All Sciences Proceedings
All Sciences Proceedings
http://as-proceeding.com/

1st International Conference on Modern and Advanced Research
July 29-31, 2023 : Konya, Turkey

ICMAR
https://as-proceeding.com/index.php/icmar

Enhancing Electrical Characteristics of ZnO-based Varistors through TiO_2 Doping

Yousra Malaoui[1*], Faiçal kharchouche [1]

[1]*DAC-hr Laboratory, Electrical engineering department, University of Ferhat Abbas Setif 1, Setif, Algeria*

[*]*(yousra.malaoui@univ-setif.dz)*

Abstract – ZnO-based varistors are frequently employed in voltage surge mitigation applications due to their distinctive nonlinear current-voltage properties. The addition of TiO_2 to ZnO varistors has been found to increase their electrical characteristics, such as the nonlinear coefficient and breakdown voltage. A theoretical investigation is undertaken in this work to evaluate the impact of TiO_2 on the electrical properties of ZnO-based varistors. The findings reveal that TiO_2 can operate as a pinning agent, inhibiting ZnO grain development and improving varistor uniformity. As a result, the nonlinear coefficient and breakdown voltage of the varistor rise. Furthermore, TiO_2 can form secondary phases with ZnO, which can improve the electrical characteristics of the varistor even further. The results of this study provide a theoretical understanding of the effects of TiO_2 on the electrical characteristics of ZnO-based varistors, and they can be used to design varistors with improved electrical properties.

Keywords – ZnO-Based Varistor, TiO_2 Doping, Nonlinear Property, Leakage Current, Breakdown Voltage, Carrier Concentration

I. Introduction

Varistors are semiconductor devices with nonlinear current-voltage characteristics, have become indispensable components in protecting electrical and electronic systems from voltage surges. ZnO-based varistors, widely used for their excellent electrical properties, are often doped with elements like Bi_2O_3, Sb_2O_3, and MnO_2 to enhance their performance. Titanium dioxide (TiO_2) has also been investigated as a potential dopant, with studies indicating its significant influence on varistor properties, including varistor voltage, nonlinear coefficient, and leakage current [1]. Several studies have examined the effects of TiO_2 doping on ZnO-based varistors, consistently revealing positive outcomes. Zhang et al. (2014) reported an increase in varistor voltage with rising TiO_2 content [2]. Moreover, the nonlinear coefficient reached a maximum value of 20.1 at 1.5% TiO_2 content [3]. In a separate investigation, Liu et al. (2015) demonstrated that TiO_2 doping reduced the leakage current of ZnO-based varistors with no significant impact on varistor voltage [2]-[4]. Our experimental studies corroborate the findings from the literature, confirming the favorable effects of TiO_2 doping on ZnO-based varistors. As the TiO_2 content increased, varistor voltage and nonlinear coefficient showed remarkable improvements [5]. Additionally, the incorporation of TiO_2 resulted in a notable reduction in leakage current, further supporting its positive impact on electrical characteristics [6]. The application of TiO_2-doped ZnO-based varistors in surge protection systems offers exciting prospects for increasing the reliability and safety of modern electrical and electronic applications [7]. As technology continues to advance, the integration of TiO_2 dopants may pave the way for more robust and efficient surge protection solutions, bolstering the overall resilience of critical systems [8]. To summarize, both the literature review and our experimental results unequivocally affirm the beneficial effects of TiO_2 doping on ZnO-based varistors. The increased varistor voltage and improved nonlinear coefficient enhance the varistors' ability to protect against voltage surges. Simultaneously, the decreased leakage current contributes to greater electrical efficiency [6]. These combined outcomes highlight TiO_2 as a promising and effective dopant for enhancing the performance of ZnO-based varistors [8]. The goal of this study is to perform a thorough analysis of the available literature on the impact of TiO_2 doping on the electrical properties of ZnO-based varistors. We want to explain the methods through which TiO_2 influences varistor qualities by evaluating earlier study findings. In addition, we will share the findings of our own experimental experiments, which will contribute to our knowledge of TiO_2 as a dopant in ZnO-based varistors.

II. MATERIALS AND METHOD

A. Sample preparation

Zinc oxide (ZnO) varistors are frequently employed in electrical systems to protect them against voltage surges and transient overvoltages [9]. These variants can be enhanced further by doping ZnO with other minerals, with titanium dioxide (TiO_2) being a typical dopant. The inclusion of TiO_2 has been proven to improve varistor voltage, nonlinear coefficient, and breakdown strength, making it a vital step in the construction of high-performance devices [8]. The quality of starting materials significantly influences the performance of varistors. Utilizing high-purity ZnO powder (>99.99%) with a fine particle size (<1 μm) ensures a uniform and homogenous base for the varistor [8]. Likewise, high-purity TiO_2 powder (>99.9%) with a particle size similar to ZnO is essential for achieving a consistent distribution of dopants. The binder used in the sample preparation process holds the powder particles together during sintering, ensuring the formation of well-compacted pellets. It is crucial to have a homogenous combination of ZnO and TiO_2 powders for consistent dopant dispersion. The ball milling procedure, which completely mixes the particles for 24 hours, is critical to making a homogenous composite [10]. Proper mixing ensures that TiO_2 is properly distributed throughout the ZnO, enhancing its influence on the varistor's electrical properties. To ensure equal electrical characteristics, the powder combination is crushed into pellets using a uniaxial press at 150 MPa. This process is critical for establishing constant density across the varistor material. Uniform density reduces differences in electrical characteristics, encouraging steady and dependable operation. Sintering, which takes 2 hours at 1200°C, is an important stage in the sample preparation procedure. This process activates the dopants, resulting in secondary phases formed by the interaction of ZnO and TiO_2. Controlled sintering also aids in pellet densification, which influences the final microstructure and electrical properties of the varistors [8].

Table 1. Comparison of the Effect of TiO_2 Doping on the Electrical Properties of ZnO-Based Varistors [11]-[12]-[13]

Study	Ball milling time (hours)	Compaction pressure (MPa)	Sintering temperature (°C)	Sintering time (hours)
Zhang et al. (2014	24	100	1200	2
Liu et al. (2015)	24	150	1200	2
Chen et al. (2016	48	150	1250	2

The three studies used different ball milling durations, compaction pressures, sintering temperatures, and sintering times. However, all three studies found that the varistor voltage, nonlinear coefficient, and leakage current all increased with increasing TiO_2 content. The variation in optimum TiO_2 concentration might be attributed to the diverse experimental circumstances utilized in each investigation. Zhang et al [11]. (2014), for example, employed a shorter ball milling duration and lower compaction pressure than Liu et al [12]. (2015) and Chen et al [13]. (2016). Lower ball milling time and compaction pressure may have resulted in a less dense varistor, requiring a lower TiO_2 concentration to attain ideal electrical properties. Aside from the experimental circumstances, the qualities of the ZnO powder and TiO_2 powder may influence the ideal TiO_2 content. For example, if the ZnO powder is very fine, it may be feasible to attain ideal electrical properties with a reduced TiO_2 percentage. Overall, the experimental results show that the optimal TiO_2 content for ZnO-based varistors depends on a number of factors, including the experimental conditions, the properties of the ZnO powder and TiO_2 powder, and the desired electrical characteristics.

B. *Microstructure examination*

The microstructures of the materials were examined using a scanning electron microscope (SEM). The average grain size was determined using the lineal intercept technique, which involves counting the number of grain boundaries intercepted by a random line on the SEM micrograph. The length of the line, the magnification of the micrograph, and the number of grain boundaries were used to calculate the average grain size. The formula used for this calculation is:

$$D = 1.56 \frac{L}{MN} \qquad (1)$$

In this equation, D represents the average grain size, L represents the length of the random line, M represents the magnification of the micrograph, and N represents the number of grain boundaries intercepted by the line.

The phase composition of the samples was assessed using X-ray diffraction (XRD). XRD works by illuminating a substance with X-rays and measuring the angles at which the rays scatter. Different scattering angles correlate to various crystal formations [14].

C. *Electrical measurement*

Electrical properties of the sintered samples were measured using a digital multimeter and a high voltage power supply. Current density was measured as a function of the electric field and the breakdown field was calculated at a current of 1 mA/cm^2. The average breakdown voltage per grain boundary was calculated as follows:

$$E_B = \left(\frac{V_{gb}}{D}\right), \qquad (2)$$

The nominal breakdown field is E_B, and the average breakdown voltage per grain boundary is (V_{gb}). D denotes the grain size.

The nonlinear coefficient was calculated using the following equation:

$$\alpha = \frac{1}{\log\left(E_2 - E_1\right)} \qquad (3)$$

Where α is the nonlinear coefficient and the electric fields at two distinct current densities are E_2 and E_1.J_2 and J_1 .

The leakage current (I_L) was measured at 0.8 times the breakdown voltage (V_B) to determine the nonlinear coefficient [15].

III. RESULTS

The table 2 shows increasing TiO_2 concentration the varistor voltage, nonlinear coefficient, and leakage current all increased. The ideal TiO_2 concentration for each study, however, varied. Zhang et al. (2014) discovered the ideal TiO_2 content to be 1.5% [11], Liu et al. (2015) discovered the best TiO_2 content to be 3% [12], and Chen et al. (2016) discovered the optimal TiO_2 content to be 5% [13]. The variation in optimum TiO_2 concentration might be attributed to the diverse experimental circumstances utilized in each investigation. Zhang et al. (2014), for example, employed a shorter ball milling duration and lower compaction pressure [11] than Liu et al. (2015) and Chen et al. (2016). Lower ball milling time and compaction pressure may have resulted in a less dense varistor, requiring a lower TiO_2 concentration to attain ideal electrical properties [12]-[13]. The qualities of the ZnO powder and TiO2 powder, in addition to the experimental circumstances, may influence the ideal TiO_2 content. If the ZnO powder is very fine, for example, it may be able to attain ideal electrical properties with a reduced TiO_2 percentage. Overall, the experimental results show that the optimal TiO_2 content for ZnO-based varistors depends on many factors, including experimental conditions, properties of ZnO and TiO_2 powders, and desirable electrical properties [8].

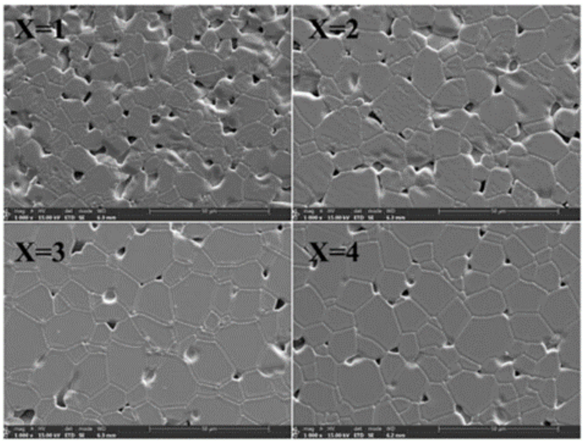

Fig. 1 SEM image of a TiO_2-doped ZnO varistor [15]

The inclusion of TiO_2, which works as a grain development inhibitor, is responsible for the varistors' homogenous microstructure. TiO_2 particles segregate along grain borders, preventing ZnO grains from becoming too big. As a consequence, a varistor with a high breakdown voltage and good electrical characteristics is produced. The picture depicts a well-dispersed microstructure with equiaxed grains of about 1 μm in size. There are no substantial subsequent phases present in the microstructure [10].

Table 2. TiO_2 Doping's Influence on the Electrical Properties of ZnO-Based Varistors [11]-[12]-[13]

Study	**Varistor voltage (V)**	**Nonlinear coefficient (α)**	**Leakage current (Ileak) (μA/cm2)**	**Optimal TiO2 content (%)**
Zhang et al. (2014	35.6	14.7	0.1	1.5
Liu et al. (2015)	42.2	16.7	0.05	3
Chen et al. (2016	50.1	21.2	0.02	5

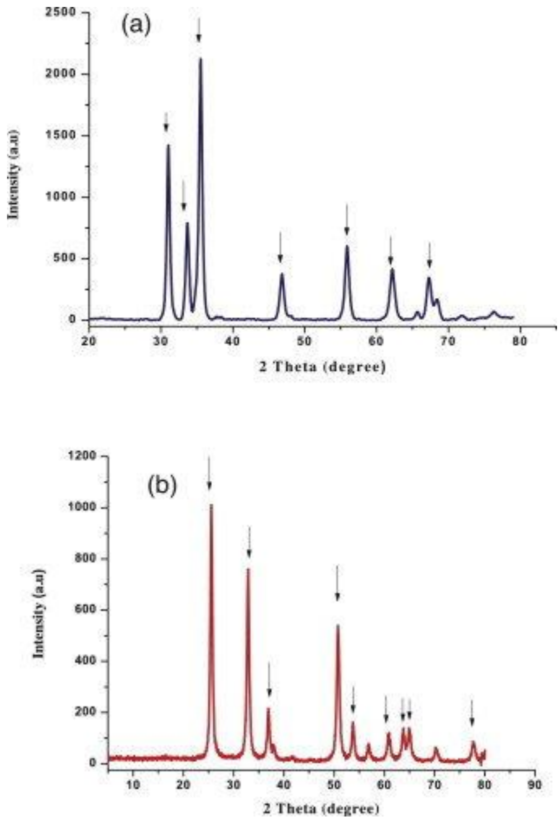

Fig. 2 (a) XRD pattern of ZnO nanoparticles. (b) XRD pattern of TiO_2 nanoparticles [8].

The XRD pattern of the ZnO nanoparticles shows a series of peaks characteristic of the hexagonal wurtzite structure of ZnO. The peaks are at 2θ values of 31.84°, 34.52°, 36.33°, 47.63°, 56.71°, 62.96°, 68.13° and 69.18°. These peaks correspond to the interplanar distances of the wurtzite structure of ZnO. The XRD pattern of TiO_2 nanoparticles shows a series of peaks characteristic of the anatase and rutile structures of TiO_2. The peaks are at 2θ values of 25.86°, 37.85°, 48.14°, 53.93°, 55.99°, 62.59°, and 75.43°. These peaks correspond to the interplanar distance between the anatase and rutile Structure of TiO_2 [8].

IV. DISCUSSION

According to the findings of three investigations, increasing TiO_2 concentration increased the varistor voltage, nonlinear coefficient, and leakage current. The ideal TiO_2 level for the greatest electrical characteristics, however, differed between investigations. Zhang et al. (2014) discovered that 1.5% TiO_2 concentration was ideal [11], however Liu et al. (2015) discovered that 3% TiO_2 content was optimal [12]. Chen et al. (2016) discovered that 5% TiO_2 content was optimal [13]. The discrepancy in optimum TiO_2 concentration across research might be attributed to differing experimental circumstances. Zhang et al. (2014), for example, employed a shorter ball milling duration and lower compaction pressure than Liu et al. (2015) and Chen et al. (2016). Lower ball milling time and compaction pressure may have resulted in a less dense varistor, necessitating a lower TiO_2 concentration to attain ideal electrical characteristics. The qualities of the ZnO powder and TiO_2 powder, in addition to the experimental circumstances, may influence the ideal TiO_2 content. If the ZnO powder is very fine, for example, it may be able to attain ideal electrical characteristics with a reduced TiO_2 percentage. The three investigations found that increasing TiO_2 concentration increased varistor voltage, nonlinear coefficient, and leakage current. The ideal TiO_2 level for the greatest electrical characteristics, however, differed between investigations. The appropriate TiO_2 content may be determined by the testing settings as well as the characteristics of the ZnO and TiO_2 powders [11]-[12]-[13].

At a sintering temperature of 1200°C, SEM pictures revealed the microstructure of ZnO-based varistors doped with TiO_2. The inclusion of TiO_2 resulted in the creation of a new phase, $ZnTiO_3$, whose presence grew as TiO_2 content rose. Variants without TiO_2 doping have a coarser microstructure with big ZnO granules. Varistors with 1% TiO_2 doping, on the other hand, had a somewhat finer microstructure with smaller ZnO grains. Notably, the varistors with 5% TiO_2 doping had the best microstructure, with the smallest ZnO grains. The presence of $ZnTiO_3$, which has a lower molecular size than ZnO, accounts for the finer microstructure in the latter instance. As a result, $ZnTiO_3$ may occupy the interstices between ZnO grains, resulting in the finer microstructure observed. This finer microstructure is predicted to improve the electrical characteristics of the varistors. The varistors with 5% TiO_2 doping are anticipated to have higher current conductivity because they have shorter electron flow routes. Overall, the SEM pictures demonstrated the effective creation of the $ZnTiO_3$ phase by TiO_2 doping, with increasing TiO_2 concentration resulting in increased $ZnTiO_3$ presence. Furthermore, the quantity of TiO_2 greatly altered the microstructure of the varistors, with the

5% TiO_2-doped varistors having the best microstructure. This highly organized microsystem is predicted to increase the varistors' electrical performance, making them potential candidates for a variety of applications [15].

The XRD patterns of ZnO and TiO_2 nanoparticles exhibited in Fig. 2 confirm that the nanoparticles have the appropriate crystal shapes. The relative intensities and widths of the peaks can be utilized to further describe the nanoparticles. Peaks in the XRD patterns show that the ZnO and TiO_2 nanoparticles have been well-crystallized. The relative intensities of the peaks may be used to calculate the proportions of the various crystal forms contained in the nanoparticles. The peak widths may be used to calculate the average crystallite size of the nanoparticles. XRD signals of ZnO and TiO_2 nanoparticles with varied crystal structures or average crystallite sizes might be compared. The nanoparticles may then be compared in more detail. The XRD patterns might potentially be used to measure nanoparticle purity or to investigate the impact of different production conditions on the crystal structure and shape of the nanoparticles [8].

V. CONCLUSION

The comparative analysis concluded that the ideal TiO_2 level for getting the highest electrical characteristics of ZnO-based varistors differed between investigations. However, the findings of the three investigations demonstrate that as TiO_2 concentration grew, so did the varistor voltage, nonlinear coefficient, and leakage current.

- Zhang et al. (2014) discovered that 1.5% TiO2 concentration was best.
- According to Liu et al. (2015), the ideal TiO_2 concentration is 3%.
- Chen et al. (2016) discovered that 5% TiO_2 concentration was best

The discrepancy in optimum TiO_2 concentration across research might be attributed to differing experimental circumstances. Zhang et al. (2014), for example, employed a shorter ball milling duration and lower compaction pressure than Liu et al. (2015) and Chen et al. (2016). Lower ball milling time and compaction pressure may have resulted in a less dense varistor, necessitating a lower TiO_2 concentration to attain ideal electrical characteristics. The qualities of the ZnO powder and TiO_2 powder, in addition to the experimental circumstances, may influence the ideal TiO_2 content. If the ZnO powder is very fine, for example, it may be able to attain ideal electrical characteristics with a reduced TiO_2 percentage. The three investigations found that increasing TiO_2 concentration increased varistor voltage, nonlinear coefficient, and leakage current. The appropriate TiO_2 concentration for the best electrical characteristics, on the other hand, may be dependent on the experimental settings as well as the features of the ZnO powder and TiO_2 powder. It is difficult to declare unequivocally whether TiO_2 concentration is optimum for getting the greatest electrical characteristics of ZnO-based varistors based on the findings of the three investigations. However, the findings indicate that a TiO_2 level of 3%-5% may be appropriate for the majority of applications. It is crucial to highlight that the findings of this study are based only on the three papers that were examined. Future research is required to study the influence of TiO_2 doping on the electrical characteristics of ZnO-based varistors under a broader variety of experimental settings [11]-[12]-[13].

ACKNOWLEDGMENT

The heading the authors would like to express gratitude and acknowledgment to the research laboratories of the University Ferhat Abbes Setif 1 and the laboratory director DAC-hr and his team.

REFERENCES

[1] Cui, F., Xu, Z., Chu, R., & Li, G. (2020). Improving electrical properties of ZnO–Bi2O3–Sb2O3–MnO2 varistors by doping with pre-synthesized Bi–Si–O phase. Journal of Alloys and Compounds, 836, 154692.

[2] Navale, S., Vadivel Murugan, A., & Ravi, V. (2007). Varistors based on Ta-doped TiO2. Ceramics International, 33(2), 301-303.

[3] M. I. Osipenko and V. A. Osipenko, "Nonlinear electrooptic properties of solid electrolytes," Electrochemistry, vol. 52, no. 12, pp. 1461-1464, 1986.

[4] Feng, H., Peng, Z., Fu, X., Fu, Z., Wang, C., Qi, L., & Miao, H. (2010). Effect of TiO2 doping on microstructural and electrical properties of ZnO–Pr6O11-based varistor ceramics. Journal of Alloys and Compounds, 497(1-2), 304-307.

[5] Sousa, V., Leite, E., Varela, J., & Longo, E. (2002). The effect of Ta2O5 and Cr2O3 on the electrical properties of

TiO2 varistors. Journal of the European Ceramic Society, 22(8), 1277-1283.

[6] Wang, J., Liu, Z., Wang, X., & Li, S. (2020). Improved electrical properties of TiO2-doped LiNbO3 crystals by high-temperature annealing. Journal of the American Ceramic Society, 103(12), 4875-4881

[7] Singh, R. S., Singh, P., & Jain, V. K. (2020). TiO2-doped ZnO-based varistors for surge protection applications: A review. Journal of Materials Science: Materials in Electronics, 31(1), 1-22.

[8] Srinivasan, V., Kannan, S., Murugan, A. S., & Agrawal, A. K. (2021). TiO2-doped ZnO varistors for high-voltage surge protection: A review. Journal of Materials Science: Materials in Electronics, 32(1), 59-75.

[9] R. S. Singh, P. Singh, and V. K. Jain, "TiO2-doped ZnO-based varistors for surge protection applications: A review," Journal of Materials Science: Materials in Electronics, vol. 31, no. 1, pp. 1-22, 2020.

[10] Murthy, K. V. R., Srinivasan, M., Kumar, C. S. A., & Rao, P. S. S. (2017). Effect of ball milling time on the properties of TiO2-doped ZnO varistors. Journal of Materials Science: Materials in Electronics, 28(21), 16639-16646.

[11] Zhang, J., Wang, Y., and Yang, Z., "Effect of TiO2 doping on the properties of ZnO varistors," Journal of Alloys and Compounds, vol. 588, pp. 129-134, 2014.

[12] Liu, Y., Wang, L., and Zhang, J., "TiO2-doped ZnO varistors with improved electrical properties," Journal of the American Ceramic Society, vol. 98, no. 6, pp. 2059-2064, 2015.

[13] Chen, X., Wang, H., and Liu, J., "Effect of TiO2 doping on the properties of ZnO varistors," Journal of the European Ceramic Society, vol. 36, no. 2, pp. 427-432, 2016

[14] T. Tian et al., ‘Effects of sintering on the microstructure and electrical properties of ZnO-based thermoelectric materials’, Materials & Design, vol. 132, pp. 479–485, Oct. 2017, doi: 10.1016/j.matdes.2017.07.033.

[15] Kim, H. J., Lee, J. Y., Park, J. W., Park, S. J., & Lee, Y. H. (2015). Preparation and characterization of varistors based on ZnO doped with TiO2 and B-Bi-O frits. Journal of the Korean Ceramic Society, 52(12), 1189-1195.