Study of BaTiO$_3$-doped Bi$_2$O$_3$/ZnO varistor microstructure and its electrical characteristics

Faiçal Kharchouche$^1$, Yousra Malaoui$^1$, Omrane Bouketic$^2$

$^1$DAC-hr Laboratory, Department of Electrical Engineering, Faculty of Technology, Setif 1 University-Ferhat ABBAS, Setif, Algeria

$^2$Mechatronics Laboratory, Department of Electrical Engineering, Faculty of Technology, Setif 1 University-Ferhat ABBAS, Setif, Algeria

ABSTRACT

This study presents the characterization and optimization of BaTiO$_3$-doped ZnO-based varistors for electrical and electronic applications. The varistors were prepared using a conventional ceramic procedure and were sintered at a temperature of 1,000 °C with different concentrations of BaTiO$_3$ (0 and 3 mol%) added to the Bi$_2$O$_3$/ZnO-based varistor composition (99.5 mol% ZnO and 0.5 mol% Bi$_2$O$_3$). The results showed that the addition of BaTiO$_3$ led to the formation of various oxides and solid solutions, such as Bi$_2$TiO$_5$, BaTiO$_3$ and (Bi$_2$O$_3$)$_{0.80}$ (BaO)$_{0.20}$. The dielectric constant and grain size decreased with increasing BaTiO$_3$ content, while the non-linearity coefficient, electric fields (Eb) increased, and dielectric loss (tan$\delta$) decreased. The optimized varistor contains 2 mol% BaTiO$_3$ and an electric field of 148.08 V/mm, which are superior to those of the BaTiO$_3$/Bi$_2$O$_3$/ZnO-based varistor. During this study, we were able to observe that a slight addition of BaTiO$_3$ will increase the breakdown voltage and the coefficient of nonlinearity and this will allow us to develop low-dimensional varistors and install them in the high-voltage domain.

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Corresponding Author:

Faiçal Kharchouche

DAC-hr Laboratory, Department of Electrical Engineering, Faculty of Technology

Setif 1 University-Ferhat ABBAS

Setif, Algeria

Email: faical.kharchouche@univ-setif.dz

1. INTRODUCTION

Varistors made of Zinc oxide (ZnO) are polycrystalline ceramic semiconductors, non-linear resistors that are used for protecting electronic components and electrical installation from surges. They are also largely employed to stabilize voltage and suppress transient surges in electric power systems as well as in electronic circuits. Various types of such varistors are being used in lightning arrestors [1]–[6]. The chemical constitution of this type of varistors is 98% mol of ZnO and 2% represents additives. The non-linearity of I-V characteristics is due to the formation of double Schottky barrier layers at the grain boundaries. Commercial ZnO-Bi$_2$O$_3$ varistors are traditionally manufactured by mixing the oxides in a direct manner, where it is not easy to get the exact desired microstructure and hence the electrical properties [7]–[12]. The choice of a good chemical structure and composition will determine the non-linear coefficients of the varistors. These coefficients are determined through extensive experimental and empirical studies. Adding metal oxides during manufacturing or shaping will alter the electrical properties and/or the microstructure of the final product [13]–[15]. In the subsequent sections, the main constituents of a varistor are introduced. The effects of these elements on material properties are also investigated. Special emphasis will be on the conditions of further development of ZnO-based varistors to achieve optimal manufacturing processes.

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Production of varistors by the longest method of sintering a mixture of ZnO powder as a milieu and small amounts of metal oxides such as SrTiO$_3$, SnO$_2$, WO$_3$, Bi$_2$O$_3$, TiO$_2$, Sb$_2$O$_3$, CeO$_2$ is discussed in [14]–[21].

These oxides have been considered because of their wide bandgap properties (Eg > 3 eV). Some studies have also been conducted to investigate the influence of specific dopants such as Ce$_2$O$_3$, Ho$_2$O$_3$, La$_2$O$_3$, Dy$_2$O$_3$, and Y$_2$O$_3$ [22]–[24]. The following relationship was used to determine the variation of current $I$ as a function of voltage $V$ and determine the coefficients of non-linearity for varistors [25]–[27].

$$I = kV^\alpha$$

(1)

or

$$J = kE^\alpha$$

(2)

$\alpha$ signifies the coefficients of non-linearity, $E$ is the electric field and $J$ is the electric current density. This study focuses on the effects of the BaTiO$_3$ perovskite type as an addition to a matrix consisting of 99.5% ZnO + 0.5% Bi$_2$O$_3$ and microstructure analysis and electrical properties were studied on all samples.

2. EXPERIMENTAL PROCEDURE

Powder of Nano ZnO with high purity (99.99% Nanogard) and particle size of 60 nm was considered in this study. Bi$_2$O$_3$ powder was added to the ZnO with standard proportion according to the formula below: 99.5% ZnO + 0.5% Bi$_2$O$_3$ (all in mol%). Four samples Z0 (ZB), Z1 (ZB+1mol% BaTiO$_3$), Z2 (ZB+2mol% BaTiO$_3$), and Z3 (ZB+3mol% BaTiO$_3$) were prepared for the experimental investigation. The basic composition of this formula is: 99.5% ZnO + 0.5% Bi$_2$O$_3$ + X mol% BaTiO$_3$ (ZB + X mol% BaTiO$_3$). Our experimental protocol for the elaboration of varistors was carried out using the classic method of mixing oxides. A small amount (approximately 50 g) of the selected powder is mixed in a polypropylene bottle filled with 5 mm diameter zirconia beads in deionized water containing the zirconia beads and ethanol using a mixer. The mixing operation took 3 hours with a rotation speed (2 rpm) using zirconia beads; these beads promote the homogenization of the mixture and prevent pollution of the mixture. The powder is dried at 110 °C for 12 hours. Then calcined isothermally at 800 °C for 2 hours (rise rate 10 °C/min). However, the powder mixture was ground and after this step, it was sieved through a 200 µm sieve. before pressing and for each sample, we use 0.5 g of powder and 4% polyvinyl alcohol (PVA) as an organic binder. This results in the formation of so-called “soft” deformable agglomerates that support particle alignment during pressing. Incorporate in a porcelain mortar at the rate of 2 drops per 10 g of powder to form a paste. During this operation several advantages can be found among which the relative density will increase, that is to say, the porosity will decrease which can be seen through the scanning electron microscopy SEM on the microstructure of each sample also the use of PVA will be prevented the creation and appearance of cracks which will disrupt and degrade the electrical characteristics. After drying the latter in an oven at 80 °C for 1h, it is extracted, ground in a mortar, and passed through a 200 µm sieve. Our technique consists of shaping starting powder. We implemented two complementary compression protocols. A uniaxial pressure of 40 MPa was applied to the powder mixture in a cylindrical press to obtain the desired shape. Then an isostatic pressure of 300 MPa was applied for 5 minutes on all samples. The final dimensions of the samples after pressing are approximately 8 mm in diameter and approximately 1.5 mm in thickness. Sintering all samples at 1,000 °C at a speed of 5 °C/min for 2 hours, sintering considers the last stage of the development of the sample as illustrated in Figure 1 which presents the different stages of the development of the varistor. Using the Archimedes method, we were able to measure and determine the density of the sample. High-resolution SEM was used to understand the microstructural changes and monitor the microstructural evolution, and the mapping of the four samples was also examined by EDX (Hitachi S-3500N). Using the linear intercept method to calculate the grain size [4]–[7], [19]. Using this method, several segments of length L were traced on the micrograph, and the number N of intercepted grains was counted. Grains not completely cut are counted as half a grain, as presented by Mendelson [17], [18], the average grain size $G$ is determined by this expression:

$$G = 1.5L/MN$$

(3)

Where M is the magnification of the micrograph, L is the random line length on the micrograph, and N is the number of grain boundaries intercepted by the lines. A thin layer of silver paste is applied to both sides of the pellet and annealed in a conventional oven at 650 °C for 10 min to establish better contact with the electrode whose diameter was 10 mm. The parameters $E_b$ is the breakdown field, $J_l$ is the leakage current, and $\alpha$ could
then be determined from the use of a voltage source with an integrated nanometer (measure source unit, Keithley 237) which determines the current/voltage characteristics. By convention, we define the non-linearity coefficient $\alpha$ as,

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

(4)

with $J_1 = 1$ mA.cm² and $J_2 = 10$ mA.cm². Graphically, it corresponds to the slope of the log $J = f(\log E)$ curve. As part of this work, we were interested in some of these parameters, in particular, the dielectric constant $\varepsilon'$, the loss factor $\varepsilon''$, and the loss tangent $\tan\delta$. These parameters were measured using an impedance analyzer HP4194A. Also, the dielectric constant could be calculated using (5). The relative permittivity $\varepsilon_r$ is given by:

$$\varepsilon_r = \frac{C}{C_v}$$

(5)

where $C$ is the capacity of the material under test and $C_v$ is the capacity of air. In an alternating electric field, the complex dielectric permittivity $\varepsilon$ given by:

$$\varepsilon = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

(6)

where $\varepsilon'$ is the dielectric constant, $\varepsilon''$ is the dielectric loss factor (the dielectric dissipation factor). It is given by (7):

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

(7)

a horizontal pushrod dilatometer Dil 402 PC (Netzsch) with a temperature range of 25–1,400 °C was used for dilation measurement. Pellets with a diameter of 7 mm were pressed at a pressure of 1t for 20 s. Then they were sintered at a constant heating rate of 5 °C/min and held at 1,000 °C for 2h before they were cooled to room temperature in air.

![Diagram](image.png)

Figure 1. Diagram, presenting the different stages of varistor elaboration
3. RESULTS AND DISCUSSION

We have chosen to work on three commercial powders. They have heterogeneous grain sizes, according to the SEM image of Figure 2. It can be seen that the agglomeration of the commercial ZnO powder is composed of grains of the lower order of 1 μm, and a very weak agglomeration. Regarding the commercial powder of barium oxide titanate (BaTiO₃), we see that the grains are very fine in the order of a nanometer.

3.1. Microstructural studies

3.1.1. EDX mapping

The study of the micrograph and the analysis of the SEM images according to the experimental protocol of sintering varistors at a temperature of 1,000 °C for 2 hours makes it possible to precisely illustrate the sizes of precipitates and shows secondary phase precipitation on a fractured surface of the sample Z1 as shown in Figure 3. The result of this study is supported by EDX mapping which allowed us firstly to see all the chemical components incorporated into the main zinc oxide matrix of the varistor and also shows that these secondary phases are rich in Ti and Ba but completely free of ZnO and bismuth. The microstructure is quite homogeneous (no bimodal distribution). The cracking is intergranular. We have only seen extra-granular porosities since the intra-granular porosities are specifically spherical and localized in the grains. We are therefore dealing with normal growth of the microstructure without pore-grain boundary separation and then abnormal growth.

Small porosities are observed at the grain boundaries and on the faces of the grains as well as a liquid phase (white) at the triple points and at the grain boundaries. White nodules are observed in the middle of the faces of the grains and perhaps inside the grains. It is difficult to tell if the white nodules are inside the grains since the fracture is essentially intergranular.

The liquid phase is observed at the grain boundaries but not between the grains. On the other hand, the white nodules are located on the faces of the grains and sometimes at the triple points. The hypothesis that can be made is that the nodules have a different composition from the liquid phase.

Figure 4 Let's take a look at the SEM-EDX elemental mapping for one of the samples which contain all the stoichiometry required in this study: (99.5% ZnO + 0.5% Bi₂O₃ + 1% BaTiO₃) (all in mol%). The electron image shows the distribution of chemical elements in the internal matrix of the samples, this image shows two very important points such as the homogeneous dispersion of atoms and the appearance of secondary phases through the chemical reactions after sintering, the corresponding elementary element maps are (Zn, Ba, Bi, Ti, and O). The spectrum of the EDX region and the table of atomic and weight ratios of the different elements obtained after the sintering process. Grain boundary analysis by EDX indicates that the grain boundary between grains is richer in Ba, Ti, and Bi and sometimes at triple points compared to other elements (Zn, Ba, Bi, Ti, and O), so there is the possibility of a chemical reaction at the grain boundary.

3.1.2. Dilatometry

Dilatometry is the measurement of change in a linear dimension of a sample during a programmed thermal cycle. In principle, therefore access to the change in volume of a sample subjected to a thermal program, through an appropriate combination of measures linear. The dilatometer measures the linear variation in the dimension of a sample up to a temperature of 1,400 °C in this work and under a controlled atmosphere. This device is very useful for following shrinkage during sintering according to the time and temperature and provides access to the expansion coefficients of sintered materials. Figure 5 illustrates the full cycle of the sintering shrinkage process. The main events in this process are shown; these include mainly the temperature of the sintering beginning, the temperature of the start point of densification (950 °C), and the point where the open porosity is eliminated. Moreover, the final phase of sintering where the gradient is big with a final linear shrinkage of the neighborhood (0.08) is demonstrated as well. The shrinkage behavior during sintering in our case of varistor production is due to the existence of the liquid phase of the varistor substance, which contains additives like Bi₂O₃ and BaTiO₃.

3.1.3. SEM observation

Figure 6 shows the microstructure of the varistors observed by scanning electron microscope on the fractures after metallization with gold. The micrographs of the varistors show that the varistors are quite dense. These justify the high densities obtained. They also show distinct grain boundaries, very low intergranular porosity, and homogeneous grain distribution in each sample. The average grain sizes are shown in Table 1. Table 1 presents the approximate values of the grain size which varies respectively from 3.12 μm to 2.5 μm for Z0 to Z3. It is shown from the microstructure analysis that there were no significant differences in the shape of the grains of the four samples. However, there are substantial differences in their grains’ size, where it is notably small for Z3 as compared to other samples. It should be noted that the more quantity of BaTiO₃ powder we add to the sample, the more we notice that there is a reduction in grain size.
It is also mentioned that the appearance of the precipitation of secondary phases and nodal points at grain boundaries will lead to the augmentation of grain size. These microstructures present a significant proportion of sub-joints and are characterized by a bimodal distribution of grain sizes. In addition, the microstructure shows the composition of a massive phase and an intergranular phase. The sample Z0 appears to be further porous compared to the other three samples which are doped by BaTiO$_3$, the amount of BaTiO$_3$ added improves grain size and advances micro-structural uniformity. All of these results are in agreement with the work cited in references [17]–[22]. The measured density values are given in Table 1, the density varies respectively from 93.42, 95.42, 96.06, and 96.86 for Z0, Z1, Z2 to Z3. So, we notice that the density of the samples improves as we add a quantity of BaTiO$_3$ powder. In this case, we can say that the porosity has decreased due to the powder effect of BaTiO$_3$.

Figure 2. SEM image of Bi$_2$O$_3$, BaTiO$_3$, and ZnO powder

Figure 3. Presentation of the micrograph of a fractured surface by SEM for sample Z1

3.1.4. XRD analysis

Figures 7 and 8 show a typical X-ray diffractogram (XRD) of a zinc oxide varistor from sample Z1 and all samples, recorded on all the samples at 1,000 °C for 2 h, calcined at 800 °C. According to the JCPDS data sheet (01-089-7102) presented in Figures 7 and 8, the lines constituting these spectra are the well characterization of ZnO crystallizing in the hexagonal structure and which is featured by a peak looking at an angle of 2θ = 36.256°. In these spectra, we observe the presence of small lines corresponding to the secondary phases of the doping elements, we obtained three phases with weak peaks like Bi$_2$TiO$_{20}$ has a compound name (SGD+$^+$Bi$_2$O$_3$), BaTiO$_3$, and (Bi$_2$O$_3$)$_{0.80}$(BaO)$_{0.20}$, has a compound name (Bismuth Barium Oxide) according to the JCPDS data sheet (00-042-0186), (01-074-1968) and (00-032-0109) which indicates that there is a dissolution of the Bi$_2$O$_3$ and BaTiO$_3$ dopants within the ZnO crystal lattice by occupying the Zn ionic sites. Note also that the spectra show that, for all the pure and doped samples, the line diffracted by the (101) planes are the most intense. It is deduced that the solid solutions that are detected by XRD are situated in the grain limitations of ZnO. As shown in the SEM of Z1 (Figure 2).
3.2. Electrical properties

The electrical characteristics $E=f(J)$ of the studied samples is given in Figure 9. These samples have been sintered at 1,000 °C for 2 hours as stated above. It is clear from the curves that all samples have the same $E=f(J)$ shape. However, the values of the current densities and electric fields are very different from one sample to another. The addition of the doping powder BaTiO$_3$ increased the nonlinear coefficient and the electric field in the Bi$_2$O$_3$-based ZnO varistor. The nonlinearity coefficients measured for each varistor are shown in Table 2. The existence of the nonlinearity region is the most important property of varistors. The varistors present their conducting phase here. The current increases much faster than the voltage in this region of nonlinearity. So, the electrical characteristics obtained through this elaboration of Bi$_2$O$_3$-based ZnO varistor doped with BaTiO$_3$ illustrate the transition from the insulating phase to the conductive phase, has occurred very fast.
Table 1. The main data of the microstructural
Composition (99.5% ZnO + 0.5% Bi₂O₃+Xmol% BaTiO₃) | Grain size (µm) | Relative density (%) \\
--- | --- | --- \\
Z0 (x=0) | 3.12 | 93.42 \\
Z1 (x=1) | 2.88 | 95.42 \\
Z2 (x=2) | 2.67 | 96.02 \\
Z3 (x=3) | 2.5 | 96.86 \\

Figure 7. X-ray diffractogram (XRD) of a zinc oxide varistor from sample Z1

Figure 8. X-ray diffractogram (XRD) of all samples sintered at 1,000 °C

Figure 9. J-E characteristic of all samples sintered at 1,000 °C

Table 2. The main data of the electrical characterization
Composition (99.5% ZnO + 0.5% Bi₂O₃+Xmol% BaTiO₃) | Breakdown field Eb₅mA (V/mm) | The nonlinearity coefficients α \\
--- | --- | --- \\
Z0 (x=0) | 12.09 | 1.53 \\
Z1 (x=1) | 44.35 | 2.03 \\
Z2 (x=2) | 148.08 | 3.58 \\
Z3 (x=3) | 176.15 | 2.74 \\

3.3. Dielectric property

The evolution of the real part $\varepsilon'$ and the imaginary part $\varepsilon''$ of the permittivity as a function of frequency are first carried out at room temperature on all samples with and without BaTiO$_3$. Figure 10 regroups the permittivities of the four samples in the interval of 100-2 MHz. $\varepsilon'$ decreases quickly at the beginning and then stabilizes when the frequency increases. On the other hand, the loss tangents $\varepsilon''$ present very low values, not exceeding 0.1. We can deduce that $\varepsilon'$ decreased with the increase in the concentration of BaTiO$_3$. From these results, we see that the surfaces and grain boundaries of the samples can be charged and contain charge carriers which can orient themselves under the action of an electric field and thus contribute to the polarization of the material. This phenomenon is called the interfacial polarization mechanism. It is inferred that there is a decrease in the number of conductive carriers, which may accompany the test frequency during the dielectric constant. It should be noted that the dissipation factor at 10 kHz shows a fluctuation between 0.119 and 0.32 as the amount of BaTiO$_3$ increases. The tan$\delta$ of the dielectric property includes heat loss due to leakage current and heat loss due to friction due to rotation of the electric dipole [24]. It is believed that the reason all samples have high tan$\delta$ is that the leakage current is quite high. More detailed dielectric property parameters are summarized in Table 3.

The dielectric constant is an important parameter in the design of passive devices for integrated circuits and advanced packaging technologies. Figure 11 demonstrates that the dielectric constant is inversely proportional with the frequency in the range of 1 kHz to 2 MHz after heating at different temperatures. For most dielectric materials, the dipole rotation rate at high frequencies is insufficient to accommodate changes in applied AC bias voltage, so dielectric relaxation is expected to decrease the permittivity with increasing frequency. We also found that the decrease in permittivity with increasing temperature is uniform at low and high frequencies.

![Figure 10. Evolution of dielectric constant and dielectric loss versus frequency](image)

![Figure 11. Evolution of dielectric constant versus frequency for sample Z1](image)

<table>
<thead>
<tr>
<th>Composition (99.5% ZnO + 0.5% Bi$_2$O$_3$+Xmol% BaTiO$_3$)</th>
<th>Dielectric constant $\varepsilon'(10$KHz$)$</th>
<th>Dielectric loss Tan$\delta$ (10$KHz$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z0 (x=0)</td>
<td>4444</td>
<td>0.119</td>
</tr>
<tr>
<td>Z1 (x=1)</td>
<td>2576</td>
<td>0.034</td>
</tr>
<tr>
<td>Z2 (x=2)</td>
<td>2404</td>
<td>0.032</td>
</tr>
<tr>
<td>Z3 (x=3)</td>
<td>3246</td>
<td>0.102</td>
</tr>
</tbody>
</table>

Table 3. The main data of the dielectric characterization

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*Study of BaTiO$_3$-doped Bi$_2$O$_3$/ZnO varistor microstructure ... (Faïçal Kharchouche)*
4. CONCLUSION

This study consists of three main parts. Thus, we focus in the first part on the development and elaboration process of the varistors, while the second part depends on the precise microstructural characterization, and the third on the electrical and dielectric properties. BaTiO$_3$-doped Bi$_2$O$_3$/ZnO varistors were developed traditionally. The added amount of BaTiO$_3$ is 0 to 3 mol%. The sintering temperature chosen in this work is 1,000 °C. The results are summarized below: i) Expansion measurements show that the samples started to shrink at the wanted temperature, with compression onset at 950 °C; ii) As the BaTiO$_3$ concentration increases, the grain size of the sample significantly reduces from 2.16 µm to 1.89 µm; iii) XRD analysis confirmed the formulation of the ZnO hexagonal crystal structure. According to the JCPDS database (01-089-7102), all major peaks can be indexed as zinc oxide phases. The spectrum of Z1 shows that the microstructure consists of three phases: ZnO grains (primary phase) and other solid phases, Bi$_2$ZnO$_{20}$-BaTiO$_3$ and (Bi$_2$O$_3$)$_{0.80}$ (BaO)$_{0.20}$, described by the appearance of peaks; iv) Determine the nonlinear coefficients of the curve $E=f(J)$. This study shows that as the BaTiO$_3$ content increases, the nonlinear coefficients increase; v) The electric field ($E_b$) and relative density as the grain size increases; vi) When we use a small amount of BaTiO$_3$, the dielectric constant and dielectric loss will decrease; vii) The findings suggest that BaTiO$_3$-doped ZnO-based varistors have the potential for use in electrical and electronic applications requiring high-performance non-linear behavior.

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REFERENCES


### BIOGRAPHIES OF AUTHORS

**Faïcal Kharchouche**
- He obtained a baccalaureate in chemistry.
- He holds degrees in electrical engineering from Farhat Abbas University Setif 1, Setif, in 2002 and a Ph.D. Degree in Electrical Engineering from Farhat Abbas University Setif 1, 2014. From 2006 to 2023, he was a researcher in the Dac Hr Lab. Since 2009, he has been an Assistant Professor in the Department of Electrical Engineering. He has many articles and publications in the field electricity and protection of electrical appliances. He can be contacted at email: faical.kharchouche@univ-setif.dz.

**Yousra Malaoui**
- Completed her Bachelor of Science degree in Electrical Engineering at the Department of Electrical Engineering at the University of Ferhat Abbas Setif.
- She also finished her Master of Science degree at the same department and has been working on her research topic, which involves the study and elaboration of semiconductors for protection against electrical disturbances, specifically focusing on ZnO-based varistors. She can be contacted via email: yousra.malaoui@univ-setif.dz.

**Omran Bouketir**
- Is currently an associate professor at Ferhat Abbas University Setif 1 since 2016.
- Prior to this, he has been a faculty member at several international universities namely King Fahd University of Petroleum and Minerals (KFUPM, KSA), University of Nottingham Malaysia Campus (UNMC) and Multimedia University (Malaysia).
- Omран has more than 20 years of teaching experience in Electrical engineering field; his main research interests are in renewable energy storage systems, power electronics, and CAD systems for teretiary teaching. He can be contacted at email: omrane@univ-setif.dz.