

LOW-TEMPERATURE SINTERING OF ZnO–Bi₂O₃-BASED VARISTOR CERAMICS FOR ENHANCED MICROSTRUCTURE DEVELOPMENT AND CURRENT-VOLTAGE CHARACTERISTICS

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ZnO–Bi₂O₃-based varistor ceramics are typically sintered at temperatures above 1100°C to ensure the proper microstructure development and the required current-voltage (I-U) characteristics. In this investigation the influence of the sintering regime at temperatures between 800 and 950°C on the microstructure development and the I-U characteristics of varistor ceramics was studied. It was shown that the presence of a sufficient amount of Bi₂O₃-based liquid phase at the proper Sb₂O₃-to-Bi₂O₃ ratio enhanced the sintering and also promoted grain growth under the influence of the inversion boundaries (IBs) triggered in the ZnO grains by the Sb₂O₃. The well-developed microstructures with high density and grain sizes from 4 to 8 μm resulted in good current-voltage characteristics of the samples with a coefficient of nonlinearity α equal to about 30 and a low leakage current I_L of below 1 μA. Depending on the composition and the sintering regime, the threshold voltages V_T were in the applicable range from 270 V·mm⁻¹ to 850 V·mm⁻¹, even though values much greater than 1000 V·mm⁻¹ are typically obtained with such low sintering temperatures.

INTRODUCTION

ZnO–Bi₂O₃-based varistors are characterized by an exceptional current-voltage (I-U) nonlinearity; at a particular, so-called breakdown voltage they switch within a few nanoseconds from a highly resistive to a highly conductive state so that the current through the varistor increases by several orders of magnitude for a small change of voltage. As they also have a high energy-absorption capability, varistors have the right combination of properties for the effective protection of electrical devices, electronic circuits and power systems against impulse-voltage transients generated by lightning, switching and electrostatic discharges. They are essential for safe and undisturbed operation, and prevent unnecessary costs due to a loss of working hours and damage to equipment.

The unique characteristics of ZnO–Bi₂O₃-based varistor ceramics are closely related to their microstructure and arise from the combined effects of the I-U nonlinearity of the grain boundaries and the high conductivity of the ZnO grains. At voltages below the breakdown voltage the electrical characteristics of the varistor ceramics are controlled by the resistivity of the grain boundaries and their I-U nonlinearity, which results from the electrostatic barriers caused by the presence of Bi₂O₃ at the grain boundaries. An ideal “varistor” grain boundary has a breakdown voltage of about 3.2 V. Hence,

the breakdown voltage of a varistor is the sum of the breakdown voltages of all the non-linear grain boundaries between the electrodes of the varistor. In other words, it is proportional to the number of grain boundaries, which is determined by the thickness of the varistor and the ZnO grain size. At voltages above the breakdown voltage and at high currents the I-U characteristics and energy-absorption capability of a varistor depend on the conductivity of the ZnO grains. Hence, oxides of Co, Mn and Ni are added, which incorporated into the ZnO grains act as donors and enhance their conductivity [1, 2]. Control of the grain size is important for tailoring the breakdown voltage of varistor ceramics. Typical dopants added to the starting composition for the control of the grain growth are either Sb₂O₃ to obtain fine-grained, high-voltage ceramics or TiO₂ for coarse-grained, low-voltage ceramics. Both dopants influence the grain growth primarily by triggering the inversion boundaries (IBs) in the ZnO grains and also slightly with the formation of the Zn₇Sb₂O₁₂ or Zn₂TiO₄ spinel phase at the grain boundaries of the ZnO [3].

Accordingly, the composition of the starting varistor powder mixture is rather complex, composed of ZnO with the addition of about 7 - 12 wt. % of oxides of Bi, Sb, Co, Mn, Ni and Cr, while each of the dopants plays a unique role. Nevertheless, the reactions and hence the phase composition of the varistor ceramics are basically determined by the ZnO–Bi₂O₃–Sb₂O₃ system.

A Bi₃Zn₂Sb₃O₁₄ pyrochlore-type phase in which the Sb₂O₃-to-Bi₂O₃-ratio is 1 forms already at temperatures above 600°C; hence, the Sb₂O₃-to-Bi₂O₃ ratio in the starting composition has an important influence on the microstructure development. For a Sb₂O₃-to-Bi₂O₃ ratio > 1 all the Bi₂O₃ is bounded into the pyrochlore phase and the Bi₂O₃-based liquid phase is formed only after the decomposition of the pyrochlore phase at temperatures above 1000°C. In contrast, for a Sb₂O₃-to-Bi₂O₃ ratio < 1 free Bi₂O₃, being in excess to the Sb₂O₃, can result in the occurrence of the Bi₂O₃-based liquid phase already at a temperature of 740°C (i.e., the eutectic between ZnO and Bi₂O₃); it dissolves other dopants and ensures their uniform distribution, promotes sintering and enhances grain growth, which all benefit the I-U characteristics of the varistor ceramics [4-7].

The ZnO–Bi₂O₃-based varistor ceramics are typically sintered in the temperature range between 1100°C and 1300°C. Sintering varistor ceramics at temperatures below 1100°C usually results in a poor microstructure development with reduced and uneven grain growth, high breakdown voltages much above 1000 V·mm⁻¹, low I-U nonlinearity and poor reproducibility of the electrical characteristics [8]. However, the preparation of varistor ceramics at temperatures below 1000°C with proper characteristics would be very desirable. A reduced sintering temperature could possibly be used for the preparation of fine-grained varistor ceramics and can represent significant energy savings and cost reductions for the manufacturers of high-voltage energy varistors. In the technologies of “two-dimensional” varistor structures with a large aspect ratio between the surface and the thickness, like multilayer and thick-film varistors, lower sintering temperatures are preferred to reduce the evaporation of the Bi₂O₃ and the interactions with the electrodes and the substrate, which result in the degradation of the varistor characteristics. Temperatures below 1000°C would also enable the use of cheaper Ag contacts instead of the much more expensive Pd- or Pt-containing ones [9-15]. Different approaches have been reported in order to prepare dense varistor ceramics with good I-U characteristics at temperatures below 1000°C, such as the use of fine starting powders with a high

sinterability prepared by a polymerized complex method [16], a two-stage, low-temperature thermal processing [17,18], hot pressing [19] or the addition of low-melting glass frit [10,20]. They resulted in a high density of varistor ceramics; however, the breakdown voltages of the ceramics were still above 1000 V·mm⁻¹, which is much too high for most applications. The addition of glass frit increases the chemical complexity of an already very complex system and is quite delicate due to the effects on the varistor characteristics of the grain boundaries.

In this work the preparation of ZnO–Bi₂O₃-based varistor ceramics using a classic ceramic procedure at temperatures below 1000°C was studied. The strategy to prepare dense varistor ceramics with a good current-voltage I-U nonlinearity aimed to exploit the influence of the Bi₂O₃-based liquid phase and the Sb₂O₃-triggered inversion boundaries for enhancing the grain growth and the microstructure development at such low firing temperatures [3, 21-23]. Accordingly, the varistor compositions were carefully set with regard to the amounts of Bi₂O₃, Sb₂O₃ and the Sb₂O₃-to-Bi₂O₃ ratios to ensure either higher or lower amounts of Bi₂O₃-rich liquid phase in the system at the sintering temperature. Furthermore, the samples were sintered with different heat-treatment regimes, which were set in regard to the sintering behaviour of the studied varistor compositions for possible additional enhancement of the microstructure development. The microstructural and current voltage characteristics of the varistor ceramics prepared at temperatures below 1000°C are discussed with respect to the influence of the starting composition and the heat-treatment regime.

EXPERIMENTAL

The samples of varistor ceramics with the compositions VC1 and VC2, having added the same amount of Bi₂O₃ and different amounts of Sb₂O₃, appropriate for the Sb₂O₃-to-Bi₂O₃ ratios (Sb/Bi) 0.25 and 0.50, were prepared using ZnO powder (Pharma 4, Grillo Zinkoxid GmbH, Goslar, Germany) and the reagent-grade varistor dopants Bi₂O₃, Sb₂O₃, Co₃O₄, Mn₃O₄, NiO and Cr₂O₃, added in total amounts of 1.8 and 2.0 mol. %, respectively.

Table 1. Different heat-treatment regimes used for sintering the samples.

Regime	Rate (°C·min ⁻¹)	T ₁ (°C)	t ₁ (min)	Rate (°C·min ⁻¹)	T ₂ (°C)	t ₂ (min)	Rate** (°C·min ⁻¹)
R1	D*	950	120	10	850	0	1
R2	D*	950	15	10	850	105	1
R3	D*	800	120	1	–	–	–
R4	D*	800	15	10	950	105	1
R5	D*	800	15	10	900	105	1
R6	D*	950	15	10	900	105	1
RS	5	1200	120	1	20	–	–

* sample were placed directly into furnace heated to temperature T₁

** cooling rate to room temperature

respectively. Stable water suspensions of the varistor powder mixtures with the addition of organic binders and plasticizers were prepared and dried on a spray drier to obtain granulates. The densification characteristics of the granulates for both compositions were recorded using a heating-stage microscope up to 1300°C at a heating rate of 10 K·min⁻¹. The granulates were pressed into discs with a diameter of 10 mm and a height of about 1.0 mm at a pressure of 150 MPa. The samples were sintered in a chamber furnace in an air atmosphere using various heat-treatment regimes, which were either single-stage processes (R1, R3) or two-stage-processes (R2, R4, R5, R6), given in Table 1. They were set in accordance with the observed densification behaviour of the granulates so that the samples were sintered at characteristic temperatures along their sintering curve (Figure 1): at the beginning of the sintering, at the end of the sintering, at the fastest sintering rate or two of these. For comparison, samples of both compositions were also sintered under typical sintering conditions for varistor ceramics, i.e., at 1200°C for 2 h (regime RS).

The density of the sintered samples was determined using Archimedes' method. The microstructures of the samples were 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 analysed 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. The surface of each grain was measured and the grain size was determined for a circular geometry as the diameter of a circle having the same surface area as the grain; the average ZnO grain size was determined from measurements of 100 to 800 grains per sample. For the DC current-voltage (I-U) characterization, silver electrodes were painted on both parallel surfaces of the discs and fired at 600°C. The nominal varistor voltages (U_N) at 1 mA·cm⁻² and 10 mA·cm⁻² were measured using a Keithley 2410 Digital SourceMeter and the threshold voltage U_T (V·mm⁻¹) and the non-linear coefficient α were determined. The leakage current (I_L) was measured at 0.75V_N (1 mA·cm⁻²).

RESULTS AND DISCUSSION

The sintering characteristics of the analysed varistor compositions are shown in Figure 1. The sample VC1, with more Bi₂O₃ and hence a larger amount of Bi₂O₃-rich liquid phase, starts to densify at about 750°C and the maximum sintering rate is at about 785°C. In the sample VC2 with a larger addition of Sb₂O₃ and hence less Bi₂O₃-rich liquid phase the onset of sintering is shifted to an about 35°C higher temperature, while the sintering rate remains the same. For both samples the densification ended at about 1050°C and the final linear shrinkage was 13 to 14 %. The sintered samples had a high density in the range from 96 to 97 % of the theoretical density, regardless of the heat-treatment regime.

The microstructural analysis of the samples on the SEM showed a well-developed microstructure in all the samples sintered at temperatures above 800°C and below 1000°C, regardless of the heat-treatment regime, similar to the microstructure of the varistor ceramics sintered at

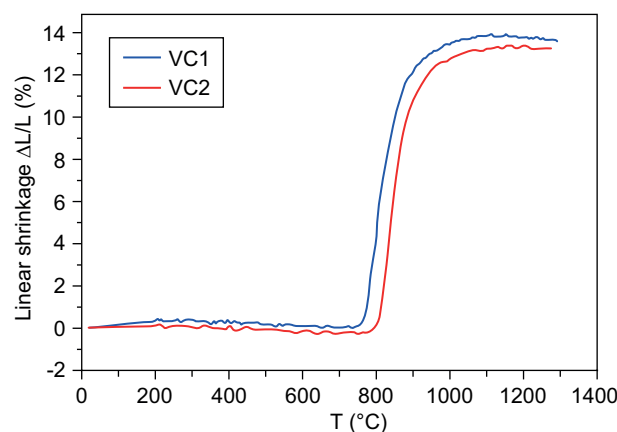


Figure 1. Densification curves of the samples.

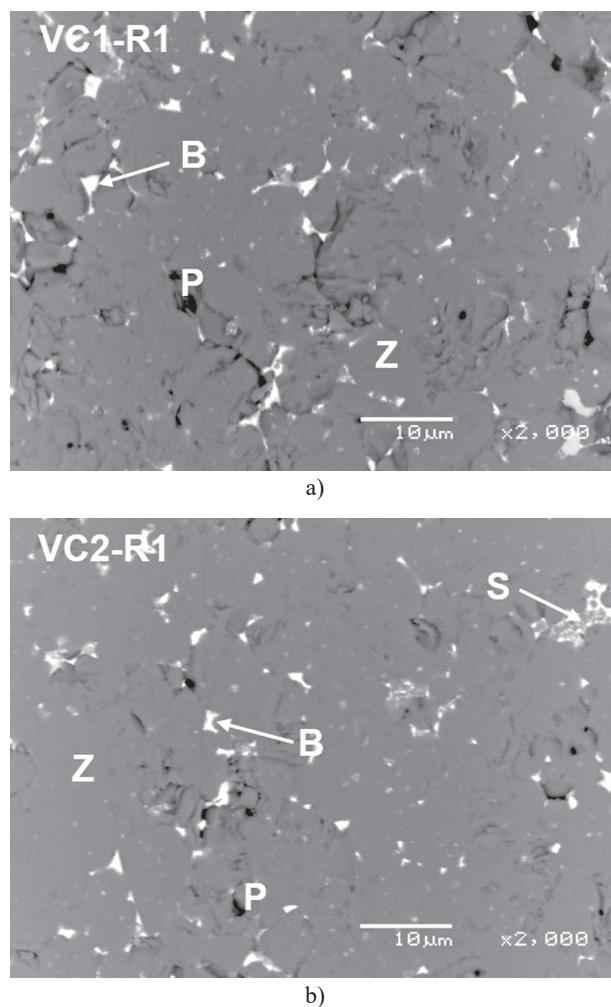


Figure 2. Microstructures of the samples VC1 and VC2 sintered in the single-stage regime R1 at 950°C for 2 h. Z: ZnO; B: Bi₂O₃-rich phase; S: Zn₇Sb₂O₁₂ spinel phase; P: pore.

typical temperatures above 1100°C. This confirmed that the compositions were properly set with regard to the amount of added Bi₂O₃ and also the Sb₂O₃-to-Bi₂O₃ ratio to ensure the microstructure development by the presence of the appropriate amount of Bi₂O₃-based liquid phase in the samples at temperatures above 740°C; it enhanced the sintering of the samples and promoted grain-growth under the influence of the inversion boundaries (IBs) triggered in the ZnO grains by the presence of the Sb₂O₃ already at such low temperatures. Typical microstructures of the samples are shown in Figure 2. The samples had homogeneous microstructures with a uniform distribution of the Bi₂O₃ phase as the main secondary phase at the grain boundaries of the ZnO. In the samples with the composition VC2 some minor amounts of a fine-grained Zn₇Sb₂O₁₂ spinel phase were observed, while in the samples VC1, with an even smaller addition of Sb₂O₃, some traces of spinel phase could not be excluded. Only the samples sintered at 800°C had a poorly developed varistor microstructure with a non-uniform distribution of the Bi₂O₃ phase and a strongly reduced grain growth. At temperatures above 1100°C, which are typically used

for the sintering of varistor ceramics, rapid grain growth takes place and often has to be hindered to obtain the desired breakdown voltages. However, at lower sintering temperatures varistor ceramics usually suffer a lack of sufficient grain growth and consequently have extremely high breakdown voltages with poor I-U nonlinearity due to the very fine ZnO grains, which are not sufficiently doped and have a too high resistivity. At such low temperatures a uniform distribution of the Bi₂O₃-based liquid phase is important to facilitate a uniform distribution of the other varistor dopants across the microstructure and the development of the electrostatic barriers at the grain boundaries for their varistor nature. It also promotes grain growth under the influence of inversion boundaries (IBs) and at the same time ensures appropriate and uniform doping of the ZnO grains with oxides of Co, Mn and Ni, all contributing to usable breakdown voltages in the range of several 100 V·mm⁻¹ for a proper I-U nonlinearity. Typical microstructures of the samples studied in this work, showing ZnO grains and their size distribution, are given in Figure 3. The results of the stereological analysis of the average ZnO grain size (G)

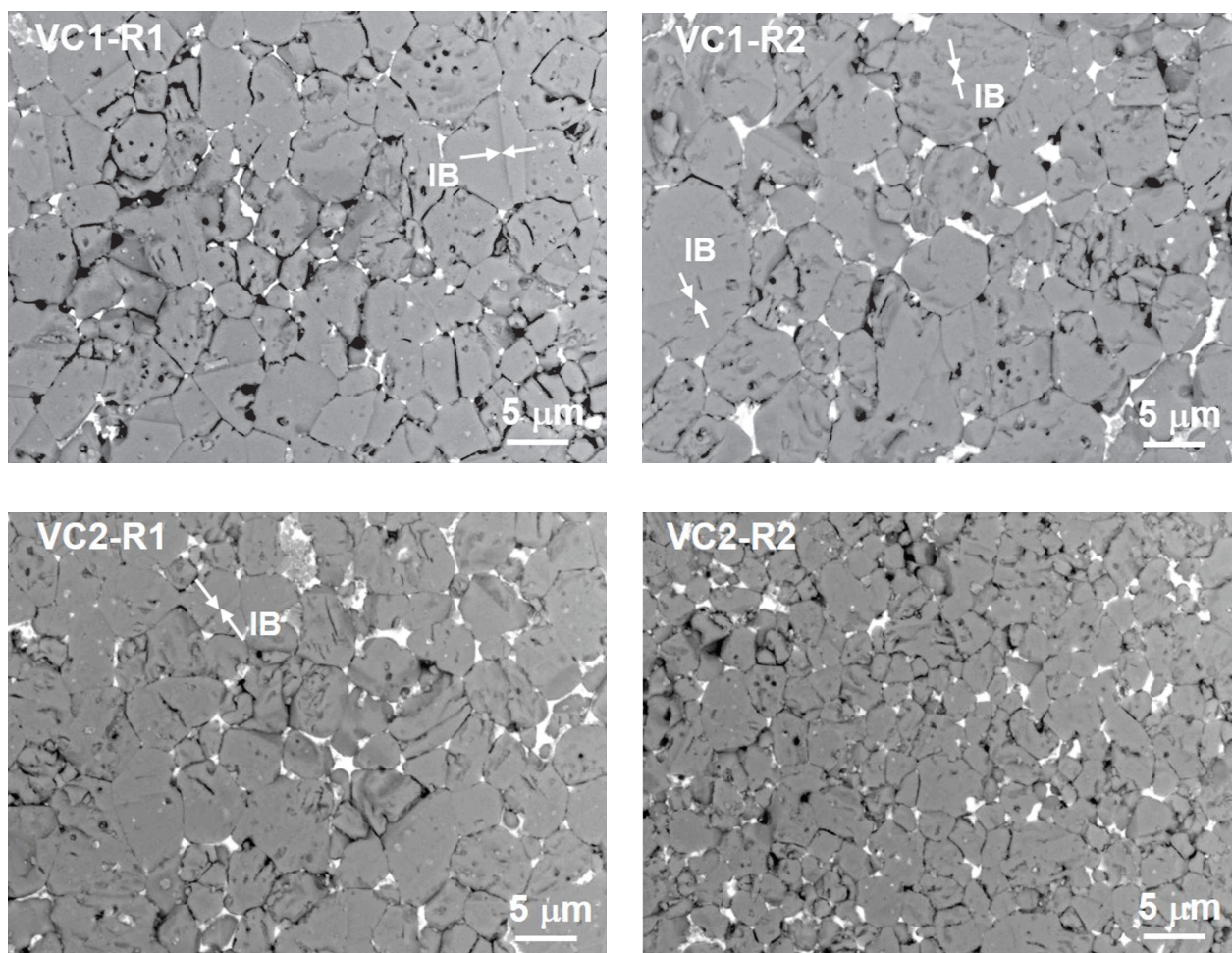


Figure 3. Etched microstructures of the samples VC1 and VC2 sintered under regimes R1 (950°C – 120 min) and R2 (950°C – 15 min + 850°C – 105 min). IB: inversion boundary.

are given in Table 2. Microstructural analyses showed a relatively uniform grain growth in all the samples studied in this work, with the exception of the samples fired at 800°C (R3). In these samples minor or practically no grain growth was observed, so that the grains remained around 1.0 μm for both compositions, VC1 (0.8 μm) and VC2 (1.2 μm), which is comparable to the starting particle size of the ZnO powder (0.5 μm). In all the other samples the pronounced grain growth resulted in ZnO grains with an average size for various samples in the range from 4 to 8 μm . For some of the larger ZnO grains the IBs are particularly evident. In general, for most of the heat-treatment regimens the samples with composition VC2 (larger addition of Sb_2O_3 and hence a lower amount of Bi_2O_3 -rich liquid phase) have a smaller average grain size than the samples with the composition VC1. Also, the heat-treatment regime with the higher temperature of the main heat-treatment stage resulted in a larger average ZnO grain size. As could be expected, the samples sintered at 1200°C for 2 h (regime RS) had much larger grains of about 24 μm for the composition VC1 and about 22 μm for the composition VC2; the grains are also more rounded with “smooth” grain-boundary lines in comparison to the grains in the samples sintered at temperatures below 1000°C, which have a more irregular shape with “rough” grain boundaries.

Proper microstructure development resulted in good current-voltage (I-U) characteristics for most of the samples. It showed, however, that even for these thoroughly set compositions, with the formation of the proper amount of the Bi_2O_3 -rich liquid phase already at 740°C, the sintering temperature of 800°C (regime R4) was too low for sufficient grain growth; hence, the samples had a breakdown voltage much above

the measuring range of the instrument, so they could not be measured. Other firing regimes with sintering temperatures between 850°C and 950°C resulted in samples with very suitable breakdown voltages U_T in the range from about 250 $\text{V}\cdot\text{mm}^{-1}$ to about 850 $\text{V}\cdot\text{mm}^{-1}$. The samples also had a good I-U nonlinearity, with a coefficient of nonlinearity α between 18 and 33, and a low leakage current I_L below 1 μA . The U_T is strongly correlated with the grain size G ; samples with smaller G have larger U_T and vice versa. The heat-treatment regimes with a higher temperature of the main sintering stage resulted in the larger average ZnO grain size and hence a lower U_T . The average breakdown voltages of the grain boundaries U_{GB} are in the range from 2.0 V to 3.4 V, which also indicates good nonlinearity of the samples. In general, samples with the composition VC2 with a larger addition of Sb_2O_3 have a higher U_T , α and U_{GB} , and lower I_L for the same sintering regime than

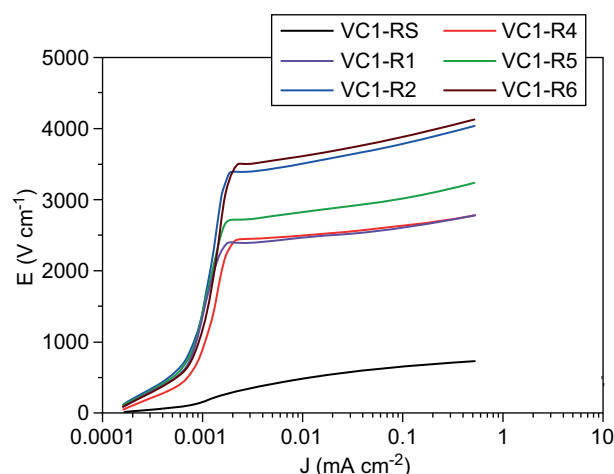


Figure 4. Electric field E vs. current density J of the varistor samples with the composition VC1, sintered under different heat-treatment regimes R.

Table 2. Average ZnO grain size (G) of the samples with compositions VC1 and VC2, sintered under different heat-treatment regimes and their current-voltage (I-U) characteristics.

Regime	Sample	U_T ($\text{V}\cdot\text{mm}^{-1}$)	α	I_L (μA)	G (μm)	U_{GB} (V)
RS	VC1	79	18	0.48	23.7	1.9
	VC2	110	19	0.34	21.5	2.4
R1	VC1	268	33	0.06	7.3	2.0
	VC2	376	32	0.06	6.2	2.4
R2	VC1	390	28	0.05	6.2	2.4
	VC2	845	25	0.09	3.7	3.1
R3	VC1	–	–	–	0.8	–
	VC2	–	–	–	1.2	–
R4	VC1	279	23	0.39	6.4	1.8
	VC2	420	33	0.10	6.1	2.6
R5	VC1	313	28	0.05	8.0	2.5
	VC2	830	27	0.12	4.1	3.4
R6	VC1	405	26	0.11	5.3	2.2
	VC2	569	26	0.13	3.8	2.2

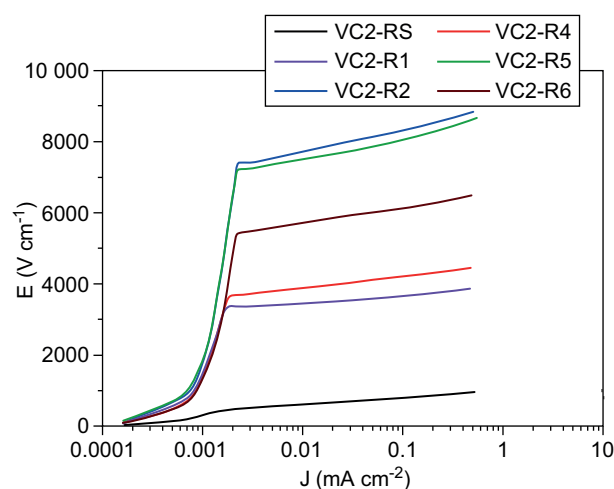


Figure 5. Electric field E vs. current density J of the varistor samples with the composition VC2, sintered under different heat-treatment regimes R.

samples with the composition VC1. The results of the current-voltage (I-U) characterization of the samples are collected in Table 2. A sharp transition at the breakdown voltage from ohmic to nonlinear I-U characteristics of the samples is also evident from the measurements of the electric field E versus the current density J, presented in Figures 4 and 5.

CONCLUSIONS

In this work ZnO–Bi₂O₃-based varistor ceramics were developed by sintering under different heat-treatment regimes, either in a single-stage or two-stage process at low temperatures in the range from 800°C to 950°C with a total time at the sintering temperatures of 2 hours. The results confirmed that the proper amount of the Bi₂O₃-based liquid phase controlled by the amount of added Sb₂O₃ (Sb₂O₃-to-Bi₂O₃ ratio < 1) enhanced the sintering and also promoted the grain growth at temperatures above 800°C. Hence, the samples had a high density of at least 96 % of the theoretical density and microstructures with a uniform distribution of the main Bi₂O₃-rich secondary phase at the grain boundaries and minor traces of the Zn₇Sb₂O₁₂ spinel phase.

The well-developed microstructures resulted in good current-voltage characteristics of the samples. Depending on the composition and sintering regime, the samples had breakdown voltages U_T in the range from 270 V·mm⁻¹ to 850 V·mm⁻¹, a coefficient of nonlinearity α between 23 and 33, and a low leakage current I_L below 1 μ A. The average breakdown voltages of the grain boundaries U_{GB} are in the range from 2 V to 3.4 V, which also indicates the good nonlinearity of the samples. In the two-stage heat-treatment process the temperature of the main (longer) firing stage has a major influence on the average ZnO grain size and consequently on the breakdown voltage U_T of the sample.

The results fully confirmed that the correct strategy when setting the starting varistor composition for the amount of added Bi₂O₃ and the Sb₂O₃-to-Bi₂O₃ ratios in combination with an appropriate sintering regime enable the proper microstructure development at temperatures below 1000°C and consequently current-voltage characteristics of the varistor ceramics suitable for a broad range of varistor applications.

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