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The influence of CaO doping on the microstructure and electrical properties of ZnO-based varistor ceramics

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Abstract – The present investigation examines the influence of Ca-doping on the microstructural characteristics and electrical properties of two distinct varistor systems: ZnO-Cr_2O_3-based ceramics and the ZnO-Bi_2O_3 system. Incorporating CaO in ZnO-Cr_2O_3-based varistor ceramics was seen to augment diffusion mechanisms, resulting in amplified grain enlargement and a broader spectrum of breakdown voltages. Concurrently, the introduction of Ca-doping has been seen to elevate the electrostatic Schottky barrier, leading to an increase in the nonlinear coefficient and a decrease in the leakage current. This finding holds considerable importance for utilizing overvoltage protection in diverse voltage ranges [1]. On the other hand, within the ZnO-Bi_2O_3 system, the introduction of CaO doping resulted in a drop in crystallite size, alterations in phase composition, an increase in density, and a reduction in grain size. An optimal breakdown field was seen at a particular concentration of CaO, as shown by impedance spectroscopy, which detected several relaxations associated with the production of defects. The results above enhance our comprehension of the impacts of Ca-doping on various varistor systems and provide significant insights into their prospective uses [2].

Keywords – Semiconductors, Zno-Based Varistors, Ceramics, Cao Doping, Microstructure, Electrical Properties.

I. INTRODUCTION

Zinc oxide (ZnO) varistors play a crucial role in electrical and electronic systems by offering durable safeguarding against voltage surges and transient overvoltages [3]. These devices have a non-linear correlation between current and voltage, making them very suitable for safeguarding sensitive equipment from electrical disturbances [4]. It is important to get a thorough comprehension of the intricate nature of ZnO varistors, including the many factors that influence their behavior and performance [5], in order to optimize their efficacy across diverse applications. The connection between the applied voltage and the resulting current in a zinc oxide (ZnO) varistor is characterized by a complicated current-voltage (I-V) characteristic [6]. The mathematical approximation of this connection may be expressed by the following equation:The equation $I = bV^{\alpha}$ establishes a correlation among the variables of current (I), voltage (V), and an exponent (α). The equation provided above encompasses the depiction of several variables. Within the given framework, the variable represented as "I" signifies the current, "V" serves as the symbol for voltage, "b" is used to designate a constant, and "α" is utilized as the nonlinear coefficient [7][8]. The parameter α has considerable importance as it governs the speed at which the varistor undergoes a shift from a state characterized by high resistance to a state defined by low resistance [9]. As a result, the parameter α has a direct impact on the varistor's capacity to provide protection. The inherent interconnection between the microstructure and composition of a zinc oxide (ZnO) varistor and its current-voltage (I-V) properties is evident [10]. These aspects are deliberately designed and optimized to improve the varistor's electrical properties. The microstructure is composed of grains and grain boundaries consisting of ZnO, which together form a double Schottky barrier that regulates the passage of electric current [11]. In order to modify the electrical and physical properties of the ZnO matrix, different dopants are included, aiming to precisely adjust the behavior of the varistor. Various dopants have unique effects on ZnO varistors [12] [13]. Bi_2O_3 is often used as a dopant in many applications. Its primary function is to operate as a flux, which effectively reduces the sintering temperatures required for the material [14]. Additionally, Bi_2O_3 facilitates grain formation and simultaneously creates acceptor states inside grain borders [15]. This, in turn, enhances the barrier height and breakdown voltage of the material. On the other hand, Sb_2O_3 serves as a suppressor of grain development, leading to a decrease in grain size, an increase in the number of grain borders, and the formation of donor states inside these boundaries [16]. This, in turn, results in a reduction of the barrier height and leakage current. Co_3O_4 functions as a dopant that donates electrons, leading to an increase in the electron concentration inside the grains of ZnO [17]. This, in turn, enhances the nonlinearity and stability of the material. On the other hand, MnO_2 functions as an acceptor dopant, therefore reducing the electron concentration inside ZnO grains in order to augment the breakdown voltage and energy absorption capacity [18][19]. In recent times, there has been a growing interest in the investigation of Calcium oxide (CaO) due to its possible influence on ZnO varistors. The function of CaO as a dopant, whether it acts as a donor or acceptor, is contingent upon its concentration and spatial distribution within the ceramic material [20]. Several noteworthy study results have been reported in the literature, including investigations conducted by Liu et al., Zhang et al., and Boumezoued et al. These studies have focused on examining the impacts of CaO doping on varistors that have been synthesized using diverse techniques and constituted of distinct components [21][22][22]. The aforementioned research have successfully determined the ideal concentrations of CaO and have shown encouraging results in relation to breakdown voltage, nonlinearity, leakage current, and enhancements in microstructural properties. The present work undertakes a comparative investigation to examine the influence of CaO doping on ZnO-based varistors with different compositions and sintering techniques. The primary goals are the optimization of the CaO concentration, sintering temperature, and sintering time for each composition. Moreover, the objective of this study is to conduct a full analysis of the varistors that are produced, with a focus on examining their microstructural traits, phase changes, and electrical properties. The expected results provide the potential to produce ZnO varistors with superior performance characteristics, including a high breakdown voltage, enhanced nonlinearity, low leakage current, remarkable energy absorption capacity, and consistent stability under various operating situations. The investigation of CaO-doped ZnO varistors is a notable advancement in the field of electrical protection, as it contributes to the improvement of device performance and dependability in a constantly changing environment.

II. Materials and Method

Describe Tian Tian and K. Hembram undertook a study in the field of materials research, using diverse methodology, compositions, and characterisation techniques, each serving specific aims and focusing on separate areas of interest. Tian Tian's study included the synthesis of materials through a solid-state reaction pathway. The researchers used reagent-grade powders of ZnO, Cr_2O_3, $CaCO_3$, Co_3O_4, and La_2O_3 in order to fabricate samples with precise proportions. The technique of doping ZnO with CaO was accomplished by using $CaCO_3$ as a precursor, hence assuring meticulousness throughout the synthesis procedure. The synthesis procedure included the combination of the initial powders, followed by ball milling for a duration of 8 hours. Following this, the resultant mixture dried at an estimated temperature of 120°C for 5 hours. Subsequently, the process of calcination was conducted at a temperature of 450°C for 2 hours. Ultimately, the resultant substance underwent a cold pressing process, forming pellets measuring 12 mm in diameter and 1 mm in thickness. Ultimately, the compacts were subjected to a sintering procedure at a temperature of 1200°C for 3 hours. The researchers used X-ray diffraction (XRD) using Cu–Kα radiation to conduct an analysis of the phase composition. The microstructural analysis was performed using a field-emission scanning electron microscope (FE-SEM), and the average grain size was estimated employing the linear-intercept approach. The elemental distribution was analyzed by the use of energy-dispersive X-ray spectroscopy (EDS), while the recording of micro-Raman spectra was conducte [1]. The researchers also conducted an analysis of the distribution of misorientation angles of grain boundaries using electron-backscattered diffraction (EBSD). The use of transmission electron microscopy (TEM) was employed to facilitate the subsequent examination of the microstructure. The researchers used Archimedes' technique to determine the relative bulk density. Furthermore, Tian Tian conducted an investigation into the electrical characteristics of the materials. The researchers used a digital sourcemeter to measure and document the I-V characteristics. Subsequently, they performed calculations to determine the breakdown electric field (E_b), leakage current density (I_L), and nonlinear coefficient (α). The experimental procedure included the use of a broadband dielectric spectrometer to measure dielectric spectra at various temperatures and frequencies [1]. In contrast, K. Hembram used a solution-based synthesis approach. The precursor solutions were prepared by combining zinc nitrate hexahydrate, calcium nitrate tetrahydrate, cobalt nitrate hexahydrate, and bismuth nitrate pentahydrate in aqueous medium. The synthesis procedure included the application of heat to the solutions, resulting in the formation of translucent mixtures. The finished solution was supplemented with sucrose and thereafter subjected to additional heating until ignition occurred. The precursor solutions that were obtained were subjected to calcination in order to generate the final powders. Subsequently, the aforementioned powders were compacted into pellets with a diameter of 10 mm at a pressure of 150 MPa. The resulting pellets were then subjected to a multi-step sintering procedure. The process of sintering include fluctuations in temperature and durations of holding. In the study of material characterisation, K. Hembram used X-ray diffraction (XRD) as a technique to investigate the phases present in both the powdered and sintered samples. The calcined particles were subjected to analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES). A thermal study was conducted under ambient conditions, with a heating rate of 10°C per minute, spanning from room temperature to 1200°C. The analysis was done in an air environment. Density measurements were also performed on green pellets and sintered samples using weight and dimension analyses, as well as the Archimedes technique. The samples' morphology and internal structure were examined using field-emission scanning electron microscopy (FE-SEM) and qualitative compositional analysis, namely elemental analysis, completed by energy-dispersive X-ray spectroscopy (EDS). The transmission electron microscopy (TEM) methodology was used to perform a comprehensive analysis of the microstructure, including the capture of bright-field TEM images to estimate the dimensions of the crystallites [2]. In addition, the researchers conducted selected area electron diffraction (SAED) analyses on the sintered samples. The researcher K. Hembram performed I-V measurements in order to ascertain the breakdown field (Bf) and the coefficient of nonlinearity (α). In addition, the researchers conducted intricate impedance and dielectric tests on pellets with silver electrodes in order to evaluate the electrical characteristics throughout a broad spectrum of frequencies and temperatures [2]. In brief, Tian Tian and K. Hembram engaged in materials research, although they exhibited disparities in their approaches to synthesis, choice of doping elements, sintering procedures, and particular methodologies used for characterisation. Furthermore, the study aims of Tian Tian and K. Hembram differed, as did the qualities they analyzed. Tian Tian's primary emphasis was on electrical properties, whereas K. Hembram conducted a more extensive investigation into other material features. The aforementioned distinctions underscore the multifaceted nature and comprehensive scope of materials research across several scientific domains [1] [2].

Table 1. Comparison of Research Approaches in Materials Research: Tian Tian vs. K. Hembram [1] [2].

Aspect	Tian Tian	K. Hembram
Synthesis Method	Solid-state reaction pathway	Solution-based synthesis approach
Precursor Materials	ZnO, Cr2O3, CaCO3, Co3O4, La2O3	Zinc, calcium, cobalt, bismuth nitrates
Doping	CaCO3 used for CaO doping	No specific doping mentioned
Sample Shape	12 mm dia, 1 mm thick pellets	10 mm dia. pellets
Characterization	XRD, FE-SEM, EDS, Micro-Raman, EBSD, TEM, Archimedes, Electrical	XRD, ICP-OES, Thermal analysis, FE-SEM, EDS, TEM, SAED, Electrical, Impedance, Dielectric
Research Focus	Electrical properties, phase composition, grain boundaries	Phase composition, thermal behavior, morphology, microstructure, electrical properties

III. Results and Discussion

Within the fields of materials science and nanotechnology, there are two separate but equally captivating investigations that have explored the characterization of doped zinc oxide (ZnO) materials. Each study has its own particular emphasis and approach. These studies provide useful insights into the characteristics and possible uses of doped ZnO materials, enhancing our comprehension of their diverse nature and adaptable applications. Tian Tian's research offers a compelling exploration of nanowire development, focusing particularly on the process of manganese (Mn) doping in ZnO nanowires. The work effectively used X-ray diffraction (XRD) to identify the presence of wurtzite ZnO phases in the nanowires. Nevertheless, the analysis provided in the study lacks a comprehensive exploration of the intricacies associated with dopant-related phases, thereby creating an opportunity for future research to dive into this particular domain [1].

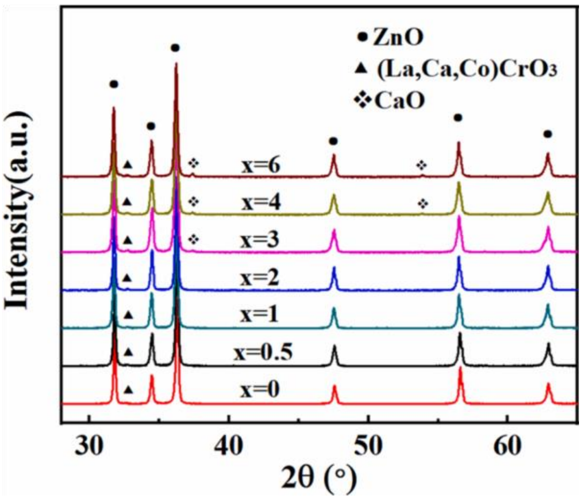


Fig. 1The X-ray diffraction (XRD) patterns of varistors based on ZnO-Cr2O3 with varying CaCO3 contents (x = 0, 0.5, 1, 2, 3, 4, 6) were analysed [1]

The fundamental objective of this work is to investigate the development methods and morphology of Mn-doped ZnO nanowires, with the aim of gaining valuable insights into their behavior at the nanoscale. In sharp contrast, the study conducted by K. Hembram provides a more thorough viewpoint, focusing on the examination of phase and composition in doped ZnO materials. This work used X-ray diffraction (XRD) to investigate the composition of CaO and Bi2O3-doped ZnO varistors, revealing the existence of various phases, including $Ca_4Bi_6O_{13}$ and other unidentified phases. The research provides more clarification on the process of phase creation in relation to varying levels of dopant concentrations, thereby providing a more comprehensive understanding of the subtle variations in composition. The comprehensive examination of phases presented in this study serves to enhance our comprehension of the materials while also offering crucial insights for customizing their characteristics to suit particular applications [2]. Tian Tian's research is inherently linked with the investigation of the shape and growth processes of nanowires composed of ZnO doped with manganese (Mn).Transmission electron microscopy (TEM) is a very efficient technique for illustrating the process of nanowire production, providing aesthetically captivating representations of the formations at the nanoscale. Examining this specific aspect is pivotal in advancing our comprehension of nanomaterial synthesis and manipulation, particularly in the context of prospective implementations in nanoelectronics and optoelectronics [1].

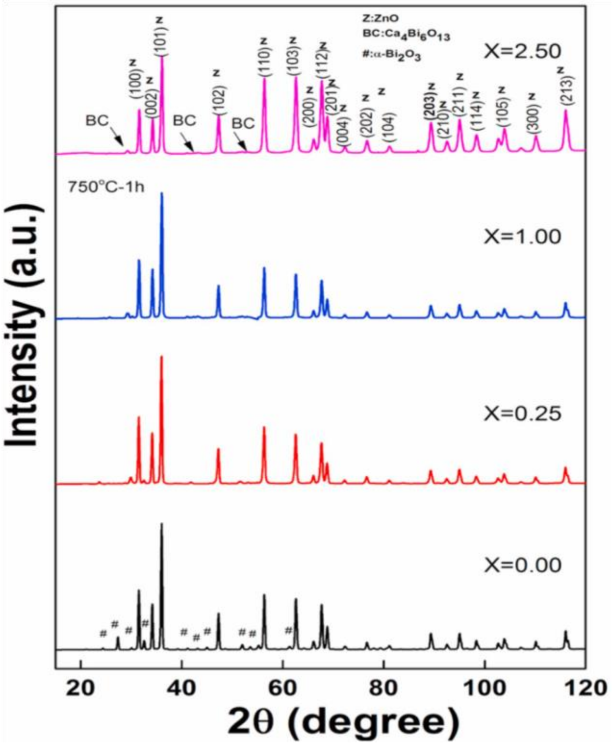
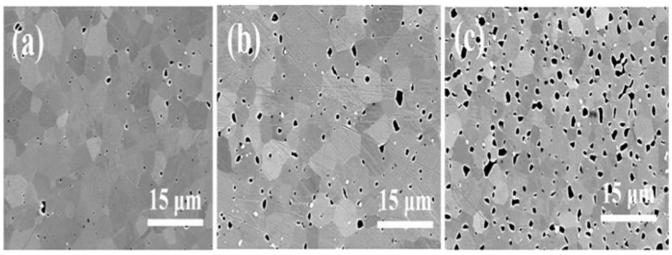


Fig. 2 XRD patterns of UDZB and CDZB powder samples calcined at 750 ◦C for 1 h [2].

On the other hand, the research conducted by K. Hembram diverges from the aforementioned approach as it delves deeply into the examination of the microstructure of ZnO varistors doped with CaO and Bi_2O_3. The present study provides a thorough examination of several aspects, including the distribution of grain sizes, the phases present at grain boundaries, and the distribution of liquid phases inside the examined materials. The research reveals the occurrence of aberrant grain development when larger quantities of CaO are present, which is a feature that has major importance for varistor applications. Gaining a comprehensive understanding of these intricate microstructural characteristics is of utmost importance in order to effectively enhance the performance and dependability of varistors. Tian Tian's research, however rich in insights on the development of nanowires, does not extensively explore the distinct electrical characteristics or



Backscattered-electron (BSE) pictures were obtained for the ZnO-Cr2O3-based varistors with varying CaCO3 concentrations, specifically on polished surfaces. The values of x in the given set are as follows: (a) x = 0, (b) x = 2, (c) x = 6 [1]

Conductivity evaluations of Mn-doped ZnO nanowires. In sharp contrast, the study conducted by K. Hembram offers comprehensive elucidation on the electrical characteristics shown by varistors composed of ZnO doped with CaO and Bi_2O_3. The document presents essential characteristics, such as breakdown fields and coefficients of nonlinearity. Under controlled sintering circumstances, the varistors demonstrate remarkably elevated breakdown voltage and nonlinearity coefficients, therefore emphasizing their considerable potential for use in electrical applications, namely surge protection devices and voltage regulation. In K. Hembram's work, the electrical properties of doped ZnO varistor materials are revealed via impedance and dielectric measurements [2]. These experiments provide significant insights into the relaxation peaks, fluctuations in the dielectric constant, and behavior of tan δ with respect to different amounts of CaO doping. These discoveries provide a substantial contribution to the comprehension of the electrical characteristics and potential uses of these materials in electronic devices and power systems. In conclusion, the aforementioned investigations, albeit investigating different aspects of doped ZnO materials, highlight the adaptability and promise of compounds based on ZnO. The emphasis placed by Tian Tian on the development of nanowires and the incorporation of Mn-doping underscores the complexities associated with materials at the nanoscale, providing valuable insights into the synthesis and morphology of such materials at a basic level. In contrast, the comprehensive examination conducted by K. Hembram regarding the electrical characteristics, phase behavior, and microstructure of ZnO varistors doped with CaO and Bi_2O_3 offers valuable insights into their complex nature. This research serves as a fundamental basis for the potential use of these varietals in practical applications. Collectively, these investigations enhance our comprehension of doped zinc oxide (ZnO) substances, providing significant perspectives for further scholarly inquiries, technological progress, and the creation of pioneering materials throughout diverse sectors.

IV. CONCLUSION

Tian Tian's research is on investigating the effects of CaO doping on the properties of varistor ceramics based on ZnO-Cr_2O_3. The findings of the study indicate that the inclusion of CaO, within the confines of its solid solubility limit, has a beneficial impact on grain development, the electronic states present at grain borders, the electrostatic Schottky barriers, and the nonlinearity. Nevertheless, the introduction of an excessive amount of CaO above its solubility limit has detrimental consequences on the integrity of grain boundaries and electronic states, ultimately leading to a degradation of electrical properties. The optimal degree of CaO doping enhances the range of switching fields, nonlinearity, and lowers leakage current, hence conferring significant value for the purpose of overvoltage protection [1]. The work conducted by K. Hembram examines the effects of CaO doping inside a ZnO-Bi_2O_3 system. The introduction of CaO as a dopant results in a decrease in the size of crystallites, the development of $Ca_4Bi_6O_{13}$ and Ca0.89Bi3.11O5.56 phases, an increase in density, and a reduction in grain size. The observed phenomenon may be ascribed to the inhibitory effects of secondary phases, which impede grain formation via processes such as Zener pinning. The breakdown field exhibits an initial rise when the CaO concentration is increased up to 1wt. %, followed by a subsequent reduction. The 1 wt% CaO sample exhibits a significant coefficient of nonlinearity. Two instances of defect relaxations and two-stage activation energy of conductivity are detected, which have resemblance to those seen in commercial ZnO varistors [2]. Both studies generally emphasize the beneficial impacts of CaO doping on diverse material properties, including grain size, density, and electrical characteristics, within distinct ceramic systems. The use of CaO as a dopant has been seen to significantly augment the performance characteristics of varistor ceramics, hence broadening their potential utility in various electronic systems, particularly those involving overvoltage protection. Nevertheless, the appropriate degree of doping and its subsequent effects might differ based on the particular ceramic system and its composition.

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