

# CHARACTERISTICS OF SnO<sub>2</sub> DOPED ZnO-Bi<sub>2</sub>O<sub>3</sub> CERAMICS

## ZNAČILNOSTI SnO<sub>2</sub> DOPIRANE ZnO-Bi<sub>2</sub>O<sub>3</sub> KERAMIKE

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The influence of SnO<sub>2</sub> additions on the sintering, microstructure development and nonlinear characteristics of ZnO based ceramics in the ZnO - Bi<sub>2</sub>O<sub>3</sub> - SnO<sub>2</sub> system was studied. Introduction of SnO<sub>2</sub> to the ZnO - Bi<sub>2</sub>O<sub>3</sub> system results in the formation of the Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase and the Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase. For Sn/Bi < 1 ratio the pyrochlore phase forms and bounds all the SnO<sub>2</sub>, while excess Bi<sub>2</sub>O<sub>3</sub> results in the formation of a liquid phase at 740°C which enhances sintering. In samples with a Sn/Bi ≥ 1 ratio all the Bi<sub>2</sub>O<sub>3</sub> is bounded in Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlore phase and sintering is hindered. Sintering is promoted at the decomposition of the pyrochlore phase into a Bi<sub>2</sub>O<sub>3</sub> melt and Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase at temperatures above 1000°C. The addition of 0.1% of SnO<sub>2</sub> promotes ZnO grain growth. In compositions with larger amounts of SnO<sub>2</sub>, growth of ZnO grains is already inhibited by the increasing amount of Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase. Moderate doping with SnO<sub>2</sub> improved the nonlinear characteristics of the basic ZnO - Bi<sub>2</sub>O<sub>3</sub> binary system, while a large amount of SnO<sub>2</sub> resulted in its degradation.

Key words: ZnO, varistor ceramics, SnO<sub>2</sub> doping, sintering, microstructure

Preiskovali smo vpliv dodatka SnO<sub>2</sub> na sintranje, razvoj mikrostrukture in tokovno-napetostno nelinearnost keramike na osnovi ZnO v sistemu ZnO - Bi<sub>2</sub>O<sub>3</sub> - SnO<sub>2</sub>. Pri dodatku SnO<sub>2</sub> v sistem ZnO - Bi<sub>2</sub>O<sub>3</sub> pride do nastanka piroklorne faze tipa Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> in spinelne faze tipa Zn<sub>2</sub>SnO<sub>4</sub>. Pri razmerju Sn/Bi < 1 piroklorna faza Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> veče ves SnO<sub>2</sub>, preostali Bi<sub>2</sub>O<sub>3</sub> pa povzroči pri 740°C nastanek tekočih faz, ki pospešijo sintranje. V vzorcih z razmerjem Sn/Bi ≥ 1 je ves Bi<sub>2</sub>O<sub>3</sub> vezan v piroklorno fazo, zato je sintranje zavrtlo. Sintranje v teh vzorcih je pospešeno, ko pride pri temperaturi nad 1000°C do razpada piroklorne faze v talino Bi<sub>2</sub>O<sub>3</sub> in spinelno fazo Zn<sub>2</sub>SnO<sub>4</sub>. Dodatek 0.1% SnO<sub>2</sub> pospešuje rast zrn ZnO. Pri sestavih z večjim dodatkom SnO<sub>2</sub> je rast zrn zavrtla zaradi vedno večje količine spinelne faze Zn<sub>2</sub>SnO<sub>4</sub>. Zmerni dodatki SnO<sub>2</sub> izboljšajo nelinearno karakteristiko binarnega sistema ZnO - Bi<sub>2</sub>O<sub>3</sub>, večji dodatki pa jo poslabšajo.

Ključne besede: ZnO, varistorska keramika, dopiranje z SnO<sub>2</sub>, sintranje, mikrostruktura

## 1 INTRODUCTION

Varistor ceramics are produced by sintering ZnO with minor additions of different metal oxides. They exhibit highly non-ohmic behaviour and excellent energy absorption capability. As a consequence of this, varistors are widely used for the protection of electronic devices against voltage transients and power overloads.

The non-linear relationship between current (I) and voltage (V) is expressed according to equation 1:

$$I = CV^\alpha \quad (1)$$

where  $\alpha$  is the nonlinear exponent and C is a constant. In commercial varistors the value of  $\alpha$  is usually between 20 and 70. The breakdown voltage separates the linear and non-linear regions and depends on the number of grain boundaries between the electrodes. Therefore, for high voltage applications fine-grained ceramics are required, whereas low voltage applications demand coarse-grained varistor ceramics.

The addition of Bi<sub>2</sub>O<sub>3</sub> to ZnO is essential for the non-ohmic behaviour to occur ( $\alpha$  below 10). In the process of sintering, Bi<sub>2</sub>O<sub>3</sub> introduces a liquid phase into the system and forms a skeleton of Bi-rich phases around the ZnO grains. The addition of metal oxides such as Sb<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> and others improves the electrical characteristics of the basic binary varistor ZnO-Bi<sub>2</sub>O<sub>3</sub> system in different ways: (i) by influencing

ZnO grain growth during the sintering process with the formation of pyrochlore and spinel phases, (ii) by altering the conductivity of ZnO grains, (iii) by influencing the characteristics of intergranular phases and (iv) by the formation of inversion boundaries (IB's) in ZnO grains<sup>12</sup>.

The influence of SnO<sub>2</sub> on ZnO-based varistor ceramics has been investigated by Viswanath et al.<sup>3</sup>. They reported that the addition of SnO<sub>2</sub> increases the nonlinear exponent ( $\alpha$  up to 20), electrical resistivity in the prebreakdown region, and promotes linear shrinkage of the basic ZnO-Bi<sub>2</sub>O<sub>3</sub> binary varistor system.

In this paper the influence of SnO<sub>2</sub> doping on sintering, microstructural characteristics, formation of secondary phases and electrical characteristics in the ZnO-Bi<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> system is reported.

## 2 EXPERIMENTAL PROCEDURES

The samples were prepared according to conventional ceramic procedures. The reagents: ZnO (99.8%, Union Minier), Bi<sub>2</sub>O<sub>3</sub> (99.8%, Alfa) and SnO<sub>2</sub> (99%, Alfa) were weighed and mixed using absolute ethanol as the media for homogenisation in a planetary mill. The homogenised mixtures were dried at 70°C. The powders were pressed into pellets using a pressure of 200 MPa. The samples were sintered in a tube furnace at

1200°C for 2 hours in air with a heating and cooling rate of 5 K/min.

Samples with the following compositions (in molar percentages) were prepared:

(99-x) % ZnO + 1 % Bi<sub>2</sub>O<sub>3</sub> + x % SnO<sub>2</sub> for x = 0 (ZB), 0.1 (SN01), 0.5 (SN05), 2 (SN2), 10 (SN10)

For comparison, samples of "pure" ZnO (label Z) were also prepared.

Sintering curves were obtained on a Leitz heating microscope by heating to 1300°C at a heating rate of 10°C/min.

The crystalline phases, present in the sintered samples, were determined by the use of X-ray powder diffractometry using a Philips PW 1710 with Ni filtered CuK $\alpha$  radiation in the range 2 $\Theta$ =10°-60° with a step of 0,04° and recording time 1 sec/step.

Microstructural investigations were performed on a Jeol 5800 scanning electron microscope (SEM), operated at 20kV and equipped with an energy dispersive X-ray spectrometer (EDS).

For SEM investigations, samples were diametrically cut and mounted in acrylic resin. Cross-sections of the samples were ground and polished. Half of each polished microstructure was etched with dilute hydrochloric acid.

The ZnO grain sizes were estimated using an equivalent-circle-diameter function, that computes the area of an irregular shape and transforms it to an equivalent-circle-diameter.

For electrical measurements, silver electrodes were fired on both sides of the samples at 600°C. The nominal varistor voltages (V<sub>N</sub>) at 1 mA and 10mA, and leakage current I<sub>L</sub> at 0.5V<sub>N</sub> (1mA) were measured. The threshold voltage V<sub>T</sub> (V/mm) and the nonlinear coefficient  $\alpha$  of the samples were determined.

### 3 RESULTS AND DISCUSSION

Sintering curves, showing the shrinkage of samples with different nominal composition, are compared in Fig. 1. In pure ZnO sintering starts at 650°C, maximum densification rate is at 840°C and shrinkage ends at 1130°C. In samples ZB, SN01, SN05 and SN2 sintering starts at 740°C, while in sample SN10 the onset of sintering is delayed up to 900°C. The lowest temperature of maximum densification rate is observed for sample ZB at 760°C. In samples SN01, SN05 and SN10 maximum densification rates are at 780°, 800° and 1070°C respectively. The sintering curve of sample SN2 shows enhanced sintering around 770° and 1050°C, while it is slowed in the temperature range from 780° to 1010°C. The shrinkage is completed at 980°C in sample ZB, at 1040°C in samples SN01 and SN05, while in pure ZnO and samples SN2 and SN10 densification ends at 1130°C. The final linear shrinkage  $\Delta L/L_0$  of pure ZnO is 14.6% and for the ZB sample 12.5%. In samples doped with SnO<sub>2</sub> the final shrinkage is in the range 14 to 16%

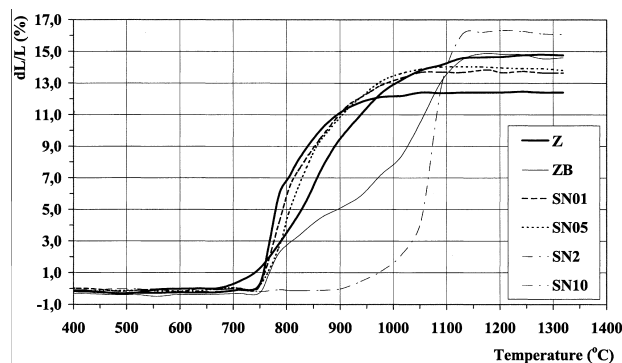


Figure 1: Densification curves of samples with different starting compositions

Slika 1: Krivulje zgoševanja vzorcev z različno izhodno sestavo

and increases with higher amounts of SnO<sub>2</sub>. X-ray diffraction patterns of samples with varying amounts of SnO<sub>2</sub> are given in Fig. 2.

Results of XRD analysis show that the major phase present in all the samples is ZnO. Since the quantity of Bi<sub>2</sub>O<sub>3</sub> is the same in all samples, the type and amount of secondary phases depend on the amount of SnO<sub>2</sub> addition. The secondary phases determined by XRD analysis in the SnO<sub>2</sub> doped samples are:  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase, Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase and Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase. The Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase was determined by XRD analysis to be in all SnO<sub>2</sub> doped samples. In the samples SN01 and SN05, XRD analysis also revealed the presence of the  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase, while in samples SN2 and SN10, characteristic XRD peaks of  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> are not observed. SEM/EDS analysis revealed traces of an intergranular Bi<sub>2</sub>O<sub>3</sub> rich phase (probably  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>) in the sample SN2. However, in the sample SN10, the presence of a Bi<sub>2</sub>O<sub>3</sub> rich phase was not detected by SEM/EDS analysis. The presence of the Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase is evident from XRD patterns

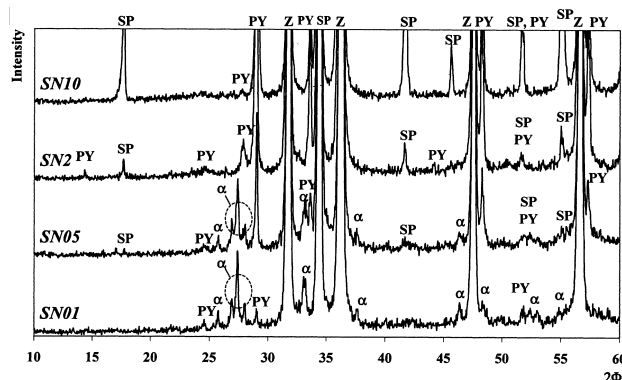
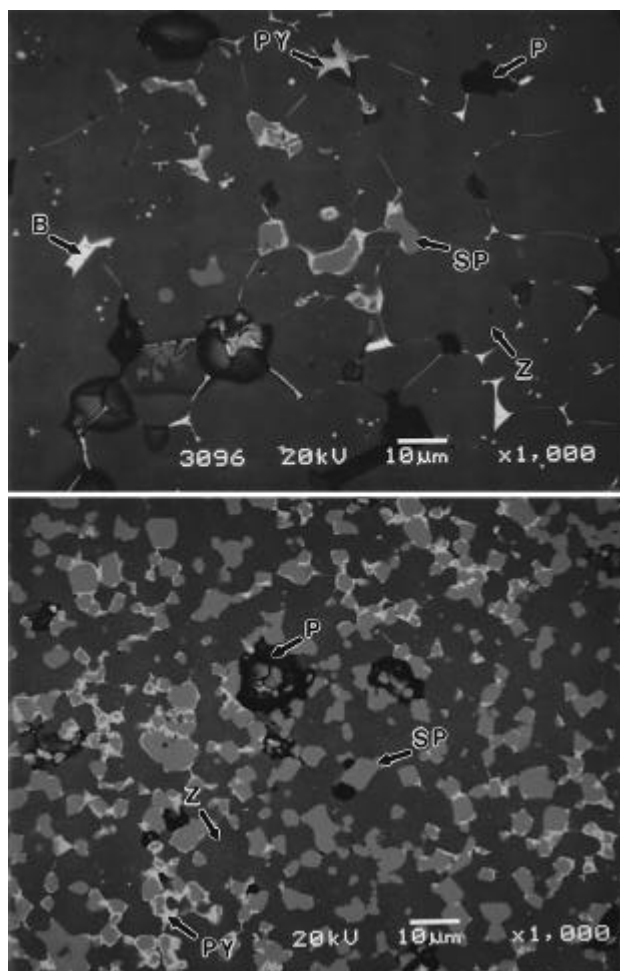


Figure 2: X-ray diffraction patterns of SnO<sub>2</sub> doped samples: (a) SN01, (b) SN05, (c) SN2, (d) SN10. Z: ZnO, SP: Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase, PY: Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase and  $\alpha$ :  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> phase

Slika 2: Rezultati pražkovne difrakcije vzorcev dopiranih s SnO<sub>2</sub>: (a) SN01, (b) SN05, (c) SN2, (d) SN10. Z: ZnO, SP: Zn<sub>2</sub>SnO<sub>4</sub> spinelna faza, PY: Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> piroklorna faza in  $\alpha$ :  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> faza



**Figure 3:** SEM backscattered electron (BE) images of non-etched microstructures of samples, fired at 1200°C for 2 hours; a) SN05, b) SN10. Z: ZnO phase, B: Bi<sub>2</sub>O<sub>3</sub>-rich phase, PY: Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase, SP: Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase and P: pore

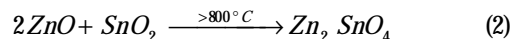
**Slika 3:** Mikrostrukturni vzorci vzorcev, ganih pri 1200°C 2 uri; a) SN05, b) SN10. Z: ZnO faza, B: Bi<sub>2</sub>O<sub>3</sub>-bogata faza, PY: Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> piroklorna faza, SP: Zn<sub>2</sub>SnO<sub>4</sub> spinelna faza in P: pora

in all SnO<sub>2</sub> doped samples, except in sample SN01. SEM/EDS analysis showed that a small amount of spinel phase, below the XRD detection limit, is also present in this sample.

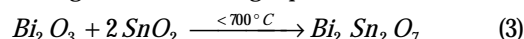
In **Fig. 3**, SEM backscattered electron (BE) images of samples SN05 and SN10 are shown. In sample SN10 a significantly larger amount of Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase is present in comparison with sample SN05. While in sample SN05, the Bi<sub>2</sub>O<sub>3</sub> rich and pyrochlore phases form an intergranular layer at the grain boundaries of the ZnO, the pyrochlore phase is the only Bi-containing phase in the SN10 sample.

The sintering behaviour (see **Fig. 1**) of the investigated samples can be explained by phase formation e.g. the presence of a liquid phase. In comparison with the ZnO sample, where solid state sintering has already started at 650°C, the onset of sintering is shifted to higher temperatures in the other samples, due to the presence of additives. In the sample

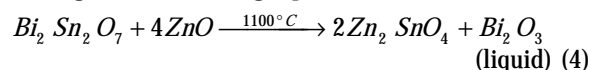
BZ, the presence of Bi<sub>2</sub>O<sub>3</sub> results in liquid phase formation at 740°C (melting of the Bi<sub>33</sub>ZnO<sub>33</sub> phase<sup>4</sup>). It promotes rapid shrinking, which is finished at 980°C. The addition of SnO<sub>2</sub> to the ZnO-Bi<sub>2</sub>O<sub>3</sub> system results in the formation of pyrochlore and spinel phases. Our previous investigations<sup>5</sup> of the Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase showed that it starts to form between 800° and 900°C according to the reaction:



The Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase<sup>5</sup>, however, already formed at temperatures below 700°C in the binary system Bi<sub>2</sub>O<sub>3</sub>-SnO<sub>2</sub> as well as in the presence of ZnO, according to the following equation:

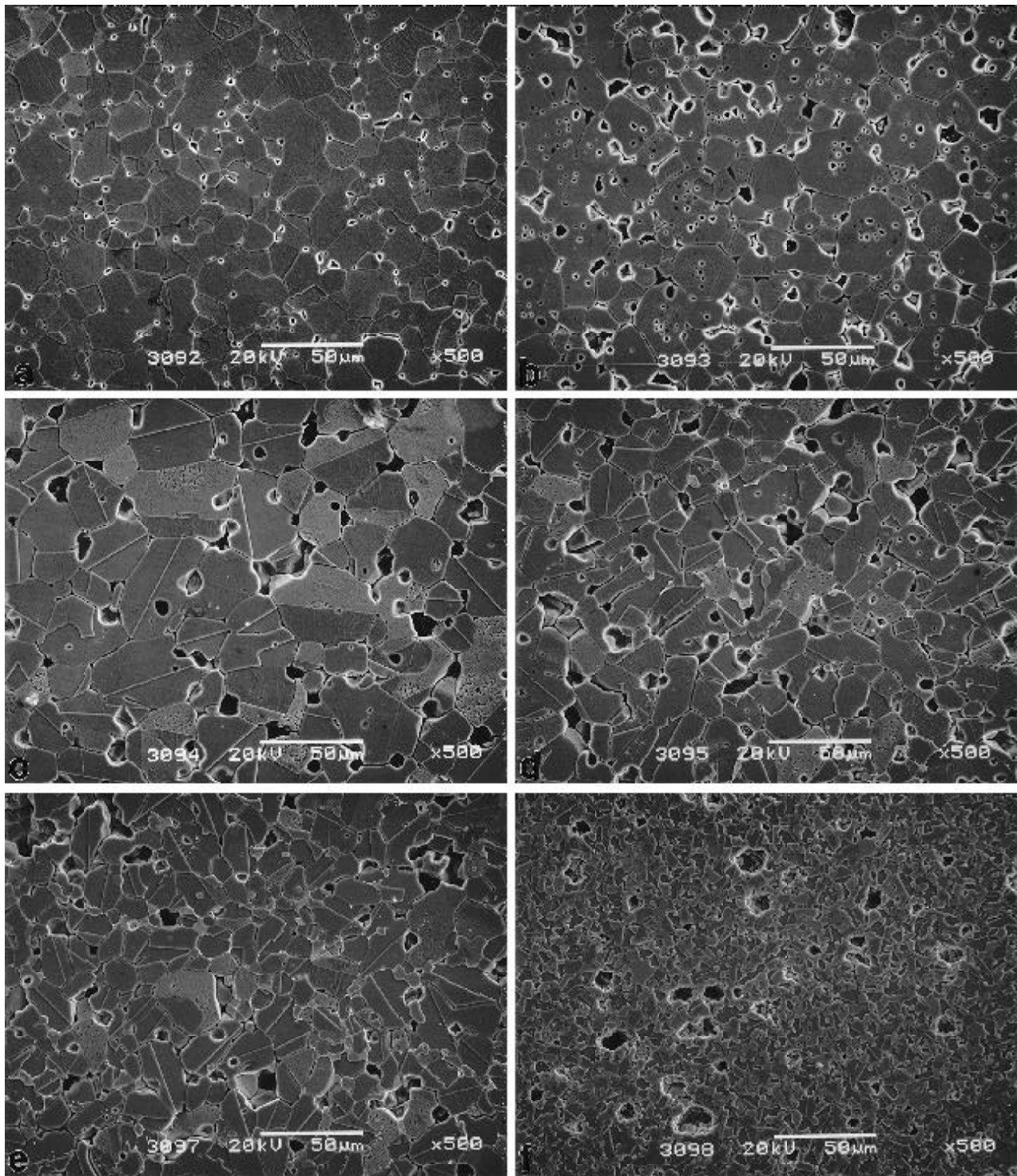


In the presence of ZnO approximately 1-1,5 at.% of Zn<sup>2+</sup> incorporates on Bi<sup>3+</sup> sites of the Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase. It was also observed that in the presence of ZnO the pyrochlore phase decomposes to the Bi<sub>2</sub>O<sub>3</sub> liquid phase and Zn<sub>2</sub>SnO<sub>4</sub> spinel phase at 1100°C, according to the following equation:



This results show that in samples containing SnO<sub>2</sub>, the pyrochlore phase already forms at relatively low temperatures, before the sintering starts. In the pyrochlore phase the atomic ratio Sn/Bi is 1. Consequently in samples SN01 and SN05 with a Sn/Bi ratio below 1, free Bi<sub>2</sub>O<sub>3</sub> is present and forms a liquid phase at 740°C, which enhances the sintering process. The shift of the maximum sintering rate to higher temperatures for the samples SN01 and SN05 in comparison with samples BZ is explained by formation of the pyrochlore phase and hence a reduced amount of liquid phase. In sample SN2, where the Sn/Bi ratio is 1, the formation of the pyrochlore phase is not yet completed at 740°C. Therefore in the early stages, sintering is enhanced by the presence of a small amount of liquid phase and later hindered due to the pyrochlore phase. In sample SN10, with a large amount of SnO<sub>2</sub> (Sn/Bi ratio 5), all the Bi<sub>2</sub>O<sub>3</sub> is bounded in the Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlore phase and no liquid phase is present at lower temperatures. The beginning of sintering is delayed till 900°C in this sample by the presence of the pyrochlore phase and the Zn<sub>2</sub>SnO<sub>4</sub> spinel phase which results from a reaction between ZnO and excessive SnO<sub>2</sub>. The maximum sintering rates at 1050°C and 1070°C in samples SN2 and SN10, respectively, are associated with the decomposition of the pyrochlore phase above 1000°C and formation of the Bi<sub>2</sub>O<sub>3</sub> liquid phase.

The Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase was present in the SN samples, despite sintering at 1200°C for two hours, which is well above the decomposition temperature (equation 4) of this phase. It is well known that the Bi<sub>3</sub>Zn<sub>2</sub>Sb<sub>3</sub>O<sub>11</sub> type pyrochlore phase in ZnO - Bi<sub>2</sub>O<sub>3</sub> - Sb<sub>2</sub>O<sub>3</sub> system decomposes at a temperature of about 1000°C into the Zn<sub>7</sub>Sb<sub>2</sub>O<sub>12</sub> type spinel phase and



**Figure 4:** SEM images of etched microstructures of samples, fired at 1200°C for 2 hours; a) Z, b) ZB, c) SN01, d) SN05, e) SN10  
**Slika 4:** Mikrostruktura vzorcev `ganjih pri 1200°C 2 uri; a) Z, b) ZB, c) SN01, d) SN05, e) SN10

Bi<sub>2</sub>O<sub>3</sub> liquid phase. On cooling, it forms again with the reaction between the spinel and Bi<sub>2</sub>O<sub>3</sub> phases<sup>67</sup>. Similarly, the Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase forms during cooling in the ZnO - Bi<sub>2</sub>O<sub>3</sub> - SnO<sub>2</sub> system.

The secondary phases in the investigated samples strongly influence ZnO grain growth. Microstructures of

samples with various compositions are presented in **Fig. 4** and their corresponding average ZnO grain sizes are given in **Table 1**. In the pure ZnO sample, the average ZnO grain size is 11 μm. In the presence of the Bi<sub>2</sub>O<sub>3</sub>-liquid phase, grain growth is promoted and sample ZB has an average ZnO grain size of 14 μm. In the pure

ZnO sample intergranular porosity dominates, while in the ZB sample intragranular porosity is clearly evident as well. The addition of a small amount of SnO<sub>2</sub> in sample SN01 results in a significantly larger average ZnO grain size of 22 μm. However, in comparison with the ZB sample, intragranular porosity is significantly lower in sample SN01 as well as in other SN samples and intergranular porosity is the dominant feature. The addition of 0.1% of SnO<sub>2</sub> only results in a small amount of Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase which does not influence significantly the ZnO grain growth. The amount of Bi<sub>2</sub>O<sub>3</sub> rich liquid phase in samples ZB and SN01 is practically equal. Therefore increased ZnO grain growth in the SN01 sample can be attributed to the influence of SnO<sub>2</sub> on the wettability of the Bi<sub>2</sub>O<sub>3</sub>-rich liquid phase. In samples with larger additions of SnO<sub>2</sub> the grain growth of ZnO is already inhibited due to the increasing amount of Zn<sub>2</sub>SnO<sub>4</sub> spinel grains at the grain boundaries. The inhibition of grain growth is especially significant in the SN10 sample where a large amount of spinel phase is already formed at much lower temperatures with the reaction between ZnO and excess SnO<sub>2</sub> (Eq. 2). In samples with a Sn/Bi ≤ 1 ratio, the spinel phase forms at higher temperature with the decomposition of the pyrochlore phase (Eq. 4). In these samples, intergranular and intragranular spinel grains can be observed. In addition, inclusions of the Bi<sub>2</sub>O<sub>3</sub> containing phase are occasionally present in ZnO grains. In these cases, the pyrochlore phase was most probably overgrown by ZnO. The mechanism of grain growth inhibition by the spinel phase is known and has been studied in other ZnO based compositions with spinel forming additives, such as Sb<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and others<sup>89</sup>.

**Table 1:** Average grain sizes of the investigated samples

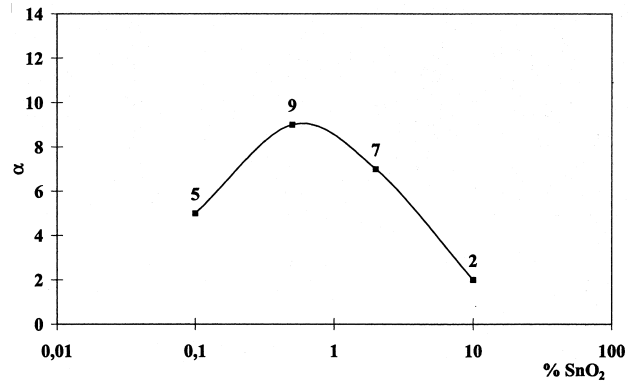
**Tabela 1:** Povprečne velikosti zrn preiskovanih vzorcev

Sample	Average grain size (μm)
Z	10,8 ± 5,1
ZB	14,1 ± 6,7
SN01	21,7 ± 9,5
SN05	16,1 ± 6,1
SN2	12,8 ± 5,5
SN10	5,6 ± 1,9

All investigated samples exhibit nonlinear current-voltage (I-V) characteristics (Fig. 5). The nonlinear coefficient obtained for the ZB sample is 3. Doping with SnO<sub>2</sub> increased the non-linearity and the highest nonlinear coefficient α of 9 shows in the sample doped with 0.5% of SnO<sub>2</sub>. A large addition of SnO<sub>2</sub> results in the degradation of the nonlinear characteristics in sample SN10.

#### 4 CONCLUSIONS

The influence of SnO<sub>2</sub> addition on the sintering, microstructure development and nonlinear characteristics



**Figure 5:** Nonlinear coefficient α of SnO<sub>2</sub> doped samples, fired at 1200 °C for 2 hours

**Slika 5:** Koefficient nelinearnosti α vzorcev dopiranih s SnO<sub>2</sub>, ganih pri 1200°C 2 uri

of ZnO based ceramics in the ZnO - Bi<sub>2</sub>O<sub>3</sub> - SnO<sub>2</sub> system was studied.

Introduction of SnO<sub>2</sub> into the ZnO - Bi<sub>2</sub>O<sub>3</sub> system results in the formation of the Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> type pyrochlore phase and the Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase. The pyrochlore phase forms at temperatures below 700°C and the spinel phase starts to form between 800°C and 900°C. Therefore for a Sn/Bi < 1 ratio the pyrochlore phase forms and bounds all the SnO<sub>2</sub>, while free-Bi<sub>2</sub>O<sub>3</sub> results in the formation of a liquid phase at 740°C which enhances sintering. On cooling the liquid phase stabilises as an α-Bi<sub>2</sub>O<sub>3</sub> modification. In samples with a Sn/Bi ≥ 1 ratio all the Bi<sub>2</sub>O<sub>3</sub> is bounded in Bi<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> pyrochlore phase and sintering is hindered due to the absence of a Bi<sub>2</sub>O<sub>3</sub> liquid phase. The excess SnO<sub>2</sub> results in the formation of the Zn<sub>2</sub>SnO<sub>4</sub> spinel phase. In compositions with Sn/Bi ≥ 1 sintering is promoted after decomposition of the pyrochlore phase into the Bi<sub>2</sub>O<sub>3</sub> melt and the Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase at temperatures above 1000°C. The pyrochlore phase recrystallises during cooling from the firing temperature.

The addition of SnO<sub>2</sub> strongly influences ZnO grain growth. The addition of 0.1% of SnO<sub>2</sub> promotes ZnO grain growth due to the influence on the properties, most probably wettability, of the Bi<sub>2</sub>O<sub>3</sub> rich liquid phase. In the sample SN01 the average ZnO grain size was determined to be 22 μm and in sample ZB to be 14 μm. Larger amounts of SnO<sub>2</sub> in samples SN05, SN2 and SN10 resulted in a smaller ZnO grain size, due to an increasing amount of the Zn<sub>2</sub>SnO<sub>4</sub> type spinel phase. While in the sample ZB, besides intergranular, also intragranular porosity is clearly evident, in SnO<sub>2</sub> doped samples there is practically no intragranular porosity.

Moderate doping with SnO<sub>2</sub> improved the nonlinear characteristics of the basic ZnO - Bi<sub>2</sub>O<sub>3</sub> binary system, while a large amount of SnO<sub>2</sub> resulted in its degradation.

## ACKNOWLEDGMENTS

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