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ZnO varistors from intensively milled powders

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Abstract

Two ways of application of intensive milling in ZnO varistors processing were compared. First was intensive milling of mixture of previously prepared constituent phases. In this case, intensive milling was applied only to obtain highly activated nanocrystalline varistor powder mixtures. Second application is intensive milling of simple mixture of oxides that could result not only in activation and formation of nanocrystalline powders, but also in mechanochemical reaction and synthesis of constituent phases. Powders and ceramics samples were characterized by XRD and SEM analysis, as well as by dc electrical measurements (nonlinearity coefficients, leakage current and breakdown field). Differences in microstructural and electrical properties of obtained varistors were discussed and optimal milling and processing conditions were recommended. The best electrical characteristics were found in sample Z1-DMCP-m, which exhibited leakage current of 2.5 μA/cm^2, nonlinear coefficient reaching 58 and breakdown field of 8950 V/cm.

Keywords: ZnO; Varistors; Milling; Grain boundaries; Electrical properties

1. Introduction

ZnO varistors are composite materials, consisting typically of three phases: ZnO, spinel and intergranular Bi-rich phase.[1–3] Conventional method of mixing of oxides is common method of preparation of commercial ZnO varistors. Reactive sintering and appropriate thermal treatment provide desirable microstructure and electrical properties. This method makes difficult supervision of composition and amount of phases in ZnO varistors. Therefore, in recent years more attention has been addicted to new methods of preparation, which enable precise control of microstructure. One of these methods is method referred as direct mixing of constituent phases (DMCP).[4,5] Method is based on sintering of mixture of previously prepared constituent phases, whereby process of reaction sintering does not take place. The result is the same phase composition of varistors as in the powder mixture.

Intensive milling of varistor powder can improve ZnO varistor characteristics, providing the narrow grain size distribution, homogenous distribution of phases and high sintering activity of the powders.[5,6] The aim of this work was investigation of influence of intensive milling on electrical and microstructural properties of varistors obtained by conventional method from simple mixture of oxides and by DMCP. Also, a comparison of samples obtained by DMCP and conventional method was performed for the first time on the samples processed under the same conditions of milling and sintering.

2. Experimental procedure

Two powder mixtures, marked as Z1 and Z2, were prepared by both methods—DMCP and mixture of oxides, therefore four varistor powder mixtures were obtained.

Two powder samples, marked as Z1-DMCP and Z2-DMCP, were prepared using DMCP and their compositions (in wt.%) were the following:

$$\text{Z1}: 85\%\,\text{ZnO} + 10\%\,\text{spinel} + 5\%\,\gamma\text{-}Bi_2O_3,$$

$$\text{Z2}: 92.5\%\,\text{ZnO} + 5\%\,\text{spinel} + 2.5\%\,\gamma\text{-}Bi_2O_3.$$

Compositions of constituent phases were:

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

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Based on compositions of constituent phases of samples used for preparation of varistors by DMCP, masses of oxides for synthesis of samples Z1-MO and Z2-MO, obtained by simple mixing of oxides, were calculated (in g) and measured:

$$\text{Z1–MO}: 4.5410\,\text{ZnO} + 0.0218\,\text{MnO}_2 + 0.1442\,\text{Sb}_2\text{O}_3 + 0.0340\,\text{Cr}_2\text{O}_3 + 0.0044\,\text{Co}_3\text{O}_4 + 0.0122\,\text{NiO} + 0.2422\,\text{Bi}_2\text{O}_3$$

$$\text{Z2-MO}: 4.7705\,\text{ZnO} + 0.0109\,\text{MnO}_2 + 0.0721\,\text{Sb}_2\text{O}_3 + 0.0170\,\text{Cr}_2\text{O}_3 + 0.0022\,\text{Co}_3\text{O}_4 + 0.0061\,\text{NiO} + 0.1211\,\text{Bi}_2\text{O}_3$$

Here MO marks conventional method from the simple mixture of oxides. Details of preparation of phases can be found in our previous article.[5]

Two groups of ceramics samples were prepared: "unmilled" and "milled". "Unmilled" varistors were obtained by homogenization of all four mixtures in an agate planetary ball mill with agate balls 20 mm in diameter under the following conditions: w_b/w_p was 7:1, time of homogenization was 2 h and the disc rotation speed was 70 2π rad/s. These mixtures were not subjected to intensive high-energy ball milling before sintering. On the other hand, "milled" varistors were prepared by intensive milling 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, w_b/w_p was 20:1, and disc rotation speed was 360 2π rad/s. Powders were pressed into pellets sized 1 mm × 8 mm and sintered in air for 1 h at 1200 °C (heating rate was 10° min^{-1}, cooling rate was 5° min^{-1}).

The characterization of powders and ceramics was made by scanning electron microscopy (JEOL JSM-5800 equipped with EDS detector and Oxford Instruments Link Isis 300 analytical system), density measurements (Archimedes method) and X-ray powder diffraction. Rietveld refinements were performed with the program General Structure Analysis System (GSAS).[7] The peak profile function was modeled using a convolution of the Thompson-Cox-Hastings pseudo-Voigt (pV-TCH)[8] with the asymmetry function described by Finger et al.,[9] which accounts for the asymmetry due to axial divergence.

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 (E_b) was measured at 1 mA/cm^2, and the leakage current (J_L) was determined at the voltage of 0.8 K_C.

3. Results and discussion

In this work properties of intensively milled varistors prepared by DMCP method and by simple mixing of oxides were compared. Mixtures Z1-DMCP and Z2-DMCP were chosen because they exhibited good electrical characteristics in our previous investigations.

Table 1
Microstrain (ε) (%) and crystallite size $\langle t \rangle$ (nm) for the investigated varistor powders

Samples	ε_{100}	ε_{110}	ε_{111}	$\langle t_{//} \rangle$ (nm)	$\langle t_{\perp} \rangle$ (nm)	τ
Z2-DMCP-m	1.728	0.576	0.758	81	58	1.40
Z2-MO-m	2.14	0.713	0.879	72	76	0.95
Z1-DMCP-m	1.69	0.563	0.756	70	51	1.37
Z1-MO-m	2.325	0.775	0.881	39	56	0.69
Z1-MO	0	0	0.013	233	216	1.08

Crystallite shape anisotropy τ, defined here as $\tau = \langle t_{//} \rangle / \langle t_{\perp} \rangle$.

As it was expected, XRD analysis of intensively milled powders prepared by DMCP showed the presence of the same phases as existed in starting mixtures. Although intensive milling of varistor powders obtained by mixing of oxides was applied with intention to achieve mechanochemical synthesis of constituent phases along with activation and formation of nanocrystalline powders, XRD results of Z1-MO and Z2-MO powders did not show formation of new phases. According to our earlier investigation of possibility of mechanochemical synthesis of γ-Bi_2O_3 and spinel, γ-Bi_2O_3 could be easily formed under this milling conditions.[10] On the other hand, it is difficult to obtain pure zinc antimony spinel phase by mechanochemical synthesis, but it will be formed in some amount. The possible explanation of absence of γ-Bi_2O_3 and spinel peaks in XRD pattern could be small amount of formed phases, but also the possible amorphization of these phases during high-energy ball milling.

To compare powder properties of all samples, Rietveld refinement was performed and crystallite size and microstrains were calculated (Table 1). Besides obvious reduction in crystallite size and increase in microstrains, intensive milling also had influence on crystal shape. The crystal shape anisotropy is more pronounced in samples prepared by DMCP and also in samples with higher amount of dopants. Change in crystallite size and shape, as well as increase in microstrains, have significant influence on sintering and microstructure of the final ceramics, as it will be discussed later.

Electrical properties of ZnO varistors were determined from U-I characteristics (Fig. 1), which were obtained using dc method. In Fig. 1 only results for Z1 samples were shown

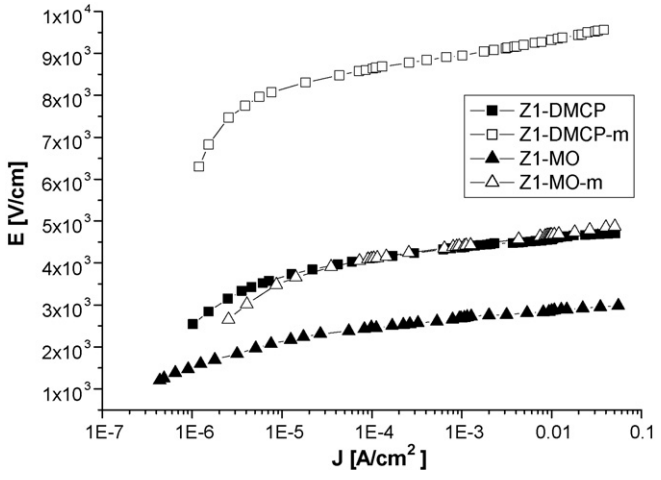

Fig. 1. U-I characteristics of the sample Z1, prepared by different methods.

because of limited space, but similar curves were obtained for Z2. Electrical parameters were summarized in Table 1. It can be seen that samples Z1-DMCP and Z2-DMCP comparing to Z1-MO and Z2-MO have higher values of α_1 and α_2, higher values of E_b and lower J_L. The same was concluded comparing varistors Z1-DMCP-m and Z2-DMCP-m with varistors Z1-MO-m and Z2-MO-m. Also, in comparison to "unmilled" varistors, "milled" samples had higher values of α_1 and α_2, higher values of E_b and lower values of J_L.

Samples Z1 and Z2 are of the same composition as the samples Z70 and Z85 from our earlier investigation,[5] but Z1 and Z2 showed better electrical properties due to additionally optimized processing, especially sintering conditions and samples packing. Optimization of all important processing parameters, performed during several investigations, resulted in excellent electrical properties of intensively milled samples Z1 prepared by DMCP.

Differences in electrical properties could be explained by analyzing grain size distribution (GSD) and average grain size (AGS) of all varistors. GSD of "milled" samples were narrower, and also AGS were smaller, in comparison to "unmilled" varistors. For example, Z1-DMCP has AGS $d = 5.92\,\mu m$ and Z1-DMCP-m has AGS $d = 2.99\,\mu m$. Also, AGS of "unmilled" samples obtained by DMCP were smaller comparing to AGS of "unmilled" samples obtained by mixing of oxides. For example, sample Z2-DMCP has AGS $d = 6.24\,\mu m$ and Z2-MO has $d = 6.42\,\mu m$. Narrower GSD indicates the more uniform and the more homogeneous microstructure, which has influence on the uniform conducting and increasing number of active grain boundaries. The consequence is decrease of leakage current and increase of the nonlinearity coefficients and breakdown field. Varistor samples obtained from intensively milled powders have a remarkably more homogeneous and denser 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.

Great difference in microstructures of "milled" and "unmilled" samples (Fig. 2) was already expected due to great difference in powder properties (Table 1). Crystallite shape anisotropy observed in intensively milled powders resulted in grain size anisotrpy in sintered samples. Also, more activated intensively milled powders provided higher densities in sintered samples. From Table 2 and from Fig. 2a and b it could be concluded that the densities of samples Z2-DMCP-m and Z2-MO-m were slightly different. However, it was observed that sample Z2-MO-m contained pyrochlore phase, which could be the explanation for its worse electrical characteristics comparing to Z2-DMCP-m. Same was concluded by observing the microstructure of samples Z1-DMCP-m and Z1-MO-m.

The obvious difference in microstructure of the "milled" and "unmilled" varistors was extremely increased percent of inver-

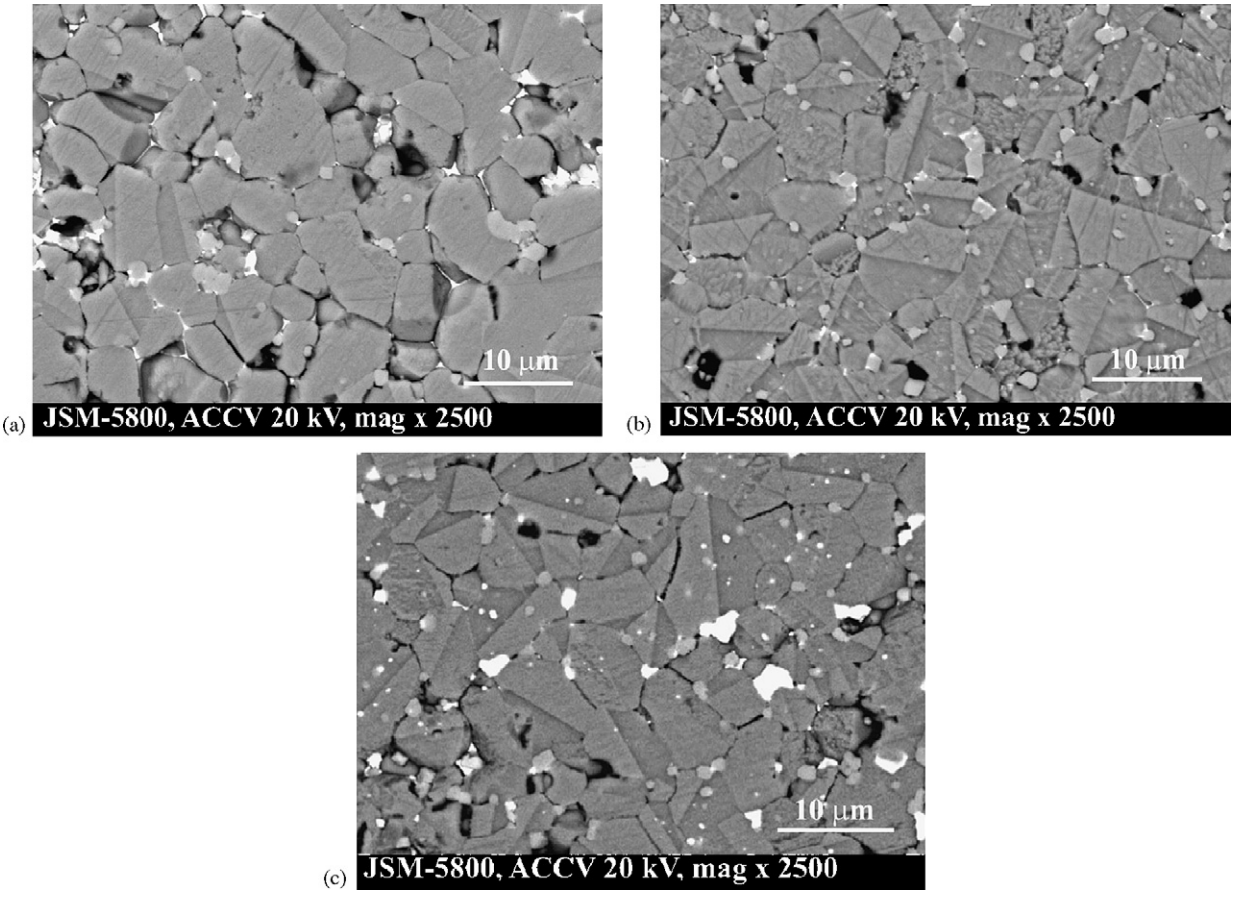

Fig. 2. SEM of the polished and chemically etched surfaces of the sintered varistor samples: (a) "unmilled" sample Z2-DMCP, (b) intensively milled sample Z2-DMCP-m, (c) intensively milled sample Z2-MO-m.

Table 2
Electrical characteristics of investigated varistors

Mixture	ρ/ρ_T (%)	d (μm)	α_1	α_2	J_L (μA/cm^2)	E_b (V/cm)
Z1-DMCP	95	5.92	44	50	4.5	4370
Z2-DMCP	93	6.24	26	43	17.9	4969
Z1-MO	92	6.30	27	41	19.2	2677
Z2-MO	90	6.42	21	37	30.7	2343
Z1-DMCP-m	98	2.99	58	53	2.5	8950
Z2-DMCP-m	96	4.09	41	51	6.4	6270
Z1-MO-m	94	3.51	36	46	12.4	4408
Z2-MO-m	94	3.83	29	40	22.0	3730

sion boundaries (IBs) in "milled" samples. Milling of initial powders results in several effects: (1) it increases the availability of Sb_2O_3 from the spinel phase for the formation of IBs and also improves homogeneity of its distribution, (2) increases the number of defects in the ZnO grains which also contribute to enhancement of IBs nucleation in the ZnO.[11] This is important, because presence of inversion boundaries have influence on the electrical properties of varistor ceramics and tailors the growth of ZnO grains via IB-induced grain-growth mechanism.[12] There was no significant difference in number of IBs between samples Z2-DMCP-m and Z2-MO-m (Fig. 2b and c), which could be explained by the same amount of Sb_2O_3 in their mixtures and the same conditions of milling of powders. Same was concluded for the samples Z1-DMCP-m and Z1-MO-m. Sb_2O_3 is the dopant that triggers the formation of IBs in ZnO grains which strongly influences their grain growth. Although its amount was higher in the samples obtained by mixing of oxides comparing to DMCP samples, where it was bonded in the spinel, the same number of IBs was found in the both types of the samples. It could be supposed that during the milling of DMCP samples sufficient amount of Sb_2O_3 for IBs forming was extracted from spinel, but it is more likely that milling increases the number of defects in the ZnO grains which contribute to enhancement of IBs nucleation in the ZnO. Further, IBs have great influence on the grain size and final microstructure.

It is very important to underline that the observed features of the investigated varistors were valid for the both compositions, Z1 and Z2, although the mixture Z2 had two times less amount of the spinel and Bi_2O_3 phase. The presence of the same effects, regardless their different compositions, provides the direct observation of the milling effects and its separation from the effect of dopants amounts.

4. Conclusions

It was found that varistors obtained from the powders subjected to intensive milling before sintering showed significantly better electrical properties in comparison to unmilled samples: lower values of leakage current, higher breakdown fields and higher values of nonlinear coefficients α_1 and α_2. Microstructures of the "milled" varistors were more homogeneous with narrow grain size distribution, lower values of the average grain size and high percentage of inversion grain boundaries.

The "milled" samples obtained from the mixture of oxides, unlike "milled" samples obtained by DMCP, contained small amount of pyrochlore, which partially explained their worse electrical characteristics.

The best electrical characteristics were found in sample Z1-DMCP-m, which exhibited J_L of 2.5 μA/cm^2, α reaching 58 and E_b of 8950 V/cm.

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