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ZnO varistors with reduced amount of additives prepared by direct mixing of constituent phases

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Abstract

The aim of this work was to reduce number of additives using new method of preparation, refered as "direct mixing of the constituent phases". The method is based on sintering of a mixture of constituent phases with the following compositions: ZnO phase uniformly doped with 0.1 mol% Mn^{2+} and 0.1 mol% Co^{2+}, γ-Bi_2O_3 stabilized with Mn^{2+} and spinel phase of composition $Zn_{1.86}Co_{0.46}Sb_{0.67}O_4$ or $Zn_{1.971}Ni_{0.090}Co_{0.030}Cr_{0.247}Mn_{0.090}Sb_{0.545}O_4$. The varistors sintered at 1030 °C showed good electrical properties, with nonlinearity coefficient reaching 50 and low values of leakage current. To improve microstructure some powder mixtures were intensively milled and further processed on the same way as unmilled powder mixtures. Electrical and microstructural properties of milled and unmilled samples were compared.
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1. Introduction

Semiconducting ceramics based on zinc-oxide are widely used for voltage stabilization and transient surge suppression in electric power systems and electronic circuits.[1,2] These ceramics devices, named varistors, exhibit high nonlinearity of current–voltage characteristics. The quality, electrical properties and application depend on their microstructure, phase composition, additives distribution and homogeneity.

There are many different methods for varistor fabrication, but there are still dilemmas and disagreements about role of additives and secondary phases, their influence on electrical properties and necessity of their presence. Ideal varistor should consist only of homogenously distributed ZnO grains with highly resistive grain boundaries and without secondary phases.[3] Unfortunately, we cannot reach this ideal with current knowledge about ZnO varistors production. One of the main reasons for that is conventional treatment from the mixture of ZnO and additives, where reaction sintering takes place making difficult supervision of composition of phases.

The main goal of this study was to reduce number of additives using new method of preparation, refered as "direct mixing of the constituent phases" (DMCP), solely or in combination with intensive milling. Milling should make this reduction easier because it enables better contact between ZnO, as well as formation of inversion boundaries, which improves microstructure and electrical properties of varistors.[4]

2. Experimental procedure

DMCP method enables preparation of the bulk type varistors with precisely defined composite structure. This method is based on the fact that ZnO varistors are composite materials, consisting typically of three phases: ZnO, spinel, and intergranular Bi-rich phase.[5–7] Each phase could be prepared separately and the final varistor could be formed by sintering the mixture of constituent phases. Details about the method can be find elsewhere.[8,9]

Composition of the starting phases were the following:

- ZnO phase: 99.8 mol% ZnO + 0.2 mol% (Co^{2+} + Mn^{2+});
- Spinel phases: $Zn_{1.971}Ni_{0.090}Co_{0.030}Cr_{0.247}Mn_{0.090}Sb_{0.545}O_4$ (Zn-all) and $Zn_{1.86}Co_{0.46}Sb_{0.67}O_4$ (Zn–Co);
- Bi_2O_3 phase: $6Bi_2O_3 \cdot MnO_2$.

ZnO phase was prepared by suspending ZnO in an aqueous solution of $Mn(CH_3COO)_2$ and $Co(NO_3)_2$, followed by evaporation of suspension, calcinations and milling of the powder.

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Table 1
Phase composition of varistor mixtures

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

Table 2
Electrical characteristics of investigated varistors

Sample	α_1	α_2	K_C (V/cm)	J_L (μA/cm^2)	ρ/ρ_T (%)
Z12	39	46	4838	4.1	90
ZnCo	31	46	3573	10.5	88
Z13	16	38	4429	49.6	89
Z14	13	32	4368	78.9	89
Z15	11	29	4164	120.2	89
Z12-m[a]	60	53	8238	2.3	91
ZnCo-m	49	60	6675	4.7	93
Z13-m	40	50	5271	5.6	98
Z14-m	36	44	5065	7.7	95
Z15-m	25	35	4256	20.3	97

[a] m—marks intensively milled powder.

Bi_2O_3 phase was prepared by solid state reactions of appropriate amounts of oxides. Among possible additives for γ-Bi_2O_3 stabilization, MnO_2 was chosen for this study, because it is common component of ZnO varistors and already exists in ZnO phase. The mixture was homogenized by dry milling in an agate mortar and heated at 800 °C for 3 h in a platinum crucible to obtain the single γ-Bi_2O_3 phase.

Spinel phases were prepared by solid state reaction. Conditions of thermal treatment were 1150 °C/8 h for Zn–Co and 1100 °C/1 h for Zn-all. The compositions were chosen based on previously performed optimization of spinel phase composition.[10]

The obtained phases were used for preparation of varistor mixtures with phase compositions listed in Table 1.

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 1 h at 1030 °C. This temperature was slightly lower than the commonly used temperatures in varistor preparation,[11] but allows easier distinguishing between "good" and "bad" varistors. In the further discussion samples prepared on this way will be called "unmilled".

With intention to improve powder and consequently varistor characteristics all powder mixtures were intensively milled for 2 h and further processed on the same way as unmilled powder mixtures. Milling was carried out in the agate planetary ball mill with agate balls 20 mm in diameter and w_b/w_p was 20:1.

The characterization of initial powders and the resulting ceramics was made by X-ray powder diffraction (Philips PW 1710 powder diffractometer with graphite-monochromatized Cu Kα radiation), scanning electron microscopy (JEOL JSM-5800 equipped with EDS detector and Oxford Instruments Link Isis 300 analytical system).

Electrical properties were registered within the 0.1–10 mA/cm^2 using a dc method. 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 (K_C) was measured at 1 mA/cm^2, and the leakage current (J_L) was determined at the voltage of 0.8K_C.

3. Results and discussion

The investigation was parallely conducted in two directions. To reduce overall amount of additives by reduction of number of additives in spinel phase or by reduction of amount of secondary (Bi_2O_3-rich and spinel) phases in comparison to starting composition. 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 typical composition of varistors with good electrical properties.[9]

The main difference between DMCP and conventional method of synthesis is that during sintering of varistor samples prepared by former method reactive sintering does not take place. All constituent phases were formed before sintering which means that only densification and grain growth occurred during sintering. The X-ray diffraction analysis of sintered samples showed the existence of the same phases as those introduced into the varistor powder mixtures: ZnO, spinel and γ-Bi_2O_3.

The electrical properties of ZnO based varistors were characterized by their current density–electric field (*J–E*) properties. The *J–E* curves for the samples are shown in Fig. 1 and the corresponding electrical parameters are summarized in Table 2.

Sample ZnCo has a spinel phase with reduced number of additives in comparison to Z12. There was not significant difference between nonlinearity coefficients of these samples, but ZnCo has lower breakdown filed and higher leakage current J_L. On the other hand, intensively milled Z12-m and ZnCo-m has significantly higher α_1 and α_2, higher breakdown field K_C and lower J_L in comparison to corresponding "unmilled" samples (Fig. 1b and Table 2). Although the results are encouraging, it is necessary to perform additional optimization of processing parameters to reduce leakage current of varistor ZnCo. The properties of ZnCo are worse in comparison to Z12, but it has to be emphasized that ZnCo composition contains only five different oxides.

Results of electrical characterization showed that decrease of spinel and γ-Bi_2O_3 contents caused a serious damage of varistor characteristics; nonlinearity coefficients α_1 and α_2 of "unmilled" samples became lower and J_L higher (Table 2). Reduction of amount of secondary phases is not possible only by DMCP method of processing and some new technologies should be included.

Comparing, for example, "unmilled" Z12 and intensively milled varistor Z13-m, contents of spinel and Bi_2O_3 phase in Z13-m were two times lower, but α_1 and α_2 of Z13-m were higher and J_L has similar value. Same was concluded for samples Z13 and Z14-m and for samples Z14 and Z15-m, where even significantly lower values of J_L were obtained in samples

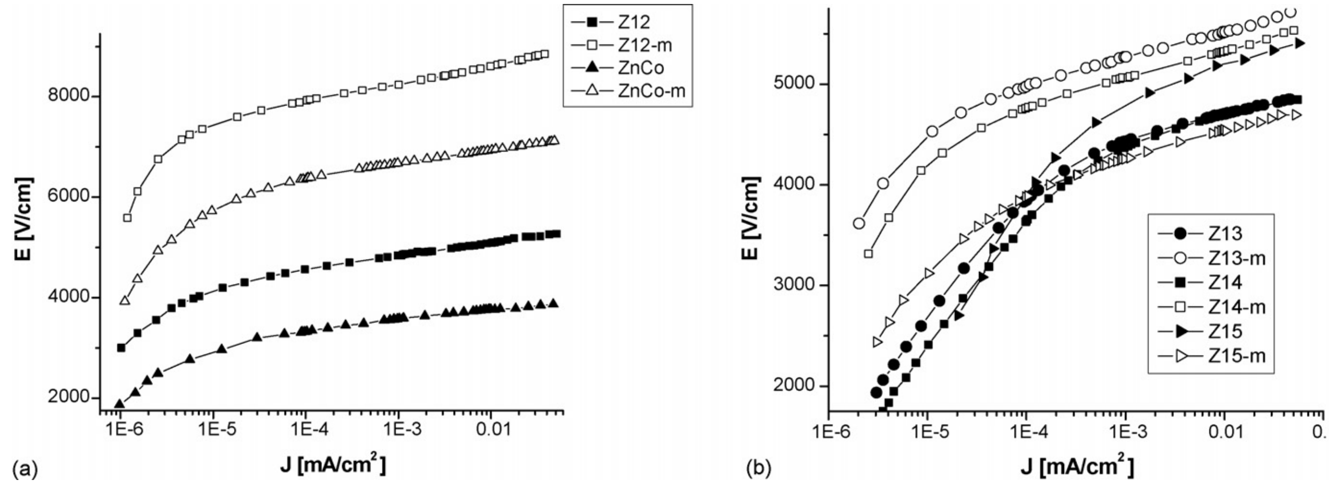

Fig. 1. (a) The current density/electric field (*J*–*E*) curves for "unmilled" and intensively milled varistors Z12 and ZnCo. (b) The current density/electric field (*J*–*E*) curves for "unmilled" and intensively milled varistors Z13, Z14 and Z15.

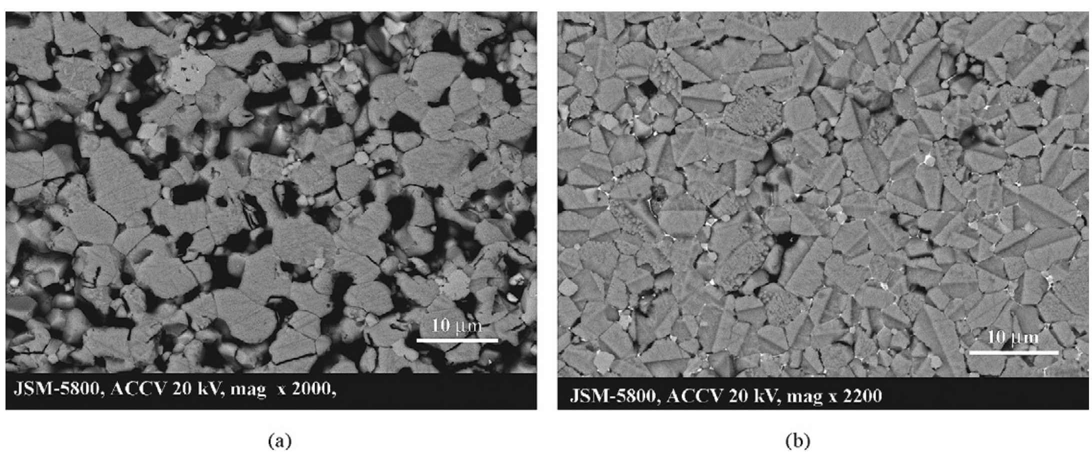

Fig. 2. SEM of the polished and chemically etched surfaces of the sintered varistor samples: "unmilled" sample Z14 (a) and intensively milled sample Z14-m (b).

with reduced content of spinel and/or Bi_2O_3 phase if they were intensively milled before sintering.

Also, there was observed an important change in microstructural characteristics of intensively milled samples compared to the "unmilled" one (Table 2). The main difference is that the intensively milled samples have higher sintering densities (reaching 98% of theoretical value in composition Z13-m). For example, sample Z12 has the highest density of all unmilled samples, only 91% of theoretical density. Varistor samples obtained from intensively milled powders have a remarkably

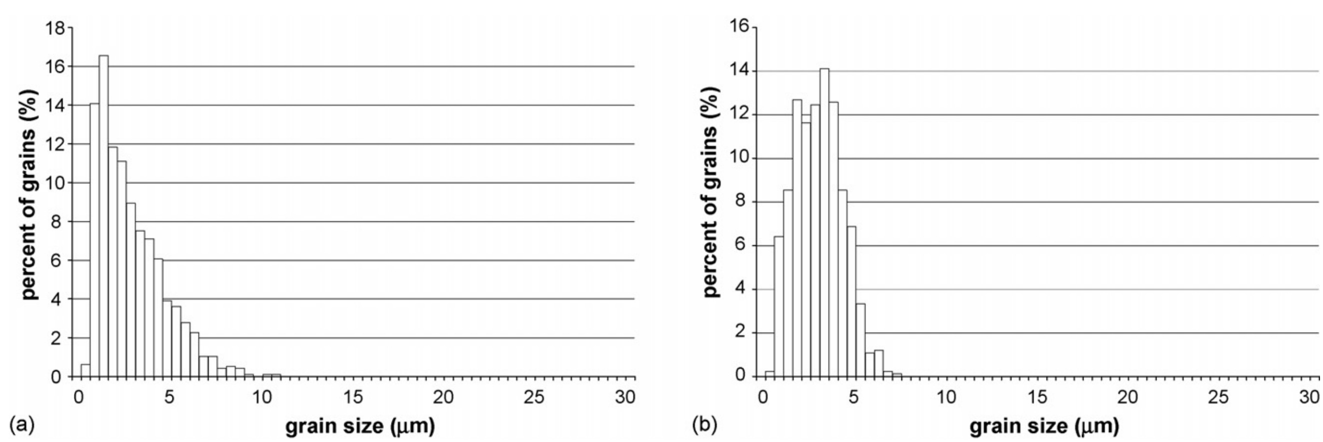

Fig. 3. Particle size distribution of samples Z14 (a) and Z14-m (b).

more homogeneous and more dense microstructure in comparison to the "unmilled" samples (Fig. 2). It could be expected that these varistors exhibit improved stability because of increased density and homogeneity. The percent of inversion boundaries (IBs) is extremely increased in milled samples. This is important, because the inversion boundaries influence the electrical properties of varistor ceramics and tailor the growth of ZnO grains via IB-induced grain-growth mechanism.[4] The particle size distribution of intensively milled varistors was narrower than "unmilled" (Fig. 3), indicating better homogeneity, which was very important for uniform conduction. Our investigation confirmed that intensive milling can produce highly activated powders for sintering. As a consequence the sintering temperature of milled samples is generally lower in comparison to conventionally processed one. The comparison of these results with results of characterization of samples prepared from intensively milled powders that were simple mixture of oxides[12] showed that combination of intensive milling and DMCP method give much better results, especially from the microstructural aspect. The focus of our further investigations should be preparation of improved varistors by optimizing sintering conditions.

4. Conclusions

Five different varistor mixtures were prepared by DMCP method or by DMCP in combination with intensive milling. Investigated varistors mostly showed good electrical properties, nonlinearity reaching 50 and low values of the leakage current.

Varistors with reduced number of additives in spinel phase exhibited partially worse electrical properties in comparision to starting composition. Nonlinearity coefficients were similar, but leakage currents were slightly increased. Bearing in mind significant reduction of number of additives in ZnCo varistor, this is good result. Some additional investigation can be performed to reduce leakage current.

It was shown that significant reduction of amount of secondary phases also is not possible only by application of DMCP method; α_1 and α_2 were lower and values of J_L were significantly higher. Intensive milling facilitates this reduction, because it improves contact between ZnO grains and significantly increase density and homogeneity of the varistors. Intensively milled varistors showed better microstructure and electrical properties in comparison to varistors with higher content of secondary phases prepared only by DMCP method.

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