Chemical Composition of γ-Bi_2O_3 Phase and Its Influence on Varistor Properties

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Abstract

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. Compositions of constituent phases in sintered samples were investigated by changes of their lattice constants, and by EDS analysis. After sintering phase compositions of all investigated samples were the same: ZnO phase, spinel and γ-Bi_2O_3. It was found that γ-Bi_2O_3 phase is mainly stabilized with Zn^{2+} ions. All samples showed good electrical properties with nonlinearity coefficients up to 50 and small values of the leakage current. Electrical properties of the samples were discussed in terms of diffusion processes and redistribution of additives during sintering.

Keywords: E: varistors, A. powders-solid state reaction, B: X-ray methods, C: electrical properties

Introduction

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Main feature of the ZnO varistors is a high nonlinearity of the current-voltage characteristics. Varistors contain three main phases: doped ZnO grains, spinel and intergranular phase.[1,2] The composition of Bi_2O_3 phase in varistors may be very different[1,2] and probably depends on chemical composition of initial varistor powder mixture and sintering conditions. Any of four polymorphs, α-, β-, γ-, and δ-Bi_2O_3, could be present in varistors[3,4], but most of authors believe that γ-modification of Bi_2O_3 provides the best characteristics to the ZnO varistors.[4,5] γ-Bi_2O_3 is a metastable modification of Bi_2O_3 but it could be stabilized with some additives such as ZnO, PbO, B_2O_3, Al_2O_3, SiO_2, MnO_2, *etc*.[6]

The analysis of intergranular phase in ZnO varistors usually confirmed the presence of Bi, Zn, Sb and Cr[1], as well as small quantities of some other elements, such as Co, Mn, and Si.[7] Unfortunately, in all previous investigations, intergranular phase did not contain γ-Bi_2O_3. Although there is no literature data about chemical composition of γ-Bi_2O_3 phase in ZnO varistors, Cerva supposed that it is stabilized with Zn^{2+} ions.[2]

In this work varistor microstructural and electrical properties were investigated as a function of chemical composition of Bi_2O_3 phase. Several powder mixtures, differing only in starting chemical and phase composition of Bi_2O_3 phase, were prepared using DMCP method,[8,9] which means that each phase was prepared separately and final ceramics was obtained by sintering the mixture of the crystal phases. Therefore the composition of the starting Bi_2O_3 and other phases was known. The changes in phase composition and redistribution of additives after sintering were determined from chemical analysis of constituent phases in final ceramics. The electrical properties of the varistors were related to the phase composition of the intergranular phase.

Experimental procedure

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).

ZnO phase was prepared by suspending ZnO in solution of $Co(NO_3)_2$ and $Mn(CH_3COO)_2$, followed by evaporation of suspension, calcination and milling of the powder. Spinel and Bi_2O_3 phases were prepared by solid state reactions of appropriate amounts of oxides. The formula of spinel phase is calculated by averaging results of chemical analysis of spinel phase given by other authors.[1,5,10]. Thermal conditions for its preparation are given elsewhere.[8,9]

Oxides chosen for stabilization of desired Bi_2O_3 phases (γ- or β-Bi_2O_3) were metal oxides, which are commonly present in varistors. Ratio between Bi and Me ions was based on literature data.[6,11]. Thermal treatment used for preparation of Bi_2O_3 phases, as well as composition of obtained samples are given in Table 1. Single γ-Bi_2O_3 phase was obtained in compositions Bi-Mn and Bi-Zn, and the mixture of two γ-Bi_2O_3 phases was obtained in composition Bi-Si-Zn. After thermal treatment of composition Bi-Sb the mixture of γ-Bi_2O_3 and β-Bi_2O_3 in approximate mass ratio 1:5 was found, although literature data suggested that the pure β-Bi_2O_3 should be obtained.[11] The lattice constants of the obtained phases are in accordance with literature data.[6,11]

Varistor mixtures with a composition 85 wt.% of ZnO phase + 10 wt.% of spinel + + 5 wt.% of Bi_2O_3 phase were homogenized in an agate planetary ball mill for 2 h, pressed into pellets sized approximately 8 mm × 1 mm and sintered at 1473 K, for 1 h. Sintering conditions were chosen according to the earlier results.[8, 9] In further discussion varistor mixtures will be designated according to the Bi_2O_3 phase (for example: Bi-Mn varistor is varistor that contains Bi_2O_3 phase designated Bi-Mn).

Characterization of the initial powders and the resulting ceramics was made by X-ray powder diffraction, XRPD, (Philips PW 1710 powder diffractometer with graphite-monochromatized CuKα radiation), optical and scanning electron microscopy (JEOL JSM-T330A) and energy dispersive X-ray analysis (EDS).

Electrical properties were registered within the 0.1-10 mA/cm^2 region using a dc measurements. The nonlinearity coefficients were determined within the ranges 0.1-1.0 mA/cm^2 (α_1) and 1.0-10 mA/cm^2 (α_2), the breakdown field (K_C) was measured at 1A/cm^2, and the leakage current (J_L) was determined at an electrical field of $0.8 \cdot K_C$. Voltage per barrier (U_b) was determined from the values of K_C and D (where D is ZnO grain size), according to the equation $U_b = K_C \cdot D$.

Results and discussion

X-ray diffraction analysis of sintered samples showed that all samples had the same phase composition: ZnO, spinel and γ-Bi_2O_3. This means that the thermal treatment lead to formation of only one γ-Bi_2O_3 in samples Bi-Si-Zn and Bi-Sb. XRPD pattern of Bi-Sb sample after sintering (Fig. 1) confirms change in phase composition of intergranular phase.

Due to low Bi_2O_3 content only few well-separated, but weak maxima, belonging to γ-Bi_2O_3 phase were visible in varistor XRPD patterns. Therefore it was possible to calculate only approximate lattice constants of resulting γ-Bi_2O_3 phases. They were in the range 10.13-10.21 Å and were changed in respect to the starting values. EDS analysis of intergranular phase showed that it contains γ-Bi_2O_3 stabilized mainly with Zn^{2+}. Depending on starting compositions traces of several elements, such as Mn, Sb, Cr, Co were also detected (Fig. 2). According to Takemura and co-workers the wide range of observed lattice constants can be attributed to the volume contractions and stresses at grain boundaries because of phase transformations and other processes occurring during liquid phase sintering of the varistors.[5]

Diffusion processes taking place during sintering lead to partial redistribution of additives, as well as to formation of single γ-Bi_2O_3 mainly doped with Zn^{2+} ions. The formation of γ-Bi_2O_3 of this composition looks the most probable if a great excess of ZnO in all systems is taken into account. The appearance of liquid phase during sintering promote diffusion, as well as dissolution of small quantities of ZnO in liquid Bi_2O_3 phase, and consequently increase probability of formation of Zn-stabilised γ-Bi_2O_3.

All samples showed almost identical composition of spinel and ZnO phases, although small variations in peak intensities were observed. EDS analysis of ZnO phase showed only presence of Zn and no traces of Co or Mn (Fig.3a), probably because they are present in quantities which are under detection limits. X-ray diffraction analysis of the ZnO phase showed slight increase (0.02-0.2 %) of lattice constants in comparison to starting phase. EDS spectra of typical spinel phase composition are given in Fig. 3b. Lattice constants of spinel phase also increased for maximally 0,3 % in comparison to the starting spinel.

Results of microstructural analysis showed similar shape and distribution of phases, as well as porosity and homogeneity of the samples. Based on these results and fact that all samples has the same phase composition, similar electrical properties of the samples could be expected. Nevertheless, Bi-Mn sample showed pronounced differences in electrical properties (Table 2).

Bi-Mn samples showed significantly higher values of nonlinearity coefficient α_2 and voltage per barrier-U_b, while Bi-Zn sample had the lowest value of leakage current J_L. These results are a consequence of diffusion processes taking place during sintering and could be rationalized as follows. Bi-Zn sample is the most stable composition, changed in the lowest extent, since it already contained γ-Bi_2O_3 stabilized with ZnO. This gives a possible explanation for low value of J_L in this sample. Similar study of varistors differing only in composition of spinel phases also showed that the best characteristics are found for the most stable compositions, *i.e.* in compositions that were changed in lower extent during sintering.[9] This is in accordance with here presented results.

On the other hand, Bi-Mn samples contains higher amount of Mn than other varistors. Based on composition of the starting phases in Bi-Mn varistors it is possible to calculate that Bi_2O_3 phase in this sample contains two times higher quantity of Mn than entire ZnO phase. Mn diffuses from Bi_2O_3 phase to other phases during sintering. It could be supposed that Mn^{x+} ions are mainly incorporated into ZnO phase, which means that ZnO phase in Bi-Mn varistors contains approximately three times higher concentration of Mn than other samples. This may partially explain different electrical properties of Bi-Mn sample. Besides the quantity of Mn, valence of Mn-ions should also be considered. ZnO phase is doped with Mn^{2+} ions, but Bi_2O_3 phase contains Mn^{4+}. Driear et al.[13] investigated influence of valence state of Mn^{x+} (x = 2 or 4), and of Co^{y+} ions (y = 2 or 3) on ZnO varistor properties and concluded that charge of these ions has a significant influence on their concentration in ZnO grains, as well as on grain size and porosity, and consequently on electrical properties. It was shown that presence of Mn^{4+} ions decreases ZnO grain size and porosity. This is in accordance with our results, because we have also observed the smallest grains in Bi-Mn varistors in comparison with other compositions. Influence of Mn and Co valence state was also investigated by some other authors.[13] They found that samples prepared with MnO_2 always contain higher concentration of Mn^{4+} than samples prepared with MnO, although Mn^{2+} ions should be more stable than Mn^{4+} under used sintering conditions. A systematic investigation of electrical properties as a function of Mn^{x+} valence state showed that varistors which contains higher concentration of Mn^{4+} also have higher concentration of donors, which results in increase of potential barrier at the grain boundaries. Our results confirmed this conclusion since we also found higher U_b in Bi-Mn samples.

Conclusions

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

All varistors showed almost identical microstructures. Observed differences in electrical properties are explained by diffusion and redistribution of additives during sintering, which results in different concentrations of additives in ZnO grains, and at grain boundaries. Investigated varistors showed excellent electrical properties, nonlinearity more than 50 and low values of leakage current.

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References

[1] Inada M., Formation of non-ohmic zinc oxide ceramics. *Jap. J. Appl. Phys.,* 1980, **19**, 409-419.

[2] Cerva H. & Russwurm W., Microstructure and crystal structure of bismuth oxide phases in zinc oxide varistor ceramics. *J. Am. Ceram. Soc.*, 1988, **71**, 522-529.

[3] Olsson E. & Dunlop G.L., The Effect of Bi_2O_3 Content on the Microstructure and Electrical Properties of ZnO Varistor Materials. *J. Appl. Phys.*, 1989, **66**, 4317-4324.

[4] Cerva H. & Russwurm W., Anaysis of Bismuth Oxide Grain Junctions in ZnO Varistors by Transmission Electron Microscopy. In *Ceramic Transactions, Vol. 3, Advances in varistor technology,* ed. L.M. Levinson. The American Ceramic Society, Westerville, OH, 1989, pp. 93-100.

[5] Takemura T., Kobayashi M., Takada Y. & Sato K., Effects of contents of Bi_2O_3 and Sb_2O_3 on lattice parameters of phases of ZnO varistor ceramics. *Jpn. J. Appl. Phys.,* 1986, **25**, 293-294.

[6] Levin E.M. & Roth R.S., Polymorphism of bismuth sesquioxide. II. Effect of oxide additions on the polymorphism of Bi_2O_3. *J. Res. Nat. Bureau Stand. A, Phys. and Chem.,* 1964, **68A**, 197-206.

[7] Kanai H., Imai M., Effects of SiO_2 and Cr_2O_3 on the formation process of ZnO varistors. *J. Mater. Sci.*, 1988, **23**, 4379-4382.

[8] Branković Z., Milošević O., Poleti D., Karanović Lj. & Uskoković D., ZnO varistors prepared by direct mixing of constituent phases. *Materials Transactions, JIM,* 2000, **41**, 1226-1231.

[9] Branković Z., Branković G., Poleti D. & Varela J.A., Structural and electrical properties of ZnO varistors containing different spinel phases. *Ceramics International,* 2001, **27**, 115-122.

[10] Bäther K.H., Hinz D., Mattern N., Bitterlich M. & Brückner W., Spinel phases in ZnO varistors. *Phys. Status Solidi A*, 1980, **61**, K9-K11.

[11] Tanji H., Bradt R.C., Thermal expansion of Sb_2O_3-stabilized Bi_2O_3 polymorphs. *J. Am. Ceram. Soc.,* 1980, **63**, 715-716.

[12] Driear J.M., Guertin J.P., Sokoly T.O. & Hackney L.B., in *Grain boundary phenomena in electronic ceramics, Advances in Ceramics,* ed. L.M. Levinson. Columbus, Ohio, 1981, **1,** p. 316-330.

[13] Chen Y.-C., Shen C.-Y. & Wu L., Grain growth processes in ZnO varistors with various valence states of manganese and cobalt. *J. Appl. Phys.*, 1991a, **69**, 8363-8367.

Table 1. Thermal treatment conditions for preparation of Bi_2O_3, phase composition and corresponding lattice constants.

Mixture	Temperature (K)/Time (h) of Thermal Treatment	Phase Composition	Lattice constants (Å)
Bi-Mn	963/6 + 1073/3	γ-Bi_2O_3	10.221(1)
Bi-Zn	963/3 + 1073/3	γ-Bi_2O_3	10.196(3)
Bi-Si-Zn	963/1.5	γ_1-Bi_2O_3 + γ_2-Bi_2O_3	10.112(3)-γ_1; 10.199(2)-γ_2
Bi-Sb	963/2.5	β-Bi_2O_3 + γ-Bi_2O_3	β: a = 7.738(9), c = 5.609(3) γ: a = 10.243(6)

Table 2. Characteristic parameters of investigated samples

Varistor	α_1	α_2	J_L (μA/cm^2)	K_C (V/mm)	U_b (V)	D (μm)
Bi-Mn	28	52	8,6	420	3,2	7,5
Bi-Zn	30	28	5,4	290	2,6	8,9
Bi-Si-Zn	31	28	8,4	322	2,6	8,1
Bi-Sb	29	34	8,2	326	2,7	8,4

Figure captions:

Fig. 1. XRPD pattern of Bi-Sb sample sintered at 1373 K.

Fig. 2. EDS of intergranular phase for samples **a)** Bi-Mn, **b)** Bi-Sb.

Fig. 3. EDS of **a)** ZnO grain interior of varistor Bi-Mn, **b)** spinel phase of varistor Bi-Mn.

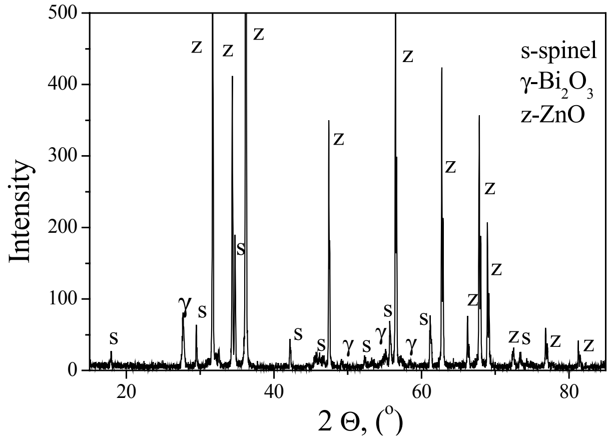
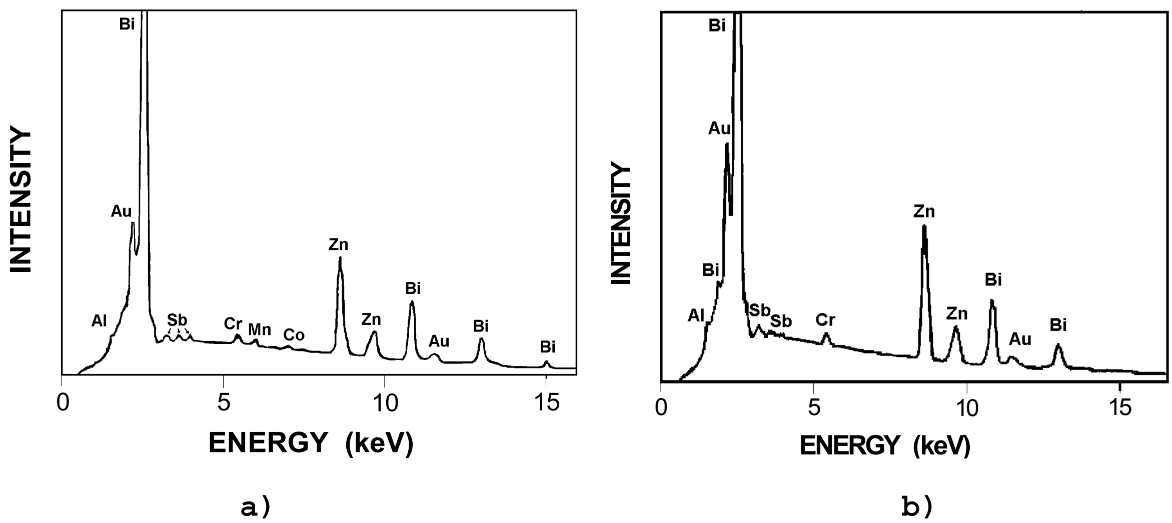


Fig. 1.


INTENSITY
ENERGY (keV)
Bi
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a)
INTENSITY
ENERGY (keV)
Bi
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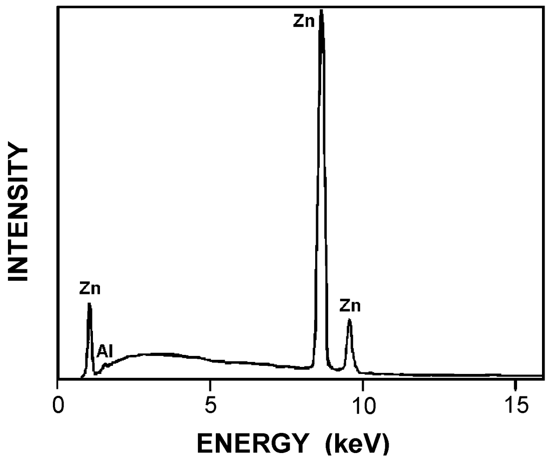
Fig. 2.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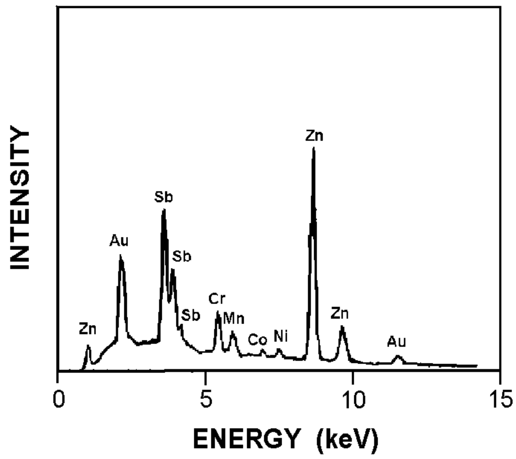
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Fig. 3.