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Microstructural evolution during sintering of Bi_2O_3-doped ZnO

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Abstract The electrical properties of a ceramic varistor depend strongly on its microstructural uniformity. In the present study, the microstructure of the Bi_2O_3-doped ZnO after sintering is characterized. A very small amount, 0.04 mol%, of Bi_2O_3-addition may induce density inhomogeneity in the early stage of sintering. A critical amount, >0.09 mol%, of Bi_2O_3 is needed to result in density uniformity. The addition of Bi_2O_3 can enhance the coarsening rate of ZnO grains; nevertheless, the grain size distribution is not affected.

Keywords ZnO · Sintering · Microstructure · Grain size distribution

1 Introduction

Zinc oxide (ZnO) varistors with multilayer structure are now frequently used as the surge protection components in many 3C (communication, computer, consumer) electronic products. To fulfill the requirement on miniaturization, the breakdown voltage of such multilayered varistors has to be low. Sometimes it may be even as low as 6 V. Since the barrier voltage of one single Bi_2O_3-rich grain boundary is around 3.5 V [1, 2], only a few grains are allowed to squeeze into the inner electrodes. Furthermore, the electrical current tends to pass through the weakest part, the part with the largest grains, within the component; the variation of grain size from one place to another place should be as small as possible. To control the microstructure uniformity is thus essential to the electrical performance of varistor.

The ZnO varistor is composing of semiconducting ceramic grains and insulating grain boundary layer. A liquid phase, Bi_2O_3-rich phase, is usually added to enhance the densification, then acted as the insulating layer after sintering. The densification and grain growth behavior of ZnO–Bi_2O_3 system have attracted much attention for their potential usage as varistor [2–7]. Apart from the average grain size, the grain size distribution after sintering attracted relatively less attention [2, 3]. In the present study, the effect of Bi_2O_3-rich liquid on the microstructure uniformity of ZnO is investigated.

2 Experimental

A high-purity ZnO powder was mixed with various amounts of Bi_2O_3 by ball milling in ethyl alcohol for 4 h. After drying, the dried lumps passed a no. 150 sieve to remove agglomerates. The green compacts, with diameter of 10 mm and thickness of 3 mm, were formed by uniaxial pressing at 50 MPa. Sintering was performed within a box furnace from 800 to 1200 °C for 1 h. The heating and cooling rates were 5 °C/min. The density was determined with the water displacement method. The cross-section of the specimens were ground with silicon carbide particles and polished with alumina particles. The grain boundaries were revealed by soaking the polished section in dilute hydrochloric acid for several seconds. The microstructure

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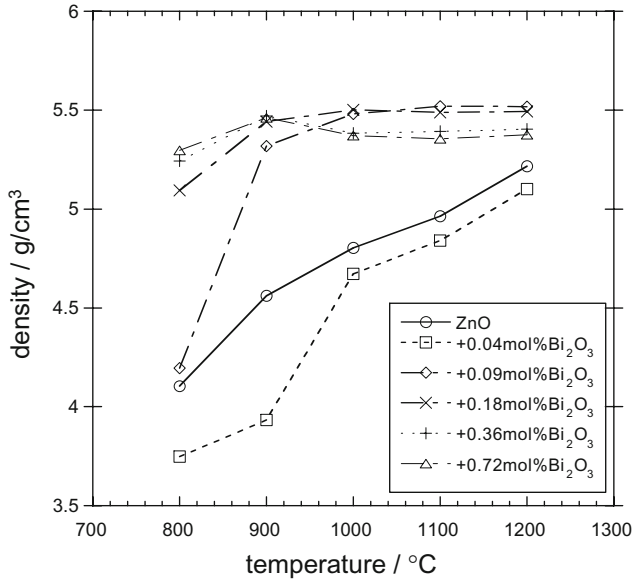


Fig. 1 Density as function of sintering temperature. The dwell time at the indicated temperatures was 1 h

was observed by using scanning electron microscopy (SEM). The SEM micrographs were then digitized by using a scanner. The image analysis was performed on the digitized images in order to determine the area of each grain. Over 500 grains were measured for each composition. The equivalent circular diameter was determined from the area, assuming that each grain was spherical. The three-dimensional mean grain size was calculated by multiplying the mean equivalent circular diameter by 1.56.

3 Results and discussion

Figure 1 shows the density of the Bi_2O_3-doped ZnO specimens as a function of sintering temperature. The addition of Bi_2O_3 induces the formation of a liquid phase in ZnO above ~750 °C [8]. The presence of such liquid phase provides a fast route for mass transportation [5]. However, the density of the 0.04 mol% Bi_2O_3-doped ZnO specimen is lower than that of the ZnO specimen. The presence of a small amount of Bi_2O_3 reduces the fired density had been related to the segregation of Bi_2O_3 phase at the ZnO/ZnO necks [7]. After conducting careful microstructural observation, an alternative is proposed here. A typical micrograph of the 0.04 mol% Bi_2O_3-doped ZnO specimen after sintering at 1100 °C is shown in Fig. 2. The microstructure is not uniform, high-density regions with coarse grains and low-density region with fine grains are co-existed within the specimen. Since the amount of the liquid phase in the 0.04 mol% Bi_2O_3-doped ZnO specimen is very small. Once the liquid phase is formed, such liquid phase is limited to

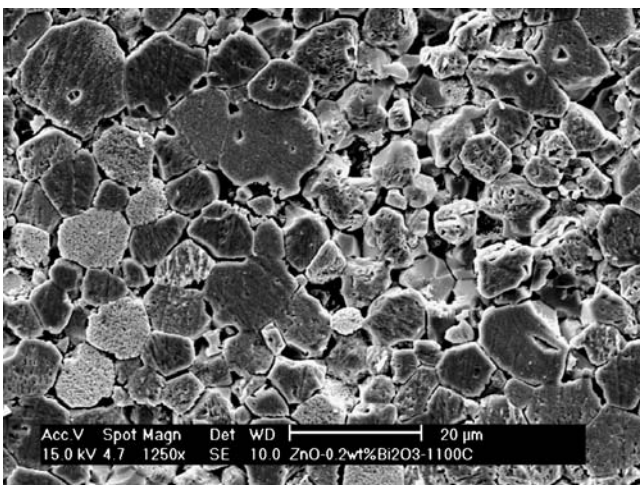
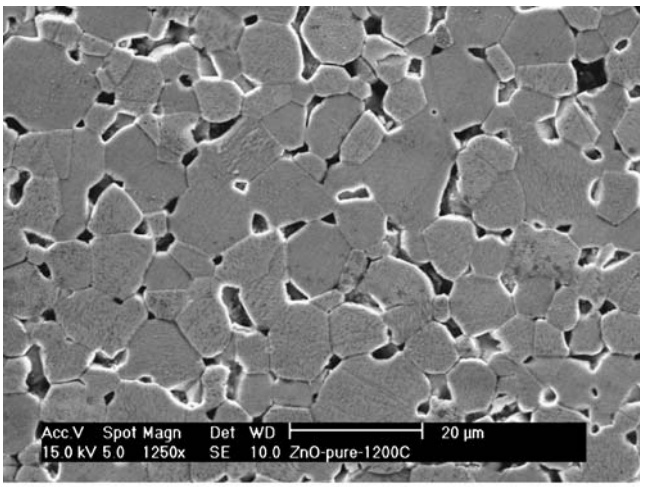
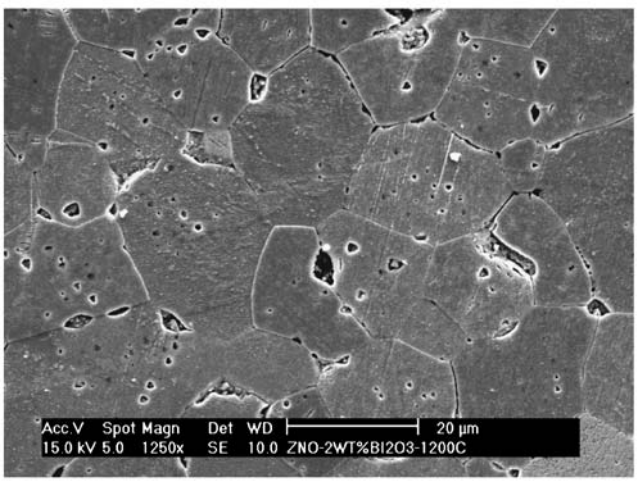


Fig. 2 Typical micrograph of the 0.04 mol% Bi_2O_3-doped ZnO specimen after sintering at 1100 °C for 1 h



(a)



(b)

Fig. 3 Typical micrographs of the (**a**) ZnO and (**b**) 0.36 mol% Bi_2O_3-doped ZnO specimens after sintering at 1200 °C

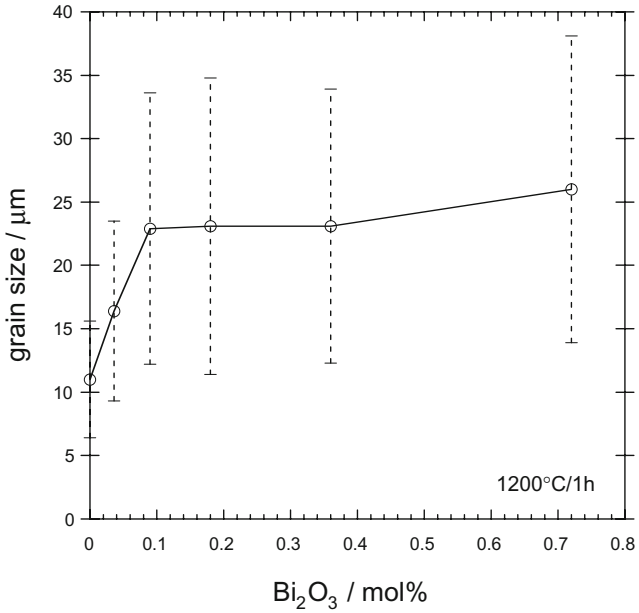


Fig. 4 Average grain size of the Bi_2O_3-doped ZnO specimens as a function of Bi_2O_3 amount

the region near the Bi_2O_3 particles. The presence of the Bi_2O_3-rich liquid can induce a capillary force which drags the nearby particles close together [9]. Dense regions are thus formed. The grain growth rate is usually faster in the dense region [10], the grains in the dense regions are therefore larger. However, the porous regions with fine grains are still existed around such dense region. As the amount of Bi_2O_3 is higher than 0.09 mol%, the densification of ZnO is enhanced. It thus suggests that there is a minimum amount of liquid phase to achieve microstructure uniformity.

Figure 3 shows typical microstructures of the ZnO and Bi_2O_3-doped ZnO specimens after sintering at 1200 °C for 1 h. The pores in the ZnO specimen are mainly located at the grain boundaries and triple junctions. The addition of the Bi_2O_3-rich liquid reduces the dihedral angle [4]. Many elliptical pores in the ZnO–Bi_2O_3 specimens, Fig. 3(b), are the evidence for such change. The reduction of the dihedral angle encourages the separation between the pore and grain boundary. Many pores are thus trapped into ZnO grains as Bi_2O_3 is added. The formation of intragranular pores results in a limiting density, ~97.5%, to the ZnO–Bi_2O_3 system, Fig. 1.

Table 1 The microstructural features of the ZnO and Bi_2O_3-doped ZnO specimens.

	Average grain size/μm	Standard deviation/μm (coefficient of variation[a]/%)	Area fraction of coarse grains[b]/%
ZnO	11	4.6 (42%)	39
ZnO+0.04 mol%Bi_2O_3	16	7.1 (43%)	42
ZnO+0.09 mol%Bi_2O_3	23	10.7 (47%)	45
ZnO+0.18 mol%Bi_2O_3	23	11.7 (51%)	47
ZnO+0.36 mol%Bi_2O_3	23	10.8 (47%)	40
ZnO+0.72 mol%Bi_2O_3	26	12.1 (47%)	44

[a] Coefficient of variation = standard deviation/average value
[b] The grains with the size larger than (average value + one standard deviation)

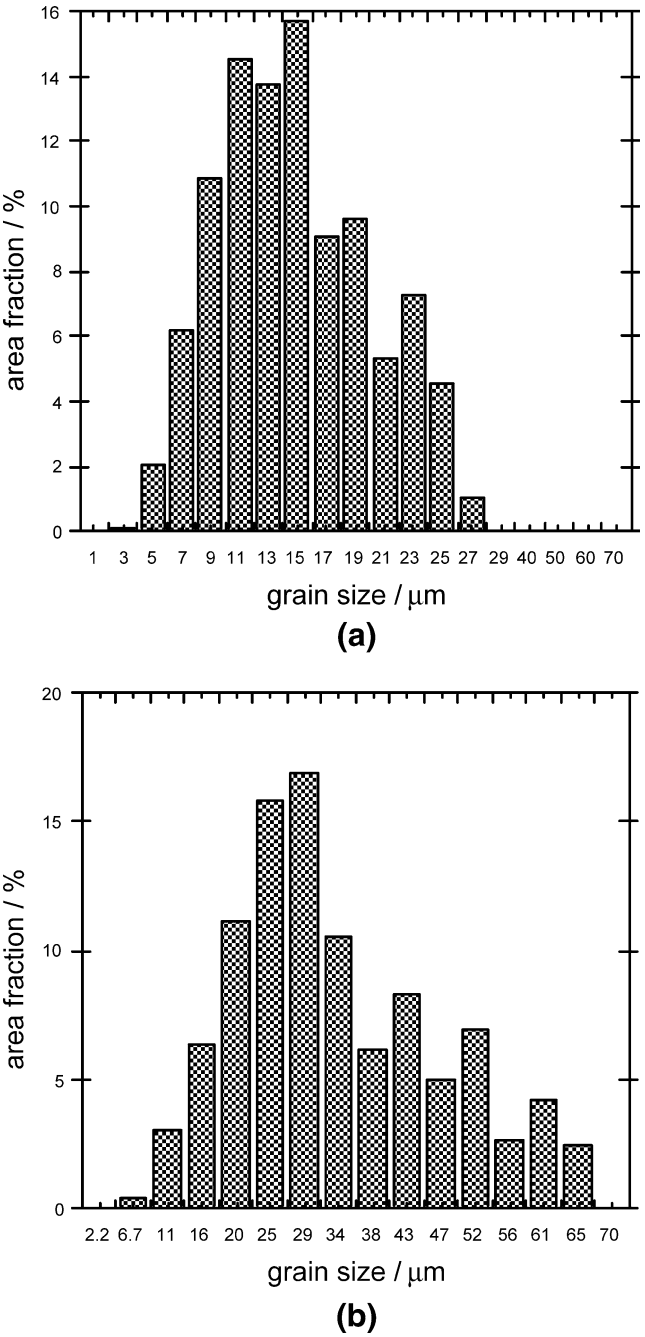


Fig. 5 Grain size distribution (area frequency) of (**a**) ZnO and (**b**) 0.36 mol%Bi_2O_3-doped ZnO specimens

Differ from the densification behavior of the Bi_2O_3-doped ZnO specimens, a very small amount of Bi_2O_3, 0.04 mol%, can also enhance the coarsening rate of ZnO. The average size of ZnO grains increases with the increase of Bi_2O_3 amount, Fig. 4. The average grain size reaches a plateau as the Bi_2O_3 amount is higher than 0.09 mol%. Table 1 shows the values of average grain size and standard deviation. Though the standard deviation of the Bi_2O_3-doped ZnO specimens is larger than that of ZnO specimen, the coefficient of variation (standard deviation/average value) is very close to each other.

Figure 5 shows the grain size distribution of the ZnO and Bi_2O_3-doped ZnO specimens. By adding Bi_2O_3 into ZnO, the size distribution curve shifts to larger size. Several coarse grains could cover relatively large area fraction; the presence of large grains can lead to unexpected breakdown. Therefore, the area fraction is used as the index to characterize the grain size distribution. In order to quantify the amount of coarse grains, we define that the grains with the size larger than (average size + one standard deviation) as coarse grains. The area fraction of the coarse grains in the Bi_2O_3-doped ZnO specimens is shown in Table 1. Similar to the coefficient of variation (Table 1), the area fraction of the coarse grains is more or less the same for the ZnO and Bi_2O_3-doped ZnO specimens, suggesting that the addition of Bi_2O_3 affects little the size distribution of ZnO grains. The amount of Bi_2O_3 also shows little influence on the size distribution of the ZnO grains. Nevertheless, one should note that the coarse grains occupy 40% of the area fraction, indicating that the coarse grains can dominate the electrical properties of the present ZnO–Bi_2O_3 system.

4 Conclusions

The effect of Bi_2O_3 addition on the microstructural evolution during sintering is investigated. The following conclusions can be drawn from the present study.

1. A minimum amount of Bi_2O_3 addition is needed to avoid the formation of density inhomogeneity in the early stage of sintering.
2. Though the addition of Bi_2O_3 enhances the coarsening rate of ZnO grains, the size distribution of ZnO grains in the Bi_2O_3-doped ZnO specimens is not affected.
3. There is a limiting density, ~97.5%, to the ZnO–Bi_2O_3 specimens, due to the presence of intragranular pores.
4. The area fraction of the coarse grains, the grains with the size larger than the value of average size plus one standard deviation, is around 40%.

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