UDK 546:666
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 42(2)69(2008)

TAILORING THE MICROSTRUCTURE OF ZnO-BASED CERAMICS

KONTROLA RAZVOJA MIKROSTRUKTURE V ZnO KERAMIKI

Slavko Bernik, Matejka Podlogar, Nina Daneu, Aleksander Rečnik
Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
slavko.bernik@ijs.si

Prejem rokopisa – received: 2007-10-05; sprejem za objavo – accepted for publication: 2007-12-14

In polycrystalline materials – both metals and ceramics – understanding and controlling the microstructure is very important since vital physical properties, critical for applications, are strongly influenced by the average grain size, the grain size distribution and the porosity. The influence of the microstructure is very straightforward in the case of the exceptional current-voltage nonlinearity of ZnO-based varistor ceramics, which is closely related to the ZnO grain size: a coarse-grained microstructure results in a low breakdown voltage for the ceramics, while a fine-grained microstructure is required for a high breakdown voltage. The grain size in high-voltage varistor ceramics is controlled by the addition of a spinel-forming additive, typically Sb_2O_3. The grain-growth inhibition is due to the reduced grain-boundary mobility caused largely by the pinning effect of the spinel particles and defines the approach to the preparation of ZnO-based varistor ceramics, and hence also the composition. Spinel-forming dopants such as Sb_2O_3, TiO_2 and SnO_2 also result in the formation of inversion boundaries (IBs) in the ZnO grains. We have identified an IB-induced grain-growth mechanism and showed that it controls microstructure development, while the role of the spinel is subordinated. Fundamental research that revealed the true nature of the grain growth in varistor ceramics enabled us to take an entirely new approach to tailoring either a coarse- or fine-grained microstructure for ZnO-based ceramics, and will significantly alter the preparation of varistors for all voltage ranges.

Key words: ZnO, ceramics, microstructure, grain growth, inversion boundaries

V polikristaliničnih materialih – v kovinah in keramiki – sta razumevanje in kontrola mikrostrukture ključnega tehnološkega pomena, saj so bistvene fizikalne lastnosti za uporabo teh materialov močno odvisne od povprečne velikosti zrn, porazdelitve velikosti zrn in poroznosti. Vpliv mikrostrukture je morda najbolj neposredno izražen v primeru tokovno-napetostne nelinearnosti varistorske keramike na osnovi ZnO, ki so tesno povezane z velikostjo zrn ZnO; medtem ko grobo zrnata mikrostruktura vodi do nizke prebojne napetosti, je za keramiko z visoko prebojno napetostjo zahtevana drobnozrnata mikrostruktura. Za kontrolo velikost zrn v varistorski keramiki so dodani dopanti, ki z ZnO tvorijo spinelno fazo, navadno je to Sb_2O_3. Razumevanje zaviranja rasti zrn zaradi prisotnosti spinelne faze na mejah med zrni, kar zmanjša njihovo mobilnost, je močno vplivalo na način priprave varistorske keramike in s tem tudi na njeno sestavo. Dopanti, kot so Sb_2O_3, TiO_2 in SnO_2, ki povzročijo nastanek spinelne faze, sprožijo tudi nastanek inverznih mej (IBs) v zrnih ZnO. Identificirali smo mehanizem rasti zrn pod vplivom inverznih mej in pokazali, da le-to prvenstveno kontrolira razvoj mikrostrukture, medtem ko je vpliv spinelne faze obrobnega pomena. Osnovne raziskave, s katerimi smo pojasnili dejanske mehanizme rasti zrn v varistorski keramiki, so nam omogočile popolnoma nov način priprave bodisi grobo- ali drobnozrnate mikrostrukture keramike na osnovi ZnO, kar je izredno pomembno za pripravo varistorjev za različna napetostna področja.

Ključne besede: ZnO, keramika, mikrostruktura, rast zrn, inverzne meje

1 INTRODUCTION

In polycrystalline materials – both metals and ceramics – understanding and controlling the microstructure is very important since such vital properties as mechanical strength, electrical conductivity, magnetic susceptibility, optical transmission, etc., are strongly influenced by the average grain size, the grain size distribution and the porosity. The microstructure is a directly related to grain-growth mechanisms. Grain growth, one of the fundamental subjects in material science and processing, has been studied for more than 50 years.

The influence of grain size on the electrical characteristics of ceramics is perhaps most straightforward in the case of the exceptional current-voltage nonlinearity of ZnO-based varistor ceramics. Here, the breakdown voltage – the transition from a highly resistive to a highly conductive state – is a direct function of the grain size: a coarser grain size results in lower breakdown voltages, while for a higher breakdown voltages a finer grain size is required. ZnO-based varistor ceramics are obtained by the addition of small amounts of oxides of Bi, Sb, Ti, Co, Mn, Ni, Cr, Al and others to ZnO powder, and then sintering in air within the temperature range from 1100 °C to 1300 °C, typically at 1200 °C. The current-voltage nonlinearity of the varistors is a grain-boundary phenomenon with an ideal breakdown voltage of the grain boundary at about 3.2 V. As the breakdown voltage of a varistor is the sum of the breakdown voltages of all the non-linear (varistor) grain boundaries between the electrodes, it depends on the number of grain boundaries per unit volume of the varistor ceramic, which is inversely proportional to the ZnO grain size.[1-3] Consequently, control of the grain growth in the processing of varistor ceramics is essential for the successful application of varistors in over-voltage protection in a broad range, from a few volts up to several kilovolts. Processing varistor ceramics with varying breakdown voltages per unit thickness – low, medium or high – makes it possible to produce varistors with suitable dimensions (thickness) for any required voltage.

The microstructure development and grain growth in ZnO ceramics have been intensively studied in the past and the main emphasis was given to those varistor dopants that significantly influence the grain growth: Bi_2O_3, which not only induces the non-linearity in ZnO ceramics but also introduces a liquid phase to the system,[4-7] and spinel-forming dopants, especially Sb_2O_3 [8-10], TiO_2 [11,12] and Al_2O_3 [13-16], which are added to control the ZnO grain size in varistor ceramics. Due to the addition of Bi_2O_3, sintering and grain growth in varistor ceramics take place in the presence of a liquid phase, and the amount of added Bi_2O_3 has a major influence. [4,5] According to Bradt and coworkers, [6,7] the rate-controlling mechanism for ZnO grain growth is the phase-boundary reaction of the solid ZnO grains and the Bi_2O_3-rich liquid phase, which enhances the grain growth for additions of Bi_2O_3 up to the mole fraction 0.5 %, while for larger additions of Bi_2O_3 the rate-controlling mechanism changes to one of diffusion through the layer of the Bi_2O_3-rich liquid phase and the grain growth is slowed. While Sb_2O_3 is a standard dopant in fine-grained high-voltage varistor ceramics, TiO_2 is added to coarse-grained varistor ceramics with a low breakdown voltage. The inhibition of grain growth in Sb_2O_3-doped [8-10] and also Al_2O_3-doped [13-15] samples is generally explained by the reduced mobility of the ZnO grain boundaries due to the pinning effect of the spinel grains at the ZnO grain boundaries. A microstructure similar to that of Sb_2O_3 is obtained with SnO_2-doped varistor ceramics.[17] Sb_2O_3, SnO_2 and TiO_2 form a spinel phase with ZnO, and they also trigger the formation of inversion boundaries (IBs) in the ZnO grains. In the Sb_2O_3- and SnO_2-doped samples the IBs are present in most of the ZnO grains [9,17], and in the TiO_2-doped samples IBs are present only in some, regularly exaggeratedly grown grains.[12,18] While the possible role of IBs in the grain-growth process of Sb_2O_3-doped samples was only briefly considered [9] until recent years, in TiO_2-doped ZnO ceramics the exaggerated growth of ZnO grains in connection with IBs was observed by Makovec et al.[12]

Based on studies of microstructure development in ZnO ceramics doped with Bi_2O_3 and SnO_2 we realized that inversion boundaries (IBs) have a major influence on the grain growth of ZnO, while the influence of the spinel phase is subordinate to the role of IBs.[19] Studies of the microstructure development at lower temperatures, where the grain-growth kinetics is still slow, revealed that grains with IBs overgrow all the normal grains without an IB in their surroundings until they prevail in the microstructure. Based on these results we proposed an inversion-boundary-induced grain-growth mechanism. At temperatures below those for the formation of the spinel phase, in the early stage of sintering, IBs nucleate in some ZnO grains. ZnO grains with an IB, i.e., a nucleus, anisotropically and exaggeratedly grow in the direction of the adopted defect (IB) until they collide with each other, and finally prevail in the microstructure. Consequently, it should be possible to tailor the grain size of ZnO ceramics by controlling the number of nuclei. A coarse-grained microstructure would develop from a smaller number of nuclei as the grains could grow to a larger size before they collide with each other. In contrast, with a larger number, nuclei would collide with each other when they are still small, which would result in a fine-grained microstructure. In diffusion-doped ZnO, sintered under a slightly increased partial pressure of Sb_2O_3, we demonstrated that higher concentrations of Sb_2O_3 resulted in a fine-grained microstructure with the absence of the spinel phase, while at a low concentration of the dopant, grains several times larger than normal developed in the Sb_2O_3-poor region of the ZnO ceramic.[20] A coarse-grained microstructure was obtained for the first time in Sb_2O_3-doped ZnO ceramics. These results showed that the amount of IBs-triggering dopant (Sb_2O_3) influences the number of nuclei, which indeed results in either a coarse-grained microstructure for a small number of nuclei or a fine-grained ZnO ceramic for a larger number of nuclei formed in the early stage of sintering.

To understand the role of spinel-forming dopants on the formation of IBs, their atomic structure, chemistry and nucleation were analysed by Recnik et al. [21,22] They found that the IB plane consists of an Sb-rich monolayer that contains 1/3 of Sb^{5+} and 2/3 of Zn^{2+} octahedrally coordinated ions, giving an average oxidation state of +III for each available octahedral interstice in the boundary plane. A study of IB nucleation revealed two competing mechanisms that take place, depending on the oxidation state of the IB-forming dopant: (i) internal diffusion, and (ii) surface nucleation and growth. The first mechanism prevails for III+ dopants and is controlled by the Zn-vacancy diffusion, whereas the second mechanism holds for all IB-forming dopants (oxides of Sb, Sn and Ti) and is controlled by chemisorption of the dopants on Zn-deficient (0001) surfaces. In both cases the driving force for the inversion is the preservation of the local charge balance. The IB structure – a sort of stable two-dimensional surface compound – is thermodynamically more stable than the reactants alone (ZnO and the IBs-triggering dopant).[19,22] Due to the driving force for incorporating the IB-forming dopant into the IB, the growth of the host ZnO grain is dictated by the direction of the IB plane and, consequently, such a grain is preferred in terms of growth over the normal grains without IBs. The process is controlled by surface diffusion of the IBs-triggering dopant and its incorporation into the structure of the IB.[22] The anisotropic and exaggerated growth of grains with IBs (nuclei) is caused by a nucleation mechanism for the IBs [22,23] An understanding of this mechanism explained the preferential growth of ZnO grains with IBs over normal grains.

Diffusion doping with Sb_2O_3 demonstrated that the amount of IBs-triggering dopant indeed influenced, via the IBs-induced grain-growth mechanism, the microstructure development in ZnO ceramics: with a larger amount of Sb_2O_3 a fine-grained microstructure is obtained, while a smaller amount of Sb_2O_3 results in coarse-grained ceramics.[20] Our further studies were aimed at investigating the possibilities for tailoring the microstructure, via the IBs-induced grain-growth mechanism, of ZnO ceramics doped with varying amounts of IBs-triggering dopant (Sb_2O_3) in a more usual way. We studied the microstructure development in low Sb_2O_3-doped ZnO ceramics [24] and afterwards also in ZnO ceramics doped with Bi_2O_3 and Sb_2O_3.[25] Tailoring the microstructure in the basic varistor system of ZnO ceramics doped with Bi_2O_3 and Sb_2O_3 with the IBs-induced grain-growth mechanism would mean the same possibility also for fully doped ZnO-based varistor ceramics. While in Sb_2O_3-doped ZnO only the $Zn_7Sb_2O_{12}$ spinel phase is formed, the chemistry of the ZnO-Bi_2O_3-Sb_2O_3 system, which defines the reactions in the varistor ceramics (other varistor dopants incorporate into the phases of this system), is much more complex and is influenced by the Sb_2O_3/Bi_2O_3 ratio: at 600 °C the $Bi_3Zn_2Sb_3O_{14}$ pyrochlore phase is already formed and this decomposes into a Bi_2O_3-rich liquid phase and $Zn_7Sb_2O_{12}$ above 1000 °C. The $Zn_7Sb_2O_{12}$ phase is formed above 800 °C in a direct reaction with ZnO, only when $x(Sb_2O_3)/x(Bi_2O_3) > 1$, and the liquid phase is present in the system already at 740 °C only for $x(Sb_2O_3)/x(Bi_2O_3) > 1$, otherwise it appears in the system only after the decomposition of the pyrochlore phase at much higher temperatures.[2,3]

In this paper a review of previously reported results [24,25] about the influence of the amount of added Sb_2O_3 or Sb_2O_3 and Bi_2O_3 for different $x(Sb_2O_3)/x(Bi_2O_3)$-to-x(ZnO) ratios on the grain growth and formation of IBs in ZnO ceramics prepared by a classical ceramic procedure is discussed. The resulting microstructures of the samples sintered at 1200 °C were analyzed in terms of the grain size and the fraction of grains containing IBs, related to the starting composition and the sintering time.

2 EXPERIMENTAL

ZnO powder, Pharma A (Grillo Zinkoxid GmbH, purity > 99.9 %), with a uniform distribution of spherical particles was used for the preparation of Sb_2O_3- and Bi_2O_3-doped samples. Stable solutions of Bi-nitrate and Sb-acetate were used to add Bi^{3+} and Sb^{3+} to the ZnO powder for appropriate doping with Bi_2O_3 and Sb_2O_3. All the samples were prepared with the addition of equal amounts of a solution to 20 g of ZnO; the amounts of Bi^{3+} and Sb^{3+} solutions required for a particular sample composition were diluted to 20 mL with ethanol. The obtained ZnO slurry was homogenized in a polyethylene mill with zirconia balls for 1 h at 200 r/min. After homogenization the slurry was dried in a vacuum drier to obtain a powdered sample. Camphor was added to the powder mixture as a pressing aid, and pellets with a diameter of 10 mm and a thickness of 2 mm were pressed from the powder mixture with a pressure of 150 MPa. ZnO-Sb_2O_3 samples were prepared with additions of Sb^{3+} (1, 5, 25, 50, 100, 250 and 500) µg/g, which correspond to amounts of the mole fraction from 0.000033 % Sb_2O_3 to 0.016716 %. The samples were sintered in air at 1200 °C for (2, 10, 20, 50 and 250) h. The ZnO-Bi_2O_3-Sb_2O_3 samples were prepared with additions of the mole fraction 0.01 % Bi_2O_3, 0.02 % Bi_2O_3 and with equal additions of Bi_2O_3 for x(Sb_2O_3)-to-x(Bi_2O_3) ratios of 0.8, 1.0 and 1.2. These samples were sintered in air at 1200 °C for 2 h and 10 h. To prevent any contamination among the samples with different compositions, each sample was placed into a separate, covered Al_2O_3 crucible. In addition, the sample pellets were placed between two pellets of the same composition, a bottom sacrificial one, to prevent contamination with the Al_2O_3 of the crucible, and a top one. The microstructure of each sample was prepared by grinding and polishing the sample pellet in a cross-sectional direction. Half of each microstructure was etched with dilute hydrochloric acid. The microstructures were analyzed on a scanning electron microscope (SEM) JEOL JSM-5800. Several SEM/BE images per sample were used for a stereological analysis of the ZnO grain size and the grain size distribution. The surface of each grain was measured and its size was calculated in terms of a diameter for circular geometry; the average ZnO grain size and the size distribution were determined from measurements of 400–1200 grains per sample. Details are given in references 24 and 25.

3 LOW Sb_2O_3-DOPED ZnO CERAMICS

The results of the ZnO grain-size analyses are summarized in **Table I** and graphically presented in **Figure 1**. The grain sizes of the ZnO samples doped with small amounts of Sb (Sb_2O_3) were strongly influenced by the amount of dopant and also by the sintering time. As expected, the ZnO grain size increased with longer sintering times; however, the increase in the grain size with time was very different with respect to the amount of added Sb. With the exception of the sample doped with 500 µg/g of Sb, all the other Sb-doped samples had a noticeably larger ZnO grain size – ranging from 26 µm to 32 µm – than the undoped ZnO (23 µm) after sintering for 20 h, which indicates a faster growth rate in the case of Sb-doped samples than in the case of pure ZnO. Longer sintering times resulted in a steady and more moderate increase in the ZnO grain size; in comparison to the undoped ZnO sample the

Table I: Results of the ZnO grain-size analysis of the ZnO samples doped with varying amounts of Sb and sintered at 1200 °C : average ZnO grain size *G* /µm with its standard deviation *σ* /µm and the fraction (in %) of the ZnO grains that contain an inversion boundary (IB).

Sample ZnO + *y* Sb *y*/(µg/g) ($x(Sb_2O_3)$/%)	1200 °C														
	2 h			10 h			20 h			50 h			250 h		
	G µm	*σ* µm	*IBs* %	*G* µm	*σ* µm	*IBs* %	*G* µm	*σ* µm	*IBs* %	*G* µm	*σ* µm	*IBs* %	*G* µm	*σ* µm	*IBs* %
0 (0)	**9.5**	4.3	0	**16.3**	7.6	0	**23.1**	9.8	0	**25.2**	10.5	0	**44.5**	19.4	0
1 (0.000033)	**11.4**	5.1	8	**19.6**	10.0	5	**26.1**	12.6	8	**29.3**	12.8	5	**56.2**	23.6	24
5 (0.000167)	**10.0**	4.9	10	**18.9**	9.2	15	**27.6**	11.6	20	**30.8**	14.1	10	**58.4**	25.4	31
25 (0.000835)	**9.2**	4.6	18	**20.2**	10.7	51	**32.3**	14.9	58	**43.4**	19.1	59	**71.3**	30.9	77
50 (0.001671)	**9.0**	4.6	24	**18.9**	9.7	56	**30.6**	13.0	62	**36.4**	16.2	63	**58.9**	24.6	77
100 (0.003342)	**9.9**	4.7	42	**18.7**	8.5	68	**27.4**	11.8	71	**30.3**	13.2	74	**54.0**	21.9	77
250 (0.008356)	**9.1**	4.8	43	**18.7**	8.9	70	**29.1**	13.3	72	**33.2**	15.5	73	**53.5**	22.4	78
500 (0.016716)	**3.4**	2.0	69	**8.5**	4.1	76	**9.7**	4.6	75	**10.0**	4.8	74	**11.9**	6.2	77

increase in the grain size was higher in the samples doped with (1, 5, 50 and 100) µg/g of Sb, being the highest in the sample doped with 25 µg/g of Sb, and similar in the sample doped with 250 µg/g of Sb. Consequently, the differences in ZnO grain size among the samples sintered for 20 h, and 50 h in the case of the sample with 25 µg/g Sb, remained either at the same level or increased even more after a longer sintering time. An exception was the sample with the addition of 500 µg/g of Sb, which has a lower growth rate than the other samples, even for sintering times shorter than 10 h, and especially for longer times. It has a much lower average ZnO grain size (about 10 mm) than all the other samples after 20 h of sintering, and the grain growth ceased so that further sintering for as long as 250 h resulted in only a slight increase in the grain size, to about 12 µm.

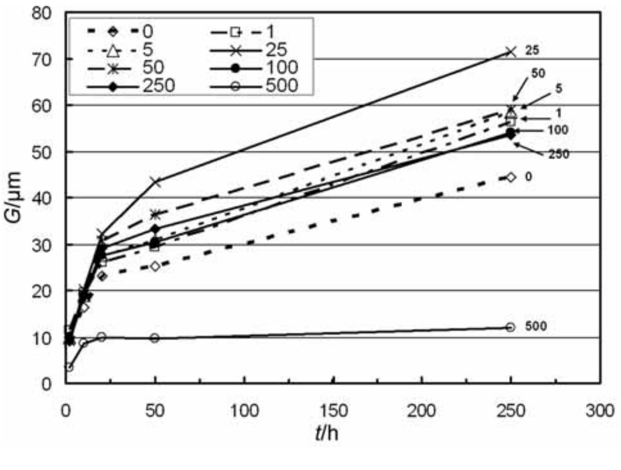

Figure 1: Average size of ZnO grain vs. sintering time at 1200 °C for samples with a varying amount of added Sb to the ZnO

Slika 1: Povprečna velikost zrn ZnO v odvisnosti od časa sintranja pri 1200 °C za vzorce z različnim dodatkom Sb v ZnO

Besides the differences in ZnO grain size, the fraction of ZnO grains that contains IBs is also different, depending on the amount of added Sb and the sintering time. The microstructures of the samples sintered for 10 h are presented in **Figure 2**. The results of the assessment of the fraction of ZnO grains with IBs in the samples with different amounts of Sb added to ZnO after different times at the sintering temperature are given in Table I and graphically presented in **Figure 3**. Both parameters, the amount of Sb and the sintering time, are dependent on each other and strongly influence the fraction of ZnO grains with IBs. In general, the fraction is higher in the samples with larger additions of Sb, it increases with the increasing time of sintering, and the grains with IBs develop in the microstructures after a shorter sintering time when the amount of added Sb in the sample is greater. However, in the ZnO sample doped with 500 µg/g of Sb the ZnO grains with IBs prevail (70 %) in the microstructure after 2 h of sintering, and after 10 h of sintering the grains with IBs completely dominate the microstructure.

The doping of ZnO with Sb resulted in coarse-grained microstructures for the samples with an average ZnO grain size noticeably larger than in the sample of undoped ZnO after sintering at 1200 °C. The only exception in this study was the sample with the largest amount of Sb added to the ZnO, 500 µg/g, which was fine-grained after prolonged sintering. These results contradict the standard understanding of the grain growth and microstructure development, i. e., that Sb_2O_3 doping results only in the inhibition of ZnO grain growth by the formation of spinel grains at the grain boundaries to reduce the grain mobility by the so-called Zener

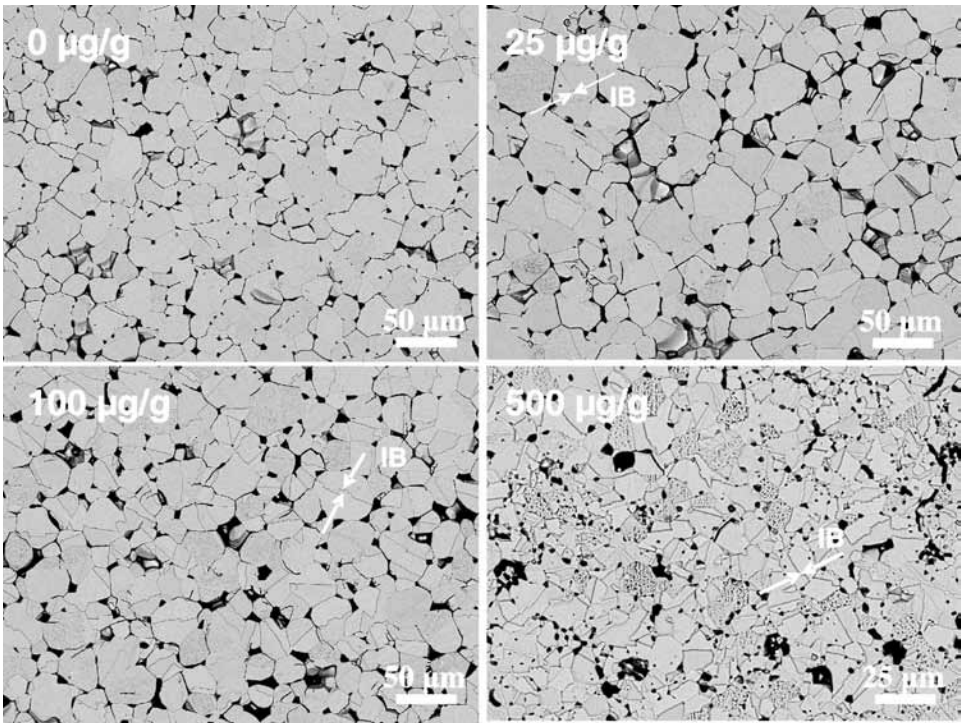

Figure 2: Microstructures of un-doped ZnO sample and ZnO samples doped with (25, 100 and 500) μg/g Sb, sintered for 10 h at 1200 °C
Slika 2: Mikrostrukture nedopiranih vzorcev ZnO in vzorcev ZnO dopiranih s (25, 100 in 500) μg/g Sb, ki so bili sintrani 100 h pri 1200 °C

pinning effect. The actual microstructure development can be explained by an IBs-induced grain-growth mechanism,[19] and this is in agreement with other grain-growth studies.[20]

In this study it was observed that even the addition of just 1 μg/g of Sb to the ZnO results in the formation of IBs in some ZnO grains. With larger additions of Sb increasingly larger numbers of ZnO grains contain IBs, even after sintering for 2 h, and their fraction increases with longer sintering times. Consequently, ZnO grains with IBs dominate in the microstructures of the samples with the larger additions of Sb after shorter sintering times. In the sample with 500 μg/g of Sb, as many as 70 % of the ZnO grains contain an IB after 2 h of sintering, which showed that for a sufficient addition of Sb, grains with an IB completely dominate in the microstructure of the sample after a relatively short sintering time. The increase in the fraction of ZnO grains containing IBs with the sintering time is accompanied by an increase in the average grain size. A larger increase in the grain size with sintering time in Sb-doped samples in comparison to pure undoped ZnO can, therefore, be attributed to the presence of IBs in the ZnO grains. ZnO grains with IBs (nuclei) exhibit an enhanced grain growth when compared to normal grains; they grow at the expense of the normal grains, while their fraction increases and after a certain time of sintering, ZnO grains with IBs completely prevail in the microstructure.

After a short sintering time, most of the samples have a similar ZnO grain size. However, once the influence of the preferred growth of grains containing IBs starts to dominate in the microstructure, with a longer sintering time, the differences in the grain sizes among the samples become evident. Consequently, the grain sizes of the samples doped with Sb become larger than in the un-doped ZnO sample and the Sb-doped samples start to differ in terms of the ZnO grain size. The exception was the single sample with the largest addition of Sb, 500 μg/g, which is fine grained even after sintering for 250 h. In the 500 μg/g Sb sample the ZnO grains with IBs dominate in the microstructure even after a short

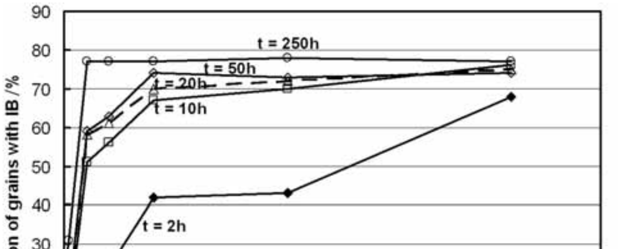

Figure 3: Fraction of ZnO grains with inversion boundaries (IBs) versus the amount of added Sb to ZnO for various sintering times
Slika 3: Delež ZnO zrn z inverznimi mejami (IBs) v odvisnosti od dodatka Sb v ZnO za različne čase sintranja

sintering time of 2 h, hence, their fraction and consequently also their grain size increased very little with an extended sintering time compared to other Sb-doped samples. The results indicated that with an increased amount of added Sb more ZnO grains contain IBs in the early stage of sintering, which determines the subsequent course of the grain growth and the final microstructure development. ZnO grains with IBs consume normal ZnO grains during their growth, and with their increasing fraction in the microstructure, the average ZnO grain size of the sample increases until the stage at which the grains with IBs completely dominate in the microstructure.

The longer is the period in which ZnO grains with IBs can grow at the expense of normal ZnO grains before they impinge upon each other, the larger they can grow and the coarser is the microstructure. In the sample with the addition of 25 μg/g of Sb, just the appropriate number of ZnO grains with IBs was formed in the early stage of sintering to take them a longer sintering time to prevail in the microstructure than in other Sb-doped samples, so the ZnO grains with IBs can grow larger than in any other sample. With the addition of 50 μg/g of Sb there was a slightly larger fraction of ZnO grains with IBs after sintering for just 2 h, which meant that the sintering time for their growth before they finally impinge on each other was somehow shorter and they are smaller after 20 and especially after 250 h (58 μm) than in the sample with 25 μg/g of Sb (71 μm). This is even more pronounced in the case of samples with 100 μg/g and 200 μg/g of Sb. The sample with the addition of 500 μg/g of Sb has a significantly smaller grain size of about 12 μm than all the other samples after sintering for 250 h. In this sample the ZnO grains with IBs prevail in the microstructure after sintering for 2 h.

From the graph of grain size vs. sintering time in **Figure 1** three regimes of noticeably different growth rates are evident: (i) an enhanced grain growth for sintering times up to 20 h, (ii) a modest growth rate for sintering times longer than 20 h and (iii) a grain growth that is practically terminated after 20 h of sintering. In the pure ZnO sample the grain growth is controlled by the solid-state diffusion of Zn^{2+} ions and follows Oswald-ripening growth kinetics. As long as the driving force for the reduction of a specific surface and hence the surface energy is sufficient, the grain growth is enhanced. However, as the average ZnO grain size of the sample noticeably increased after a longer sintering time, the driving force for grain growth decreased and the grain size increased modestly for sintering times longer than 20 h. In the Sb-doped samples, however, the regimes of the grain growth are related to the presence of IBs in the ZnO grains. In "regime I" ZnO grains with IBs coexist with normal ZnO grains. Because of the preferential growth of ZnO grains with IBs at the expense of normal grains, the grain growth is enhanced until ZnO grains with IBs dominate the microstructure. The amount of added IB-forming dopant directly influences the number of grains with IBs, which develop in the early stage of sintering, and hence, also the time span of the grain-growth "regime I" in which the grains with IBs can grow at the expense of the normal grains. The longer is the duration of "regime I" of the microstructural development, the larger can grow the grains with IBs before they impinge on each other, and the coarser is the final microstructure of the sample. Once ZnO grains with IBs impinge on each other "regime II" of the grain growth starts and the grain growth is noticeably slowed. With large enough additions of Sb to make "regime I" short, resulting in a very fine-grained microstructure, and followed by "regime II", one observes "regime III" in which the ZnO grains practically do not grow any more and the Sb-doped ZnO ceramics remain fine grained, even after an extended sintering time. In this study that condition was observed only with the sample doped with 500 μg/g of Sb, which resulted in the nucleation of IBs in almost every ZnO grain so that they were in very close proximity of each other, even at the very beginning of the grain-growth process, and had a very small number of normal grains available for recrystallisation. Also, the addition of Sb to the 500 μg/g Sb sample was sufficient for the formation of the $Zn_7Sb_2O_{12}$ spinel phase.

The results fully confirmed the possibility of controlling the grain growth and microstructure development via an IBs-induced grain-growth mechanism with the amount of IBs-triggering dopant (Sb_2O_3) in ZnO ceramics prepared by a classic ceramic procedure. However, it also showed that a reduced number of ZnO grains infected with IBs in the early stage of sintering, depending on the amount of added Sb – lower for smaller and higher for larger additions of Sb – results only in a very narrow compositional range of added Sb_2O_3. Only within this range of amount of Sb_2O_3 added to ZnO can the grain size be varied from coarse to fine grained. With a larger amount of added Sb_2O_3 practically all the ZnO grains are infected with IBs in the early stage of sintering and the resulting final microstructure is fine grained. A detailed presentation and discussion of these results are given in ref. 24.

4 Bi_2O_3- AND Sb_2O_3-DOPED ZnO CERAMICS

The results of the ZnO grain-size analysis confirmed the uniform grain growth in the un-doped ZnO samples from the observation of the microstructure (**Figure 4**). In contrast, the addition of the mole fraction 0.01 % and 0.02 % of Bi_2O_3 to ZnO resulted in the exaggerated growth of some ZnO grains, while others remained fine grained, with a size in the range from below 1 μm to a few micrometers (**Figure 4**). The result of the grain-size measurements indicates a moderate, average ZnO grain size of about 11 μm for the Bi_2O_3-doped samples; however, the microstructures of these samples are

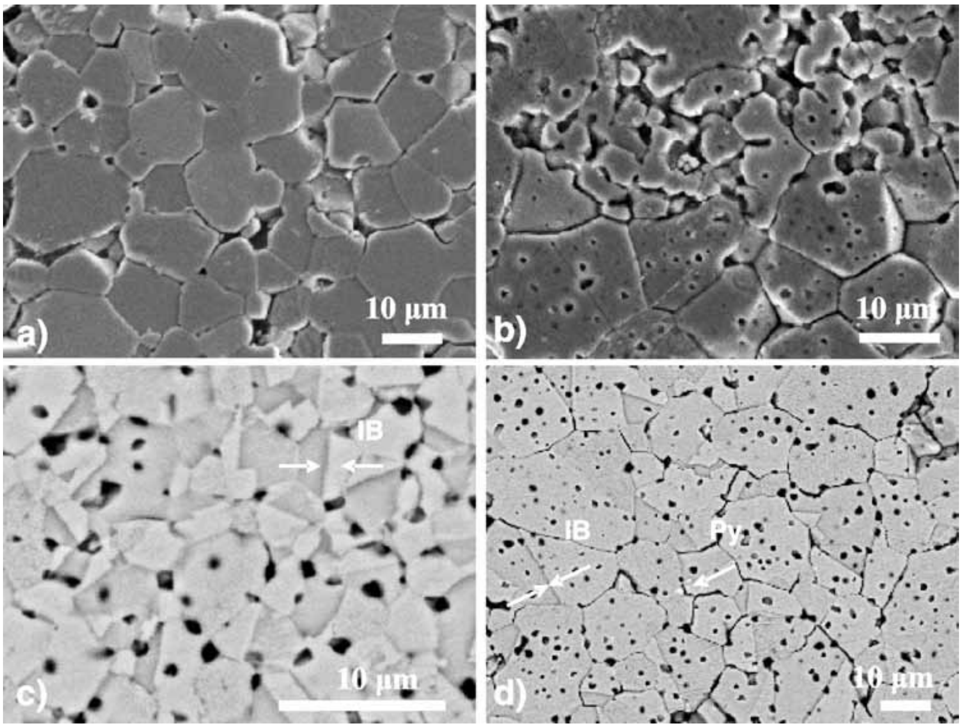

Figure 4: Microstructures of the samples sintered at 1200 °C for 2 h. a) ZnO; b) ZnO + 0.02 % Bi_2O_3; c) ZnO + 0.01 % Bi_2O_3 + 0.008 % Sb_2O_3; d) ZnO + 0.02 % Bi_2O_3 + 0.016 % Sb_2O_3. IB: inversion boundary; Py: pyrochlore phase; Bi_2O_3, Sb_2O_3 in mole fractions

Slika 4: Mikrostrukture vzorcev sintranih 2 uri pri 1200 °C. a) ZnO; b) ZnO + 0.02 % Bi_2O_3; c) ZnO + 0.01 % Bi_2O_3 + 0.008 % Sb_2O_3; d) ZnO + 0.02 % Bi_2O_3 + 0.016 % Sb_2O_3. IB: inverzna meja; Py: piroklorna faza; Bi_2O_3, Sb_2O_3 v molskih deležih

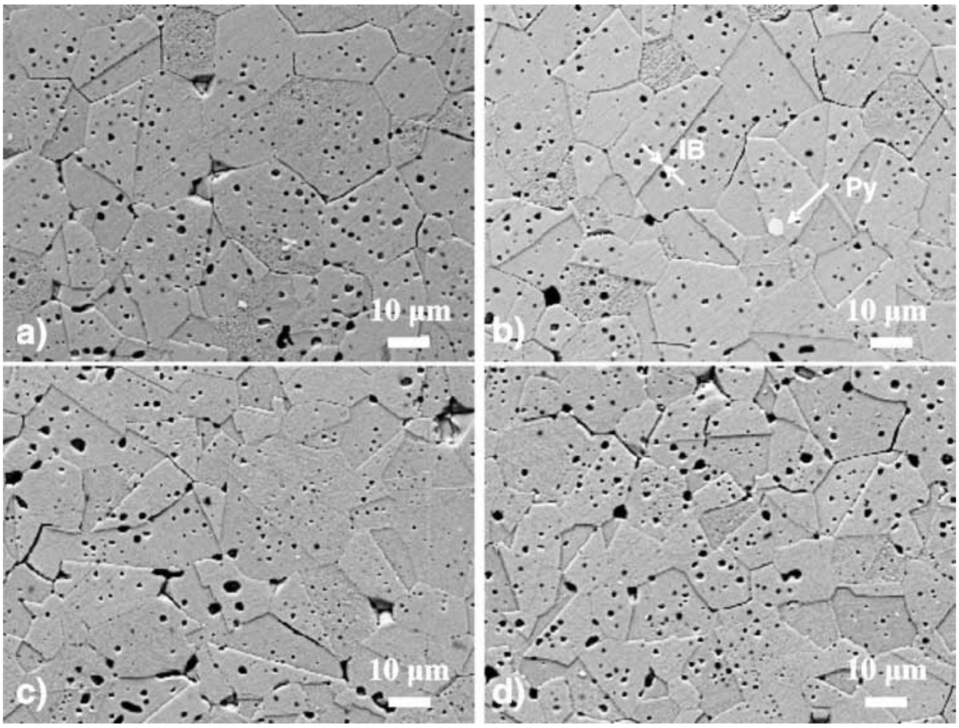

Figure 5: Microstructures of the samples sintered at 1200 °C for 10 h. a) ZnO + 0.01 % Bi_2O_3 + 0.008 % Sb_2O_3; b) ZnO + 0.02 % Bi_2O_3 + 0.016 % Sb_2O_3; c) ZnO + 0.01 % Bi_2O_3 + 0.012 % Sb_2O_3; d) ZnO + 0.02 % Bi_2O_3 + 0.024 % Sb_2O_3. IB: inversion boundary; Py: pyrochlore phase; Bi_2O_3, Sb_2O_3 in mole fractions

Slika 5: Mikrostrukture vzorcev sintranih 10 ur pri 1200 °C. a) ZnO + 0.01% Bi_2O_3 + 0.008 % Sb_2O_3; b) ZnO + 0.02 % Bi_2O_3 + 0.016 % Sb_2O_3; c) ZnO + 0.01 % Bi_2O_3 + 0.012 % Sb_2O_3; d) ZnO + 0.02 % Bi_2O_3 + 0.024 % Sb_2O_3. IB: inverzna meja; Py: piroklorna faza; Bi_2O_3, Sb_2O_3 v molskih deležih actually highly bimodal and consist of very large ZnO grains surrounded by fine grains. In the sample with the mole fraction of 0.01 % Bi_2O_3 the largest grains have a size of about 60 μm, while in the sample with the mole fraction of 0.02 % Bi_2O_3 the largest grains are about 30 μm. At the grain boundaries of some grains a sufficient amount of Bi_2O_3-based liquid phase is present to ensure the exaggerated growth of these grains, while at the other boundaries the grain growth is hindered due to a lack of liquid phase.

The microstructures of the ZnO-Bi_2O_3 samples doped with Sb_2O_3 are shown in **Figures 4 and 5**. These results show that the addition of Sb_2O_3 strongly affects the microstructure development and the grain growth of ZnO doped with Bi_2O_3. In the reaction of Bi_2O_3 and Sb_2O_3 with ZnO the pyrochlore phase is formed, and its fine inclusions can be observed in the microstructures. Inversion boundaries (IBs) are clearly evident in most of the ZnO grains of Sb_2O_3-doped samples, regardless of the sintering time at 1200 μC. In comparison to the ZnO-Bi_2O_3 samples with exaggerated grain growth, the introduction of Sb_2O_3 resulted in a uniform grain growth. Samples with the addition of the mole fraction 0.01 % Bi_2O_3 and sintered for 2 h are fine grained with a grain size of about 2 μm for all Sb_2O_3/Bi_2O_3 ratios, while samples doped with the mole fraction of 0.02 % have an average ZnO grain size of about 6 μm, which is comparable to the un-doped ZnO, except the sample with a Sb_2O_3/Bi_2O_3 ratio of 1, which is fine grained. After sintering for 10 h most of the Sb_2O_3 doped samples have a similar ZnO grain size of about 10 μm, which is comparable to the grain size of the pure ZnO sample (12 μm), except for samples with a Sb_2O_3/Bi_2O_3 ratio of 1, which have a smaller grain size, especially the sample with the addition of the mole fraction 0.01 % Bi_2O_3; this sample remained fine-grained (2.8 μm).

The results of the microstructure analysis for the ZnO ceramics doped with small amounts of Sb_2O_3 and Bi_2O_3 indicated the complex influence of several factors on the grain growth: the amount of added Bi_2O_3, the formation of the pyrochlore phase, the Sb_2O_3/Bi_2O_3 ratio and the inversion boundaries (IBs) in the ZnO grains. The amount of added Bi_2O_3 defines the amount of liquid phase at the sintering temperature, while the amount of added Sb_2O_3 affects the nucleation of IBs in ZnO grains at the early stage of sintering and hence, the number of grains infected by IBs that can grow exaggeratedly. The formation of the pyrochlore phase bounds both the Bi_2O_3 and Sb_2O_3 at a very low temperature of about 600 °C, and hence affects their presence at temperatures below its decomposition at 1040 °C. In ZnO samples doped with such a small amount of Bi_2O_3, exaggerated grain growth occurs. The addition of Sb_2O_3 to ZnO doped with Bi_2O_3 results in uniform grain growth and the occurrence of inversion boundaries (IBs) in most of the ZnO grains. Grain growth is promoted by a sufficient amount of the Bi_2O_3 liquid phase at the grain boundaries and also the presence of IBs in the ZnO grains. With a large enough addition of Bi_2O_3 the grain growth of ZnO grains with IBs is additionally promoted by the liquid phase and the grain size of the samples with a Sb_2O_3/Bi_2O_3 ratio smaller or larger than 1 is comparable to the grain size of the undoped ZnO samples. In the absence of a sufficient amount of the Bi_2O_3 liquid phase, the ZnO grains with IBs grow at a slower rate; however, after a longer sintering time the grain sizes of the samples with a Sb_2O_3/Bi_2O_3 ratio smaller or larger than 1 are comparable to the pure ZnO sample. The influence of the $Bi_3Zn_2Sb_3O_{14}$ pyrochlore phase formation is especially evident in the case of samples with a Sb_2O_3/Bi_2O_3 ratio of 1, where neither free Bi_2O_3 nor free Sb_2O_3 is present at temperatures below the decomposition of the pyrochlore phase, which consequently have a smaller ZnO grain size than the other samples.

5 CONCLUSIONS

The results fully confirmed the IBs-induced grain-growth mechanism and the possibility to use it for tailoring the microstructure in conventionally prepared ZnO ceramics doped with Bi_2O_3 and Sb_2O_3. For ZnO ceramics doped with Sb_2O_3, either a coarse-grained microstructure or a fine-grained microstructure, in comparison to pure ZnO, was obtained. Such results can be explained by the influence of IBs on the grain growth. The results showed that only very small amounts of Sb_2O_3, within a very narrow compositional range, result in a reduced number of ZnO grains infected with IBs (nuclei), so: i) for smaller amounts of Sb_2O_3, fewer nuclei are formed, which means they can grow for longer at the expense of normal ZnO grains before they impinge on each other and prevail in the microstructure, which results in a larger average ZnO grain size; and ii) for larger additions of Sb_2O_3, more nuclei are formed, which can grow to a lesser extent at the expense of normal ZnO grains before they impinge on each other and the final grain size is smaller. However, larger additions of Sb_2O_3 are sufficient to trigger the formation of IBs in most of the ZnO grains during the early stage of sintering and the resulting microstructure is fine-grained. In ZnO ceramics doped with Bi_2O_3 and Sb_2O_3 the complex influence of several factors on the grain growth is present: the amount of added Bi_2O_3, the formation of the $Bi_3Zn_2Sb_3O_{14}$ pyrochlore phase, and the Sb_2O_3-to-Bi_2O_3 ratio. They influence the amount of Bi_2O_3-rich liquid phase at the grain boundaries and also the presence of IBs in the ZnO grains, which strongly influence the grain-growth process. The results of these and previous investigations give us a comprehensive understanding of grain growth in ZnO ceramics under the influence of IBs; this enabled us to prepare ZnO ceramics doped with Bi_2O_3 and Sb_2O_3 with an average ZnO grain size that is either much larger or finer than for undoped ZnO ceramics.

Acknowledgement The authors acknowledge the financial support by the Slovenian Research Agency (Program Contract No. P2-0084-0106/05 and Project Contract No. L2-9175).

6 REFERENCES

[1] D. R. Clarke, *J. Am. Ceram. Soc*., 82 (**1999**), 485–502

[2] T. K. Gupta, *J. Am. Ceram. Soc*., 73 (**1990**), 1817–1840

[3] M. Inada, *Jpn. J. Appl. Phys*., 19 (**1980**). 409–419

[4] J. Kim, T. Kimura, T. Yamaguchi, *J. Am. Ceram. Soc.*, 72 (**1989**), 1541–1544

[5] J. Wong, *J. Appl. Phys*., 51 (**1980**), 4453–4459

[6] T. Senda, R.C. Bradt, *J. Am. Ceram. Soc*., 73 (**1990**), 106–114

[7] D. Dey, R. C. Bradt, *J. Am. Ceram. Soc.*, 75 (**1992**), 2529–2534

[8] J. Kim, T. Kimura, T.Yamaguchi, *J. Mater. Sci.*, 24 (**1989**), 2581–2586

[9] T. Senda, R.C. Bradt, *J. Am. Ceram. Soc*., 74 (**1991**), 1296–1302

[10] M. Ito, M.Tanahasmi, M.Uehara, and A.Iga, *Jpn. J. Appl. Phys*., 36 (**1997**), L1460–L1463

[11] H. Suzuki, R.C. Bradt, *J. Am. Cer. Soc.*, 78 (**1995**), 1354–1360

[12] D. Makovec, D. Kolar, M. Trontelj, *Mater. Res. Bull*., 28 (**1993**), 803–811

[13] S. I. Nunes, R. C. Bradt, *J. Am. Ceram. Soc*., 78 (**1995**), 2469–2475

[14] J. Han, P. Q. Mantas, A. M. R. Senos, *J. Mater. Res*., 16 (**2001**), 459–468

[15] M. Tanahashi, M. Ito, M. Murao, A. Iga, *Jpn. J. Appl. Phys*., 36 (**1997**), L573–L576

[16] S. Bernik, N. Daneu, *J. Europ. Ceram. Soc*., 27 (**2007**), 3161–3170

[17] S. Bernik, N. Daneu, *J. Europ. Ceram. Soc.*, 21 (**2001**), 1879–1882

[18] S. Bernik, N. Daneu, A. Rečnik, *J. Europ. Ceram. Soc*., 24 (**2004**), 3703–3708

[19] N. Daneu, A.Recnik, S. Bernik, and D. Kolar, *J. Am. Ceram. Soc*., 83 (**2000**), 3165–3171

[20] N. Daneu, A. Rečnik, S. Bernik:, *J. Amer. Ceram. Soc*., 86 (**2003**), 1379–1384

[21] A. Rečnik, N. Daneu, T. Walter, W. Mader, *J. Am. Ceram. Soc*., 84 (**2001**), 2657–2668

[22] A. Rečnik. N. Daneu, S. Bernik, *J. Europ. Ceram. Soc*., 27 (**2007**), 1999–2008

[23] A. Rečnik, M. Čeh. D. Kolar, *J. Europ. Ceram. Soc*., 21 (**2001**), 2117–2121

[24] S. Bernik, J. Bernard, N. Daneu, A. Rečnik, *J. Am. Ceram. Soc.,* 90 (**2007**), 3239–3242

[25] S. Bernik, M. Podlogar, N. Daneu, A. Rečnik, *Mat. Sci. Forum,* 558–559 (**2007**), 857–862