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The Effect of Sintering Time on The Microstructural and Nonlinear Electrical Properties of Zn-V-Mn-Nb-Nd-O Low-Voltage Varistor Ceramics

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Abstract. There is lacking of study on the prolonged sintering time effect on the microstructural and nonlinear electrical properties of ZnO-V2O5-MnO2-Nb2O5-Nd2O3-based low-voltage varistor ceramics sintered at 900 °C. The aim of this study is to investigate the effect of sintering time from 120 to 210 mins on the microstructural and nonlinear properties of the ceramics. It is expected that its properties is diminished as sintering time is increased. The sample was prepared by solid-state method and sintered at 900 °C. The XRD diffraction peaks detected V2O5 as secondary phase. The ZnO peak shifted to the low diffraction angle of 34.37° and increased the interplanar space slightly to 2.61 Å. The average grain size decreased to 2.67 μm and density decreased to 4.74 g/cm³ as sintering time increased to 180 mins. However, the presence of liquid phase at 210 min increased both value to 3.63 μm and 5.00 g/cm³. The nonlinear α value decreased to 5.74 since the barrier height decreased to 0.633 eV as sintering time increased. The value of leakage current density $J_L$ increased to 0.54 mA/cm² as sintering time increased up to 180 mins but decreased to 0.42 mA/cm² at 210 mins. The breakdown field $E_{1mA}$ value also decreased from 76.07 to 66.03 V/mm as sintering time increased.

1. Introduction
Zinc oxide (ZnO)-based low voltage varistors are semiconducting ceramic devices used to protect low voltage electrical devices from harmful overvoltage. The low voltage devices without varistor had risk being exposed to overvoltage transient repeatedly and have a high chance to damage. The ZnO-based varistor is produced by sintering ZnO powder containing additives of small amount such as vanadium (V), bismuth (Bi), manganese (Mn), and niobium (Nb) [1,2]. The nonlinear properties of ZnO-based varistors ceramics are ascribed to double Schottky barrier formed at active grain boundaries [3,4]. Double Schottky Barrier model proposed that the bulk of material behaves as an $n$-type semiconductor and the interface behaves as a $p$-type semiconductor [5].

Study shows that the prolonged sintering time from 1h to 3h deteriorates the varistor properties of the ZnO-based ceramics substituted with dysprosium oxide (Dy$_2$O$_3$) and yttrium oxide (Y$_2$O$_3$) where it reduces the nonlinear properties [8,9]. The low-voltage varistor based on Zn-V-Mn-Nb-O ceramics substituted with 0.03 mol% of Gd$_2$O$_3$ and Nd$_2$O$_3$ sintered at 900 °C shows good nonlinear α value which are 9.91 and 9.94 and low $E_{1mA}$ value which are 88.48 and 75.05 V/mm [6,7]. The Zn$_2$Mn$_2$Nb$_2$O$_9$ phases was found to enhance the nonlinear properties in ZnO-based ceramics [6,7].
However, there is lacking of study on the prolonged sintering time effect on the microstructural and non-linear electrical properties of ZnO-V$_2$O$_5$-MnO$_2$-Nb$_2$O$_5$-Nd$_2$O$_3$-based low-voltage varistor at 900 °C. The previous study of ZnO-V$_2$O$_5$ ceramics investigating the sintering time effects in range from 60 to 480 min [6,7,10]. The aim of this study is to investigate the effect of sintering time on the microstructural and non-linear electrical properties of the ceramics. The prolonged sintering time was expected to diminish the microstructural and non-linear electrical properties of the ceramics. In this paper, the effect of sintering time from 120 to 210 min on the microstructural and electrical properties of ZnO-V$_2$O$_5$-MnO$_2$-Nb$_2$O$_5$-Nd$_2$O$_3$-based low voltage varistor ceramics have been discussed.

2. Materials and Methods

The sample was fabricated according to (97.40-x) ZnO (0.5) V$_2$O$_5$ (2) MnO$_2$ (0.1) Nb$_2$O$_5$ (0.03) Nd$_2$O$_3$ from high-purity reagent-grade raw materials (> 99.9%, Alfa Aesar). All the units were used in the bracket were in mole percentage. Raw materials were ground using ball milling with zirconia balls with distilled water for 24h. The slurry was dried at 70 °C for 12h before pre-sintered at temperature of 800 °C for 2h. Then, the binder polyvinyl alcohols 1.75 wt% was added and sieved through the 75 μm mesh screen. The powder from each ceramic combination was pressed into pellets with 10 mm diameter and 1 mm in thickness at a pressure of 10 tonne/m$^2$. The pellets were sintered at a temperature of 900 °C in air for 120, 150, 180 and 210 mins with heating and cooling rates of 5 °C/min. The crystalline phase was identified using Cu Kα radiation (λ = 1.540598 Å) with PANalytical X’Pert. XRD software X’Pert high score software Pro PW3040/60) was used to identify secondary phase and d-spacing. The d-spacing value was measured using Bragg law. The average density ($\rho_{avg}$) of sintered sample was determined using an electronic densimeter (Alfa Mirage, Model MD-300S), working based on the Archimede’s principle.

$$\rho = \frac{m}{V} = \left(\frac{W_{\text{air}}}{W_{\text{air}} - W_{\text{water}}}\right) \times \rho_{\text{water}}$$  

(1)

where $w_{\text{air}}$ is a weight of sample in air, $w_{\text{water}}$ is a weight of sample in water, and $\rho_{\text{water}}$ is a density of water. The value of $\rho_{\text{water}}$ is about 1.00 g/cm$^3$. The surface microstructures were examined by a scanning electron microscope (SEM, model: LEO 1455 VPSEM). One side of the samples was lapped and ground with SiC paper, and then polished with 0.3 μm Al$_2$O$_3$ powder to make a mirror-like surface. The average grain size ($D$) was determined by the linear intercept method [11].

The current density ($J$) – electric field ($E$) characteristics at room temperature were measured using the voltage source-measure (Keithley Model 2410) unit to obtain their non-linear coefficient ($\alpha$). All samples were coated with silver conductive paint and cured at 550 °C for 10 min to make the electrodes. The $\alpha$ value was determined through the expression (2):

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

(2)

where $E_1$ and $E_2$ are the electric fields corresponding to $J_1$ = 1.0 mA/cm$^2$ and $J_2$=10 mA/cm$^2$, respectively. The breakdown electrical field ($E_{1mA}$) was measured at 1 mA/cm$^2$ in the current density and the leakage current density ($J_L$) was measured at 0.8 $E_{1mA}$. The barrier height $\phi_B$ is estimated according to (3)

$$J = AT^2 \exp\left(\frac{\beta E^{1/2} - \phi_B}{k_B T}\right)^{-1}$$  

(3)
where $k_B$ is the Boltzmann constant ($8.167 \times 10^{-5}$ eV/K), $A$ is the Richardson’s constant (30 A/cm²K²) for ZnO, $T$ is the absolute temperature, $\beta$ is a constant related to the relation as $\beta \sim (r\omega)^{-1}$, where $r$ is grains per unit length and $\omega$ is the barrier width [12].

3. Results and Discussion

Figure 1 shows the XRD patterns of ZnO-based varistor ceramics sintered at different sintering time. The major diffraction peaks belong to ZnO (ref. No. 98-006-5190) as the primary phase and the minor diffraction peaks the V₂O₅ (ref. No. 98-010-7061) and Zn₂Mn₂Nb₂O₉ (ref. No. 98-004-3631) as secondary phase as the XRD pattern is matched to ICSD database. The V₂O₅ liquid phase detected in all sintering time with very low-intensity peaks. The ZnO peak shifts to the low diffraction angle from 34.4962° to 34.3789° and increases the $d$-spacing space slightly gain from 2.6000 Å to 2.6080 Å as the sintering time is increased.

![XRD patterns of ZnO-based varistor sintered at different time](image)

Figure 1. XRD patterns of ZnO-based varistor sintered at different time

Figure 2 shows the microstructure characterization of ZnO-based varistor ceramics at varied sintering time. The micrograph shows the large grains dispersed in a small grains at 120 mins. The disappearance of Zn₂Mn₂Nb₂O₉ phase at 150 mins inhibit the abnormal grain growth at the grain boundary by leaving the pores at the grain boundary. The pores are shrunk at 180 mins but the number of grain boundary is increased as Nd₂O₃ and MnO₂ act as grain inhibitor in the Zn-V-Mn-Nb-Nd-O ceramics [7, 13]. The liquid phase filled up the pores at the grain boundary is clearly observed at 210 mins as a result of segregation of Vanadium towards the grain boundary. The average grain size ($D$) decreases from 3.54 to 2.67 μm with increasing sintering time up to 180 mins due to pores but increases to 3.63 μm at 210 mins due to liquid phase. The pores also reduces the density ($\rho$) from 5.02 to 4.74 g/cm³ with increasing sintering time up to 180 mins and but increases to 5.00 g/cm³ at 210 mins due to liquid phase. The liquid phase act as a sintering aid that enhances the grain growth and densification by a solution and re-precipitation of ZnO [9, 14]. Assuming all additives disappear except V element, the grain boundary containing V element shown in Fig 3 confirmed the existence of V₂O₅ phase at 210 mins.
Figure 2. SEM of ZnO-based varistor ceramics sintered at different time

Figure 3. SEM attached with EDX of ZnO-based varistor ceramics sintered at 210 mins

The sintering time also affect the nonlinear electrical properties of ZnO-based varistor ceramics. Figure 4 shows the nonlinear region of $J-E$ curves shifted to the lower electrical field region with increasing sintering time. The nonlinear $\alpha$ value decreased from 9.94 to 5.21 at 150 mins as the barrier height decreased from 0.849 to 0.625 eV might due to formation of pores at the grain boundary. This indicates the pores did not contribute to the build-up of barrier height. The leakage current density $J_L$ increased from 0.45 to 0.46 mA/cm$^2$ as sintering time increased. The pores on the microstructures surfaces affecting the electrical conduction might contributes increment of $J_L$ [15]. However, the pores shrunk at 180 mins causes the barrier height increased to 0.644 eV and the nonlinear $\alpha$ value increased to 5.80, but the $J_L$ increased to 0.54 mA/cm$^2$. Assuming all additives disappear at the grain boundary might generates conduction carriers in the ZnO grain and thus weaken the insulating grain boundary [16]. Adversely, the barrier height decreased again to 0.633 eV at 210 mins and therefore, the nonlinear $\alpha$ value decreased to 5.74. It has been well accepted that the oxygen species promote density of interfaces states, thus increases the barrier height [17]. Assuming the liquid phase containing Vanadium might have promoted the oxygen vacancies $V_O$ formation and depleted the O species. Thus, it reduces the density of interface state and hence decreases the barrier height. The behavior of nonlinear $\alpha$ and barrier height dependence on the sintering time is shown in Figure 5.
Figure 4. J-E curve of ZnO-based varistor sintered at different sintering time.

The $J_L$ value also decreased to 0.42 mA/cm$^2$ at 210 mins. The liquid phase at the grain boundary might control the generation of conduction carrier in the ZnO grain and thus strengthen the insulating grain boundary [10]. The breakdown field $E_{1mA}$ value also decreased from 76.07 to 66.03 V/mm as sintering time increased. This reduction is due to pores and liquid phase formation. Table 1 shows the value of position 2$\theta$, $d$-spacing, density ($\rho$), average grain size ($D$), breakdown electrical field ($E_{1mA}$), nonlinear coefficient ($\alpha$), leakage current density ($J_L$) and barrier height ($\Phi_b$) of ZnO-based varistor ceramics sintered at varied sintering time.

Figure 5. Nonlinear $\alpha$ and barrier height ($\Phi_b$) dependence on sintering time
Table 1. Position 20, d-spacing, density ($\rho$), average grain size ($D$), breakdown electrical field ($E_{1mA}$), nonlinear coefficient ($\alpha$), leakage current density ($J_{L}$) and barrier height ($\Phi_{b}$) of ZnO-based varistor ceramics sintered at varied sintering time.

| Sintering time (min) | Position 20 ($^\circ$) | $d$-spacing (Å) | $\rho$ (g/cm$^3$) | $D$ (μm) | $\alpha$ | $\Phi_{b}$ (eV) | $E_{1mA}$ (V/mm) | $J_{L}$ (mA/cm$^2$) |
|----------------------|------------------------|-----------------|------------------|---------|---------|---------------|-----------------|-----------------|
| 120                  | 34.4962                | 2.6000          | 5.02             | 3.54    | 9.94    | 0.849         | 76.07           | 0.45            |
| 150                  | 34.4163                | 2.6059          | 4.91             | 3.08    | 5.21    | 0.625         | 68.03           | 0.46            |
| 180                  | 34.3939                | 2.6075          | 4.74             | 2.67    | 5.80    | 0.644         | 66.07           | 0.54            |
| 210                  | 34.3789                | 2.6080          | 5.00             | 3.63    | 5.74    | 0.633         | 66.03           | 0.42            |

4. Conclusion
The effect of sintering time on the nonlinear coefficient of Zn-V-Mn-Nb-Nd-O varistor ceramics was studied systematically. The prolonged sintering time disrupts the microstructure and nonlinear electrical properties as expected. The pores were formed which retarded the densification which causes of decreasing in density and inhibited the grain growth which causes of decreasing in average grain size. The pores did not contribute to the build-up of barrier height which lead to decrement in the nonlinear $\alpha$ value. It also affecting the electrical conduction which contributes increasing in $J_{L}$ value up as the sintering time increased to 180 mins. The liquid phase at 210 mins promoted the densification which causes of increase in density and grain growth which lead to increase in the average grain size with increasing sintering time. It also strengthens the insulating grain boundary which causes decrease in $J_{L}$ value but promoted the $V_{O}$ formation and depleted the O species, thus reduced the barrier height to 0.633 eV and consequently decreased the nonlinear $\alpha$ value to 5.74. The $E_{1mA}$ value decreased from 76.07 to 66.03 V/mm as sintering time increased.

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