Enhancement of Microstructure Development and Current-voltage Characteristics of ZnO-Bi$_2$O$_3$ Varistor Ceramics Sintered with Sintering aids at the Low-Temperature

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Abstract. ZnO-Bi$_2$O$_3$ based varistor ceramics doped with SnO$_2$ or with SnO$_2$, B$_2$O$_3$ and SiO$_2$ were prepared by traditional solid–state reaction method respectively. The microstructure and properties of samples sintered at a low temperature range from 910 to 950°C were studied. Results show that: by low-temperature sintering, the sintering aids can improve the sample’s density and homogeneity, and therefore the overall properties of the samples. It was found that the samples sintered at 910°C with SnO$_2$ as sintering aid possess the best performance, and the breakdown voltage is 1368 V/mm, nonlinear coefficient is 12.2, and the leakage current is less than 0.1 μA.

1. Introduction

ZnO-Bi$_2$O$_3$ varistor ceramics have been widely used to protect the electrical and electronic circuits from transient voltage surges due to their excellent nonlinear coefficient, low leakage current and high response speed[1-3]. The ceramic materials are usually sintered at the temperatures between 1100°C and 1300°C. Bi$_2$O$_3$ plays an essential role in liquid-phase sintering and the formation of nonlinear characteristics of the material[4]. However, the Bi$_2$O$_3$ of ZnO–Bi$_2$O$_3$ based ceramics will volatilize at the sintering temperatures over the melting point of Bi$_2$O$_3$ during sintering process, which cause the performance deterioration. Even worse, in the Multilayer Co-fired Ceramic (MLCC) field, the performance deterioration often occurred because Bi$_2$O$_3$ is easy to react with Pd within the Ag-Pd inner electrode at the temperatures mentioned above 950°C [5-6]. The probably best solution is to lower the sintering temperature below 950°C, which would be helpful in the replacement of Pd with pure Ag as inner electrode.

The application of sintering aids is effective in lowering the sintering temperature. By taking into account of the environmental protection, SnO$_2$, B$_2$O$_3$ and SiO$_2$ were used as sintering aids[7-13]. Yongvanich et al.[9] reported the evolution of microstructure of ZnO–Bi$_2$O$_3$ based varistor ceramics doped with different amounts of SnO$_2$. However, the sintering temperature is as high as 1200°C. Xu et al.[8] and Bai et al.[12] reported separately B$_2$O$_3$-doped and SiO$_2$-doped, and the both dopants are conducive to promoting the electrical properties of ZnO varistor ceramics and lowering the sintering temperature. As is reported that the SnO$_2$ doping could influence grain growth and increase nonlinear and breakdown voltage, the B$_2$O$_3$ and SiO$_2$ which have low melting point temperature.
In this paper, ZnO-Bi₂O₃ based varistor ceramics doped with SnO₂ or with SnO₂, B₂O₃ and SiO₂ were prepared by low temperature sintering (lower than 950°C) to study the effect of different dopants on microstructure and electrical properties.

2. Experimental procedure
The ZnO-Bi₂O₃ based varistor samples with basic composition of ZnO, Bi₂O₃, Sb₂O₃, MnO₂, Co₂O₃, Cr₂O₃, Ni₂O₃, Al₂O₃, marked as M1. The samples with SnO₂-doped composition were marked as M2, that with SnO₂, B₂O₃ and SiO₂–doped basic composition were marked as M3. All samples were prepared by traditional solid–state reaction method. The M1 samples sintered at 910°C, 930°C, 950°C for 2 h were recorded as samples M1-910, M1-930, M1-950, and M2, M3 similarly. The final size of the samples with silver as electrode was φ10×1 (mm×mm).

The electrical characteristics of the samples were measured using varistor voltage test instrument (MY-1KV, Hunan, China). The crystalline phases were identified by an X-ray diffractometer (XRD, Rigaku, Japan) using a CuKα radiation. The microstructure was examined by a scanning electron microscope (SEM, Sigma, Japan).

3. Results and discussion
Figure 1 showed the XRD patterns of the samples sintered at 950°C. The main phases of all samples were ZnO (PDF NO. 75-0576), (Zn₇Sb₂O₁₂)₁.₂₆₇ (PDF NO. 74-1858), Zn₆Al₂O₉ (PDF NO. 51-0037) and Bi₂O₂.₇ (PDF NO. 75-0993). Doping didn’t change the ceramic phase. No Sn-based phase was observed, probably due to the detection limit of the instrument.

![Figure 1. XRD patterns of samples.](image)

Figure 2 showed the typical microstructures of all samples. All of the samples possessed satisfied density. Further observation revealed that the doping of sintering aids improved the homogeneity of microstructure and decrease the average grain size, especially for SnO₂, B₂O₃ and SiO₂–doping. SnO₂ was beneficial to lower the sintering temperature. SnO₂ readily reacted with ZnO to form a spinel phase (Zn₂SnO₄), and with Bi₂O₃ to form pyrochlore phase (Bi₂Sn₂O₇)[9]. The low melting point dopants, SiO₂ and B₂O₃, are conducive to promoting the uniform growth of grain and the homogeneous distribution of second phases[14]. In addition, B₂O₃ is helpful to form glass phase on grain boundary and stabilized grain boundary, and SiO₂ is beneficial to form the second phase and inhibiting grain growth[12].
Figure 2. Microstructure of samples: (a) M1-910, (b) M2-910, (c) M3-910; (d) M1-930, (e) M2-930, (f) M3-930; (g) M1-950, (h) M2-950, (i)M3-950.

Table 1. Electrical Parameters, Density and Grain Size of Samples.

| Breakdown Voltage (V/mm) | Nonlinear Coefficient $\alpha$ | Density (g/cm$^3$) | Average Grain Size ($\mu$m) |
|-------------------------|-------------------------------|-------------------|---------------------------|
| 910$^\circ$C 930$^\circ$C 950$^\circ$C | 910$^\circ$C 930$^\circ$C 950$^\circ$C | 910$^\circ$C 930$^\circ$C 950$^\circ$C | 910$^\circ$C 930$^\circ$C 950$^\circ$C |
| M1 | 1206 | 1035 | 885 | 8.2 | 7.0 | 9.1 | 5.36 | 5.42 | 5.48 | 1.5 | 2.0 | 2.9 |
| M2 | 1368 | 1245 | 1043 | 12.5 | 10.3 | 6.6 | 5.40 | 5.46 | 5.53 | 1.4 | 1.9 | 2.5 |
| M3 | 1040 | 877 | 712 | 7.8 | 6.6 | 8.3 | 5.50 | 5.55 | 5.59 | 1.1 | 1.7 | 2.1 |

Note: The leakage current is less than 0.1 $\mu$A, and could not be read due to the equipment test limit.

By studying the relationship between microstructure and sintering temperature, it’s found that with the rise of sintering temperature, the grain size and the density of samples increased. The average size of the samples range from 1 to 3 mm, and the relative density is above 90%, according to theoretical density 5.60 g/cm$^3$[15]. The explanation could be given as follows. As the sintering temperature increased, the liquid phase formed during the sintering process becomes richer, which is beneficial to the mass transfer and promotes the grains growth and improves the microstructure uniformity. At each sintering temperature, the grain size order was M3<M2<M1. It is considered that the spinel phase formed with SnO$_2$ could prevent grain growth during sintering process. In M3, Which were doped with SnO$_2$, SiO$_2$ and B$_2$O$_3$, the average grain size of the samples obtained at each sintering temperature is the smallest among the three, and the average grain size increases slowly with the increase of sintering temperature. The last but not least, the microstructure of M3 is most homogeneous. The
homogeneous distribution of second phases formed by dopants as explained above in M3 will be the first reason for the improved performance of samples.

Details of the electrical properties, density and average grain size are listed in Table 1. The leakage current was less than 0.1 µA which cannot be read from the instrument, so it was not shown in the table. From Table 1, the breakdown voltage value of the samples were in the range of 700 ~1400 V/mm, and the nonlinear coefficient of all samples was in the range of 6.0~12.5. When sintering at 910°C, the M2 samples exhibited the best comprehensive performance. The M2-910 displayed the breakdown voltage of 1368 V/mm, the nonlinear coefficient of 12.5, and the leakage current less than 0.1 µA.

The breakdown voltage of the samples decrease gradually with the rising sintering temperature. The reason is that the voltage is theoretically equal to the product the grain boundaries number per unit thickness and the voltage drop of a single grain boundary. In general the value of voltage drop is invariable about 2.0–4.0 V, so the breakdown voltage is proportional to the number of grain boundaries per unit thickness and inversely proportional to the grain size[5]. With the rise of sintering temperature, the average grain size increase and the grain boundaries number decrease, therefore the voltage decreases.

It is clearly shown in Table 1 that the breakdown voltage increase from 1206 V/mm in M1 to 1368 V/mm in M2 doped with SnO₂ under sintering at 910°C, the nonlinear coefficient of M2 is larger. The discussion of the nonlinear coefficient difference is so far difficult[16]. But it is certain that the addition of sintering aids not only causes the change of grain size, but also changes the grain boundary characteristics, such as grain boundary barrier, interfacial state density and so on which will affect the nonlinear coefficient and breakdown voltage[6, 14]. M3, sintered at 910°C, whose average grain size of is smaller and the microstructure is more uniform than M1 and M2, obtain the best performance of microstructure. But the voltage of M3 is smaller than M1 and M2.

4. Conclusions
ZnO varistor ceramics doped with SnO₂, B₂O₃ and SiO₂ is expected to reduce sintering temperature below 950°C and be applied in MLCC field. The study prepared respectively different samples doped with SnO₂ or with SnO₂, SiO₂ and B₂O₃ by traditional solid–state reaction method. The results showed that with the increase of sintering temperature, the average grain size and the density of samples increased, and the breakdown voltage decreased gradually. The doping of sintering aids can improve the microstructure compactness and uniformity the distribution of the second phase and particle size. M3 exhibit the smallest average grain size and achieve high density below 950°C. In terms of electrical properties, the breakdown voltage of the samples was 700~1400 V/mm, and the nonlinear coefficient ranged at 6.0~12.5. The best electrical properties is obtained by M2, which doping with SnO₂, sintered at 910°C: voltage of 1368.3 V/mm, nonlinear coefficient of 12.2, leakage current less than 0.1 μA, the average grain size of 1.4 μm.

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