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Microstructure and electrical properties of $ZnO–Bi_2O_3$-based varistor ceramics by different sintering processes

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Abstract

The effect of sintering processes, such as open sintering, sintering inside a closed crucible, and sintering within a powder bed, on the microstructure and *V–I* characteristics of $ZnO–Bi_2O_3$-based varistor ceramics was investigated at sintering temperatures in the range 1000–1200 °C. The results from the experiments showed that the microstructure and electrical properties of the samples varied according to the sintering method and temperature. Optimal values for the electrical characteristics of the varistor ceramics by different sintering processes were obtained when the sintering was conducted at 1100 °C. At the same sintering temperature, the different processes affected the properties differently. At 1000 °C, the samples sintered within a powdered bed showed better electrical properties than those subjected to the other two processes, while at 1100 or 1200 °C, the samples sintered in an open crucible exhibited the best electrical properties.

Keywords: Varistors; ZnO; Sintering; Final microstructure; Electrical properties

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1. Introduction

Varistor ceramics are electronic ceramic devices whose function is to limit voltage surges by becoming strongly conducting at a breakdown voltage.[1,2] ZnO-based varistor ceramics play a leading role in making surge protection devices, which are commonly used to protect electric power systems from transient voltages.[3–5] The nonlinear current–voltage characteristic of ZnO-based varistor ceramics is a grain-boundary phenomenon, and the electrical characteristics of the varistor are directly related to the size of the ZnO grain.[6,7] The method of preparation, crystalline size, and homogeneity of the additive are critical for producing good varistor materials. Varistor ceramics with inhomogeneous microstructure can cause a large spread in current–voltage characteristics due to high local currents, which lead to the degradation of the varistor during electrical operation.[1] Varistor ceramics are rather complex, being mainly composed of ZnO to which small amounts of oxides such as Bi_2O_3, Sb_2O_3, Co_2O_3, MnO_2 and Cr_2O_3 have been added.[6] The powder is mixed, then pressed and sintered at higher temperatures to make the dense, final products. The microstructure of the sintered material comprises a matrix of highly conductive ZnO grains with two major secondary phases: a spinel-type phase mainly located at the grain boundaries and triple points, and a Bi-rich phase surrounding the ZnO grains and promoting the formation of potential barriers to electrical conduction at the ZnO homojunctions.[3,8]

In the classical ZnO-based varistor, Bi_2O_3 is used as the varistor-former,[9] thus it is essential for inducing the nonlinearity of the ZnO ceramics.[10] Bi_2O_3 is particularly important since it provides the medium for liquid-phase sintering, enhances the growth of ZnO grains, and affects the stability of the nonlinear current–voltage characteristics of the material. The melting point of Bi_2O_3 is 825 °C. The eutectic temperature of $ZnO–Bi_2O_3$ is only 740 °C, thus a liquid is formed in the $ZnO–Bi_2O_3$ specimens below 800 °C. As soon as the eutectic liquid is formed, the weight loss starts to increase. This indicates that the vaporization of Bi_2O_3 starts immediately after the eutectic liquid has been formed.

Peiteado and his co-workers[11,12] used the X-ray fluorescence method to investigate the effect of the area/volume ratio on

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the vaporization of Bi in ZnO varistors. To reduce the loss of material, Metz et al.[13] suggested using a new route, in which ceramics are produced by mixing pre-synthesized spinel and pyrochlore phases with the other classical single-oxide additives. Onreabroy et al.[14] have noted that the nonlinear coefficient depended primarily on the sintering temperature, which significantly decreased at higher temperatures, probably due to the volatilization of Bi_2O_3. Weight loss by uncontrolled Bi_2O_3 vaporization is a crucial parameter in the manufacture of varistor ceramics.[15] However, the effects of the sintering process on the electrical properties and vaporization of the Bi_2O_3 in varistor ceramics have seldom been reported.

In this paper, the microstructure and the electrical response of varistor ceramics sintered at differing temperatures and by differing processes were studied in order to obtain a sintering process which can control the vaporization of Bi_2O_3 more effectively.

2. Experimental procedure

2.1. Sample preparation

ZnO–Bi_2O_3-based varistor samples with a nominal composition of 96.5 mol.% ZnO, 0.7 mol.% Bi_2O_3, 1.0 mol.% Sb_2O_3, 0.8 mol.% Co_2O_3, 0.5 mol.% Cr_2O_3, and 0.5 mol.% MnO_2 were used. Reagent-grade raw materials were mixed and homogenized in absolute ethanol media in a polyethylene bowl with zirconia balls for 5 h at 500 rpm by planetary high-energy ball milling. The ratio of balls to the mixed powder was, respectively, 20:1. The slurry was dried at 70 °C for 24 h, it was then pulverized by an agate mortar/pestle and after 2 wt.% polyvinyl alcohol (PVA) binder had been added, it was granulated by sieving through a 100-mesh screen to produce the starting power. The power was uniaxially pressed into discs which were 12 mm in diameter and 2 mm in thickness. The pressed disks were heated in air at 500 °C and for 2 h dwell time to release the binder. Then the disks were sintered in air at 1000–1200 °C (2-h dwell time), at a heating rate of 5 °C/min and then cooled in the furnace. The different processes used to sinter the green pellets are shown in Fig. 1, they were open sintering (OS), sintering inside a closed crucible (CS), and sintering within a powdered bed (PS). The green compacts of OS were placed on a corundum sheet covered with a ZnO powder bed in order to avoid material diffusing into the substrate (Fig. 1a). The green compacts of CS were placed on a corundum sheet covered with a ZnO powder bed, and were sealed into an inverse corundum crucible (Fig. 1b). The green compacts of PS were placed in a corundum crucible, the substrate of the crucible was covered with 99.3 mol.% ZnO and 0.7 mol.% Bi_2O_3 powder, and the same powder was then used to bury the green compacts (Fig. 1c). The detailed sintering schedules are given in Table 1. The sintered samples were lapped and polished to 1.0-mm thickness. The final samples were about 10 mm in diameter and 1.0 mm in thickness.

Table 1
Sintering schedules of samples sintered at different temperatures by different processes.

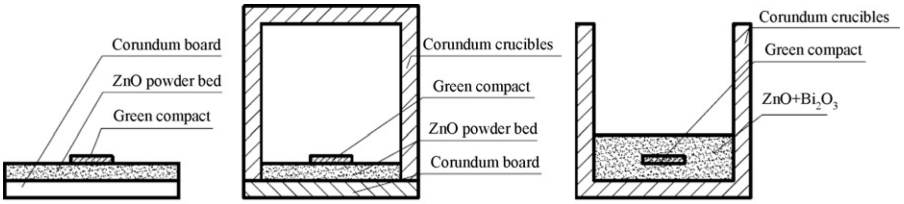
Sintering processes	Sintering temperature θ (°C)		
	1000	1100	1200
OS	C2A	C2B	C2C
CS	C3A	C3B	C3C
PS	C4A	C4B	C4C

2.2. Measurement of microstructures

To observe the microstructure, sintered ZnO samples were fractured and the fractured surface was coated with gold for examination by a scanning electron microscope (SEM) (JSM-6700F, Japan). The average grain size (G) was determined by the linear intercept method, given by $G = 1.56\,L/MN$, where L is the random line length on the micrograph, M the magnification of the micrograph, and N is the number of the grain boundaries intercepted by lines. The crystalline phases were identified by an X-ray diffractometer (Rigaku D/max 2200, Japan) using Cu Kα radiation. The density, ρ, of the pellets was measured geometrically.

2.3. Measurement of V–I characteristics

The DC current–voltage was characterized by coating silver paste onto both faces of the samples. The silver electrodes (diameter 5 mm) were formed by heating at 600 °C for 10 min. The voltage–current (V–I) characteristics were measured by using a V–I source/measure unit (model CJ1001). The nominal varistor voltages (V_N) (breakdown voltage is the voltage at which the varistor switches from a highly resistive to a highly conductive state) at 0.1 and 1 mA were measured and the threshold voltage V_T (V/mm) (breakdown voltage/unit thickness of varistor ceramic; $V_T = V_N$ (1 mA)/d, where d is the thickness of the sample in mm) and the nonlinear coefficient α ($\alpha = \log(I_{1mA}/I_{0.1mA})/\log(V_{1mA}/V_{0.1mA}) = 1/\log(V_{1mA}/V_{0.1mA})$) according to the equation describing the V–I nonlinearity of the



(a) OS (b) CS (c) PS

Fig. 1. Sintering processes: (a) OS; (b) CS; (c) PS.