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Short communication

Sintering behavior of Zn–Pr–Co–Mn–O varistor ceramics

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Abstract

Sintering and grain growth of Pr_6O_{11}-based ZnO varistors were investigated in detail over a range of temperature and holding time. The grain growth kinetics in the Zn–Pr–Co–Mn–O system was studied using the simplified phenomenological grain growth kinetics equation: $G^n - G_0^n = K_0 t \exp(-Q/RT)$ together with the physical properties of the sintered samples. From 1050 °C to 1300 °C, the grain growth exponent value (n) and the apparent activation energy for this system were found to be approximately 3.7 and 306 ± 61 kJ/mol respectively. Highly densified ceramics sintered at 1300 °C for 4 h were obtained, reaching about 96% of theoretical density (TD = 5.78 g/cm^3). These values are compared with those obtained for Bi_2O_3-based ZnO varistors. The maximum nonlinear exponent ($\alpha = 54.7$) was obtained at a sintering temperature of 1275 °C.

Keywords: A. Grain growth; D. ZnO; E. Varistors; Nonlinear; Nanocrystalline; Pr_6O_{11}

1. Introduction

ZnO varistors are a kind of ceramic semiconductor devices produced by a sintering process, which derive their nonlinear current–voltage behavior from addition of small amounts of varistors-forming oxides, such as Bi_2O_3, Pr_6O_{11}, MnO_2 and Co_3O_4 [1,2]. It is generally believed that the sintering process gives rise to the effective varistor structure, which consists of semiconducting n-type ZnO grains surrounded by very thin insulting intergranular layers [3]. Therefore, ZnO varistors exhibit highly nonlinear voltage–current (V–I) properties expressed by the relation $I = KV^{\alpha}$, where K is a constant and α is a nonlinear exponent, which characterizes the nonlinear properties of varistors. Functionally, this can result in a high-energy absorption capability to various surges. Based on above, these varistors are widely used as surge arresters in the field of electric power lines, such as transmission and electric power systems.

In recent years, Pr_6O_{11}-based ZnO varistors are being studied aiming to find a substitution for Bi_2O_3-based ZnO varistors, which have a few drawbacks due to Bi_2O_3 having high volatility and reactivity [4–6]. Pr_6O_{11}-based ZnO varistors have been reported that not only their structure is simple, but also the nonlinearity is high. However, they also have a few drawbacks [7,8]. One is the high sintering temperature. The sintering temperature of Pr_6O_{11}-based ZnO varistors is generally high, which hinders the widespread appliance of the ceramics due to the increase of production cost. Another is the dissatisfactory performance. There have been a number of studies addressing the microstructure, electrical conduction, degradation characteristics, non-ohmic properties and mechanisms of ZnO ceramics. It is proved that electrical properties of ZnO varistors are directly related to their microstructure, namely, grain size and intergranular phases [2,9]. Therefore, in this paper, microstructure and grain growth kinetic of the Zn–Pr–C–Mn–O system were investigated in detail over a range of temperatures and holding time.

2. Experimental procedure

Nanocrystalline ZnO with particle sizes in the range of 20–100 nm was used in this study. Other oxides were reagent grade. The ceramic samples used in this experiment were composed of 98.5 mol% ZnO + 0.5 mol% Pr_6O_{11} + 0.5 mol% Co_3O_4 + 0.5 mol% $MnCO_3$ (designated as ZPCM). Raw materials were mixed for 24 h in deionized water with zirconia balls and acetone in a polypropylene bottle. The mixture was then dried at 120 °C for 12 h and calcined in air at 750 °C for 2 h. The calcined mixture was again milled for 6 h in deionized water

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after 2.5 wt% polyvinyl alcohol (PVA) binder addition. After drying again, the mixture was pulverized using an agate mortar/pestle and granulated using a sieving 200 mesh screen to produce the starting powder. The powder was compacted into discs of 16.66 mm in diameter and 2 mm in thickness by employing a 30 MPa pressure in a uniaxial press. The pellets were then sintered at different time (0.5, 1, 2, 4 and 8 h) and temperature (1050, 1150, 1200, 1250, 1275 and 1300 °C) with heating and cooling rates of rate of 3 °C/min. The sintered densities (ρ) of the green samples were determined by the Archimedes method with distilled water. The reference theoretical density (TD) of pure ZnO was taken to be 5.78 g/cm^3.

For microstructural observations, the top and bottom surfaces were lapped and ground with SiC paper and finally polished with 0.3 μm-Al_2O_3 powder to mirror-like finish. The polished surfaces were etched with 2% natal (2 vol.% nitric acid with alcohol) for about 1–2 min. The microstructure was examined by scanning electron microscopy (SEM, JSM-6360LA, Japan). The average grain sizes were measured directly form the micrographs of the etched samples by the lineal intercept method, as described by Mendelson [10],

$$G = 1.56\frac{L}{MN} \tag{1}$$

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.

Before electrical measurements, silver electrodes were applied to both surfaces of the samples and ohmic contacts electrodes formed by heating at 600 °C for 10 min. The size of electrodes was 10 mm in diameter. The breakdown field ($E_{1\ \mathrm{mA/cm}^2}$) was measured at 1.0 mA/cm^2 and the leakage current (J_{leak}) was defined as the current at 0.83 $E_{1\ \mathrm{mA/cm}^2}$. The nonlinear exponent (α) is defined by $\alpha = (\log J_2 - \log J_1)/(\log E_2 - \log E_1)$, where J_1 and J_2 are the electric fields responding to $J_1 = 0.1$ mA/cm^2 and $J_2 = 1$ mA/cm^2.

3. Results and discussion

Fig. 1a shows the relative density of ZPCM ceramics as a function of the sintering time for samples sintered at 1300 °C. The relative densities of the sintered samples increase from 92% to 96% of TD with the increase in sintering time and almost reach a plateau when heated for 4 h. However, the effect of sintering temperature on the densities shows a different trend (Fig. 1b). Samples treated below 1150 °C show densities less than 77% of TD. Density increases significantly when heated above 1150 °C and reaches 96% of TD at 1300 °C. The densification process is essentially complete at 1300 °C.

Fig. 2 presents the microstructure of ZPCM samples sintered at varied temperatures and times. It can be observed that all the samples show uniform equiaxed grain and are free of abnormal grain growth. In general, the grain size increased with increasing temperature and holding time, from about 2.3–8.3 μm, which is much smaller than those of pure nanocrystalline zinc oxide (about 10 μm) sintered at same condition [11,12]. Therefore, the ceramics contained more grains per unit thickness that can affect the electrical properties.

In order to understand grain growth behavior during the sintering, grain growth analysis is necessary. These parameters can be obtained from the phenomenological kinetic grain growth equation:

$$G^n - G_0^n = K_0 t \exp\left(-\frac{Q}{RT}\right) \tag{2}$$

where G is the average grain size at time t, G_0 is the initial grain size which is usually negligibly small, the n value is the kinetic grain growth exponent, K_0 is a pre-exponential constant, Q is the apparent activation energy for the grain growth process, R is the universal gas constant, and T is the absolute temperature. Eq. (2) can be readily changed into the form as followed (G_0 being neglected):

$$\ln G = \frac{1}{n}\ln t + \frac{1}{n}\ln K0 - \frac{Q}{nRT} \tag{3}$$

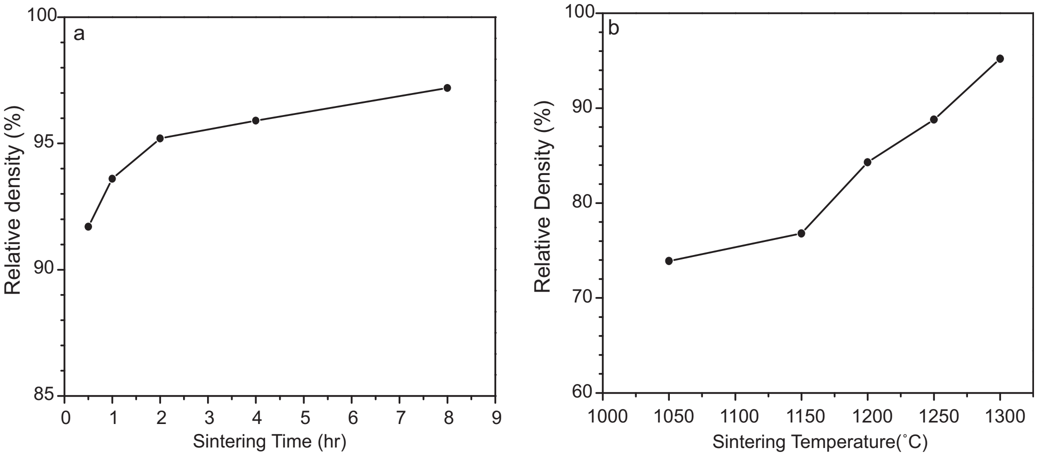

Fig. 1. Effect of sintered density of ZPCM samples with sintering time (sintered at 1300 °C); (b) sintering temperature (sintered for 2 h)

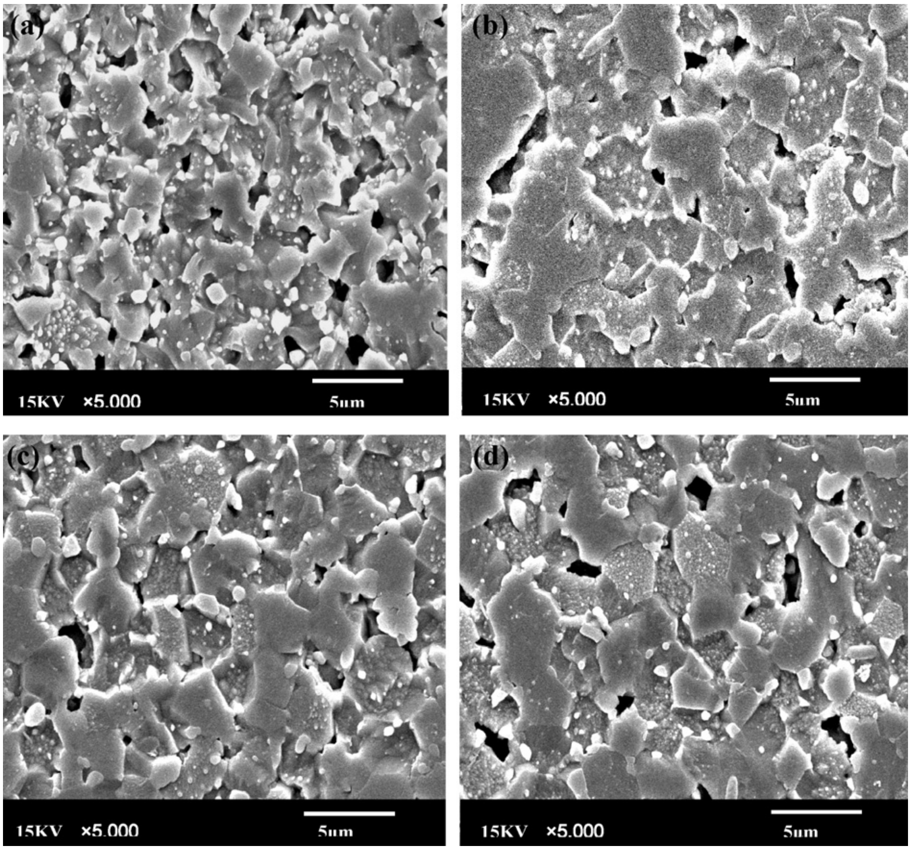

Fig. 2. Microstructures of ZPCM samples sintered at: (a) 1250 °C for 2 h, (b) 1300 °C for 2 h, (c) 1300 °C for 1 h, (d) 1300 °C for 4 h.

According to the slope of the ln G versus ln t line, which is $1/n$, the grain growth kinetic exponent n is found to be equal around 3.7 (Fig. 3). Hence, grain growth of this system during sintering is described by:

$$G^{3.7} = K_0 t \exp\left(-\frac{Q}{RT}\right) \tag{4}$$

This value of n is slightly lower compared to the value of 5 for Bi_2O_3-based ZnO varistors [5]. This small value of n illustrates that the grain growth of ZPCM varistors is faster than that of Bi_2O_3-based ZnO varistor ceramics. The highly reactive nanocrystalline ZnO is believed to be the cause of this excessive growth.

The grain growth activation energy can be obtained from the Arrhenius plot (Fig. 4). Eq. (4) can also be changed into another form as:

$$\ln\left(\frac{G^{3.7}}{t}\right) = \ln K_0 - \frac{Q}{RT} \tag{5}$$

The slope of which yields the apparent activation energy for the grain growth process. Data scatter exists because the grain growth does not exactly ascribe to the 1/3.7 power of the time as shown in Fig. 1b. However, there generally exists a reasonably good linear relationship between $\ln(G^{3.7}/t)$ and $1/T$ from 1050 °C to 1300 °C, implying that the mechanism for grain growth in this selected temperature range is the same. Thus, the apparent activation energy for grain growth is calculated from the slope of the fitted line in Fig. 4 to be approximately 306 ± 61 kJ/mol. From the same plot, the value of pre-exponential constant K_0 is also determined to be 3.43×10^{12} $\mu m^4/h$.

The kinetic parameters for various ZnO varistors are summarized in Table 1. The grain growth kinetic exponent of Pr_6O_{11}-based ZnO varistors is lower than that of Bi_2O_3-based

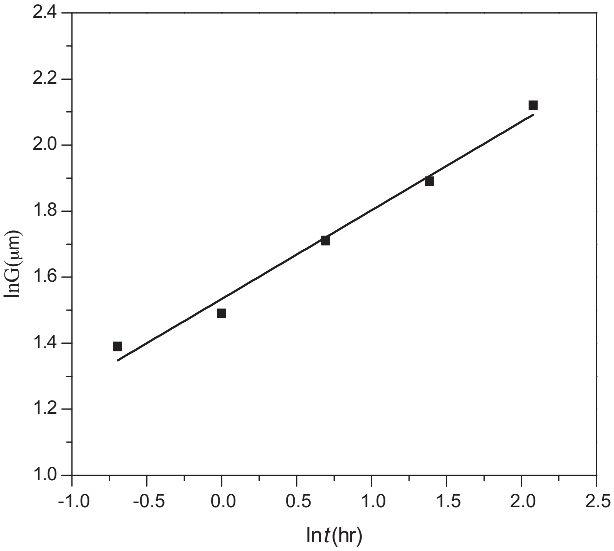

Fig. 3. Grain size ln G versus time ln t for growth of ZPCM samples sintered at 1300 °C.

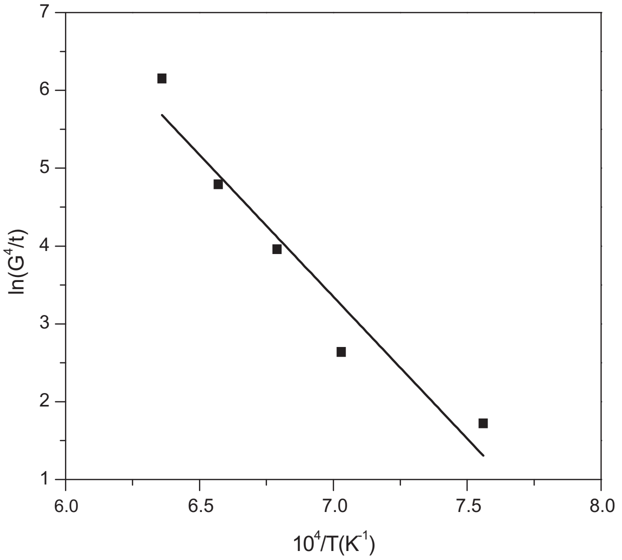

Fig. 4. Arrhenius plot for grain growth of ZPCM systems: ln ($G^{3.7}/t$) versus $10^4/T$.

Table 1
Comparison of grain growth parameters of various ZnO varistor ceramics.

Composition	n	K_0	Q (kJ/mol)	Reference
Pure nanocrystalline ZnO	6	2.95×10^{11} μm^3/h	64 ± 6	[10]
Bi_2O_3-based varistor	5	8.89×10^{12} μm^5/h	148 ± 31	[5]
Pr_6O_{11}-based varistor	3.7	3.43×10^{12} μm^4/h	306 ± 61	This work

Table 2
Summary of varistor parameters for ZPCM ceramics sintered at different temperatures.

Sintering temperature (°C)	Sintering time (h)	Average ZnO grain size (μm)	$E_{1\ \mathrm{mA/cm}^2}$ (V/cm)	Nonlinear exponent (α)	J_{leak} (μA/cm^2)
1200	2	3.2	6750	7.4	53.2
1250	2	4.0	5400	20.6	46.2
1275	2	5.1	4850	54.7	37.9
1300	2	5.5	4550	35.4	61.7

ZnO varistors, which has a value of 5. This shows that a higher grain growth rate is obtained for Pr_6O_{11}-based ZnO varistor system. The different activation energy observed in these two systems might be due to the presence of Bi-rich liquid phase at grain boundary for Bi_2O_3-based ZnO varistors during the sintering process [10–13].

The characteristic parameters of the Zn–Pr–Co–Mn–O system with different sintering temperatures are summarized in Table 2, where the point at which nonlinearity begins is given by the onset electric field $E_{1\ \mathrm{mA/cm}^2}$ and leakage current density J_{leak}.

The breakdown field ($E_{1\ \mathrm{mA/cm}^2}$) decreased over a wide range from 6750 V/cm to 4550 V/cm with the increase of sintering temperature. This is attributed to the decease in the number of grain boundaries caused by the increase in ZnO grain size during sintering process. The nonlinear exponent (α) increased as the sintering temperature increase from 1200 °C to 1275 °C. The samples sintered at 1275 °C exhibited the highest α value, whereas the α value abruptly decreased at 1300 °C. This shows that sintering temperature greatly affects nonlinear properties. While the variation of J_{leak} value was opposite to that of α value, this is because the high α value leads to low leakage current due to relatively high tunneling current and the low leakage current due to relatively high thermionic emission current [14].

4. Conclusion

Sintering behavior of Zn–Pr–Co–Mn–O varistor ceramics was systematically investigated in air. Sintering temperature and time have great effect on the microstructure and the electrical properties. The relative density of sintered ZPCM ceramics increased from 72% to 96% with the temperature in the range of 1050–1300 °C. From 1050 °C to 1300 °C, the grain growth kinetic exponent is about 3.7, lower than for Bi_2O_3-based ZnO varistors. The apparent activation energy for grain growth in this temperature range is around 306 ± 61 kJ/mol, which is higher than that of Bi_2O_3-based ZnO varistors. An optimum sintering temperature of 1275 °C gave the best electrical properties, with the nonlinear exponent (α) attaining a highest value of 54.7.

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