International Journal of Automotive and Mechanical Engineering (IJAME)
ISSN: 2229-8649 (Print); ISSN: 2180-1606 (Online); Volume 9, pp. 1630-1638, January-June 2014

DOI: http://dx.doi.org/10.15282/ijame.9.2013.13.0135

# INVESTIGATING THE PHYSICAL AND MECHANICAL PROPERTIES OF $TIO_2$ VARISTOR MATERIALS PREPARED WITH VARIOUS DOPANTS

**I. R. Daud[1,*], S. Begum[1, 2], M. M. Rahman[1,2], S. Gholizadeh[1,2] and Z. Kothandapani[1,2]**

[1]Department of Mechanical Engineering, Universiti Tenaga Nasional
43009 Kajang, Selangor, Malaysia
Phone: +603-89212020; Fax: +603-89212065
Email: *ida.rasyada@gmail.com
[2]Centre for Advanced Materials
Universiti Tenaga Nasional
43009 Kajang, Selangor, Malaysia

## ABSTRACT

Varistors are the most efficient devices for the protection of power transmission lines and electronic devices against excessive transient surges. The current trends that require varistors with more functions have led to research to develop new ceramic varistor material and titanium dioxide ($TiO_2$) is the emerging new material. In this research nanosized $TiO_2$ was taken as the base materials to which a small amount of impurities was added as dopants for enhancing the properties. $Ta_2O_5$, $WO_3$, $Bi_2O_3$ and $Co_3O_4$ were used as dopants where the percentage of $Bi_2O_3$ and $Co_3O_4$ was fixed; 0.5% and 0.2% respectively. Samples were prepared with different weight percentages of dopants and sintered at a constant temperature of 1300˚C with 2 hour's holding time to observe the effect of these dopants on physical and mechanical properties of nanosized $TiO_2$. Analysis was undertaken to evaluate the properties of the nanosized $TiO_2$, such as green density, fired density, fired strength, axial and radial shrinkage. It was found that with the composition of 98.1% $TiO_2$+0.7% $Ta_2O_5$+0.5% $WO_3$+0.2%$Co_3O_4$+0.5%$Bi_2O_3$ have a significant influence on the physical and mechanical properties, which is anticipated to improve the performance of varistor. With the improvement in the physical and mechanical properties of $TiO_2$, the composite material has potential application in low voltage application devices.

***Keywords:*** $TiO_2$ varistor; dopants; fired density; fired strength; hardness.

## INTRODUCTION

Varistor is a ceramic material which has unique nonlinear current-voltage characteristics, and is used in circuit to protect the system against transient surge voltage. The most important characteristic of varistor is its nonlinear current voltage behavior that can be expressed by the equation $I=KV^{\alpha}$, where $\alpha$ is the nonlinear coefficient (Santana, Dos Santos, Sousa, & Chui, 2008). A higher value of this coefficient signifies a better device. Ceramics such as silicon carbide, zinc oxide (ZnO), and tin dioxide ($SnO_2$) are some of the varistors studied before (Keating & Nesic, 1999). Up to now, ZnO has been the most extensively studied due to its excellent properties, so as to be employed in both the power industry and the semiconductor industry, and shown high nonlinear coefficient than SiC (Choon, 2012). However, the use of $TiO_2$ as a semiconductor is relatively new and research is ongoing to improve its functional properties. Investigation shows that current trends require varistor to have a low capacitance and low breakdown voltage, thus the use of ZnO varistor is restricted in low voltage circuits due to its low permittivity, which weakens its ability to absorb sparks (Luo, Tang, Li, & Zhang, 2008). Titanium dioxide ($TiO_2$), also known as titania, is a versatile material with a high density (4.0 g/cm$^3$) and very low percentage of porosity that has attracted many due to properties that can satisfy the new functional demand.

In study to develop a useful $TiO_2$ based ceramic, it is important to investigate the effect of dopants on varistor performance. Up until now, study of $TiO_2$ was based on either one or two dopants to increase its properties and performance. Addition of dopants should promote properties of nanosized $TiO_2$ to increase electrical conductivity through a process of crystallization. Titanium dioxide has been investigated since 1982, by (Yan & Rhodes, 1982) who first reported the nonlinear coefficient for (Nb, Ba) doped $TiO_2$ ceramic varistor around $\alpha$=3-4 and that an oxidizing atmosphere during cooling would be necessary. According to previous researchers, tantalum pentaoxide ($Ta_2O_5$) and tungsten trioxide ($WO_3$) act as substantial donors and increase the electrical conductivity of $TiO_2$. It was observed that a high nonlinear coefficient and low breakdown voltage could be obtained by addition of $Ta_2O_5$ into the system (Luo et al., 2008). Furthermore, the addition of $WO_3$ would cause the formation of a solid solution with $TiO_2$ lattice due to ionic similarity, thus influencing the grain growth of $TiO_2$ (Su et al., 2003; Wang et al., 2012). On the other hand, cobalt (II,III) oxide ($Co_3O_4$) was reported as one of the effective dopants that promotes densification of $TiO_2$, as it creates oxygen vacancies, increases oxygen diffusion at grain boundaries, and promotes densification (Metz et al., 2007). Meanwhile, the addition of bismuth(III) oxide ($Bi_2O_3$), should promote the growth of $TiO_2$ grains and the stability of the nonlinear current-voltage by providing the medium for liquid-phase sintering (Wang et al., 2012; Xu, Cheng, Yuan, Yang, & Lin, 2011 ). There is still a lack of research and study on the effect of the addition of $Bi_2O_3$ to a $TiO_2$ powder based varistor. Although there are previous researchers who have studied the effect of various dopants towards the electrical properties of the $TiO_2$ powder based varistor, there is still a lack of research done on the physical, mechanical, and microstructural properties of nanosize $TiO_2$ based varistor. In this study the effect of dopants on the properties of $TiO_2$ ceramic was therefore examined.

## EXPERIMENTAL WORK

Nano size of titanium dioxide ($TiO_2$) based varistor with the appropriate percentage of weights dopants was prepared as shown in Table 1. The percentage of $Co_3O_4$ (ALDRICH), and $Bi_2O_3$ (ALDRICH) remained constant, and the percentage of $Ta_2O_5$ (ALDRICH) and $WO_3$ (ALDRICH) varied throughout the experiment. The mixing composition was ball milled with zirconia balls and ethanol as solvent inside a jar for one hour. The slurry produced was dried in an oven at 60°C for 24 hours. The resulting powder was sieved and pelletized into disks 20mm in diameter and 4mm thick at uniaxial pressure, 2.76MPa. The green pellet was sintered at a constant temperature of 1300°C for two hours and cooled at constant rate of 10°C/min. Samples were polished using different sizes of abrasives, followed by diamond paste, and carefully washed in water. The properties of $TiO_2$ were investigated by calculating the density and the shrinkage rate of the sample. The fired densities were determined after sintering with the Archimedes Method. Axial and radial shrinkage were also calculated based on the dimension of the pellet. For mechanical properties, the sintered strength was calculated using a Vickers hardness test machine; the Wolpert Wilson Instrument model. Samples was coated with gold to identify microstructural characterization using Scanning Electron Microscope (SEM) model Hitachi S-3400N to determine the porosity and grain size using the intercept method. The average grain size, *G*, was calculated with Eq.(1):

$$G = \text{Number of intercepts/ Line length} \quad (1)$$

The ceramic phases were identified by X-Ray Diffraction model Shimadzu XRD-6000 using Cu Kα radiation. The samples were scanned in $2\theta$ ranges of 20-60˚ for the period of a 0.02 step scan mode.

Table 1. Composition of Samples.

| Samples | Composites (wt%) |
|---|---|
| A | $TiO_2$ |
| B | $TiO_2$+0.2wt% $Ta_2O_5$+0.25wt% $WO_3$+0.2wt % $Co_3O_4$+0.5wt % $Bi_2O_3$ |
| C | $TiO_2$+0.2wt % $Ta_2O_5$+0.5wt% $WO_3$+0.2wt% $Co_3O_4$+0.5wt % $Bi_2O_3$ |
| D | $TiO_2$+0.4wt % $Ta_2O_5$+0.1wt % $WO_3$+0.2wt % $Co_3O_4$+0.5wt % $Bi_2O_3$ |
| E | $TiO_2$+0.7wt % $Ta_2O_5$+0.5wt % $WO_3$+0.2wt % $Co_3O_4$+0.5wt % $Bi_2O_3$ |

## RESULTS AND DISCUSSION

### Green Density and Fired Density

The variation of density with the different composition of nanosized $TiO_2$ based varistor disc is presented in Figure 1. It can be seen that the results of densification after the sintering process was highly dependent on the concentrations of dopants. According to Figure 1, the increment in fired density shows the trend in general, becoming more densified with the increments in the concentration of dopants. These are due to the behavior of $Ta_2O_5$ and $WO_3$, which formed a solid solution with the $TiO_2$ lattice at high temperature, thus increasing the density of nanosized $TiO_2$.

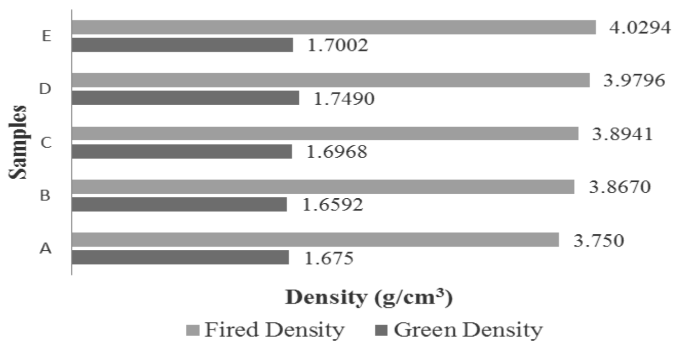


Figure. 1. Green and fired density of $TiO_2$ disc with different concentration of dopants.

Moreover, the addition of $WO_3$ influences grain growth, and thus influences the density of the samples. The addition of $Co_3O_4$ should promote densification of nanosized $TiO_2$, with an influence similar to that of CoO over $SnO_2$ (Metz et al., 2007).

Only with the addition of $Ta_2O_5$ and $WO_3$ content around 0.7% and 0.5%, did the samples exhibit high fired density (4.0294 g/cm$^3$), which is 0.7% higher compared to a theoretical density of $TiO_2$ (4.000 g/cm$^3$).

## Axial and Radial Shrinkage

To determine the shrinkage rate of nanosized $TiO_2$, the thickness and diameter of pellets were measured before and after the sintering process. The percentage of thickness and diameter reduction was calculated with the following Eq. 2 and Eq. 3:

$$\%t = \left[ \left( \frac{\delta t}{t_g} \right) \times 100\% \right] \tag{2}$$

$$\%d = \left[ \left( \frac{\delta d}{d_g} \right) \times 100\% \right] \tag{3}$$

where *t* is the thickness of the pellet, *d* is diameter of the pellet.

Figure 2 and Figure 3 present the axial and radial shrinkage rate at different dopant concentrations. Sample E shows the average highest reduction of other samples. It is well documented that the maximum shrinkage rate is highly dependent on the concentration of dopants (Wang, Tang, Yua, & Cao, 2011). The increase in $Ta_2O_5$ and WO3 has a great influence on the sintering process of the system. At maximum shrinkage temperature (1300 °C), highly doped samples cause segregation at grain boundaries which results in a decrease in grain size, and thus will increase the strength of the samples (Navale, Vadivel Murugan, & Ravi, 2007)

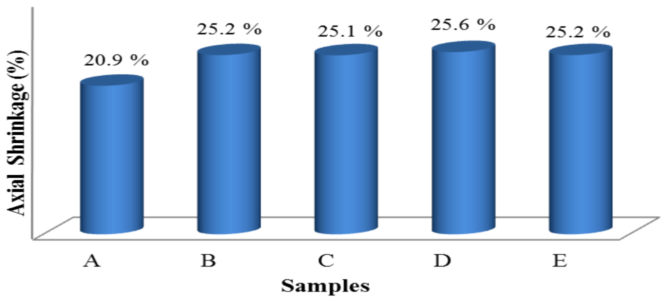


Figure. 2. Axial shrinkage (%) $TiO_2$ disc with different concentration of dopants.

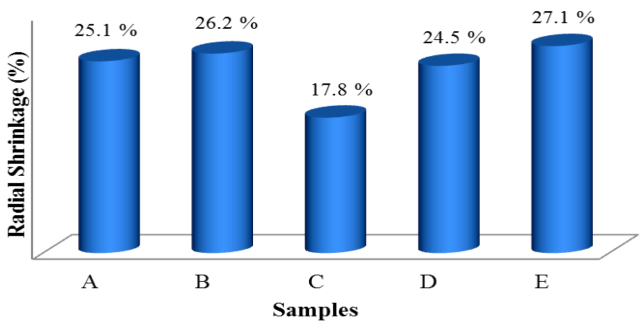


Figure. 3. Radial shrinkage (%) $TiO_2$ disc with different concentration of dopants.

## Sintered Strength

The hardness values of ceramic material are frequently analyzed to characterize resistance to deformation as well as densification, despite poor performance on ceramic material due to experimental issues such as cracking or chipping. However, it is important to observe whether a small impurity added to $TiO_2$ can increase the mechanical properties to relate it with electrical behavior of the material. The sintered strength was determined by using a Vickers hardness test by allowing the diamond-tipped fall into the sample to observe the maximum load that samples can withstand without causing damage. As shown in Figure 4, Sample E, which previously showed the highest density apparently shows highest hardness values as well. Sample E, $TiO_2$ doped with 0.7% $Ta_2O_5$, 0.5% $WO_3$, 0.2% $Co_3O_4$ and 0.5% $Bi_2O_3$, has comparatively higher hardness values compared to other samples (805.05 HV1). Furthermore, compressive strength also been conducted to calculate the compressive strength of the nanosized $TiO_2$. As shown in Figure 5, once again Sample E shows the highest values of compressive strength.

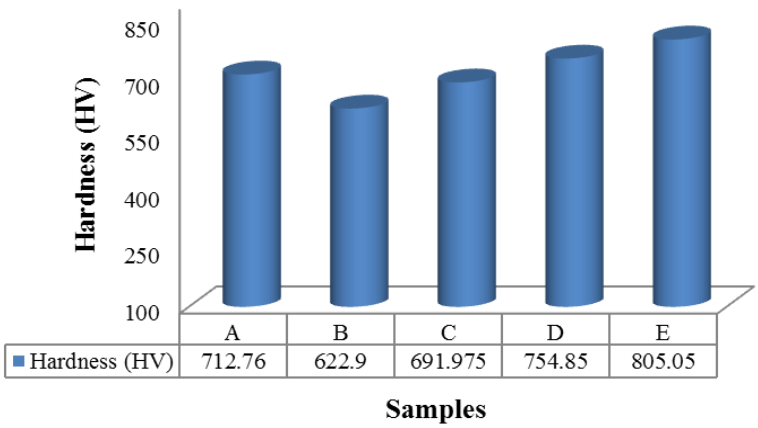


Figure 4. Hardness Values of $TiO_2$ with different concentration of dopants.

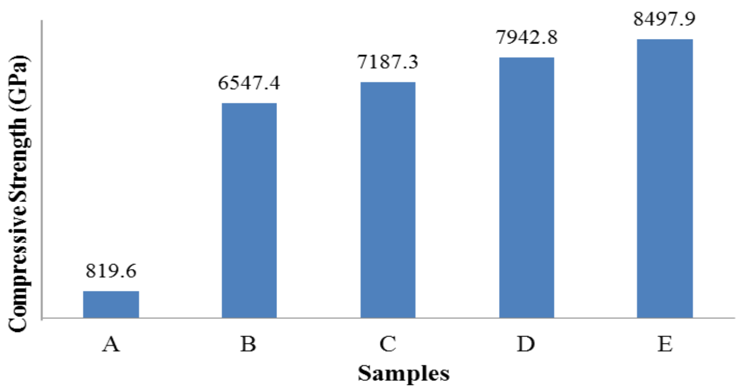


Figure 5. Compressive Strength of $TiO_2$ with different concentration of dopants.

## Scanning Electron Microscope

Figure 6 shows the SEM micrograph of the compact $TiO_2$ with different concentrations at 1300°C. The strength of samples was further confirmed by SEM micrograph. Grain size gradually decreases as the concentration of dopants increases, thus increasing the strength of the sample. The average grain size obtained through the linear intercept method was in the range of 2-10 µm. The mean grain size decreased as concentrations of $Ta_2O_5$ and $WO_3$ increased, which shows that the increment in dopants prevented the grain from growing. This is in agreement with other findings for high performance varistors (Filho et al., 2007; Silva et al., 2007; Xu et al., 2011 ). From Figure 6 it can also be seen that porosity reduced with the addition of dopants, thus increasing the physical and mechanical properties of $TiO_2$.

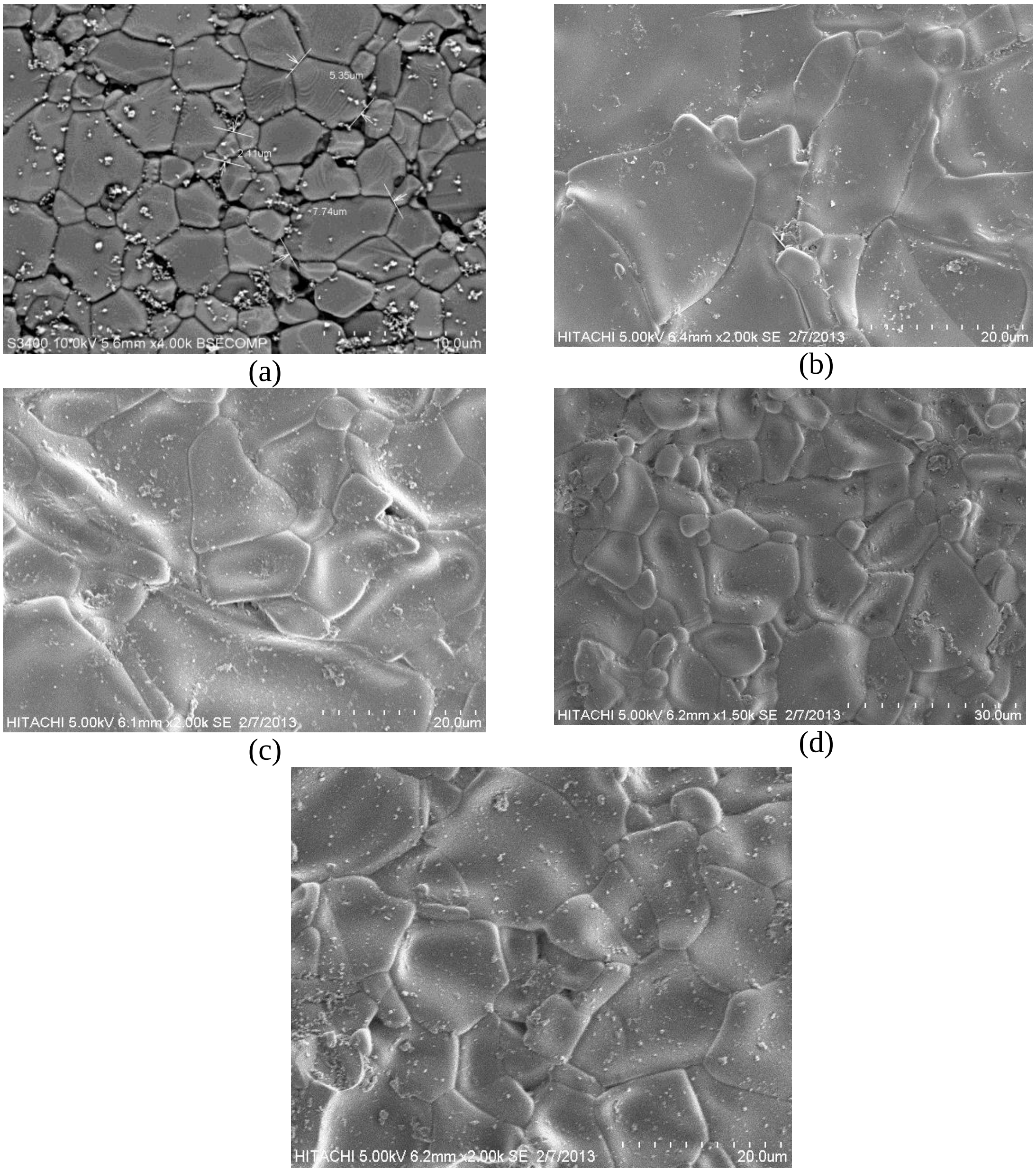


Figure 6. Microstucture of nanosized $TiO_2$ (a) 100% $TiO_2$(b) 0.2%$Ta_2O_5$+0.25%$WO_3$, (c) 0.2%$Ta_2O_5$+0.5%$WO_3$, (d) 0.4%$Ta_2O_5$+0.1%$WO_3$, (e) 0.7%$Ta_2O_5$+0.5%$WO_3$.

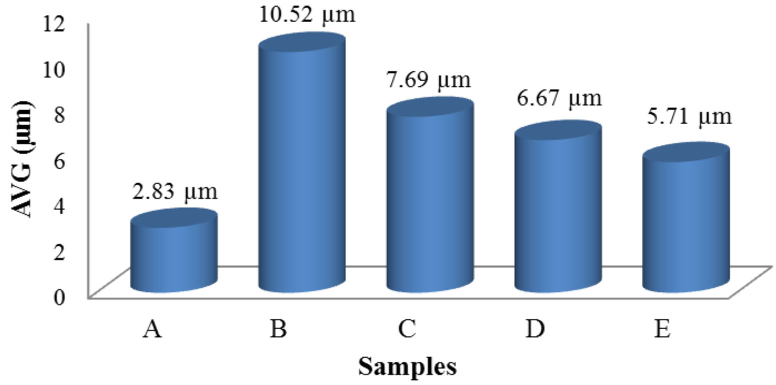


Figure 6. Average grain size (µm) of $TiO_2$ discs with different concentrations of dopants.

## X-Ray Diffraction

In order to investigate the phase structure of the $TiO_{2,\ an}$ XRD test was carried out. The pattern showed perfectly that all diffraction peaks indexed to a rutile $TiO_2$ when scanned at $2\theta$ ranges of 20° – 60° for the period of the 0.0200 step scan mode. No phases other than $TiO_2$ were observed. This could be because the amount of dopants added was very low and other possible phases may not been detected due to equipment limitations. This is in agreement with other studies. Major intensity peaks for the rutile phase of nanosized $TiO_2$ with $2\theta$ = 27.54°, 36.17°and 54.42° are clearly seen.

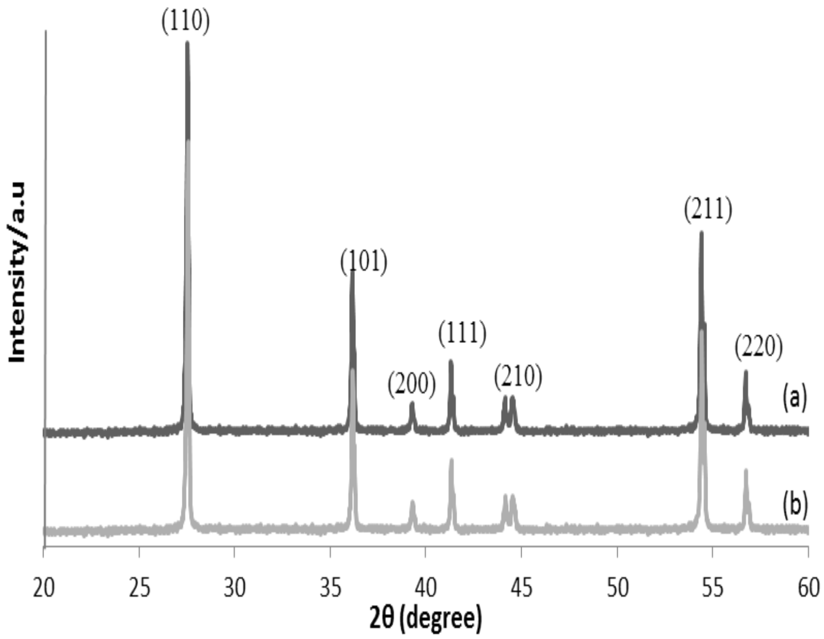


Figure 7 : XRD of $TiO_2$ disc (a) 100% $TiO_2$
(b) 0.7%$Ta_2O_5$+0.5%$WO_3$+0.2wt%$Co_3O_4$+0.5wt %$Bi_2O_3$

## CONCLUSIONS

The physical, mechanical and microstructure of nanosized $TiO_2$ doped with various dopants were evaluated. The addition of dopants significantly influenced the properties of $TiO_2$ varistor discs. The varistor discs prepared with 0.7% $Ta_2O_5$, 0.5% $WO_3$, 0.2% $Co_3O_4$ and 0.5% $Bi_2O_3$ exhibited improved properties compared to other compositions. The enhancement in strength of the nanosized $TiO_2$ signifies the reduction of porosity and enhancement of density of $TiO_2$ based ceramic varistor. Physical, mechanical and microstructure results evidence the influence of the dopants on the processing of $TiO_2$ powder at high temperature. Furthermore, influences on grain size and porosity will facilitate the performance of varistor.

## ACKNOWLEDGEMENTS

The investigation was conducted under the eScience fund of project code 03-02-03-SF0234. The authors would like to acknowledge the financial support provided by the Ministry of Science, Technology and Innovation (MOSTI).

## REFERENCES

Choon, W. N. (2012). Nb2o5 doping effect on electrical properties of zno-v2o5-mn3o4 varistor ceramics. . *Ceramic International,* 38, 5281-5285.

Filho, F. M., Simoes, A. Z., Ries, A., Perazolli, L., Longo, E., & Varela, J. A. (2007). Dependence of the nonlinear electrical behavior of sno2-based varistor on cr2o3 addition. *Ceramic International,* 33, 187-192.

Keating, A., & Nesic, S. (1999). *Prediction of two-phase erosion-corrosion in bends.* Paper presented at the Second International Conference on CFD in the Minerals and Process Industries, CSIRO, Melbourne, Australia.

Luo, H., Mittal, R., Zheng, X., Bielamowicz, S. A., Walsh, R. J., & Hahn, J. K. (2008). An immersed-boundary method for flow–structure interaction in biological systems with application to phonation. *Journal of Computational Physics,* 227(22), 9303-9332.

Luo, S., Tang, Z., Li, J., & Zhang, Z. (2008). Effect of ta2o5 in (ca,si,ta) doped tio2 ceramic varistor. *Ceramic International*, 34, 1345-1347.

Metz, R., Koumeir, D., Morel, J., Pansiot, J., Houbes, M., & Hassanzadeh, M. (2007). Electrical barrier formation at grain boundaries of co-doped sno2 varistor ceramic. *Journal of European Ceramic Society,* 28, 829-835.

Navale, S. C., Vadivel Murugan, A., & Ravi, V. (2007). Varistor based on ta-doped tio2. *Ceramic International,* 33, 301-303.

Santana, M. M. A., Dos Santos, F. S. N., Sousa, V. C., & Chui, Q. S. H. (2008). Variability sources of dc voltage-current measurements in the study of tio2-based varistor. *Journal of Measurements*, 41, 1105-1112.

Silva, I. P., Simoes, A. Z., Filho, F. M., Longo, E., Varela, J. A., & Perazolli, L. (2007). Dependence of la2o3 content on the nonlinear electrical behavior zno,coo and ta2o5 doped sno2 varistor. *Material Letters*, 2121-2125.

Su, W. B., Wang, J. F., Chen, H. C., Wang, W. X., Zang, G. Z., & Li, C. P. (2003). Novel tio2.Wo3 varistor system *Materials Science and Engineering*(B99), 461-464.

Wang, H., Gan, Y., Dong, X., Peng, S., Dong, L., & Wang, Y. (2012). Thermoelectric properties of ti-doped $WO_3$ ceramics. *Journal of Material Sciences*(23), 2229-2234.

Wang, M., Tang, Q., Yua, C., & Cao, M. (2011). Effect of zro2 dopants on the sintering behavior and performance of mcmb-derived carbon laminations. *Journal of Wuhan University of Technology-Mater. Sci. Ed*, 1, 15-18.

Xu, D., Cheng, H., Yuan, H., Yang, J., & Lin, Y. (2011 ). Microstructure and electrical properties of $Y(No_3)_3$•$6H_2O$-doped ZnO-$Bi_2O_3$-based varistor ceramics. *Journal of Alloys and Compounds*, 38, 9312-9317.

Yan, M. F., & Rhodes, W. W. (1982). *Varistor properties of (nb,ba)-doped $TiO_2$.* Paper presented at the MRS Proceedings, 5, 357 doi:10.1557/PROC-5.