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Electrical Properties of ZnO Varistors Prepared by Direct Mixing of Constituent Phases

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Abstract:
Varistor samples containing different amounts of constituent phases were prepared by direct mixing of constituent phases. Detailed electrical characterization was performed to explain the influence of minor phases (spinel and intergranular phases) on overall properties. Characterization included investigation of the non-linear coefficients (α), breakdown electric field (E_B), leakage currents (J_L), grain boundary barrier hight (Φ_B) and constant β from current-voltage characteristics, as well as calculation of activation energies for conduction (E_A) from ac impedance spectroscopy in the temperature interval 30-410 °C. Varistors sintered at 1100 °C for 1 h showed pronounced differences in electrical properties depending on relative molar ratios of the phases. Results were discussed in the sense of possible reduction of the content of minor phases in ZnO varistors.
Keywords: *ZnO varistors, Electrical properties, Phases, Microstructure.*

1. Introduction

ZnO varistors are ceramic composites widely used for voltage stabilization and transient surge suppression in electronic circuits and electric power systems [1, 2]. ZnO varistors are composite materials, consisting typically of three phases: ZnO, spinel and an intergranular Bi-rich phase [3-5]. Their quality, electrical properties and application depends on their microstructure, phase composition, additive distribution and homogeneity. The main feature of ZnO varistors is high nonlinearity of current-voltage characteristics. An ideal varistor should consist only of homogeneously distributed ZnO grains with highly resistive grain boundaries, without secondary phases. This means that it is possible to reduce the amount of minor phases, such as spinel and intergranular phase, with some improvements in the preparation procedure. To reach this goal it is necessary to understand the role of each phase and its influence on varistor properties.

The aim of this study was to observe electrical properties of varistors with different amounts of constituent phases, with the intention to reduce the amount of spinel and intergranular phases in varistors. For this purpose the method refered to as "direct mixing of the constituent phases" (DMCP) was applied in the preparation of varistors, because this method enables better control of relative amounts of constituent phases inside the

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ceramics [6].

2. Experimental procedure

The DMCP method enables preparation of bulk type varistors with an optimum and precisely defined composite structure.

Preparation of ZnO varistors by the DMCP method proceeded in two steps:

- synthesis of constituent phases (ZnO, γ-Bi_2O_3, and spinel),
- synthesis of varistor ceramics from powder mixtures of constituent phases.

Compositions of the starting phases were the following:

- ZnO phase: 99.8 mol% ZnO + 0.2 mol% (Co^{2+} + Mn^{2+})
- Spinel phase: $Zn_{1.971}Ni_{0.090}Co_{0.030}Cr_{0.247}Mn_{0.090}Sb_{0.545}O_4$ (Zn-all)
- Bi_2O_3 phase: $6Bi_2O_3 \cdot MnO_2$ (Bi-Mn)

Composition of the ZnO phase was 99.8 mol% ZnO + 0.2 mol% (Co^{2+} + Mn^{2+}). Details of the varistor preparation procedure using DMCP can be found elsewhere [6, 7]. The obtained phases were used for preparation of varistor mixtures with phase compositions listed in Tab. I. The starting composition (Z12) has the following composition written in mol%: 96.5 % ZnO + 1.87 % Bi_2O_3 + 0.03 % Co_3O_4 + 0.60 % MnO_2 + 0.29 % NiO + 0.89 % Sb_2O_3 + 0.40 % Cr_2O_3, that is a typical composition than enables good electrical properties [8].

Tab. I. Phase composition of varistor mixtures.

Mixture	Constituents (mass %)		
	ZnO	Spinel Zn-all	γ-Bi_2O_3
Z12	85	10	5
Z13	92.5	5	2.5
Z14	95	2.5	2.5
Z15	92.5	2.5	5

The mixtures were homogenized in an agate planetary ball mill for 2 h, pressed into pellets sized 1 mm × 8 mm and sintered in air for 1h at 1100 °C.

Microstructural characterization of ceramics was made by scanning electron microscopy (JEOL JSM-5800).

Electrical properties were registered using a dc method and the method of ac impedance spectroscopy (Gamry EIS300). The grain boundary barrier height *(Φ_B)* and constant β, which is inversly proportional to the barrier width (ω), were determined by fitting current-voltage characteristics in the pre-breakdown region assuming a Schottky-type barrier model. The nonlinearity coefficients were determined within the ranges 0.1-1 mA/cm^2 (α_1) and 1-10 mA/cm^2 (α_2), the breakdown field *(E_B)* was measured at 1 mA/cm^2 and the leakage current (J_L) was determined at the voltage of 0.8 E_B. Apparent activation energies for conduction *(E_A)* were determined using ac impedance spectroscopy in the temperature interval 30 - 410 °C and frequency interval 0.1 - 300000 Hz.

3. Results and discussion

The electrical properties of ZnO based varistors were firstly characterized by the method of ac impendance spectroscopy. As an example, Nyquist plots of sample Z14 at different temperatures are shown in Fig. 1. Temperature and frequency intervals were chosen to obtain only one semicircle that refers to the grain boundary region. The Arrhenius plots were constructed based on these measurements (Fig. 2). *Ln R* is a linear function of reciprocal temperature in the chosen temperature interval. Apparent activation energies (Tab. II.) were calculated from the slopes of the function:

$$\ln R = \ln A_0 + \frac{E_A}{kT} \quad (1)$$

where R is resistance of the grain boundary region, A_0 is the pre-exponential constant, E_A is activation energy of conduction, k is the Boltzman constant and T is the temperature.

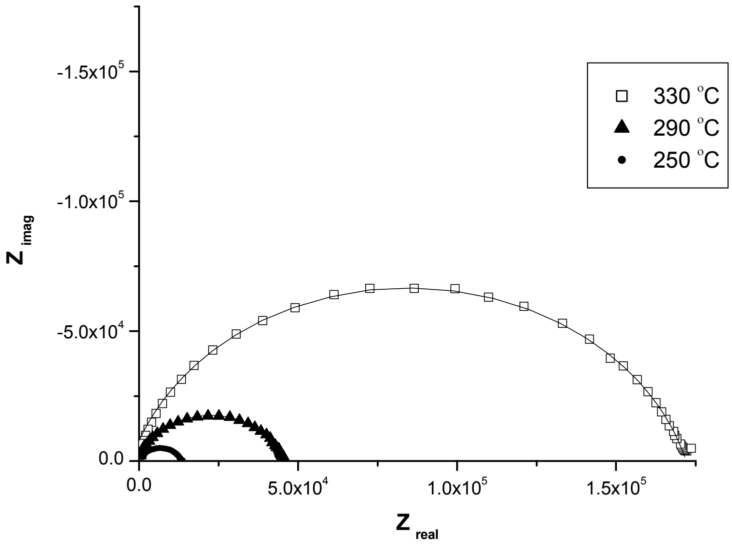


Fig. 1. Nyquist plots of the varistor Z14 measured for different temperatures.

Values of the activation energies were in the range 0.95-1.02 eV. Some dopants were introduced to grain the boundary region during sintering due to redistribution of dopants between phases, as shown in [7]. Since all samples contained the same type of dopants, i.e. the same composition of the constituent phases, but different relative amounts of phases, it could be expected that they differ only in the concentration of particular deffects, but not in their type. In accordance with this conclusion, only small differences in E_A were registered suggesting a difference in the concentration of some of defects and interface states.

Further electrical characterization was performed using current density-electric field (*J-E*) properties. *J-E* curves of the samples are shown in Fig. 3a and 3b and the corresponding electrical parameters α, J_L and E_B are summarized in Tab. II. A significant difference in electrical parameters of the investigated samples existion: coefficients α ranging from 11 - 46 and the leakage currents from 4.1 to 120.2 μA/cm^2, depending on the relative amount of constituent phases. Obviously, a reduction of the content of minor phases results in worse electrical properties. To obtain good electrical properties in these samples it is necessary to change processing parameters, first of all homogenization and sintering conditions, in order to reach homogeneous distribution of dopants and more homogeneous microstructures.

Values of E_B were relatively high in all samples and they were in the range from 4164 to 4838 V/cm, because of relatively small grains of ZnO. Values of the breakdown electric field are inversely proportional to the grain size:

$$U_B = E_B \cdot D \quad (2)$$

Obtained values of U_B are given in Tab. II. A comparison of values for E_B and D for different samples showed that E_B values did not follow the linear change of D, suggesting an inhomogeneous distribution of dopants between grain boundaries inside one sample and consequently the existence of some inactive boundaries and different current paths.

Tab. II. Characteristic parameters of investigated samples (α - nonlinearity coefficient, J_L - leakage current, E_B - breakdown electric field, D - grain size, U_B - voltage per barrier, E_A - apparent activation energy of conduction, Φ_B - grain boundary barrier height, β - constant, ρ - density, ρ_T - theoretical density).

Sample	α_1	α_2	J_L [μA/cm^2]	E_B [V/cm]	D [μm]	U_B [V]	E_a [eV]	Φ_B [eV]	1000β [eVm$^{1/2}$V$^{-1/2}$]	ρ/ρ_T [%]
Z12	39	46	4.1	4838	3.70	1.79	1.02	1.07	0.541	90
Z13	16	38	49.6	4429	3.40	1.50	0.98	0.94	0.431	89
Z14	13	32	78.9	4368	3.76	1.64	0.99	0.91	0.411	89
Z15	11	29	120.2	4164	3.10	1.29	0.95	0.91	0.399	89

The parameter U_B is calculated assuming a very idealized brick-layer model and because of that it is significantly more sensitive to microstructural imperfections, inhomogeneous distribution of dopants and existence of inactive boundaries. As a result significant changes in U_B were detected in samples of different compositions.

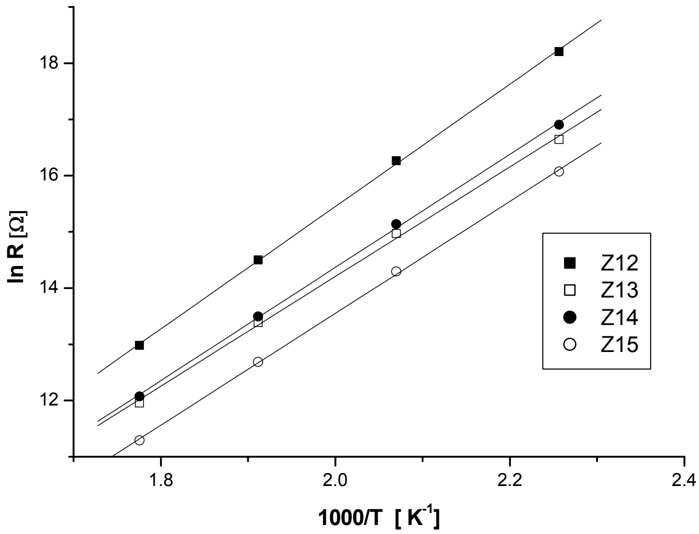


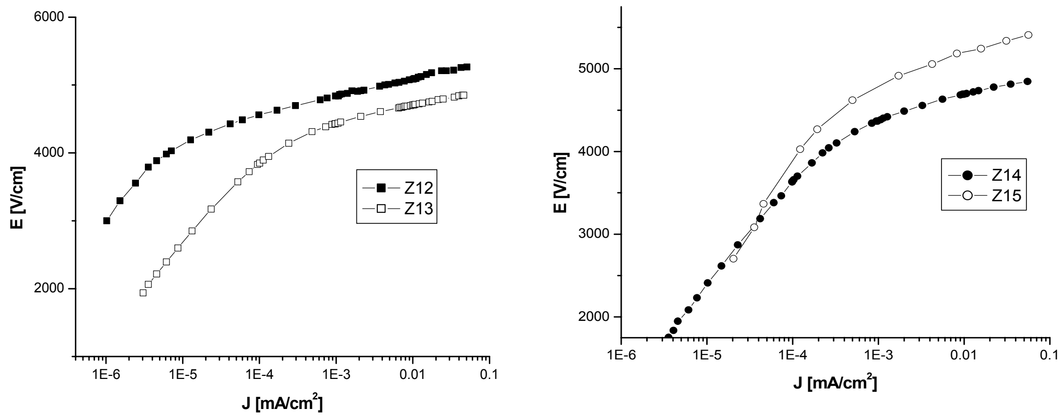
Fig. 2. Arrhenius plots of resistance vs. temperature for Z12, Z13, Z14 and Z15 varistors.

Usually, a Schottky-type barrier model is used to explain the nonlinear electrical behavior of varistors. The relevant equation is:

$$J_S = A^* T^2 \exp\left[-\left(\Phi_B - \beta\sqrt{E}\right)kT\right] \quad (3)$$

where J_S is the current density, A^* is the Richardson constant, T is the temperature and E is the electric field.

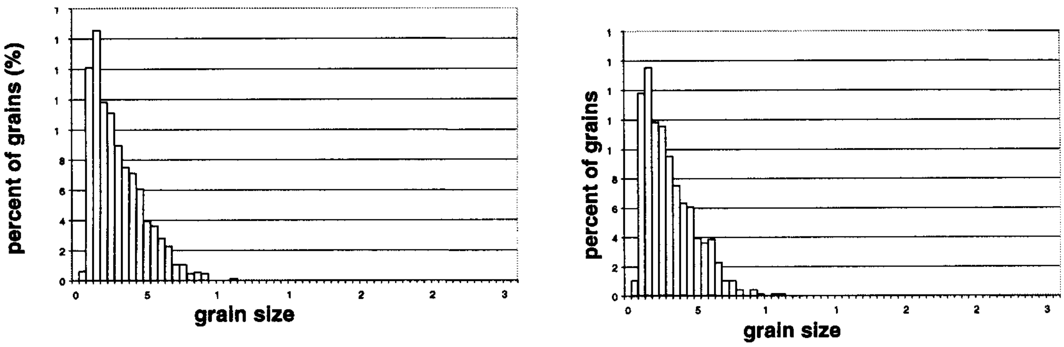
Parameters β and Φ_B were obtained by fitting eq. 3 (Tab. II). It could be seen that the barrier height increses with increase of the amount of spinel. It is well known that the main role of the spinel phase is control of ZnO grain growth. Also, according to some authors [9, 10] spinel has no *direct* influence on electrical properties, but according to Brankovic et al. [7] spinel *indirectly* influences electrical properties due to redistribution of dopants during sintering. For example, Cr^{3+} and Sb^{3+} diffuse from spinel to grain boundaries. As a consequence the grain boundary barrier height increases with increasing amount of spinel.



a) b)

Fig. 3a. Current density vs.electric field (J-E) curves for varistors Z12 ,Z13. (a) and Z14, Z15 (b)

The Z12 varistor has the best electric properties, with the highest values of nonlinearity coefficients and grain boundary barrier height, as well as with the lowest values of leakage current. On the other hand, sample Z15 showed very poor electrical properties. The Z12 varistor has same amount of γ-Bi_2O_3 as Z15 and a four times higher amount of spinel.



a) b)

Fig. 4. Particle size distribution of samples Z12 (a) and Z15 (b).

Both samples have almost the same densities and a similar particle size distribution (Fig. 4), which leads to the conclusion that the amount of spinel in Z15 is sufficient for grain growth control, but not for uniform doping of grain boundary regions through redistribution during sintering. Z14 and Z15 varistors also had the same amount of spinel but sample Z15 contained a two times higher amount of intergranular Bi_2O_3-based phase. Both samples had the same values of Φ_B, but Z14 had slightly higher values of nonlinearity coefficients and the breakdown field. Obviously, the relative molar ratio of spinel and intergranular phase is a very important parameter and a large amount of intergranular phase in comparison to spinel results in worse electrical properties. This is in accordance with the results of other authors who found that an optimal range of Bi_2O_3 concentrations in varistors exists [11].

4. Conclusions

Detailed characterization of varistors containing different amounts of constituent phases confirmed the significance of minor phases and their influence on electrical properties. Analysis of results of measurements performed showed that spinel influences electrical properties through redistribution of dopants during sintering. Redistribution of dopants could change the defect concentration at grain boundaries. This results in different values of barrier height and width, as well as in different voltages per barrier. Changes in dc electrical properties, such as nonlinearity coefficients and leakage currents were more pronounced, indicating an inhomogeneous distribution of dopants and the existence of inactive grain boundaries in varistors with a lower content of spinel. It was also found that the relative molar ratio of spinel and intergranular phases is a very important parameter and that a large amount of intergranular phase in comparison to spinel results in worse electrical properties.

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Садржај: *Методом дириговане синтезе конститутивних фаза припремљени су варисторски узорци са различитим количинама конститутивних фаза. Извршена је детаљна електрична карактеризација са циљем да се објасни утицај секундарних фаза (спинелске и интергрануларне фазе) на карактеристике варистора. Карактеризација* *је обухватила одређивање коефицијената нелинеарности (α), поља пробоја (E_B), струја ширења (J_L), висине потенцијалне баријере на граници зрна (Φ_B) и константе β из струјно-напонске карактеристике, као и израчунавање енергија активације провођења (E_A) из ас импендансне спектроскопије у температурном интервалу 30-410^{0}C. Варистори синтеровани на 1100^{0}C током 1 h показали су значајну разлику у електричним својствима у зависности од релативног молског односа фаза. Резултати су разматрани с тачке гледишта могуће редукције садржаја секундарних фаза у ZnO варисторима.*

Кључне речи: *ZnO варистори, електрична својства, фазе, микроструктура.*