Effect of sintering temperature on microstructure and nonlinear electrical characteristics of ZnO varistor

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The nonlinear properties of ZBMCCS-based varistors, which are composed of ZnO–Bi₂O₃–MnO₂–Cr₂O₃–Sb₂O₃–Co₃O₄ and SiO₂ are studied in relation to sintering temperature, in the range of 1280–1350°C. The samples are investigated for grain morphology by using scanning electron microscope (SEM). These samples were examined by using X-ray diffraction patterns (XRD) and DC electrical measurements. X-ray diffraction analysis of the samples show the presence of ZnO, Zn₂SiO₄ willemite phase and Co_{2.33}Sb_{0.67}O₄ spinel phases. The average grain size of ZnO increased as the sintering temperature increased from 2.57 to 6.84 μm. In the examined temperature range, the breakdown field decreased from 2992 to 127 V/cm with the increase of sintering temperature. This system gives a relatively high nonlinearity coefficient $\alpha = 33.61$ (at a sintering temperature of 1280°C) with a low leakage current of 0.21 mA/cm².

Keywords: ZnO varistor ceramics; microstructure; nonlinear coefficient; sintering temperature.

1. Introduction

Zinc oxide varistors are ceramic semiconductor devices with high nonlinear current–voltage characteristics. This latter and the energy absorption capability are the two most important parameters of the ZnO varistor.¹ The nonlinearity coefficient is defined as:

$$I = KV^\alpha, \quad (1)$$

where K is a constant, α is the nonlinear coefficient. ZnO varistors are used as surge protection devices in different electrical and electronic circuits, where many studies have already focused on electrical properties of varistor. Various techniques of elaboration have been used, such as ceramic method and chemical method. The size of the grains and the homogeneity of the microstructure are essential elements for the development of efficient ZnO varistors. In this context, the choice of a ceramic method makes it possible to envisage obtainment of fine grains as well as a good dopant distribution. The varistor devices were formed by sintering ZnO powder with a number of other metal oxides of small amount (Bi₂O₃, MnO₂, Co₃O₄, Cr₂O₃, Sb₂O₃, Al₂O₃ and SiO₂, etc) where all these oxides are milled together before sintering.² Each of them has a special function both in the sintering temperature and in the resulting varistor. The addition of Bi₂O₃ and Cr₂O₃ were needed to increase the breakdown voltage,^{3–5} and manganese and cobalt dopants enhance the degree of nonlinearity.^{4,6} Al₂O₃ was added to increase the electrical conductivity of the zinc oxide grains.⁷ Shuai *et al.* have reported that Cr₂O₃ did not react with ZnO at such low

sintering temperature of 950°C.⁸ The reactions between ZnO and oxide additives in high-temperature lead to the formation of different phases in the ZnO grain boundary.⁹ These phases are the spinel phase and the willemite phase.¹⁰ For this reason, sintering temperature is one of the most important parameters in making varistors, because approximately all properties of varistors are affected by temperature. More recently, published research has shown that the addition of SnO₂ significantly influences ZnO grain growth, and nonlinear properties.¹¹ In 2014, Guangliang Hu *et al.* studied the microstructure and the electrical properties of MgO-doped SnO₂ varistor ceramics. It indicates that 1350°C is the best sintering temperature for this system.¹² Thus, Nahm investigated the microstructure and electrical properties of the ZnO–Pr₆O₁₁–Bi₂O₃-based varistor ceramics with sintering changes in the range of 1100–1250°C.¹³ There are no published reports studying the effect of the sintering temperature on the varistor properties in ZBMCCS-based varistor ceramics, especially, in the range of 1280–1350°C.

The aim of this work is to investigate the effect of sintering temperature on the microstructure and electrical properties of the ZBMCCS-based varistors.

2. Experimental Procedure

2.1. Sample preparation

Reagent-grade raw materials were used in proportions of 96 mol% ZnO, 0.5 mol% Bi₂O₃, 0.5 mol% MnO₂, 0.5 mol% Cr₂O₃, 1 mol% Sb₂O₃, 0.5 mol% Co₃O₄ and 1 mol% SiO₂.

High-purity commercial ZnO-micro (purity of 99.7%), and the other oxides were mixed and homogenized in absolute ethanol, using porcelain balls within a polypropylene bottle for 24 h. The mixture was dried at 100°C for 24 h and calcined in air at 750°C for 2 h. The resulting powders are pressed into discs of 13 mm in diameter and 2 mm thickness at a pressure of 1000 kg/cm². The discs were sintered at four fixed different temperatures 1280°C, 1300°C, 1320°C, 1350°C, for 2 h with heating and cooling rates of 5°C/min. These samples are labeled FB1, FB2, FB3 and FB4, respectively, in the following parts of the text. The size of the final samples were about 8 mm in diameter and 1.0 mm in thickness. Both sides of the sintered samples were polished and coated in a silver paste and ohmic contacts were formed by heating at 600°C for 10 min in air. The electrodes were 5 mm in diameter.

2.2. Microstructure examination

The microstructures of samples were examined via the scanning electron microscope (JEOL, JSM-6360LV). The average grain size (D) was determined by the lineal intercept method using the following equation:

$$D = 1.56 \frac{L}{MN} \quad (2)$$

where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of grain boundaries intercepted by the lines.^{14,15}

The phase composition of samples was characterized by means of X-ray diffraction (XRD) in D8 advance BRUKER diffractometer with Cu-K α ($\lambda = 1.54 \text{ \AA}$).

2.3. Electrical measurement

The electrical properties for sintered samples were performed with a Keithley 2015 digital multimeter and an Extra high voltage (Power supply) (LB2615-001, Australia). The current was recorded by increasing the applied voltage manually to characterize the electric field current density (E, J) behavior of all samples. The nominal breakdown field $E_B = V_1 \text{ mA}$ (V/cm) was measured when the current flowing through the varistor is 1 mA/cm². Breakdown electrical field of varistors can be expressed by the following equation:

$$E_B = \left(\frac{V_{gb}}{D} \right), \quad (3)$$

where V_{gb} is the average breakdown voltage per grain boundaries. From the measured values of E_B and D , V_{gb} could be obtained.¹⁶

The leakage current (I_L) is measured at 0.8 V_B .^{15,17} The nonlinear coefficient α is obtained by the following equation:

$$\alpha = \frac{\log \left(\frac{J_2}{J_1} \right)}{\log \left(\frac{E_2}{E_1} \right)} = \frac{1}{\log(E_2 - E_1)}, \quad (4)$$

where E_1 and E_2 are the electric fields corresponding to $J_1 = 1 \text{ mA/cm}^2$ and $J_2 = 10 \text{ mA/cm}^2$,¹⁸ respectively.

3. Results and Discussion

3.1. Microstructure analyses

Figure 1 shows SEM micrographs of ZBMCCSS-based varistors sintered at different temperatures. The grain sizes of ZBMCCSS ceramic varistors were shown to increase from 2.57 to 6.84 μm when the sintering temperature increases from 1280°C to 1350°C. The detailed microstructural parameters are summarized in Table 1. It is clear that the sample FB1 has smaller average grain size than the others, which demonstrates that the higher sintering temperature has played an effective role in controlling the growth of the grains.

3.2. X-ray powder diffraction

The XRD patterns for all samples sintered with four different temperatures are given in Fig. 3. The XRD pattern reveals the presence of three diffraction peaks, namely, primary phase ZnO (JCPDS No. 065-3411), as the predominant compound and secondary phase willemite Zn₂SiO₄ (JCPDS No. 037-1485) and spinel phase Co_{2.33}Sb_{2.67}O₄ (JCPDS No. 15-0517). As can be seen in Fig. 3, it is revealed that the spinel

Fig. 1. SEM micrographs of the samples for different sintering temperatures.

Table 1. E - J and microstructure characteristic parameters of the samples for different sintering temperatures.

Samples	T°C	D (μm)	E_B (v/cm)	α	V_{gb} (v)	I_L (mA/cm ²)
FB1	1280	2.57	2991.57	33.61	0.77	0.21
FB2	1300	3.61	543.94	7.87	0.19	0.27
FB3	1320	4.5	127.84	3.19	0.05	0.56
FB4	1380	6.84	664.79	6.96	0.45	0.33

Fig. 2. Variation of nonlinear coefficient α and leakage current I_L with different sintering temperature.

phase exists as a minor phase for all the samples. The intensity of these peaks decreases with the increase of sintering temperature. This phase can inhibit the grain growth during the sintering process of the varistor.¹⁸

3.3. Current–voltage characteristics

Figure 5 shows the electric field and current density (E - J) curves of samples with different sintering temperatures. It is

clearly seen that all the samples have varistor property. The (E - J) curves of ZBMCCSS-based varistor ceramics can be divided into two regions. The first region is in the low-field, where the varistor is an insulator, which allows low leakage current. The second region clearly shows nonlinear behavior (upturn region). The (E - J) characteristic parameters with various sintering temperatures are summarized in Table 1.

The breakdown field E_B decreased over a wide range from 2991.57 to 127.84 V/cm with the increase of sintering temperature. This fact can be explained by: firstly, the increase in the average grain size, equivalent to a reduction of the number of grain boundaries as shown in Fig. 4. Secondly, the decrease of varistor voltage per grain boundary V_{gb} , as shown in Table 1. In general, smaller the grain size, higher the varistor voltage.

The nonlinearity coefficient α decreased sharply from 33.61 to 7.87 until the sintering temperature is 1280°C. However, when the sintering temperature exceeded 1300°C, α increased to a slight extent from 3.19 to 6.96, the tendency of change in α is very unusual because of sharp change of α between 1280°C and 1350°C. So the sample sintered at 1280°C exhibited the breakdown field as high as 2991 V/cm and the non-ohmic coefficient as high as 33. For the sintering temperature used in this work, the best value of α was found for FB1 varistor sintered with 1280°C.

Figure 2 shows the variation of α and leakage current I_L as a function of sintering temperature. The variation of I_L value

Fig. 3. XRD patterns of the samples for different sintering temperatures.

Fig. 4. Variation of grain size D and breakdown field E_B with different sintering temperature.

is observed to be opposite to α . The minimum value of leakage current I_L was found for FB1 varistor ceramic. The V_{gb} was in the range of 0.76 to 0.06 V/gb.

Many researchers have been studying the impacts of microstructure, metal oxide additives and processing methods on the degradation of ZnO varistors.¹⁹ Nahm *et al.* reported the degradation behavior by DC-accelerated stress and pulse-current stress of varistors with different sintering temperatures. They have found that the sample sintered at 1300°C exhibited the highest stability for E - J characteristics after application of the DC-accelerated stress state and they confirmed that the sintering temperature has a strong effect on degradation behavior by the stress.²⁰ The degradation phenomena in ZnO varistors occurs under ac, dc, and pulse electric field resulting in changes in nonlinear coefficient and leakage current.

As a result, the best sample exhibits low leakage current, high nonlinear coefficient and high breakdown voltage. The

Fig. 5. E - J characteristics of the samples for different sintering temperatures.

varistor FB1 sintered at 1280°C is better than FB2, FB3 and FB4. The nonlinear coefficient α is above 33, the breakdown field E_B is 2991.57 v/cm, and leakage current is $J_L = 0.21$ mA/cm².

4. Conclusions

The properties of ZBMCCSS-based varistor prepared by the ceramic method, which was discussed in the preparation section of the samples, were investigated as a function of different sintering temperatures, and investigated for phase identification and grain morphology by using XRD and SEM techniques. The XRD pattern showed the presence of ZnO, Zn₂SiO₄ willemite and Co_{2.33} Sb_{2.67}O₄ spinel.

For sintering temperatures ranging from 1280°C to 1350°C, the average grain size increased from 2.57 to 6.84 μm, which leads to a substantial decrease in breakdown field of the varistors from 2991 to 127 v/cm. The nonlinearity coefficient α measured for the material sintered at 1280°C was 33.61. This coefficient decreased with the increase of sintering temperature.

Finally, it can be inferred from the above results that the ZBMCCSS ceramic varistors sintered at 1280°C would be very useful in the fabrication of a good varistor, because, first, they exhibit excellent electrical properties of 2991.57 v/cm, $\alpha = 33.61$ and $J_L = 0.21$ mA/cm², second, the electrical characteristics of the degraded sample are partially restored after heat treatment in an oxygen-rich atmosphere. Hence, these varistors could be applied to the nonlinear resistors for high-voltage field.

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