Effects of Ta$_2$O$_5$ Addition on Electrical Properties of ZnO-V$_2$O$_5$ Based Varistor Ceramics

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Abstract. ZnO varistors are widely used for the protection of electronic and electrical equipment against transient surges. ZnO–V$_2$O$_5$ based varistor system is a potential candidate which can co-fire with Ag, and avoids the use of expensive Pa and Pt as the inner electrode in making multilayer chip varistors. However, the study of ZnO–V$_2$O$_5$-based ceramics is still in the initial stage for practical applications. The current work reports the effects of Ta$_2$O$_5$ on the electrical properties of ZnO-V$_2$O$_5$ based varistor ceramics. It shows that within 850–925°C experimental sintering temperature, the addition of Ta$_2$O$_5$ (0.05-0.20 mol%) may not improve the nonlinear coefficient but reduces the breakdown field of ZnO–V$_2$O$_5$ varistor ceramics.

1. Introduction
Zinc oxide (ZnO) is non-stoichiometric materials possessing excessive Zn ion and thus it is n-type oxide semiconductor. ZnO is proven as a very promising candidate for application to high performance electrical/electronic devices. Due to their highly nonlinear I-V characteristics and excellent energy handle capabilities, ZnO varistors are widely used for protection of electronic and electrical equipment against transient surge and overvoltage. Since its invention in 1968, ZnO varistor has been intensively studied and developed. The development of ZnO varistors has been one of great successes of functional ceramics [1-7].

Most of commercial ZnO varistors are made based on ZnO-Bi$_2$O$_3$ or ZnO-Pr$_5$O$_{11}$ systems, these two systems exhibit excellent nonlinear I-V characteristics [1-7]. Currently, the research and development in electronic design have tended toward miniaturization and with higher packaging density. Hence many different miniaturized multilayer chip ZnO varistor components are produced. However, due to the low melting temperature of silver (Ag, 961°C), the commercial Bi$_2$O$_3$ or Pr$_5$O$_{11}$ based ZnO varistor ceramics cannot be co-fired with the Ag inner electrode in multilayered chip components because of their relatively high sintering temperature above 1000°C [8, 9], they can only co-fired with expensive palladium (Pa) or platinum (Pt) metals. Therefore, the new varistor ceramics are required in order to use Ag inner electrodes. Among the various ceramics, one candidate is the ZnO–V$_2$O$_5$ based system [10, 11]. This system can be sintered at relatively low temperature of approximately 900°C. This is quite important to miniaturized multilayer chip component applications, because it can be co-sintered with Ag inner-electrode without using expensive Pa or Pt as electrodes.
Since the nonlinearity coefficient $\alpha$ (the parameter of nonlinearity) of binary ZnO–V$_2$O$_5$ is low [10,11], a study of ZnO–V$_2$O$_5$-based varistor ceramics is still in the initial stage for practical application. Nahm [12] reported that the ternary ZnO–V$_2$O$_5$–MnO$_2$ ceramics could possess improved nonlinear properties with a nonlinear coefficient of 17–19. Some metal oxide are concerned as additives for ZnO–V$_2$O$_5$ system varistor ceramics. Ta$_2$O$_5$ has been used as a dopant in the ZnO-Bi$_2$O$_3$ based varistor ceramic systems, it can enhance $\alpha$ value of ZnO-Bi$_2$O$_3$ varistors. Nahm [13] added Ta$_2$O$_5$ into ZnO–V$_2$O$_5$–MnO$_2$ ceramics and reported the $\alpha$ value increasing with the rising of sintering temperature. However, the effects of Ta$_2$O$_5$ doping on the ZnO–V$_2$O$_5$ ceramics are still unclear. In this study, the investigation of different amount of Ta$_2$O$_5$ doped ZnO–V$_2$O$_5$ ceramics with sintering temperatures are reported and some new results are obtained.

2. Experimental Procedures

The ceramic samples used in this study were based on the compositions: ZnO: (96.5–X)mol%; V$_2$O$_5$: 0.5mol%; MnO$_2$: 2.0mol%; Co$_2$O$_3$: 1.0mol%; Ta$_2$O$_5$: (X=0, 0.05, 0.10, 0.20mol%). All oxides were analytic grade chemicals. They were mixed in deionized water with agate balls for 20 hours ball milling. After drying, granules were obtained by passing the dried powders through a screen having an aperture mesh of nominally 0.3mm. The small disc shape samples (12 mm in diameter and 2.5 mm in thickness) were pressed by a uniaxial press at 80MPa. The samples were sintered at 850, 875, 900 and 925°C for 2 hour in air, with both heating and cooling rates at 3°C/min.

The microstructural observation of samples was examined by a scanning electron microscope (JSM-6360LV, Japan). The crystalline phases of samples were identified by X-ray diffractometry (D/MAX2500C, Japan) with CuK$_\alpha$ radiation.

Before electrical measurements, sliver electrodes were applied to both polished sides of the samples. The nonlinearity coefficients ($\alpha$) and the breakdown electric field ($E_b$) were determined by using an instrument for dc parameters of varistors (Type: CJ1001, Chuangjie Ltd. China).

3. Results and Discussion

For crystalline phase characterization of Ta$_2$O$_5$ doped ZnO–V$_2$O$_5$ ceramics, the XRD pattern of the 0.2mol% Ta$_2$O$_5$ doped sample sintered at 900°C are shown in Fig. 1. The phase patterns revealed the presence of Zn$_3$(VO$_4$)$_2$, and TaVO$_5$ as minor secondary phases in addition to a major phase of hexagonal ZnO, which is agreement to the finding of Nahm.[13] These minor secondary phases may act as liquid-phase sintering aids.[13,14].

![Fig. 1. The XRD pattern of the 0.2mol% Ta$_2$O$_5$ doped sample sintered at 900°C](image-url)
Figure 2 shows the nonlinearity coefficients ($\alpha$) of $\text{Ta}_2\text{O}_5$ doped samples at different sintered temperatures. From Fig. 2 it can be seen that the addition of $\text{Ta}_2\text{O}_5$ has a reverse effect on the nonlinearity coefficients of samples sintered at all sintering temperatures. The highest $\alpha$ value, 9.2, was obtained on the samples without $\text{Ta}_2\text{O}_5$ doping and sintered at 850°C, and second highest $\alpha$ value, 5.8, was obtained on the samples doped with 0.05mol% $\text{Ta}_2\text{O}_5$ doping and also sintered at 850°C. This finding is in the region to that by reported Nahm,¹⁴ which is 8 obtained on the sample doped with 0.05mol%$\text{Ta}_2\text{O}_5$ sintered at 875°C. However, with addition of $\text{Ta}_2\text{O}_5$ within the experimental doping levels, the $\alpha$ value of samples dropped no matter of at what sintering temperatures, and trended to a certain value between 3 to 6. This result is different with the finding of Nahm [13], who reported that the $\alpha$ value of 0.05mol% $\text{Ta}_2\text{O}_5$ doped sample increased with the increasing of temperature, it could reach 28 at 950°C sintered sample, but no results on the $\alpha$ value of samples doped with $\text{Ta}_2\text{O}_5$ at higher doping level.

![Nonlinearity Coefficients](image)

**Fig. 2.** The non-linearity coefficients ($\alpha$) of samples as the function of sintering temperature

![Breakdown Field](image)

**Fig. 3.** The breakdown field ($E_b$) of samples as the function of sintering temperature

Figure 3 shows the breakdown field ($E_b$) as the function of sintering temperature. The $E_b$ value obviously decreased as the content of $\text{Ta}_2\text{O}_5$ increases at the 850°C sintering temperature, and this
reduction became not obvious at 875°C and 900°C. It can also be seen that the $E_b$ value is quite sensitive to the sintering temperature, the breakdown field ($E_b$) of samples drop significantly with the increase of sintering temperature. This is because that nonlinear $I$-$V$ characteristics of ZnO varistors can be ascribed to the double Schottky type electrical barrier at the ZnO grain boundary [1-6]. The parameters controlling the value of $E_b$ are the grain size and barrier voltage ($V_{gb}$) according to the following equation:

$$E_b = V_{gb}N_g$$  \hspace{1cm} (1)$$

where the $N_g$ is the average number of grains per centimeter [1-6]. From the results of Fig. 3, it suggests that the addition of Ta$_2$O$_5$ could enhance the grain size of ZnO–V$_2$O$_5$ samples. The higher sintering temperature usually results in lower breakdown electric field because of the increasing grain size as a result of increase of sintering temperature.

4. Conclusion
Except main phase ZnO, the Zn$_3$(VO$_4$)$_2$ and TaVO$_5$ as minor secondary phases were detected on the Ta$_2$O$_5$ doped ZnO–V$_2$O$_5$ varistor ceramics.

The addition of Ta$_2$O$_5$ did not improve the nonlinear coefficient, but decreased the breakdown field of ZnO–V$_2$O$_5$ varistor ceramics. Within experimental doping level and sintering temperature, the highest value of nonlinear coefficient 9.2 was obtained on the simple without Ta$_2$O$_5$ doping and sintered at 850°C. The more detail investigation is carrying on.

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