

ZnO Varistors Prepared by Direct Mixing of Constituent Phases

Zorica Branković¹, Olivera Milošević¹, Dejan Poletić², Ljiljana Karanović³ and Dragan Uskoković¹

¹*Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez-Mihailova 35/IV, 11000 Belgrade, Yugoslavia*

²*Department of General and Inorganic Chemistry, Faculty of Technology and Metallurgy, University of Belgrade, P.O. Box 494, 11001 Belgrade, Yugoslavia*

³*Laboratory of Crystallography, Faculty of Mining and Geology, University of Belgrade, Djušina 7, 11000 Belgrade, Yugoslavia*

ZnO varistors with non-linearity coefficients reaching 50 and low values of the leakage current (~ 0.01 A/m²), were obtained by a method referred to as "direct mixing of constituent phases". The method is based on sintering of a mixture of the constituent phases with the following compositions: ZnO phase uniformly doped with Co²⁺ and Mn²⁺; intergranular phase: γ -Bi₂O₃ stabilized with Mn²⁺ or Zn²⁺; spinel phase: Zn_{1.971}Ni_{0.090}Co_{0.030}Cr_{0.247}Mn_{0.090}Sb_{0.545}O₄. As proved, the obtained varistors are composed of the same phases as those introduced into the system. The influence of composition as well as milling and sintering parameters on the varistor characteristics were investigated. Some varistor powder mixtures were intensively milled before sintering. As a result, high density ceramics with highly homogeneous microstructure were obtained after sintering.

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1. Introduction

ZnO varistors are ceramic devices widely used for voltage stabilization and transient surge suppression in electric power systems and electronic circuits.^{1,2)} Main feature of the ZnO varistors is a high nonlinearity of the current-voltage characteristics. Electrical properties, quality, and application of ZnO varistors are directly related to their microstructure, phase composition, additives distribution and homogeneity.

A conventional and the most frequently used method for varistor fabrication is sintering of ZnO powder with small amount of additives such as oxides of bismuth, antimony, cobalt, manganese, nickel, chromium, aluminum, and some other metals. In three decades long history of ZnO varistors a great number of new methods for their preparation have been reported. According to varistor structure and principle of forming nonlinear effects, all these methods could be classified into three groups: surface type, bulk type and junction type.³⁾ For the bulk type varistors, many new fabrication technics have been developed improving significantly some of the varistor characteristics. For example, chemical methods of powder synthesis such as sol-gel,⁴⁾ evaporation of solutions and suspensions,⁵⁾ coprecipitation,^{6,7)} and evaporative decomposition of solutions⁸⁾ improve varistor characteristics through better homogeneity of the microstructure. Advanced methods of consolidation, such as hot pressing,⁹⁾ hot-isostatic pressing,¹⁰⁾ microwave sintering,¹¹⁾ etc., have also been applied in varistor technology.

In this study the new method of direct mixing of constituent phases (DMCP) was developed to obtain the bulk type varistors with an optimum and defined composite structure. The method is based on the fact that ZnO varistors are composite materials, consisting typically of three phases: ZnO, spinel, and intergranular Bi-rich phase.¹²⁻¹⁴⁾ The presence of small quantities of pyrochlore-type phase was also confirmed in cer-

tain varistor samples.^{13,15,16)} As found, pyrochlore degrades varistor properties,¹⁷⁾ so this phase was not included in our investigation. Consequently, each phase could be prepared separately and the final varistor could be formed by sintering the mixture of constituent phases. This logical approach was applied in our investigation. The main question was whether the composition of phases would be retained after sintering of their mixture. Results confirmed the presence of phases with composition very close to the starting one for which we believed to be optimum. Preliminary investigations of the method efficiency have already been reported.^{18,19)} After the first positive results obtained for only one composition, investigation was directed to the optimization of milling and sintering conditions, as well as of the phase ratio in varistors prepared by DMCP. In this work, results of this investigation are presented.

2. Experimental Procedure

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

- synthesis of constituent phases (ZnO, γ -Bi₂O₃, and spinel),
- synthesis of varistor ceramics from mixtures of constituent phase powders.

Schematic presentation of the method is given in Fig. 1.

The most common dopants found in ZnO phase are Co²⁺ and Mn²⁺. In order to obtain a good homogeneity, doped ZnO phase was prepared by a chemical technique, which is a modification of our previously described method for varistors preparation.²⁰⁾ The composition of ZnO phase was: 99.8 mol% ZnO + 0.2 mol% (Co²⁺ + Mn²⁺). ZnO was suspended in an aqueous solution containing Mn(CH₃COO)₂ and Co(NO₃)₂ and the suspension was stirred on a hot plate. After evaporation of water, the material was dried at 408 K, calcined at 1473 K for 2 h and homogenized in an agate planetary

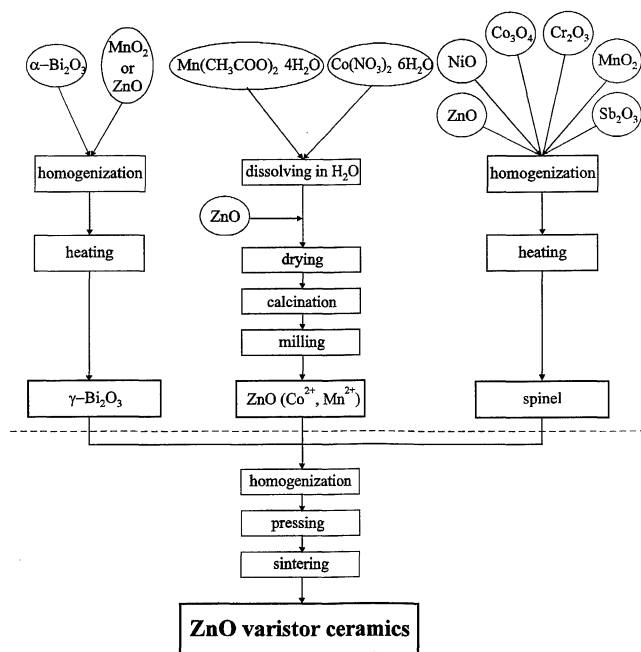


Fig. 1 Schematic presentation of the direct mixing of the constituent phases method.

ball mill (Retsch, type PM4) for 4 h. The ZnO phase was examined by X-ray powder diffraction analysis and the lattice parameters were $a = 0.32507(4)$ and $c = 0.5207(3)$ nm. Obtained values are very close to that of pure ZnO [$a = 0.32496(1)$, $c = 0.52070(9)$ nm; JCPDS card 36-145].²¹⁾

Intergranular phase may contain any of four possible Bi_2O_3 polymorphs,²²⁻²⁵⁾ but most of authors believe that γ -modification provides the best characteristics of the ZnO varistors.^{18,25,26)} Among possible additives for γ - Bi_2O_3 stabilization, ZnO and MnO_2 were chosen for this study, because they are common components of ZnO varistors and already exist in ZnO phase. Two mixtures were used for preparation of γ - Bi_2O_3 phases: $6\text{Bi}_2\text{O}_3 \cdot \text{MnO}_2$ (A) and $6\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$ (B). The compositions, as well as thermal treatment were based on phase diagrams of Bi_2O_3 - MnO_2 and Bi_2O_3 -ZnO binary systems given by Levin and Roth.²⁷⁾ Both mixtures were homogenized by dry milling in an agate mortar and heated at 1073 K for 6 h in a platinum crucible to obtain the single γ - Bi_2O_3 phase. The lattice constants of the obtained γ - Bi_2O_3 phases were: $a = 1.0221(1)$ for mixture A and $a = 1.0196(3)$ nm for mixture B. In both cases, γ - Bi_2O_3 phase was easily prepared and its lattice parameters agree with the literature data.²⁷⁾

The composition of the spinel was chosen as a re-

sult of summation and averaging of compositions determined by other authors,^{13,28,29)} as well as from our previous studies.³⁰⁾ A mixture of components (ZnO, NiO, Co_3O_4 , Cr_2O_3 , MnO_2 , Sb_2O_3) corresponding to the formula $\text{Zn}_{1.971}\text{Ni}_{0.090}\text{Co}_{0.030}\text{Cr}_{0.247}\text{Mn}_{0.090}\text{Sb}_{0.545}\text{O}_4$ of the spinel phase, was homogenized in an agate mortar, and heated at 1373 K for 2 h. X-ray powder diffraction analysis confirmed the existence of pure spinel phase with the lattice parameter $a = 0.8546(1)$ nm.

The obtained phases were used for preparation of varistor mixtures with phase compositions listed in Table 1. The first prepared and investigated composition was Z70A, which was chosen as the optimal composition from our previous studies of varistors prepared by other methods.²⁰⁾ Compositions Z85 and Z92.5 were prepared to investigate the possibility of reduction of additives content in varistors prepared by the DMCP method.

Mixtures Z70A and Z70B were homogenized in an agate planetary ball mill under the following conditions: milling intensity (basic sundiscs rotation) = 90 min^{-1} , milling time = 2 h, and ball-to-powder weight ratio (w_b/w_p) = 2 : 1. These samples will be called "untreated" in the further discussion.

With intention to improve powder and consequently varistor characteristics some powder mixtures were intensively milled (Table 2). Milling was carried out in the agate planetary ball mill with agate balls 10 and 20 mm in diameter. Balls of 10 and 20 mm were used when w_b/w_p was 10 : 1 and 20 : 1, respectively. In order to determine the crystallite size as a function of milling time, the mill was stopped at certain intervals and some amount of powder (about 1 g) was picked up for examination. Ball-to-powder weight ratio was kept constant by removing some of the balls.

The resulting powders were pressed into pills sized 1 mm in height and 8 mm in diameter and sintered in air. Varistor mixtures Z70A and Z70B were sintered in a temperature range 1073–1573 K for 0–8 h. Intensively milled powders of Z70A composition were sintered at 1373 K for 1 h, while powders

Table 1 Phase composition of varistor mixtures.

Mixture	Constituents (mass%)			
	ZnO	Spinel	γ - Bi_2O_3 (A) *	γ - Bi_2O_3 (B) **
Z70A	70	20	10	—
Z70B	70	20	—	10
Z85	85	10	5	—
Z92.5	92.5	5	2.5	—

* $6\text{Bi}_2\text{O}_3 \cdot \text{MnO}_2$; ** $6\text{Bi}_2\text{O}_3 \cdot \text{ZnO}$

Table 2 Milling parameters of intensively milled varistor powders.

Mixture	Z(90.20.4)*	Z(250.20.2)*	Z(90.10.4)*	Z(250.10.2)*	Z85, Z92.5
Milling parameters					
Intensity (min^{-1})	90	250	90	250	250
w_b/w_p	20 : 1	20 : 1	10 : 1	10 : 1	10 : 1
Time (h)	4	2	4	2	2

*Mixtures of composition Z70A (see Table 1), symbols in parentheses refer to milling conditions

Z85 and Z92.5 were sintered at temperatures within 1073–1573 K for 1 h.

The characterization of initial powders and the resulting ceramics was made by the methods of particle size distribution (COULTER MULTISIZER), X-ray powder diffraction (Philips PW 1710 powder diffractometer with graphite-monochromatized $\text{CuK}\alpha$ radiation), optical and scanning microscopy of polished, chemically etched (HNO_3 solution, for 5 s) samples, and fractured surfaces. Changes in crystallite size were calculated from the peak widths of two nonoverlapping maxima [at 47.55° (2θ) for ZnO (102) reflection and at 42.22° (2θ) for spinel (400) reflection], using the Scherrer formula.³¹⁾ The peak widths were corrected for $\text{K}\alpha_1/\alpha_2$ doublet, and instrumental broadening. Sample Z70A sintered at 1473 K for 8 h and having the narrowest diffraction maxima, was used as the reference material.

The mean grain size of ZnO and spinel grains was determined from the optical micrographs of the chemically etched sintered samples by the intercept method.

Electrical properties of sintered samples were registered using a direct current method. The nonlinearity coefficients were determined within the ranges 1–10 A/m^2 (α_1) and 10–100 A/m^2 (α_2), the breakdown field (K_C) was measured at 10 A/m^2 , and the leakage current (J_L) was determined at the voltage of $0.8K_C$.

3. Results and Discussion

The X-ray powder diffraction analysis of sintered samples Z70A and Z70B confirmed the existence of the same phases as those introduced into the varistor powder mixtures. Diffraction patterns of samples Z70A and Z70B are almost the same with small differences in peak intensities. The ZnO phase is the dominant one in all cases exhibiting the highest degree of crystallinity in the samples sintered at 1573 K. The lattice parameters of ZnO and spinel in Z70A samples, sintered at 1073–1573 K for 1 h, are shown in Table 3.

The changes in spinel and ZnO lattice parameters were generally small and could be a result of cation redistribution between different phases. The $\gamma\text{-Bi}_2\text{O}_3$ phase was identified at all temperatures except at 1573 K, where weak peaks of $\beta\text{-Bi}_2\text{O}_3$ were registered.

3.1 Influence of sintering conditions

Considering electrical properties there are no significant

differences between the varistors Z70A and Z70B. This means that the type of oxide (ZnO or MnO_2) used for $\gamma\text{-Bi}_2\text{O}_3$ stabilization is irrelevant for electrical behaviour of the varistors. First varistor effects were obtained in samples sintered at 1073 K for 30 min. However, these samples had high values of the leakage currents ($>0.1 \text{ A}/\text{m}^2$) and low values of the nonlinearity coefficients (<20) indicating a high degree of porosity and poor microstructural characteristics of the varistors obtained. Microstructural examination of the samples confirmed these results. Maximum densities (94% of the theoretical value) were achieved at sintering temperatures 1373 and 1473 K.

The breakdown fields were from 200 to 1600 kV/m depending on the ZnO grain size which is proportional to the sintering time and temperature. Slightly larger ZnO grains and smaller spinel grains were found in Z70B samples. ZnO grain size, depending on the sintering parameters, was in the range 4–13 and 4–14 μm for varistors Z70A and Z70B, respectively. Spinel grain size was in the range 1.5–4 and 1.5–5 μm for Z70B and Z70A compositions, respectively.

Electrical characteristics of varistors Z70A and Z70B could be summarized in the following way. The minimum J_L values were found for samples sintered at 1373 and 1473 K, for 1–2 h and they were in the range 0.01–0.02 A/m^2 . The maximum nonlinearity coefficients, α_1 , were found for samples sintered at 1373 K and their values were 50 and 45 for varistors Z70A and Z70B, respectively. The nonlinearity coefficient, α_2 , was in the ranges 20–36 and 20–40 for varistors Z70A and Z70B, respectively, depending on the sintering parameters.

Bearing in mind presented results it could be concluded that optimal sintering conditions for “untreated” varistors Z70A and Z70B are 1373 K and 1 h.

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. On the other hand, during sintering of samples prepared by conventional method, depending on sintering and cooling conditions, several reactions can take place. These are pyrochlore type phase formation as well as spinel phase formation from pyrochlore and ZnO.^{13,16)} The reaction of spinel phase formation can be reversed during slow cooling due to reaction of spinel phase with liquid Bi_2O_3 .^{13,16)} Additionally, additives can largely influence these reactions.¹³⁾ Complexity of those reactions suggest that it is very hard to control all processes, as well as final composition of phases and their molar ratio. During sintering of varistor samples prepared by DMCP method, the same phases introduced into the system are present in varistor ceramics after sintering. Moreover, small differences in lattice constants of starting phases and phases in sintered samples mean that only small amounts of components present in particular phases diffused from one to another phase. It follows that the role of liquid Bi_2O_3 -rich phase is sintering promotion only, because there is no chemical reaction during sintering.

3.2 Effects of intensive milling

The preparation of a powder mixture is the first step in production of ZnO varistors with desired structural and electrical characteristics. The main requirements are to obtain powders

Table 3 Lattice constants of ZnO and spinel phases in Z70A varistor samples.

Temperature, (K)	ZnO Phase		Spinel <i>a</i> (nm)
	<i>a</i> (nm)	<i>c</i> (nm)	
Starting sample	0.32507(4)	0.5207(3)	0.8550(3)
1073	0.32518(7)	0.5211(4)	0.8551(3)
1173	0.32530(6)	0.5208(4)	0.8549(5)
1273	0.32530(9)	0.5210(6)	0.8552(3)
1373	0.3259(2)	0.522(1)	0.8561(6)
1473	0.32520(5)	0.5211(3)	0.8550(3)
1573	0.32556(8)	0.5217(5)	0.8559(2)

with narrow particle size distribution, homogeneous phase distribution and high sintering activity.^{32,33} Intensive milling was previously included in processing of powder mixture of varistor components, in order to better fulfilled these requirements.^{34,35} Some progress was achieved suggesting that intensive milling could improve varistor properties. For that reason, the intensive milling was applied on powder mixtures prepared by DMCP method.

The mean particle size of intensively milled powders in comparison to the "untreated" sample is given in Table 4. As shown, the mean particle size of intensively milled samples is considerably decreased. The comparison of powders treated under same milling conditions (intensity and time), but with different w_b/w_p parameters, shows that the increase in w_b/w_p from 10 : 1 to 20 : 1 has no significant influence on D_{50} . In the case of higher w_b/w_p value only slightly smaller particles were observed. The increase in mean particle size with prolonged milling, at a milling intensity of 250 min^{-1} , is the consequence of particles agglomeration. The particle size distribution showed that milling could provide narrower particle size distribution, but not under all milling conditions. The optimal milling parameters are: milling intensity = 250 min^{-1} , $w_b/w_p = 20 : 1$, milling time = 2 h.

The X-ray powder diffraction analysis of varistor powder mixtures milled for various milling times revealed no appearance of new phases and insignificant differences in lattice parameters. However, changes in peak intensities and widths are evident. In accordance to the results of particle size analysis, the peak intensities only slightly decreased with the change in w_b/w_p ratio from 10 : 1 to 20 : 1.

In the samples treated at a milling intensity equal to 90 min^{-1} , the peak intensities of $\gamma\text{-Bi}_2\text{O}_3$ and spinel are very similar, but changes in peak intensities of ZnO are significant. When the milling intensity was increased to 250 min^{-1} , the changes in diffraction patterns became much more pronounced, especially for $\gamma\text{-Bi}_2\text{O}_3$. After an initial decrease in intensity, the $\gamma\text{-Bi}_2\text{O}_3$ peaks disappeared after 60 min of milling indicating a complete amorphization of this phase. Figures of X-ray diffraction patterns of powders milled under different milling conditions which illustrate above given statements have been already published.¹⁹ The broadening of the ZnO and spinel peaks, due to intensive milling, was used to follow the reduction of crystallite size. The crystallite size as a function of milling time is shown in Fig. 2. The curve shape is typical and was found for many other powder systems subjected to intensive milling.^{36,37}

Sintered samples of composition Z70A, prepared from intensively milled powders were composed of the same phases as the "untreated" one with negligible differences in lattice parameters of particular phases. Also, no important change in

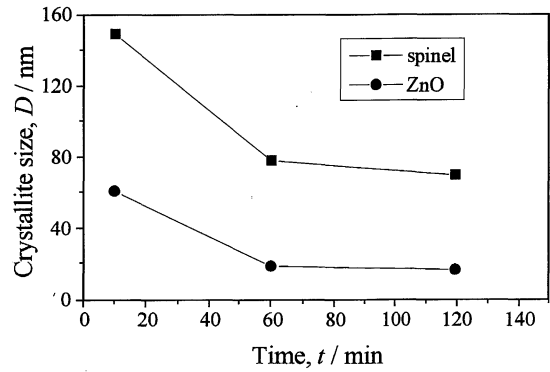


Fig. 2 Changes in ZnO and spinel crystallite size as a function of milling time (milling intensity = 250 min^{-1}).

Table 5 Electrical characteristics of intensively milled varistors ($w_b/w_p = 10 : 1$) compared to that of "untreated" sample.

Sample	α_1	α_2	K_C (kV/m)	J_L (A/m ²)
Z70A	37	27	450	0.046
Z(90.10.4)	37	30	460	0.040
Z(250.10.2)	35	25	415	0.024

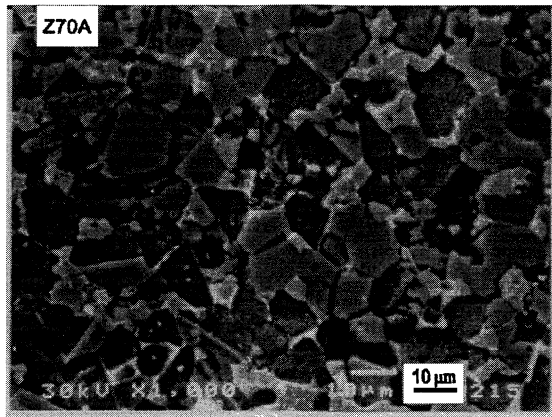
electrical characteristics of intensively milled samples compared to the "untreated" one is observed (Table 5), except that slightly lower values of leakage currents were obtained in former samples. The main difference is that the intensively milled samples have higher sintering densities (reaching 99% of theoretical value). Varistor samples obtained from intensively milled powders have a remarkably more homogeneous microstructure in comparison to the "untreated" samples (Fig. 3). It could be expected that these varistors exhibit improved stability as a result of increased homogeneity. The comparison of these samples with samples prepared from intensively milled powders that were simple mixture of oxides^{34,35} showed that combination of intensive milling and DMCP method give much better results, especially from the microstructural aspect.

3.3 The influence of spinel and $\gamma\text{-Bi}_2\text{O}_3$ content

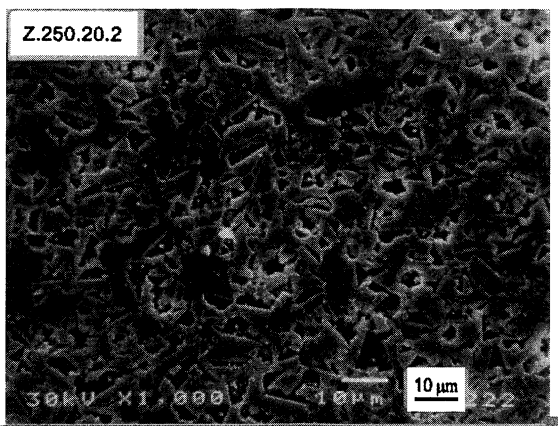
Positive effects of intensive milling were used in preparation of varistor samples with different phase compositions. The content of spinel and $\gamma\text{-Bi}_2\text{O}_3$ was decreased from Z70A, over Z85, to Z92.5 powder mixture (Table 1). Varistor mixtures Z85 and Z92.5 were also intensively milled before sintering with milling parameters given in Table 2. Then, they were processed in the usual manner and sintered in a temper-

Table 4 Mean particle size, D_{50} , of varistor powders Z70A treated under different milling conditions.

Milling parameters:											
Milling intensity (min^{-1})	90	90	90	250	250	250	90	90	250	250	250
Time (h)	2	0.17	4	0.17	1	2	0.17	4	0.17	1	2
w_b/w_p	2 : 1	10 : 1	10 : 1	10 : 1	10 : 1	10 : 1	20 : 1	20 : 1	20 : 1	20 : 1	20 : 1
D_{50} (μm)	12	10.5	5	5.5	7	9.2	9.5	4.8	6	9.5	9.5



(a)



(b)

Fig. 3 SEM of the polished and chemically etched surfaces of the sintered varistor samples: “untreated” sample Z70A (a), and intensively milled sample Z.250.20.2 (b). Both samples were sintered at 1373 K for 1 h.

ature range 1073–1573 K, for 1 h.

For sintering time of 1 h the minimum sintering temperature needed to obtain varistor effect from powders Z85 and Z92.5 was 1273 K. At an optimal sintering temperature of 1373 K the samples showed very high densities similar to that of intensively milled samples of composition Z70A and higher than that of “untreated” samples Z70A (Fig. 4).

Values of the breakdown field of sample Z92.5 are lower than of sample Z85 due to increase in ZnO grains size. The increase in ZnO grains size is a consequence of reduction of spinel content. The nonlinearity coefficient α_2 and leakage current values of varistors with different compositions, as a function of sintering parameters are shown in Figs. 5 and 6. Comparison of these results with the results obtained for varistors Z70A shows similarity between samples Z70A and Z85. However, further decrease in spinel and γ -Bi₂O₃ content caused a serious damage of varistor characteristics; samples Z92.5 have lower α_2 and higher J_L values in the whole temperature interval. Similar results were obtained for the nonlinearity coefficient α_1 . Therefore, use of DMCP method in combination with intensive milling allows reduction of γ -Bi₂O₃ and spinel content down to 50% relative to the Z70A

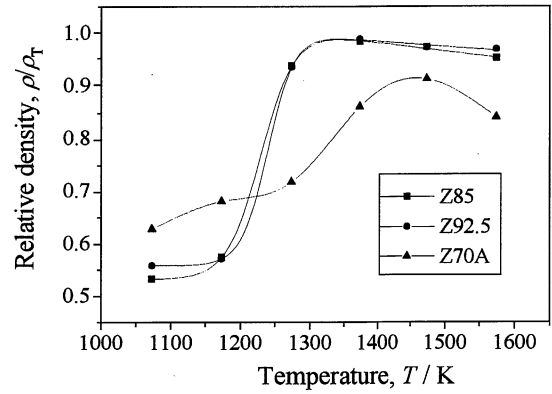


Fig. 4 Relative density (ρ/ρ_T) as a function of sintering temperature for varistors Z85 and Z92.5. A curve for “untreated” sample Z70A is included for comparison.

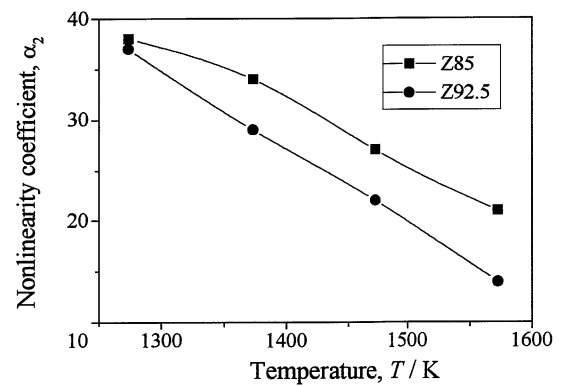


Fig. 5 Nonlinearity coefficient (α_2) as a function of sintering temperature for samples Z85 and Z92.5.

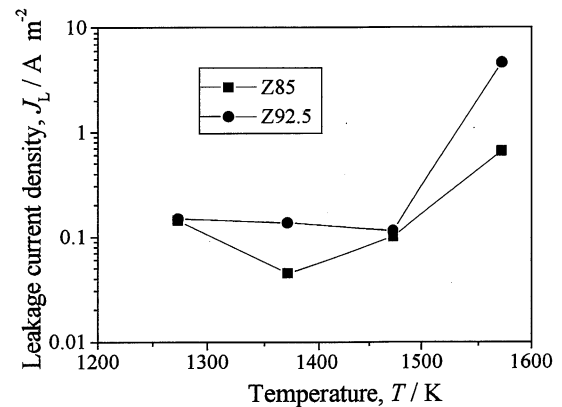


Fig. 6 Leakage current density (J_L) as a function of sintering temperature for samples Z85 and Z92.5.

composition with no significant changes in varistor characteristics. Considering these results the composition Z85 is proposed as the optimal for the investigated compositions of the constituent phases, and for given processing parameters.

The method of direct mixing of constituent phases enables preparation of varistors with good electrical characteristics, and, if the intensive milling is included in processing procedure, with almost theoretical density. Obtained values of the

α_1 , α_2 , and J_L are typical and in the ranges cited by other authors for good varistors.^{14,38,39} This method also enables better control of phase composition, as well as phase ratio, than conventional methods. DMCP method is particularly convenient for the investigation of the role of phases and additives in varistor processing. This will be the subject of our future work.

4. Conclusions

A new method of direct mixing of constituent phases was developed for the preparation of ZnO varistors. The method is based on the controlled synthesis of the constituents, which have well-defined structure and phase composition:

- ZnO phase uniformly doped with Co^{2+} and Mn^{2+} ,
- intergranular phase: $\gamma\text{-Bi}_2\text{O}_3$ stabilized with Mn^{2+} or Zn^{2+} ,

- spinel phase: $\text{Zn}_{1.971}\text{Ni}_{0.090}\text{Co}_{0.030}\text{Cr}_{0.247}\text{Mn}_{0.090}\text{Sb}_{0.545}\text{O}_4$.

Prepared varistors exhibit good electrical characteristics with nonlinearity coefficients reaching 50 and low values ($\sim 0.01 \text{ A/m}^2$) of the leakage currents.

The influence of composition as well as milling and sintering parameters on the characteristics of varistors prepared by the DMCP-method was investigated and optimal composition and parameters were estimated.

To reduce the amount of additives in the system, the composition 85 mass% ZnO (Co^{2+} , Mn^{2+}) + 10 mass% spinel + 5 mass% $\gamma\text{-Bi}_2\text{O}_3$ was proposed as optimum.

Intensive milling of varistor powders mixtures produces nanostructured powders. The optimal milling parameters are: milling intensity = 250 min^{-1} , $w_b/w_p = 20 : 1$, milling time = 2 h. Varistor samples prepared from powders treated under these milling conditions show extremely homogeneous microstructure and high densities reaching 99% of the theoretical value. The optimal sintering conditions, which provides the best electrical characteristics and especially the lowest leakage currents are 1373 K for 1 h.

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