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Inversion boundary induced grain growth in TiO_2 or Sb_2O_3 doped ZnO-based varistor ceramics

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Abstract

In low-voltage varistor ceramics, the phase equilibrium and the temperature of liquid-phase formation are defined by the TiO_2/Bi_2O_3 ratio. The selection of a composition with an appropriate TiO_2/Bi_2O_3 ratio and the correct heating rate is important for the processing of low-voltage varistor ceramics. The total amount of added Bi_2O_3 is important as the grain growth is slowed down by a larger amount of Bi_2O_3-rich liquid phase at the grain boundaries. Exaggerated grain growth in low-voltage varistor ceramics is related to the occurrence of the liquid phase and the presence of TiO_2 which triggers the formation of inversion boundaries (IBs) in only a limited number of grains, and as a result the final microstructure is coarse grained. The Zn_2TiO_4 spinel phase only affects grain growth in compositions with a TiO_2/Bi_2O_3 ratio higher than 1.5. In high-voltage varistor ceramics, just a small amounts of Sb_2O_3 trigger the formation of IBs in practically every ZnO grain, and in compositions with a Sb_2O_3/Bi_2O_3 ratio lower than 1, grain growth that is controlled entirely by an IBs-induced grain growth mechanism results in a fine-grained microstructure. The spinel phase interferes with the grain growth only at higher Sb_2O_3/Bi_2O_3 ratios.

Keywords: Grain growth; Powders: solid-state reaction; Sintering; Grain size; Microstructure-final; ZnO; Varistors

1. Introduction

The non-linear characteristic of ZnO-based varistor ceramics is a phenomenon related to the grain boundaries between the ZnO grains. The breakdown voltage of an ideal, non-linear grain boundary is approximately 3.2 V, and the threshold voltage of a varistor ceramic—the breakdown voltage per unit thickness of a ceramics is usually expressed in V/mm—is the sum of the breakdown voltages of all the grain boundaries per unit thickness of ceramic.[1,2] As the breakdown voltage of ZnO-based varistor ceramics is directly related to the size of the ZnO grains, the control of grain growth is of great importance when it comes to developing varistor ceramics for particular voltage ranges. The use of varistor ceramics with the proper threshold voltage—low, medium or high—is necessary for the production of high-quality varistors with a particular breakdown voltage and a suitable thickness.

Bi_2O_3 is the dopant that induces the non-linear characteristics in ZnO ceramics and contributes a Bi_2O_3-rich liquid phase along the grain boundaries. As a result, its influence on sintering and grain growth in ZnO-based ceramics has been intensively studied in the past.[2–6] Sintering in combination with some spinel-forming dopants also allows the microstructure development and grain growth to be controlled.[7,8] Sb_2O_3 is a standard spinel-forming dopant to produce fine-grained high-voltage varistor ceramics. It enhances the nonlinearity of varistor ceramics and reduces the evaporation of Bi_2O_3 during sintering. However, the major role of Sb_2O_3 is to control the growth of the ZnO grains. The inhibition of ZnO grain growth in Sb_2O_3-doped samples is generally explained by a reduction in the mobility of grain boundaries by a pinning effect, caused either by secondary spinel particles or a fine Sb-rich film on the surface of the ZnO grains[9–12]—with larger additions of Sb_2O_3, more spinel grains form and the ZnO grains are smaller. The addition of Sb_2O_3 also triggers the formation of IBs in ZnO grains.[13] The structure and chemistry of IBs in Sb-doped ZnO were determined by Rečnik et al.[14]

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Low-voltage varistor ceramics are characterized by a coarse-grained microstructure, where TiO_2 is commonly used as the grain-growth-enhancing additive.[15–18] The influence of TiO_2 on grain growth is not yet fully understood: the enhancement of the grain growth was explained in broad terms by an increased reactivity of the Bi_2O_3-rich liquid phase with the solid ZnO in the presence of TiO_2; however, much more indicative was the observation that the addition of TiO_2 causes exaggerated grain growth, which is controlled by the presence of IBs in the anomalously large ZnO grains that are typically found in a matrix of smaller grains.[17] The addition of TiO_2 also results in the formation of the Zn_2TiO_4 spinel phase, which has no obvious influence on the microstructure development of low-voltage varistor ceramics. Like Sb_2O_3 and TiO_2, the addition of SnO_2 to the ZnO-based ceramics also results in the formation of the Zn_2SnO_4 spinel phase and triggers the formation of the IBs in the ZnO grains. The substitution of Sb_2O_3 with SnO_2 results in an identical microstructure and a comparable breakdown voltage of ZnO-based varistor ceramics.[19]

Based on the investigations of the SnO_2-doped ZnO, we showed that the microstructure development is controlled by the growth of grains with IBs, and proposed an IB-induced grain growth mechanism.[7] We also confirmed this mechanism by diffusion doping the ZnO with Sb_2O_3: in the absence of any spinel phase, fine ZnO grains had their growth inhibited in the high-concentration region on the surface of the pellet, whereas in the low-concentration region in the central parts of the grains, several-times-larger grains were obtained as a result of the exaggerated growth.[8] By controlling the number of nuclei with IBs we can actually design, not only fine grained, but also a coarse-grained microstructure, even with Sb_2O_3 doping.

In this study the grain growth in TiO_2- or Sb_2O_3-doped ZnO–Bi_2O_3 ceramics, as well as low-voltage and high-voltage varistor ceramics, was examined to evaluate and elucidate the different aspects of the above-mentioned grain-growth-control mechanisms in ZnO-based varistor ceramics.

2. Experimental

The samples were prepared by a conventional ceramic procedure: reagent-grade oxides were mixed in the appropriate molar ratios and homogenized in absolute ethanol using a planetary mill. The powders were then dried and pressed at 200 MPa into discs with a diameter of 10 mm and a thickness of 1.5 mm. The pellets were fired at temperatures in the range from 700 to 1260 °C for 0.25–3 h. Whereas the heating rate to the sintering temperature was typically 10 °C/min, the cooling rate was either 10 °C/min or quenching (samples pulled from the oven at the sintering temperature and allowed to cool rapidly to room temperature).

The phase composition of the samples was analyzed by X-ray powder diffraction (XRD) analysis. The microstructures were examined using a scanning electron microscope (SEM) in back-scattered electron (BE) mode. The phase compositions of the samples and the compositions of the individual phases were determined by energy-dispersive X-ray spectroscopy (EDS) in the SEM. The average ZnO grain size (*D*) was determined for each sample from measurements of 300–800 grains per sample. The surface of each grain was measured and its size was calculated in terms of a diameter for circular geometry. The elongation of the grains was determined as the ratio of the length of the major (longest) axis across the grain and the length of the minor axis (the longest axis perpendicular to the major axis). This means that if the elongation is 1, the object is roughly circular or square; however, as the ratio increases to more than 1, the object becomes more elongated.

3. Results and discussion

The Bi_2O_3-rich liquid phase strongly affects the development of the microstructure in ZnO-based varistor ceramics. The amount of liquid phase at the sintering temperature of varistor ceramics in the temperature range from 1100 to 1300 °C depends on the amount of Bi_2O_3 added to the starting composition. At lower temperatures, the amount of Bi_2O_3-rich liquid phase is determined by the phase equilibrium at a particular temperature, which again depends on the starting composition. The typical phase compositions of varistor ceramics make it clear that the phase equilibrium is determined by the phase equilibrium in "the ZnO corner" of ternary systems: the ZnO–Bi_2O_3–TiO_2 system and the TiO_2/Bi_2O_3 ratio in the case of low-voltage varistor ceramics, and the ZnO–Bi_2O_3–Sb_2O_3 system and the Sb_2O_3/Bi_2O_3 ratio in the case of high-voltage varistor ceramics.

The influence of TiO_2/Bi_2O_3 ratios of 0, 0.11, 0.17, 0.33, 0.60, 1.00, 1.50 and 4.00 on the phase equilibrium, the microstructure development and the ZnO grain-size was analyzed in samples with 98 and 92 mol% ZnO doped with Bi_2O_3 and TiO_2. In the samples with 92 mol% of ZnO, four times more Bi_2O_3 was added than in the samples with 98 mol% of ZnO. In the samples with a TiO_2/Bi_2O_3 ratio of 0 (no added TiO_2), the $Bi_{38}ZnO_{58}$ phase is formed, and this phase melts at 740 °C. The addition of TiO_2 results in the formation of $Bi_{12}TiO_{20}$, which melts at 860 °C. By increasing the TiO_2/Bi_2O_3 ratio to 0.17, the TiO_2 bounds an equivalent, increasing amount of Bi_2O_3 to form the $Bi_{12}TiO_{20}$ phase, and hence less Bi_2O_3 remains to form the $Bi_{38}ZnO_{58}$ phase, i.e., there is less Bi_2O_3-rich liquid phase in the temperature range between 740 and 860 °C. For $0.16 < TiO_2/Bi_2O_3 < 1.5$, the $Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ phases form in equilibrium amounts; by increasing the TiO_2/Bi_2O_3 ratio toward 1.5, the amount of $Bi_4Ti_3O_{12}$ phase increases, while the amount of $Bi_{12}TiO_{20}$ phase decreases, and so does the amount of liquid phase in the temperature range between

860 and 1040 °C, i.e., the decomposition of $Bi_4Ti_3O_{12}$ in a reaction with ZnO to form the Bi_2O_3 liquid phase and the Zn_2TiO_4 spinel phase. At a TiO_2/Bi_2O_3 ratio 1.5, the $Bi_4Ti_3O_{12}$ phase is the only secondary phase at the grain boundaries of the ZnO. For $TiO_2/Bi_2O_3 > 1.5$, in addition to the $Bi_4Ti_3O_{12}$ phase, the Zn_2TiO_4 spinel phase also forms, and as the ratio increases the amount of Zn_2TiO_4 increases while the amount of $Bi_4Ti_3O_{12}$ remains constant—because it is limited by the amount of Bi_2O_3. The compositions with a TiO_2/Bi_2O_3 ratio equal to or greater than 1.5 contain the liquid phase only at temperatures above 1040 °C. The microstructures of the samples sintered at 1200 °C with TiO_2/Bi_2O_3 ratios of 1.0 and 4.0 are shown in Fig. 1. With the addition of oxides of Co and Mn to the ZnO–Bi_2O_3–TiO_2 system to obtain low-voltage varistor ceramics, the phase equilibria in the ZnO corner of the ternary system are similar to those described above; however, the decomposition of the $Bi_4Ti_3O_{12}$ phase in a reaction with ZnO decreases from 1040 to 940 °C. Therefore, in low-voltage varistor ceramics with a TiO_2/Bi_2O_3 ratio ≥ 1.5, the Bi_2O_3-rich liquid phase occurs at a lower temperature than in the basic ternary system.[20]

A microstructural analysis of the samples fired at 800, 900, 1100 and 1200 °C confirmed that the TiO_2/Bi_2O_3 ratio strongly influences the microstructure development and the grain growth of the ZnO samples doped with Bi_2O_3 and TiO_2. At 800 °C, the grain growth is only obvious in the samples with a TiO_2/Bi_2O_3 ratio below 0.17, whereas in the samples with a higher ratio the grain growth is retarded due to the absence of the liquid phase and by the presence of the secondary phases—$Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$, $Bi_4Ti_3O_{12}$ only, or $Bi_4Ti_3O_{12}$ and Zn_2TiO_4, depending on the TiO_2/Bi_2O_3 ratio. At 900 °C, the liquid phase is also present in the samples with a TiO_2/Bi_2O_3 ratio above 0.17 and below 1.5 due to the melting of the $Bi_{12}TiO_{20}$ at 860 °C; however, the grain growth is progressively hindered by the increased amount of $Bi_4Ti_3O_{12}$ phase at the grain boundaries as the TiO_2/Bi_2O_3 ratio increases toward 1.5. In the absence of the liquid phase at temperatures up to 1040 °C, the grain growth is slowed in the samples with a TiO_2/Bi_2O_3 ratio equal to or greater than 1.5, by the presence of $Bi_4Ti_3O_{12}$ and Zn_2TiO_4 phases at the grain boundaries. At temperatures above 1040 °C, all the Bi_2O_3 added to the starting composition is present as the Bi_2O_3-rich liquid phase in all the samples, regardless of the TiO_2/Bi_2O_3 ratio. The results of the grain size analysis are given in Table 1. The amount of added Bi_2O_3, and hence the amount of liquid phase, significantly influences the grain size: for the same TiO_2/Bi_2O_3 ratio the grain size is consistently smaller in the samples with large additions of Bi_2O_3 than in the samples with small additions of Bi_2O_3.

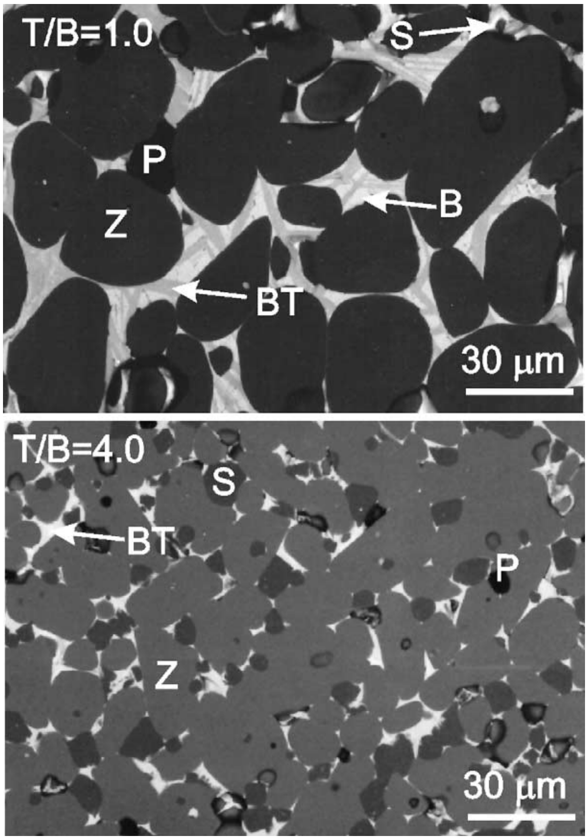

Fig. 1. BE SEM of samples with 92 mol% of ZnO doped with Bi_2O_3 and TiO_2 at a TiO_2/Bi_2O_3 (*T*/*B*) ratio of 1 and 4, fired at 1200 °C. Z: ZnO; B: Bi_2O_3-rich phase; BT: $Bi_4Ti_3O_{12}$ phase; S: Zn_2TiO_4 spinel phase.

Table 1
Influence of the TiO_2/Bi_2O_3 ratio and the sintering temperature on the ZnO grain size (in µm). In samples with 92% of ZnO, four times higher amounts of Bi_2O_3 were added (label HBi) than in the samples with 98 mol% of ZnO (label LBi)

TiO_2/Bi_2O_3	900 °C (2 h)		1000 °C (2 h)		1200 °C (2 h)	
	LBi	HBi	LBi	HBi	LBi	HBi
0	6.9	–	10.9	–	18.8	–
0.11	5.0	3.7	11.3	5.0	22.7	8.50
0.17	5.8	–	13.9	–	24.8	–
0.33	3.6	1.7	5.7	4.5	24.9	13.9
1.00	2.7	2.0	5.0	4.1	23.1	17.9
1.5	2.0	–	6.0	–	26.2	–
4.0	1.4	<1.0	4.8	2.3	17.4	11.8

Microstructural observations show a significant influence of the composition on the morphology of the ZnO grains and the distribution of the grain sizes. In the ZnO–Bi_2O_3 sample without the addition of TiO_2, the grain growth is uniform for all the sintering regimes and the ZnO grains are relatively spherical (Fig. 2a). In the samples doped with TiO_2, exaggerated grain growth occurs, and is especially evident in the samples sintered at temperatures just above the temperature at which the liquid phase occurs. Exaggerated grain growth results in a bimodal grain size distribution, with small grains among huge ones, as shown in the case of the sample with a TiO_2/Bi_2O_3 ratio of 0.17, sintered at 900 °C for 1 h (Fig. 2b). The large grains are elongated and they contain IBs (Fig. 2d), as observed by Makovec et al.[17] In general, the ZnO grains in the samples doped with TiO_2 are elongated (Fig. 2c) in comparison to the ZnO samples

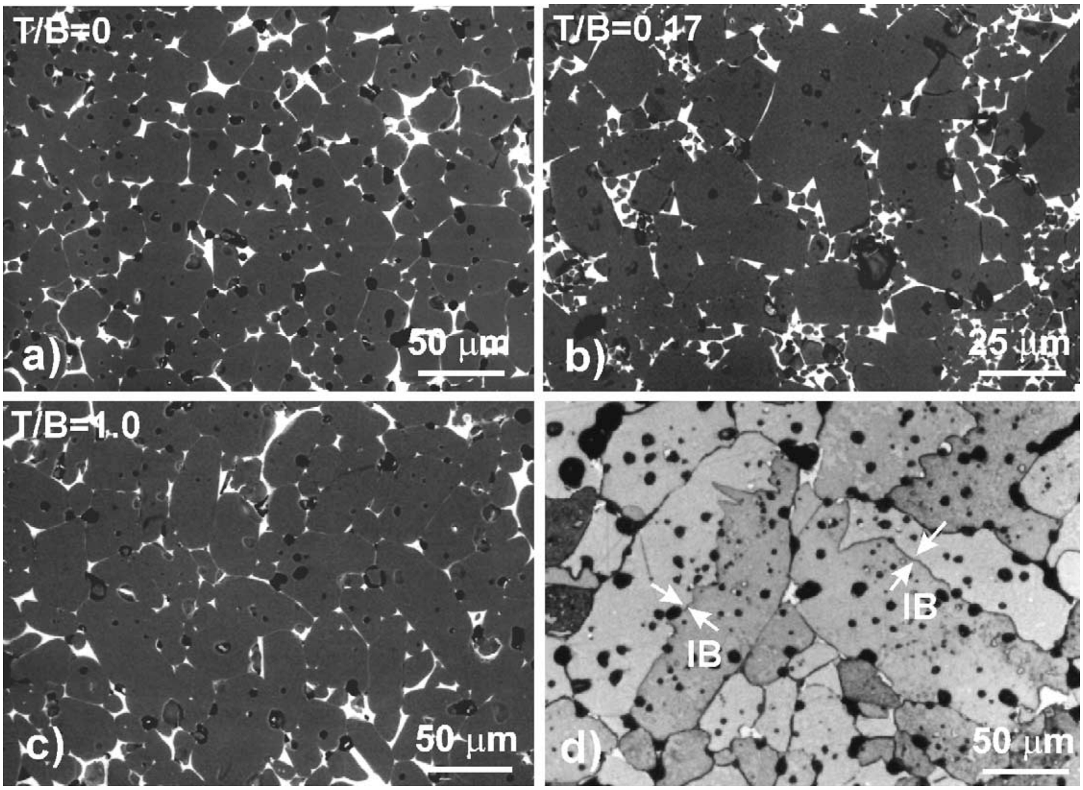

Fig. 2. Microstructures of the samples with 98 mol% of ZnO doped with Bi_2O_3 and TiO_2: (a) sample with the TiO_2/Bi_2O_3 ratio (*T*/*B*) of 0, sintered at 1200 °C; (b) sample with the TiO_2/Bi_2O_3 ratio of 0.17, sintered at 900 °C; (c) sample with the TiO_2/Bi_2O_3 ratio of 1.0, sintered at 1200 °C; and (d) microstructural detail showing IBs in exaggeratedly grown ZnO grains.

doped only with Bi_2O_3 (Fig. 2a). The maximum elongation observed in the TiO_2-doped samples after sintering at 1100 °C was between 1.8 and 2.1, and it decreased slightly after sintering at 1200 °C. The elongation of grains in the ZnO sample doped only with Bi_2O_3 was 1.6.

The X-ray diffraction analysis and the microstructural analysis showed that equilibrium phases for particular TiO_2/Bi_2O_3 ratios—the $Bi_{12}TiO_{20}$ phase, the $Bi_4Ti_3O_{12}$ phase and the Zn_2TiO_4 phase—are well formed after sintering at 700 °C for just 1 h. This indicated that the phase equilibrium is established relatively quickly for a given TiO_2/Bi_2O_3 ratio and temperature. Hence, the phase equilibrium at a particular temperature during heating to the sintering temperature, which depends on the heating rate, can influence the final microstructure and the characteristics of the low-voltage varistor ceramics. To examine this possibility, low-voltage varistor samples with varying TiO_2/Bi_2O_3 ratios were heated to the sintering temperature at different heating rates, and the results of their grain size analysis are given in Table 2. The results clearly show that the heating rate matters and that it has different effects on the samples with different compositions, i.e., different TiO_2/Bi_2O_3 ratios.

The influence of the Zn_2TiO_4 spinel phase on the ZnO grain size is evident in the sample with the TiO_2/Bi_2O_3 ratio of 4 (Fig. 1). Only in the samples with TiO_2/Bi_2O_3 ratios larger than 1.5 does the primary spinel phase, which can affect the grain growth, form at lower temperatures via a reaction between the ZnO and excess TiO_2 to form $Bi_4Ti_3O_{12}$. In the samples with TiO_2/Bi_2O_3 ratios in the range from 0.17 to 1.5, the spinel phase forms together with Bi_2O_3 liquid in the decomposition reaction of $Bi_4Ti_3O_{12}$ with ZnO. Fine spinel grains are mobile in the Bi_2O_3-rich liquid phase and do not have a significant influence on the grain growth. Whereas the $Bi_4Ti_3O_{12}$ phase is clearly present in the samples, even after quenching from the sintering temperature to room temperature, spinels are difficult to detect. Most previous studies of low-voltage varistor ceramics were limited to compositions with a TiO_2/Bi_2O_3 ratio of 1.5 or below, i.e., to compositions in which the spinels are barely present,

Table 2
The influence of the heating rate on the ZnO grain size (in μm) for low-voltage varistor samples with the composition of $ZnO + 0.7Bi_2O_3 + xTiO_2 + 0.5Co_3O_4 + 0.5Mn_2O_3$, sintered at 1260 °C for 1 h

TiO_2/Bi_2O_3	2 °C/min	10 °C/min	Soaking 800 °C[a]
0.14	23.0	26.4	23.3
0.71	29.9	29.4	30.3
1.43	26.8	24.8	22.1
4.3	22.5	22.8	26.7

[a] Heating rate 10 °C/min to 800 °C (2 h) and to sintering temperature.

Table 3
ZnO grain size of high-voltage varistor ceramics (ZnO doped with $0.9Bi_2O_3$, Co_3O_4, Mn_3O_4, NiO, Cr_2O_3 and varying amount of Sb_2O_3) sintered at 1200 °C for 2 h

Sb_2O_3/Bi_2O_3	D (μm)
0.75	10.6
1.10	7.1
1.55	6.5
1.94	5.9
2.22	5.7
2.50	5.7
2.78	5.6

and hence they have no significant influence on the development of the microstructure. The influence of the spinel phase on the grain growth occurs in compositions with larger additions of TiO_2, which are not interesting for low-voltage varistor ceramics.

A similar, although opposite, situation occurs in the case of high-voltage varistor ceramics doped with Sb_2O_3, where the phase equilibria are determined by the basic system $ZnO–Bi_2O_3–Sb_2O_3$ and the Sb_2O_3/Bi_2O_3 ratio. It is generally known that for a Sb_2O_3/Bi_2O_3 ratio equal to 1 or less the $Zn_7Sb_2O_{12}$ spinel phase forms together with the Bi_2O_3 liquid—in the basic ternary system above 1000 °C and in varistor compositions above 900 °C—only after the decomposition of the $Bi_3Zn_2Sb_3O_{11}$ pyrochlore in a reaction with ZnO. Nowadays, typical high-voltage varistor compositions normally have a Sb_2O_3/Bi_2O_3 ratio larger than 1, where the primary $Zn_7Sb_2O_{12}$ spinel phase forms at a low temperature, via the reaction of Sb_2O_3 with ZnO, and may contribute to the inhibition of the ZnO grain growth during sintering. Table 3 summarizes the results of the grain size analysis of high-voltage varistor ceramics with varying Sb_2O_3/Bi_2O_3 ratio. The microstructures of the samples with Sb_2O_3/Bi_2O_3 ratios of 1.1 and 2.5 are given in Fig. 3. The results show that an increase in the Sb_2O_3/Bi_2O_3 ratio to more than 1 results in a significant decrease in the size of the ZnO grains. A further increase in the amount of added Sb_2O_3, and hence an increase in the Sb_2O_3/Bi_2O_3 ratio, however, results in only a slight decrease in the grain sizes, especially for a Sb_2O_3/Bi_2O_3 ratio above 1.5, while the amount of the spinel phase at the grain boundaries is increased significantly (Fig. 3).

In low-voltage varistor ceramics with a TiO_2/Bi_2O_3 ratio equal to or below 1.5 spinels formed by the decomposition of the $Bi_4Ti_3O_{12}$ phase have no influence on the ZnO grain growth. The same also applies to the spinel phase in high-voltage varistor ceramics for Sb_2O_3/Bi_2O_3 ratios equal to or below 1, when it forms by the decomposition of the $Bi_3Zn_2Sb_3O_{14}$ pyrochlore phase. In view of our recent reports,[7,8] it is reasonable to conclude that at the final sintering temperature in high-voltage varistor ceramics with a Sb_2O_3/Bi_2O_3 ratio equal to or below 1, the dominant controlling mechanism is an IB-induced grain-growth mechanism, whereas the influence of the spinel phase is, if anything, negligible.

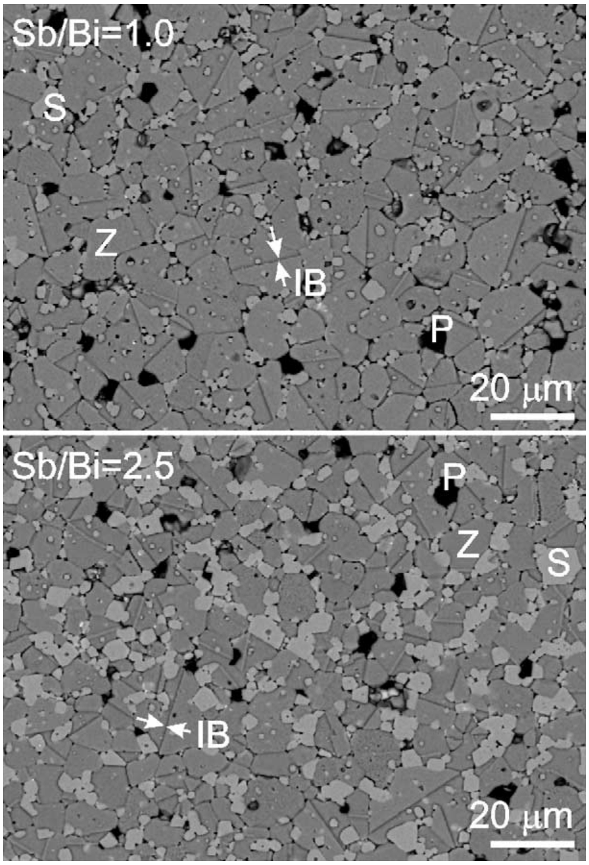

Fig. 3. BE SEM images of the microstructures of high-voltage ZnO-based varistor samples with Sb_2O_3/Bi_2O_3 ratios (Sb/Bi) 1.0 and 2.5 sintered at 1200 °C for 2 h.

4. Conclusions

In low-voltage varistor ceramics, the TiO_2/Bi_2O_3 ratio defines the phase equilibrium and hence the temperature at which the liquid phase occurs in the system. The phase equilibrium is established relatively quickly for a given temperature; hence, the heating rate to the sintering temperature can influence the final microstructure of the varistor ceramics, and the selection of a proper TiO_2/Bi_2O_3 ratio and the heating rate matter when it comes to obtaining the required low-voltage varistor ceramics. In addition, the amount of added Bi_2O_3 to the starting composition, which defines the amount of liquid phase at the sintering temperature, is important as the grain growth is slowed down by the increased thickness of the liquid film at the grain boundaries of the ZnO. In low-voltage varistor ceramics, the increase in the ZnO grain size is considerable, and so, also, is the decrease in the specific surface of the grains, and this can influence significantly the thickness of the Bi_2O_3 liquid layer at the grain boundaries during sintering.

Sintering at temperatures just above the temperature of liquid-phase formation in the samples with a particular TiO_2/Bi_2O_3 ratio results in the exaggerated grain growth of large elongated grains with IBs surrounded by much smaller, normal ZnO grains. Sintering at higher temperatures, well above the temperature of the appearance of the liquid phase, also results in exaggerated grain growth; however, the grain size distribution of the elongated grains is broad, but not bimodal. Large elongated grains often contain an inversion boundary (IB). The exaggerated grain growth in low-voltage varistor ceramics is related to the occurrence of a liquid phase in the system and the presence of TiO_2, which triggers the formation of IBs in only certain grains. A relatively low partial pressure of TiO_2 is responsible for the poor distribution of TiO_2 along the grain boundaries, and this leads to a relatively low nucleation rate for the formation of ZnO grains that contain IBs. Hence, in TiO_2-doped ZnO-based varistor ceramics, grain growth controlled by an IB-induced grain growth mechanism results in a coarse-grained microstructure. In low-voltage varistor ceramics the grain growth is affected only by the primary Zn_2TiO_4 spinels in compositions with a TiO_2/Bi_2O_3 ratio higher than 1.5, whereas in compositions with a lower ratio, the spinels that form together with the Bi_2O_3-liquid phase in the decomposition reaction of the $Bi_4Ti_3O_{12}$ phase have no effect on the grain growth.

In high-voltage ZnO-based varistor ceramics, just small amounts of Sb_2O_3 trigger the formation of IBs in practically every ZnO grain. Sb_2O_3 has a high partial pressure at low temperatures and effectively distributes along the grain boundaries—so triggering the formation of IBs in practically every ZnO grain. Therefore, in Sb_2O_3-doped varistor ceramics with a Sb_2O_3/Bi_2O_3 ratio below 1, the major growth-controlling mechanism is an IB-induced grain growth mechanism, whereas the spinel phase that forms together with the Bi_2O_3-rich liquid phase in the decomposition reaction of the $Bi_3Zn_2Sb_3O_{14}$ pyrochlore phase has a minor influence. Similarly as in low-voltage also in high-voltage ZnO-based varistor ceramics only primary spinel phase formed via the reaction of Sb_2O_3 with ZnO in compositions with a Sb_2O_3/Bi_2O_3 ratio larger than 1 can have an influence on the grain growth.

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