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The characteristics of $ZnO–Bi_2O_3$-based varistor ceramics doped with Y_2O_3 and varying amounts of Sb_2O_3

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Abstract

$ZnO–Bi_2O_3$-based varistor samples doped with 0.45 mol% of Y_2O_3 and varying amounts of Sb_2O_3 in the range from 1.8 to 0.0 mol% were fired at 1230 °C. Only in the samples co-doped with Sb_2O_3 did doping with Y_2O_3 resulted in the formation of a fine-grained Bi–Zn–Sb–Y–O phase (the Y_2O_3-containing phase) at the grain boundaries, which very effectively hinders the grain growth. Despite of a decrease in the amount of added Sb_2O_3 from 1.8 to 0.45 mol% and a significant decrease in the amount of spinel phase the samples had a similar ZnO grain size and a threshold voltage of 200 V/mm. The results confirmed that doping with Y_2O_3 is a very promising route for the production of fine-grained high-voltage $ZnO–Bi_2O_3$-based varistor ceramics, and determining the proper amounts of added Sb_2O_3 and Y_2O_3 is of great importance.

Keywords: Electrical properties; Grain size; Microstructure-final; Varistor; ZnO

1. Introduction

As the non-linear current-voltage characteristic of ZnO-based varistor ceramics[1] is a grain-boundary phenomenon, with the breakdown voltage of the non-ohmic grain boundary at 3 V, the ZnO grain size is directly related to the electrical characteristics of the varistor. Hence, tailoring of the ZnO grain size is essential for controlling the breakdown voltage of varistor ceramics. The composition of varistor ceramics is rather complex, composed mainly of ZnO to which small amounts of oxides such as Bi_2O_3, Sb_2O_3, Co_3O_4, Mn_3O_4, Cr_2O_3 and others are added. Sb_2O_3 is generally considered as the grain-growth-controlling dopant since its addition results in the formation of the $Zn_7Sb_2O_{12}$ spinel-type phase that reduces the mobility of grain boundaries and hence hinders the grain growth.[2] Sb_2O_3 also results in the formation of so-called inversion boundaries (IBs) in practically every ZnO grain of the varistor ceramics. Daneu et al.[3] revealed their influence on the grain growth and the possibility to tailor the ZnO grain size with an IBs-induced grain-growth mechanism was confirmed in the ZnO ceramics doped with small amounts of Sb_2O_3.[4] It has been reported recently that the breakdown voltage and the energy characteristics of varistor ceramics can also be significantly increased by doping with rare-earth oxides.[5] Reports on Y_2O_3-doped[6] as well as Pr_6O_{11}- and Nd_2O_3-doped[7] $ZnO–Bi_2O_3$-based varistor ceramics have confirmed the possibility of preparing fine-grained varistor ceramics with a high breakdown voltage.

Following our previous results on Y_2O_3-doped varistor ceramics,[6] in this study we report on the influence of the amount of added Sb_2O_3 on the microstructural, current-voltage (I–V) and capacitance-voltage (C–V) characteristics of $ZnO–Bi_2O_3$-based varistor ceramics doped with Y_2O_3.

2. Experimental

$ZnO–Bi_2O_3$-based varistor samples with the nominal composition (96.65-x) mol% ZnO + 0.9 mol% Bi_2O_3 + 2.0 mol% (Co_3O_4 + Mn_3O_4 + NiO + Cr_2O_3) + 0.45 mol% Y_2O_3 + x mol% Sb_2O_3 for x = 1.8, 1.35, 1.0, 0.9, 0.65, 0.45, 0.225 and 0.0 (samples labeled S1.8, S1.35, S1.0, S0.9, S0.65, S0.45, S0.225 and S0, respectively) were prepared by the classical ceramic procedure. For comparison a composition with 1.0 mol% of Sb_2O_3 and

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without added Y_2O_3 was also prepared (labeled RS). Reagent-grade oxides were mixed in proper ratios and powder mixtures were pressed into discs of 10 mm diameter and 2 mm thick. The pellets were fired at 1230 °C for 2 h in air.

The phase composition of the samples was analyzed by X-ray powder diffraction (XRD) analysis. The samples' microstructures were examined using a scanning electron microscope (SEM) in back-scattered electron (BE) mode. The phase compositions of the samples and the composition of the individual phases were determined by energy-disperse X-ray spectroscopy (EDS) in the SEM. The average ZnO grain size (D) was determined for each sample from measurement of 500 to 800 grains per sample.

For the DC current-voltage (I–V) characterisation, silver electrodes were painted on both surfaces of the disk and fired at 590 °C in air. The nominal varistor voltages (V_N) at 1 and 10 mA were measured and the threshold voltage V_T (V/mm) and non-linear coefficient α were determined. The leakage current (I_L) was measured at 0.75 V_N (1 mA).

3. Results and discussion

XRD patterns of the investigated samples are presented in Fig. 1. While in the RS sample without added Y_2O_3 the ZnO phase, the $Zn_7Sb_2O_{12}$ spinel phase and the γ-Bi_2O_3 phase were identified by XRD analysis, in samples co-doped with Y_2O_3 and Sb_2O_3 the additional peaks of the Bi–Zn–Sb–Y–O (Y_2O_3-containing phase)[6] phase were observed. The XRD peak intensities of the spinel phase decrease with decreasing amount of added Sb_2O_3 and in the Y_2O_3 doped sample S0 without Sb_2O_3 added the spinel phase is absent. Also, no Y_2O_3-containing phase was detected in this sample, while the Bi_2O_3 phase was identified as Bi–Y–O phase ($Bi_{1.9}Y_{0.1}O_3$ phase according to JCPDF 39-0275). In the S0 sample a Zn–Cr–O phase was also detected ($ZnCrO_4$ phase according to a JCPDF 19-1456).

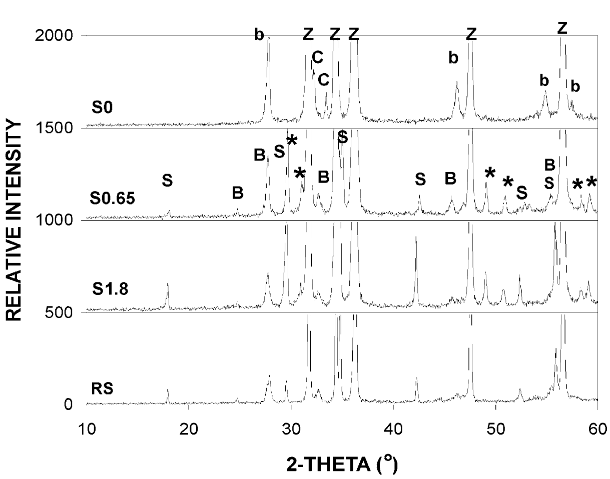

Fig. 1. XRD patterns of ZnO–Bi_2O_3-based varistor samples RS, S1.8, S0.65 and S0, fired at 1230 °C for 2 h; Z: ZnO phase, S: spinel phase, B: γ-Bi_2O_3 phase, b: Bi–Y–O phase, *: Y_2O_3-containing phase, C: Zn–Cr–O phase.

BE images from the SEM that reveal the main microstructural characteristics of the varistor samples are given in Figs. 2 and 3. The phases were identified by EDS analysis and the results confirmed the phase composition of the samples already determined by the XRD analysis. In all the Y_2O_3- and Sb_2O_3-doped varistor samples, in addition to the ZnO phase, the $Zn_7Sb_2O_{12}$ spinel-type phase and the Bi_2O_3-rich phase, the Bi–Zn–Sb–Y–O phase (Y_2O_3-containing phase) was identified at the grain boundaries of the ZnO. It is evident from Fig. 2, and was confirmed by a measurement of the area of the BE images that belongs to the spinel phase, that the amount of spinel phase in the samples decreases with decreasing amounts of added Sb_2O_3. Also, with decreasing amounts of Sb_2O_3 the composition of the Y_2O_3-phase alters and contains less Sb. It is evident from Fig. 2 that in sample S1.8, with the largest amount of added Sb_2O_3, the Y_2O_3-containing phase is fine grained and clustered, while it is fine grained and uniformly distributed along the grain boundaries of the Y_2O_3- and Sb_2O_3-doped samples with less added Sb_2O_3. The distribution and morphology of the Y_2O_3-containing phase are clearly evident in Fig. 3a. The Y_2O_3-containing phase is fine grained with grains of micrometer size and less, which is significantly smaller when compared to the grain size of the spinel phase. In sample S0, without added Sb_2O_3, the spinel and the Y_2O_3-containing phase are not present. At the ZnO grain boundaries of this sample the Bi_2O_3-rich phase containing Y_2O_3 and ZnO (most probably detected from the neighbouring ZnO grains) was determined by EDS analysis in which small grains of a Zn–Cr–O phase were also identified (Fig. 3b). In the Y_2O_3- and Sb_2O_3-doped samples the grain size can be inhibited by the spinel phase and the Y_2O_3-containing phase. However, despite the decrease in the amount of spinel phase in these samples due to the decrease in the amount of added Sb_2O_3 the size of the ZnO grains is rather similar, around 8 μm, in all varistor samples doped with Y_2O_3 and Sb_2O_3; this is except for sample S0.225 with the lowest addition of Sb_2O_3 where it is higher, at 10 μm, and is comparable to the grain size of the RS sample without added Y_2O_3 (10.4 μm). Sample RS has a similar amount of spinel phase as sample S1.35 does, and a significantly larger amount of spinel phase than sample S1.0; however, it does not contain the Y_2O_3-containing phase, and hence it has a significantly larger ZnO grain size than the other two samples. The results indicate that a fine-grained Y_2O_3-containing phase that is uniformly distributed along the grain boundaries of the

ZnO inhibits the grain growth very effectively. The ZnO grain size is significantly larger, at 20 μm, in sample S0, because the phases that inhibit ZnO grain growth, namely the spinel phase and the Y_2O_3-containing phase, are absent. The ZnO grains in this sample do not contain inversion boundaries (IBs), which can influence the grain growth as well.[3,8]

The starting composition does not influence the non-linear coefficient α, which is 40 for all the samples. The threshold voltage (V_T) of the samples strongly correlates

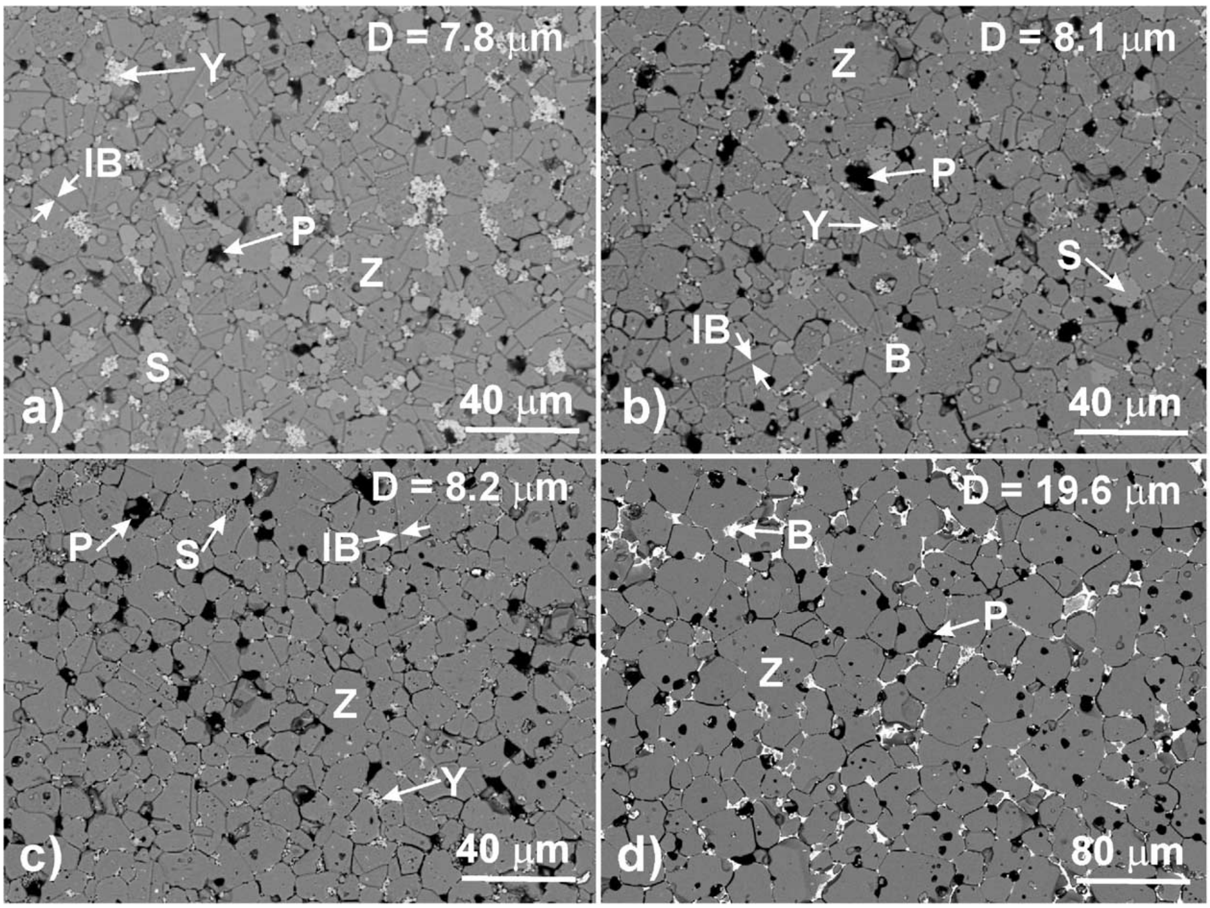

Fig. 2. Backscattered electron (BE) images of varistor samples fired at 1230 °C for 2 h. (a) S1.8, (b) S0.9, (c) S0.45 and (d) S0. Z: ZnO(Co,Mn) phase; S: $Zn_7Sb_2O_{12}$(Cr,Mn,Co,Ni) spinel-type phase; B: Bi_2O_3(Zn,Y) phase; Y: Bi–Sb–Zn–Y–O (Cr,Mn,Co,Ni) phase; C: Zn-Cr-O(Mn,Co,Ni) phase; P: pore; IB: inversion boundary.

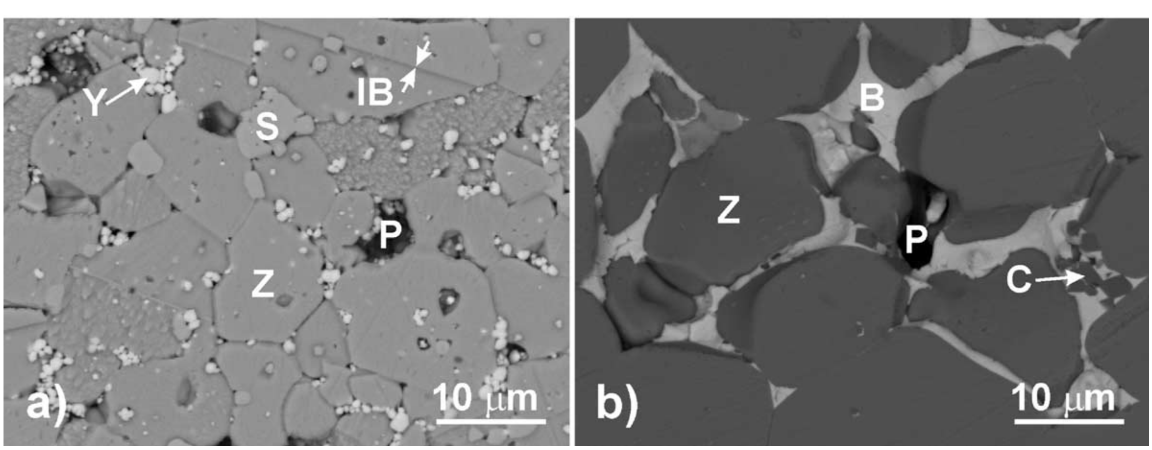

Fig. 3. Backscattered electron (BE) images of varistor samples (a) S0.45 and (b) S0, fired at 1230 °C for 2 h. Z: ZnO(Co,Mn) phase; S: $Zn_7Sb_2O_{12}$(Cr,Mn,Co,Ni) spinel-type phase; B: Bi_2O_3(Zn,Y) phase; Y: Bi–Sb–Zn–Y–O (Cr,Mn,Co,Ni) phase; C: Zn–Cr–O(Mn,Co,Ni) phase; P: pore; IB: inversion boundary.

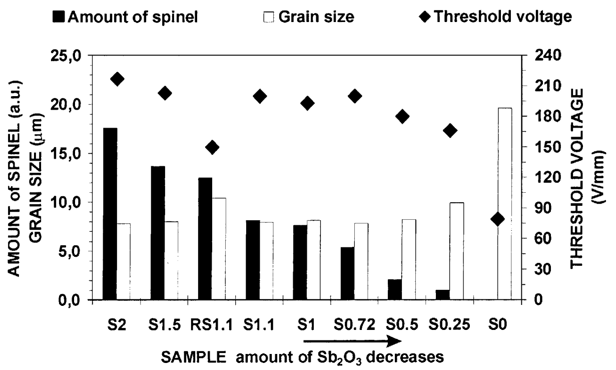

Fig. 4. Influence of the samples composition (amount of Sb_2O_3 added) on the amount of spinel phase, the average ZnO grain size and the threshold voltage (V_T) of varistor samples, fired at 1230 °C for 2 h.

with the ZnO grain size and is higher in samples with a smaller ZnO grain size, and vice versa. As the ZnO grain size is similar for most of the samples that are doped with Y_2O_3 and Sb_2O_3 they have similar threshold voltages (V_T) of 200 V/mm. The V_T is slightly higher in sample S1.8, with the largest Sb_2O_3 addition of 1.8 mol%, and starts to decrease significantly for amounts of added Sb_2O_3 below 0.45 mol%. Correlations between samples' composition, amount of spinel phase, average ZnO grain size and threshold voltage (V_T) are graphicaly presented in Fig. 4. The average breakdown voltage per grain boundary (V_{GB}), calculated from V_T and the average ZnO grain size, is 1.6 V for all samples, which indicates that the starting composition does not influence the fraction of all the grain boundaries in the sample that have non-ohmic characteristics. The leakage current (I_L) of the samples is at 0.1 μA for the Y_2O_3-free sample RS and Y_2O_3-doped samples with amount of added Sb_2O_3 0.90 mol% and higher. In samples with a lower amount of added Sb_2O_3 the I_L steadily increases and reaches 2.2 μA in sample S0 without added Sb_2O_3. This can be attributed to a week donor effect of the Y_2O_3[6] and the influence that decreasing the amount of Sb_2O_3 has on the distribution of all other varistor dopants along the grain boundaries of ZnO.

4. Conclusions

The influence of the amount of added Sb_2O_3 in the starting composition on the characteristics of Y_2O_3-doped ZnO–Bi_2O_3-based varistor ceramics was investigated. In the Sb_2O_3-Y_2O_3 co-doped samples the spinel and the Bi–Zn–Sb–Y–O phase (the Y_2O_3-containing phase) are present at the grain boundaries and hinder the grain growth. Despite of a decrease in the amount of added Sb_2O_3 from 1.8 to 0.45 mol% and a significant decrease in the amount of spinel phase the samples had a similar ZnO grain size and a threshold voltage of 200 V/mm. This indicates that a uniformly distributed and fine-grained Y_2O_3-containing phase is a very effective grain-growth inhibitor. The Y_2O_3-containing phase forms only in the presence of the Sb_2O_3, otherwise the Y_2O_3 incorporates into the Bi_2O_3-rich phase and the average ZnO grain size of sample without added Sb_2O_3 is more than doubled in comparison to the Sb_2O_3- and Y_2O_3-doped samples.

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