Jurnal Teknologi

Full Paper

EFFECT OF MnO_2 DOPING ON NONLINEAR COEFFICEINT OF ZN-BI-TI-O VARISTOR CERAMICS

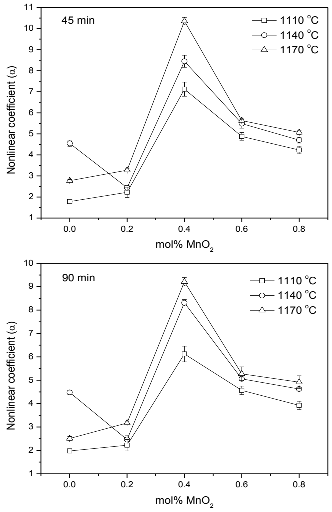
Mohd Sabri Mohd Ghazali[a*], Wan Rafizah Wan Abdullah[b], Azmi Zakaria[c], Zahid Rizwan[d], Khamirul Amin Matori[c], Mohd Hafiz Mohd Zaid[c]

[a]School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
[b]School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia
[c]Department of Physics, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[d]Department of Applied Sciences, Convener Purchase, National Textile University, Faisalabad (37610) Pakistan

Article history
Received
15 August 2015
Received in revised form
15 November 2015
Accepted
30 December 2015

*Corresponding author
mohdsabri@umt.edu.my

Graphical abstract



Abstract

The work aims the improvement of nonlinear coefficient (α) can achieve by the addition of MnO_2. The investigation regarding to the α variation of MnO_2 doping on ZnO-Bi_2O_3-TiO_2 system is discussed. The crystalline phases were identified by an XRD (PANalytical (Philips) X'Pert Pro PW3040/60) with CuKα radiation and the data were analyzed by using X'Pert High Score software. The density of varistor ceramics was measured by the geometrical method. The current-voltage characteristics of the varistor ceramics were evaluated. The average grain size (d) was determined by lineal intercept method. The α of ZnO doped with 0.5 mol% of Bi_2O_3, 0.5 mol% of TiO_2 and x mol% of MnO_2 was calculated from data analysis of current-voltage characteristics obtained through a Source Measure Unit (Keithley 236). The calculation of α is done by using Origin Pro8.0 software which at low concentration at 1170 °C has the value 10.36 and 9.21 at 45 and 90 min sintering time, respectively, and then decreases to 5.63 and 5.27 at 0.8 mol% MnO_2 concentrations. The addition of MnO_2 dopant in Zn-Bi-Ti oxide ceramics sintered at 45 minutes cause the value of α to increase up to 0.4 mol% and decrease after further addition.

Keyword: Electrical properties, MnO, Sintering, ZnO varistors

Abstrak

Penyelidikan ini bertujuan meningkatkan pekali ketaklinearan (α) boleh dicapai dengan penambahan MnO_2. Siasatan mengenai variasi α dengan pendopan MnO_2 pada sistem ZnO-Bi_2O_3-TiO_2 dibincangkan. Fasa-fasa hablur telah dikenal pasti oleh XRD (PANalytical (Philips) X'Pert Pro PW3040/60) dengan sinaran CuKα dan data dianalisis dengan menggunakan perisian X'Pert High Score. Ketumpatan seramik varistor diukur dengan kaedah geometri. Ciri-ciri arus-voltan daripada seramik varistor telah dinilai. Purata saiz butiran purata (d) telah ditentukan dengan kaedah pintasan lurus. α ZnO didopkan dengan 0.5 mol% Bi_2O_3, 0.5 mo%l TiO_2 dan x mol% daripada MnO_2 dikira daripada analisis data pencirian arus-voltan diperolehi melalui Source Measure Unit (Keithley 236). Pengiraan α dilakukan dengan menggunakan perisian Origin Pro8.0 pada kepekatan rendah pada 1170 °C mempunyai nilai 10.36 dan 9.21 pada 45 dan 90 min masa pensinteran, masing-masing, dan kemudian berkurangan kepada 5.63 dan 5.27 pada 0.8 mol% kepekatan MnO_2. Penambahan pendopan MnO_2 dalam Zn-Bi-Ti seramik oksida disinter pada 45 minit menyebabkan nilai α meningkat sehingga 0.4 mol% dan berkurangan selepas penambahannya lagi.

Kata kunci: Sifat-sifat elektrik, MnO, pensinteran, varistor ZnO

1.0 INTRODUCTION

Zinc oxide (ZnO) varistors are polycrystalline ceramics that consist of ZnO as the base and traces of additives as dopants. A unique feature of grain boundaries is created in the ceramics during sintering and they are responsible for determining the nonlinear current-voltage (*I-V*) characteristics of the device [1, 2]. The varistors are useful for protecting a variety of electrical equipments against voltage surges and they can operate repeatedly without damage. Nowadays, rapid developments of micro-electronic technology and large-scale integrated circuits have encouraged the production of varistors for low-voltage applications in automobile and semiconductor electronics.

Small amount of essential metal oxides such as Bi_2O_3, TiO_2, Co_3O_4, MnO and Sb_2O_3 is required in varistor formulations for enhancing the nonlinear response and improving the stability of ZnO varistor against aggressive operating conditions [3-8]. The addition of Bi_2O_3 can increase the low-voltage resistivity of polycrystalline ZnO and it acts as a sintering aid due to the formation of a ZnO-Bi_2O_3 eutectic at 750 °C [9]. The highly non-ohmic behavior in varistor is related to mechanism involving the grain boundaries and the associated defect concentration gradients [10]. The above mentioned additives are the main components required for improving the nonlinear response and the stability of ZnO varistor [11-17]. This paper presents the influence of Mn dopant on surface morphology and nonlinear coefficient in Zn-Bi-Ti oxide system.

2.0 METHODOLOGY

Oxide precursor powders (Alpha Aesar, USA) of 99.9% purity were used. Samples were prepared by solid state route ceramic processing. Based on nominal composition of (100-0.5-0.5-x) mol% ZnO +0.5 mol% Bi_2O_3+0.5 mol% TiO_2+x mol% MnO_2, with x are 0.2, 0.4, 0.6 and 0.8. The mixtures of oxides powder were milled with zirconium balls and deionised water for 24 h. After that, the mixture was dried at 150 °C for 24 h and followed with pre-sintering at 800 °C for 2 h. 1.75 wt.% polyvinyl alcohol (PVA) binder was added and the granulated was sieved with 75 μm mesh screen to produce a starting powder. Finally, the powder was pressed into discs of 10 mm in diameter and 1 mm in thickness approximately at a pressure of 2 tons and sintered at 1110, 1140 and 1170 °C sintering temperatures for 45 and 90 minutes sintering time with heating and cooling rate of 2.66 °C min^{-1}. Silver paste was coated on both faces 5 mm in diameter of the sample and was heating at 550 °C for 10 minute to prepare the Ohmic contact.

The crystalline phases were identified by an XRD (PANalytical (Philips) X'Pert Pro PW3040/60) with CuKα radiation and the data were analyzed by using X'Pert High Score software. The density of ceramic varistors was measured by the geometrical method [18]. The either surface of samples was lapped and ground with SiC paper and polished with 1 μm diamond suspension to a mirror-like surface. The polished samples were thermally etched. The surface microstructure was examined by SEM (JEOL JSM-6400). The average grain size (d) was determined by lineal intercept method [19], given by d = 1.56L/MN, where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of the grain boundaries intercepted by lines. The compositional analysis of the selected areas was determined by an attached EDAX microanalysis system.

The *I-V* characteristic of the ceramic varistors were evaluates using a source measure unit (Keithley 236). The varistor voltage (V_{1mA}) was measured at a current of 1.0 mA and the leakage current (I_L) was measured at 0.80 V_{1mA}. In addition, the nonlinear coefficient, α, was determined from the following Eq. 1:

$$\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \quad (1)$$

where I_1 = 1 mA, I_2 = 10 mA, and V_1 and V_2 are the voltages corresponding to I_1 and I_2; respectively.

3.0 RESULTS AND DISCUSSION

3.1 Density and Microstructure

The XRD analysis, Figure 1, reveals diffraction peaks which belong to two phases observed in XRD patterns are ZnO (ICSD code: 067454) and secondary phases, Zn_2MnO_4 (ICSD code: 039196), $Bi_4Ti_3O_{12}$ (ref. code: 00-065-2527) and $Zn_2Ti_3O_8$ (ICSD code: 083525). They were observed at all concentration except $Bi_4Ti_3O_{12}$ only seen at 0.2 mol%. Above 0.2 mol%, a few peaks of extra phase Mn_3O_4 (ref. code: 00-001-1127) were observed.

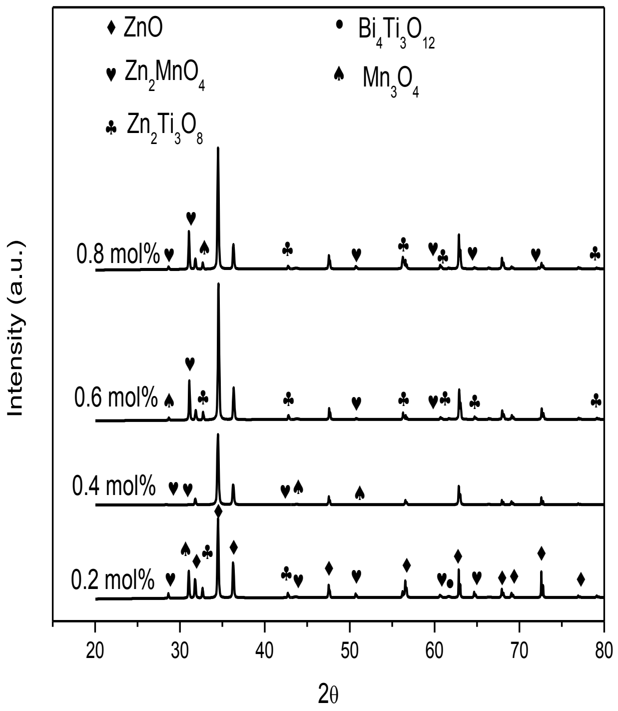


Figure 1 XRD patterns ZnO based varistor at 1140°C for 45 min sintering time at different MnO_2 dopant concentration

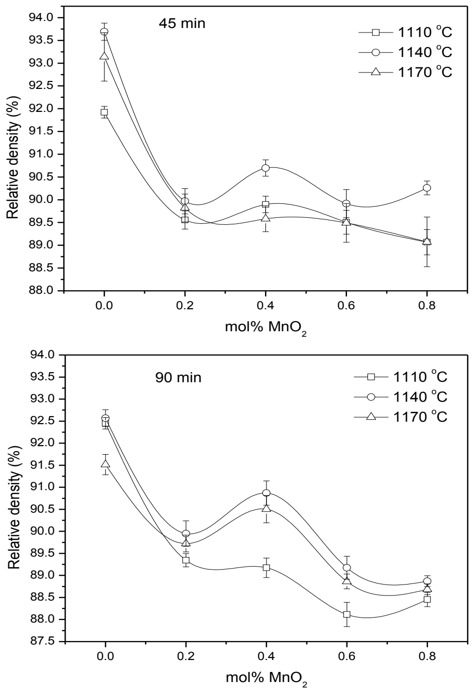


Figure 2 Relative density of 45 min (top) and 90 min (bottom)

The relative density of the ceramic without MnO_2 increases from 91.92% up to 93.69% at 1140°C and slightly decrease at 1170°C, Figure 2. Relative density is decreases when prolong sintering time. When dopant of MnO_2 is added in the ceramic the relative density decreases or remains constant with the increase of doping level at 45 minutes sintering time. However, further prolong sintering time; the relative density is decreases from 90.25 to 88.35%. This indicates the pores are increasing with the increase of sintering time. It is also observed that the overall density with the doping of MnO_2 at all sintering condition is low indicating that the MnO_2 lowering the densification manner.

Average grain size of the ceramics increases with the increase of doping level, sintering temperature and sintering time, Figure 3. It is observed and agreed that Bi_2O_3 and TiO_2 are the grain enhancer as TiO_2 is a strong grain enhancer [22, 23]. Further addition of MnO_2 average grain size increases at all doping level indicating the MnO_2 acts as a grain enhancer in this combination.

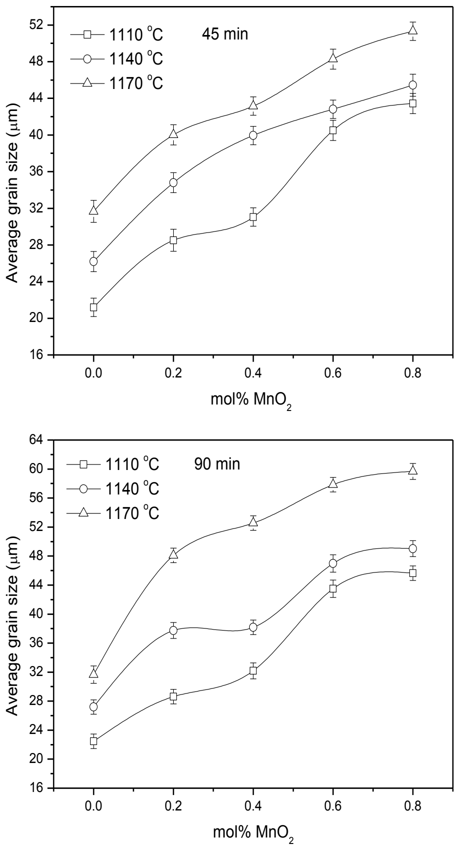


Figure 3 Average grain size of 45 min (top) and 90 min (bottom)

3.2 Nonlinear Coefficient

It is found that large as well as small grains coexists and can be seen in the SEM micrographs, Figure 4. In Figure 4, the pores are clearly observed and many have been seen at higher sintering temperature and time, as an additional proof with relative density, Figure 2. Some patches of additives can be seen in the ceramics. EDX results, Figure 5, show that the Bi is segregated in the grain boundaries at all sintering temperatures. It was found also that Mn and Ti were present near the grain boundaries; hence, this indicates that these elements are able to substitute in the ZnO lattice.

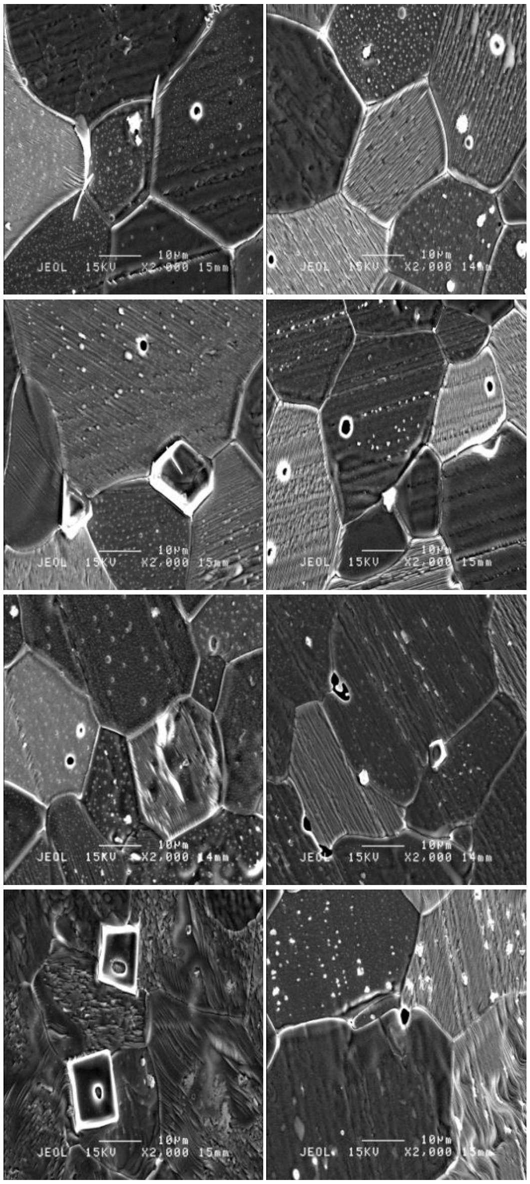


Figure 4 SEM micrographs of sintered varistor ceramics: from left (45 min) and right (90 min) from up to below is 0.2 mol%, 0.4 mol%, 0.6 mol% and 0.8 mol% of MnO_2 dopant at 1140 °C sintering temperature

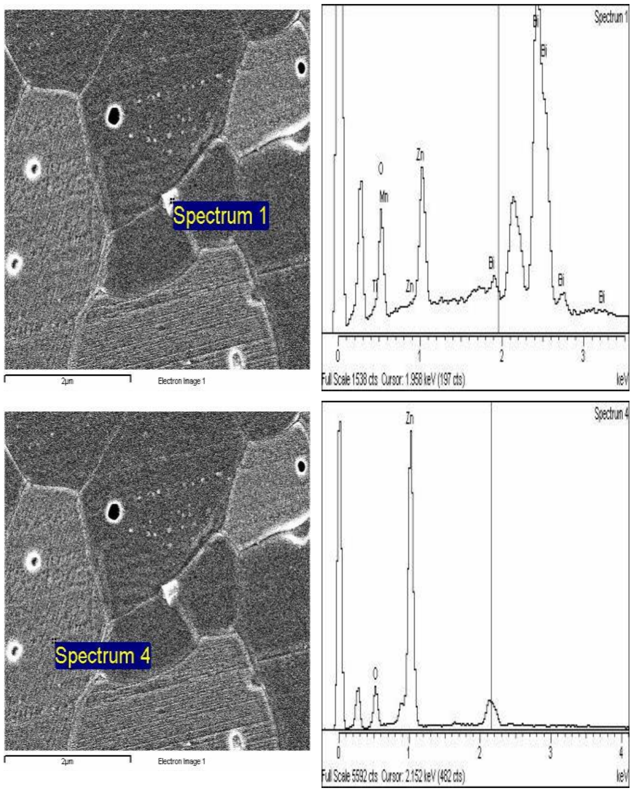


Figure 5 EDX micrographs and spectrum of varistor ceramics

Figure 6 shows α of undoped and doped ceramics with MnO_2 dopant. The α value is increasing with the increase of MnO_2 until 0.4 mol% and slightly decreases at further addition of doping level. It increases from 2.22 up to optimum value 10.36 at 1170 °C at 0.4 mol% and reduces to 4.88 to 5.63 for further addition at 45 min sintering time. At longer heat treatment (90 min), the α value increases from 2.20 up to optimum value of 9.21 at 1170 °C at 0.4 mol% and reduces to 4.57 to 5.27 for further doping. When the amount of additives is increased then the value of the nonlinear coefficient increases up to 0.4 mol% and then the value is slightly dropped after further addition. It can be seen that for this sample the incorporation of intermediate concentration, 0.4 mol%, is enough to obtain optimum α value.

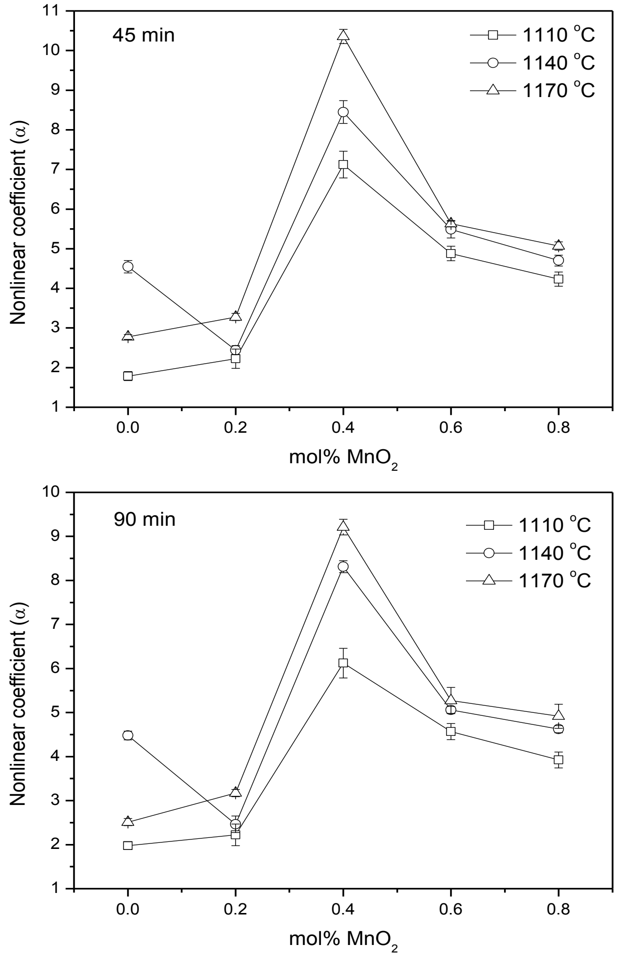


Figure 6 Variation of a of varistor ceramics at 45 min (top) and 90 min (bottom)

4.0 CONCLUSION

The evolution of surface morphology due to MnO_2 dopants was observed in the ZnO based ceramic varistors and is correlated to their electrical characteristics. The ceramic sintered sample of 0.4 mol% of MnO_2 dopant at 1170 °C for 45 minutes was found as the optimal features for Zn-Bi-Ti-Co oxide ceramics which is exhibited a of 10.36.

Acknowledgement

The authors gratefully acknowledge the financial support for this work from Research University Grant Scheme (RUGS) of Project No. 05-01-09-075RU. The corresponding author is grateful to Universiti Malaysia Terengganu and Ministry of Education for supporting the studies.

References

[1] Clarke, D. R. 1999. Varistor Ceramics. *Journal of the American Ceramic Society*. 82(3): 485-502.

[2] Souza, F. L., Gomez, J.W., Bueno, P.R., Cassia-Santos, M. R., Araujo, A. L., Leiti, E. R., Longo, E., Varela, A. J. 2003. Effect Of The Addition Of ZnO Seeds On The Electrical Properties Of ZnO-Based Varistors. *Materials Chemistry and Physics*. 80: 512-516.

[3] Matsuoka, M. 1971. Nonohmic Properties Of Zinc Oxide Ceramics. *Japanese Journal of Applied Physics*. 10(6): 736-746.

[4] Snow, G. S., White, S. S., Cooper, R. A., Armijo J. R. 1980. Characterization Of High Field Varistors In The System ZnO-CoO-PbO-Bi_2O_3. *American Ceramic Society Bulletin*. 59(6): 617-622.

[5] Eda, K. 1989. Zinc Oxide Varistor. *IEEE Electrical Insulation Magazine*. 5: 28-41.

[6] Bai S. N., Shieh J.S. and Tseng T.Y. 1995. Characteristic Analysis Of ZnOvaristors Made With Spherical Precipitation Powders. *Materials Chemistry and Physics*. 41: 104-109.

[7] Toplan O., Gunay V. and Ozkan O.T. 1997. Grain Growth In The MnO Added ZnO-6 wt% Sb_2O_3 Ceramic System. *Ceramics International*. 23(5): 251-255.

[8] Fah, C. P., Wang, J. 2000. Effect Of High-Energy Mechanical Activation On The Microstructure And Electrical Properties Of ZnO-Based Varistors. *Solid State Ionics*. 132: 107-117.

[9] Lauf, R. J., Bond, W. D. 1984. Fabricating of High-field Zinc Oxide Varistors by Sol-gel Processing. *Ceramics Bulletin*. 63 (2): 278-281.

[10] Einzinger, R. 1979. Grain Junction Properties of ZnO Varistors. *Applied Surface Science*. 3: 390-408.

[11] Fauzana, A. N., Azmi, B. Z., Sabri, M. G. M., Wan Abdullah, W. R., Hashim, M. 2013. Microstructural and Nonlinear Electrical Properties of ZnO Ceramics with Small Amount of MnO_2 Dopant. *Sains Malaysiana*. 42(8): 1139-1144.

[12] Han, J., Mantas, P. Q., Senos, A. M. R. 2001. Effect of Al and Mn Doping On The Electrical Conductivity Of ZnO. *Journal of European Ceramic Society*. 21: 1883-1884.

[13] Han, J., Mantas, P. Q., Senos, A. M. R. 2002. Varistor Behaviour Of Mn-Doped ZnO Ceramics. *Journal of European Ceramic Society*. 22: 1653-1660.

[14] Han, J., Mantas, P.Q., Senos, A. M. R. 1999. Nonisothermal Sintering Of Mn Doped ZnO. *Journal of European Ceramic Society*. 19: 1003-1006.

[15] Han, J., Mantas, P. Q., Senos, A. M. R. 2002. Deep Donors In Polycrystalline Mn-doped ZnO. *Journal of European Ceramic Society*. 75: 117-120.

[16] Han, J., Mantas, P. Q., Senos, A.M.R. 2002. Defect Chemistry And Electrical Characteristics Of Undoped And Mn-Doped ZnO. *Journal of European Ceramic Society*. 22: 49-59.

[17] Sedky, A., Sawalha, A., Abu-Abdeen, M. 2009. Electrical Conductivity Study N Pure And Doped ZnO Ceramic System. *Physica B*. 404: 1316-1320.

[18] Wang, J. F., Wen-Bin Su, Hong-Cun Chen, Wen-Xin Wang, Guo-ZhongZang. 2005. (Pr, Co, Nb)-Doped SnO_2Varistor Ceramics. *Journal of the American Ceramics Society*. 88(2): 331-334.

[19] Wurst, J. C., Nelson, J. A. 1972. Lineal Intercept Tec-Hnique For Measuring Grain Size In Two-Phase Polycrystalline Ceramics. *Journal of the American Ceramics Society*. 55: 109-111.

[20] Toyoda, T., Shimamoto, S. 1998. Effect Of Bi_2O_3 In Ceramic ZnO On Photoacoustic Spectra And Current Voltage Characteristics. *Japanese Journal of Applied Physics*. 37: 2827-2831.

[21] Suzuki, H., Bradt, R. C. 1995. Grain Growth of ZnO in ZnO-Bi_2O_3 Ceramics With TiO_2 Additions. *Journal of the American Ceramics Society*. 78(5): 1354-1360.

[22] Sabri, M. G. M., Azmi, B. Z., Zahid Rizwan, Halimah, M. K., Hashim, M., Sidek H. A. A. 2009. Application Of Direct

Current And Temperature Stresses Of Low-Voltage ZnO Based Varistor Ceramics. *American Journal of Applied Sciences*. 6(8): 1591-1595.

[23] Sabri, M. G. M., Azmi, B. Z., Zahid Rizwan, Halimah, M. K., Hashim, M., Zaid, M. H. M, Reza Zamiri. 2011. Use Of Reflectance Spectroscopy Accessory For Optical Characterization Of ZnO-Bi_2O_3-TiO_2 Ceramics. *International Journal of Molecular Sciences*. 12: 1496-1504.