STABILITY OF ZINC OXIDE VARISTORS

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School of Materials
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ABSTRACT

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Ceramic varistors based on ZnO, Bi$_2$O$_3$, Sb$_2$O$_3$, MnO and Co$_3$O$_4$ were prepared by the mixed oxide route. After milling the powders, disc shaped samples were pressed and sintered for 2 hours at temperatures in the range 950°C to 1250°C. Products were characterised in terms of phase development and microstructure by X-ray diffraction and scanning electron microscopy; electrical characterisation included current-voltage (I-V), capacitance-voltage (C-V) and degradation behaviour. Most varistors contained a three phase microstructure comprising ZnO grains (3–54 μm in size), a Bi-rich grain boundary phase and a spinel phase. Product densities were approximately 5.45 g cm$^{-3}$, and nonlinear coefficients were typically in the range 5 to 53. By selective removal of either Sb$_2$O$_3$, or MnO or Co$_3$O$_4$, the role of individual components was investigated. The absence of Sb$_2$O$_3$ encouraged grain growth (to 40 μm) but reduced nonlinearity (to 5) and degraded the stability. The absence of Co$_3$O$_4$ improved the stability whilst the absence of MnO reduced the nonlinear coefficient and leakage current. The use of attrition milling yielded powders of small particle size (0.3 μm). The resulting sintered varistors exhibited a slightly smaller grain size (~ 5 μm) lower nonlinear coefficients (~30) but higher breakdown fields and leakage currents. Samples sintered at high temperatures (1050°C to 1250°C) degraded under electrical stress more slowly than the samples sintered at low temperature (950°C). Al-doping enhanced the nonlinearity but reduced the stability. In contrast Ag-doping reduced the nonlinearity but improved the ageing behaviour. An appropriate combination of Al and Ag doping led to varistor improvements in both nonlinearity and stability. The optimum aluminium nitrate and silver oxide levels for the varistor composition studied were found to be 500 ppm and 250 ppm, respectively. C-V measurements on this material gave barrier heights of ~ 1.7 V, and donor densities of 1.3×10$^{18}$ cm$^{-3}$. One batch of samples was prepared Ga$_2$O$_3$ additions of 750 – 4000 ppm. Doping with Ga caused a significantly decrease in grain size to ~ 6 μm), and reduced the nonlinear coefficients (to ~25) but increased the stability in terms of breakdown fields and leakage currents.
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## ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BC</td>
<td>Base composition</td>
</tr>
<tr>
<td>BCM</td>
<td>Base composition prepared without MnO</td>
</tr>
<tr>
<td>BCC</td>
<td>Base composition prepared without Co₃O₄</td>
</tr>
<tr>
<td>BCS</td>
<td>Base composition prepared without Sb₂O₃</td>
</tr>
<tr>
<td>AMBC</td>
<td>Base composition prepared by the attrition milling</td>
</tr>
<tr>
<td>CMBC</td>
<td>Base composition prepared by conventional milling</td>
</tr>
<tr>
<td>BCAG</td>
<td>Base composition prepared by adding Ag₂O</td>
</tr>
<tr>
<td>BCAL</td>
<td>Base composition prepared by adding Al(NO₃)₃·9H₂O</td>
</tr>
<tr>
<td>BCAA</td>
<td>Base composition prepared by adding Ag₂O and Al(NO₃)₃·9H₂O</td>
</tr>
<tr>
<td>BCG</td>
<td>Base composition prepared by adding Ga₂O₃</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>α</td>
<td>Nonlinear coefficient</td>
</tr>
<tr>
<td>E_B</td>
<td>Breakdown field</td>
</tr>
<tr>
<td>V_B</td>
<td>Breakdown voltage</td>
</tr>
<tr>
<td>I_L</td>
<td>Leakage current</td>
</tr>
<tr>
<td>K_T</td>
<td>Degradation rate coefficient</td>
</tr>
<tr>
<td>C-V</td>
<td>Capacitance-voltage</td>
</tr>
<tr>
<td>C_b</td>
<td>Barrier capacitance</td>
</tr>
<tr>
<td>N_d</td>
<td>Donor density</td>
</tr>
<tr>
<td>φ</td>
<td>Barrier height</td>
</tr>
<tr>
<td>L</td>
<td>Width of depletion layer</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

Varistors or variable resistors are sintered polycrystalline ceramic and have been used as a surge protective device for decades. The main reason is their nonlinear current-voltage (I-V) characteristics and good energy absorption capability. ZnO varistors were first used for the purpose of protection of semiconductor devices against transient surges in TV sets, microwave ovens, and other consumer electronic equipment. Later, ZnO varistors were extensively used as surge absorbers in industrial electronic equipment, and the fields of application have risen regularly. ZnO varistors have become one of the most useful protection devices and are very important devices in transient surge suppression technology. ZnO varistors are applicable as characteristics elements in gapless-type lightning arresters used in electric power systems. Moreover, automotive use has also been by the improvements of the characteristics for high operating temperature and low operating voltages [1-3].

At low voltage, varistors act as resistors, however they become conductors at high voltage. To protect components from high voltage transients, these varistors are used in parallel with circuits as shown in Figure 1-1. In normal situations, a small current is passed from the power supply. However there may be a large current in abnormal situations and varistor draws the current to ground. In the past, ceramics used as varistors were made of silicon carbide (SiC) [4]. Zinc oxide has largely replaced silicon carbide-materials because of their superior high nonlinear behaviour, providing improved circuit protection.

![Figure 1-1 Parallel connection of varistor to a circuit (after Moulson and Herbert [4]).](image)

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The properties of zinc oxide varistors were first discovered by Matsuoka et al. in 1969 [5]. The study indicated that zinc oxide with alkaline earth-additives exhibited nonlinear behaviour in current-voltage properties. Afterwards, many researchers focused on the improvement of nonohmic properties. The electrical property characteristics of zinc oxide varistors are equivalent to that of back-to-back Zener diodes. In a similar way to diodes, varistors can limit overvoltage equally in both polarities therefore the current-voltage characteristics of a varistor, which is analogous to that of two back-to-back diodes, can increase significantly. Varistors can be operated in ac or dc fields ranging from a few volts to tens of kilovolts per metre and a wide range of current as well. Moreover, varistors have the additional property of high energy absorption capability over wide range energy from a few joules to thousands of joules [6]. Now ZnO arrestors can be used in 1000kV electric networks.

ZnO varistors consist of ZnO as the major ingredient and several kinds of additives. The additives such as Bi$_2$O$_3$, MnO$_2$, Cr$_2$O$_3$, and etc. can generate the nonohmic property and improve the electrical properties and the stability. A typical varistor formation could be from 96.5mol% ZnO, 0.5mol% Bi$_2$O$_3$, 1 mol% CoO, 0.5 mol% MnO, 1 mol% Sb$_2$O$_3$, and 0.5 mol% Cr$_2$O$_3$ [7]. Amongst these additives, Bi$_2$O$_3$ plays the most important role and segregates to the grain boundary interface [8-9]. Furthermore, some metal oxides of transition metal oxides e.g. V, rare earths e.g. Pr and alkaline earths e.g. Ba serve a similar role as Bi$_2$O$_3$ in ZnO varistors [10-16]. The additives such as Mn, Co, Sb, etc improve the specific properties for the ZnO varistors [17].

High purity and fine particle size are desirable to produce a homogeneous sintered body from the viewpoint of raw materials. Moreover, the process of mixing and pressing affects the electrical properties and their homogeneity. ZnO varistors are typically prepared by the mixed metal oxides route in addition the techniques such as sol-gel, and combustion, etc have been used [18-20]. The sintering process is the most important and strongly affects the resultant electrical properties. The same composition can lead to different polycrystalline phases and electrical properties due to different sintering conditions, for example, temperature and atmosphere.

Varistor ageing is thought to be caused by intrinsic defects formed during processing which migrate to the grain boundaries thereby lowering the electrical barriers. This process can be reversed by annealing the varistors however the treatment is not practical.
in a working environment. Therefore the researchers have paid attention to improving the stability of ZnO varistors. It has been proposed that the stability may be enhanced by using the selective metal oxide dopants. The doping ions are introduced to prevent the ageing ion migrating and to allow them to occupy interstitial sites within the grain boundary region. Consequently the formation of intrinsic defects or the migration of defects towards the grain boundaries is hindered. For example with Ag$_2$O doping, the dopant improves the stability but it degrades the nonlinearity [21].

There were four objectives of this study:

(i) To study the role of different additives on the electrical properties of the varistors. The additives including manganese, cobalt and antimony were removed from the base composition to investigate their roles.

(ii) To study the effect of milling processes on phase development. The base composition was prepared by two milling techniques: conventional milling and attrition milling.

(iii) To study the role of aluminium and silver as an additive. Aluminium and/or silver were added to the base composition at ppm levels. The role of these additives as donor or acceptor was examined.

(iv) To study the role of gallium as an additive. Gallium was added to the base composition at ppm levels. The role of these additives as donor or acceptor was examined.
2. LITERATURE REVIEW

2.1 Properties of zinc oxide varistors

Zinc oxide (ZnO) is an n-type semiconductor which has a wurtzite-type structure. As presented in Figure 2-1, oxygen atoms are located in a hexagonal close-packed type of lattice and zinc atoms occupy half of the tetrahedral sites. The two types of atoms, zinc and oxygen, are tetrahedrally coordinated to each other and are also in equivalent positions. The availability of all the octahedral and half the tetrahedral sites means the ZnO structure is relatively open. This allows atoms or ions to be accommodated relatively easily in these interstitial voids. The relatively open structure also influences both the defects and the diffusion mechanism in ZnO.

Figure 2-1 Wurtzite structure of ZnO [22].
2.2 Microstructure of ZnO varistors

The microstructure of a varistor plays a key role in the nonlinear properties. The electrical characteristics are defined by microstructure development, and the inter-relationship between microstructure, the chemistry, and the physics of the varistor. The microstructure can be manipulated by controlling the processing conditions and using various dopants.

ZnO varistors are polycrystalline materials consisting of semiconducting ZnO grains with associated grain boundaries. Three main crystalline phases have been seen in the typical ZnO-Bi$_2$O$_3$ based varistors prepared with the other additives [23-25]. These phases are ZnO grains, the spinel phase Zn$_7$Sb$_2$O$_{12}$ and Bi-rich phases. The microstructural components of the ZnO varistor including various crystalline phases, their chemical formulation and dopants in various phases are shown in Figure 2-2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formulation</th>
<th>Doping element</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>ZnO</td>
<td>Co, Mn</td>
<td>Grains</td>
</tr>
<tr>
<td>Spinel</td>
<td>Zn$_7$Sb$<em>2$O$</em>{12}$</td>
<td>Co, Mn, Cr</td>
<td>Intergranular phase</td>
</tr>
<tr>
<td>Pyrochlore</td>
<td>Bi$_6$(Zn$_4$Sb$<em>2$)O$</em>{18}$</td>
<td>Co, Mn, Cr</td>
<td>Intergranular phase</td>
</tr>
<tr>
<td>Bi-rich phase</td>
<td>β-Bi$_2$O$_3$, α-Bi$_2$O$_3$, δ-Bi$_2$O$_3$</td>
<td>Zn, Sb</td>
<td>Triple point</td>
</tr>
</tbody>
</table>

Figure 2-2 Microstructural components of ZnO varistor (after Gupta [6]).
The microstructure of ZnO-varistors can be fundamentally explained in term of a block model as shown in Figure 2-3. The distance between two electrodes is D. The rectangular blocks of conducting ZnO grains with size of d are divided by insulating barriers of thickness t at the grain boundaries. When a current is applied, an electrical current is passed through the grains. The shortest electrical pathway is the route that has the least number of grains between the electrodes.

\[ V_B = nV_g = \frac{D}{d} V_g \]  

where \( V_g \) is the breakdown voltage per intergranular barrier.
ZnO grains make up the bulk of the varistor. The sizes range from 3 \( \mu \text{m} \) to 50 \( \mu \text{m} \) depending on the processing conditions and system used. Pure ZnO was studied by Wong [26]. It was found that sintering pure ZnO at 700°C for 1 hour produced a highly porous ceramic. However this high porosity pellet did not show the non-ohmic property.

The microstructure of pure ZnO presented from the scanning electron micrograph shows that in pure ZnO sample ZnO grains had the hexagonal-shape as shown in Figure 2-4. The grain size of ZnO grain increases with increasing sintering temperature. From the work of Asokan et al. [27], the grain size increased from about 3 \( \mu \text{m} \) to about 20 \( \mu \text{m} \) as the sintering temperature increased from 900°C to 1300°C.

![Figure 2-4 SEM micrograph of pure ZnO sintered at 1300°C for 2 hours [27].](image)

The microstructures at the grain boundaries are classified into three types of structures as shown in Figure 2-5 [8]. First, type I is the grain boundary including a \( \text{Bi}_2\text{O}_3 \)-rich intergranular layer with relatively thickness approximately of 0.1-1 \( \mu \text{m} \). \( \text{Bi}_2\text{O}_3 \) has the melting point at 825°C thus during sintering procedure, a liquid phase is formed. The liquid phase is accommodated by initial porosity between the ZnO grains. Second, type II structure is the \( \text{Bi}_2\text{O}_3 \)-rich intergranular layer approaching the contact points of the ZnO particles. The thick \( \text{Bi}_2\text{O}_3 \)-rich intergranular layer becomes thinner to the size of 10-1000 Å. Last, type III structure refers to the contact point where the intergranular layer cannot be detected.
2.3 Conduction mechanism

The conduction mechanism in ZnO varistors is not fully understood even though many models have been proposed. In effect, eight models have been proposed as shown in Table 2-1.

(1) The first model was the theory of space charge limited current (SCLC) proposed by Matsuoka [28]. The concept was that the segregation layer consisted of many different oxides and was assumed to contain many traps.

(2) The second model was tunnelling through a thin layer at the grain boundaries by Levinson and Philipp [29].

(3) The third model was tunnelling through Schottky barriers proposed by many groups [30-36]. One model did not take the account to consider the heterojunction [30-32, 36]. For example in model proposed by Morris [31] the conduction mechanism showed the electron tunnelling and hopping in the intergranular layers of amorphous Bi₂O₃-ZnO. Two main factors supporting this mechanism were first a slight reduction in both the polarisability and ac resistivity with frequency and second the low activation energy. The other model took into consideration the heterojunctions [33, 34]. In model proposed by Emtage [33] the conduction mechanism is based on the grain boundary. The main
evidence supporting this model is the large apparent permittivity obtained for the varistors \((\approx 1000\varepsilon_0)\) where \(\varepsilon_0\) is the permittivity of free space \((8.854\times10^{-12} \text{ F m}^{-1})\). This value is larger than that for either the ZnO grains \((10\varepsilon_0)\) or the intergranular layer \((16\varepsilon_0)\). In addition Eda suggested that there is a semiconductor-insulator-semiconductor (SIS) structure at the grain boundary [34]. Therefore SIS composed of the intergranular layer (insulator) sandwiched between two Schottky barriers formed at ZnO grain surfaces. Moreover the thickness of the intergranular layer was reportedly less than 500 Å, much thinner than that reported by Matsuoka.

(4) The fourth model was tunnelling through homojunctions of ZnO [35]. Regarding the theory, thermal equilibrium of defects which are formed during cooling at the grain boundaries is important.

(5) The fifth model was tunnelling through Schottky barrier with the hole creation [37]. This model proposed the importance of minority carriers (holes) at the grain boundaries.

(6) The sixth model was the bypass effect at heterojunctions. This model represents the vital role of Bi$_2$O$_3$-rich intergranular layer in the small current region and assumed that parallel current paths through the heterojunctions and the Bi-rich intergranular layers should be considered.

(7) The seventh model was hole induced breakdown [38-40]. The model demonstrated that the highly nonohmic property is caused by the lowering of the potential barriers at the grain boundaries because of the hole accumulation. The holes were formed by accelerated electrons in the depletion region. The dependence of potential barriers on the interface states and or the bulk traps was proposed.

(8) The eighth model was induced space charge current at the heterojunction composed of thin films of ZnO and Bi$_2$O$_3$ [41].
Table 2-1 Timeline of the proposed conduction mechanisms in ZnO varistor (after Eda [8]).

<table>
<thead>
<tr>
<th>Year</th>
<th>Model</th>
<th>Researchers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1971</td>
<td>Space charge limited current</td>
<td>Matsuoka [28]</td>
</tr>
<tr>
<td>1975</td>
<td>Tunnelling through a thin layer</td>
<td>Levinson and Philipp [29]</td>
</tr>
<tr>
<td></td>
<td>Tunnelling through Schottky barrier</td>
<td>Levine [30]</td>
</tr>
<tr>
<td>1976</td>
<td>Tunnelling through Schottky barrier</td>
<td>Morris, Bernasconi et al. [31,32]</td>
</tr>
<tr>
<td>1977</td>
<td>Tunnelling through Schottky barrier with heterojunction</td>
<td>Emtage [33]</td>
</tr>
<tr>
<td>1978</td>
<td>Tunnelling through Schottky barrier with heterojunction</td>
<td>Eda [34]</td>
</tr>
<tr>
<td></td>
<td>Tunnelling through heterojunction</td>
<td>Emtage [35]</td>
</tr>
<tr>
<td>1979</td>
<td>Tunnelling through Schottky barrier</td>
<td>Hower and Gupta [36]</td>
</tr>
<tr>
<td></td>
<td>Hole assisted tunnelling through Schottky barriers</td>
<td>Mahan [37]</td>
</tr>
<tr>
<td>1982</td>
<td>Bypass effect at heterojunction</td>
<td>Eda</td>
</tr>
<tr>
<td>1984</td>
<td>Hole induced breakdown</td>
<td>Pike [38]</td>
</tr>
<tr>
<td>1986</td>
<td>Bypass effect at heterojunction</td>
<td>Levinson and Philipp</td>
</tr>
<tr>
<td></td>
<td>Hole induced breakdown</td>
<td>Blatter and Greuter [39, 40]</td>
</tr>
<tr>
<td>1987</td>
<td>Space charge induced current</td>
<td>Suzuoki et al. [41]</td>
</tr>
</tbody>
</table>

Even though many conduction mechanisms have been proposed the back-to-back double Schottky barrier model has been widely accepted by many studies. It has been used to interpret the various electrical properties of ZnO varistors.

2.4 Chemical defects within ZnO varistors

From optical studies, the energy band gap at room temperature for a ZnO crystal free from dopant is about 3.4 eV. The thermodynamically formed intrinsic defects occupy donor and acceptor levels within the band gap. The fastest diffusion among the natural defects is by the interstitial Zn$_i$, playing a significant role in varistor stability. On heating to high temperatures in air, oxygen atoms are lost. For this reason, oxygen
vacancies lead to the formation of nonstoichiometry of zinc atoms on the interstitial sites. It is accepted that the defect is a neutral oxygen vacancy and the thermal energy at room temperature is sufficient to ionize the vacancy. Thus the electrons are promoted into the conduction band.

![Diagram of electronic energy levels](image)

Figure 2-6 shows the schematic electronic energy levels of native defects in ZnO and the width of forbidden gap. The location of defects is reported with respect to the defect energy. The symbol such as $V_{O}/V_{O}^{x}$ represents that the defect of $V_{O}$ is on the right side of the equation and $V_{O}^{x}$ is on the left side as shown in Equation 2-2. Zinc interstitial is represented by $Zn_{i}$, oxygen and zinc vacancies are represented by $V_{O}$ and $V_{Zn}$ respectively. The symbol $x$ means an electrically neutral species. It is clearly seen that two possible defects may control the electrical conductivity of ZnO e.g. oxygen vacancies and zinc interstitials. As their donor levels are located close to the conduction band (0.05 eV), full ionisation can occur at room temperature by the following reactions:

$$V_{O}^{x} \leftrightarrow V_{O} + e' \quad (2-2)$$

$$Zn_{i}^{x} \leftrightarrow Zn_{i} + e' \quad (2-3)$$

Moreover there could be a second ionisation step as the following reactions:

$$V_{O} \leftrightarrow V_{O}^{x} + e' \quad (2-4)$$
However, from many defects in ZnO, it is believed that the major defect is interstitial zinc in the interstitial voids. This leads to nonstoichiometric Zn an n-type semiconductor having the formula \( \text{Zn}_{1+x} \text{O} \). This defect state was confirmed by the work of Mohanty and Azaroff [43]. The electron distributions in ZnO were studied for the samples exposed to liquid Zn or Zn vapour. It was concluded that the excess interstitial Zn occupied the octahedral sites. Moreover the conductivity of ZnO increases when the samples were exposed to liquid Zn or Zn vapour [43].

In order to provide an explanation for the donor and acceptor effects on the I-V curves, the defect models for these dopants in the grain and grain boundary of the entire ZnO varistor microstructure have been developed. The defect equilibrium of ZnO and Al will be explained as follows [44].

The donor and acceptor effects with Al doping assume that Al acts as a donor on lattice sites, \([\text{Al}_{2\text{zn}}]\), and an acceptor on an interstitial sites, \([\text{Al}^3']\). In order to simplify the explanation, only the singly ionised defects were considered by Gupta [44]. Furthermore, association or pairing of defects and interaction with other dopants was also neglected.

### 2.5 Chemical routes for the preparation of ZnO varistors

ZnO varistors are typically prepared by conventional ceramic processing i.e. the mixing of ZnO powder with additives (oxides) by ball milling (dry or wet), then compressing and sintering. The particle size distribution and homogeneity of the mixture play the important roles for controlling the properties of sintered ceramics. The milling methods, the milling medium and the milling time are also important factors.

Several chemical routes have been employed for preparation of ZnO varistors [45-48]. Sol-gel processing is the method that uses a kind of chemical wet-mixing route in order to obtain the very fine and homogeneous powders. Moreover this method can yield materials with high breakdown fields because of the small grain size. Pillai et al. reported a mixed precursor method (MPR) involving soluble metal salts, oxalic acid,
diethanolamine and ethylene glycol in ethanol solution [48]. The average particle size of powder was 15 nm. The varistors fabricated from this route showed the breakdown voltage at 941 V/mm, higher than that of commercial varistors sintered at 1050°C. It means that this technique may provide a simple route using inexpensive starting materials and giving good electrical properties at lower sintering temperature.

Meng et al. synthesised a varistor composite involving a double core shell structure [49]. The ZnO nanoparticles were coated with SiO$_2$ through the hydrolysis of tetraethyl orthosilicate (TEOS) and the additives were subsequently coated on the core of SiO$_2$. The homogeneity is attributed to the narrow size distribution with the average diameter of 85 nm. Using the optimum amount of TEOS yielded ZnO varistors with superior electrical performance [49]: a breakdown voltage of 1123 V/mm, the nonlinear coefficient of 43 and the leakage current of 8.5 $\mu$A.

Chemical routes can produce pure, fine, compositionally homogeneous powder for the preparation of ZnO varistors; however they are not as convenient as the conventional mixed oxides route. The latter is still the main processing method in both small scale for academic study and large scale for industrial production.

2.6 Electrical properties

2.6.1 Current-voltage characteristics

The current-voltage characteristics are the most important property of a ZnO varistor. The varistor functionally behaves as a near insulator (resistor) prior to reaching a voltage known as the breakdown or threshold voltage and it behaves as a conductor thereafter. The attractive features of the ZnO varistor are the nonlinear or nonohmic characteristic in the conductive mode and the low leakage (power loss) at the steady operating voltage in the resistive mode. The nonohmic properties of ZnO varistors have a close connection to the microstructure, characterised by the Bi$_2$O$_3$-rich intergranular layer. The threshold voltage in the I-V curve and the surge current withstand capability are proportional to the number of intergranular layers in series connection and the number of intergranular layers in parallel connection, respectively.
The I-V characteristics of ZnO varistors include three regions i.e. the pre-breakdown region, the nonlinear region, and the upturn region as shown in Figure 2-7. The first region is the pre-breakdown region which is low current linear region, <10^{-4} A/cm^2. In the pre-breakdown region the varistors exhibit ohmic I-V characteristic. The dc current is about 2 orders of magnitude lower than the ac current for a given operating voltage. The difference can be ascribed to the contribution of the dielectric loss upon application of an ac voltage. The total ac current consists of a capacitive current (I_C) and a resistive current (I_R) and is determined by the impedance of ZnO grain boundaries. Therefore, it is believed that this region is related to grain boundary controlled processes.

In the second region, the nonlinear or breakdown region is the heart of ZnO varistors. In this intermediate nonlinear region, the device conducts an increasingly large amount of current for a small increase in voltage. The nonlinear region may extend over 6 to 7 orders of magnitude of current. This large nonlinearity over a wide range of current densities makes the device is useful for the variety of applications. The degree of nonlinearity is determined by the flatness of the nonlinear region i.e. the flatter I-V curve in this region leads the better device. The breakdown voltage per intergranular barrier is expected to be 2-3 V/barrier considering the bulk material. The current-voltage relation can be expressed in a term of

\[ I = kV^\alpha \]

where \( k \) is a constant, and \( \alpha \) is nonlinear coefficient. Therefore a nonlinear coefficient is defined by

\[ \alpha = \frac{\log(I_2/I_1)}{\log(V_2/V_1)} \]

where \( V_1 \) and \( V_2 \) are the voltage at current \( I_1 \) and \( I_2 \) (\( I_2>I_1 \)), respectively.

The addition of Bi_2O_3 has been found to be essential to provide the nonohmic behaviour. However addition of transition oxides e.g. Co_3O_4 and MnO_2 also improve nonlinearity. Furthermore multiple dopants have produced greater nonlinearity than single dopant. Increasing dopants concentration up to some optimum amount has enhanced nonlinear behaviour. Zinc oxide varistors show nonlinear coefficients in the range of 20-100.
The third region is the high current upturn region. In the high current region (>10^2 A/cm^2) again the varistor acts as a resistor and the I-V characteristic is linear similar to that in low current region. Moreover in this region the voltage rises faster with current than in the nonlinear region. The up-turn region is controlled by the impedance of the grain in ZnO microstructure; therefore the property is related to grain controlled processes. As a result dopants are known to control electrical resistivity of the ZnO grains and additives such as aluminium and gallium greatly influence the upturn properties.

![Diagram showing current-voltage characteristics of ZnO varistors](image)

Figure 2-7 Typical current-voltage characteristics of ZnO varistors [50].

### 2.6.2 Breakdown voltage/field

The ZnO varistor is characterised by a voltage which points to the transition from linear to nonlinear modes. The voltage at the onset of this nonlinearity above the knee of the I-V curve is the nonlinear voltage determining the voltage rating of the device. Due to the lack of sharpness of the transition in the I-V curve, the exact location of this voltage is difficult to determine in most varistors. Therefore a breakdown voltage V_{1mA} is purposely defined as the voltage at which the current through the varistor is 1 mA. This current is usually at the knee of the I-V curve between the pre-breakdown region and the nonlinear region. However a breakdown field should be used instead of a breakdown voltage to normalise the data and avoid uncertainties caused by different dimensions.
breakdown field is thus defined as the electric field at which the current density through the varistor is between 0.5 mA/cm² and 1.0 mA/cm².

### 2.6.3 Capacitance-voltage characteristics

The relationship between the capacitance and the applied voltage of ZnO-Pr₆O₁₁ varistor was studied by Mukae et al. [51]. It was found that capacitance decreased with the applied voltage. A similar dependence was reported in the case of the Bi₂O₃ system [31, 33]. In ZnO-Bi₂O₃ the barrier height ($\phi$) and donor density ($N_d$) were obtained from the plot of $1/C^2$-$V$ [31]. In the study of Mukae a modified $1/C^2$-$V$ method was applied to obtain the barrier height and donor density on the basis of the Schottky barrier model. The band structure of a grain boundary back-to-back double Schottky barrier is shown in Figure 2-8.

![Band structure of a double Schottky barrier](image)

Figure 2-8 Band structure of a double Schottky barrier at the grain boundary of a ZnO varistor: (a) no applied voltage; (b) applied voltage=$V$ [52].

Since the intergranular layer can be considered as highly conductive, the voltage drop in the layer is negligible. In this case the capacitance per unit area of a grain boundary was defined as $C_b$ and can be expressed as:
where \( q \) is the electron charge, \( \varepsilon_s \) is permittivity of ZnO (\( \varepsilon_s = 8.5 \varepsilon_0 \)), \( N_d \) is the donor density of ZnO, \( \phi \) is the barrier height, \( V_g \) is the applied voltage per grain boundary and \( C_{b0} \) is the value of \( C_b \) when no voltage is applied.

According to Equation 2-8, if the left hand term is plotted against the applied voltage per grain boundary then a linear trend should be obtained. The donor density and the barrier height can be calculated from the slope and the intercept of the line, respectively. The donor density is typically in the range \( 10^{17} \) to \( 10^{18} \) cm\(^{-3}\) and the barrier height is about 1 V for ZnO-Pr\(_6\)O\(_{11}\) system [53-56]. The \( N_d \) and \( \phi \) values are in the range \( 10^{15} \) to \( 10^{19} \) cm\(^{-3}\) and 0.5-2.5 V for the ZnO-Bi\(_2\)O\(_3\) system [57-59].

### 2.6.4 Effect of additives oxides

Since the invention of ZnO varistors, most of the developments and investigations have been based on the ZnO-Bi\(_2\)O\(_3\) system because of its simplicity and efficiency. However, the nonlinearity of the ZnO-Bi\(_2\)O\(_3\) binary system did not show the most effective results as the nonlinear coefficient was less than 10 [5]. It means that additives play an important role for ZnO varistors because they can improve the nonlinearity. Metal oxide additives affect various properties of ZnO varistors [60]. For instance, cobalt and manganese enhance the nonlinear characteristics. These \( M^{2+} \) ions go into a solution in ZnO. Furthermore, it is believed that the transition metal oxides are involved in the formation of interfacial states and deep bulk traps, both of which contribute to highly nonohmic behaviour. The addition of titanium, aluminium and antimony retards the grain growth; on the other hand, silicon increases grain growth. Antimony forms the spinel phase and a pyrochlore phase blocking grain growth. Moreover Sb promotes the formation of twins in ZnO grains and improves the nonlinearity. Thus the I-V characteristics become better stabilised against electrical stresses, and the breakdown voltage increases. The roles of Sb\(_2\)O\(_3\) were proposed as: (i) grain growth suppression and (ii) the solubility enhancement of ions such as Zn in the Bi\(_2\)O\(_3\)-rich liquid phase [9]. The latter role is very important in order to control the defect distribution at the grain boundaries during the cooling. To improve the reliability, NiO, Cr\(_2\)O\(_3\), or a small
amount of glass frit are used. These additives stabilise the intergranular layer against the
electric load and ambient conditions e.g. temperature and humidity. Table 2-2 shows
roles of additives in ZnO varistors. Furthermore, some metal-oxide additives are
specific to grains and/or grain boundaries. For example, Gupta studied the effect of the
additive-induced defects on grain, grain boundaries, or both when the additives were
sodium, and aluminium [44]. It can be noted that aluminium addition is both grain and
grain boundary specific, whereas, the addition of sodium is only grain boundary
specific.

Table 2-2 Roles of additives in ZnO varistors (after Eda [8])

<table>
<thead>
<tr>
<th>Roles</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolation among ZnO grains and supplying required elements to grain boundaries (O₂, Co, Mn, Zn, etc.)</td>
<td>Bi, Pr &gt; Ba, Sr, Pb, U</td>
</tr>
<tr>
<td>Improvement of non-ohmic exponent -formation of interface states</td>
<td>Co, Mn &gt; (Sb)</td>
</tr>
<tr>
<td>Improvement of stability</td>
<td>Sb, glass, Ag, B &gt; Ni, Cr</td>
</tr>
<tr>
<td>Improvement of non-ohmic exponent in a high current region -formation of donors in ZnO</td>
<td>Al, Ga &gt; F, Cr</td>
</tr>
<tr>
<td>Grain growth suppression</td>
<td>Sb, Si</td>
</tr>
<tr>
<td>Grain growth promotion</td>
<td>Be &gt; Ti &gt; Sn</td>
</tr>
</tbody>
</table>

From Table 2-2, the approximate degree of effectiveness of the additives is roughly indicated by the symbol >.

2.7 Ageing (Degradation) of ZnO varistors

One of the challenges in the development of varistors has been to reduce their long term ageing. The ageing phenomena have been investigated under ac, dc and pulse electric field [61-64]. Amongst ageing mechanisms ion migration is strongly supported on the
basis of experimental evidences [65]. Thermally stimulated current (TSC) of stressed varistor is a strong evidence of ion migration [66]. Collected work on varistor ageing suggests that first, ageing is a grain boundary phenomenon, second, the ageing is caused by ion migration in the depletion region and third, the migrating ion is predominantly zinc interstitials. Regarding these suggestions, the ageing arises as a result of field-assisted diffusion of zinc interstitial in the depletion layer and thereby chemical interaction with the grain boundary defects. This process leads to a reduced barrier height and increased leakage current. The zinc interstitial originates from the nonstoichiometric nature of ZnO which can form excess zinc donors during heating, even under an oxidizing atmosphere. These donors are then accommodated at interstitial sites in the lattice and are frozen-in at room temperature during the cooling. The frozen interstitials trapped in the depletion layer degrade varistor stability. Based on this concept a grain boundary defect model for the varistor has been proposed [67].

A defect model analogous to the band model involving the Schottky barrier was developed by Gupta and Carlson [67]. The basic concept is that the depletion layer including the barrier comprises two components: a stable component consisting of spatially fixed, positively charged ions and a metastable component containing mobile, positively charged zinc interstitials. The former ions are the trivalent ions such as bismuth, antimony, etc. These ions so are called donor ions, \( D_{Zn} \). In addition, the oxygen vacancies, \( V_O \) and \( V_O^- \), are positive and in this group too (Figure 2-9b). The latter ions are the singly and doubly charge native zinc interstitials, \( Zn_{i}^{+} \) and \( Zn_{i}^{+} \). These trivalent positive charged donors extend from both sides of the grain boundary into the adjacent grains and are compensated by a layer of negatively charged ions at the grain-boundary interface, consisting primarily of native zinc vacancies, \( V_{Zn}^{−} \) and \( V_{Zn}^{−} \). The oxygen interstitials, \( O_{i}^{+} \) and \( O_{i}^{−} \), are not considered as major types of defect in ZnO. Figure 2-9 shows the defect model analogous to Schottky barrier model.
Figure 2-9 Band and defect model for varistor grain boundary [6].

Figure 2-9a shows the band model whereas Figure 2-9b illustrates the corresponding defect model. For electrical neutrality, the positive charges in the depletion layers in the adjacent grains balance the negative charges on the grain boundary. The vital feature about the charges in the depletion layer is that the spatial locations of these positive ions are different. The substituted ions and vacancies are located on the lattice sites while the zinc interstitials are located on the interstitial sites in the ZnO (wurtzite) structure. Therefore, the zinc interstitials can rapidly migrate within the structure via these interstitial sites whereas the host lattice ions or the ions replaced on the host lattice site have to move via the adjacent vacancies. For the model, these ions are spatially restricted at the practical operating temperature of the varistor. An additional feature of this model is that the grain boundary acts as if it were disordered layer. There are two characteristics of the disordered layer: it (i) provides a rapid diffusion path for anions (oxygen) and (ii) behaves as an infinite source and sink for neutral vacancies, $V_x$.

2.8 Prevention of ageing

Since the zinc interstitials in the depletion layer containing the metastable component of the barrier may be responsible for the instability of the device, the removal of the metastable component can restore stability. The metastable component can be theoretically removed thermally or chemically.

Heat treatment has been used to improve the stability of varistors. Huang and Li investigated the effect of annealing on the degradation behaviour of varistors [68].
Some ZnO varistors were further annealed at 800°C for 2 hours after sintering at 1200°C for 2 hours. It was found that the percentage of changes in current density of annealed samples was less than that of the non-annealed samples. This means the stability of the ZnO varistors was substantially and consistently improved by the annealing process. It has been shown that when the zinc interstitials in the depletion layer are permanently diffused out via thermal annealing, the varistor stability improves [69]. Takada and Yoshikado also studied the thermal annealing of Sb-Bi-Mn-Co-added ZnO varistor [70]. It was found that the tolerance characteristics of varistors to electrical degradation after annealing greatly depended on the amount of Sb$_2$O$_3$ added. The tolerance characteristics of varistors to electrical degradation were improved markedly by the addition of more than 0.01 mol% Sb$_2$O$_3$. The dependence of nonlinear coefficient on annealing temperature and time shows that after electrical degradation the samples annealed between 500°C-900°C exhibited similar nonlinear coefficients of about 15 whilst the annealing time of 5 hours yielded the highest $\alpha$-value.

The addition of selective elements can slow down the degradation process because the doping ions occupy the sites that will otherwise be used by migrating zinc ions. Gupta and Miller investigated the stability of ZnO varistor through donor and acceptor doping at the grain boundary [71]. A grain boundary defect model for the effects of Na$^+$ and K$^+$ on varistor stability was presented. Both Na and K atoms can act as amphoteric dopants since they can occupy both lattice and interstitial sites. This reduces the formation and mobility of the zinc interstitial which can degrade the varistor characteristics. Table 2-3 shows a series of quasichemical reactions and corresponding mass action relations for the creation of electronic and ionic defects in the grain boundary [71]. It can be described in the same way for Na and K. Particular attention needs to be paid to the effects of zinc interstitials which influence the stability and also to carrier concentration (n) which affects the leakage currents.
Table 2-3 Quasichemical reactions and corresponding mass action relations for the incorporation of Na in the grain boundary (after Gupta and Miller [71])

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Quasichemical reactions</th>
<th>Mass action relations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Frenkel disorder:</td>
<td>[Zn_n^x \leftrightarrow Zn_i^x + V_{zn}^x]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[[Zn_i^x][V_{zn}^x] = K_F]</td>
</tr>
<tr>
<td>(2)</td>
<td>Zn interstitial ionisation:</td>
<td>[Zn_i^x \leftrightarrow Zn_i + e']</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[[Zn_i]n = K_Z]</td>
</tr>
<tr>
<td>(3)</td>
<td>Intrinsic electronic disorder:</td>
<td>[O \leftrightarrow e' + h^-]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[np = k_i]</td>
</tr>
<tr>
<td>(4)</td>
<td>Sodium interstitial:</td>
<td>[Na(g) + V_{zi}^x \leftrightarrow Na_i^x]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[[Na_i^x] = K_1 a_{Na}]</td>
</tr>
<tr>
<td>(5)</td>
<td>Sodium substitution:</td>
<td>[Na(g) + V_{zn}^x \leftrightarrow Na_{zn}^x]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[[Na_{zn}^x] = K_2 a_{Na}]</td>
</tr>
<tr>
<td>(6)</td>
<td>Donor ionisation:</td>
<td>[Na_i^x \leftrightarrow Na_i + e']</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[[Na_i]n = K_d K_1 a_{Na}]</td>
</tr>
<tr>
<td>(7)</td>
<td>Acceptor ionisation:</td>
<td>[Na_{zn}^x \leftrightarrow Na_{zn} + h^-]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[[Na_{zn}^x]p = K_a K_2 a_{Na}]</td>
</tr>
</tbody>
</table>

In the case of silver doping, which is monovalent dopant, the quasichemical reaction and corresponding mass action relations for the creation of electronic and ionic defects in the grain boundary can be described similarly to sodium and potassium doping.

In the present work the effects of the monovalent and trivalent metal dopants will be investigated. The selective removal of individual components and the effect of different powder preparation process will also be investigated to assess their contribution to the electrical properties and varistor stability.
3. EXPERIMENTAL PROCEDURE

3.1 Starting materials and sample compositions

All starting materials were of reagent grade. Chemicals, Chemical Abstracts Services (CAS) numbers, manufacturers, as well as purity are shown in Table 3-1.

Table 3-1 Details of starting chemicals

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>CAS No.</th>
<th>Manufacturer</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>1314-13-2</td>
<td>BDH</td>
<td>99.0 %</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>1304-76-3</td>
<td>Alfa Aesar</td>
<td>99.5%</td>
</tr>
<tr>
<td>MnO</td>
<td>1344-43-0</td>
<td>Aldrich</td>
<td>99%</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>1308-06-1</td>
<td>BDH</td>
<td>-</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>1309-64-4</td>
<td>Fluka</td>
<td>99.0%</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>20667-12-3</td>
<td>Alfa Aesar</td>
<td>99%</td>
</tr>
<tr>
<td>Al(NO₃)₃·9H₂O</td>
<td>7784-27-2</td>
<td>BDH</td>
<td>99%</td>
</tr>
<tr>
<td>Ga₂O₃</td>
<td>12024-21-4</td>
<td>Aldrich</td>
<td>99.99%</td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td>67-63-0</td>
<td>BDH</td>
<td>99.7%</td>
</tr>
</tbody>
</table>

In each batch, four pellets of varistor samples were prepared. Varistor formulations prepared are listed in Table 3-2.

Table 3-2 Varistor formulations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (mol% of metal)</th>
<th>Amount of compound (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZnO</td>
<td>Bi₂O₃</td>
</tr>
<tr>
<td>BC</td>
<td>97.0</td>
<td>1.0</td>
</tr>
<tr>
<td>BCM</td>
<td>97.5</td>
<td>1.0</td>
</tr>
<tr>
<td>BCC</td>
<td>98.0</td>
<td>1.0</td>
</tr>
<tr>
<td>BCS</td>
<td>97.5</td>
<td>1.0</td>
</tr>
<tr>
<td>BCAG</td>
<td>97.0</td>
<td>1.0</td>
</tr>
<tr>
<td>BCAL</td>
<td>97.0</td>
<td>1.0</td>
</tr>
<tr>
<td>BCAA</td>
<td>97.0</td>
<td>1.0</td>
</tr>
<tr>
<td>BCG</td>
<td>97.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

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3.2 Sample preparation

Varistor materials were prepared by the conventional route as follows: the amount of starting materials powders in mole percent proportions was mixed in a polypropylene bottle using propan-2-ol as a medium for 24 h in a vibrated mill. Each batch of powder had 1:1:1 ratio of powder (gram) to 6-mm-diameter zirconia balls (gram) to volume of propan-2-ol (millilitre) producing 20 g batch for the formulations of BCAG, BCAL, BCAA and BCG, and 50 g batch for the BC, BCM, BCC, and BCS. After that the mixtures were dried in an oven for 24 h.

To study the effect of the powder processing route, BC composition was prepared by attrition milling technique as well. Starting materials powder totalling 150 g was mixed in 100 mL deionised water. A few drops of DispexA40 surfactant were added to make a solution. This mixture was poured into the container into which 0.25-mm-diameter zirconia balls were added and then mixed using Szegvari attritor (Union Process Inc.) with the speed of 200 rpm for 3 h. The mixture was then filtered and freeze dried.

The flow chart in Figure 3-1 summarises the fabrication procedures.

The powders from these preparation techniques were pressed uniaxially at 80 MPa in a hardened steel die into pellets of approximately 13.0 mm diameter and 5 mm thickness. They were placed on alumina substrates with a powder bed of the same composition and covered by an alumina boat. For each batch, four pellets were sintered at temperatures from 950°C to 1250°C for 2 h in a Vecstar HF2 Furnace, with a heating and cooling rate of 3°C/min. The dimensions of the final ceramics were approximately 10 mm in diameter and 4 mm thick. The procedure used to characterise the sintered pellets is shown in Figure 3-2.
Figure 3-1 Flow chart for sample preparation.
Figure 3-2 The procedures for characterisation of the sintered samples.

- Sintered pellets → Density Measurement → Electrical Properties Measurement

  - XRD

  - SEM + EDX Analysis
3.3 Characterisation techniques

3.3.1 Particle size analysis

Particle size analysis was undertaken using a Malvern Mastersizer. This technique is based on the principle of laser ensemble light scattering. The main benefits are that it is non intrusive, fast, precise, absolute, simple, and highly versatile. The general particle sizing system is shown in Figure 3-3. A small amount of sample powder and water were mixed in the beaker. DispexA40 surfactant was added and then stirred well. Then the mixture was dropped until into the Mastersizer unit in which the fan speed 2000 rpm was used. The obstruction was measured and then since the obstruction was reached approximately 15% the Mastersizer software was used to analyse the dispersed particles.

![Diagram of particle size analysis system](image)

Figure 3-3 General particle size analysis system schematic.

3.3.2 Density determination

The densities of sintered pellets were determined by the geometric method. The weight and the dimensions of the pellets were measured. The density of specimen \( \rho_C \) was calculated from
\[ \rho_c = \frac{w}{\pi r^2 t} \]  \hspace{1cm} (3-1)

where \( w \) is the weight of the pellet, \( r \) is the radius of the pellet and \( t \) is the thickness of the pellet. The theoretical density (\( \rho_t \)) of the sample was obtained from

\[ \rho_t = \frac{ZM}{N_A V} \]  \hspace{1cm} (3-2)

where \( Z \) is the number of atoms per unit cell, \( M \) is the mass of the atoms in the unit cell, \( N_A \) is Avogadro’s number, and \( V \) is the volume of the unit cell as determined by powder X-ray diffraction. In this case, the theoretical density of each sample was based on the composition. A linear rule of mixtures between the compositions and the theoretical densities of the end members were used to calculate the theoretical density

\[ \rho_{tm} = \chi \rho_{t1} + (1 - \chi) \rho_{t2} + \ldots \]  \hspace{1cm} (3-3)

where \( \chi \) is the volume fraction of component 1, \( \rho_{t1} \) is the theoretical density of component 1 and \( \rho_{t2} \) is the theoretical density of component 2.

The relative density, \( \rho_r \) is defined as a ratio of a calculated density to a theoretical density, obtained from

\[ \rho_r = \frac{\rho_c}{\rho_{tm}} \]  \hspace{1cm} (3-4)

### 3.3.3 X-ray diffraction (XRD)

Phase formation in specimens was examined by X-ray diffraction. A set of atomic planes with indices \((h k l)\) has the distance between each plane of \( d_{hkl} \). Atoms located on a plane act as sources of scattering. The X-ray beam will be scattered in all directions however it is easier to consider only beam 1 and beam 2 whereby the beam is scattered at the same angle as the incident beam. As shown in Figure 3-4, the difference of travel distance between beam 1 and beam 2 is SQT. If both beam 1 and beam 2 are in phase constructive diffraction could occur. It means that the extra distance SQT will cause beam 2 to be shifted with beam 1 after reflection. The degree of misalignment is equal to the distance SQT. This will happen when the distance SQT is equal to an integer multiple of lambda thus it can be generally written as
\[ n\lambda = SQT \]  \hspace{1cm} (3-5)

where \( n \) is an integer. Consider the triangle PQS, it can be noticed that

\[ d \sin \theta = SQ \text{ or } 2d \sin \theta = SQT \]  \hspace{1cm} (3-6)

due to the symmetry, we have

\[ n \lambda = 2d \sin \theta \]  \hspace{1cm} (3-7)

Equation 3-7 is known as Bragg’s law.

![Figure 3-4 Principle of X-ray diffraction [72].](image)

To prepare the samples for X-ray diffraction, the pellets were ground with 1200-grit SiC paper. Afterwards, they were polished with 6 \( \mu \)m and 1 \( \mu \)m diamond paste and finally oxide powder suspension (OPS) solution. In this study a Philips APD with Cu K\( \alpha \) radiation (\( \lambda = 0.15406 \) nm) was used to study phase analysis. For normal (step) method, X-ray powder diffraction patterns of the specimens were taken in step scan mode in a 2\( \theta \) range from 25\(^\circ\) to 70\(^\circ\), step size of 0.02\(^\circ\) and step time of 8 s per step giving a total scan of eight hours. For the high temperature XRD (continuous method), X-ray powder diffraction patterns of the specimens were taken in continuous scan mode in a 2\( \theta \) range from 25\(^\circ\) to 70\(^\circ\), step size of 0.02\(^\circ\) and step time of 19 s. The pellets were heated continuously to 400\(^\circ\)C, 500\(^\circ\)C, 600\(^\circ\)C, 700\(^\circ\)C, 800\(^\circ\)C and 900\(^\circ\)C using the heating rate at 10\(^\circ\)C/min and kept at those temperatures for 30 min before collecting data. The software X’Pert Data Viewer and X’Pert High Score Plus was used for phase identification and analysis of XRD patterns, respectively.
3.3.4 Scanning electron microscopy (SEM)

The microstructure of the samples was studied by SEM. Electron and photon emissions are produced from the impact of the electron beam striking the sample surface. By scanning the sample surface with the electron beam information about the morphology of the sample can be obtained.

In this study a Philips XL30 FEG SEM with an energy dispersive X-ray analysis detector (EDX) was used. Samples were first ground to planar surface by using 1200-grit SiC paper. After that, samples were polished using 6 μm and subsequently 1 μm diamond paste. Finally, samples were polished to mirror-like surface using OPS solution. Polished samples were attached to aluminium stubs with double sided conductive carbon tape and carbon coated (by an Edwards Coating System E306A) to avoid surface charging. After carbon coating, Silver Electrograd paint was applied to complete the circuit between the sample and the stub on which it was mounted.

After the studying the sample surface and collecting micrographs, the average grain sizes were determined by the linear intercept method using the following equation [73]

\[
d = \frac{1.56L}{MN}
\]  

(3-8)

where \(d\) is the average grain size, \(L\) is the total length of line, \(M\) is the magnification of the micrograph, and \(N\) is the number of intercepts.

3.3.5 Current-voltage (I-V) characteristics

The current-voltage characteristics were obtained over a range of currents from a few microampere (μA) to thousands of microampere consequently the current density was from a few microampere per square centimetre to over ten thousand microampere per square centimetre. The voltage was normalised to the electric field using the following techniques: the current-voltage measurements were carried out by using a DC power supply (Glassman high voltage Inc) in conjunction with precision digital multimeter (Advance Instrument, Alpha II). Samples were ground flat and parallel with thickness approximately 1 mm, and 10 mm in diameter by using 1200-grit SiC paper. After that,
both sides of the specimen were coated in silver paint and then fired at 600°C for 1 hour to dry it. A schematic diagram is shown in Figure 3-5.

![DC circuit diagram for current-voltage test.](image)

For ZnO varistors the relationship of the current-voltage (I-V) is typically expressed as Equation 2-6. To determine the non linear coefficient ($\alpha$), Equation 2-7 can be expressed as

$$\alpha = \frac{\log (J_2/J_1)}{\log (E_2/E_1)} = \frac{1}{\log (E_2/E_1)}$$

(3-9)

where $E_1$ and $E_2$ represent the electric fields corresponding to current densities, $J_1 = 1$ mA/cm$^2$ and $J_2 = 10$ mA/cm$^2$, respectively.

The breakdown field ($E_B$) was estimated at current density of 1 mA/cm$^2$. The breakdown voltage can be deduced from the I-V characteristics and the dimensions of a specimen. The leakage current ($I_L$) was also obtained using the DC circuit (Figure 3-6) with a voltage determined at 0.75 $E_B$. 


Figure 3-6 E-J plot for determination of the electrical parameters.

### 3.3.6 Ageing tests

The ageing of ZnO varistors is caused by the electrical stress resulting in thermal runaway and also short circuit. The stability of I-V characteristics is then important. Since the ageing properties depend on the applied voltage and temperature, the stability of ZnO varistors can be estimated using the accelerated ageing tests.

The I-V rig used in section 3.3.5 was used to study the DC ageing behaviour. The specimens were immersed in an insulating oil bath at 115°C. The applied DC voltage was set at 0.85 breakdown voltage. Leakage currents were recorded at 0 min, 5 min, 10 min, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 12 h and 24 h.
3.3.7 Capacitance-voltage (C-V) characteristics

The capacitance-voltage (C-V) relationship is usually expressed in terms of Equation 3-10 [51]. By plotting the term \((1/C_b - 1/C_{b0})^2\) against the voltage per grain boundary \((V_g)\) the donor density \((N_d)\) and the barrier height \((\phi)\) are obtained from the slope and the intercept of this equation, respectively.

\[
\left( \frac{1}{C_b} - \frac{1}{2C_{b0}} \right)^2 = \frac{2}{q^2\varepsilon_r\varepsilon_0N_d} (\phi + qV_g)
\]  \hspace{1cm} (3-10)

where \(C_b\) is the capacitance per unit area of a grain boundary, \(C_{b0}\) is the value of \(C_b\) when \(V_g=0\), \(V_g\) is the applied voltage per grain boundary, \(q\) is the electronic charge, \(\varepsilon_r\) is the relative permittivity of ZnO and equal to 8.5, \(\varepsilon_0\) is the permittivity of free space \((8.85\times10^{-12} \text{ F/m})\).

The capacitance-voltage characteristics of samples were obtained over a voltage range of 0 - 160 V using Keithley 6487 picoammeter/voltage source DC power supply and HP 4752A LCR meter operating at a frequency of 10 kHz.
A composition of 97.0 mol% ZnO, 1.0 mol% Bi$_2$O$_3$, 1.0 mol% Sb$_2$O$_3$, 0.5 mol% Co$_3$O$_4$ and 0.5 mol% MnO was chosen as the base composition (BC). In order to study the effect of additives, three formulations of the base composition: (i) without Sb$_2$O$_3$ (BCS), (ii) without Co$_3$O$_4$ (BCC), and (iii) without MnO (BCM) were prepared using the mixed oxide route and sintered at 950°C, 1050°C, 1150°C, and 1250°C. The densification, the microstructure, the electrical properties, and ageing behaviour were studied. The results will be discussed.

4.1 Densification

The geometric method was used to determine the density of the specimen. Figure 4-1 shows the density of the BC, BCM, BCC, and BCS varistors as a function of the sintering temperature. The general trend shows that the densities dropped with the increasing sintering temperature. The densities of BC decreased from 5.50 g/cm$^3$ to 5.27 g/cm$^3$ with increasing sintering temperatures from 950°C to 1250°C.

The absence of the additives (Co, or Mn, or Sb) caused the change of the density. From Figure 4-1, it can be noted that varistors without Sb (BCS) had the lowest densities ranging from 5.18 g/cm$^3$ (1250°C) to 5.34 g/cm$^3$ (950°C). In addition, the BCC varistors had the densities in the same range as those of BC varistors.

From the results above, it can be considered that Sb$_2$O$_3$ supports the densification of the materials whilst cobalt does not affect the densification.
Figure 4-1 Density of BC, BCM, BCC, and BCS varistors as a function of sintering temperature.

Note: The relative density was above 94% theoretical density, calculated from the volume fraction of ZnO and secondary phases such as spinel phase, pyrochlore phase and bismuth oxide.
4.2 Phase analysis

XRD spectra of the varistors studied in this work are shown in Figure 4-2. At the temperature of 950°C, XRD spectra of the BC and BCC varistors show the presence of ZnO phase, spinel (Zn$_7$Sb$_2$O$_{12}$) phase, pyrochlore (Zn$_2$Bi$_3$Sb$_3$O$_{14}$) phase and β-Bi$_2$O$_3$ phase whilst the BCS varistor contains only ZnO phase and α-Bi$_2$O$_3$ phase only. Furthermore, only ZnO phase and pyrochlore phase can be detected in the BCM varistors. At higher temperatures, XRD spectra of varistors did not change except the BCM varistor. It was found that the spinel phase can be detected in the BCM ceramic sintered at and above 1050°C. All phases detected are listed in Table 4-1.

Figure 4-2 XRD spectra of BC, BCM, BCC, and BCS ceramics sintered at 950°C.

Z= ZnO, a= α-Bi$_2$O$_3$, b=β-Bi$_2$O$_3$, P= Zn$_2$Bi$_3$Sb$_3$O$_{14}$, S=Zn$_7$Sb$_2$O$_{12}$. 
Table 4-1 Phase analysis of BC, BCM, BCC, and BCS varistors

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering temperature (°C)</th>
<th>Phase</th>
<th>ZnO</th>
<th>Bi$_2$O$_3$</th>
<th>Bi$_3$Sb$_2$Zn$<em>2$O$</em>{14}$ (Pyrochlore)</th>
<th>Zn$_2$Sb$<em>2$O$</em>{12}$ (Spinel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>950</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>BCM</td>
<td>950</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>BCC</td>
<td>950</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>✓</td>
<td>β-form</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>BCS</td>
<td>950</td>
<td>✓</td>
<td>α-form</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>✓</td>
<td>α-form</td>
<td>-</td>
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</tr>
<tr>
<td></td>
<td>1150</td>
<td>✓</td>
<td>α-form</td>
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<td>-</td>
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</tr>
<tr>
<td></td>
<td>1250</td>
<td>✓</td>
<td>α-form</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The formulations, including both those prepared with antimony oxide and bismuth oxide, typically show the presence of pyrochlore phase and/or the spinel phase in the XRD spectra. According to Equation 4-1, from the reaction of ZnO, Bi$_2$O$_3$ and Sb$_2$O$_3$, the pyrochlore phase is produced below 900°C. The spinel phase can be obtained at around 900°C moreover the Bi$_2$O$_3$ is a by-product from this reaction as indicated in Equation 4-2 [74-75].

\[
2\text{ZnO} + \frac{3}{2}\text{Bi}_2\text{O}_3 + \frac{3}{2}\text{Sb}_2\text{O}_3 + \frac{3}{2}\text{O}_2 \rightarrow \text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14} \text{(pyrochlore)} \quad (4-1)
\]

\[
2\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14} + 17\text{ZnO} \rightarrow 3\text{Zn}_7\text{Sb}_2\text{O}_{12} \text{(spinel)} + 3\text{Bi}_2\text{O}_3 (l) \quad (4-2)
\]

Therefore, for the BC, BCM, and BCC varistors pyrochlore and spinel phases can be found. In previous study by Inada [76] the Bi$_2$O$_3$ phase could not be detected at 950°C in the BC, BCM, and BCC varistors whilst the δ-Bi$_2$O$_3$ was detected in BCC varistor sintered above 1150°C with the soaking period of 1 hour. β-Bi$_2$O$_3$ is the more probable form on the cooling process due to the effect of Bi$_2$O$_3$-rich atmosphere is large in the grain boundaries.

The other interesting feature is the lattice parameters. Lattice parameters (a and c) of ZnO can be calculated from the following equation

\[
sin^2 \theta - \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) = \frac{\lambda^2}{4c^2} \ell^2 \quad (4-3)
\]

In the present work, the lattice parameters vary slightly as a function of sintering temperature as shown in Table 4-2. For a-lattice parameter values, the BC, BCM and BCS varistors show the totally downward trend whilst the BCC varistor shows the opposite trend. Furthermore, for the c-lattice parameter values, each composition presents a different trend. The BC and BCC varistors show the upward trend whilst the BCM varistor has mostly the similar values and the BCS varistor shows a downward trend.
Table 4-2 Lattice parameters for BC, BCM, BCC, and BCS varitors

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (°C)</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>950</td>
<td>3.2496±0.0005</td>
<td>5.2020±0.0005</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>3.2498±0.0005</td>
<td>5.2036±0.0005</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>3.2493±0.0005</td>
<td>5.2041±0.0005</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>3.2488±0.0005</td>
<td>5.2047±0.0005</td>
</tr>
<tr>
<td>BCM</td>
<td>950</td>
<td>3.2502±0.0005</td>
<td>5.2025±0.0005</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>3.2496±0.0005</td>
<td>5.2026±0.0005</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>3.2495±0.0005</td>
<td>5.2038±0.0005</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>3.2489±0.0005</td>
<td>5.2024±0.0005</td>
</tr>
<tr>
<td>BCC</td>
<td>950</td>
<td>3.2497±0.0005</td>
<td>5.2032±0.0005</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>3.2496±0.0005</td>
<td>5.2028±0.0005</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>3.2494±0.0005</td>
<td>5.2034±0.0005</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>3.2509±0.0005</td>
<td>5.2067±0.0005</td>
</tr>
<tr>
<td>BCS</td>
<td>950</td>
<td>3.2495±0.0005</td>
<td>5.2046±0.0005</td>
</tr>
<tr>
<td></td>
<td>1050</td>
<td>3.2497±0.0005</td>
<td>5.2060±0.0005</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>3.2478±0.0005</td>
<td>5.2022±0.0005</td>
</tr>
<tr>
<td></td>
<td>1250</td>
<td>3.2478±0.0005</td>
<td>5.1989±0.0005</td>
</tr>
</tbody>
</table>
The samples sintered at a temperature of 1250°C show the most variation of the lattice parameters as a function of a composition. For the BC varistors, the lattice parameters are \(a = 3.2488 \text{ Å}\) and \(c = 5.2047 \text{ Å}\). The BCC varistors have the highest \(a\)-lattice parameter value of 3.2509 Å and \(c\)-lattice parameter value at 5.2067 Å, and the BCS varistor has the lowest \(a\)-lattice parameter value at 3.2478 Å and \(c\)-lattice parameter value at 5.1989 Å. The lattice parameters of these samples are shown in Figure 4-3.

In the binary system of ZnO and CoO studied by Koumoto et al. [77], the addition of Co resulted in the larger \(a\)-values and the smaller \(c\)-values than those of the undoped material. It was implied that the lattice parameter \(a\) of the BC varistor should be larger than that of the BCC varistor and vice versa for the lattice parameter \(c\). However, the results from the present work indicated that both \(a\)- and \(c\)-values of the BCC varistor are larger than those of the BC varistor. It might mean that the other additives in the BC composition control the lattice parameters. A comparison to the ionic radius of zinc and additives ions from Shannon [78] shows that the ionic radius of zinc ion (0.74 Å) is similar to that of antimony ion (0.76 Å). Furthermore cobalt ion has a smaller ionic radius (0.61 Å) in contrast to a larger ionic radius of manganese ion (0.83 Å). Therefore the order of the lattice parameters of the compositions in the present study should be BCM<BC=BCS<BCC. In the present study, the BCC varistors exhibited the largest lattice parameters however the BCS varistors have the smallest lattice parameters. This means other effect may influence the lattice parameters.
Figure 4-3 Lattice parameters of different compositions sintered at 1250°C.
4.3 Microstructure

SEM micrographs are shown in Figure 4-4 to Figure 4-7. It can be seen that in the BC, BCM and BCC varistors, three phases: ZnO grains, Bi-rich intergranular phase, and spinel phase can be observed (Figure 4-4 to Figure 4-6). In contrast only ZnO grains and Bi-rich intergranular network can be seen in BCS varistor (Figure 4-7). ZnO grains (A in Figure 4-4) make up the bulk of the microstructure. The Bi-rich intergranular phases (B in Figure 4-4) are located throughout the structure and particularly present at the multiple grain junctions. Moreover the spinel phase particles (C in Figure 4-4) are present in the ZnO grains and also segregate to the multiple grain junctions as well. The black areas are a mixture of grain pullout (D in Figure 4-4) and the porosity (E in Figure 4-4).

The ZnO grains act as doped semiconductors. Moreover, the grain boundary regions provide barriers to electrical conduction and Bi-rich phases are predominantly localised at triple junction 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 [79]. Above the breakdown voltage, the latter path makes a negligible contribution to the total current. On the other hand, below the breakdown voltage, the current via the former path is low. The conduction path throughout the Bi-rich network then makes an important contribution to the total current [79].
Figure 4-4 SEM micrographs of BC varistor sintered at 1250°C. A=ZnO grain; B= Bi-rich intergranular network; C=spinel phase; D= grain pullout; E=porosity

Figure 4-5 SEM micrographs of the BCM varistor sintered at 1250°C.
Figure 4-6 SEM micrograph of BCC varistor sintered at 1250°C.

Figure 4-7 SEM micrograph of BCS varistor sintered at 1250°C.
Another feature distinguishing the microstructures is the grain size. The grain size increases with the increasing temperatures. The average grain sizes of the samples are presented in Figure 4-8. The average grain sizes of the base composition (BC) for sintering temperatures of 950°C, 1050°C, 1150°C, and 1250°C are 6 μm, 14 μm, 21 μm, and 26 μm, respectively. It can be seen that the base composition without MnO (BCM) has a dramatically larger grain size than the base composition, 34 μm and 54 μm when the pellets were sintered at high temperatures, 1150°C and 1250°C, respectively. However, ZnO grain growth particularly inhibited because of the spinel phase as shown in Figure 4-4 [79]. Furthermore, the ZnO grains in the BCS varistors are slightly larger than those in the BC varistors except at the sintering temperature of 1150°C. In the BCS formulation the Bi₂O₃ has a melting point at 825°C consequently at the sintering temperature liquid phase sintering can occur. The Bi-rich liquid phase enlarges the ZnO grains in the ZnO-Bi₂O₃ system [80]. The grain size of BCS sintered at 1150°C is approximately 20 μm consistent with the study of Kim et al. [81]. Therefore, Sb₂O₃ in the base composition retards ZnO grain growth [6].
Figure 4-8 Average grain size of varistor compositions as a function of sintering temperature.
4.4 Electrical Properties

4.4.1 Current-voltage behaviour

![Current-voltage characteristics of varistor compositions sintered at 1050°C.](image)

Figure 4-9 Current-voltage characteristics of varistor compositions sintered at 1050°C.

The current-voltage characteristics for ceramics sintered at 1050°C are shown in Figure 4-9. It can be seen that the BCC varistor exhibits the highest electric field whilst BCS varistor has the lowest electric field. The nonlinear coefficient is determined from the current density across the range from 1 mA/cm² to 10 mA/cm². As shown in Figure 4-10, the absence of MnO or Sb₂O₃ causes the reduction of the nonlinear coefficient of these compositions whilst the absence of Co₃O₄ improves the nonlinear coefficient. It is found that the α-value of BCM increases with sintering temperature rises up to 1150°C in contrast the α-value of BCS shows the inverse trend.

The smaller α-values exhibited by the BCS varistors are related to the I-V characteristics. In the range used for determination of the α-value, the flatness of the I-V curve of the BCS varistor is less than that of others composition therefore it will be characterised by poorer electrical properties. Matsuoka [28] studied the nonlinearity of
ZnO varistors. It was found that for the BCS varistor sintered at 1350°C the $\alpha$-value was 22, higher than the $\alpha$-value (10) for the BCS varistor sintered at 1250°C in the present work.

In this work, an unexpected result was obtained from the BCC varistor sintered at 1050°C. Typically the addition of cobalt improves the nonlinearity [82]. The absence of this additive should result in the poor nonlinearity. However, the nonlinear coefficient of BCC varistor sintered at 1050°C is higher than that of BC varistor. In spite of repeated experiments this trend and behaviour looks unusual and must, until there is additional supporting evidence, be treated with caution.

![Figure 4-10 Nonlinear coefficient of BC, BCM, BCC, and BCS varistors sintered at different temperatures.](image)
The breakdown fields, determined at the current density of 1 mA/cm\(^2\), are shown in Figure 4-11. It can be seen that \(E_B\) values decreased as a function of temperature for all compositions, consistent with the work of Sousa et al. [82]. Considering the breakdown field as a function of composition, at 950°C the \(E_B\) values are dramatically different. The breakdown field for BCM is over 15000 V/cm whilst that of BCS is about 2000 V/cm. In general the higher sintering temperatures are expected to have limited effect on the breakdown fields. Since the spinel phase, formed through the decomposition of the pyrochlore phase between 950°C-1050°C restricts grain growth and makes the material more resistive, the absence of Sb\(_2\)O\(_3\) tends to decrease the breakdown field due to the fact that the spinel phase cannot form [82].

The breakdown voltage is typically related to grain size. A smaller grain size can effectively increase the breakdown voltage because the number of grain boundaries per unit thickness of varistor increases. According to the present study, the breakdown field increases with decreasing grain size consistent with Gupta [6]. At fixed sample thickness an increasing grain sizes leads to a reduction in the number of grains in the samples between electrodes resulting in a reduction in breakdown voltage at higher temperatures.

The leakage current \(I_L\), determined at 0.75 \(V_B\), (Figure 4-12) clearly decreases with the increasing temperature from 950°C to 1150°C for the BC, BCM, and BCC varistors. However, for the BCS varistor the leakage current trend is slightly different. At 1250°C, the \(I_L\) values of the BCC varistor increased whilst that of BCS obviously reduced. Moreover, it can be noted that BCS varistor show the highest leakage currents. In other words, the absence of antimony oxide leads the materials to exhibit poorer electrical characteristics. The leakage currents of these compositions are shown in Figure 4-12. The BCM varistor show the lowest leakage currents at high temperature.

The varistor essentially needs the leakage current to be as low as possible to avoid the heating of the material during the use. The heating causes the degradation of the varistor because the migration of Zn\(_i\) to the grain boundary modifying and reducing the barrier height and the depletion layer formed at the grain boundary. A conductive material is ultimately produced [82].
From the electrical properties, it can be considered that the absence of MnO or Sb$_2$O$_3$ reduces the nonlinear coefficient. A summary of the electrical properties is shown in Table 4-3.

Figure 4-11 Breakdown fields of varistors as a function of sintering temperature.
Figure 4-12 Leakage currents for varistors as a function of sintering temperature.
Table 4-3 Summary of electrical properties

<table>
<thead>
<tr>
<th>Composition-sintering temperature (°C)</th>
<th>Nonlinear coefficient</th>
<th>Breakdown field (V/cm)</th>
<th>Leakage current (µA)</th>
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<td>7956±10</td>
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<td>673±10</td>
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4.4.2 Capacitance-voltage characteristics

The capacitance-voltage characteristics of BC varistors are shown in Figure 4-13. It can be seen that the barrier capacitance $C_b$ (per unit area) of the samples decreased as the sintering temperature increase. According to the standard relationship between capacitance and voltage (Equation 4-4), the barrier capacitance is related to the applied voltage $V_g$ as follows [51]

$$\left(\frac{1}{C_b} - \frac{1}{2C_{bo}}\right)^2 \propto V_g$$

(4-4)

The linear relationships between $(1/C_b - 1/2C_{bo})^2$ and $V_g$ for BC varistor are shown in Figure 4-14. Consequently, the donor density ($N_d$) and barrier height ($\phi$) can be determined from the slope and the intercept of the lines, respectively (Section 3.3.7, Equation 3-10). The calculated values of $N_d$ and $\phi$ as a function of sintering temperature are shown in Figure 4-15. It can be seen that both donor density and barrier height show the same trend, decreasing with increasing temperature. The donor density decreased from $2.28 \times 10^{17}$ cm$^{-3}$ to $3.24 \times 10^{16}$ cm$^{-3}$ and barrier height decreased from 2.14 V to 1.57 V.

An increase in temperature decreases the donor density due to the increasing ion substitution at high temperature [82]. However, the donor densities in the present work are marginally lower than those reported by Sousa et al. ($4.62 \times 10^{18}$ cm$^{-3}$ at 1150°C) although a different preparation technique was used [82].
Figure 4-13 C-V characteristics of BC varistor sintered at different temperatures.

Figure 4-14 \((1/C_b - 1/2C_{b0})^2\) as a function of \(V_g\) for BC varistor sintered at different temperatures.
Figure 4-15 Donor density and barrier height as a function of temperature for BC varistor.
The capacitance-voltage characteristics of the additive removal compositions are shown in Figure 4-16. At the sintering temperature of 1050°C, the BCS varistor attained the highest barrier capacitance with increasing applied voltage whilst the BCC and BC showed similar but lower barrier capacitance values. The linear relationships between \((1/C_b - 1/2C_{h0})^2\) and \(V_g\) for BC, BCM, BCC and BCS varistors sintered at 1050°C are presented in Figure 4-17: the parameters determined from these lines are shown in Figure 4-18. By comparison with the donor density and barrier height for BC, it is shown that the absence of MnO or Sb\(_2\)O\(_3\) obviously increased the donor density and lowered the barrier height whilst the absence of Co\(_3\)O\(_4\) slightly changed these parameters.

The lower barrier heights for the BCM than that of the BC varistors are consistent with the results from the work of Eda [34]. The addition of manganese causes the low conductivity leading to the high barrier height due to the formation of surface states or traps at the grain boundary. Furthermore, the addition of cobalt decreases the donor density because of the substitution reaction of cobalt with zinc interstitials and oxygen vacancies [83].

![Figure 4-16 C-V characteristics of various varistors sintered at 1050°C.](image-url)
Figure 4-17 $(1/C_b - 1/2C_0)^2$ as a function of $V_g$ for various varistors sintered at 1050°C.

Figure 4-18 Donor density and barrier height for varistors sintered at 1050°C.
4.5 Ageing Behaviour

Ageing behaviour is one important characteristic of ZnO varistors. Therefore, DC ageing tests were carried out at 115°C in an oil bath with an applied voltage of 0.75 $V_B$. The time dependence of the leakage current was studied.

The variation of leakage current with time (for the different compositions investigated) when subjected to DC stress for periods up to 24 hours is shown in Figure 4-19. The BCS varistor could not withstand the loading during this severe test. The BCS varistors sintered at 950°C to 1150°C degraded in less than 5 minutes whilst the BCS sample sintered at 1250°C degraded within 15 minutes. Thus it can be noted that antimony oxide is an important additive in term of stability. The other formulations could withstand the stress however the ageing for each formulation was not in similar rate.

Degradation rate coefficients can be determined from the relation between leakage current and time. It was found that at sintering temperatures 950°C to 1150°C the $K_T$ values for BCC are slightly higher than that of BC and BCM. In contrast to the sintering temperature at 1250°C, BCC samples were less degraded during the tests. According to these results, it can be noted that the absence of $Co_3O_4$ improves the stability of materials. Degradation rate coefficients as a function of sintering temperature are shown in Figure 4-20.
Figure 4.19 Ageing behaviour of varistors, sintered at 1250°C, subjected to 0.85 $V_B$ DC stress at 115°C.
The ageing phenomena relate to the deformation of the barrier in the depletion region area. The migration of ions such as zinc interstitials ($Zn_i^+$ and $Zn_i^-$) the oxygen vacancies ($V_{O}^-$ and $V_{O}^-$) are believed to cause the deformation of the barrier. Leite et al. [84] proposed a model for defects in ZnO. The solid solution of MnO in the ZnO matrix produced defects according the following reaction

$$MnO \rightarrow Mn_{Zn}^x + O_{O}^x$$  \hspace{1cm} (4-5)

The same behaviour is expected in Co$_3$O$_4$ doped ZnO. At a temperature above 1000°C the reduction of Co$_3$O$_4$ will occur as

$$Co_3O_4 \rightarrow 3CoO + \frac{1}{2}O_2$$  \hspace{1cm} (4-6)
Reaction 4-5 and reaction 4-6 are responsible for the formation of a potential barrier. The ageing should be encouraged by the reactions that eliminate the defects formed during sintering process. According the defect deformation model proposed by Gupta and Carlson [67], the unstable component at the depletion regions are positive zinc interstitials. However, at the depletion layer, the oxygen vacancies are also the major concentration of ionised carriers. Therefore the defect reaction is written as

\[ \text{ZnO} \rightarrow \text{Zn}_n^{-} + O_0^+ + V_0^- + V_{2n}^{''} \]  

(4-7)

During the cooling process, the reaction can be written as

\[ 2V_0^{-} + O_2(g) \rightarrow 2O_0^+ \]  

(4-8)

\[ V_{2n}^{''} + O^x \rightarrow O_{ad}^{''} + V_{zn}^{x} \]  

(4-9)

The negatively charged components can exist at the interface are zinc vacancy \( (V_{2n}^{''}) \) and adsorbed oxygen \( (O_{ad}^{''}) \). The oxygen vacancies migrate possibly to the interface leading the following reaction

\[ V_0^- + V_{2n}^{''} \leftrightarrow V_0^{x} + V_{zn}^{x} \]  

(4-10)

\[ V_0^- + O_{ad}^{''} \rightarrow V_0^{x} + \frac{1}{2}O_2(g) \]  

(4-11)

4.6 Summary

The densification, microstructure and electrical properties of the base composition with individual additive removed were studied. The results from these characterised techniques can be summarised as follows:

- The absence of \( \text{Sb}_2\text{O}_3 \) affects all parameters. The absence of \( \text{Sb}_2\text{O}_3 \) reduces the density and supports grain growth. In term of the electrical properties, it reduces the nonlinear coefficient and breakdown field but increases the leakage current. In addition, the BCS varistor degrades rapidly in a few minutes during a test. This is because the spinel phase cannot form [82].

- The absence of \( \text{Co}_3\text{O}_4 \) improves the varistor stability. The presence of cobalt produces the unstable component at the depletion region leading the varistor degrades [84].
- The absence of MnO reduces the nonlinear coefficient and the leakage current. The presence of manganese supports the pinning of the barrier. This enhances the nonlinear coefficient [57].

- The electronic states of these compositions can usefully be investigated by deep level transient spectroscopy (DLTS) technique.
5. PHASE DEVELOPMENT IN CERAMICS PREPARED BY CONVENTIONAL AND ATTRITION MILLING

The preparation process, crystallite size and homogeneity are important parameters to produce a better varistor. Therefore two powder preparation processes were studied. The base composition of 97.0 mol% ZnO, 1.0 mol% Bi$_2$O$_3$, 1.0 mol% Sb$_2$O$_3$, 0.5 mol% MnO and 0.5 mol% Co$_3$O$_4$ was prepared by different techniques including conventional (vibration) milling (CMBC) and attrition milling (AMBC). Four pellets from each milling route were sintered at 950°C, 1050°C, 1150°C, and 1250°C for 2 hour. The phase development of these two preparations was investigated from the temperature of 400 °C to 900 °C. Moreover, the microstructure, the electrical properties and ageing behaviour were studied.

5.1 Particle size analysis

Particle size is important for most ceramic processing operation because it affects the mechanical strength and density. The base composition prepared by the conventional- and attrition-milling show that particle size of powder prepared by attrition milling (0.3 μm) was smaller than that of sample prepared by the conventional milling (2 μm) - Figure 5-1. It is because smaller beads are used in the attrition milling technique, i.e. more surface area, that it gives greater efficiency during the milling period. However, it can be seen that the other peak around 40 μm represent the agglomeration of the powder. The particle size distribution of powder prepared by both techniques is shown in Figure 5-1.
Figure 5-1 Particle size of the base composition prepared by different techniques.
The dried powder from the conventional milling and attrition milling were grey in
colour. SEM images (Figure 5-2) show the morphology of dried powder after milling
from these techniques. It can be seen that both techniques yielded the plate shaped-
grains. Furthermore, attrition milling formed homogeneous powder (Figure 5-2b) whilst
the conventional milling produced inhomogeneous powder (Figure 5-2a). This confirms
the disadvantage and the difficulty in obtaining compositional homogeneity from
conventional milling [1, 85].

![SEM images of dried powder after milling by (a) conventional milling; (b) attrition milling.](image_url)
5.2 Densification

The density of electronic ceramics plays an important role since it affects the electronic capability. Thus geometric density of the pellets prepared by the conventional milling and attrition milling was determined and is shown in Figure 5-3. Considering the density as a function of sintering temperature, it can be noted that at higher temperatures the densification of the materials reduced. This is consistent with the work of Gupta and Coble [86] that at higher sintering temperature the pore size increased and thereby the density dropped. Moreover, the different preparation processes cause a change in density. It is clearly seen that the densities of the pellets prepared by attrition milling were higher than those of the pellets prepared by the conventional milling. In this study the highest density of 5.56 g/cm$^3$ was obtained for the ATBC varistor sintered at 950°C.

Regarding the particle size (section 5-1), it is considered that a smaller particle size powder resulted in higher density pellets. The AMBC varistors which had particle sizes of approximately 0.3 μm yielded pellets which had the densities in the range of 5.4-5.6 g/cm$^3$. The CMBC varistors having particle sizes of about 2 μm yielded the pellets which had densities in the range 5.3-5.5 g/cm$^3$.  

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Figure 5-3 Densities of the AMBC and CMBC varistors as a function of sintering temperature.

Note: The relative density was above 94% theoretical density, calculated from the volume fraction of ZnO and secondary phases such as spinel phase, pyrochlore phase and bismuth oxide.
5.3 Phase development

X-ray diffraction spectra of the CMBC and AMBC are shown in Figure 5-4 to Figure 5-7. Two methods were used in order to investigate the phase development e.g. the high temperature method or continuous method, and the step method. The high temperature XRD was used to study the phase development from room temperature to 900°C by continuously collecting the data. It was found that at room temperature the starting substances of ZnO, Bi$_2$O$_3$ and Sb$_2$O$_3$ were detected in both AMBC and CMBC samples. At the temperature at 400°C, the mixed valence antimony oxide of Sb$^{3+}$Sb$^{5+}$O$_4$ can be detected for CMBC sample. This phase disappeared by 700°C, the same temperature at which the pyrochlore (Zn$_2$Sb$_3$Bi$_3$O$_{14}$) appears. Since the XRD spectra of AMBC did not show the appropriate base line, the formation of Sb$^{3+}$Sb$^{5+}$O$_4$ phase could not be seen clearly. It was observed that Sb$^{3+}$Sb$^{5+}$O$_4$ phase was detected at 400°C only. In addition the pyrochlore phase was found once the temperature rose to 700°C. The XRD spectra for the high temperature investigations for the AMBC and CMBC are shown in Figure 5-4 and Figure 5-5, respectively.
Figure 5-4 XRD spectra of the AMBC varistor at temperature ranging from RT to 900°C. * = ZnO, Δ = pyrochlore, o = Bi$_2$O$_3$, v = Sb$_2$O$_3$, x = Sb$^{3+}$Sb$^{5+}$O$_4$

Figure 5-5 XRD spectra of the CMBC varistor at temperature ranging from RT to 900°C. * = ZnO, Δ = pyrochlore, o = Bi$_2$O$_3$, v = Sb$_2$O$_3$, x = Sb$^{3+}$Sb$^{5+}$O$_4$
The step-wise heating method was carried out as follows: the pellet of the base composition was sintered at each temperature from 400°C to 1250°C for 2 hours. XRD spectra of both AMBC and CMBC samples show that ZnO, α-Bi$_2$O$_3$ and Sb$_2$O$_3$ were detected at room temperature as shown in Figure 5-6 and Figure 5-7, respectively. Similar to the high temperature method, the mixed valence antimony oxide was detected from 400°C. The α-Bi$_2$O$_3$ detected from room temperature disappeared at 700°C. The pyrochlore phase was firstly detected at 600°C. From the step method, the differences in XRD spectra between AMBC and CMBC were the spinel and β-Bi$_2$O$_3$ phases. In the sample prepared by attrition milling the spinel phase was formed earlier (800°C) than the sample prepared by the conventional milling (900°C). Furthermore, the β-form of bismuth oxide was detected at 900°C (Figure 5-6) for attrition milling whilst at 950°C for the conventional milling (Figure 5-7). The phase analysis is summarised in Table 5-1.
Figure 5-6 XRD spectra of AMBC varistor sintered at RT-1250°C.

*=ZnO, o=α-Bi$_2$O$_3$, ⊕=β-Bi$_2$O$_3$, Δ=pyrochlore, ◇=spinel, ▽=Sb$_2$O$_3$, x=Sb$^{3+}$Sb$^{5+}$O$_4$
Figure 5-7 XRD spectra of CMBC varistor sintered at RT-1250°C.

*=ZnO, o=α-Bi₂O₃, ⊙=β-Bi₂O₃, ∆=pyrochlore, ⋄=spinel, ▼=Sb₂O₃, x=Sb³⁺Sb⁵⁺O₄
Table 5-1 Phase analysis of the CMBC and AMBC varistors

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<tr>
<th>Temperature (°C)</th>
<th>ZnO</th>
<th>Sb₂O₃</th>
<th>Sb³⁺Sb⁵⁺O₄</th>
<th>α⁻Bi₂O₃</th>
<th>β⁻Bi₂O₃</th>
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<th>Spinel</th>
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Note: The symbols represented are

A= High temperature XRD of AMBC
B= High temperature XRD of CMBC
C= XRD of AMBC
D= XRD of CMBC
From results above, there are two topics to discuss: (i) powder processing and (ii) the measuring methods. A comparison of powder processing shows that attrition milling supports the formation of the spinel phase and $\beta$-Bi$_2$O$_3$ within the detection limit. These two phases appeared at lower temperature for the AMBC varistors. A consideration of measuring method can be noted that the step method and continuous method show slightly different phase development. For the step method, the pyrochlore phase appeared from 600°C whilst for the continuous method, this phase presented from 700°C. Moreover, the $\alpha$-Bi$_2$O$_3$ can be detected in the sample of the convention-milled base composition using the continuous method until 700°C.

The same composition was prepared by dry mixing and sintered at 650-1350°C for 1 hour by Inada [76]. It was found that ZnO and pyrochlore phase were detected at 950°C in addition to the spinel phase and $\beta$-Bi$_2$O$_3$ from 1050°C. This agrees with the results from the present study. The formation of the pyrochlore and the spinel phase was investigated by many researchers [76, 87-89]. Since the melting points of antimony and bismuth oxides are 820°C and 625°C, respectively, during the sintering process these phases melt and react with ZnO to form pyrochlore phase. As shown in Equation 4-1 and Equation 4-2 (Section 4.2), the pyrochlore phase was found to form at 750-850°C and stable at >900°C and to melt at 1280°C whilst the spinel phase formed at 900-1000°C [88]. The transformation of bismuth oxide was studied by Inada [76]. At low temperature the $\alpha$-Bi$_2$O$_3$ (monoclinic) was stable and changed to $\delta$- Bi$_2$O$_3$ (fcc) when it was heat to 729°C. During the cooling process the metastable $\beta$- Bi$_2$O$_3$ (tetragonal) was formed from 650°C. This metastable phase may be stabilised by the addition of cobalt or manganese oxide [90]. Moreover $\beta$-Bi$_2$O$_3$ was easily formed in the grain boundary by slow cooling [76]. Since the XRD spectra of for the AMBC varistors presented the same phases as those of the CMBC varistors at the sintering temperature from 950°C to 1250°C, the microstructure will be further investigated.
5.4 Microstructure

Scanning electron micrographs of the base composition prepared by different techniques are shown in Figure 5-8 and Figure 5-9. It is clear that ZnO grains (A in Figure 5-8) accompanied by the inversion boundaries make up the bulk of microstructure. The Bi-rich intergranular network (B in Figure 5-8) presents throughout the structure and spinel phases (C in Figure 5-8) are present at ZnO grains junctions in the micrographs of samples prepared by both techniques. The sample prepared by attrition milling (Figure 5-8a, Figure 5-9a) has a slightly smaller grain size than that of the sample prepared conventional milling (Figure 5-8b, Figure 5-9b). Another interesting feature in the micrographs is that second phase particles are found in samples prepared by both techniques. The amount of the second phase increased in samples sintered at higher temperatures.

Olsson et al. studied the microstructures of commercial ZnO varistor [79]. Three major crystalline phases found in typical ZnO-Bi$_2$O$_3$ based varistors containing: (i) ZnO (hexagonal structure) grains with dissolved Co and Mn, (ii) Zn$_7$Sb$_2$O$_{12}$ (spinel) with dissolved Co, Mn and (ii) the Bi$_2$O$_3$-rich intergranular phases consisting of Zn$_2$Bi$_3$Sb$_3$O$_{14}$ (pyrochlore) and bismuth oxides [79]. Above 700°C, Sb$_2$O$_3$ reacts with both ZnO and Bi$_2$O$_3$ to produce Zn$_7$Sb$_2$O$_{12}$ and Zn$_2$Bi$_3$Sb$_3$O$_{14}$ pyrochlore phase. During sintering, the Zn$_2$Bi$_3$Sb$_3$O$_{14}$ yields a Bi-rich liquid phase and Zn$_7$Sb$_2$O$_{12}$. The Bi-rich liquid phase changes to a β- or α-Bi$_2$O$_3$-rich intergranular layer during cooling.

According to the normal sintering behaviour, the average grain size rose as sintering temperature increased. The dependence of average grain size on sintering temperature for the base composition prepared by both techniques is depicted in Figure 5-10.
Figure 5-8 SEM images of the base composition sintered at 950 °C prepared by (a) conventional milling (b) attrition milling. A=ZnO grain; B= Bi-rich intergranular-network; C=spinel phase
Figure 5-9 SEM images of the base composition sintered at 1250 °C prepared by (a) conventional milling (b) attrition milling.
Since the secondary phase such as spinel suppresses grain growth, small ZnO grain size was observed. The microstructure of the AMBC varistor shows more spinel phase than that in the CMBC varistor and a smaller grain size was obtained. According to Gupta and Coble [86], the increase in grain size and decrease in density with increasing sintering temperature is associated with entrapment of insoluble gas in the pores during the last stage of sintering. Pore growth is controlled by zinc atoms diffusion through the ZnO lattice; the transport of gas along the interconnecting grain boundaries was rapid [86, 91]. Therefore attrition milling may be the better process to prepare the base composition regarding to the microstructure. However, the nonlinearity of varistor is the most important behaviour for varistor devices. The electrical properties of the AMBC and CMBC are reported and discussed as follows.

Figure 5-10 Average grain size of the base composition varistors prepared by different techniques.
5.5 Electrical Properties

The current-voltage characteristics of the base composition prepared by conventional milling and attrition milling are shown in Figure 5-11 and Figure 5-12, respectively. It was seen that the preparation by attrition milling caused the varistors I-V curves to be displaced to higher electric fields (upwards). Consequently, the voltage per grain of the sample prepared by attrition milling is higher than that of the sample prepared by the conventional milling. The first considered electrical property is the nonlinear coefficient. It was found that the $\alpha$-values of the varistors prepared by conventional milling were higher than those of attrition milling for sintering temperatures up to 1150°C as shown in Figure 5-13. Whilst, at 1250°C the $\alpha$-value of the AMBC varistors was higher than those of the CMBC varistors. The dependence of nonlinear coefficient on the sintering temperature shows that the $\alpha$-value decreased as a function of temperature from 950°C to 1150°C and then increased at the temperature of 1250°C for the AMBC varistors. In contrast the CMBC varistors exhibited the decrease in the $\alpha$-values with the increase in sintering temperature. This agrees with the work of Nobrega and Mannheimer [91] which showed the nonlinear coefficient decreased with a decrease in density. Balzer [92] studied the electrical properties of ZnO varistor and found that the decrease of the $\alpha$-value may be the appearance of the $\beta$-Bi$_2$O$_3$ in the sample sintered at low temperature (<1070°C). At higher temperatures the $\alpha$-Bi$_2$O$_3$ was detected in the samples exhibiting the highest nonlinear coefficient.

The next electrical parameters to be determined are the breakdown voltage and leakage current. The breakdown fields of the varistors prepared by both techniques show the same trend for the dependence of $E_B$-value on the sintering temperature (Figure 5-14). The breakdown field decreased as the sintering temperature increased. Moreover, the $E_B$-values of attrition- and convention-milled samples were significantly different at temperature 950°C. However at higher temperatures the powder processing route did not affect the breakdown field: the breakdown field decreased with increase of sintering temperature. The breakdown field is related to the grain size of ZnO. The AMBC varistors present the higher $E_B$-value due to the smaller grain size; this increases the number of grain boundaries per unit thickness of varistor.

Figure 5-15 shows the leakage current as a function of sintering temperature. It can be seen that the leakage currents show the same trend as the breakdown fields. The leakage
current gradually dropped as the sintering temperature rose for both powder processing techniques. The leakage currents of convention-milled samples were lower than those of attrition-milled samples. However, the difference of $I_L$ between these techniques reduces as a function of sintering temperature.
Figure 5-11 I-V characteristics of the CMBC varistors sintered at 950°C to 1250°C.

Figure 5-12 I-V characteristics of the AMBC varistors sintered at 950°C to 1250°C.
Figure 5-13 Nonlinear coefficient of the CMBC and AMBC varistors as a function of sintering temperature.

Figure 5-14 Breakdown field of the CMBC and AMBC varistors as a function of sintering temperature.
Figure 5-15 Leakage current of the CMBC and AMBC varistors as a function of sintering temperature.

According to the electrical properties of samples prepared by two different powders processing routes, it may be concluded that the conventional milling yields varistors with higher nonlinear coefficients and lower leakage currents. In contrast attrition milling produces varistor with the higher breakdown fields. It can be noted that each powder processing route shows different advantages therefore the other properties such as the stability of the varistors will be investigated.
5.6 Ageing behaviour

The ageing test of the base composition was carried out at 115°C under $0.85V_{1mA/cm^2}$ applied voltage. The time dependence of the leakage current is shown in Figure 5-16. It can be seen that for the preparation by conventional milling all varistors could withstand the severe conditions (Figure 5-16a) whilst for attrition milling the varistor materials could withstand the tests except for the samples sintered at 950°C (Figure 5-16b). Especially for samples processed at 1050°C the leakage current initially increased and then decreased to the equilibrium for attrition-milled sample. In comparison the leakage current shows that the $I_L$-values of the AMBC varistor were higher than those of the CMBC varistors.

Considering the powder processing techniques; for low sintering temperatures (950°C) the conventional milling technique yields stable varistors. However, for samples produced at higher temperatures, attrition milling produces the less degraded varistors. As shown in Figure 5-17, at 950°C sintering temperature the degradation rate coefficient of AMBC samples was dramatically higher than that of CMBC samples. For 1050°C sintering temperature, samples prepared by both techniques degrade at similar rates with the $K_T$-value approximately zero. For higher sintering temperatures (1150°C and 1250°C) the trend was inversed i.e. the ageing of conventionally milled samples was faster than that of attrition milled samples. The difference was that the degradation rate coefficient increased as the temperature increased. According to the ageing behaviour of the AMBC and CMBC varistors, it can be seen that the conventional milling produces the varistor which is stable at low sintering temperature. This is in contrast to attrition milling where the varistor stability is better at higher sintering temperatures.
Figure 5-16 Ageing behaviour of the base composition prepared by (a) conventional-milling and (b) attrition milling.
Figure 5-17 Degradation rate coefficient of the base composition prepared by different milling techniques.
5.7 Summary

- The particle size of powder prepared by attrition milling was smaller than that of powder prepared by the conventional milling.

- The density of the pellets prepared by both techniques decreased as a function of sintering temperature. The denser pellets were prepared by attrition milling.

- The ZnO grain size increased as a function of temperature for both powder preparations. The smaller ZnO grains were found in the samples prepared by attrition milling.

- The conventional milling yielded varistors with higher nonlinear coefficients and lower leakage currents. In contrast, attrition milling produced varistors with higher breakdown fields.

- The stability of the varistor prepared by attrition milling is better than that of CMBC samples sintered at higher temperatures (≥1150°C).

- Attrition milling produced powder of small particle size. However, producing small ZnO grain size varistor is still a challenge.
6. EFFECT OF MONOVALENT AND TRIVALENT DOPANTS

250 ppm to 1000 ppm of two dopants Ag$_2$O and/or Al(NO$_3$)$_3$.9H$_2$O were added to the base composition. The addition of Ag$_2$O, Al(NO$_3$)$_3$.9H$_2$O, as well as combined Ag$_2$O and Al(NO$_3$)$_3$.9H$_2$O are denoted by BCAG, BCAL and BCAA, respectively. The number followed these denoted symbol is the dopant level (in unit of ppm). The sintering temperature at 1050 °C was used because of the appropriate electrical properties of the base composition (high nonlinear coefficient and low leakage current). The microstructure and the electrical properties were investigated. In addition, tests to assess the ageing behaviour of these materials were carried out.

6.1 Addition of Ag$_2$O

6.1.1 Densification

The densities of the Ag$_2$O-doped varistors were determined. The results are shown in Figure 6-1. The general trends are firstly the densities are high, above 94% dense. Secondly, the addition of Ag$_2$O causes a slight increase in density of varistors, and thirdly there is a slightly difference in density as a function of silver content. The highest density was obtained from the BCAG1000 varistor.

The results in the present work are consistent with those data presented by Kuo et al. [93]. It can be implied that the addition of silver, increasing oxygen vacancy concentration, promotes densification. The effect of silver to the oxygen vacancy will be discussed later.
Figure 6-1 Density of BCAG varistors as a function of $\text{Ag}_2\text{O}$ additions.

Note: The relative density was above 94% theoretical density, calculated from the volume fraction of ZnO and secondary phases such as spinel phase, pyrochlore phase and bismuth oxide.
6.1.2 Microstructures

The microstructure of BCAG varistors (Figure 6-2) includes ZnO grains, spinel grains and Bi-rich phases. The hexagonal-shaped ZnO grains with partial inversion boundaries do not show any evidence of abnormal grain growth. These ZnO grains make up the bulk of the microstructure. The Bi-rich intergranular phases were present throughout the structure and are visible at multiple grain junctions. Furthermore, the spinel phase located at multiple grain junctions was surrounded by the Bi-rich phase.

Figure 6-2 SEM micrograph of a BCAG250 varistor.
Another feature considered is the average grain size as shown in Figure 6-3. It was found that the average grain sizes of BCAG varistors were in the range of 9.3 μm -10.9 μm. Considering the average grain size of undoped samples (14.2 μm), it can be concluded that silver doping retards grain growth. This is caused by the formation of increasing amount of spinel phase and silver segregation to the grain boundaries.

Typically, ZnO grain growth involves the migration and the diffusion of zinc interstitials [94]. When silver ions occupy some zinc interstitial sites, normally available zinc interstitial sites are blocked. Consequently, the migration of zinc interstitials will be limited (caused by the ionic radius of larger Ag\(^+\) (1.15 Å) than that of Zn\(^{2+}\) (0.88 Å) [78]) and will depress ZnO grain growth. Moreover, the secondary phase along the grain boundaries reduces the mobility of the grain boundaries and hinders grain growth [10].

Figure 6-3 Average grain size of BCAG varistors with different Ag content.
The XRD spectra of the BCAG varistors are shown in Figure 6-4: it shows the presence of hexagonal ZnO phase, the spinel phase (Zn$_7$Sb$_2$O$_{12}$) and the pyrochlore phase (Zn$_2$Bi$_3$Sb$_3$O$_{14}$). Moreover, bismuth oxide phase was present in a different form. The β-form was detected in the base composition (BC) and BCAG varistors with the low amount of Ag$_2$O (250 ppm) in contrast the α-form was detected in the samples with higher amount of Ag$_2$O. Therefore the amount of silver affects the formation of Bi$_2$O$_3$.

The ZnO-Bi$_2$O$_3$ binary system has a eutectic point at 750°C assisting liquid formation and also densification [44]. However, the presence of other additives makes the system more complicated and lowers the temperature for liquid formation [95]. The sintering temperature of 1050°C allowed the formation of both spinel phase and pyrochlore phase. Since the pyrochlore phase reacts with ZnO during heating, the spinel phase and bismuth oxide can be formed between 950°C to 1000°C [74].

Since different forms of Bi$_2$O$_3$ were detected, the transformations of these forms should be considered. The monoclinic α-form is basically formed at the ambient condition in contrast the tetragonal β-form can be formed when fcc δ-form cooled to 650 °C [26].
Figure 6-4 XRD spectra of the BCAG varistors.

*=ZnO, Δ=spinel, o=pyrochlore, α=α-Bi$_2$O$_3$, β=β-Bi$_2$O$_3$
6.1.3 Electrical properties

The current-voltage curves for the BCAG varistors are shown in Figure 6-5 (in term of E-J). The addition of Ag₂O effectively displaced the E-J characteristics to a higher current density. Furthermore, the high amount of Ag₂O (750 ppm and 1000 ppm) also caused the increase in the electric field (curve moved upwards). It can be noticed that the addition of silver degraded the nonlinear behaviour except at the smallest amount of silver oxide addition (250 ppm). As shown in Figure 6-5, compared to the undoped material, 250 ppm silver oxide increased the nonlinear coefficient from 29 to 32. Above this amount of addition, the α-values declined gradually, falling to 14 when 1000 ppm Ag₂O was added. In contrast, the breakdown field showed the inverse trend. The E_B-value decreased with a small amount of silver oxide addition but higher levels of silver oxide increased the breakdown field. The leakage current was proportional to the amount of dopant: the I_L value was 15 μA for the undoped material and 39 μA for material prepared with 1000 ppm Ag₂O addition. The nonlinear coefficients, the breakdown fields and the leakage currents are shown in Figures 6-6 and 6-7.

Figure 6-5 I-V characteristics of BCAG varistors.
Figure 6-6 Nonlinear coefficients for BCAG varistors.

Figure 6-7 Breakdown fields and leakage currents for BCAG varistors.
The displacement in the I-V curve can be understood on the basis of the following reasons. Considering the pre-breakdown region where that part of the I-V curve is known to be controlled by the impedance of the grain boundary, then acceptor doping normally makes the I-V curve move to the left, as a result of which the impedance will be increased [21]. However, as shown in Figure 6-5 the I-V curves of BCAG move to the right. This implies that the impedance of varistor is reduced and thus the dopant acts as a donor. The degradation of nonlinear behaviour caused by the addition of silver is consistent with the work of Fan and Zhu [21, 94].

According to this result, monovalent dopants such as Na, K and Ag can act as amphoteric dopants [71]. Therefore the substitution reaction of Ag$_2$O-doping can be used to explain the donor-like behaviour of BCAG varistors [21]. The reaction will be discussed later.

### 6.1.4 Ageing behaviour

DC ageing tests were carried out at 115±1°C for periods up to 24 hours (details in Section 3.3.6). The DC supply was applied the voltage at $0.85V_{1mA/cm^2}$. The variation of leakage current with time was measured.

The time dependence of the leakage current for the BC and BCAG varistors subjected to DC stress for periods up to 24 hours is shown in Figure 6-8. Under DC stress, the degradation behaviour of silver-doped ceramics was different from the usual degradation characteristics for ZnO varistors. The leakage current of BCAG varistor decreased with time whilst that of BC did not significantly change. Comparing the $I_L$-values of the BC and BCAG varistors, it is seen that addition of Ag$_2$O increased the leakage current and it increased when the amount of Ag$_2$O increased.

According to the work of Fan and Freer, addition of silver typically improves the ageing properties of ZnO varistors however their electrical parameters are poorer than those of undoped materials [21]. In general, leakage currents for the silver-doped samples dropped initially and approached an equilibrium value. The duration of the first stage of degradation depends on the amount of silver added i.e. the greater amount of silver doping, the longer is the duration of the first stage. This is consistent with the findings of Fan and Freer [21].
Figure 6-8 Typical DC ageing behaviour of BCAG series varistors subjected to $0.85V_{1mA/cm^2}$ DC stress at 115°C.
After ageing tests, the breakdown field $E_B$ of the samples was determined at room temperature. It was noted that the $E_B$ values for BC and BCAG500 are close to the values before the ageing test whilst those for BCAG750, BCAG1000, and especially BCAG250 were higher. The relative changes of the forward breakdown fields, $\Delta E_B/E_{B0}$ (where $E_{B0}$ is the breakdown field of the sample before the ageing tests) are presented in Figure 6-9. It is interesting to see that the sample doped with the smallest amount of Ag (BCAG250) exhibited the over 11 per cent positive change in breakdown field. Furthermore, the relative changes of the breakdown fields increased with dopant content for samples with doping levels greater than 500 ppm $\text{Ag}_2\text{O}$, which is consistent with the previous study [96].

From these results it appears that the optimum amount of Ag addition is 250 ppm (in $\text{Ag}_2\text{O}$). Over this range the nonlinear coefficient dropped and the leakage currents increased. Under DC stress, the breakdown field for BCAG series changed positively. For a small amount of Ag addition the effects on ageing behaviour was steady but at higher than the optimum content the electrical characteristics has the duration period to approach the equilibrium value.
Figure 6-9 The percentage change of the breakdown field at room temperature for the BCAG series samples after being subjected to DC stress for 24 hours at 115°C.
6.2 Addition of Al(NO$_3$)$_3$·9H$_2$O

6.2.1 Densification

The densities of the BCAL series are shown in Figure 6-10. The addition of Al to the base composition increased the density of the samples. Within the range of doping level used in this work, it was found that the density increased slightly with addition of aluminium.

During sintering, densification occurs by the movement of the pore surface towards the pore centre. Very small segregation of spinel particles in the microstructure can be dragged and moved together as the pore surfaces move during sintering. The particles will push a force obstructing the motion of the surface in an equivalent way to the effect of segregation on the grain boundary movement. Therefore, the drag effect of the segregation on the pore surface movement reduced the sintering stress [8].

![Figure 6-10 Density of BCAL series varistors.](image)

Note: The relative density was above 94% theoretical density, calculated from the volume fraction of ZnO and secondary phases such as spinel phase, pyrochlore phase and bismuth oxide.
6.2.2 Microstructure

An SEM micrograph of a BCAL varistor is shown in Figure 6-11. Three phases were found in such samples: ZnO grains, spinel phase and an intergranular phase. The ZnO grains had both polyhedral and rounded shapes and the inversion boundaries were visible. The bismuth-rich phase can be seen at the ZnO grains junction with spinel phase. The addition of this dopant reduced the average grain size of ZnO, consistent to the work of Nunes and Bradt [97]. The ZnO grains of a specimen with 250 ppm and 500 ppm Al are 8.3 µm and 8.6 µm, respectively. Furthermore, the average grain size slightly decreased to 5.6 µm and 5.8 µm when the amount of dopant is up to 750 ppm and 1000 ppm. The average grain sizes of BCAL series are shown in Figure 6-12.

The effect of aluminium on grain growth in ZnO-Al₂O₃ system was discussed previously by Nunes and Bradt [97]. It is well known that ZnO grain growth is retarded by the secondary phase of ZnAl₂O₄ which pins or limits the migration of the grain boundaries. In this work the ZnAl₂O₄ spinel-type could not be detected but at the low levels of Al doping used, its presence would be below the limits of resolution of X-ray diffraction. Thus the ZnAl₂O₄ spinel phase could still have been present at very low concentrations influencing grain growth. The effect of spinel particle drag on grain growth of ZnO was also studied in other system such as ZnO-Bi₂O₃-Al₂O₃ [98].

Figure 6-11 SEM micrograph a BCAL500 varistor prepared with 500 ppm Al(NO₃)₃·9H₂O.
Figure 6-12 Average grain size of BCAL varistors.
X-ray diffraction was used to confirm the phases present in the samples. XRD spectra for all BCAL series varistors are similar. As shown in Figure 6-13, the XRD spectrum of BCAL consisted predominantly ZnO phase, which is the grey area as seen in Figure 6-12 (for SEM micrograph). Furthermore, the Bi-rich phases of pyrochlore and β-Bi₂O₃ are shown as the white phase in SEM micrograph, whilst the spinel, presented in the light grey area. It is revealed that only β-Bi₂O₃ can be detected in BCAL series. It was noted above that the ZnAl₂O₄ spinel may also be present but would be below the detection limit.

Figure 6-13 XRD spectrum of the BCAL varistor with 500 ppm Al(NO₃)₃·9H₂O.

*=ZnO, Δ=spinel, o=pyrochlore, β=β-Bi₂O₃
6.2.3 Electrical properties

The current-voltage characteristics of aluminium-doped materials are shown in Figure 6-14. It can be seen that the E-J curves of BCAL series moved to the higher current density with increasing aluminium nitrate content. The nonlinear behaviour improved as the level of Al(NO₃)₃·9H₂O increased to 500 ppm. Beyond 500 ppm doping content, the nonlinear behaviour deteriorated. The dependence of the nonlinear coefficient on the aluminium nitrate content is shown in Figure 6-15. It is clearly seen that Al-doping enhanced the nonlinearity of ZnO varistor. The maximum nonlinear coefficient was obtained for the 500 ppm aluminium nitrate doping, yielding a value of 36. However, increasing the dopant further caused the nonlinear coefficient to fall moderately. The breakdown field and the leakage current show the opposite trend. Both values increased as the amount of dopant increased. These electrical parameters are shown in Figure 6-16.

Comparing with Ag doping, it can be seen that aluminium doping affects the electrical properties of varistors in a different way to silver doping. Addition of Al yields a higher nonlinear coefficient but the leakage current and breakdown field also increases. It can be concluded that aluminium improves the nonlinear behaviour for additions up to 500 ppm aluminium nitrate.

The displacement to the right hand side (higher current density) of the E-J curves of BCAL varistors means that Al behaves as the donor as expected for the trivalent metal species [3]. Under normal circumstances ZnO contains zinc atom interstitial site and oxygen vacancies. The presence of Al in ZnO generates defects introducing donor states in the forbidden band slightly below the conduction band resulting to the reduction of band gap and making the ZnO more conducting [8]. The donors are assumed to affect the interstitial zinc ion, Znᵢ. Neutral interstitial zinc atom is first ionised as

\[ \text{Zn}^x_i \rightarrow e^+ + \text{Zn}^+_i \]  \hspace{1cm} (6-1)

and then ionised again as

\[ \text{Zn}^+_i \rightarrow e^+ + \text{Zn}^{++}_i \]  \hspace{1cm} (6-2)

where \( \text{Zn}^+_i \) and \( \text{Zn}^{++}_i \) are first and second ionisation of interstitial zinc atoms. The free electron moves to the conduction band and enhances the ZnO conductivity and then can be further increased by the extrinsic defects. The aluminium atoms would act as donors
upon addition of aluminium to the varistor. This circumstance involves the accommodation of Al ions on the host lattice sites. A trivalent $\text{Al}^{3+}$ ion would replace a divalent $\text{Zn}^{2+}$ ion causing an electron moves to the conduction band. The reaction can be written as

$$\text{Al}_2\text{O}_3 \leftrightarrow 2\text{Al}_{\text{Zn}} + 2\text{O}_\text{Zn}^{\text{V}} + 2e' + \frac{1}{2}\text{O}_2(g)$$  \hspace{1cm} (6-3)

The concentration of electrons increases thereby increasing the electrical conductivity of the grains raises i.e. the resistance of ZnO grain decreases. This causes an increasing in nonlinear coefficient and leakage current.

Figure 6-14 I-V characteristics of the BCAL varistors.
Figure 6-15 Nonlinear coefficients of BCAL varistors.

Figure 6-16 Breakdown fields and leakage currents of BCAL varistors.
6.2.4 Ageing behaviour

The leakage currents for BCAL varistors subjected to DC stress as a function of time are shown in Figure 6-17. The leakage currents for BCAL varistors dramatically increased with time whilst those of BC varistors changed only slightly with time. This result means that Al causes BCAL varistors to exhibit the high degradation rates. Moreover, the stability of BCAL series is inversely proportional to the amount of Al. During an aggressive testing, the BC varistor with 250 ppm Al(NO$_3$)$_3$·9H$_2$O could withstand DC loading for about 6 hours whilst the varistors prepared with 1000 ppm Al(NO$_3$)$_3$·9H$_2$O survived less than 1 hour. The rate coefficients for ageing, $K_T$, increased up with increasing amount of dopant from 8.33×$10^{-2}$ mA/h$^{1/2}$ to 5.07×$10^{-1}$ mA/h$^{1/2}$ for 250 ppm aluminium nitrate and 1000 ppm aluminium nitrate addition, respectively. The $K_T$-values as a function of the aluminium nitrate content are shown in Figure 6-18.

![Figure 6-17 Time dependence of the leakage current for BCAL varistors subjected to DC stress for periods up to 24 hours.](image)
Figure 6.18 Ageing rate coefficients of the BCAL varistors.
After ageing tests, the breakdown fields were determined at room temperature. From Figure 6-19 it can be noted that the $E_B$-values for BCAL varistors decreased. Since Al did not enhance the stability of ZnO varistor, then the ageing test degraded the nonlinear behaviour. Therefore the breakdown fields of BCAL varistors obviously decreased. The percentage change of breakdown field for BCAL varistor is negative consistent with the trends reported by Wong and Eda et al [26, 65]. However, the changes in this study fluctuated dramatically with a maximum of about 57%, compared to the gradually change of breakdown voltage reported by (less than 10%) [65]. However the differences may in part due to differences in applied bias.

From these results it appears that the optimum amount of Al addition is 500 ppm (in Al(NO$_3$)$_3$·9H$_2$O). Above this value the nonlinear coefficient dropped. Moreover, at other doping levels the breakdown field and the leakage current were high and the ageing rate coefficient and the change in breakdown field after ageing test were also high. Under DC stress, the breakdown field for BCAL series changed negatively. The addition of Al improves the nonlinear coefficient for levels up to 500 ppm. Higher doping degrades the nonlinear behaviour.

![Graph](https://via.placeholder.com/150)

Figure 6-19 The percentage change of the breakdown field at room temperature for the BCAL series samples after being subjected to DC stress for 24 hours at 115°C.
6.3 Addition of Ag$_2$O and Al(NO$_3$)$_3$·9H$_2$O

To prepare the material with both good nonlinear behaviour and the ability to withstand stress, the optimised material was based on the compositions for the BCAG varistor with high nonlinear coefficient and low leakage current, and the BCAL varistor with a high nonlinear coefficient. Consequently, 250 ppm of silver oxide and 500 ppm of aluminium nitrate were the chosen doping levels. The base composition prepared with addition of both Ag and Al was denoted as BCAA. These were prepared with media of propan-2-ol or deionised water: these compositions are denoted as BCAA-P2Ol and BCAA-DIW, respectively.

6.3.1 Densification

Figure 6-20 shows the density of the BCAA varistors. Since addition of either Ag or Al enhanced the density of ZnO varistors, then the addition of both Ag and Al can improve the density of the materials. Moreover, it can be seen that BCAA-P2Ol varistor had slightly higher density than either Al- (BCAL) or Ag-addition (BCAG). In contrast the density of BCAA-DIW varistor was close to that of the BC sample. This suggests that the appropriate combination Ag and Al doping and use the best milling medium gives optimum sample densification.
Figure 6-20 Comparison of density for various samples.
6.3.2 Microstructure

Typical SEM micrographs of BCAA varistors are shown in Figure 6-21. The ZnO grains, spinel phase and intergranular Bi-rich network are found as in the base composition. ZnO grains make up the bulk of the microstructure. The spinel phase is located at the ZnO grain junctions and in ZnO grain as particles. A Bi-rich intergranular network is found within the microstructure and surrounding the spinel phase grains. Considering the distribution of the phases, it can be seen that in BCAA-DIW samples the secondary phases were more uniformly distributed than in those of BCAA-P2Ol samples. The main feature distinguishing the microstructure is the grain size. As the Ag or Al doping inhibits grain growth, combined Ag and Al doping also retards ZnO grain growth. Moreover, the milling medium influences the average grain size: BCAA-P2Ol samples had an average grain size at 5.8 µm whilst those of BCAA-DIW were 7.4 µm. However taking into account uncertainty values the differences are not significantly different (Figure 6-20).
Figure 6-21 SEM images of (a) BCAA-P2Ol and (b) BCAA-DIW varistors.
Since the different media, deionised water (DIW) and propan-2-ol (P2Ol), were used to prepare the BCAA varistors, the SEM-mapping was used to investigate the elemental distribution (Figure 6-22). In BCAA-P2Ol sample, primary grains consisted predominantly of zinc atoms. The bismuth-rich phase contained mainly atoms of bismuth and antimony but also manganese and aluminium. The light grey spinel phase contained antimony, manganese, cobalt and zinc. Silver atoms were found within the grain and secondary phases at low level. The phase in which aluminium dissolved is different from the other work [65] showing here that Al concentrated in the spinel phase. In the BCAA-DIW samples, the elemental distributions are similar to the distributions in BCAA-P2Ol samples (Figure 6-22).
Figure 6-22 SEM-mapping of BCAA-P2Ol and BCAA-DIW varistors.
To confirm the phases present in the Ag+Al samples, they were investigated by XRD. From an example XRD spectra (Figure 6-23), it can be noted that even though different media were used the spectra are similar. The predominant ZnO, spinel phase (Zn$_7$Sb$_2$O$_{12}$) and pyrochlore phase (Zn$_2$Bi$_3$Sb$_3$O$_{14}$) were detected. In addition $\alpha$-Bi$_2$O$_3$ was present the same as in samples prepared with a small amount of Ag$_2$O. The XRD spectra of BCAA varistors are shown in Figure 6-23. Complementary SEM results show that the primary grey area is clearly the ZnO grain containing dissolved Co, Mn, Ag and Ag; the light grey area is the spinel phase containing dissolved Co, Mn and Ag; the Bi-rich phase contains dissolved Mn, Al and Ag.

![XRD spectra](image)

Figure 6-23 XRD spectra of the base composition prepared with the addition of 250 ppm Ag$_2$O and 500 ppm Al(NO$_3$)$_3$.9H$_2$O. *$=$ZnO, $\Delta$=spinel, o=pyrochlore, $\alpha$=$\alpha$-Bi$_2$O$_3$
6.3.3 Electrical properties

The I-V characteristics of BCAA-P2Ol and BCAA-DIW varistors are shown in Figure 6-24. The nonlinear behaviour caused by Ag and Al doping can be explained in terms of the E-J curves moving to the right, to higher current density. Furthermore, the BCAA-DIW varistors exhibited a higher electric field than the BC varistors. The nonlinear coefficients are 34 and 38 for BCAA-P2Ol and BCAA-DIW, respectively. It can be noted that the medium of deionised water leads to the material having maximum α-value in this work, slightly higher than that for 500 ppm aluminium nitrate doping (36). The specimen prepared using deionised water moreover showed a breakdown field of 2700 V/cm and the lowest leakage current of 15 μA whilst for the ceramics prepared in in propan-2-ol the breakdown field was 3160 V/cm and leakage current is 18 μA. Comparing the electrical properties of BCAA series to those of BCAG and BCAL series, it can be noted that the addition of both dopants in deionised water increased the nonlinear coefficient and reduced the leakage current. The electrical parameters are shown in Figure 6-25.

Figure 6-24 E-J curves of BC, BCAA-P2Ol and BCAA-DIW varistors.
The I-V characteristics of BCAA varistors are obviously obtained from the combined effect of Al and Ag doping. For the doping levels selected the effect of Al doping may dominate the nonlinearity of BCAA varistors because the I-V characteristics of BCAA were as good as those of BCAL500 sample. In addition, the effect of Ag doping may dominate stability of BCAA as the samples could withstand the stress condition.

Figure 6-25 Electrical parameters of various varistors.
6.3.4 Ageing behaviour

Figure 6-26 shows the ageing behaviour of BCAA varistors. It can be seen that the overall ageing behaviour of BCAA varistors is similar to that of the Ag-doped samples i.e. the leakage current initially decreased and then approached a stable value. Especially for the BCAA-P2Ol samples the leakage current dramatically decreased and then gradually increased with time. The base composition exhibited the lowest leakage current whilst the BCAA-P2Ol showed the highest values. Samples prepared with addition of both Ag and Al in deionised water had the lower leakage currents than those of the Ag-doped materials.

Figure 6-26 Time dependence of the leakage current for the BC, BCAG250 and BCAA varistors.
6.4 Capacitance-voltage characteristics

Since Schottky barriers play a vital role in the conduction process, the difference between the electrical characteristics of the doped and undoped samples means their barriers are different. To estimate these parameters, capacitance-voltage (C-V) measurements were carried out. The linear relationship between the barrier capacitance (per unit area) and applied voltage (per grain boundary) is shown in Figure 6-27. The donor density \( N_d \) and barrier height \( \phi \) can be determined from the slope and the intercept of the term \( \left( \frac{1}{C_b} - \frac{1}{2C_{b0}} \right)^2 \) and \( V_g \) line, respectively. Since the donor density and barrier height are calculated, the width of the depletion layer \( L \) then can be determined from the following equation [21]:

\[
L = \left( \frac{2\phi \varepsilon S}{qN_d} \right)^{1/2}
\]

The barrier parameters for the ZnO varistors are shown in Table 6-1. The addition of Ag or/and Al has a clear effect on barrier height. The addition of silver oxide appears to have a small effect on the barrier parameters: decreasing the donor density, barrier height and width of depletion layer. In contrast, the addition of aluminium nitrate increased \( N_d \), decreased \( \phi \), and \( L \). Furthermore, the addition of both Ag and Al should show barrier parameters between those for samples prepared with Al or Ag doping. In fact, the BCAA series showed similar barrier parameters to those for the addition of Al: the parameters are not totally between those of BCAG250 and BCAL500. Looking at the effect of the milling medium, it was seen that the BCAA-P2Ol varistors had the higher donor density, lower barrier height and smaller width of depletion layer than those of BCAA-DIW. As the \( L \)-values for all doped ZnO varistors were lower than those of BC varistors, the prime reason may be the increase in sample capacitance.
Figure 6-27 \(\left(\frac{1}{C_b} - \frac{1}{2C_{b0}}\right)^2\) as a function of \(V_g\) for various samples.

Table 6-1 Calculated donor density, barrier height and width of depletion layer for the ZnO varistors chosen

<table>
<thead>
<tr>
<th>Samples</th>
<th>Donor density (\text{(cm}^3\text{)})</th>
<th>Barrier height (V)</th>
<th>Width of depletion layer (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>(1.13 \times 10^{17})</td>
<td>2.00</td>
<td>129</td>
</tr>
<tr>
<td>BCAG250</td>
<td>(9.88 \times 10^{16})</td>
<td>1.52</td>
<td>120</td>
</tr>
<tr>
<td>BCAL500</td>
<td>(8.84 \times 10^{17})</td>
<td>1.77</td>
<td>43</td>
</tr>
<tr>
<td>BCAA-P2Ol</td>
<td>(1.29 \times 10^{18})</td>
<td>1.70</td>
<td>35</td>
</tr>
<tr>
<td>BCAA-DIW</td>
<td>(8.44 \times 10^{17})</td>
<td>1.98</td>
<td>47</td>
</tr>
</tbody>
</table>
According to the work of Carlson and Gupta [67], a small amount of Al doping behaves as donor, which increases the conductivity of the ZnO grains of the varistors. It is consistent with the observed displacement of E-J curve to the higher current density in this work and the higher donor density of BCAL 500 varistors.

In the case of monovalent metal oxide doping, the substitution reaction between the monovalent metal ions and Zn ions at the lattice sites leads the metal ions to act as acceptors [71]. This may increase the resistivity and cause the deterioration of I-V characteristics. Therefore in Ag$_2$O doped samples the I-V characteristics are degraded as a result of the doping of Ag$_2$O.

The Ag$^+$ ion has a larger ionic radius than that of Zn$^{2+}$ consequently there is a limited substitution at the proximity of depletion region of ZnO grains. The reactions may be written as:

\[
Ag + V_{Zn}^x \rightarrow Ag_{Zn}^x
\]  
(6-5)

\[
Ag_{Zn}^x \rightarrow Ag_{Zn}^I + h^-
\]  
(6-6)

The generated $h^-$ combines with e$^-$ due to the formation of the acceptor level. Moreover the net donor density also decreases. The results from the present C-V measurements support the above hypothesis that donor density decreased upon Ag doping.
6.5 Ageing phenomena in monovalent and trivalent doped varistors

The back-to-back Schottky barrier model is typically accepted for presenting the conduction mechanism of ZnO varistors therefore the barriers may be deformed under long term electrical stress in the ageing process. At fixed field and temperature, the current density is proportional to the barrier height. When ageing occurs, the leakage current increases and the breakdown field decreases resulting in the decrease of barrier height.

The deformation of the barriers may be attributed to the migration of ions in the barrier region [26]. Such ions are located in the proximity of the grain boundary. The barrier depletion layer, located adjacent to the grain boundary interface, has the positive charge [65]. This positively charged defects include mobile interstitial Zn ions (\(Zn_i\) and \(Zn_{i}^{-}\)) existing from the non stoichiometric nature of ZnO, the spatially fixed ions comprising the native oxygen vacancies (\(V_{O}^{2-}\) and \(V_{O}^{\cdot}\)) and the trivalent substitutional ions such as Bi, Sb, etc. To maintain the electrical barrier, negative charges are formed at the grain boundary interface by \(O^{2-}\) ions from the oxygen gas formed during the sintering procedure and the native Zn vacancies (\(V_{Zn}^{\prime}\) and \(V_{Zn}^{\prime\prime}\)) [8,71]. The grain boundary acts as a disordered layer [56]. This layer has two characteristics: first, enabling a rapid diffusion and second, acting as an infinite source and sink for neutral vacancies, \(V^{x}\).

This defect model, analogous to Schottky barrier model, is presented in Section 2.7.

When varistor is subjected to electrical stress, field-assisted diffusion moves mobile zinc interstitials towards the negatively charged grain boundary interface. At the interface these defects are thus converted to neutral defects because of the chemical reactions between defects as follows:

\[
Zn_i + V_{Zn}^{\prime} \rightarrow Zn_{i}^{x} + V_{Zn}^{x} \tag{6-7}
\]

\[
Zn_i + V_{Zn}^{\prime} \rightarrow Zn_{i}^{x} + V_{i}^{x} \tag{6-8}
\]

and

\[
Zn_{i}^{-} + V_{Zn}^{\prime} \rightarrow Zn_{Zn}^{x} + V_{i}^{x} \tag{6-9}
\]

\[
Zn_{i}^{-} + V_{Zn}^{\prime\prime} \rightarrow Zn_{Zn}^{x} + V_{i}^{x} \tag{6-10}
\]
The neutral vacancies $V_{zn}^X$ and $V_i^X$ disappear in the grain boundary, leaving the $Zn_{zn}$ and neutral $Zn_{zn}^X$ and $Zn_i^X$ at the interface.

Meanwhile, under electrical stress the negatively charged oxygen ions $O^{2-}$ may migrate towards the depletion regions where the reaction with the immobile native oxygen ($V_o$, $V_o$) vacancies takes place as

$$O'' + V_o \rightarrow O_o^X$$  \hspace{1cm} (6-11)

the neutral oxygen is produced in the lattice of the depletion region and

$$O'' + V_o \rightarrow O_o'$$ \hspace{1cm} (6-12)

thus the new ZnO lattice may be created by

$$Zn_{zn} + O_o' \rightarrow ZnO$$ \hspace{1cm} (6-13)

The negatively charged oxygen ions would possibly react with the positively charged interstitials moving towards the grain boundary interface. This reaction leaves neutral oxygen ions and zinc interstitial ions at the grain boundary interface.

The simultaneous migration process of zinc interstitials and oxygen ions leads the decline in the negative charges at the grain boundary interface, responsibly caused the decrease of barrier height, as shown in Figure 6-28.

Figure 6-28 Defect diffusion and chemical interaction at grain boundary during electrical stress: (a) diffusion of $Zn_i$ and $O''$ and (b) reaction of defects ad resulting reduction of barrier height [67].

139
In the case of Al-doping, Al$^{3+}$ easily substitutes for Zn$^{2+}$ in the lattice [8]. The Zn ions substituted may be located in other available vacant interstitial sites. Since more zinc interstitials exist in the bulk ZnO including the depletion region, under electrical stress the BCAL varistors may be more degradable than the BC varistor. Moreover, the higher donor density at the interface depletion region needs more negative charges at the other side of interface to equalise the balance. Therefore the density of negatively charged oxygen ions at the interface of Al-doping is higher than that of Ag-doped samples. This may be one reason to explain the lower stability of Al-doped samples.

In the case of Ag-doping, it is assumed that Ag$^{+}$ can act as both donors and acceptors (amphoteric) as the same as Na$^{+}$ and K$^{+}$ [65]. Metal ions are able to occupy both the lattice and the interstitial sites. In the case of donor type behaviour, the substitution reaction at interstitial sites is shown as

$$Ag_2O \rightarrow 2Ag_i + \frac{1}{2}O_2(g) + 2e'$$

(6-14)

These reactions assume that Ag$^{+}$ having larger ionic radius of (1.15 Å) than Zn$^{2+}$ (0.88 Å) will substitute preferentially region of the grain boundary as opposed to the interior of the grain. This will encourage the depletion layer to become the most favourable region to contain the dopants.

Due to dual mode of substitution, silver atoms partially occupy the sites where zinc interstitials would otherwise occupy. This will essentially block the formation of zinc interstitials in available sites. If the available sites are occupied by silver atoms, the migration of zinc interstitials via available sites will also be diminished.

The available interstitial vacancies at a local region will be limited when Ag$^{+}$ is substituted for Zn$_i$ at the available sites. Therefore the number of Ag$_i$ and Zn$_i$ will be stable. The excess Zn$_i$ diffuses out of the crystal along with its electron at the fabrication temperature of the varistor. It combines with absorbed oxygen and then disappears via the formation of the new ZnO lattice sites at the surface or grain boundary [65]. Thus the Ag doped ZnO varistors may have less zinc interstitials.

The results for BCAA varistors may be explained in terms of the balance between Ag and Al doping. If the balance is optimum, the effect of both Ag and Al will be obtained. The large donor density caused by Al doping and the low concentration of zinc
interstitials in depletion region controlled by Ag doping are the predominant effect. The combined effect will provide both good nonlinearity and stability for the Al+Ag doped samples.

6.6 Summary

- The addition of Ag enhances the stability of ZnO varistor but reduces the nonlinearity. The stability is because the Ag\(^+\) ion occupies the interstitial site [21].

- The addition of Al improves the nonlinearity but reduces the stability. The degradation is because the Al\(^{3+}\) ion replaces Zn\(^{2+}\) ion on the host lattice site [3].

- The addition of both Al and Ag improves both the nonlinearity and stability. Samples containing both additives have a low density of interstitial zinc ions in the depletion layer benefitting the degradation resistance [3].

Table 6-2 Grain size and electrical properties of BCAL, BCAG and BCAA varistors.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ave. grain size ((\mu m))</th>
<th>(\alpha)</th>
<th>Breakdown field (V/cm)</th>
<th>Leakage current ((\mu A))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>14.2±1.7</td>
<td>29±1</td>
<td>3068±10</td>
<td>18±2</td>
</tr>
<tr>
<td>BCAG250</td>
<td>11.4±1.1</td>
<td>32±2</td>
<td>2960±10</td>
<td>18±2</td>
</tr>
<tr>
<td>BCAG500</td>
<td>12.9±0.8</td>
<td>23±1</td>
<td>2660±10</td>
<td>25±2</td>
</tr>
<tr>
<td>BCAG750</td>
<td>10.6±1.0</td>
<td>21±1</td>
<td>3600±10</td>
<td>29±2</td>
</tr>
<tr>
<td>BCAG1000</td>
<td>10.2±0.9</td>
<td>14±1</td>
<td>4160±10</td>
<td>39±2</td>
</tr>
<tr>
<td>BCAL250</td>
<td>9.3±0.8</td>
<td>32±2</td>
<td>3032±10</td>
<td>29±2</td>
</tr>
<tr>
<td>BCAL500</td>
<td>10.5±0.8</td>
<td>36±2</td>
<td>3360±10</td>
<td>29±2</td>
</tr>
<tr>
<td>BCAL750</td>
<td>5.7±0.5</td>
<td>22±2</td>
<td>4240±10</td>
<td>39±2</td>
</tr>
<tr>
<td>BCAL1000</td>
<td>7.1±0.65</td>
<td>21±2</td>
<td>4100±10</td>
<td>44±2</td>
</tr>
<tr>
<td>BCAA-P2O1</td>
<td>7.7±1.0</td>
<td>34±2</td>
<td>3165±10</td>
<td>18±2</td>
</tr>
<tr>
<td>BCAA-DIW</td>
<td>8.1±1.0</td>
<td>38±2</td>
<td>2703±10</td>
<td>15±2</td>
</tr>
</tbody>
</table>
7. EFFECT OF GALLIUM OXIDE DOPING

Using BC as the base composition a series of varistors were prepared by adding gallium oxide at the concentrations are 750 ppm, 1000 ppm, 1500 ppm, 2000 ppm and 4000 ppm. These formulations are denoted as BCG followed by Ga$_2$O$_3$ content in ppm. The BC varistor was used as a reference to compare the results. The varistors were prepared by a conventional mixed oxide route. The pellets were sintered at 1050°C for 2 hours. The densification, microstructure and the electrical properties of Ga doped varistors were investigated.

7.1 Densification

The specimen densities determined from weight and dimensional measurements are shown in Figure 7-1. It was found that the density of Ga-doped varistors are high, typically above 94% theoretical density and there is no significant difference in sintered density as a function of gallium content. According to Gupta and Coble, the development of a liquid phase during processing led to the high densities.
Figure 7-1 Densities of BCG varistors as a function of Ga$_2$O$_3$ additions.

Note: The relative density was above 94% theoretical density, calculated from the volume fraction of ZnO and secondary phases such as spinel phase, pyrochlore phase and bismuth oxide.
7.2 Microstructure

Scanning electron micrographs are shown in Figure 7-2. They show typically three phases of ZnO, spinel and the Bi-rich intergranular network. The ZnO grains make up the bulk of the microstructure and many exhibit inversion boundaries. The spinel phase is located predominantly at the ZnO junctions and surrounded by the Bi-rich phase. Unlike the Ga-free samples (Figure 7-2a), there appear to be less spinel particles in the ZnO grains for the Ga doped sample (Figure 7-2b). The Bi-rich intergranular network is present along the grain boundary. Barf et al. studied the creation of twins and corresponding boundaries in ZnO prepared with a small amount of Ga₂O₃ [99]. It was found that gallium migration into ZnO encourages the creation of twins and corresponding boundaries. Figure 7-3 shows the location of elemental analysis for a BCG4000 varistor. Table 7-1 shows the corresponding elemental analyses. It can be considered that in ZnO grains only Co was dissolved whilst in spinel phase Co, Mn, and Ga were dissolved. We also expect to see Mn dissolved in the ZnO grains but perhaps because of the small amount of Mn, it was not detected.
Figure 7-2 SEM micrographs of ZnO varistors (a) BC and (b) BCG4000.
Figure 7-3 SEM image for BCG4000 sample showing locations of analysis.

Table 7-1 Point scanning elemental analysis of BCG4000 varistor

<table>
<thead>
<tr>
<th>Point</th>
<th>Amount (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>A/ZnO</td>
<td>16.37±0.81</td>
</tr>
<tr>
<td>B/Spinel</td>
<td>16.23±1.25</td>
</tr>
<tr>
<td>C/Bi-rich boundary phase</td>
<td>37.65</td>
</tr>
</tbody>
</table>

NB: spot C has only one measurement
Another feature considered is the grain size. From the micrographs the average grain sizes were determined by the linear intercept method. Data are present in Figure 7-4. It is clearly seen that addition of gallium oxide suppressed grain growth and therefore the grain size of the varistors. The average grain size of the gallium free varistor was about 14 μm whilst the maximum average grain size of Ga₂O₃ doped varistors was approximately half that at 6 μm. The results from this study are broadly consistent with other studies of Ga doped varistors. Gilbert and Freer reported that the grain sizes slowly increased (7-9 μm) as the amount of gallium gradually increased (1000-10000 ppm) [100]. Furthermore, comparison with other dopants such as aluminium (similar ionic charge and ionic radius to Ga ion: 0.54 Å for Al³⁺ and 0.62 Å for Ga³⁺) shows that the grain size decreased (15 μm to 7 μm) as the aluminium content increased (from zero to 1%Al) in the study of Carlson and Gupta [101].

![Figure 7-4 Average grain size of gallium-doped ZnO varistors at different amount.](image-url)
The phases found by SEM analysis were confirmed by X-ray diffraction analyses. Three phases of ZnO (A in Figure 7-3), a spinel (B in Figure 7-3) and $\beta$-Bi$_2$O$_3$ C in Figure 7-3) were detected. Moreover, it was found that all XRD spectra of BCG varistors were similar. Therefore only the XRD spectrum of BCG4000 varistor is shown in Figure 7-5.

Figure 7-5 XRD spectrum of a BCAG4000 varistor.

*=ZnO, Δ=spinel, $\beta$=$\beta$-Bi$_2$O$_3$
7.3 Electrical properties

7.3.1 Current-voltage characteristics

The current-voltage characteristics of the base composition with different amount of gallium oxide are shown in Figure 7-6. It can be noted that the reference material (sample BC, without gallium oxide doping) commenced the nonlinear region at the current density of $2 \times 10^2 \mu A/cm^2$. It can be seen that addition $Ga_2O_3$ also moved the I-V characteristics upward to a higher electric field. In addition, the addition of gallium oxide caused displacement of the nonlinear region to the right i.e. to higher current density. This indicates that Ga acts as a donor. The greater additions of gallium up to 1500 ppm increased the displacement of the I-V characteristics further to the right. In contrast increasing the $Ga_2O_3$ to 2000 ppm modified the E-J curve to be displaced backward to the lower current density. This means a reduction in the leakage current and the transition from the donor type to the acceptor type behaviour.

On the basis of the earlier work [101-103], the change in the I-V characteristics was expected. Gupta reported that the transition from donor to acceptor of Ga doped varistor was found between 750-1800 ppm Ga [102]. Since, gallium doping has been known to affect both the grain and grain boundary regions a displacement to the higher current density of the E-J curves confirmed the effect to the grain. However the effect on the grain could not be formally assessed in the present work. This was because the I-V curve did not extend into the upturn region. The upturn region represents the effect of the ZnO grain in contrast at pre-breakdown region it should be controlled by the effects of the grain boundaries.
Figure 7-6 I-V characteristics of gallium-doped varistors sintered at 1050 °C.
The electrical parameters of BCG series are as follows: the nonlinear coefficients were determined from the I-V characteristics over the current density range 1-10 mA/cm^2. The results (Figure 7-7) show that Ga doping reduced nonlinearity. The nonlinear coefficient of the Ga free samples (29) was higher than that of Ga doped samples (15-26) as shown in Figure 7-7. The samples with the gallium oxide content of 750 ppm and 1500 ppm had the $\alpha$-values over 25, typical for that of a commercial varistor. In contrast the varistor with gallium content over 2000 ppm had $\alpha$-values below 20. Since the nonlinear coefficients were determined over the range as mentioned above, the I-V characteristics of the BCG varistors are in both the pre breakdown region and nonlinear region. Thus an apparent decrease in the nonlinear coefficients is not a real effect but due to a displacement to the higher current density region of the I-V curves of these samples.
Figure 7-7 Nonlinear coefficients of gallium-doped varistors sintered at 1050 °C.

Figure 7-8 Breakdown fields and leakage currents of BCG varistors sintered at 1050 °C.
The leakage current was determined at 75% breakdown field and the results are shown in Figure 7-8. It can be noted that addition of gallium increased the leakage current. As the gallium content increased to 2000 ppm, the $I_L$ reaches a maximum value over 100 μA. Addition of gallium over this amount, led to a reduction in the leakage current value. As shown in Figure 7-8, the increase in leakage current with increasing gallium content up to a maximum at 2000 ppm is higher than that reported by Gilbert and Freer [100] for addition of 1500 ppm Ga$_2$O$_3$.

Miyoshi et al. discussed the effect of trivalent metal dopants such as Al and Ga on the I-V characteristics of varistors [103]. Both dopants indicated the same effect i.e. addition of these dopants increased the leakage current in the pre-breakdown region and decreased the resistivity in the upturn region. In donor type behaviour the carrier concentration increased whilst the acceptor type exhibit the inverse effect. The donor type behaviour is caused by the substitution of gallium on zinc lattice sites as indicated in Equation 7-1.

$$Ga_2O_3 \rightarrow 2Ga_{2n} + 2O_2^u + 2e' + \frac{1}{2}O_2(g) \quad (7-1)$$

Substitution of Ga$^{3+}$ onto a zinc lattice site leads to an increase in carrier concentration. The leakage current rises because the resistivity of the grain boundary falls.

According to Gupta [71], the change in I-V characteristics of BCG varistors can be interpreted on reflecting the change in behaviour of Ga from donor to acceptor. One made for acceptor type behaviour could be based on the gallium ions beginning to occupy the sites that usually occupied by zinc interstitial ions as shown in the following reaction [100]

$$2Ga_2O_3 \leftrightarrow 4Ga_i' + 4h' + 3O_2(g) \quad (7-2)$$

Alternative reactions include:

$$Ga_2O_3 \rightarrow 2Ga_{2n} + V_{Zn}'' + 3O_2 \quad (donor) \quad (7-3)$$
The breakdown field was determined at current density of 1 mA/cm$^2$. The reference varistors have the breakdown fields of approximately 3000 V/cm. Addition of gallium to the base composition increased the $E_B$-value to the maximum over 4600 V/cm for the 1500 ppm Ga$_2$O$_3$. At 2000 ppm Ga$_2$O$_3$, the breakdown field dropped. Since the breakdown field is directly related to grain size, decreasing grain size effectively increased the $E_B$ value due to the increase in the number of grain boundaries per unit thickness. However it should be noted that for the BCG samples the displacement of I-V characteristics again effects to the breakdown field. To determine the actual breakdown voltage, it may necessary to choose a higher current density than the normal at 1 mA/cm$^2$ because at this current density the samples were still within the pre-breakdown region.

In addition to the proposed mechanism based on donor/acceptor behaviour there is a further possibility. As a result of gallium oxide doping, the resistivity of each grain boundary is reduced (reduction in barrier height drops proves this, see Figure 7-11) therefore the leakage current increases. However because of the smaller grain size caused by Ga$_2$O$_3$ doping, there are increased numbers of grain boundaries/barriers in series (even doubled) in a unit thickness. This led to the sample breakdown voltage/field being increased and the leakage current also increased. When doping of Ga is beyond certain level (here 2000 ppm), as a consequence of the grain size increase, the total number of grains in series connection reduced and hence the breakdown voltage/field decreased.

7.3.2 Capacitance-voltage characteristics

The C-V characteristics of the BCG varistors are shown in Figure 7-9. The capacitance decreased for all BCG varistors as a function of applied voltage per grain boundary ($V_g$). The capacitances of the reference sample was low ranging from approximately 100-110 pF, thus this data is not plotted in Figure 7-9. The linear relationship between the barrier capacitance per unit area ($C_b$) and $V_g$ was plotted to calculate the conduction parameters. Figure 7-10 shows the data for $(1/C-1/C_{b0})^2$ versus $V_g$. It can be seen that $(1/C-1/C_{b0})^2$ increased with applied voltage. The BCG 4000 varistors exhibited the greatest value of $(1/C-1/C_{b0})^2$ in this study. The linear relationship between barrier capacitance and applied voltage is consistent with that observed in other studies [34].
Figure 7-9 Capacitance-voltage characteristics for BCG varistors sintered at 1050°C.

Figure 7-10 Barrier capacitance \((1/C-1/2C_{b0})^2\) as a function of applied voltage per grain for BCG varistors sintered at 1050°C.
The donor density ($N_d$) and barrier height ($\phi$) can be determined from the slope and the intercept of the line, respectively. The donor densities for the gallium oxide doped varistor are presented in Figure 7-11. It is seen that the donor densities of BCG varistors were higher than that of the Ga free sample. This means that Ga behaves as a donor. The $N_d$-values increased ($9 \times 10^{17}$-$1 \times 10^{18}$ cm$^{-3}$) as the Ga$_2$O$_3$ content increased (750-2000 ppm). When Ga$_2$O$_3$ content was more than 2000 ppm, the donor density dropped to $9 \times 10^{17}$ cm$^{-3}$. In contrast, the barrier height shows the inverse trend. The $\phi$ values of BCG varistors are obviously lower than those of the BC reference samples. Comparison of the barrier height as a function of Ga$_2$O$_3$ content shows that the $\phi$ value slightly decreased (1.15-1.11 V) as a content of Ga$_2$O$_3$ up to 1500 ppm. The samples with Ga$_2$O$_3$ content over 1500 ppm show an increase in barrier height to 1.3 V.

![Figure 7-11 Donor density and barrier height as a function of Ga$_2$O$_3$ content of BCG varistors.](image-url)
7.4 Summary

- Addition of gallium oxide retarded grain growth. The average grain sizes reduced dramatically for the BCG varistors.

- The I-V characteristics of BCG varistors with the addition of 750 ppm to 1500 ppm Ga$_2$O$_3$ were displaced to the right, meaning to higher current density. At 2000 ppm Ga$_2$O$_3$ there appeared to be a transition from donor to acceptor behaviour since the I-V characteristics moved towards lower current densities. The I-V characteristics move because of the impedance of grain changes [102].

- The nonlinear coefficients of BCG series varistors were lower than those of Ga free sample possibly because of the displacement of I-V characteristics of BCG [100]. The addition of gallium oxide increased both the breakdown field and the leakage current.

- The C-V characteristics indicated that the donor density of BCG varistors were higher than those of Ga free varistors and increased up to 2000 ppm gallium oxide doping. This donor type is caused by the substitution of gallium on zinc lattice sites [100]. The barrier heights of BCG samples were much lower than those of the reference samples and decreased as a function of Ga$_2$O$_3$ content up to 1500 ppm.
8. CONCLUSIONS

High quality ZnO-based varistors were prepared by the mixed oxide route. The base composition was 97 mol% ZnO, 1.0 mol% Bi₂O₃, 1.0 mol% Sb₂O₃, 0.5 mol% MnO and 0.5 mol% Co₃O₄. The sintered products were typically more than 94% dense. They all exhibited nonlinear current-voltage characteristics, with non-linear coefficients in the range 5 – 53. The nonlinear coefficient was a very good parameter for the primary assessment of degradation behaviour. Ageing processes play an important role in defining the life of varistors.

It was found that the selective removal of primary oxide components, such as Sb, Mn and Co differently affected the microstructure and electrical behaviour. The effects of additives can be summarised as follows:

(i) The absence of Sb₂O₃ affects all characteristics. Density decreases and grain size increases. Moreover the nonlinear coefficient and breakdown fields reduce, but the leakage currents increase. Furthermore these (BCS) varistor exhibit poor degradation characteristics, surviving only a few minutes.

(ii) The removal of Co₃O₄ tends to improve the varistor stability

(iii) The absence of MnO leads to a reduction of the nonlinear coefficient and the leakage current.

This means Sb has significantly more influence than Co and Mn on the properties of ZnO varistor, since the spinel phase did not form in the BCS varistors.

The effect of two different powder milling processes was investigated in Chapter 5. It was found that particle size of powder prepared by attrition milling (0.3 µm) was smaller than that of powder prepared by conventional milling (3 µm). Moreover, attrition milling enabled the preparation of pellets of higher densities than those prepared by conventional milling. The study of phase development showed that α-Bi₂O₃ was still present at 700°C for the CMBC samples prepared by the continuous heating method. In contrast for the AMBC samples prepared using stepwise heating method, the
spinel phase and the β-Bi₂O₃ were found from 700°C and 900°C, respectively. The conventional milling yields the varistors with higher nonlinear coefficients and lower leakage currents. In contrast attrition milling produces varistors with higher breakdown fields because of a smaller grain sizes in AMBC samples. The samples prepared by conventional milling are more stable than those prepared by the attrition milling at low sintering temperature (950°C). However, for higher sintering temperature (≥1150°C) the samples prepared by conventional milling are more degraded than those prepared by the attrition milling.

Doping the base composition with monovalent (Ag⁺) and trivalent (Al³⁺) showed that Ag improved the stability of the ZnO varistors but reduced the nonlinearity, whilst the addition of Al improved the nonlinearity but encourages ageing. The addition of combined Al and Ag enhances both the nonlinearity and stability. From C-V results, it was found that Ag acts as the acceptor whilst Al acts as a donor because of generating lower and higher donor densities respectively than the reference material.

The addition of gallium oxide to the base composition retarded grain growth resulting in a reduction of average grain sizes for the BCG varistors. Ga acts as a donor up to the 1500 ppm Ga₂O₃ level. At 2000 ppm Ga₂O₃ there appears to be a transition from donor to acceptor behaviour since the I-V characteristics move towards lower current densities. The nonlinear coefficients of BCG series varistors are lower than those of reference sample possibly due to the displacement of I-V characteristics of BCG. Ga-doping caused an increase in both the breakdown field and the leakage current. The C-V results confirmed the transition from donor to acceptor behaviour.
RECOMMENDATIONS FOR FURTHER WORK

As the grain size has a dramatic effect on varistor properties, routes should be explored to produce varistors of smaller size. This could include chemical methods to prepare the powders, and the use of very short sintering times such as by Spark Plasma Sintering. In addition more work on attrition milled powders should be undertaken as they appear to offer advantages over conventionally processed powders.

Since varistors are grain-boundary controlled devices, the compositional and microstructural variations near to grain boundaries should be investigated in by high resolution electron microscopy, including TEM EDX.

As trap states in varistors are known to control many important electrical properties, including degradation of the barriers, then the initial work on C-V characteristics for Al-Ag doped materials should be extended to include an investigation of trap states in barrier depletion regions by the deep level transient spectroscopy (DLTS).
9. REFERENCES


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