JOURNAL OF ENGINEERING RESEARCH

Refereed and issued twice annually by the
Faculty of Engineering - University of Tripoli

Issue 27 March 2019

INVESTIGATION OF I–V ELECTRICAL CHARACTERISTICS OF SINTERED FINE-GRAINED ZINC OXIDE

Nabile Hassine and Alzaera Ali Shteep

Department of Materials and Metallurgical Engineering,
Faculty of Engineering, University of Tripoli, Libya
E-mail: nabs65@hotmail.com

الملخص

تحظى المواد ذات البنية النانومترية باهتمام بالغ وذلك لما ينتج عن استخدامها من تحسن كبير في خواص المادة مقارنة بالمواد الميكرومترية. يعدّ أكسيد الزنك (ZnO) شبه موصل من النوع السالب وله تطبيقات هندسية كثيرة من أهمها صناعة جهاز الفارستر (Varistor) والذي تتغير مقاومته الكهربية وفقاً لفرق الجهد المسّلط. الهدف الأساسي من البحث الحالي هو دراسة مدى تأثير البنية النانومترية على بعض الخواص الكهربية لعينات تمّ معالجتها حراريا (ملبّدة) من أكسيد الزنك. الخواص الكهربية المختارة شملت ما يُعرف بمعامل اللاخطية (α) حيث أنّه من الخواص الأساسية التي يجب توفرها في ZnO لكي يستخدم في انتاج الفارستر. تمت الدراسة البحثية بطحن مسحوق خشن من ZnO بواسطة طاحونة عالية الطاقة لفترات زمنية تتراوح من 5 الى 15 ساعة. وتم الحصول على مساحيق حبيباتها بحجم النانومتر وأثبتت ذلكِ القياسات والحسابات التي أجريت باستخدام تحليل حيود الأشعة السينية. هذه المساحيق النانومترية شكّلت باستخدام مكبس هيدروليكي وتم اجراء عملية التلبيد عليها عند درجات حرارة تراوحت بين 1100 و 1350 درجة مئوية في فرن عالي الحرارة لفترات زمنية امتدت من 2 الى 4 ساعات. أعلى درجة تكثيف تم انجازها كانت 86% ولكن كان هذا مصحوب بنمو حبيبي جزئي غير مرغوب فيه حيث وصل الحجم الحبيبي الى 399 نانومتر والذي يفوق الحد الأعلى وهو 100 نانومتر لكي تعتبر المادة ذات بنية نانومترية. وتضمن هذا البحث أيضا قياس خصائص التيار– فرق الجهد عن طريق مصدر طاقة عالي الفولت (DC) حيث أوضحت النتائج المتحصل عليها ظاهرة جديدة من السلوك اللاخطي لأكسيد الزنك النقي ذو البنية النانومترية. وتمّ حساب المعامل α وكانت أعلى قيمة له تساوي 6 وهذه في الواقع أقل من القيم المعروفة للفارستر التجاري والتي تتراوح بين 30 و 50. وقد يعزى هذا الى غياب أي أكاسيد أخرى مضافة وكذلك درجة التكثيف المنخفضة التي تم الحصول عليها.

ABSTRACT

Special attention has been devoted to nanostructured materials due to their potential of having greatly improved properties compared to their micro-structured counter-parts. Zinc oxide, ZnO, is an n-type semiconductor which has been applied to many practical devices such as varistors. This present research work involved the subjection of as-received coarse grained ZnO powder to high energy centrifugal ball milling for time periods ranging from 5 to 15 hours. The obtained nano-sized powder particles were characterized via X-ray diffraction analysis, XRD. These powders were then compacted into cylindrical shapes using a hydraulic press and sintered in a temperatures range 1100 to 1350°C in a high temperature furnace for holding times ranging from 2 to 4 hours. The highest degree of achieved densification was 86%, however, this came at the expense of undesired grain growth reaching a gain size of 399 nm which is well above the upper limit of 100 nm for the material to be considered nano-grained. I-V electrical characteristics of the sintered zinc oxide samples were measured using a DC high voltage power supply

device. The results obtained showed a novel phenomenon of non-linearity for a pure nanocrystalline zinc oxide material. The highest calculated value of non-linear coefficient, α, came to be 6. This value is lower than the typical values 30 – 50 widely reported for commercial varistors. This is thought to be due to the absence of any metal oxides additives and the low degree of densification achieved.

KEYWORDS: I-V Characteristics; Nanocrystalline; Zinc Oxide; Varistor; Ball Milling.

INTRODUCTION

The basic idea behind nanotechnology is the ability to form nanoparticles, which are usually less than 100 nm in size. Another more specific definition states, that nano-materials would be those that have properties which depend inherently on their size, and such properties can be significantly different when compared to the properties of micro-sized or bulk materials [1]. Nanometer sized powder particles, prepared by the method of high energy ball milling, has resulted in a new class of ultrafine-grained materials. These nanocrystalline materials typically have grain sizes ranging from about 19 to 47 nm and can exhibit properties that are very different from those of conventional materials [2]. Zinc oxide (ZnO) has received much attention over the past few years because it has a wide range of properties including a range of conductivity from metallic to insulating, it has a high transparency, piezoelectricity, wide band gap semi-conductivity, room-temperature ferromagnetism, and huge magneto-optic and chemical-sensing effects.

Zinc oxide and zinc-oxide-based powders have been widely studied recently because of their unique optical and electrical/electronic properties and thus they can be used in many demanding technological applications, such as low-voltage varistors [3].

In order to obtain high-quality zinc oxide powders with fine particle size, narrow size distribution and special morphology, various preparation techniques have been used to synthesize ultrafine zinc oxide powders, including precipitation, sol–gel, micro emulsion, etc. One of the success stories of solid-state ceramics is the development of zinc oxide varistors. Varistors are defined as voltage-dependent resistors (VDR) used as protective devices to regulate transient voltage surges of unwanted magnitudes. Unwanted over-voltage transient surges normally refer to damaging voltage transients that exceed more than 10% of the operating voltage of the equipment being protected. Zinc oxide varistors have now become commodity items and mass-produced in many countries [4-8].

The main objectives of the present work included the following;

- Measurement of the conduction non-linear coefficient, α, of sintered Nano-grained zinc oxide bodies. The higher the value of α, the better the varistor is and the higher the protection level.
- Studying the compaction and sintering of Nano-zinc oxide at a range of temperatures and holding times to determine the optimum sintering conditions that produce the least grain growth,
- Relating the obtained electrical characteristics to the sintered nanostructure of the zinc oxide samples.

EXPERIMENTAL WORK

Materials

As received zinc oxide (ZnO) powder of high purity was used as the starting powder in the present work manufactured by the (BDH) Laboratory supplies, PooleBH15 1TD, England. The chemical composition of the ZnO powder is as given in Table (1) shown below.

Table 1: Chemical composition of as-received ZnO powder

Chemical element or compound	Weight (%)
Chloride	0.001
Nitrogen compounds	0.0005
Sulphate	0.01
Arsenic	0.01
Cadmium	0.0001
Calcium	0.005
Copper	0.001
Iron	0.0005
Lead	0.0005
Manganese	0.002
Nickel	0.002
Sodium	0.0005

The trace impurities give a total of 0.0316 wt.% and hence the degree of purity of ZnO powder is over 99.96 %. The powder granules had an initial overall average crystallite size of about 0.1645μm, and a density of 5.606 g/cm^3. The crystallite size was determined via the use of X-ray diffraction analysis and calculated by a modified Scherrer equation. Figure (1) shows the XRD pattern for the as-received zinc oxide powder.

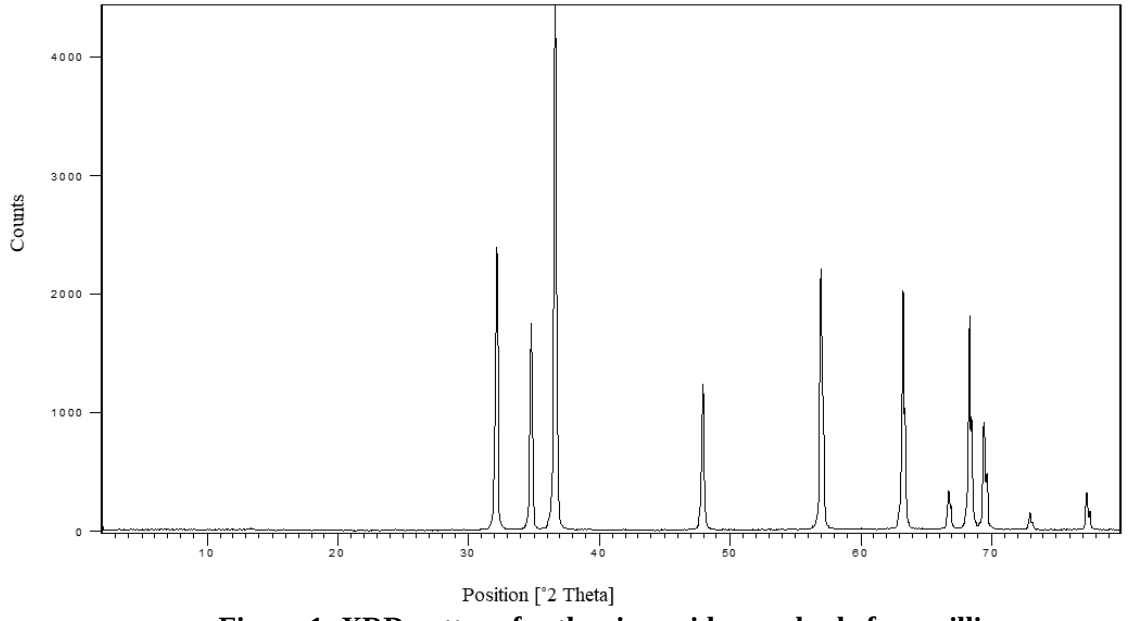

Figure 1: XRD pattern for the zinc oxide powder before milling.

Mechanical Milling

Milling of zinc oxide powder was performed using a high energy centrifugal ball mill [Model S100, Retsch GmbH]. Dry milling was carried out in a 250 ml steel jar using hardened steel balls weighing about 500 grams as the grinding medium. The jar was loaded with a fixed amount of 50 grams of ZnO powder for all runs. The ratio of the weight of steel balls to zinc oxide powder was chosen to be 10:1. This ratio is taken to be high in order to minimize the chance of adhesion of powder particles together and also due to the fact that the quantity of the material to be milled should not exceed approximately 1/3 of the grinding jar volume. Grinding was carried out for a varying time periods of 5, 10, and 15 hours.

X-Ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) was used to estimate the crystallite size of the milled powder particles. The XRD patterns were taken using a computerized X-ray Diffractometer (Model: PW 1800 of M/s Philips NV, Holland) at the Petroleum Research Centre, Tripoli. All X-ray diffract grams were taken by Cu-Kα radiation (wavelength, λ = 0.15405 nm) at a scanning speed of 0.10 per second in 2θ. A tube voltage of 40 kV, a tube current of 30 mA, and a time constant of 10 seconds were used. The fine powder was run at 0.0200 °θ step and scan step time of 0.5000.

Scherrer equation, $L = K\lambda / \beta \cos\theta$, was developed in 1918, to calculate the nano crystallite size (L) by XRD radiation of wavelength λ (nm) from measuring full width at half maximum of peaks (β) in radian located at any 2θ in the pattern. Shape factor of K can be 0.62–2.08 and is usually taken as about 0.89. But, if all of the peaks of a pattern are going to give a similar value of L, then $\beta\ cos\theta$ must be identical. This means that for a typical 5 nm crystallite size and $\lambda\ Cu\ k\alpha_1$ = 0.15405 nm, the peak at $2\theta = 170°$ should be more than ten times wide with respect to the peak at $2\theta = 10°$, which is never observed. A Modified Scherrer equation [9] plots ln β against $ln(1/cos\theta)$ and obtains the intercept of a least squares line regression, $ln = K\ \lambda\ /\ L$, from which a single value of L is obtained through all of the available peaks. This novel technique is applied for calculating the average crystallite size of the milled zinc oxide powder.

Compaction Process

Powder samples were compacted in a die by a hydraulic press into the shape of a cylinder of a radius of 0.5 cm and about 1.6 cm height using a selected pressing pressure of 27.5 MPa. Values of compaction pressure reported in the open literature ranged from 25 to 60 MPa [6], however, initial pressing trials showed that the selected value mentioned above was most suitable as it produced cohesive and un-cracked green bodies.

Sintering Process

Sintering trials of the green shaped powder samples were carried out at holding temperatures of 1100, 1300, and 1350°C and using periods of soaking time of 2, and 4 hours with a heating rate of 15°C/min. At the end of each of the soaking time periods, the

furnace would be switched off and the sample left to cool inside. This was done for the purpose of determining the optimum conditions of sintering temperature and time. The sintering runs were performed in a conventional high temperature sintering furnace, (Nabertherm Gmbh) with a maximum working temperature of 1400°C.This part of the present study involved the sintering of green shaped cylindrical bodies made from the ZnO powder batch which was milled for 10 hours and had an overall average particle size of 52 nm. The latter Nano-particulate powder was selected for the sintering trials as it had a lesser degree of iron contamination compared to the powder batch with the particle size of 12 nm. The other remaining batch of milled powder had a much larger particle size of 99 nm which is too close to the allowed upper limit. For powders particles to be classified as Nano-sized they must have a particle size less than 100 nm. Sintering runs were carried out at temperatures ranging from 1100 to 1350°C and for holding times of 2 and 4 hours as shown in Table (2).

Table 2: Densification (%) and grain size of sintered samples (Initial powder particle size 52 nm)

Sample Designation	Sintering Temp. (°C)	Holding Time (hours)	Densification (%)	Sintered samples grain size (nm)
A	1100	2	70	42
B	1300	4	80	203
C	1350	4	86	399

Densification (%) was calculated by dividing the bulk density of the sintered samples by the theoretical density of ZnO. The bulk density, in turn, was obtained simply by dividing the mass of sintered samples by their volume. While, grain sizes of the sintered samples were calculated via the use of the modified Scherrer equation with the required data being obtained from the samples XRD patterns. Reflective properties it is also used in sunblock's and can often be seen on the nose and lips of lifeguards at the beach.

Electrical Properties (I-V Curves) Measurement

Current-Voltage Characteristic Curves or simply I-V curves of an electrical device or component, are a set of graphical curves which are used to define its operation within an electrical circuit. As the name suggests, the curves show the relationship between the current flowing through an electronic device and the applied voltage across its terminals. These curves need not be a straight line. There are resistive elements such as varistors, and even the light bulb, whose I-V characteristic curves are not straight or linear lines but instead are curved or shaped and are therefore called non-linear devices because their resistances are non-linear.

Zinc oxide without any additives, such as the powder used in the present work, is a non- stoichiometric n-type semiconductor with linear I–V behavior. I–V electrical characteristics of sintered zinc oxide samples were measured using a DC high voltage

power supply device. The non-linear coefficient (α) was determined from the obtained I-V curves. The ZnO sintered test specimens were prepared from nanocrystalline powders as it is well known that finer grain size would lead to a higher value of α. This is one of the properties required for a good and an efficient varistor.

RESULTS AND DISCUSSION

The Prepared Nano-Crystalline Zinc Oxide Powder

The as-received zinc oxide powder was subjected to high energy ball milling to convert it to Nano-sized powder and the results obtained are as given in Table (3).

Table 3: XRD Crystallite size of nano-crystalline powder

Milling time (hours)	Crystallite size (nm)
5	99
10	52
15	12

The conversion of the initial coarse powder to the nanometer size was found to be possible using a high energy ball milling technique using variously sized steel balls as a grinding medium. This sort of grinding medium appears to reduce the problem of the powder caking onto the sides of the mill and not receiving any further size reduction. In other words, the use of differently sized steel balls as the grinding medium seems to facilitate the subjection of powder particles to continuous impact and size reduction leading eventually to the required Nano-sized particles. The crystallite size was successfully reduced to the size range of 99 to 12 nm over an increasing milling time from 5 to 15 hours. However, a colour change of the milled powder was observed as a result of the grinding process. The powder sample was originally white, and after 5 hours of grinding it became pale yellow. The colour got even darker after grinding for the longer period of 10 hours. This colour change may possibly be due to iron contamination picked up from the steel balls grinding medium during milling. Iron contamination is most severe in high energy mills like the one used in the present research work. One measure of reducing contamination is by coating the grinding media steel balls with the product powder. Using as short milling times as possible can also be helpful [10-12].

The obtained sizes are all less than 100 nm and hence the powder can be considered as Nano-sized and should have the potential advantages and properties improvement exhibited by nanomaterials. Achieving this aim of obtaining Nano-crystalline powder is highly significant, since the main theme of the present work is to investigate the influence of Nano-structure on the non–linear coefficient, α, of sintered ZnO bodies. This is one of the essential properties required for the application of ZnO in the manufacturing of varistors.

An illustration of the computer software used for the crystallite size calculations is shown in Figure (2).

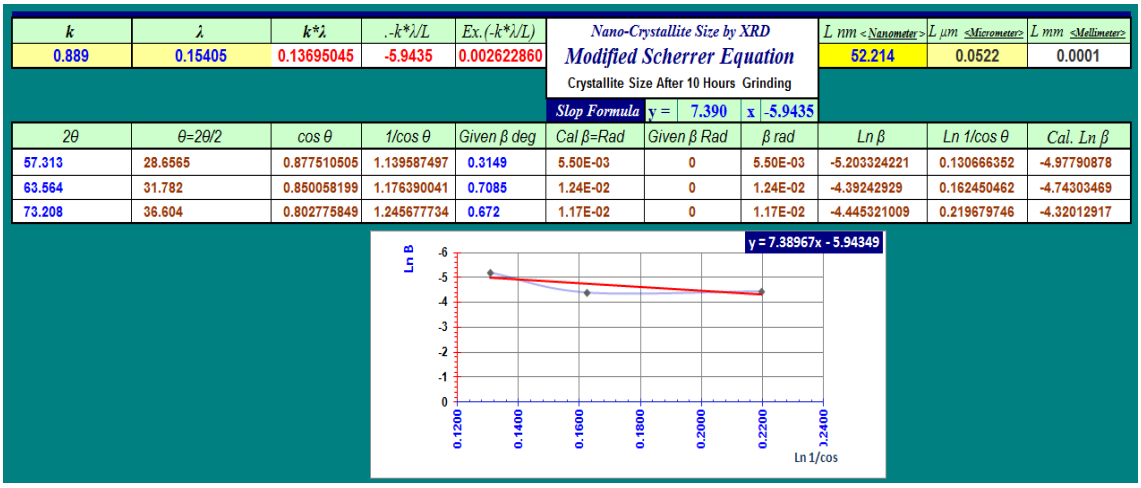

Figure 2: Computerized calculations of Nano-powder crystallite size

The XRD pattern for the powder milled for ten hours is shown below in Figure (3).

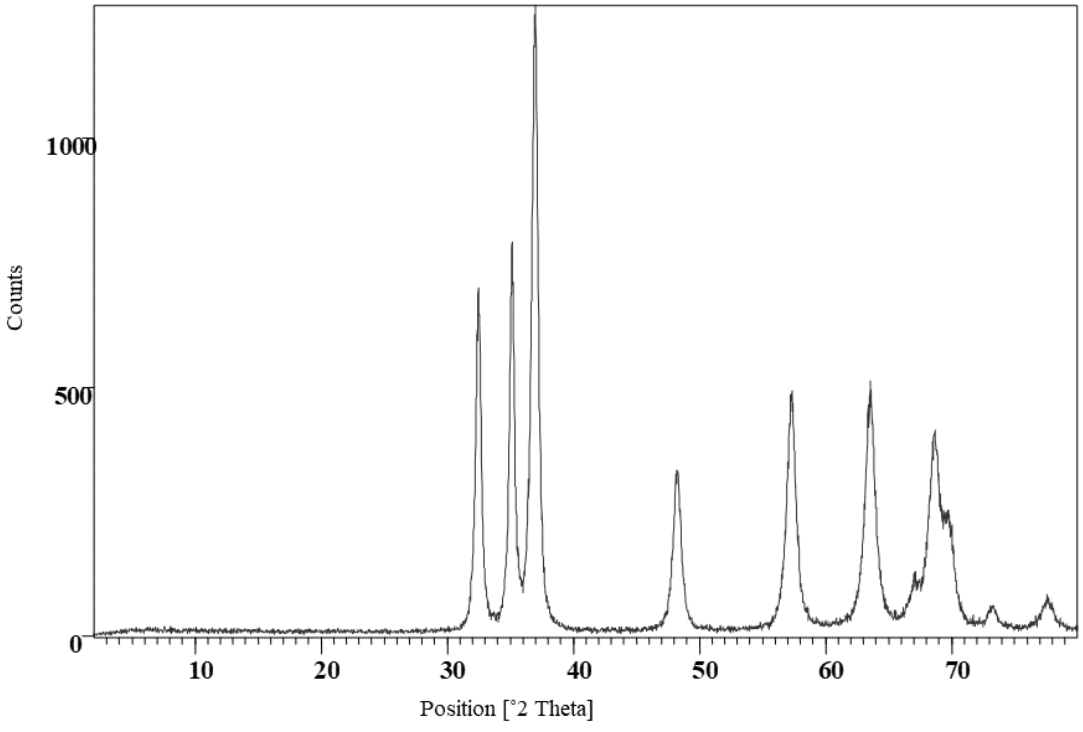

Figure 3: XRD pattern for the powder milled for 10 hours

Figure (4) shows the XRD pattern for sample (C).

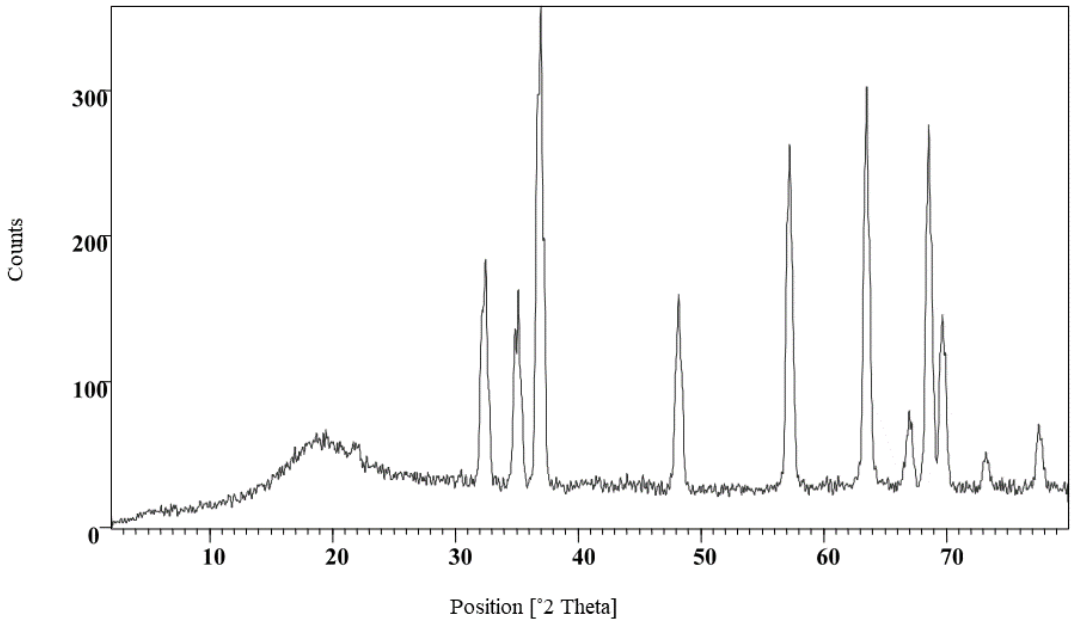

Figure 4: XRD pattern for sample (C)

Sintering Trials

As can be seen from Table (2), significant grain growth occurred as the sintering temperature increased to 1350°C and the highest densification achieved being 86%. Hence, sintered specimen's B and C cannot be considered as nanostructured. On the other hand, specimen A is within the nan grained range, however, the densification is low 70% and therefore is not expected to have any significant practical applications [13-16].

The present work results further prove the widely reported difficulty in achieving full densification while maintaining Nano-grained structure. Because of their small size, nanocrystalline particles are quite susceptible to the formation of interparticle London – van der Waals bonds, in either the wet or dry state. Even if no bonds are formed during synthesis, the van der Waals attraction can cause the powder particles to bond together into agglomerates during handling, drying, or storage. The compaction of these agglomerates then produces an inhomogeneous particle packing structure within the green body and poor green density [17,18]. Once a powder compact is made, it needs to be densified. The primary method of doing so is by applying heat (with or without added pressure) to reach the elevated temperatures necessary to allow significant diffusion to take place. Unfortunately, the fact that diffusion is required for densification leads to a fundamental problem. Grain growth also occurs by the same mechanism, i.e. diffusion, and so it is difficult to plan a sintering strategy that encourages densification without simultaneously stimulating grain growth. Unfortunately, this is exactly what is needed to produce fully dense ceramics with a less than 100 nm grain size; i.e. a decoupling of the densification and grain growth processes during sintering. One technique is simply to add solutes or second phase particles to a single phase ceramic, to reduce grain boundary mobilities or to pin grain boundaries, respectively.

For the present work, ZnO powder had no solutes nor second phase particles. The intention was to investigate the influence of the nano-size of powder particles on electrical properties without having any other factors which might influence these properties in one way or another. And since no second phase was added, solid state sintering was the

operative mechanism and liquid phase sintering was not applicable to the present work system.

Electrical Properties Measurement

ZnO is a very important material for varistors. Its extra conduction nonlinearity is due to the special current – voltage characteristics of the special grain boundary phase, which is formed by diffusion of additives such as Bi_2O_3 and Sb_2O_5. However, it is well known that pure ZnO, as the material used in the present research work, is a semiconductor with linear conduction. The current – voltage measurements were carried out on the sintered ZnObulk samples A, B, and C using an adjustable DC power supply operating in the range 0 – 900 V. The non – linear exponent (α), Table (4), was determined for each sample from I-V plots (as in Figure (5) which shows the I-V plot for sample (C) using current values 0 – 6000 µA.

Table 4: Non-linear coefficient (α) values as a function of sintered samples grain size.

Sample Designation	Sintered samples grain size (nm)	Non-linear coefficient (α)
A	42	2
B	203	2
C	399	6

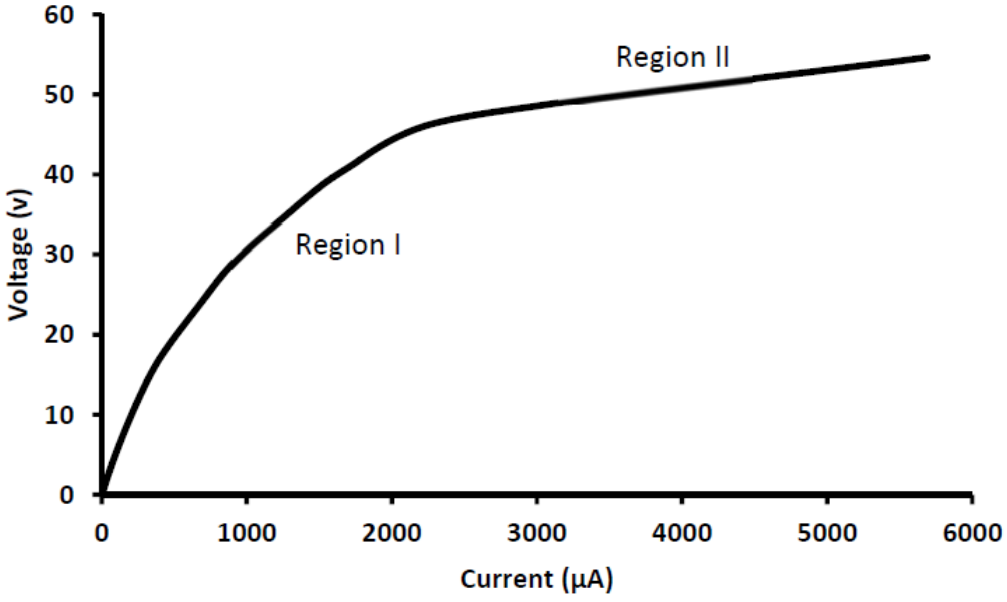

Figure 5: I-V plot for sample C

The obtained plot for the present work, pure nanocrystalline ZnO, material show a novel phenomenon of non-linear I-V characteristics. The curve for sample C show the regions I and II typically exhibited by commercial varistors. However, region III, which would give the ZnO material break down voltage, was not reached by the present work specimens. The latter over-heated due to the Joule heating effect and the test runs had to be abandoned.

It is well known that the proportion of grain boundaries has a pronounced effect on the properties of ZnO varistors [6,19]. The larger number of grain boundaries present in the fine-grained research work sintered samples and the anticipated special amorphous boundaries phase may possibly be the reasons behind the observed novel phenomenon of non-linearity.

The degree of non-linearity (represented by the nonlinear coefficient, α) is determined by the flatness of the nonlinear region, the flatter the I-V curve (i.e., the greater α) in this region, the better the device.

The non-linear coefficient was calculated to be 6 for the highest densified, 86 % sintered, sample with an overall grain size of 399nm (or 0.399 μm). The commercial varistors typically have a grain size of 10–100 μm with a non-linear coefficient values ranging from 30 to 50. The obtained value of non-linear coefficient is clearly lower than that of commercial varistors. This may possibly be due to firstly the absence of any additives of metal oxides and a second factor could be the fact that the highest densification achieved is far from full densification required for good and acceptable varistor properties. Hence, for a fair assessment of the influence of nano-crystalline structure on varistor properties to be made, a much greater effort has to be expended in order to produce fully dense, nano-grained ZnO material [6].

CONCLUSIONS

Based on the present research work, the following conclusions may be drawn;

- Nano-sized powder may be obtained by subjecting the starting coarse ZnO powder to high energy centrifugal ball milling for 5 to 15 hours, with the 10 hour time period being considered the optimum milling time. Milling for longer periods of time has the disadvantage of picking up increased amounts of iron contamination.
- Grain growth became significant in the ZnO samples conventionally pressure-less sintered at temperatures of 1300-1350 °C with the highest densification achieved being 86%.
- The measured I-V plots for the present work, pure nanocrystalline ZnO material, showed a novel phenomenon of non-linear I-V characteristics. The obtained curves had the same regions I and II typically exhibited by commercial varistors.
- The non-linear coefficient, α, for the present research work (ZnO) material was calculated to be 6 which is clearly lower than that of commercial varistors (30-50). This may possibly be due to the absence of any additives of metal oxides and the relatively low degree of densification achieved.

ACKNOWLEDGEMENTS

The authors would like to thank Eng. Lotfi Suissi, Civil Eng. Dept., Tripoli University, for his help and assistance with the hydraulic pressing machine. Thanks are also extended to Eng. Asma Marie, Oil Research Centre, and Dr. Siddiq Al-Zindah, Materials and Metallurgical Eng., Dept., Tripoli University for their kind help with the X-ray diffraction technique measurement and analysis. Sincere thanks are also due to Dr. Khaled Dadesh, Electrical Eng. Dept., Tripoli University, for his assistance with I-V electrical measurements.

REFERENCES

[1] Leach, C., "Crystal plane influence of the EBIC contrast in zinc oxide varistors", J. European Ceramic Society, Vol. 21, 2001, pp. 2127-2130.

[2] Koch, C., and Cho, Y., "Nanocrystals by high energy ball milling", J. Nanostructured Materials, Vol. 1, 1992, pp. 207-212.

[3] Ivanchenko, A. V., et al., "Desorption thermal degradation model of zinc oxide ceramics", J. European Ceramic Society, Vol.24, 2004, pp. 3709-3712.

[4] Suvaci, E., and Özer, İ., "Processing of textured zinc oxide varistors via templated grain growth", J. European Ceramic Society, Vol. 25, 2005, pp. 1663-1673.

[5] Leach, C., et al., "The effect of sintering temperature variations on the development of electrically active interfaces in zinc oxide based varistors", J. European Ceramic Society, Vol. 20, 2000, pp. 2759-2765.

[6] Gao, L., et al., "Preparation and electric properties of dense nanocrystalline zinc oxide ceramics", J. Am. Soc., Vol. 85, No. 4, 2002, pp. 1016-1018.

[7] Žunić, M., et al., "ZnO varistors from intensively milled powders", J. European Ceramic Society, Vol. 27, 2007, pp. 3897-3900.

[8] Hynes, A., et al., "Sintering and characterization of nano-phase zinc oxide", J. Am. Soc., Vol. 85, No. 8, 2002, pp. 1979-1987.

[9] Monshi, A., et al., "Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD", World Journal of Nano Science and Engineering, Vol. 2, 2012, pp. 154-160.

[10] Benchelia, S., et al., "Synthesis, characterization and cytotoxic effect of ZnO nanoparticles obtained by mechanical alloying", J. New Technology and Materials, Vol. 4, 2014, pp. 34-40.

[11] Ketabchi, M., and Parvin, N., "Nanocrystalline/nanoparticle ZnO synthesized by high energy ball milling process", Materials Letters, Vol. 86, 2012, pp. 122-124.

[12] Salah, N., et al., "High-energy ball milling technique for ZnO nanoparticles as antibacterial material", International J. Nanomedicine, Vol. 6, 2011, pp. 863-869.

[13] Gupta, T., and Coble, R., "Sintering of ZnO: I, densification and grain growth", J. Am. Ceram. Soc., Vol. 51, 1968, pp. 521-525.

[14] Gupta, T., and Coble, R., "Sintering of ZnO: II, density decrease and pore growth during the final stage of the process", J. Am. Ceram. Soc., Vol. 51, 1968, pp. 525-528.

[15] Senda, T., and Brandt, R., "Grain growth in sintered ZnO and ZnO-Bi_2O_3 ceramics", J. Am. Ceram. Soc., Vol. 73, 1990, pp. 106114.

[16] Chu, M., et al., "Effect of heating rate on sintering and coarsening", J. Am. Ceram. Soc, Vol. 74, 1991, pp. 1217-1225.

[17] Mayo, M. J., "Processing of nanocrystalline ceramics from ultrafine particles", J. Int. Mater. Rev, Vol. 41, 1996, pp. 85-115.

[18] Gleiter, H., "Nanostructured materials: basic concepts and microstructure", Acta Mater, Vol. 48, 2000, pp. 1-29.

[19] Kiselev, A., et al., "High-resolution electron microscopy of ZnO grain boundaries in bicrystals obtained by the solid-phase intergrowth process", Philos. Mag. A, Vol. 76, 1997, pp. 633-55.