OPTIMAL COMPOSITION OF ZINC OXIDE VARISTOR DEVELOPED IN NIGERIA

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ABSTRACT

The successful development of zinc oxide varistors using locally available materials in Nigeria is presented in this work. This functional semiconductor device protects circuit against voltage surges. The physical dimensions, electrical properties, capacitance, the effect of supply frequency variation on the capacitance of the locally fabricated ZnO varistors were examined and a comparison of these properties with the imported ones undertaken. The composition of the samples includes ZnO 97-100mol% and 0-3mol% additives (Bi_2O_3 and CoO). The compositions were mixed in a polyethylene container using zirconia balls, with cassava starch as binder. The samples were pressed using steel rings as moulds, and sintered at 1260^{O}C for 3hours. The results of the electroded samples subjected to electrical property measurements indicates that the current-voltage characteristics, plots of nonlinear coefficient α, against peak current and plots of α against β were similar to the foreign made ZnO varistors. Optimal varistor properties were obtained in sample C with a composition of ZnO 98%, Bi_2O_3 1% and CoO 1%, having a voltage clamping ratio of 1.17, a breakdown voltage of 240volts and the non-linear coefficients α and β were 71 and 1.03 respectively. The effect of supply frequency on the capacitance revealed that the capacitance-frequency curves over a wide range of frequencies decay exponentially. The production of ZnO varistor will promote economic activities in the electrical and solid mineral sectors of Nigerian economy, thereby enhancing her capacity building and developmental goals in Africa.

KEYWORDS: Development, Zinc Oxide, Additives, Furnace, Varistor, Electrical Properties

INTRODUCTION

The production of lightning arresters using locally available materials in Nigeria was carried out Usifo and Edeko (1998). They used a mixture of haematite and calcium carbonate to produce the arrester. Usifo (2001) conducted s further work on these materials which resulted in the present day Oriaghe (named after the inventor) lightning arresters which have the same characteristics as that of the silicon carbide based lightning arrester. It would be interesting to note that these lightning arresters were the spark gap types which have several fundamental limitations (Paul and Venugopalan, 1993). These limitations include the valve elements, the gaps, and the power follow-through current. It has nonlinearity coefficient in the range of 2 to 6 and negative temperature coefficient.

The discovery of zinc oxide ceramics exhibiting nonlinearity coefficients between 40 and 60 allowed a surge arrester to be manufactured without the use of spark gaps and its inherent limitations. Matsuoka (1971) developed the first ZnO varistor in Japan in 1970, using the conventional ceramic process. The varistors were produced by a ceramic sintering process that gave rise to structure comprised of conductive ZnO grains surrounded by electrically insulating barriers. These barriers are derived from trap states at the grain boundaries induced by additive elements such as Bi, Co, Pr, Mn (Lagrange, 1991). Small amount of these metal oxide additive added, is to control the electrical characteristic of the ZnO grain boundaries to optimize the varistor behaviour.

Nigeria has the human and natural capacity for the development of these functional semiconductor devices for electrical circuit protection (Evbogbai, Edeko and Ajuwa, 2011)a. The nonlinear coefficients of the developed varistor compared favourably with the imported ones (Evbogbai, Edeko and Ajuwa, 2011)b. The prospects and challenges for the commercial production of these devices have been identified (Evbogbai, Ajuwa and Edeko ,2011). In this work a modest attempt is made to determine the optimal composition of zinc oxide varistor developed in Nigeria by constituting samples of different percentage compositions. The conventional production process and electrical properties measurement were also carried out. The commercial production of zinc oxide varistor in Nigeria will enhance human and material capacity building for rapid national development.

EXPERIMENTAL PROCEDURES

MATERIALS

Chemical substances used for the experiment were zinc oxide, bismuth oxide (Bi_2O_3) and cobalt oxide (CoO), deionized water and cassava starch.

The following equipment were used electronic weighing machine, electric furnace. VD890G digital multimeter, Fluke model 117 True-rms digital display multimeter, DT2905A digital multimeter, AC/DC variable power supply (OMEGA TYPE LTV-005),10Ω choke resistors, Gw INSTEK GDS-1062 digital storage oscilloscope, Farnell sine squarewave oscillator model LF, FEEDBACK power circuits BEE 4210 model, FEEDBACK power supply 441model and other standard labouratory equipment.

METHOD

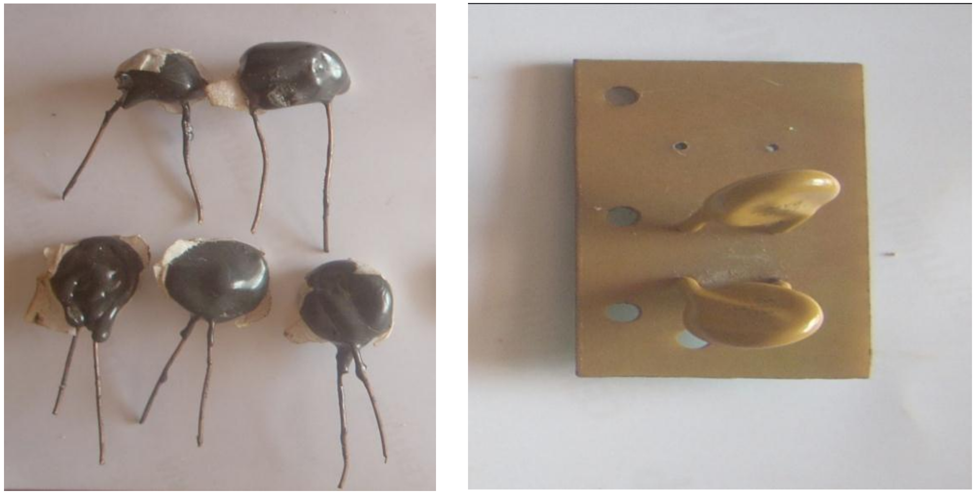
Materials Preparation

. Adventurertm, OHAUS CORP electronic weighing machine, model AR1530 was used in weighing the powder substances used in this study. The compositions of the various zinc oxide varistors is shown in Table1.

The zinc oxide and additive oxide weighed were poured into a polyethylene container. The oxides were thoroughly mixed using zirconia balls and 20 grams of starch and 20 milliliretres of deionised water were used for ball milling. The detailed experimental procedure of the conventional ceramic process for the local production of ZnO varistors had been reported elsewhere (Evbogbai, Edeko and Ajuwa, 2011). The discs in each sample that withstood and survived processing conditions such as sintering, polishing, electroding and encapsulation were labeled using Arabic numeral as subscripts. The discs produced under sample A were labeled A_1, A_2 and A_3. Similarly, the discs produced in samples B, C and D were labeled accordingly. Plate 1(a) shows the photograph of the developed zinc oxide varistors, Plate 1(b) the photograph of the foreign made varistors.

Table 1: Composition Of The Zinc Oxide Varistors

Samples	ZnO mol%	Bi_2O_3 mol%	Co mol%
A	100	-	-
B	99	0.5	0.5
C	98	1	1
D	97	1.5	1.5



(a) :Developed Zinc Oxide Varistors. (b) :Foreign Made Varistors.

Plate 1

Electrical Measurement

The capacitance of the each bulk ZnO varistor samples was measured using VD890G digital multimeter.

Current-Voltage Measurement

Figure 1 shows the circuit diagram to determine experimentally the ZnO varistors samples current-voltage data. The dc current source for these experiments was obtained using voltage to current sources converter, which comprises of AC/DC variable power supply (OMEGA TYPE LTV-005) in series with ten, 1Ω choke resistors. The dc current source was varied from zero, no readings appeared on the voltmeter, between 5μA to 1A, the corresponding voltage drop across the ZnO varistors were measured using DT2905A digital voltmeter, while Fluke model 117 True-rms digital display multimeter, was used to measure the dc source current. These experiments were conducted for all the developed ZnO samples. The experimental current-voltage data were used to determine the voltage-clamping ratio, nonlinear coefficients, varistor voltage, and continuous operating voltage.

Figure 2 shows the circuit diagram for the investigation of the effect of supply frequency variation on the capacitance of the developed ZnO varistor samples. The equipment used were, Gw INSTEK GDS-1062 digital storage oscilloscope, Farnell sine squarewave oscillator model LF, 10 volts peak-peak amplified by FEEDBACK power circuits BEE 4210 model energized by FEEDBACK power supply 441model. The supply frequency of the sinewave function generator was varied from 10Hz to 1MHz. The current flowing through the varistor samples and the voltage drop across each sample was measured using Fluke digital ammeters and voltmeter respectively. These experimental data were recorded and the experiment was conducted for all the developed ZnO varistor samples

RESULTS AND DISCUSION

Some of the ZnO varistor pellets after sintering, were properly densified, hence good stability, they could withstand drop impact test (about 2m) and could be handled without breakage, while some got fractured, and others got burnt due to small thickness and long sintering hours. Those with larger thickness were porous, not properly compacted, hence poorly densified and lack stability. These defects could be attributed to inadequate compactness resulting from manual pressing.

The results of the capacitance measurement at room temperature revealed that the chemical composition, surface area and thickness of the ZnO varistor affects it capacitance. The thickness of the ZnO varistors samples controls the nominal voltage, the electrode surface area controls the surge current withstanding capability and the volume controls the transient energy capability.

The experimentally measured current-voltage data were used to plot the current-voltage characteristics for the various ZnO varistor samples. Figure 3 shows the various distinct regions current-voltage curve for sample D_3.

A comparative analysis of these characteristics with those in the literatures (Lagrange, 1991; Harris, 1999; Brass, 2004) shows similar behaviour confirming that the developed samples had varistor properties similar to the foreign ones. From the I-V characteristic curves the varistor voltage occurs at 1mA dc for all ZnO samples. Above this voltage, the varistor action takes place by providing an alternative path for the surge current to flow. During this action theresistance of the varistor which was initially high during low voltage operation reduces to a very low value when transient over voltage occurs. The nonlinearity in this region is high. Figure 4 shows a family of current-voltage characteristics curves for all the ZnO varistor samples C. The curves for all samples were similar, but they have different electrical properties which depend on the chemical composition, thickness, surface area and volume.

Using the V-I characteristics curve for each of the ZnO varistor samples, the voltage-clamping ratio was computed for all the samples. These ratios were approximately 1 for most of the zinc oxide varistors samples, which was in agreement with the voltage-clamping ratio of the foreign made ZnO varistor computed from experimental data and in the literatures. As defined in the literature ((Lagrange, 1991), the closer the clamping ratio tends towards 1, the better the protective function of the ZnO varistors

A study of the voltage-clamping ratio for ZnO varistor samples shows that this value varies from one sample to another based on varistor voltage at 1mA dc and the voltage at peak current. Amongst the A samples, sample A_1 has a voltage clamping ratio of 2.48, while samples A_2 and A_3 have1.164 and 1.07 respectively.

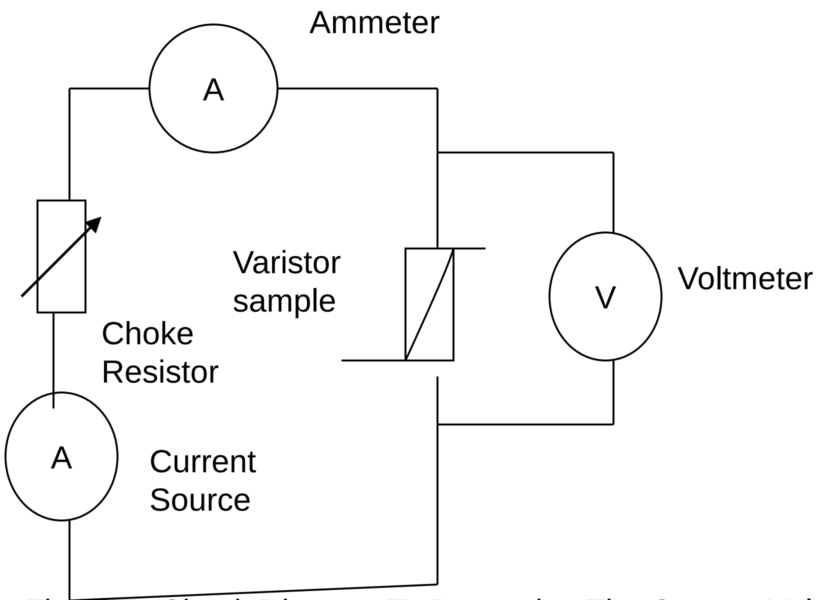


Figure 1: Circuit Diagram To Determine The Current-Voltage Characteristics Of ZnO Varistor Samples.

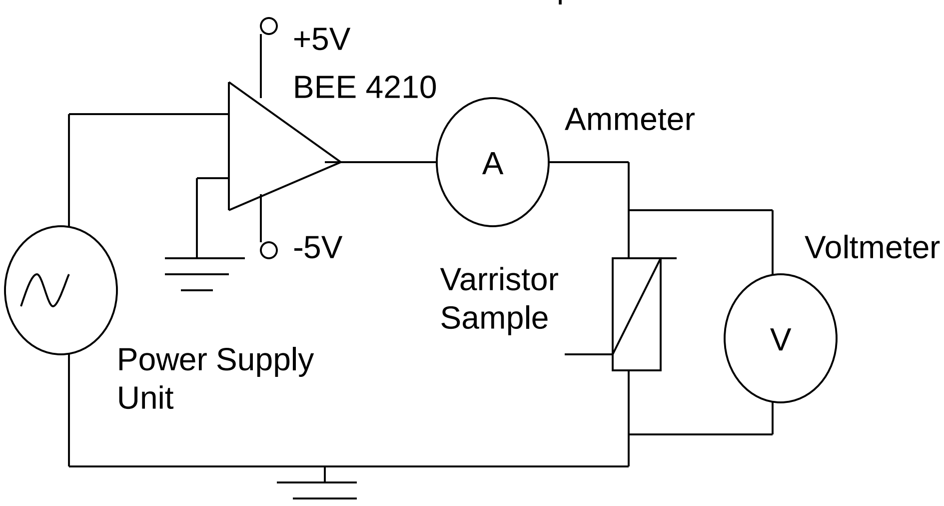


Figure 2: Circuit Diagram For Experimental Determination Of The Effect Of Frequency On ZnO Varistor Samples.

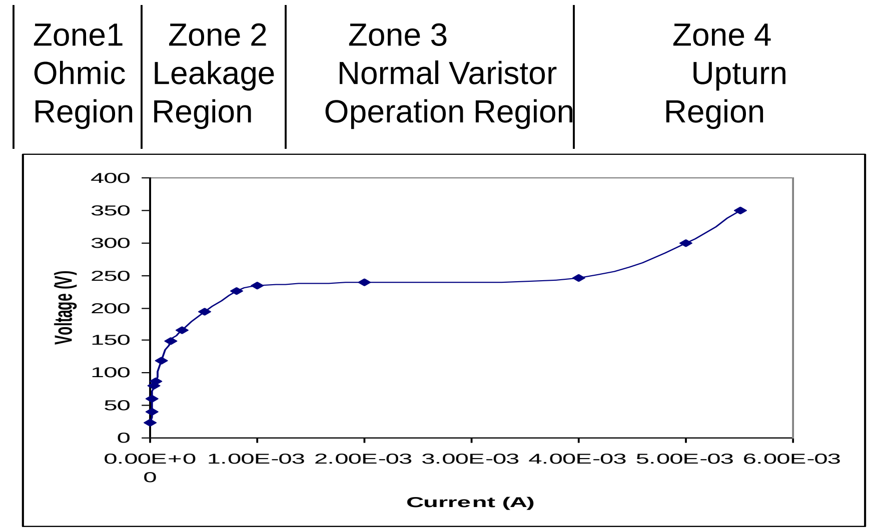


Figure 3: Current-Voltage Characteristics For ZnO Varistor (Sample D_3).

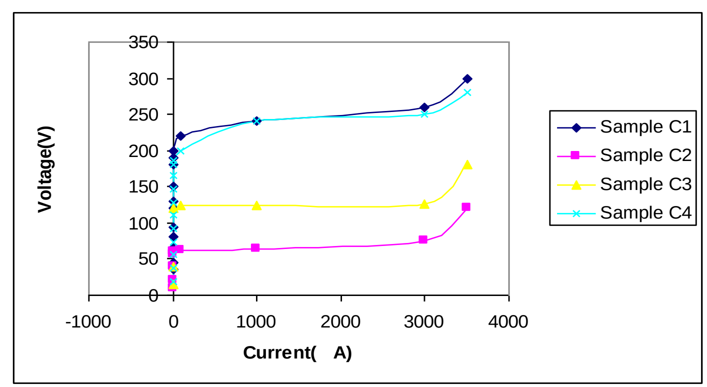


Figure 4: Current-Voltage Characteristics For ZnO Varistors(Sample C).

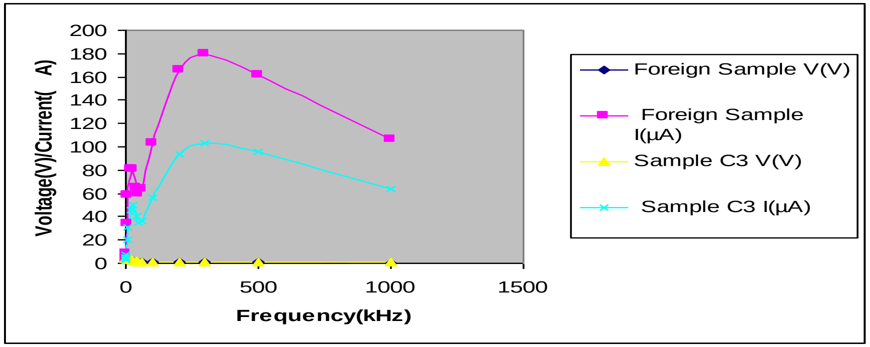


Figure 5: Comparison Of The Frequency Dependence Of Voltage And Current Of Developed ZnO Varistor(Sample C_3) With The Foreign Counterpart VF10M10271K.

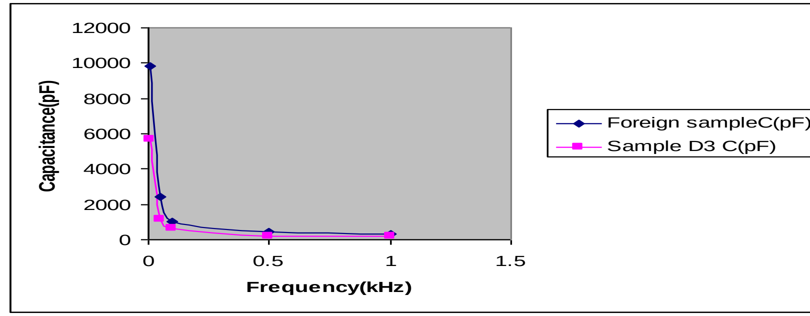


Figure 6: Comparison Of The Frequency Dependence Of Capacitance Of The Developed ZnO Varistor Sample D_3 With The Foreign Counterpart In The Frequency Range Of 0.01-1 kHz.

The varistor voltages for samples A_1, A_2 and A_3 were 1.45V, 124.6V and 280V respectively. At a peak current of 5mA, the corresponding voltage was 3.6V for sample A_1. In the case of sample A_2, at a peak current of 4mA the voltage was measured to be 145V, while for sample A_3, at a peak current of 2mA, the voltage was 300V. In samples B, only B_2 had voltage clamping ratio greater than 2. Samples C and D voltage clamping ratios were computed to be approximately 1. The varistor voltage depends solely on the thickness of ZnO varistor since, the same ZnO grain sizes were used for the samples preparation. The voltage which the varistor can withstand continuously in operation has been computed for all zinc oxide samples, which was approximately equal to $0.8V_{1mA}$ and the corresponding leakage current were in the microampere range as can be seen on the current-characteristic curves. The lower the leakage current, the lower is the dissipated power.

A comparative study of the nonlinear coefficients of all the samples shows that the highest value of α occurs near 1mA. Sample A_3 has the highest α of 13.34, while α value for A_1 and A_2 were 3.01 and 6.35 respectively. In the sample B categories, sample B_3 has highest α value of 29.2, followed by B_1 and B_2 with α value of 4.90 and 1.95 respectively. The lowest nonlinearity, α for samples C, was C_1, which had 26, while that of C_2, C_3 and C_4 were 48, 71 and 71 respectively. On the other hand α for D_1, D_2 and D_3 were 12.3, 12.4 and 8.64 respectively. These analyses shows that the nonlinear coefficients α of ZnO samples A, which was composed of purely 100% zinc oxide without any additive oxides lack the basic varistor forming ingredient, heavy elements such as Bi having a large ionic radii and varistor performance ingredient transition metal element such as Co, hence low value of α for the samples. It was observed that samples C had the highest value of α, followed by samples B. These implies that based on the chemical composition, the varistor effects were optimized in sample C with a nonlinear coefficient of about 71, followed by sample B with an α value of 29.2. This compares favourably with the imported samples with nonlinear coefficient of 50 (Levinson and Philipp, 1986; Brass, 1999).

The origin of the nonlinearities was attributed to the presence of electrostatic barriers located in the region of direct ZnO grain-to-grain contact. The barriers result from the interfacial trapping of free charges within the narrow physical boundary. From the composition, it was evident that the use of additive oxides in the composition improves the nonlinear coefficient α to a great extent, further increase in the additive oxide shows a decrease in the values of α as observed in samples D. The small additive oxides added to these materials, controls the electrical characteristics of the zinc oxide grain boundaries, and thus optimizes the varistor behavior. The number of grain boundaries between electrodes determines the varistor voltage itself. In addition to a very high value of α in sample C, high densification and stability were equally observed.

An important observation of the breakdown region for all the ZnO samples shows that it was relatively insensitive within reasonable limits to temperature, chemical composition and processing. The voltage breakdown of varistors depends on the number of barriers (thickness) in the direction of the electric field. The voltage breakdown per barrier had been defined to be 3V in the literature. However Einzinger, (Einzinger, 1975) in his varistor model postulated that potential barriers doesn't exist at each grain boundary, which implies that varistor action can be absent between two grains. He concluded that the electrical properties are closely correlated with the homogeneity of the grain size, barrier distribution and homogeneous distribution of the additives (characteristics in the bulk). Therefore applying Einzinger varistor model, the variations observed in the electrical characteristics for different samples and within the samples were due to non-uniform distribution of the barriers within the volume of the ceramic and non-homogeneity of grain size.

The better the homogeneity of barrier distribution, the better is the performance of the ZnO varistors. However, this could not be achieved under the prevailing conditions of powder preparation by conventional steps of mixing and milling the elements. To improve homogeneity of the barrier distribution and grain growth control, powder preparation by a chemical method have been recommended. Several chemical methods had been reported in the literatures. The zinc oxide grains used in all the developed ZnO samples were assumed to be of the same size. Bi_2O_3 and CoO were the only additives available for these experiments. During processing (mixing and milling) these additives were located in the intergranular layer between ZnO-ZnO grain boundaries. As a result of varistors processing, the ZnO in the ZnO varistors were semi conducting, while the intergranular layer offered potential barriers. Varistor samples A were 100% ZnO, no additives in the grain boundaries gave poor varistor action. Varistors Samples B, C and D have Bi_2O_3 and CoO as its constituents, but in different proportions. They were varied from 0.5% to 1.5%. The maximum varistors performance was observed in sample C having 1% each for the two additives used in the experiment. From the foregoing there exist limit for which additive oxides can be added for optimal varistor characteristics. Further increase of the additives beyond this limit to 1.5% in the case of sample D showed a decrease in the nonlinear coefficients α. It should be pointed out here that the Bi_2O_3 was a varistor-forming ingredient, which has effect on the basic structure, while the CoO was the varistor performance ingredient responsible for the non ohmic properties and stability of the varistor. High sintering temperature of $1260^{O}C$ and sintering time of three hours further enhanced the stability and densification of the developed ZnO varistor samples. Each additive control one or several or several parameters, such as voltage breakdown, nonlinear coefficient, surge current withstanding, surge energy absorption capability and stability. The I-V characteristic varies from sample to sample based on the powder composition. Comparatively from the families of curves, zinc oxide varistor composition of sample C has the best characteristics.

Comparatively the voltage/current-frequency characteristics depicted by the developed zinc oxide varistors with that of their foreign counterpart is identical as evident in Figure 5. The current is maxima in the vicinity of 300 kHz. These peaks are reminiscent of a (broadened) Debye resonance (Buchanan, 1991). The voltages across the varistors were fairly constant from 10Hz to 1kHz, but beyond this it decreases steadily as the frequency increases to 1MHz.

Comparing the figures of samples A to those of B, C and D having additives, it was evident that the additives to a large extent, alters the insulating resistance at the intergranular layers of the ZnO grain boundaries. The experimental results show a clear indication that the voltage and current parameters of zinc oxide varistors are frequency dependent.

The capacitance-frequency curves in Figure 6 shows that the developed ZnO varistors and their foreign counterpart exhibit analogous behaviour similar to the exponential decay curve of a discharge capacitor. The frequency dependence of capacitance of varistors limits their usage in high frequency applications (Lagrange, 1991).

The values of capacitive reactance computed from the experimental data decreases with increase in frequency, hence the decrease in voltage across the varistors. These results were virtually analogous to that described by (Levinson and Philipp, 1986). The capacitive reactance, hence the capacitance were due to the presence of insulating potential barriers on either side of each grain boundary and it depends on the surface area and thickness of the varistors. The result clearly indicates that the depletion layer largely controls the varistors low-voltage capacitance. From the results it was observed that varistors have frequency limitation, which would hinder its suitability in high frequency applications.

A Comparison of the current-voltage characteristics, nonlinear coefficients and effect of supply frequency on the capacitance for both the developed zinc oxide varistors and the imported ones exhibit analogues behaviour.Table 2 shows the comparison of the electrical parameters of the developed zinc oxide varistors. The results revealed that optimal electrical properties occurred in sample C, having a voltage clamping ratio of about 1 and highest nonlinear coefficient of approximately 71. Based on this result, it therefore means that the composition of sample C is the best formulation suitable for zinc oxide varistor production, hence sample C is recommended.

Table 2: Comparison Of The Parameters Of The Developed Zinc Oxide Varistor Samples With The Foreign One.

		A			B			C				D		
Samples of Varistor	Foreign	A_1	A_2	A_3	B_1	B_2	B_3	C_1	C_2	C_3	C_4	D_1	D_2	D_3
Voltage Clamping Ratio	1.15	2.48	1.164	1.07	1.25	2.81	1.24	1.08	1.03	1.12	1.17	1.15	1.08	1.28
Varistor Voltage(V)	280	1.45	124.6	280	40	11.19	30.3	240.5	64	125	240	36.2	120.5	235
Nonlinear Coefficient(α)	60	3.01	6.35	13.34	4.9	1.95	29.2	26	48	70.8	70.6	12.3	12.4	8.64
Nonlinear coefficient(β)	1.25	1.04	1.44	1.273	1.6	3.26	1.08	1.09	1.05	1.03	1.03	1.21	1.21	1.31
Capacitances(pF) at 1kHz)	330	2E+07	239	120	4E+06	4340	145	142	7230	290.2	425.4	2200	2E+05	162.5

CONCLUSION

A modest attempt has been made to develop an optimal composition of zinc oxide varistor in Nigeria. Optimal varistor properties were obtained in sample C with a composition of ZnO 98%, $B_{i2}O_3$ 1% and CoO 1%, having a voltage clamping ratio of 1.17, a breakdown voltage of 240volts and the non-linear coefficients α and β were 71 and 1.03 respectively.

To facilitate the growth and further work on zinc oxide varistors, the private sector is expected to assume a leadership role in mining and processing activities of the raw materials, such leadership is aided, among other variables by government support and protection. This action will promote local content development and capacity building, thereby creating employment, boast revenue and help to eradicate poverty.

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