also due to the presence of large grains in the matrix, material containing second phase and also impurities of high concentration.

1.7 Electrical Characteristics

The combination properties of ZnO varistor such as nonohmic behaviour, large energy handling capabilities and their amazing versatility make them a very high demand protective device to regulate transient voltage surges of unwanted magnitudes. ZnO varistor have energy handling capabilities as high as 300 J/cm^3. Some other investigators reported the achieving of energy handling capabilities up to 1000 J/cm^3. Their ability to absorb or handle energy levels are important because most materials would vaporize if they are expose to energy levels even less than 100 J/cm^3.

The very thin grain boundaries of ZnO varistor have amazingly high resistivity in the range of $10^8 – 10^{12}$ Ω.cm compared to ZnO grains which have the resistivity of 1-10 Ω.cm. The difference between ZnO grain and ZnO boundary resistivity is the existence of electrostatic potential barrier located at the depletion layers inside the ZnO grain, very close to the grain boundaries. The concentrations of donors inside the depletion region create trap states that prevent the flow of charge carriers across the grain boundaries. Therefore, large potential barriers exist at the area close to the grain boundaries.

Table 1.1: Electrical Characteristics of ZnO Varistors

ZnO Varistor Characteristics	Electrical Characteristics Values
Depletion Layer Thickness	50-100 nm
Grain Boundary Resistivity	$10^8 – 10^{12}$ Ω.cm
Grain resistivity	1 – 10 Ω.cm
Donor Concentration	10^{17} /cm^3
Interfacial Trap Density	10^{14} /cm^2
Nonlinear Voltage Range	1 V – 10 kV
Nonlinear Coefficient (α)	10 - 100
Energy Absorption Capability	100 – 300 J/cm^3
Response Time	5 -10 ns
Power Loss	10– 100 mW/cm^3

The very thin grain boundaries of ZnO varistor have amazingly high resistivity in the range of $10^8 – 10^{12}$ Ω.cm compared to ZnO grains which have the resistivity of 1-10 Ω.cm. The difference between ZnO grain and ZnO boundary resistivity is the existence of electrostatic potential barrier located at the depletion layers inside the ZnO grain, very close to the grain boundaries. The concentrations of donors inside the depletion region create trap states that prevent the flow of charge carriers across the grain boundaries. Therefore, large potential barriers exist at the area close to the grain boundaries.

1.7.1 Degradation – Electrical Relationship

ZnO based varistors are widely used to protect circuits against excessive transient voltages by incorporating them into the circuit in such a way that, when triggered, they will shunt the current created by the high voltage away from the sensitive components because of their extreme nonlinearity in their I-V characteristics. The chosen suitable additives are the main tools that are used to improve the nonlinear response and the stability of ZnO varistor ceramics (Eda, 1989). Therefore, the stability of ZnO based varistor ceramics against constant biases, AC and DC or voltage surge is recognized as one of crucial subjects to be investigated (Gupta, 1990). In practical application, ZnO varistors are always subjected to a continuous electrical stress, switching surge and lightning surge. If the stability against these stresses is poor, the application of such varistor is extremely limited even if the nonlinearity is high. The ZnO varistor begin to degrade due to the gradual increase in leakage current with stress time. Eventually, they cause thermal runaway and loss of varistor function. Therefore, the stability of varistor is more important than any other varistor property. In addition to nonlinearity, the electrical stability is a technologically important characteristic of ZnO varistor. The stability of varistors can be estimated from the empirical equation: $I_L = I_{L0} + K_T t^{1/2}$. where K_T, is the degradation rate coefficient indicating the aging degree. The lower the K_T value, the better the stability.

1.7.2 Nonlinear Current- Voltage Characteristics

Due to the strong semiconducting behaviour of ZnO varistors, many prominent varistor scientists such as (Matsuoka 1971 and Clarke, 1999) have reported that the most important property of ZnO varistor is it nonlinear current-voltage (I-V) characteristics, as shown in Figure 1.7. Since ZnO varistors are manufactured with many voltage and current ratings, the diameter and its thickness values would have large variations, from a few a few millimetres to 400 millimetres in diameter and from micrometres to 40 centimetres in thickness. Consequently the current density-electric field (J-E) graph will also experience big variations in terms of its shape and turning points. Therefore if the varistor samples have large physical variations, it would be it would be wise to report the current and voltage values with respect to a certain denominator; that is current is represented by current density J (amperes/cm^2) while voltage is represented by electric field E (voltage/ cm). However, if an analysis is focused on a certain model, say low – voltage models, then the current-voltage (I-V) characteristics do not vary that much; therefore it is relatively accurate if the common denominator is not used.

J-E curve has three characteristic regions which are the pre-breakdown region (the sleep mode), the breakdown region (triggered mode) and the upturn region (the high current zone).

Pre-Breakdown Region

In this low-current region, the ZnO varistor acts as an ohmic resistor. Current increases linearly with voltage and the resistivity (or resistance) can be directly calculated from the slope of the J-E Graph in Figure 1.7. This pre-breakdown region is the **“sleep mode”** of the varistor whereby the varistor action is not triggered and it does not interact with the normal operation of the electrical circuit being protected. This ohmic region normally ranges from a current density of 1 nA/cm^2 up to 0.1mA/cm^2, which is a variation of up to six orders of magnitude. With regard to varistor application, this pre-switch region refers to the region of operation in the absence of all over-voltage transients.

Another name of this pre-switch region is leakage region that corresponds to the presence of a small leakage current ((Kutty and Ezhilvalavan, 1996) and (Clarke, 1999)). For commercial use, this leakage current must be lower than 60 μA/cm^2 in order to reduce to the watt loss of the circuit being protected.

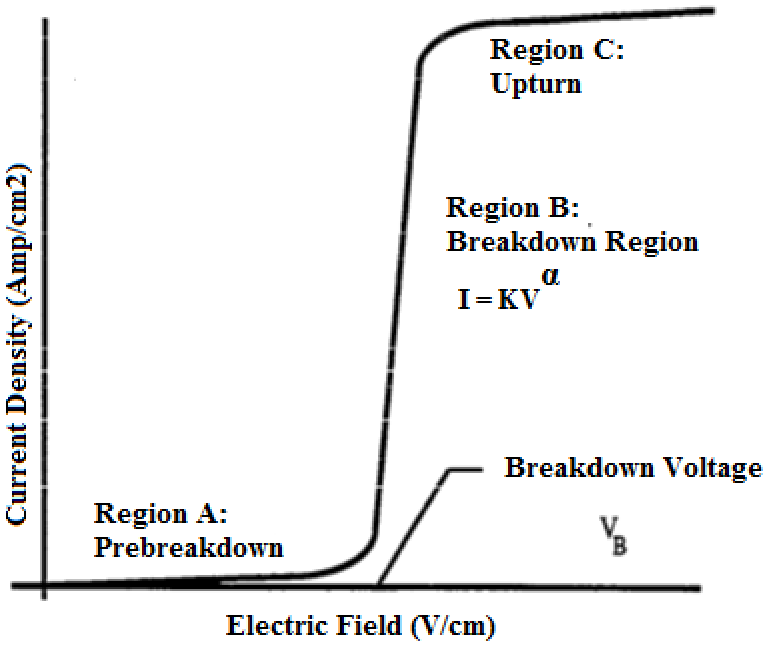

Figure 1.7: Nonlinear Current density-Electric field Characteristics Regions. (Nies, 1989)

This watt loss can be regarded as an amount of energy stolen from the power supply during the normal operation of circuit, and this stolen energy would reduce the power efficiency of the circuit and also it can make the resistor to become hot.

Breakdown Region

In this current-voltage region, the ZnO varistor acts as a very good conductor and as a very effective power surge absorber. From the J-E graph in Figure 1.7, flat peak of the graph refers to the switched region; the flatter peak, the better the protective function of the varistor.

The breakdown region, also called the nonlinear region, has one critical point known as switch-on voltage (V_{on}). It is also known as threshold Voltage or onset voltage. The switched-on voltage (V_{on}) is the voltage at which the varistor action is triggered. One intriguing fact about the switch-on voltage (V_{on}) is that, it is conveniently chosen to be 0.5 mA/cm2 current density or the voltage at 1mA. This chosen voltage (V_{1mA}) is found to be a convenient measuring parameter for varistor manufacturers to compare ZnO varistors of different voltage ratings. Another reason for choosing V_{1mA} as the critical parameter is that, most ZnO varistors exhibit the minimum nonlinearity at current value of about 1 mA. V_{on} must be at least 20% higher than the steady-state voltage of the normal operation of the circuit being protected by the varistor. This more than 20% voltage requirement is set by varistor manufacturers and varistor buyers. If the switch-on voltage is less than 20%, there will a danger of premature triggering of the varistor action that can cause harm to the circuit.

If the incoming supply voltage to the circuit suddenly increases to a dangerous level, that is more than 20%, then the varistor action of the ZnO varistor will be “switched on”. When the varistor senses over voltage, it becomes highly conductive and conducts the large quantity of current from the transient; thus preventing the damaging over-voltage from reaching the circuitry.

The current-voltage (I-V) characteristics in this nonlinear region do not obey Ohm’s law because the resistivity (ρ) of the varistor changes at different voltage values. For both the pre-switch and switched regions, the electrical characteristics of the ZnO varistor is controlled by the ZnO grain boundaries. Grain boundary resistivity, Grain boundary potential barrier, depletion layers and interfacial trap states are the grain boundary phenomena that contribute to the electrical characteristics of ZnO varistor.

Upturn Region

The upturn region is also called high-current region due to the high impulse current that the ZnO varistor has to endure. Because the ZnO grains becomes the controlling parameter that determine how the current-voltage characteristics response to transient surges, where the grain boundary potential barrier is completely removed by the large electric fields from the transients.

Referring to Figure 1.7, the onset of the upturn region also called E_{upon} can also be written as V_{upon}. The upturn onset electric field (E_{upon}) occurs at about 100A/cm^2 current density; and for low- voltage varistors, it may be about 1A/cm^2 current density. One unique characteristic about the high current region is that the ZnO varistor becomes more ohmic as the current/voltage increases, in which the current density-electric field (J-E) graph appears like a straight line.

Another crucial property of this high current region is that, the high current surges can cause permanent damage, physically and electrically on ZnO varistor; which almost means that the electrical properties are no longer reversible. In most cases, the electrical properties of the ZnO varistor become worse after every encounter with a high current transient surge. But luckily enough, high current surges do not occur regularly since they are cause by lightning and serious power faults.

The upturn region can extend up to a few thousands amperes/cm^2 current density or until the ZnO device is physically destroyed. For low-voltage varistors, the upturn region ranges from 0.1 A/cm^2 to 100A/cm^2 current density. Higher voltage varistor models can withstand higher level current surges up to one million amperes.

1.7.3 Nonlinear Coefficient

The nonlinear coefficient (α) is the most important property of the varistor because it is the heart of the varistor action that provides the protection against over-voltage transient surges (Wang et al., 2008). Over-voltage transient triggers the varistor to transform from a highly resistive state ($\rho \sim 10^{12}$ Ω.cm) into a highly conductive state

($\rho < 10$) in just a few nanoseconds, thus short-circuiting the incoming transient into the varistor device.

The higher the nonlinear coefficient value, the better the protection function of the varistor. The nonlinear coefficient equation is derived from the current – voltage (I-V) characteristics in switched region (Figure 1.7). The transformation from a highly resistive into a highly conductive state is made possible by the highest value of nonlinear coefficient of ZnO varistor.

The majority carriers (electrons) are rich with kinetic energy which allow them to cross the potential barrier at the grain boundary, thus gives the highest value of nonlinear coefficient. ZnO gives the highest value of nonlinear coefficient (α) if compared with any other varistor materials; this property makes ZnO the best choice for protection. Older varistor materials such as silicon carbide and selenium have much lower α value which explains why they are totally replaced with ZnO varistors. Pure resistors should have α value equal to 1 because referring to equation 1.1, if $\alpha = 1$ the equation becomes $I = KV$ which is the equation of straight line that agrees with Ohm's law. Here K is constant that is known as reciprocal of resistance, that is $K = 1/R$.

1.8 Research Problems

In operation, ZnO varistor materials are often subjects to various stresses such as continuous leakage current and resultant heat that can affect their performances. It has been found that the effect of applied field stresses on the stability of ZnO varistor ceramics can be taken care-off by the introduction of small amount of metal oxides as additives in the system. To develop a high performance of ZnO ceramics, small amount of CMO is added to ZnO system where this additive improves the stability of ZnO varistor.

Wide applications of ZnO inspire extensive research working on ZnO doped with transition metal oxides. In last few years, quite a substantial number of researchers have investigated ZnO doped with transition metal ions, but must of them paid their attention to its microstructure and electrical properties, but little report on the effect of applied field stresses on the stability of ZnO varistor ceramics.

In spite of many investigations carried out on ZnO varistor, investigation concerning the stability of ZnO ceramic containing small amount of metal oxides has not been sufficiently elucidated. Hence in this research the effect of applied field stresses on the stability of ZnO ceramics with $CaMnO_3$ as additive for varistor application was studied.

1.9 Objectives

In this present research work, different mole percentages of the dopant (CMO) with the same sintering temperature and different sintering time were performed. The objectives of this project are;

1. To study the effect of CMO contents on nonlinearity coefficient (α) enhancement of ZnO based low voltage varistor derived through modified citrate gel solution coating,
2. To study the nonlinear stability of ZnO based varistor ceramic against DC electrical field and thermal stresses as a function of CMO contents.

1.10 Hypothesis

1. Using wet chemical method to synthesize CMO, the nonlinearity coefficient value is expected to have an optimum value with the increase in the CMO contents
2. A good stability is expected after subjecting the ZnO + CMO varistor to DC electrical and thermal stresses at certain CMO content

1.11 Scope of Research

This work focuses on these areas:

1. ZnO material doped only with CMO. The dopant is added to investigate its contribution on electrical properties of ZnO varistor.
2. Microstructure characteristics are analysed using X-ray diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), and Thermogravimetric/Differential Thermal Analysis (TG/DTA).
3. Electrical characteristics are analysed through the current density-electric field (J-E) characteristics of the sintered samples. The variation of nonlinear coefficient (α), degradation of the samples with various formulation, leakage current and stability.

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LIST OF PUBLICATIONS

The following journal publications were achieved from the output of this research and during the period of candidature:

Accepted

I. I. lakin, A. Zakaria, Y. Abdollahi, D. Umaru, (2014). Effect of Sintering Temperature on Microstructure and Electrical Properties of ZnO + $CaMnO_3$ Ceramics used in Low-Voltage Varistor. Digest Journal of Nanomaterials and Biostructures.

Submitted

I. I. lakin, A. Zakaria, H. M. Kamari, R. S. Aziz and R. Wan Abdullah, (2014). Degradation Characteristics of Low Voltage Varistor from ZnO + $CaMnO_3$ Ceramics. Solid State Communications.