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Structural and electrical properties of ZnO varistors containing different spinel phases

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Abstract

Structural and electrical properties of ZnO varistors were investigated as a function of spinel composition. Six varistor mixtures differing only in chemical composition of spinel, were prepared by mixing separately synthesized constituent phases (DSCP method). Compositions of constituent phases in sintered samples were investigated by changes of lattice parameters of the phases, as well as by EDS analysis of the constituent phases. It was found that compositions of ZnO, intergranular and spinel phases were partially changed during sintering due to redistribution of additives, that was controlled by starting spinel composition and its stability. Electrical characterization showed significant difference in electrical properties of investigated varistors: nonlinearity coefficients ranging from 22 to 55 and leakage currents differing by the order of magnitude. Activation energies of conduction were obtained from ac impedance spectroscopy measurements. Calculated values of activation energies were in the range 0.61–1.0 eV confirming difference in defect structure of ZnO grain boundaries in varistors containing different spinel phases. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: B. X-ray method; C. Electrical properties; D. Spinels; E. Varistors

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1. Introduction

ZnO varistors are ceramic composites used for voltage stabilization and transient surge suppression in electric power systems and electronic circuits [1]. Main feature of the ZnO varistors is its high nonlinearity of the current-voltage characteristics. The electrical properties of ZnO varistors are determined by their microstructure, composition, additives distribution and homogeneity. Varistors contain three main phases: doped ZnO grains, intergranular, and spinel phase [2–4]. If the varistor is prepared by a conventional method, then these phases are formed during the reactive sintering of ZnO powder with a small amount of additives such as oxides of Bi, Sb, Co, Mn, Cr, Al, Ni, etc.

Spinel phase, whose basic formula in ZnO varistors is $Zn_{2.33}Sb_{0.67}O_4$ [5,6], may dissolve almost all other elements present in the system [5,7,8]. Its actual formula depends on the initial varistor mixture composition and sintering conditions.

Although ZnO varistors were investigated from many different aspects (microstructural, chemical, electrical) by a great number of authors, there are only several articles dealing with spinel phase, its composition and influence on varistor characteristics. There is general agreement that spinel acts as ZnO grain growth inhibitor and indirectly influences the breakdown voltage that depends on ZnO grain size (see, for example [9,10]). Only a few comprehensive studies about the spinel phase composition were reported [5,7,8]. Most of the works are based on the investigation of Sb_2O_3 influence on sintering, as well as on densification of ZnO varistors [11–13], and rarely on electrical properties [14,15].

Absence of systematic investigation of influence of spinel phase composition on varistor properties can be explained by the fact that conventional method of varistor fabrication is not convenient for control of the phase composition. That is why the method of direct synthesis of the constituent phases (DSCP) [16] was chosen for our investigation. This method enables synthesis

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of varistor ceramics with more defined composition of each phase. To investigate the relation between chemical composition of the starting spinel phase and varistor properties several varistor samples containing different spinel phases were prepared. Structural and electrical properties of the resulting ceramics were investigated by changes of lattice constants of the phases, SEM and EDS analysis, as well as by electrical measurements. Conclusions about influence of spinel composition on varistor properties were made based on these results.

In addition, this investigation also tested the possibility of using DCSP method in synthesis of varistors with desired and controlled composition.

2. Experimental procedure

According to DSCP method each phase was prepared separately and final ceramics was obtained by sintering the mixture of the crystal phases. Preparation procedures are given elsewhere and resulted from our earlier investigations [16–18]. Compositions of phases used in preparing varistors were the following:

- ZnO phase: 99.8 mol% ZnO + 0.2 mol% of Co^{2+} + Mn^{2+} ions,
- γ-Bi_2O_3 phase: $6Bi_2O_3{\cdot}MnO_2$,
- spinel phases: (1) $Zn_{2.33}Sb_{0.67}O_4$ (Zn–Sb), (2) $Zn_2Mn_{0.5}Sb_{0.5}O_4$ (Zn–Mn); (3) $Zn_2Cr_{0.5}Sb_{0.5}O_4$ (Zn–Cr); (4) $Co_{2.33}Sb_{0.67}O_4$ (Co–Sb); (5) $Zn_{1.86}Co_{0.46}Sb_{0.67}O_4$ (Zn–Co); (6) $Zn_{1.971}Ni_{0.090}Co_{0.030}Cr_{0.247}Mn_{0.090}Sb_{0.545}O_4$ (Zn–all).

Spinel phase compositions were chosen based on the following consideration. There is general agreement that the formula of spinel in ZnO varistors is approximately $Zn_{2.33}Sb_{0.67}O_4$ [3,5]. This spinel was the starting point in our work. Spinels Zn–Mn, Zn–Co and Zn–Cr, whose general formula is $Zn_xMe_ySb_zO_4$, were obtained by replacing a certain percentage of Zn^{2+} ions with Me ions, where is Me = Mn, Co or Cr. These ions are common additives in ZnO varistors. Formulas of spinels Zn–Mn, Zn–Co and Zn–Cr were calculated based on two main requests: a) sum of atoms $x+y+z$ must be equal to 3, and (b) overall charge of cations must be equal to 8 [17]. Spinel Co–Sb was chosen because its existence in real varistors was also reported [3]. The last spinel, Zn–all, has the composition most similar to common composition of spinels in varistors obtained by conventional method. Its formula is calculated by averaging results of chemical analysis of spinel phase given by other authors [5,7,8]. These compositions enable systematic investigation of spinel phases stability, as well as their influence on varistor properties.

Varistor mixtures with a composition 85 wt.% of ZnO phase, 10 wt.% of spinel and 5 wt.% of γ-Bi_2O_3 were homogenized in agate planetary ball mill for 2 h, pressed into pellets sized approximately 1 mm in height and 8 mm in diameter and sintered at 1200°C, for 1 h. Sintering conditions were chosen according to the preliminary results [19]. In further discussion varistor mixtures will be designated according to the spinel composition (for example: Zn–Co varistor is varistor that contains spinel designated Zn–Co).

Characterization of the initial powders and the resulting ceramics was made by X-ray powder diffraction (Philips PW 1710 powder diffractometer with graphite-monochromatized CuK_α radiation), optical and scanning electron microscopy (JEOL JSM-T330A) with energy dispersive X-ray analysis (EDS), as well as by electrical measurements.

Electrical properties were registered within the 0.1–10 mA/cm^2 region using a direct current method. The nonlinearity coefficients were determined within the ranges 0.1–1.0 mA/cm^2 (α_1) and 1.0–10 mA/cm^2 (α_2), the breakdown field (K_C) was measured at 1 mA/cm^2, and the leakage current (J_L) was determined at an electrical field of 0.8 K_C. Voltage per barrier (U_b) was determined from the values of K_C and D, according to the equation $U_b = K_C{\cdot}D$, where D is ZnO grain size.

For ac impedance spectroscopy (IS) measurements sintered samples were polished and coated with silver paste at both sides. Electrode area was 38.5 mm^2 and samples were approximately 1 mm thick. IS measurements were carried out on a HP4276A LCZ-meter, in the frequency region of 100 Hz–20 KHz, and in temperature interval 23–207°C.

3. Results and discussion

DSCP method enables full control of composition of phases in starting varistor powder mixtures. After preparation, powder mixtures are subjected to liquid phase sintering and it was expected that compositions of the constituent phases would be partially changed due to diffusion of additives. Composition of constituent phases in final ZnO varistors were determined by X-ray and EDS analysis.

X-ray diffraction analysis of sintered samples reveals no formation of new phases, but lattice constants of the phases were changed after sintering. Lattice constants of each sample were changed in different extents depending on the phases affinity to a particular ion and on overall varistor composition.

In comparison to the starting ZnO powder lattice constant of ZnO phase slightly increased in all sintered samples (Table 1). This means that some ions diffuse into ZnO phase. Mn^{2+} ions are present in all mixtures because intergranular γ-Bi_2O_3 phase contains Mn component, so Mn^{2+} is probably one of the components that diffuses into ZnO and raises lattice constant value. Another ion that could diffuse is Co^{2+}, when it is present in the spinel phase, as in Zn–Co and Co–Sb mixtures. Changes of ZnO lattice constant were the greatest in Co–Sb varistors. EDS analysis of this sample showed the presence of great amount of Co^{2+} ions in ZnO grain (Fig. 1a). The increased amount of Co^{2+} in ZnO grains are also detected in Zn–Co varistor, but not in such high concentration as in case of Co–Sb varistors (Fig. 1b). The lattice constant of ZnO in samples Zn–all and Zn–Co sample is the most similar to the starting one.

Table 1
Lattice constants of ZnO phase in sintered varistors[a]

Varistor[b]	a (Å)	c (Å)
Zn–Mn	3.2552 (3)	5.2120 (2)
Zn–Sb	3.2550 (4)	5.2110 (5)
Zn–Cr	3.2537 (3)	5.2110 (5)
Co–Sb	3.260 (2)	5.230 (4)
Zn–Co	3.2523 (4)	5.205 (1)
Zn–all	3.2520 (4)	5.212 (3)

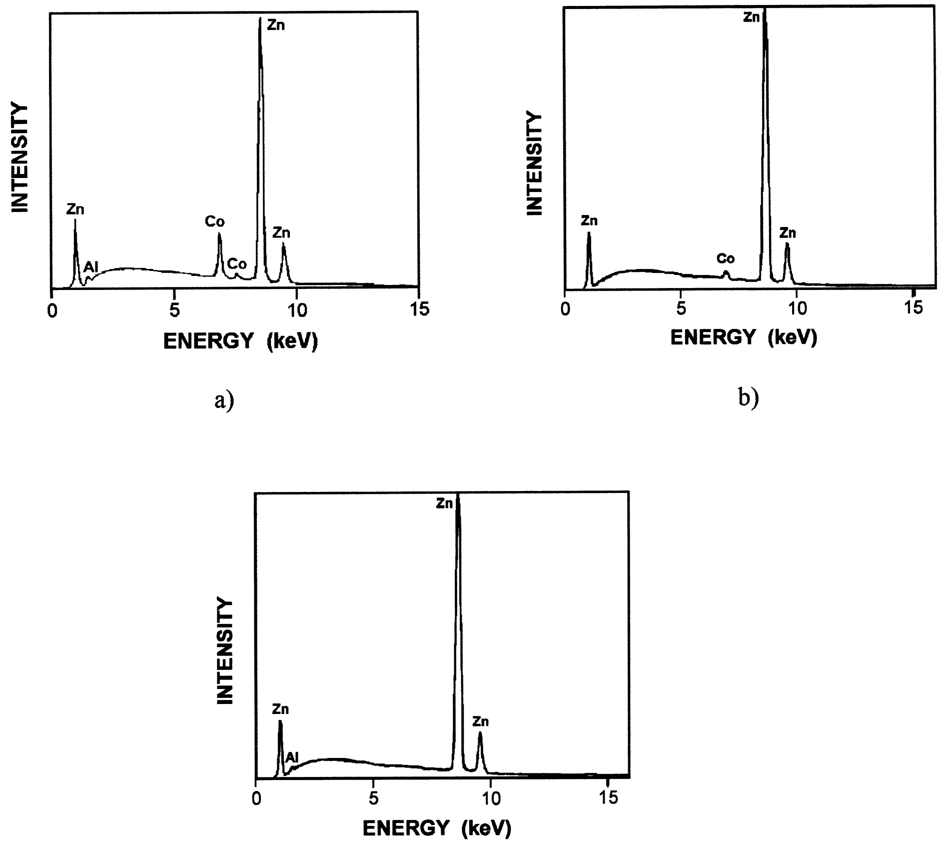
[a] Starting ZnO: $a = 3.2507$ (4), $c = 5.207$ (3) Å.

[b] Varistor mixtures are designated according to the spinel composition

According to our earlier investigations [17], the lattice constant of ternary $Zn_xMe_ySb_zO_4$ spinels (Me=Cr, Co, Mn, or Ni) decreases linearly with increasing content of Me ions. Applied to this investigation it means that in most cases Me ions leave the spinel (Table 2) and are incorporated into other phase(s). Considering above mentioned linear relation between spinel lattice constant and Me-ions content it is possible to calculate approximately amount of Me ions to be substituted.In the case of Zn–Mn varistors, Zn^{2+} was probably substituted for about 25% of Mn-ions, because Zn^{2+} and Co^{2+} are the only ions that could be incorporated into the spinel, but

Table 2
Lattice constants of the spinel phase in sintered varistor samples

Varistor	Starting spinel	After sintering
Zn–Mn	8.548 (2)	8.561 (4)
Zn–Sb	8.594 (1)	8.580 (2)
Zn–Cr	8.5259 (7)	8.538 (1)
Co–Sb	8.561 (1)	8.604 (5)
Zn–Co	8.587 (2)	8.594 (1)
Zn–all	8.550 (2)	8.550 (3)



a)

b)

c)

Fig. 1. EDS of ZnO grain interior of varistors (a) Co–Sb, (b) Zn–Co, (c) Zn–Sb.

much higher concentration of Zn^{2+} is present in the system. For Zn–Cr composition, it is more complicated to conclude what happened during sintering process. For example, change of spinel lattice constant of Zn–Cr varistor showed that certain amount of Cr-ions were substituted, but there are three possible substituents — Zn^{2+}, Mn^{2+} and Co^{2+} — and all of them should increase the spinel lattice constant [17]. Co^{2+} is less probable, considering relative amounts of these ions in the system, so the expected substituents were Zn^{2+} and Mn^{2+}. EDS analysis showed only higher amount of Zn^{2+} and no Mn^{2+}, therefore the composition of the resulting spinel was changed only in amount of Cr^{3+} ions in comparison to starting spinel (Fig. 2a). According to lattice constants changes approximately 10% of Cr^{3+} were substituted with Zn^{2+}. EDS analysis of

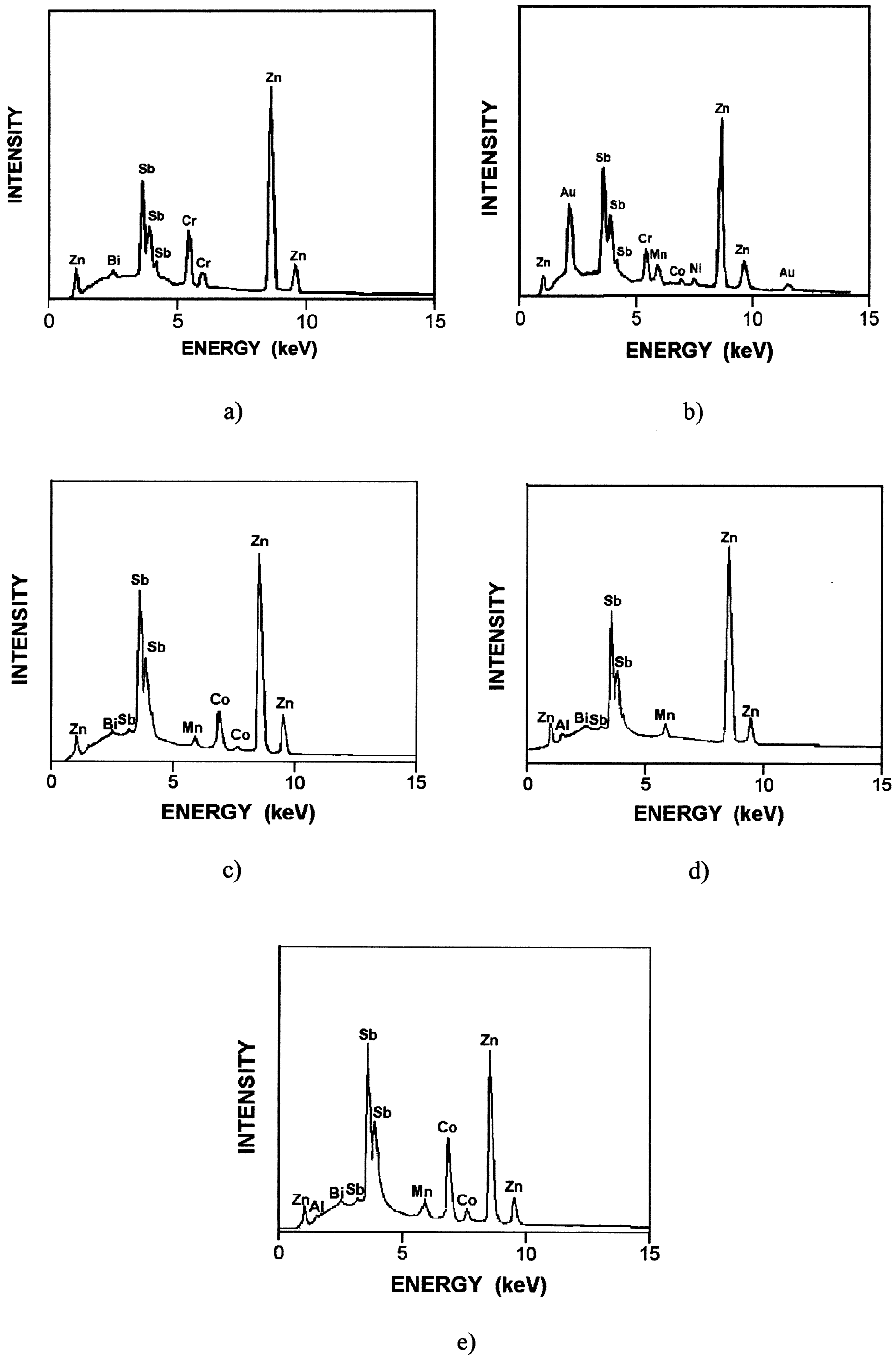


Fig. 2. EDS of spinel phase of varistors (a) Zn–Cr, (b) Zn–all, (c) Zn–Co, (d) Zn–Sb, (e) Co–Sb.

intergranular phase of Zn–Cr samples showed presence of Cr^{3+} (Fig. 3a), so it can be concluded that following processes took place:

- Mn^{2+} diffuse from γ-Bi_2O_3 to ZnO grains,
- Small amount of Cr^{3+} diffuse from spinel into intergranular phase,
- Zn^{2+} diffuse from ZnO grains into spinel and intergranular phase.

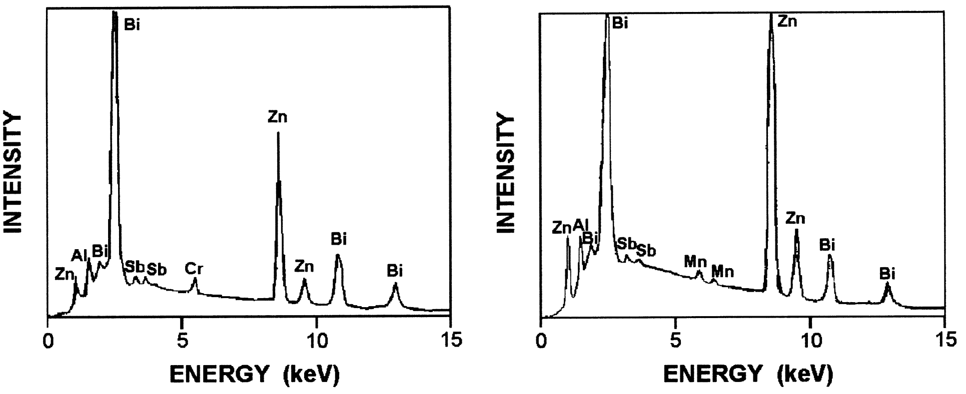
In the case of spinel Zn–all, changes of lattice constants are not registered, implying that there is no significant change in spinel composition, which was also confirmed by EDS (Fig. 2b). According to results of calculation of lattice constants, the same situation is with Zn–Co spinel, which also remained almost unchanged after sintering. Nevertheless, EDS analysis of spinel phase in samples Zn–Co showed the presence of small quantity of Mn^{2+} (Fig. 2c), which obviously diffused into spinel from intergranular phase. At the same time, Co^{2+} from spinel diffuses to ZnO phase and EDS analysis confirmed higher amount of Co^{2+} inside ZnO grains in comparison to the samples without Co in spinel (Fig. 1b and c).

Decrease in lattice constant in sample containing non-doped $Zn_{2.33}Sb_{0.67}O_4$ spinel means that certain amounts of Me ions were introduced into the spinel. EDS analysis of this sample showed presence of Mn^{2+} ions in spinel phase (Fig. 2d). Based on linear relation between spinel lattice constant and Me ions content, it is possible to calculate that about 5% of Zn^{2+} were replaced with Mn^{2+}. This means that the composition of spinel Zn–Sb is similar to composition of spinel Zn–Mn in sintered varistors.

In the case of Co–Sb varistor changes in spinel lattice constant were great and suggest that Zn^{2+} substituted a great amount of Co^{2+}. EDS analysis also showed the presence of small amount of Mn^{2+}, similar as in Zn–Co composition (Fig. 2e).

Due to low Bi_2O_3 content, only two or three well-separated, but very weak maxima belonging to this phase were visible in diffractograms. Therefore, it was not possible to calculate γ-Bi_2O_3 lattice constants with high precision. Estimated values range between 10.13 (1) and 10.174(6) Å that is typical for γ-Bi_2O_3 in ZnO varistors [20,21]. These values are lower than the starting one [10.221(1) Å]. Possible explanation of decrease in lattice constants is that sintered samples contain γ-Bi_2O_3 stabilized mainly with Zn^{2+}. This means that Mn^{2+} is substituted by Zn^{2+}, but this kind of substitution can not explain such a low values of lattice constants, since our previous investigation of γ-Bi_2O_3 stabilized with Zn^{2+} showed that this phase of composition $6Bi_2O_3 \cdot ZnO$ has the lattice constant $a = 10.196(3)$ Å. Second possible explanation is that amounts of Bi^{3+} and Mn^{2+} or Zn^{2+} in γ-Bi_2O_3 does not follow the ratio 12 Bi^{3+}:1Me^{2+}, but some others. Unfortunately, there are no reliable literature data about influence of relative amount of Me-ions in γ-Bi_2O_3 on its lattice constants. EDS analysis of intergranular phase in investigated samples showed that its composition is γ-Bi_2O_3 stabilized mainly with Zn^{2+}. Mn^{2+} ions were not detected, except in Zn–Mn samples (Fig. 3b), meaning that Mn^{2+} diffused to ZnO grains, as well as into spinel when it is possible. Lower values of lattice constants in comparison to pure $6Bi_2O_3 \cdot ZnO$ are probably due to change in relative amounts of Bi^{3+} and Zn^{2+}, as well as due to presence of small amount of some other ions, such as Sb^{3+} and Cr^{3+} which were detected in some compositions (Fig. 3).

The main conclusion of above given consideration is that redistribution of additives took place, even in varistors prepared from mixture of constituent phases. These processes resulted in partial change of composition in sintered samples in comparison to starting mixtures. In some compositions (Zn–all, Zn–Co) these changes were less pronounced than in others and they



a) b)

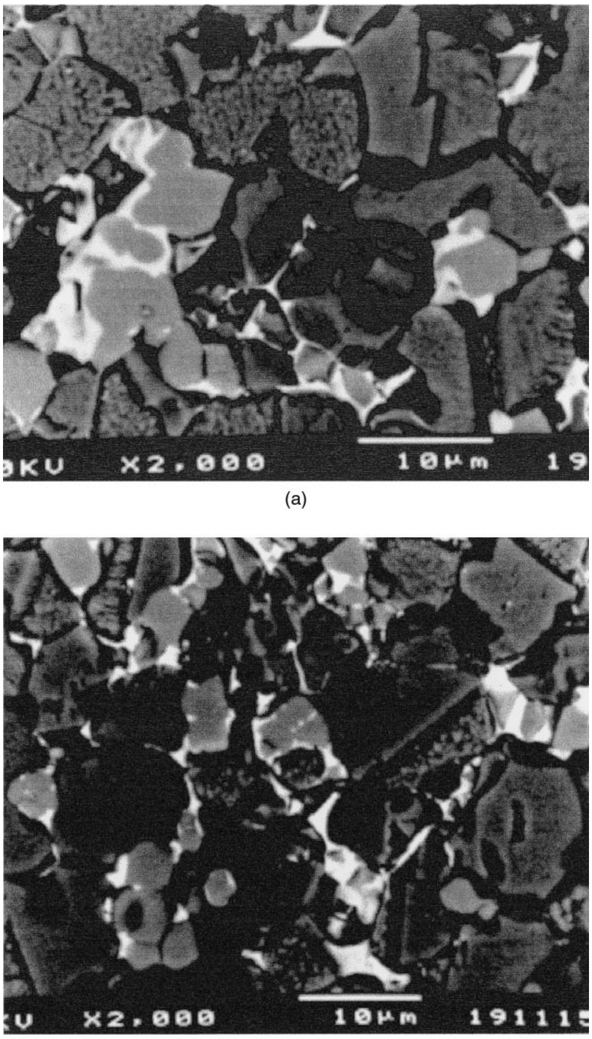
Fig. 3. EDS of intergranular γ-Bi_2O_3 phase of varistors (a) Zn–Cr, (b) Zn–Mn.

have compositions more similar to the starting ones. Redistribution of additives does not depend on number and amount of additives present in system, but on chemical composition of spinel phase and its stability during sintering. It was shown that some spinels are more stable and should be used in preparation of varistors with really controlled composition. These spinels are $Zn_{1.86}Co_{0.46}Sb_{0.67}O_4$ (Zn–Co), and $Zn_{1.971}Ni_{0.090}Co_{0.030}Cr_{0.247}Mn_{0.090}Sb_{0.545}O_4$ (Zn–all), which chemical composition did not change significantly after sintering.

Electrical parameters of obtained varistors, as well as ZnO mean grain size values are given in Table 3. Obviously, spinel composition has influence on electrical properties of varistors. There were significant differences in electrical parameters of the investigated samples: coefficients α ranging from 22 to 55, and leakage currents from 8.6 to 57 $\mu A/cm^2$. Also, investigated varistors showed great differences in ZnO grain size and values of breakdown voltage per barrier. Varistors Zn–Mn and Zn–Sb exhibit very similar values of electrical parameters, as well as of ZnO grain size. This result was expected since structural analysis showed similar compositions of the constituent phases in these varistors after sintering. Electrical properties of these varistors were poor, with low values of nonlinearity coefficients and high leakage currents.

The best varistors were Zn–Co and Zn–all. They exhibited the highest values of nonlinearity coefficients and the lowest values of leakage currents. According to structural analysis, these varistors had composition of phases more similar to starting ones. It has to be emphasized that varistors Zn–Co contain only five components and show excellent electrical properties: nonlinearity coefficients equal to 43 (α_1) and 55 (α_2), as well as leakage current of 9.0 $\mu A/cm^2$.

Co–Sb samples showed very poor electrical properties that could be consequence of inhomogeneous microstructure found in these samples. Comparison of microstructures of Co–Sb sample with other samples showed that there is significant difference in spinel grain size, shape and distribution. More irregularly shaped and larger spinel grains were found in Co–Sb samples (Fig. 4). Spinel grains are mainly present as large agglomerates, without clear, sharp boundaries. Also, lower crystallinity of Co–Sb spinel phase in comparison to other compositions was detected by X-ray diffraction analysis. This is consequence of instability of Co–Sb spinel resulting in great changes in composition. At the same time ZnO grains in Co–Sb varistors contains too much Co^{2+} ions. According to literature data [22], as the concentration of Co^{2+} is increased, the upturn region occurs at lower and lower currents, i.e. concentration of Co^{2+} strongly influences varistor properties. High Co^{2+} content also increases value of breakdown voltage, i.e. voltage per barrier, which was also observed in our samples.



(a)

(b)

Fig. 4. SEM of the varistors (a) Co–Sb, (b) Zn–Co (polished and chemically etched surfaces).

Table 3
Electrical parameters of investigated varistors

Varistor	α_1	α_2	J_L ($\mu A/cm^2$)	K_C (V/mm)	D (μm)	U_b (V)
Zn–Mn	25	24	16	489	5.9	2.9
Zn–Sb	22	23	16	428	5.5	2.4
Zn–Co	43	55	9.0	399	7.8	3.1
Zn–Cr	27	35	11	487	7.9	3.8
Co–Sb	13	19	57	478	8.9	4.3
Zn–all	28	52	8.6	420	7.5	3.2

Further electrical characterization was performed by the method of ac impedance spectroscopy. Impedance plots of investigated samples are shown in Fig. 5. Considering frequency and temperature range of measurements obtained semicircles present grain boundary regions.

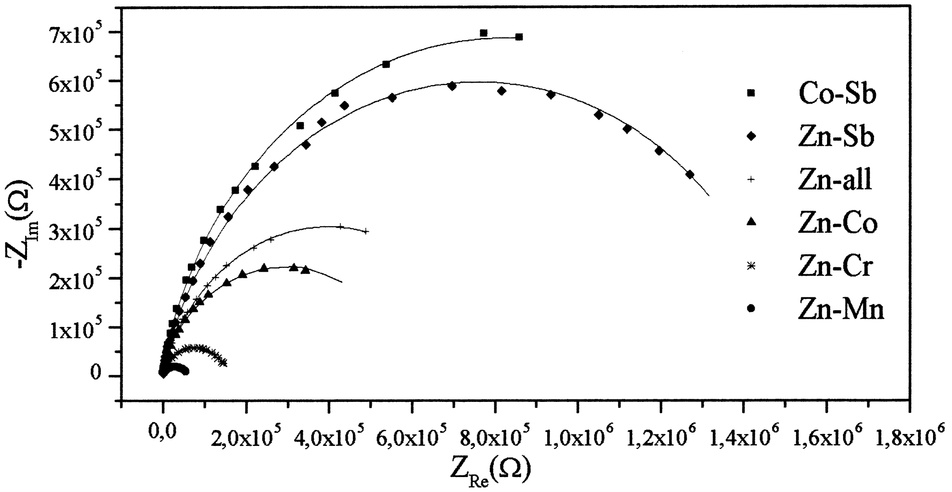


Fig. 5. Nyquist plots of investigated varistors. Measurements temperature was 190°C.

Diffusion and redistribution of additives during sintering, that were detected by X-ray diffraction and EDS analysis, results in different grain boundary properties of investigated samples. Arrhenius plots for sintered samples are shown in Fig. 6. Ln R of the samples is linear function of reciprocal temperature in chosen temperature interval. Apparent activation energies (Table 4) were calculated from the slopes of the functions:

$$\ln R = \ln A_o + \frac{E_A}{k}\cdot\frac{1}{T},$$

where R is resistance of the grain boundary region, A_o is pre-exponential constant, E_A is activation energy of conduction, k is Boltzman constant, and T is temperature.

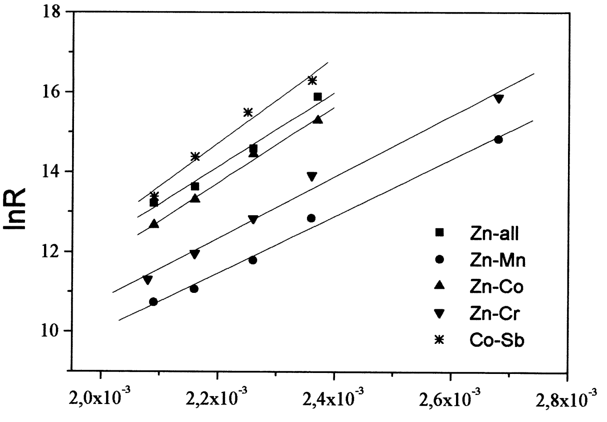


Fig. 6. Arrhenius plots of investigated varistors.

Table 4
Activation energies of investigated varistor samples

E_A (eV)				
Zn–Mn	Zn–Co	Zn–Cr	Co–Sb	Zn–all
0.61	0.83	0.73	1.0	0.81

Activation energies (E_A) of varistor samples were in the range 0.61–1.0 eV. These values are similar to values reported by other authors for similar measurements conditions [23–25]. Different values of E_A suggest non-identical defect structure of ZnO grain boundaries of investigated samples. This means that defect structure of ZnO grain boundaries was changed because of redistribution of additives. Samples Zn–all and Zn–Co, containing more chemically stable phases, i.e. phases more similar to the starting ones, showed almost identical values of E_A. Activation energy of sample Zn–Sb was not calculated, because of its unstable electrical properties resulting in unreliable fitting results. High activation energy of 1.0 eV, found in samples Co–Sb, is in accordance with already mentioned literature data that increase in Co^{2+} concentration results in higher values of breakdown voltage.

Phase constituents of ZnO varistors are classified on phases that have direct or indirect influence on electrical properties [9,10]. Phases which take part in electrical conduction, such as ZnO grains and intergranular phase, have direct influence on electrical properties. Spinel phase has no direct influence on varistor properties [9,10] because it is highly resistive phase which does not take part in electrical conduction. Most of authors believe that spinel phase act as ZnO grain growth inhibitor and on that way indirectly influence varistor properties [4,9,10,26]. Nevertheless, our investigation showed that spinel phase indirectly influence varistor properties but not only through tailoring microstructure, but also because of redistribution of additives between spinel and other phases. Diffusion and redistribution of additives changed properties of ZnO grains, as well as of grain boundaries. Bearing in mind that the compositions of ZnO and intergranular phases were the same in all varistors powder mixtures, it has to be concluded that diffusion of additives during sintering is controlled by chemical composition of spinel phase, as well as by its stability. It was shown that varistor containing phases more similar to starting ones exhibit superior electrical properties.

This investigation also confirmed advantages of DSCP method in controlling chemical composition of constituent phases in ZnO varistors. DSCP method enables systematic investigation of influence of phase composition on varistor properties.

4. Conclusion

Structural and electrical properties of ZnO varistor were investigated as a function of chemical composition of spinel phase. According to results of X-ray and EDS analysis redistribution of additives took place, even in varistors prepared from mixture of constituent phases. Redistribution of additives does not depend on number and amount of additives present in system, but on composition of spinel phase and its stability.

Electrical properties of varistors prepared by DSCP method also depend on spinel composition. It was shown that composition of spinel phase indirectly influence varistor properties but not only through tailoring microstructure, but also because of redistribution of additives between spinel and other phases. Diffusion and redistribution of additives changed properties of ZnO grains, as well as of grain boundaries. Higher values of nonlinearity coefficients and lower values of leakage currents were found in samples with compositions more similar to the starting ones. One of these composition is Zn-Co with nonlinearity coefficients 43 (α_1) and 55 (α_2) and low values of the leakage current.

Comparison of the grain boundary properties of investigated varistors was performed based on IS measurements. Activation energies of conduction were in the range 0.61–1.0 eV depending on varistor composition. Different values of E_A confirmed nonidentical defect structure of the ZnO grain boundary regions in samples containing spinels of different compositions.

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