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Conventional Sintering Effects on the Microstructure and Electrical Characteristics of Low-Voltage Ceramic Varistor

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Abstract

Conventional, free or pressure less sintering is the simplest technique which involves heating of a powder compact, previously prepared at ambient temperatures, without applying any external pressure. It can be conducted with various box furnaces or tube furnaces under different atmospheres (oxidizing, reducing, inert, and vacuum). Through the use of this method, a highly applicable varistor can be mass produced. Varistors are of a particular interest for modern surge protection of over-voltage. Nowadays, ZnO ceramic varistors are most favorable in electronic industry due to their excellent electrical characteristics and high energy handling capabilities. By optimizing the method during sintering process, the number of potential barriers formed can be controlled thus improving the capability of the low-voltage varistor.

Keywords: conventional sintering, microstructure, electrical properties, low-voltage varistors

1. Introduction

Sintering or firing of ceramic materials is the heat treatment to provide the energy to the ceramic powder particle to bond together to remove the porosity exist from compaction

stages. The sintering process involves strengthening of powder compact by heating to a high temperature. During sintering process, the ceramic powders of the separate particles disperse to the neighboring powder particles. The sintering process reduces the surface energy of the particles by decreasing their vapor-solid interfaces. The pores take places in the disc/pellet where it diminishes, resulting in densification of the compact ceramic powders, and increases its mechanical properties. The porosity will be decrease from the effect of sintering temperature and time. Sintering will be improved if a liquid phase takes part in the process and a long time and high temperature are needed for the dispersion happens in solid state.

Sintering can result in high-strength bonds, particularly in ceramic materials with a crystalline structure. Sintering is the final step in the ceramic fabrication process where it will provide ceramic powders with density. The sintering operation is carried out in many stages such as heating up, annealing at specified temperature and cooling. The atmosphere, temperature and duration need to be chosen carefully for ceramic materials in order to provide a ceramic material with particular characteristics. The required characteristics of ceramic material are needed to design processing methods that will provide this required properties. The aim of sintering process is to increase the mechanical strength of the material and to prevent deformation and cracking of samples. Sintering of ceramic powder compacts will undergo several significant changes including chemical reactions in the solid state such as decomposition, oxidation and phase transformations. The sintering proceeds in different ways for different ceramic materials to provide densification of ceramic powder compact to improve the properties of the material [1].

Fabrication of varistor ceramics is normally achieved via conventional solid-state ceramic fabrication method by applying sintering temperature. Varistor is a solid state electronic ceramic component used to protect electronic devices against overvoltage surges. Varistor are of particular interest to modern surge protection, which commonly made from zinc oxide. The application of ZnO varistor as high or low-voltage varistors is related to the presence of potential barriers and improves their microstructure, which can be controlled during sintering [2]. The sintering temperature has a prominent effect on the electrical characteristics of varistor ceramics where the process will contribute to the formation of a multi-phase microstructure and promoting the formation of potential barriers and also gives rise to a distinctive microstructure of ZnO varistor ceramics [3, 4]. ZnO varistor ceramics with minor additions of other oxides exhibit nonlinear electrical characteristic and, therefore are widely used as varistors devices to protect electronic equipment against overvoltage [5]. Conventional preparation of varistors are preparing of powder by weighing, milling, mixing and spray drying the milled of different metal oxide materials. After that, for electrical characterization the powder is pressed into disc-shapes (pellets) form with predetermined thickness in order to obtain a desired application. Finally, the pressed powder, which is the green pellets, will be expose to heat treatment by using conventional sintering at different sintering temperature, time and atmosphere, in order to improve their microstructure and electrical properties for desired application and method.

The sintering temperature of ceramic compact powder will transforms into a dense body with varistor characteristics. The physical properties are mostly developed during sintering,

which involves the final densification of the ceramic material at high temperature. Sintering process of varistor ceramic was commonly achieved at three stages. At the first stages, a liquid phase is formed due to the dispersion and the homogeneous distribution of the dopants and contribute to the grain growth at the second stage. For the second stage at the end the of the process which is for in the beginning of the last stage, the grain growth, crystallization of the secondary and spinel phase, formation of the potential barriers, and retraction of the liquid phase from the two grain boundaries to the triple junctions are taking place [6]. The sintering process gives a microstructure with conductive ZnO grains and improves the grain boundaries with additive. The sintered varistor pellets was then silver paste for electrical characteristics. This processing method is still preferred in varistor industries due to their low cost of production, processing viability, only need basic instrumentation tools for preparation of varistors, reduce risks and hazards leads to the attraction of this processing method.

2. Tailoring the properties of grain and grain boundaries during the fabrication process

As one of the most widely used electronic tool in the world, designing and tailoring the microstructure of ceramic play a big role in determining their properties for a specific application. Nowadays, the usage of modern ceramic can be seen almost virtually in any modern devices. In fact, without the existence of ceramic, there would not be a \$2 trillion global industry today [7]. The only reason it manages to come this far is none other because of its capability to fit in various emergence of new products. Thus, researching and discovering a better method to tailor the properties of ceramic on the atomic level are of a great importance to future generation of technology. The focused of this topic will be dealing on the subject of tailoring the properties of grain and grain boundaries of ZnO ceramic varistor by reviewing previous related studies.

Zinc oxide is an interesting and useful material, which produces various applications such as optical devices, sensors, FET devices, SAW devices, and varistor by a few processing procedure. Between all of them, the effects of varistor with using zinc oxide have become interesting nowadays [8]. Zinc oxide based varistor (ZnO) is one of material electronic semiconductor ceramic that have properties high energy absorption which capable to defend electronic device from excess voltage flow that sent to the electronic components that will cause breakdown [9]. Commonly, sintered zinc oxide ceramics produce their own microstructure with numerous grains and grain boundaries. The microstructure unit consists of grain–grain and boundary–grain, which is 3-dimensional series and parallel connection and it is distributed into entire bulk. Pure zinc oxide will show a linear voltage (V)–current (I) connection that obey the Ohm’s Law [10]. However, the main features of ZnO possess the attribute of non-linear current-voltage (I-V) with a grain size suitable for enhancement to improve the breakdown voltage of a varistor. By decreasing the grain size below 10 μm the material become qualified to be applied in high voltage application while larger grain size ($>30 \mu\text{m}$) is fitting for low-voltage application [10].

There are several factors, which contribute to controlling specific desired microstructure properties of ZnO ceramic varistor such as the temperature of sintering, hold time, addition of impurities (dopant), and so on [11]. By selecting a suitable combination of these factors during the fabrication process will an acceptable result is produced. For this topic, tailoring the microstructure of ceramic through a conventional method will be discussed and explained. The fabrication of ceramic generally begins with ceramic powder is processed into a compact form and pass through a heat treatment (sintering) where the structure starts to significantly change [12]. Changes include phase transformation and chemical reaction such as oxidation and decomposition. In different term, sintering is a diffusional process that occurred when the temperature of the material is increase to half or three quarters of its melting temperature [13]. Frankly, sintering can be considered as one of the major step in developing a desired outcome of a ceramic since during this process the densification begins to take place. The step is crucial due to density affect desirable properties such as dielectric constant and mechanical strength [14]. Detailed explanation on densification will be further explained later in the subtopic.

2.1. Process of powder through solid-state route

Necessity to understand the importance of an appropriate techniques in the powder preparation is derived from a fact that the step will determine the outcome properties of the finished product. The process usually begins by setting a specific ratio of chemical composition without any presence of impurities with smallest grain size possible. By selecting a smaller and better developed material, the capability of the powder to produce a desired microstructure will significantly increase. Several studies have suggested the method of applying particle growth technique as well as disintegrating the grained materials as means to create smaller size powder [15]. However, such technique mostly required the researcher to spend large amount of money to obtained specific equipment with no real capability for mass production.

Previously, a technique consisting of ball mills are generally selected to fulfill the role of crushing the powder into fine form. Not only the technique is easier to operate, but the mechanism is also relatively simple. Moreover, it has wider control on the powder distribution by choosing a proper size and shape of the mill balls [16]. Nowadays, with the advance of technology the technique has been further develop and a better technique known as high energy ball milling has been introduced. The new technique is more adaptable and able to deal with lower particle size unlike the previous version where it can only function up till the micron size particle. By constantly colliding the particles of powder with the mill balls and bowl will result in mechanical energy, which promotes the phase reaction among the reactant reducing the size of particles to the size of nano. The use of the technique will also ensure the mixed oxide powder are evenly and homogenously mix up. Reportedly, the usage of high energy ball milling is a promising approach for the starting mixture of powder in the varistor ceramic preparation [17].

The mixed powder will later undergo calcination process where the materials are subjected to high temperature for the purpose of removing humidity and gases [18]. Due to

its function of dispelling unwanted composition, sometimes the process is also called as a purification process. The process will begin by increasing the temperature inside the furnace slowly until it reached the designated values usually above 500°C and below 900°C in an average spent of 2 hours [19]. After the heating process is finished, the inside furnace is cooled down slowly and turned off at specific temperature. Point to be noted is the temperature used in this step does not exceed the value of sintering temperature of the later procedure.

The process will then proceed with remilling the mixed powder while adding binder for the purpose of increasing the mechanical strength of green ceramic body. Binder such as polyvinyl alcohol (PVA) are commonly added in a small quantity and mix together using mortar and pestle [20]. There is supposedly an ideal method suggested i.e. through the use of spray-dry system. However, the disadvantages are it requires longer time, difficult to clean the mobile parts and mostly applied for a large amount of mixed powder. Thus, using agate-mortar is not only simpler but also proves to be fully functional. Selecting a suitable binder is also a key in producing a good pellet with adequate electrical properties. A good binder must yield high density and high fired strength, which are essential to increase the electrical properties of the ceramic varistor [21]. PVA is extensively chose in various study mainly due to its high affinity for adsorption reaction when reacts with dispersed oxide particle in water.

The following procedure is pressing where the finalized mixed powder is pressed under a high pressure forming a pellet or disk. The thickness of pellet depends upon the application to be tested. If for the purpose of producing an applicable low voltage ceramic varistor, the thickness is under 1.5 mm while above is for high voltage application. After the pellet is formed, then it will be sintered with the goal of converting a compact porous powder into a well-structured grain form possessing the desired mechanical and electrical properties. The optimum range of temperature used in the process is still debatable since many studies revealed different result when testing different substance under different temperature. But, the range of the best temperature generally falls between 800 and 1200°C [4, 22]. The sintering procedure sometimes continue to pre-sintering step where the products are once again sintered under the same condition due to the previous step unable to produce the desired grain structure or have some defects. By repeating the process, the structure will be further enhance result in superior mechanical and macro properties.

Conventional sintering technique can be considered as one of the commercially accepted method presently. Although there are other better methods such as sol-gel, hydrothermal and co-precipitation but this method is much more simple, faster and easier to use while ensuring a decent quality output.

2.2. Microstructure and electrical properties

Microstructure is defined as structure of material that is extremely small in size. The structure of material can only be observed by using 25× magnification of microscope. The importance of understanding the microstructure lies in its capability to affect physical properties of material,

which is metals, ceramics and composite and also polymers. Such physical properties include strength, toughness, ductility, corrosion resistance, temperature behavior, and hardness or wear resistance [23]. Moreover, it is important to carefully decide the scale of magnification during conducting observation on microstructure since the characteristic of material microstructural may have a huge distinct when observed from various length scales. In ZnO-based varistor, the microstructure refers to the grain and grain boundaries.

Nowadays, all of the electrical and electronic devices have varistor's help. ZnO-based varistor is usually used due to its ability to surge protection from overvoltage current. This is because, ZnO provide an electrostatic potential that act as a barrier between the grains in the sintered body of an electronic tools. Generally, the production of ZnO based varistor is prepared by the addition of additive, which is needed to improve the efficiency varistor for further application [12]. Through the sintering process, ZnO based varistor will form a polycrystalline structure that consist of semiconductor ZnO grains after sintering process [9].

Typically, ZnO is a material that controlled by grain boundaries. It is expected that the properties of the samples will be modified due to the many defect present. Microstructurally, the doped-ZnO samples consist of a very high conductive n-type ZnO grains that is surrounded by an electrically insulating regions of grain boundary. Increasing the sintering temperature up to limited temperature will cause the average size of grain gradually increased. This will reduce the discontinuity between the grains that happen when the microstructure became more compact with less grain boundaries. Due to the increasing of sintering temperature, larger driving forces for internal atomic diffusion enhance the grain growth and pore elimination [5].

In general, the structure of the grains, grain boundaries morphology, density and also distribution of second phase are some of the factors influenced the electrical properties of ZnO such nonlinear coefficient (α), breakdown field (E_b), leakage current density (J_L), and barrier height (ϕ_b) [11, 24]. The mechanical, magnetic piezoelectric and electrical properties of ceramic also will improve if the grain size is smaller which also can help to enhance the application of ceramics [5]. The parameter of the sintering process such as temperature and hold time is really important in getting grain structure. In order to form ceramic with good varistor characteristic, a homogeneous distribution of dopant and correct concentration of oxygen is necessary, as the conductivity of zinc oxide depends on oxygen defect in the structure [11]. Methods that involve during sintering process are important to investigate in order to achieve the solids microstructure and final properties [25].

2.3. Densification

Density is defined as the amount of substance that occupies a defined volume at stated pressure and temperature. In the production of ceramic varistor, density is one of the essential component, which requires a special concern. Without a good control on the development of density, the material will not be able to achieved its desired performance [25]. If we take a look generally on the densification step occurred during sintering, the process can be considered to be divided in three stages i.e. initial, intermediate and final stage. During the first stage, when the particles of powder are exposed to sintering force it begins to rotate and slide into a stable

arrangement. The movement of the particle will cause the microstructure to shrink contributing to the overall increase in the density. Moreover, the stage also leads the particles to form necks between one another as shown in **Figure 1** as the interparticle contact is increased. The first stage is assumed to finish when the extent of neck growth of particle reach to 0.4 and 0.5 of its total radius.

The intermediate stage starts immediately right after the end of the first when the pores of the powder have achieved their equilibrium configuration. Although the particles have begun to develop at this point, the overall density is still low with the pores are mostly linked to one another. Thus, in the second stage the densification will cause the length of cross section between the pores to significantly reduce which eventually result in the pores develop into an unstable state and break away. The second stage can in fact be regards as the major stage out of the three. With the particles are fully individualize, the final stage will take place. At this section, the sintering process generally covers the elimination of isolated pores present in the powder increasing the total density to its theoretical value. Furthermore, the growth of grains is also reach its crucial step at this point where larger grains will exponentially increase by sacrificing smaller grains [27].

The importance of densifying the green bodies of ceramic varistor lies in the formation of continues 3D structure for further selected application. The mechanisms, which are generally responsible for densification, are migration of grain boundaries and diffusion of grain boundaries where the first oversee the last stage of the whole sintering process. Migration of grain boundary refers to the movement of boundary, which separates different grain body through diffusion of atoms from one body to another. Several factors act as the driving force impacting the movement such as strain and elastic energy. The second mechanism of grain boundary diffusion will further densify the ceramic varistor until it reaches highest density capable by the mixed materials [28].

Additionally, the whole densification process can also be seen in three different scales i.e. global, microstructure and atomic scale. Through global scale it shows the densification process which occurred because of surface energy minimization which leads to grain boundaries replacing solid–gas interface. The second scale of microstructure focused on the differences in pressure and concentration gradient due to the presence of vacancies that act as a driving force for the transfer of mass. Finally, the atomic scale reveals the condition of all atoms either in a convex or concave surfaces where there is higher concentration of atoms on the surface of

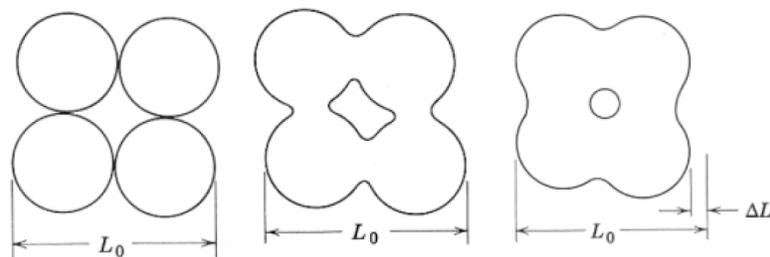


Figure 1. Diagrammatic depiction of (a) powder compact, (b) partial densification of neck growth and (c) fully densified neck growth [26].

concave than convex. The movement on this scale can be seen as a flow of atom from higher place (higher concentration) to the lower region with the upper region having more energy and mobility [29].

Up to date, several researches have shown the relationship between sintering temperature and how it affects the densification of ceramic varistor. Such example includes decreasing in sintering temperature cause an increase in pores, which directly decrease the density and vice versa [8, 30, 31]. The truth is each material has its own properties that cause this kind of situation to happen. Thus, for every material present and included in the production of ceramic varistor it requires an elaborate investigation to determine their specific characteristics before any conclusion can be made.

2.4. Sintering technology

Sintering is the densification of powder compact with the help of thermal treatment. It is also the key for processing the ceramic and powder metallurgical [32]. Sintering can be divided by two categories, which is conventional sintering and advanced sintering. Advanced sintering included spark plasma sintering (SPS), hot pressing sintering and microwave sintering. Unfortunately, some of the technique produce different final product that might not help the economy due to it possessing a non-viable property. Thus, the conventional method is considered to be more appealing for the purpose of mass producing ceramic product since it has lower cost maintenance. For conventional method, minimum grain growth can be controlled by maximization the last density that determine by the heating curve. By controlling the procedure of the heating curve, high densification of grain size can be controlled [25].

2.4.1. Conventional sintering

Conventional sintering technology is the simplest form in sintering that also known as pressureless sintering. It only involves heating of the powder compact after prepared at ambient temperatures without any external pressure applied during the process. Nanostructured ceramic materials that have dense properties normally acquire nanopowder that have undergo pressing process, which is done through a pressure assisting method. The pressure assisted method includes hot pressing, sinter forging, hot isostatic pressing, and others [33]. Hot pressing technique can also use to produce the mixture of two or more types of metals powder base product that can be improved the mechanical properties. When using the hot pressing method, some of the ceramic materials are found to be densified even at lower temperature when compared to conventional method. The benefits in using hot pressing sintering technique are firstly improving the densification kinetic and limited of grain development, where disadvantages are the end product have limited geometry and equipment needed highly in cost [34].

2.4.2. Microwave sintering

Generally, it has been 3 decades since the microwave sintering of ceramics have been introduced. Respectively, it has some superiority, which is fast processing and heating selective.

Furthermore, the processed materials are mostly enhanced via inhibition of the grain for it to develop while reducing the processing time and energy required to complete the process. The application of microwave technology is not really something new in the field of processing and material science. Its applications are actually widely applied in various field such as calcination, drying of ceramic and decomposition of gaseous species. Processing materials it is only limited to only 2000 ceramics with the use of microwave, polymeric materials, semiconductors and inorganic. The advantages of this sintering technique are great microstructure control, improved the material mechanical properties, the product have no limit geometry and reduce the manufacturing cost due to low temperature, energy used and processing time. Microwave sintered sample also reported that hardly reveal any development and cobalt does not exhibit any dissolution of tungsten while there are nearly 20% dissolved in cobalt binder phase in the conventional sintering. The researcher also found that sample that sintered in microwave always showed improvement in mechanical properties compared to the conventional sintered one [34].

2.4.3. Spark plasma sintering

Spark Plasma Sintering or in a more complex Pulsed Electric Current Sintering (PECS) is a new technology in the field of metals, ceramics and composite fabrication starting from powders. With the nanostructured features, it has the potential of densifying powders while avoid it become rough which follow the densification routes [34]. This spark plasma sintering mechanism has been investigated in the 1960s and began to be used in metal powder compressed. But there is no wider use of it since the price of the equipment are very expensive coupled with inferior efficiency in sintering. To heat the specimens, the use of pulsed direct current is commonly used in these systems. SPS consist of several parts of uniaxial pressure machine where the water-cooled punches also work as electrodes, a pulsed DC generator a water cooled reaction chamber, position, pressure and temperature regulation system. The relatively low homogenous temperature and short duration required for this technique because it is really suitable for the preservation and nanocrystalline densification feature in the ceramics material. Nowadays SPS is widely used due to the possibility in performing a fast consolidation of ceramic that tough to sinter and composite ceramics during decreased temperature [33].

3. Low-voltage ZnO-based varistor

Zinc oxide (ZnO) ceramic materials are commonly used for overvoltage protection in electronic industry. ZnO varistor ceramic is nonlinear electrical component and high energy handling capabilities. Low-voltage varistor are now highly demand for surge protection in electronic devices with fast response, highly nonlinear current-voltage properties and energy absorption capabilities. The performance of low-voltage ZnO varistors can be improve by increasing the grain size, which allows the decreased grain boundary per unit volume and improves the nonlinear electrical characteristics. Low-voltage varistors are improved when their thickness is decrease to increase the size of ZnO grains. However the strength and energy absorption

capabilities of the thin ZnO varistor are very poor due to its small volume [35]. In addition to grains size and the additives, sintering temperature is an important parameter in the manufacture process of varistor-based ceramics. Low-voltage ZnO varistors are now being used for surge protection in integrated circuits and in automobiles. The electrical properties of low-voltage ZnO varistors are based on their composition and microstructure. Optimizing the process, the composition and microstructure of conventional varistors are used to achieve low-voltage varistor. Therefore, it is important to find a new method to fabricate high performance varistors without reducing their thickness.

In low-voltage ZnO varistors, the most influence additives are titanium oxide (TiO_2) which can greatly improve the grain growth of ZnO, thus is commonly used as a grain growth enhancing additive to produce low-voltage ZnO varistors. But, the doping of TiO_2 reduces the degree of nonlinearity [36]. The degree of nonlinearity (α) is used to explain the characteristics of varistor ceramics with excellent surge withstanding capabilities. The coefficient α is the measure of efficiency of the device, the higher its values the more is the effectiveness of device in protecting a circuit from overvoltage [37]. The nonlinearity strongly depends on the microstructure and directly affects their electrical properties that can be adjusted by the means of sintering process. The performance of microstructure and electrical characteristics of varistor ceramic can be improve by adding additives by thermal treatment. A unique properties of grain boundaries is formed in the ceramics during sintering and they are responsible for determining the nonlinear electrical characteristics of varistor component. The chemical composition, sintering temperature, sintering time, heating and cooling rates are variables that can be adjust fundamentally to control the electrical performance of ZnO varistors [38].

The sintering temperature reaction between ZnO and additives lead to the formation of different phases in the ZnO grain boundary and the nonlinear properties are ascribe to the formation of potential barriers at the ZnO grain boundaries. The performance of ZnO-based components is sensitive to the presence of additive even though their amount is very small and the processing environment has significant effect on the microstructure of varistor ceramics. Development of specific microstructure at varying sintering condition in ZnO based varistor ceramics will determine its electrical characteristics especially at varistor voltage of the ceramic device, since it is directly related to the grain size and grain boundary of ZnO varistor ceramics. Therefore, the temperature at which these reactions take place will lead to different grain sizes, and different electrical properties will be obtained when fabricating the varistor device [39]. Industrially, varistor manufacturing is commonly by the conventional solid-state preparation method and ZnO varistors were manufactured through a high-temperature reaction called sintering. A dense varistor product was normally obtained through the sintering process, since the varistor performance depends on the final sintered microstructures, the sintering process must be carefully carried out. For sintering, the varistor powder needs to be hard-pressed to ceramic discs/pellets and should be heated at a temperature in the range of 1100–1250°C [40, 41]. The improvement of ZnO varistor with excellent electrical properties and high energy handling capability can be obtain through grain size control by using nanosize-doped ZnO powder and manage the excess of grain growth by step sintering process.

3.1. Barium titanate and calcium manganite as additive

A new processing technique in the production of low-voltage ZnO varistor are now being investigated for overvoltage protection in low-voltage electronic due to highly demand. The breakdown voltage (varistor voltage) is directly proportional to the number of ZnO grains in series between the electrodes, therefore, it can be achieve by decreasing the thickness of the disc/pellet or increase the size of ZnO grains. However, the thin ZnO varistor are weak, thus by using additives or improve their processing technique are important to optimize the performance of low-voltage varistor ceramics. In low-voltage varistor, a grain growth-enhancer titanium oxide (TiO_2) is mostly used and can influence the degree of non-linearity of conduction. As barium titanate (BaTiO_3) consist of TiO_2 , its addition can attribute to the formation of grain growth [42]. BaTiO_3 is one of the members of perovskite (ABO_3) family that has wide applications in electronic industry. Doping with BaTiO_3 on ZnO based varistor ceramics has significant effect due to the rich variety of physical properties such as high-temperature superconductivity and colossal magnetoresistance observed in these compounds makes them very attractive from both fundamental and applied perspectives.

Perovskite oxides have attracted much attention due to their structure properties formed by substitution make it outstanding functional materials which is exhibit various properties and one of the important usages of perovskite oxides is in the capacitor application because of their excellent dielectric properties [43]. The combination of varistor-capacitor characteristics makes it a promising material in the field of overvoltage protection of electronic devices. The presence of large BaTiO_3 grains on the ZnO microstructures will greatly improve the electrical properties of the varistor since BaTiO_3 as the doping of ZnO based varistor possess the ability to control the microstructural development of the ceramic. According to previous research reveals that the heavily ZnO doping on the BaTiO_3 ceramic are very interesting for the purpose of capacitor-varistor integration [44]. BaTiO_3 is a prototypical ferroelectric material with a tetragonal distortion characteristic of the cubic perovskite structure. The ferroelectric distortion is facilitated by the large size of the Ba cation. Barium titanate is a good candidate for a variety of applications due to its excellent dielectric, ferroelectric, and piezoelectric properties [45]. It is extensively used in the electronic industry as capacitor and positive temperature coefficient of resistivity (PTCR) sensors.

The used of calcium manganite (CaMnO_3) as additive material to produce low-voltage varistor is extensively studied due to their unique properties that make them attractive in enhancing the performance of the existing materials. Perovskite manganite AMnO_3 , where A is an alkaline earth metal such as Ca, Sr, Ba and Pb, has been the subject of intense research during the last decade and it has a significant effect on the microstructure of ZnO varistor ceramics [4]. In addition, the varistors prepared from ZnO with CaMnO_3 perovskite as the only forming additive, exhibit voltage-limiting electrical properties while the combination of perovskite structure CaMnO_3 with the microstructure of ZnO varistor ceramics is simple consisting of only ZnO grain and CaMnO_3 as intergranular layer [46].

Additive of CaMnO_3 on the microstructure of ZnO varistor ceramics shows a good properties in order to produce low-voltage varistors. The combination of ZnO with perovskite manganite gives multifunctional properties for low-voltage electrical characteristics with large

nonlinear coefficients, which is suitable for semiconductor electronic and magnetoelectric devices due to magnetotransport properties of polycrystalline multi-phase ceramic [47]. The influence of perovskite CaMnO_3 as the only additives in the microstructure of ZnO varistor ceramics shows a significant effect on the electrical characteristics of low-voltage ZnO based varistor and with the new formulation for low-voltage ceramic varistor containing CaMnO_3 as varistor former in spinel phase and doping elements of rare-earth also shows a potential to be used as doping low-voltage varistor [48]. The new generation of varistor that introduced perovskite as additive and as varistor former, make this device less use of additives as compared to first generation, which is use bismuth oxide as a varistor former [49–52].

3.2. Effects of ZnO + perovskite on the development of microstructure

The further improvement of the electrical characteristics is associated to the ability to control the microstructural development in the ceramic materials. The used of barium titanate (BaTiO_3) as an additive on the microstructure and grain growth in the ZnO varistor ceramics shows a significant effect, where it contains titanium oxide (TiO_2) which has mostly used as grain growth enhancer and can influence the nonlinear coefficient of varistor. BaTiO_3 is a ceramic material with a characteristic of the cubic perovskite structure and facilitated by the large size of the Ba cation. The displacement of atoms in BaTiO_3 as a function of an external electric field will induce to a nonlinear behavior. ZnO- BaTiO_3 -based varistor ceramic sintered at 1300°C enhances their grain size and improves microstructural uniformity. The microstructure consists of two phase which is ZnO grain (primary phase) and inter-granular phase with concentration of BaTiO_3 solid solution in the ZnO grain boundaries. The BaTiO_3 as additive increase the grain size of ZnO compared to the sample without BaTiO_3 at the same sintering temperature. From the microstructure, the ZnO grains reveal high concentration of additives with BaTiO_3 element. The distribution of the chemical elements is homogeneous except near the grain boundaries where the solid solutions are located. The inhomogeneity is characterized by a strong concentration in the grain boundaries, which contain of excess BaTiO_3 in ZnO microstructure. The secondary phase is located near triple-grain junctions and nodal points in the grain boundaries with the high concentration of the additives. The competition between dissolution and segregation of the BaTiO_3 into the grain boundaries of ZnO are present and this chemical and physical reaction depends on the sintering temperature and amount of concentration between them. From **Figure 2**, the microstructure of ZnO doped with BaTiO_3 is shown to be larger as the sintering temperature is increase from 900 to 1300°C .

Additive of calcium manganite (CaMnO_3) on the ZnO based varistor reveals the presence of ZnO as dominant in the microstructure and the secondary phase formed at the grain boundaries and also at the triple point junction which consist of CaMnO_3 as varistor former for grain growth. The ionic radii of Mn^{2+} is larger than ZnO^{2+} ions, therefore, it segregated at the grain boundaries as secondary phases. However this phase reduces when the sintering temperature was increased to 1300°C due to the reactive melting of CaMnO_3 . The non-uniformity of the grain structure of ZnO- CaMnO_3 based varistor ceramics are reduce when the sintering temperature are increase which a uniform grains are present and free from abnormal grain growth by doping of CaMnO_3 as an additive. ZnO ceramics doped with perovskite phase of

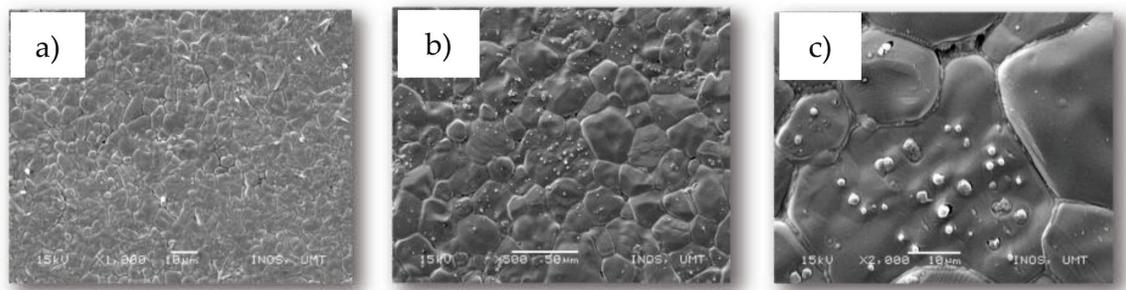


Figure 2. SEM micrographs of ZnO-BaTiO₃ at sintering temperature in (a) 900°C, (b) 1100°C and (c) 1300°C.

CaMnO₃ as the additive improves the microstructure with the support of sintering process. The sintering temperature influences the microstructure of ZnO-CaMnO₃ by segregate of CaMnO₃ dopants at grain boundaries with the increase in sintering temperature.

3.3. Effects of ZnO + perovskite on the electrical properties

The incorporation of large barium titanate (BaTiO₃) grains on the ZnO microstructures will greatly improve the electrical properties of the varistor since BaTiO₃ as the doping of ZnO based varistor possess the ability to control the microstructural development of the ceramic. The effect of BaTiO₃ on the electrical properties can be seen clearly with the increase of BaTiO₃ content as the additive and the varistor voltage increase significantly with BaTiO₃. The varistor voltage is enhanced with the increase of the number of active grain boundaries because of the decrease of ZnO grain size with increasing of BaTiO₃ percentage. It is well known that titanium oxide (TiO₂) are commonly used to produce low-voltage varistor, since BaTiO₃ consist of TiO₂ it will increase the grain size but restrict the nonlinear properties. When the grain size are increase it lowering the varistor voltage with the increase in of BaTiO₃ concentration at the grain boundaries. The present of TiO₂ in the perovskite structure BaTiO₃ act in inverse since nonlinear coefficient (α) increases with the addition of BaTiO₃. The varistor sintered at 1300°C decreases the varistor voltage due to the homogeneous microstructure of grain boundaries and increasing the grain size compared to varistor sintered at temperature 1250°C that possess high varistor voltage. The breakdown voltage of current-voltage characteristics for ZnO varistor is much better with BaTiO₃. For low-voltage ZnO varistors it can be improve by increasing the grain size, which allows the decreased grain boundary per unit volume and improves the nonlinear electrical characteristics. The addition of perovskite structure BaTiO₃ is attribute to the formation of potential barriers at the grain boundaries where the large grain size of BaTiO₃ will greatly increase the grain size and the present of Barium will contribute to the increase in nonlinearity of ZnO varistor, since it more dominant in comparison with the effect of titanium oxide. The used of BaTiO₃ as an additive for grain growth will produce a suitable range of varistor voltage with the conventional sintering technology in order to produce low-voltage varistor.

In addition, the perovskite manganite CaMnO₃ as an additive changes the breakdown voltage of the ZnO varistor system. It presents a good electrical properties for low-voltage varistor

with large nonlinearity coefficients [47] and surpasses the results as reported by using ZnO-Bi₂O₃ based and ZnO-Pr₆O₁₁ based varistor [53, 54]. The low-voltage nonlinearity originates as a result of higher concentration of manganese present at the grain boundary layer regions, being charge compensated by zinc vacancies [47]. The effect of sintering temperature on microstructure and electrical properties of low voltage varistor ceramics fabricated from a mixture of ZnO with CaMnO₃ perovskite gives a broad idea to researcher for their further research on production of low-voltage varistor [55]. The effect sintering temperature at certain composition of this additives can exhibit a voltage-limiting in the electrical properties of ZnO varistor. The varistor sintered at 1200°C provided low varistor voltage per thickness of the ZnO ceramics for low voltage varistor [4].

4. Overview

The preceding chapter in this book has presented the best available knowledge the conventional sintering effects as a driving force on the microstructure and electrical characteristics of low-voltage ceramic varistor. The aim of this chapter is to provide sufficient knowledge related to sintering technology that has been used for ceramic varistors fabrication industry. Almost the past century there has been a discovery of ceramic varistors and a few decade later, a varistor with simple formulation of ZnO-Bi₂O₃ based varistor was successfully fabricated in industries and start from that, varistor have been growing, whereas, ZnO-perovskite introduced. At the heart of this magnificent semiconductor device is the sintering technology—a way of heat treatment to make the ceramic varistor become compacted and less porosity.

The methodology in this chapter present low-voltage ZnO based varistor and its additives. The discussion part elaborates the recent studies related to microstructure and electrical properties of ZnO-perovskite based varistor as compared in citation to first generation and second generation, which are ZnO-Bi₂O₃ based and ZnO-Pr₆O₁₁ based varistor; respectively. The discussion concludes with driving force through sintering process in solid-state route, the desired low voltage ZnO-Bi₂O₃ and ZnO-perovskite based varistor with favorable nonlinearity coefficient, α , is successfully fabricated.

5. Conclusion

The effects of conventional sintering on the microstructure and electrical properties of low-voltage ceramic varistor in this chapter are describe based on their useful properties which are determined by their properties of grain and grain boundaries during the fabrication process. The processing technique through solid-state route shows a significant effect with sintering process in the microstructural development of ZnO varistor ceramics. The densification of sintered ceramic varistor can be controlled by using different sintering technology in order to improve their microstructure and electrical properties especially for production of low-voltage varistor. It was also determined that a steady increase in sintering temperature and time until certain limitations results in larger size of grains which in turn will decrease the grain

boundary per unit volume improving the nonlinear parameters. Moreover, the low-voltage ZnO varistor ceramics can be improved by using suitable additives such as Barium Titanate and Calcium Manganite since it exhibits perovskite structure where these materials possess the ability to control the microstructure development during sintering process.

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