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# CORRELATION BETWEEN CHEMICAL COMPOSITION OF THE $\gamma$–$Bi_2O_3$ PHASE AND THE PROPERTIES OF ZnO VARISTORS

*Four varistor samples differing in chemical and phase composition of the starting $Bi_2O_3$ phase were prepared by the method of direct mixing of the constituent phases (DMCP), i.e. by sintering the mixture of the previously prepared phases. The compositions of the constituent phases in the sintered samples were investigated by changes of their lattice constants and by EDS analysis. After sintering, the phase compositions of all the investigated samples were the same: ZnO phase, spinel and $\gamma$–$Bi_2O_3$. It was found that the $\gamma$–$Bi_2O_3$ phase was mainly stabilized with $Zn^{2+}$ ions. All the samples showed good electrical properties with non-linearity coefficients up to 50 and small values of the leakage current. The electrical properties of the samples were discussed in terms of diffusion processes and the redistribution of additives during sintering.*

*Key words: Varistors, $Bi_2O_3$ phase, Solid state reaction, X–ray diffraction analysis, Electrical properties.*

ZnO varistors contain three main phases: doped ZnO grains, spinel and an intergranular phase [1,2]. The composition of the $Bi_2O_3$ phase in varistors probably depends on the chemical composition of the initial varistor powder mixture and the sintering conditions. Any of four polymorphs, $\alpha$–, $\beta$–, $\gamma$–, and $\delta$–$Bi_2O_3$, could be found in varistors [3], but most authors believe that the $\gamma$–modification of $Bi_2O_3$ provides the best characteristics for ZnO varistors [3,4]. $\gamma$–$Bi_2O_3$ is a metastable modification, but could be stabilized with additives such as ZnO, PbO, $B_2O_3$, $Al_2O_3$, $SiO_2$, $MnO_2$, etc [5].

Analysis of the intergranular phase in ZnO varistors has usually confirmed the presence of Bi, Zn, Sb and Cr [1], as well as small quantities of other elements, such as Co, Mn, and Si [6]. Unfortunately, these investigations were performed on intergranular phases containing other polymorphs, but not $\gamma$–$Bi_2O_3$. Although there are no data about the chemical composition of the $\gamma$–$Bi_2O_3$ phase in ZnO varistors, Cerva supposed that it was stabilized with $Zn^{2+}$ ions [2].

Varistor microstructural and electrical properties were investigated as a function of the chemical composition of $Bi_2O_3$ phase in this study. This is part of a systematic investigation of the influence of the chemical composition of minor phases on varistor properties. Several powder mixtures, differing only in the starting chemical and phase composition of the $Bi_2O_3$ phase, were prepared using the DMCP method [7,8], meaning that each phase was prepared separately and the final ceramic material was obtained by sintering a mixture of the crystal phases. Therefore, the composition of the starting $Bi_2O_3$ and other phases was known. The changes in the phase composition and redistribution of additives after sintering were determined from the chemical analysis of the constituent phases in the final ceramics. The electrical properties of the varistors were related to the phase composition of the intergranular phase, based on the changes in the concentrations of dopants introduced by different intergranular phases.

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## EXPERIMENTAL

Four varistor samples containing ZnO and spinel phases of the same chemical composition, but differing in the chemical and phase composition of the starting $Bi_2O_3$ phase were prepared. The compositions of the starting phases were the following:

- ZnO phase: 99.8 mol% ZnO + 0.2 mol% of $Co^{2+}$ + + $Mn^{2+}$ ions,
- spinel phase: $Zn_{1.971}Ni_{0.090}Co_{0.030}Cr_{0.247}Mn_{0.090}Sb_{0.545}O_4$,
- $Bi_2O_3$ phases: $6Bi_2O_3 \cdot MnO_2$ (Bi–Mn), $6Bi_2O_3 \cdot ZnO$ (Bi–Zn), $12Bi_2O_3 \cdot ZnO \cdot SiO_2$, (Bi–Si–Zn) and $20{,}28Bi_2O_3 \cdot Sb_2O_3$ (Bi–Sb).

In further discussion the varistor mixtures will be designated according to the $Bi_2O_3$ phase (for example: V–Bi–Mn is the varistor that contains the $Bi_2O_3$ phase designated as Bi–Mn).

The ZnO phase was prepared by suspending ZnO in a solution of $Co(NO_3)_2$ and $Mn(CH_3COO)_2$, followed by evaporation of the suspension, calcination and milling of the powder. The spinel and $Bi_2O_3$ phases were prepared by solid state reactions of appropriate amounts of oxides. The starting formula of the spinel phase was calculated by averaging the results of the chemical analysis of the spinel phase given by other authors [1,4,9]. The thermal conditions for its preparation are given elsewhere [7,8].

The oxides chosen for stabilization of the desired $Bi_2O_3$ phases ($\gamma$– or $\beta$–$Bi_2O_3$) were metal oxides, which are commonly present in varistors. The ratio between Bi and the Me ions was based on literature data [5,10]. The thermal treatment used for preparation of the $Bi_2O_3$ phases, as well as the composition of the obtained samples are given in Table 1. A single $\gamma$–$Bi_2O_3$ phase was obtained in $Bi_2O_3$–phases of the compositions Bi–Mn and Bi–Zn, and a mixture of two $\gamma$–$Bi_2O_3$ phases was obtained in the composition Bi–Si–Zn. After thermal treatment of the $Bi_2O_3$–phase of composition Bi–Sb, a

*Table 1. Thermal treatment conditions for the preparation of the $Bi_2O_3$, phase composition after thermal treatment and the corresponding lattice constants*

| $Bi_2O_3$ phase | T (K)/t (h) | Phase Composition | Lattice constants (Å) |
|---|---|---|---|
| Bi–Mn | 963/6 + 1073/3 | $\gamma$–$Bi_2O_3$ | 10.221(1) |
| Bi–Zn | 963/3 + 1073/3 | $\gamma$–$Bi_2O_3$ | 10.196(3) |
| Bi–Si–Zn | 963/1.5 | $\gamma_1$–$Bi_2O_3$ + $\gamma_2$–$Bi_2O_3$ | 10.112(3)–$\gamma_1$; 10.199(2)–$\gamma_2$ |
| Bi–Sb | 963/2.5 | $\beta$–$Bi_2O_3$ + $\gamma$–$Bi_2O_3$ | $\beta$: a = 7.738(9), c = 5.609(3), $\gamma$: a = 10.243(6) |

mixture of $\gamma$–$Bi_2O_3$ and $\beta$–$Bi_2O_3$ in an approximate mass ratio of 1:5 was found, although literature data suggested that pure $\beta$–$Bi_2O_3$ should be obtained [10]. The lattice constants of the obtained phases were in accordance with literature data [5,10].

Varistor mixtures with the composition 85 wt.% of the ZnO phase +10 wt.% of spinel + 5 wt.% of the $Bi_2O_3$ phase were homogenized in an agate planetary ball mill for 2 h, pressed into pellets (8 mm x 1 mm) and sintered at 1473 K for 1 h. The sintering conditions were chosen according to previous results [7,8].

Characterization of the initial powders and the resulting ceramics was performed by X–ray powder diffraction, XRPD (Philips PW 1710 powder diffractometer with graphite–monochromatized CuK$\alpha$ radiation), scanning electron microscopy (JEOL JSM–T330A) and energy dispersive X–ray analysis (EDS).

The electrical properties were registered within the 0.1–10 mA/cm$^2$ region using dc measurements. The non-linearity coefficients were determined within the ranges 0.1–1.0 mA/cm$^2$ ($\alpha_1$) and 1.0–10 mA/cm$^2$ ($\alpha_2$), the breakdown field ($K_C$) was measured at 1 A/cm$^2$, and the leakage current ($J_L$) was determined at an electrical field of $0.8 \cdot K_C$. The voltage per barrier ($U_b$) was determined from the values of $K_C$ and D (where D is the ZnO grain size), according to the equation $U_b = K_C \cdot D$.

## RESULTS AND DISCUSSION

X–Ray diffraction analysis of the sintered samples showed that all the samples had the same phase composition: ZnO, spinel and $\gamma$–$Bi_2O_3$ (Figure 1). This result implies that the thermal treatment led to the formation of only one $\gamma$–$Bi_2O_3$ in samples V–Bi–Si–Zn and V–Bi–Sb. The XRPD pattern of the V–Bi–Sb sample after sintering (Figure 1) confirms a change in the phase composition of the intergranular phase.

Due to the low $Bi_2O_3$ content only a few well–separated, but weak maxima, belonging to the $\gamma$–$Bi_2O_3$ phase were visible in the varistor XRPD patterns. Therefore, it was possible to calculate only approximate lattice constants of the resulting $\gamma$–$Bi_2O_3$ phases. They ranged from 10.13 to 10.21 Å and were changed in respect to the starting values. Based on EDS analysis of the intergranular phase, it is evident that $\gamma$–$Bi_2O_3$ is stabilized mainly by $Zn^{2+}$. Depending on the starting compositions, traces of several elements, such as Mn, Sb, Cr, Co were also detected (Figure 2). According to Takemura and co–workers, the wide range of observed lattice constants could be attributed to volume contractions and stresses at the grain boundaries because of

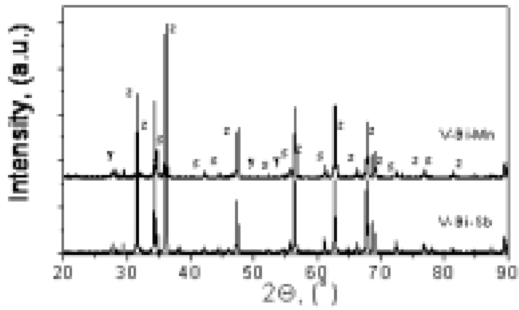


*Figure 1. XRPD patterns of samples V–Bi–Sb and V–Bi–Mn, sintered at 1473 K*

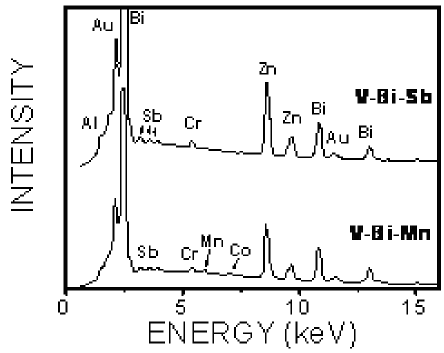


*Figure 2. EDS of the intergranular phase of varistors V–Bi–Mn and V–Bi–Sb (the Au peak originate from the metallization of some samples to obtain better micrograhs)*

phase transformations and other processes occurring during liquid phase sintering of the varistors [4].

The diffusion processes taking place during sintering led to partial redistribution of the additives, as well as to the formation of single $\gamma$–$Bi_2O_3$ mainly doped with $Zn^{2+}$ ions. The formation of $\gamma$–$Bi_2O_3$ of this composition seems the most probable if a great excess of ZnO in all systems is taken into account. The appearance of a liquid phase during sintering promotes diffusion, as well as the dissolution of small quantities of ZnO in the liquid $Bi_2O_3$ phase, and consequently increases the probability of the formation of Zn–stabilised $\gamma$–$Bi_2O_3$.

All the samples showed an almost identical composition of the spinel and ZnO phases, although small variations in the peak intensities were observed (Figure 1 and Table 2). EDS analysis of the ZnO phase showed only the presence of Zn and no traces of Co or Mn (Fig. 3a), probably because they are present in quantities which were under the detection limits. X–Ray diffraction analysis of the ZnO phase showed a slight increase (0.02–0.2%) of the lattice constants in comparison to the starting phase. EDS spectra of typical spinel phases are given in Figure 3b. Obviously, the spinel phase has an almost identical composition in all the samples, which is in accordance with the results of XRPD that shows very small differences in the lattice parameters of the spinel phases in different varistors (Table 2).

The results of microstructural analysis showed a similar shape and distribution of the phases, as well as porosity and homogeneity of the samples. Values of the characteristic microstructural parameters, such as the ZnO grain size (D), linear shrinkage (Δl/l) and apparent densities (ρ) are given in Table 3. Based on these results and the fact that all the samples had the same phase composition, similar electrical properties of the samples could be expected. Nevertheless, the V–Bi–Mn sample showed pronounced differences in electrical properties (Table 3).

The V–Bi–Mn samples showed significantly higher values of $\alpha_2$ and Ub, while the V–Bi–Zn sample had the lowest value of $J_L$. These results are a consequence of the diffusion processes taking place during sintering and could be rationalized as follows. The V–Bi–Zn sample is the most stable composition, changed to the lowest extent, since it already contained the $\gamma$–$Bi_2O_3$ stabilized with ZnO. This gives a possible explanation for the low value of $J_L$. A similar study of varistors differing only in the composition of the spinel phases also showed that the best characteristics were found for the most stable compositions, *i.e.* in compositions that were changed to a lower extent during sintering [8]. This is in accordance with the presented results here.

On the other hand, the V–Bi–Mn samples contain a higher amount of Mn than the other varistors. Based on the composition of the starting phases in the V–Bi–Mn varistors, it is possible to calculate that the $Bi_2O_3$ phase in this sample contains a two times higher quantity of Mn than the entire ZnO phase. Mn diffuses from the $Bi_2O_3$ phase to other phases during sintering. It could be

a)

b)

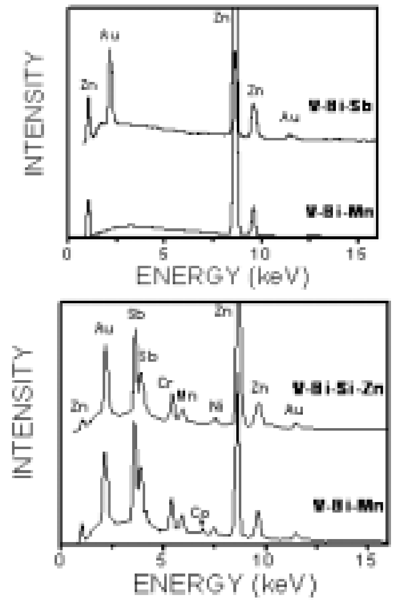


*Figure 3. EDS of a) the ZnO grain interior of varistors V–Bi–Mn and V–Bi–Sb, b) the spinel phase of varistors V–Bi–Mn and V–Bi–Si–Zn*

supposed that $Mn^{x+}$ ions are mainly incorporated into the ZnO phase, which means that the ZnO phase in V–Bi–Mn varistors contains an approximately three times higher concentration of Mn than the other samples. This may partially explain the different electrical properties of the V–Bi–Mn sample. Besides the quantity of Mn, the valence of Mn–ions should also be considered. The ZnO phase is doped with $Mn^{2+}$ ions, but the $Bi_2O_3$ phase contains $Mn^{4+}$. Driear et al. investigated the influence of the valence state of $Mn^{x+}$ ($x = 2$ or 4) and $Co^{y+}$ ions ($y = 2$ or 3) on ZnO varistor properties [11]. They showed that the presence of $Mn^{4+}$ ions decreases ZnO grain size and porosity and, consequently, influences the electrical properties. This statement is in accordance with our results, because we have also observed the smallest grains in V–Bi–Mn varistors in comparison with other compositions. Some other authors [12] have found that samples prepared with $MnO_2$ always contain a higher concentration of $Mn^{4+}$ than samples prepared with MnO, although $Mn^{2+}$ ions should be more stable than $Mn^{4+}$ under the applied sintering conditions. A systematic investigation of the electrical properties as a function of the $Mn^{x+}$ valence state showed that varistors containing $Mn^{4+}$ have a higher concentration of donors, which results in an increase of the potential barrier at the grain boundaries. Our results confirmed this conclusion since we also found a higher $U_b$ in the Bi–Mn samples.

*Table 2. The lattice constants of the ZnO and spinel phases in varistors of different compositions (the lattice constants of the starting phases were: ZnO – a = 3.2507(4), c = 5.207(3), spinel – a = 8.550(2) Å)*

| | ZnO | | Spinel |
|---|---|---|---|
| Varistor | a (Å) | c (Å) | a (Å) |
| V–Bi–Mn | 3.2520(4) | 5.212(3) | 8.550(3) |
| V–Bi–Zn | 3.2524(4) | 5.210(2) | 8.553(2) |
| V–Bi–Si–Zn | 3.2521(6) | 5.209(1) | 8.576(3) |
| V–Bi–Sb | 3.259(1) | 5.218(2) | 8.579(5) |

*Table 3. Electrical and microstructural parameters of the investigated samples*

| Varistor | $\alpha_1$ | $\alpha_2$ | $J_L$ ($\mu A/cm^2$) | $K_C$ (V/mm) | $U_b$ (V) | D ($\mu$m) | Δl/l(%) | $\rho/\rho_T$ (%) |
|---|---|---|---|---|---|---|---|---|
| V–Bi–Mn | 28 | 52 | 8,6 | 420 | 3,2 | 7,5 | 11.2 | 95.3 |
| V–Bi–Zn | 30 | 28 | 5,4 | 290 | 2,6 | 8,9 | 11.0 | 96.4 |
| V–Bi–Si–Zn | 31 | 28 | 8,4 | 322 | 2,6 | 8,1 | 10.8 | 94.8 |
| V–Bi–Sb | 29 | 34 | 8,2 | 326 | 2,7 | 8,4 | 11.0 | 95.6 |

## CONCLUSIONS

Four different varistor mixtures differing only in the chemical composition of the starting $Bi_2O_3$ phases were prepared by the DMCP method. Although the starting mixtures contained different polymorphs of $Bi_2O_3$, after sintering all the samples had the same phase composition: the ZnO phase, spinel and $\gamma$–$Bi_2O_3$. It was found that $\gamma$–$Bi_2O_3$ was stabilized by Zn and contained traces of some other elements, such as Cr, Mn and Sb.

All the varistors showed almost identical microstructures. The observed differences in the electrical properties were explained by the diffusion and redistribution of additives during sintering, which resulted in different concentrations of additives in the ZnO grains and at the grain boundaries. The investigated varistors showed excellent electrical properties, non-linearity more than 50 and low values of the leakage current.

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## IZVOD

UTICAJ HEMIJSKOG SASTAVA $\gamma$–$Bi_2O_3$ FAZE NA SVOJSTVA ZnO VARISTORA

(Naučni rad)

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Varistori su elektronske komponente koje se odlikuju izrazitom nelinearnošću strujno–naponske karakteristike. Osnovna namena varistora je odvođenje prenapona iz bilo kog izvora čime se obezbeđuje zaštita električnog kola. Klasičan postupak dobijanja ZnO varistora podrazumeva sinterovanje ZnO sa malom količinom aditiva kao što su oksidi bizmuta, antimona, kobalta, mangana, nikla, hroma, aluminijuma i drugi. Na ovaj način se dobija kompozitna keramička struktura čiji su osnovni konstituenti: zrna ZnO, intergranularna i spinelska faza. Intergranularna faza može da sadrži pirohlornu fazu kao i bilo koju od četiri moguće polimorfne modifikacije $Bi_2O_3$, ali većina autora smatra da $\gamma$–modifikacija $Bi_2O_3$ obezbeđuje najbolje karakteristike ZnO varistora.
Cilj rada bio je da se utvrdi uticaj hemijskog sastava $\gamma$–$Bi_2O_3$ na mikrostrukturna i električna svojstva ZnO varistora, kao i da se ispita difuzija i preraspodela dopanata između faza tokom sinterovanja. U tu svrhu najpogodnije je bilo primeniti metodu dirigovane sinteze konstitutivnih faza koja se bazira na dobijanju ZnO varistora iz smeše prethodno sintetizovanih faza. Pripremljene su četiri varistorske smeše koje su se razlikovale samo u hemijskom sastavu $\gamma$–$Bi_2O_3$. Nakon sinterovanja na 1473 K tokom 1 h dobijeni su gusti uzorci varistora. Sastav pojedinih faza u sinterovanim uzorcima ispitan je rendgenskom difrakcionom analizom kao i EDS analizom. Utvrđeno je da sva četiri izorka imaju isti fazni sastav: ZnO, spinelsku i $\gamma$–$Bi_2O_3$ fazu. Nađeno je da je $\gamma$–$Bi_2O_3$ faza stabilisana $Zn^{2+}$ jonima, a da se u tragovima mogu naći još i Cr, Mn i Sb.
Svi varistori pokazuju skoro identične mikrostrukture. Uočene razlike u električnim karakteristikama objašnjene su difuzijom i preraspodelom aditiva tokom sinterovanja koji rezultiraju različitim koncentracijama aditiva u ZnO zrnima, kao i na granicama zrna. Ispitivani uzorci pokazuju odlične električne karakteristike, nelinearnost veću od 50 i niske vrednosti struje curenja.

Ključne reči: varistori, $Bi_2O_3$–faza, reakcije u čvrstom stanju, rendgenska difrakciona analiza, električna svojstva.