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$BaBiO_{2.77}$ as a promoter of the varistor property in zinc oxide ceramics

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Abstract

Metal oxide varistors typically are made by bulk ceramic technology. The homogeneity of ceramics and the grain interface profile are of primary concern in varistor design and processing. The nonohmic property in the ZnO varistor is attributed to the Bi enrichment at ZnO grain boundaries and Bi-rich intergranular layer. The Bi susceptibility for formation of agglomerates and volatilization during varistor sintering is a problem. To overcome it, we decided to pre-react Bi_2O_3 with Ba and add the varistor mixture with $BaBiO_{2.77}$ instead of Bi_2O_3. As it appeared, $BaBiO_{2.77}$ addition benefits varistor ceramics in many ways. Varistors have better electrical properties. The origin of nonohmic behaviour takes place at a lower temperature, 1100 instead of 1250°C. The Bi phase distribution in the ceramics is homogenous. Also, the volume of not contributing with break-down voltage intergranular phase is restrained. Taking into account that due to it the amount of additives decrease and that at lower sintering temperature, less volatile Bi is liberated to ambient, $BaBiO_{2.77}$ addition benefits varistors not only technologically but also from the point of view of economics and environment protection. © 2001 Published by Elsevier Science Ltd.

Keywords: $BaBiO_{2.77}$; Electrical properties; Microstructure-final; Varistors; ZnO

1. Introduction

Varistors exhibiting non-linear resistance are widely used as protection devices against voltage surges. One of the several materials which exhibits non-linear current–voltage characteristics is zinc oxide containing a small amount of bismuth oxide and other metal oxide additives.

Non-ohmic behaviour of the $ZnO–Bi_2O_3$ system was first discovered by Kosman et al.[1,2] It is usual to say that ZnO ceramics with five additives of Bi_2O_3, Sb_2O_3, Co_2O_3, MnO_2 and Cr_2O_3 was revealed by Matsuoka.[3,4] Also, in this system Bi_2O_3 has been found essential for imposing non-ohmic property to the ZnO.

During varistor processing, the additive oxide powders are mixed with ZnO, which is then pressed and sintered between 1000 and 1300°C. For the time of continuance of sintering, the ZnO grains are three-dimensionally separated from each other by an intergranular layer formed by the reaction of additives with each other and with ZnO. The main and most important component of the intergranular layer is the Bi_2O_3. The Bi_2O_3–ZnO system, liquid at high (>740°C) temperatures, penetrates and modifies the boundaries of ZnO matrix grains.[5–8] As a result, the potential barriers, responsible for non-ohmic behaviour are formed.

In the intergranular layer, besides Bi-rich liquid phase dissolving several elements (Bi, Zn, Sb, Cr, Co, Mn), secondary solid phases such as spinel $Zn_7Sb_2O_{12}$, pyrochlore $Zn_2Sb_3Bi_3O_{14}$ and Bi_2O_3 crystal phases are also present.

The pyrochlore $Zn_2Sb_3Bi_3O_{14}$ phase was primarily identified by Wong.[5] It forms at 750–850°C and over 1000°C[13,14] reacts to ZnO forming spinel and an additional amount of bismuth-rich liquid.

$$Bi_2(Zn_{4/3}Sb_{2/3})O_6 + ZnO = Zn(Zn_{4/3}Sb_{2/3})O_4 + Bi_2O_3$$

Bi_2O_3 which, as mentioned above, is directly responsible for varistor non-ohmic behaviour, also affects the varistor electrical properties indirectly by promotion of ZnO grain growth during sintering. The α-$Zn_7Sb_2O_{12}$ spinel particles, by pinning migrating ZnO grain boundaries, retard the ZnO grain growth.[15,16]

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Unfortunately, the bismuth-rich liquid phase, due to thermal expansion mismatch between Bi_2O_3 and ZnO, also develops the tensile stresses in varistor ceramics. Besides, the tensile stresses are developed by the secondary phases present in Bi-rich liquid (spinels, pyrochlore, Bi_2O_3 crystallite phases). For example, during the solidification of Bi_2O_3 as β-phase, the increase of volume is assumed to be 2.7%.[17] The β to γ transition during the additional annealing (to decrease electrical degradation effect) results in a volume contraction of 3 vol.%. With these in mind, we aimed at the restraint of the volume of the intergranular phase.

Because the operation of varistors results from a Bi and other additives enrichment at ZnO–ZnO grain boundaries rather than from Bi_2O_3 quantity, there was no risk that the limitation of volume of liquid phase would impose undue effects to electrical properties of varistors. The volumetric Bi-rich liquid intergranular phase, like the ZnO junction containing a pyrochlore phase, does not provide a barrier to electrical conduction. Only ZnO junctions separated by thin Bi-rich intergranular amorphous film or having Bi atoms pinned in barriers give the breakdown voltages 3.2 and 3.6 V, respectively.[8,9] Because there is no variation in wettability of ZnO grains with respect to the volume of Bi-rich liquid, we decided to limit the amount of Bi liquid by the restraint of the $Zn_2Sb_3Bi_3O_{14}$ pyrochlore phase and finding out the other compound capable of decomposing with liberation of Bi liquid during the heating, but in less quantity. Examining varistor ceramics additives able to form compounds with Bi, we ran against Ba and Ti.

The role of Ba and Ti additives is known in literature.[10,11] Low voltage varistor ceramics are usually added with TiO_2 or $Bi_4Ti_3O_{12}$ (BIT).[12] The fact that Ba compounds benefit varistor nonlinearity was obvious to Matsuoka[18] as early as 1969. He was followed by others[19–21] who added varistor ceramics with Ba compounds of various type and amounts. Yang and Wu[22] established that TiO_2 varistor samples containing Ba provided better barriers to electrical conduction than samples containing Bi. The best barriers were formed in samples containing both Ba and Bi.

Looking through Ba–Bi compounds, we noticed that $BaBiO_{2.77}$ reacts more readily with varistor ceramics additives (with Ti especially), than with ZnO. $BaBiO_{2.77}$ reacts with Ti at 650–750°C forming barium titanate and Bi_2O_3. Our rights to the varistor mixture with barium bismuth oxide addition are secured by patent.[23]

The functional dependence of current I on applied voltage V in the non-ohmic regime may be expressed by $I = KV^{\alpha}$ where α is the nonlinear exponent and K is a constant.

2. Experiments

For comparison purposes, two mixtures of varistor ceramics were prepared. They had the same chemical composition but differed in the manner of addition. The first mixture was added with $BaBiO_{2..77}$. $BaBiO_{2..77}$ was synthesised and identified on the basis of the crystal data of the Powder Diffraction Files (PDF 38-1151). The other mixture was added with $Bi_2Ti_2O_7$ and $Ba(OH)_2$.

The other additives of the mixtures were typical. They were analytically pure metal oxides. The details on powder mixtures composition are given in Table 1.

Additionally, A3 mixture, with a triple amount of sample A components, was prepared in order to make crystal phase identification easier. The varistor ceramics is a multicomponent structure and some components may form solid solutions and rearrange diffraction spectrum. In addition, some weak reflections may lie below the XRD detection limits.

Varistor samples were prepared using a conventional ceramic technique. Mixtures were wet milled for 18 h, then dried. The dried powders were sifted through a nylon mesh and pelletised in discs. The pressed discs containing about 7 wt.% of binder, weighing 1.6 g, 15 mm in diameter and 2.5 mm thick were sintered at two different temperatures: 1100 and 1250°C for 1 h and furnace cooled.

For electrical measurements, Ag electrodes were formed on both polished surfaces of discs by vacuum evaporation.

The microstructure of varistor samples was examined by scanning electron microscopy (SEM). SEM micrographs and mapping images of element distribution were taken using Jeol JXA-5A X-ray microanalyser. The crystal phases of the samples were identified using X-ray diffraction (XRD) method by means of DRON-2 powder diffractometer using Co K_{α} radiation and Fe filter. X-ray powder patterns were recorded in a scan

Table 1
Compositions of samples used in this study

Sample	ZnO	Amount of additives (mol%)								
		$Bi_2Ti_2O_7$	$Ba(OH)_2$	$BaBiO_{2.77}$	TiO_2	Sb_2O_5	Co_2O_3	NiO	MnO	Cr_2O_5
A	95.75	–	–	1.5	0.75	0.5	0.5	0.5	0.25	0.25
B	96.1	1.7	0.2	–	–	0.5	0.5	0.5	0.25	0.25

mode so that $\Delta 2\theta = 0.05°$. The crystal phases were identified on the basis of the crystal data of the PDF.

3. Results

The phase transitions with temperature in sample A3 (with a triple amount of sample A components) are shown in Fig. 1.

As can be seen $BaBiO_{2..77}$ reacts with TiO_2 already at 650°C, what is confirmed by appearing of reflections of $BaTiO_3$, disappearing the diffraction lines of $BaBiO_{2..77}$ and some weak reflections of γ-Bi_2O_3 and rearranged reflections from subcrystallite pyrochlore phase are also present.

At 850°C, the pyrochlore phase is still present and Bi_2O_3 crystallises in γ form. Further increase of temperature up to 950°C causes the strong crystallisation of the all phases present in varistor ceramics. Bi_2O_3 crystallises in distorted β-form and diffraction lines of zinc titane-antimony spinel appear. The barium titanate reflection lines are also present.

X-ray powder pattern of the sample sintered at 1150°C gives evidence that there is no more phase changes resulted from the temperature increase.

Table 2 gives the another view on crystal phases present in sample A3. The measurements of characteristic X-ray intensities were carried out on the surface and polished surface of sintered body.

On the surface of the sample $BaCr_2O_4$ (PDF 20-0372) and $BaTiO_3$ (PDF 31-0174) were traced. Taking into account that Bi_2O_3 above 740°C diffuses out from the sample body and entrains the dissolved elements on sample surface, the presence of $BaTiO_3$ and $BaCr_2O_4$ on sample surface proves that Ba, Ti and Cr elements dissolve in Bi_2O_3 liquid.

XRD studies of the A3 body (polished sample) revealed the existence of matrix ZnO phase, $BaTiO_3$ (PDF card No 31-0174), Bi_2O_3 (27-0050) and zinc titane–antimony spinel.

The lattice parameter a of spinel elementary cell was 8.517 Å and was smaller than a lattice constants of both $Zn_7Sb_2O_{12}$ ($a = 8.585$ Å, PDF 15-0687) and $Zn_{1.91}Ni_{0.15}Co_{0.08}Mn_{0.07}Cr_{0.23}Sb_{0.57}O_4$ ($a = 8.56$ Å) spinels, the last one modified by conventional additives of waristor ceramics. On the other hand the $a = 8.517$ Å is higher than a parameter ($a = 8.45$ Å) of $Zn_{1.54}Ni_{0.16}Co_{0.1}Mn_{0.42}Ti_{0.78}O_4$ titan–zinc spinel.[24] So, the diminished lattice parameters of our zinc–antimony spinel we attributed to Ti-enrichment. Its chemical composition we expressed as $Zn_7(Sb,Ti)_2O_{12}$.

As was anticipated, not all phases present in sample A3 were identifiable in varistor samples A and B. Anyway, besides the matrix ZnO phase some reflections of

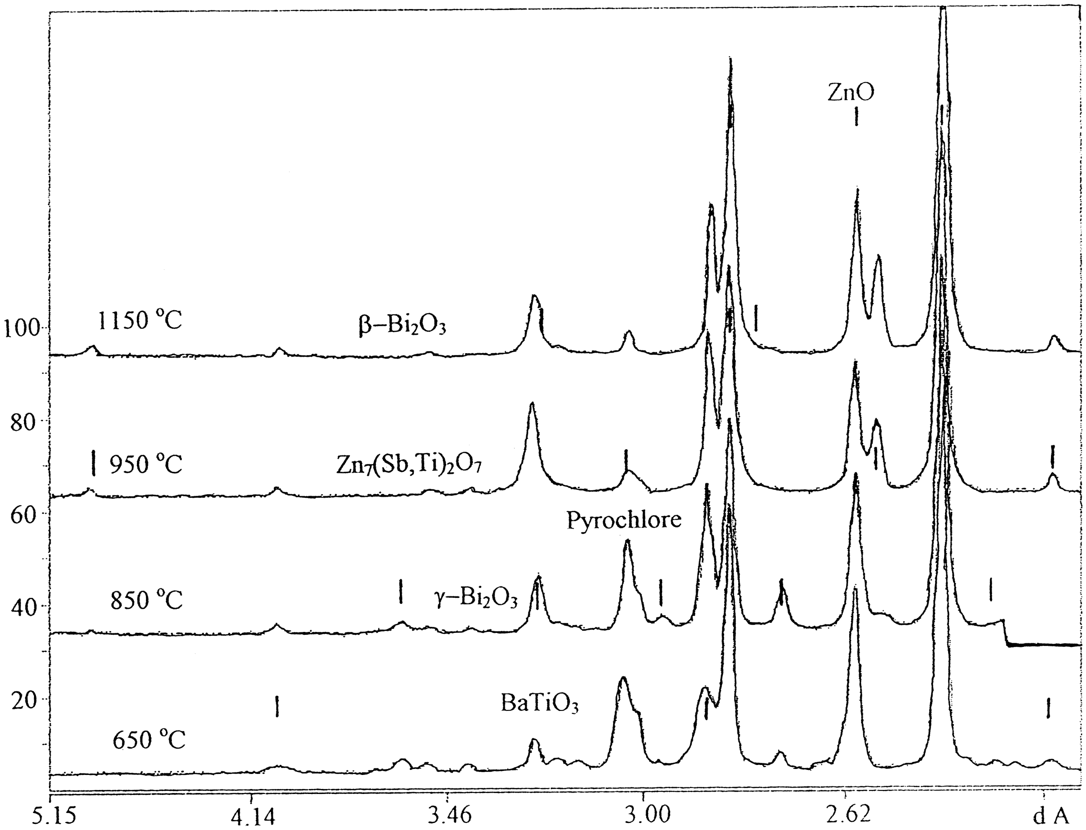

Fig. 1. X-ray (Co radiation) patterns of A3 sample. The phase transitions with sintering temperature.

Table 2
X-ray diffraction measurements of A3 sample sintered at 1150°C

Measured pattern	Surface	Polished samples		Data of identyfied phases									
				ZnO 05-0644		$BaTiO_3$ 31-0174		$Zn_7(Sb,Ti)_2O_{12}$		Bi_2O_3 27-0050		$BaCr_2O_4$ 20-0372	
2θ	*d* (Å)	*I*	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*	*d* (Å)	*I*
21.1	4.889	6	3					4.917	18	5.464	2	5.291	8
22.8	4.529	1										4.505	15
23.4	4.414	1										4.367	20
25.7	4.025	7	2			4.032	12						
26.1	3.964	7										3.937	30
26.7		1										3.817	10
28.3	3.662	11										3.636	33
29.6	3.504	33	1							3.466	3	3.509	100
30.6	3.392	14	2									3.375	43
32.2	3.228	18	15									3.205	45
32.8	3.175	22	-							3.195	100	3.155	75
34.7	3.002	11	8					3.011	45	2.950	2		
36.1	2.889	11	-										
36.6	2.851	78	34			2.849	100					2.857	35
37.1	2.814	100	62	2.817	70					2.817	15		
37.8	2.763	9								2.740	25	2.740	55
40.2	2.605	89	42	2.604	55					2.646	1	2.525	8
40.8	2.568	54	23					2.568	100				
42.4	2.475	100	100	2.475	100			2.458	25				
44.7	2.354	2								2.347	1	2.358	30
45.2	2.329	11	3			2.326	30						
47.0	2.245	3										2.237	15
48.8	2.167	11								2.183	1	2.160	55
49.2	2.150	8								2.146	1	2.146	70
49.7	2.130	9	5					2.129	35				
50.3	2.106	3										2.105	20
52.7	2.017	22	8			2.016	35			2.004	1		
53.8	1.992	4	6					2.007	14	1.961	20	1.953	15
56.0	1.907	24	23	1.912	25					1.934	11		
58.6	1.829	1								1.876	1	1.894	10
59.6	1.801	2				1.802	10			1.783	2		
62.0	1.738	3	2					1.738	20				
64.0	1.689	7	4							1.689	11		
66.0	1.643	22	15					1.639	25	1.656	20		
66.8	1.626	78	41	1.626	40					1.650	12	1.626	30
73.0	1.505	13	9			1.505	20	1.505	40	1.595	8		
74.7	1.475	26	33	1.477	35								

β- or δ-Bt_2O_3 were identified in both sintered samples. In sample A, zinc–antimony spinel was traceable.

To obtain more detailed information on phase spatial arrangement, the SEM photomicrographs of samples A and B sintered at 1100°C were taken. The microstructure of polished A sample is shown in Fig. 2a. Bright areas in photomicrograph indicate heavy elements, in for case for bismuth and antimony. The more contrasted area (grey) shows the presence of ZnO matrix grains. Strong contrasts indicate pores.

The area distribution maps of Ba, Bi, Sb, Ti elements visible in Fig. 2b–e reveal that element clusters actually do not exist in sample A. The uniform distribution is characteristic in particular to the Bi-rich phase (Fig. 2b). The distribution of Ba (Fig. 2c) is not so uniform. Ba occurs in the company of Ti (Fig. 1d) and these must be the places where $BaTiO_3$ particles are present. There are Ba particles which are in common with Cr (Cr distribution map is not included here). In all probability, they are $BaCr_2O_4$ phase. At last, for reasons that are not well known, some Ba particles are present together with Sb (Fig. 1e) and Ti.

The distribution of Ti and Sb is, in general, the same, i.e. Ti and Sb are identified in the same places, which suggests the existence of zinc–antimony spinel enriched with titanium.

In respect to structure character, sample B differs from sample A. The SEM images of sample B are seen in Fig. 3. As can be seen, the crystalline phases in sample B are clearly separated from the ZnO matrix grains

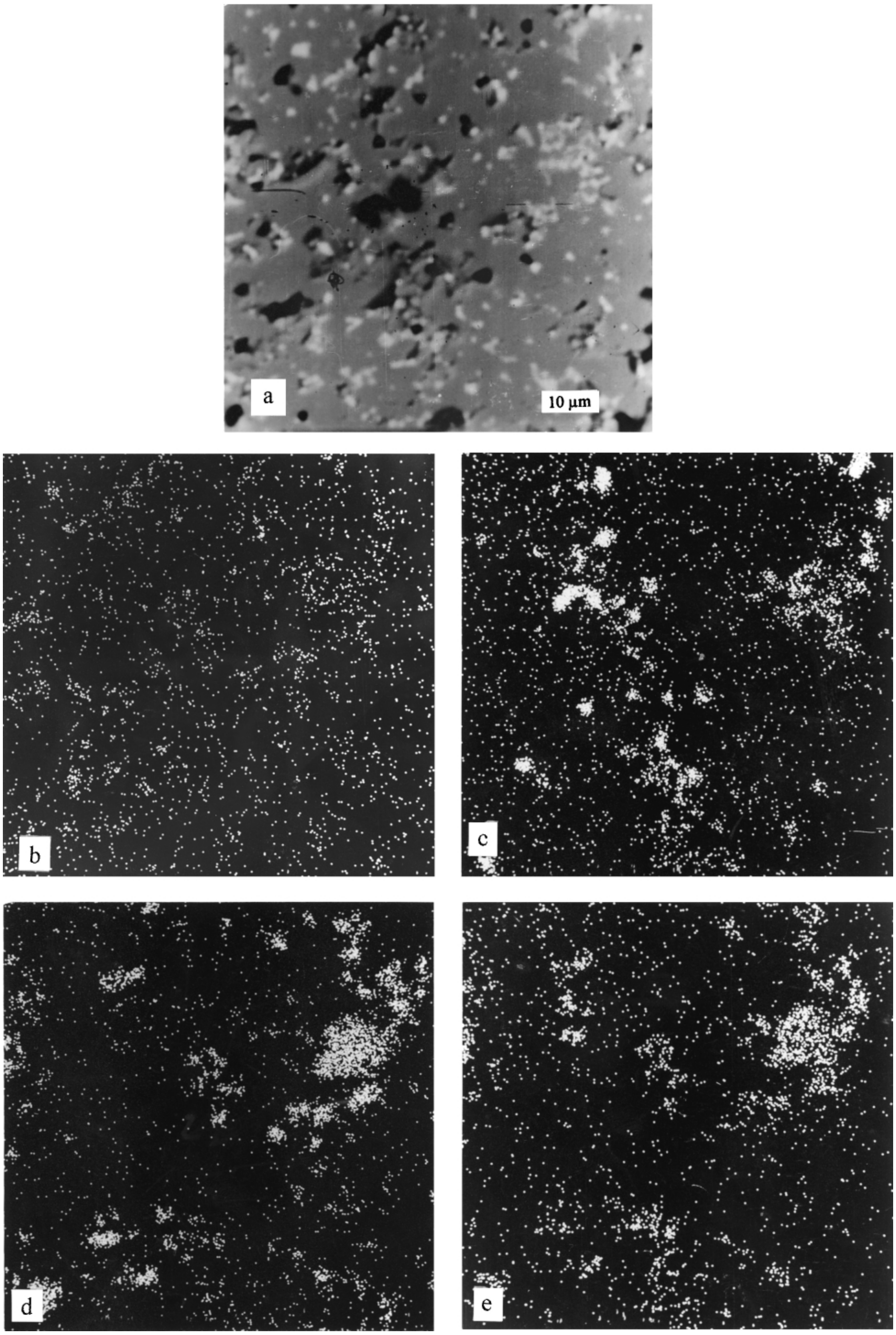

Fig. 2. SEM micrographs of sample A: (a) microstructure of polished sample; the area distribution maps of elements (b) Bi, (c) Ba, (d) Ti, (e) Sb.

(Fig. 3a), i.e. there is not saturation and penetration of ZnO grain boundaries by Bi_2O_3 phase. Bi_2O_3-rich intergranular regions (Fig. 3b) form a few microns large clusters. Ba phase distribution is shown in Fig. 3c. Ba occurs in the company of Ti and in the form of large clusters also containing Sb Ti (Fig. 3d and e) and Bi.

These microstructural differences of A and B samples vary markedly the varistor electrical properties. The *I–V* characteristics of A and B varistor samples sintered at 1100 and 1250°C are shown in Table 3.

The varistor samples were examined by passing through their bodies dc current in range from 10 μA up to 10 mA. As can be seen, sample A, in comparison to sample B, was characterised by higher breakdown voltages and higher nonlinear exponents. Nonlinear coefficients α for sample A were in the range 40–50 while α

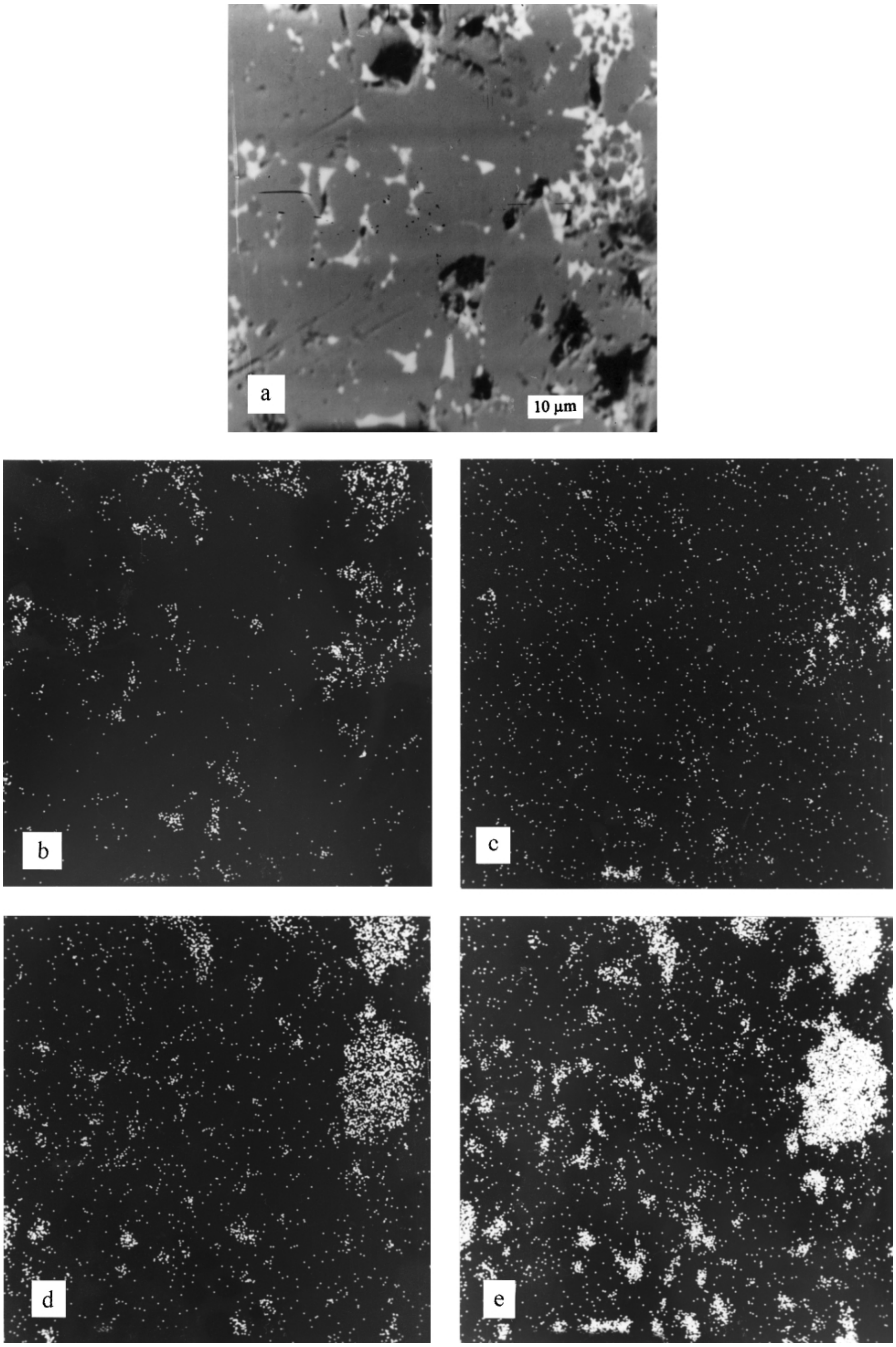

Fig. 3. SEM micrographs of sample B: (a) microstructure of polished sample; the area distribution maps of elements (b) Bi, (c) Ba, (d) Ti, (e) Sb.

Table 3
The I–V characteristics of A and B varistor samples sintered at 1100 and 1250°C

Varistor sample	Sintering temperature (°C)	10 uA	α coefficient	100 uA	α coefficient	1 mA	α coefficient	10 mA	$U_{1\ \mathrm{mA/1mm}}$ (V)
A	1100	428	54	447	46	470	39	498	235
A	1250	227	36	243	40	258	40	274	117
B	1100	155	11	190	21	212	24	234	95
B	1250	50	8	67	6	96	14	114	41

values for sample B were less than 24. The breakdown voltages and nonlinear exponents decreased with increasing sintering temperature for both studied samples. The comparison of *I–V* characteristics of sample A sintered at 1250°C and B sintered at 1100°C gives another proof that the ZnO grain interfaces of sample A are better profiled and decorated with Bi and other additives (higher α coefficient and the same characteristic voltage).

4. Conclusion

The research carried out proved that $BaBiO_{2.77}$, due to $BaBiO_{2.77}$ reaction to TiO_2, actively modifies the nonohmic property in metal oxide varistor ceramics. This is true not only for TiO_2 but also for other metal (Cr, Mn, Sb) oxides. XRD reflections of $BaTiO_3$ appear at 650°C along with weak crystallised γ-Bi_2O_3 phase. At 850°C, Bi_2O_3, liberated during $BaBiO_{2.77}$ reaction to TiO_2, is already well crystallised in γ-Bi_2O_3 and pyrochlore $Zn_2Sb_3Bi_3O_{14}$ phase is present. At 950°C, all the crystal phases constituting the ZnO ceramics are formed. They are distorted β-Bi_2O_3, barium titanate– and zinc titane–antimony spinel. The diminished lattice parameter of zinc–antimony spinel ($a = 8.517$ Å) identified in ceramics added with $BaBiO_{3-x}$,in comparison to $a = 8.585$ Å of α-$Zn_7Sb_2O_{12}$ spinel is the effect of embodiment of Ti in crystal lattice of the identified spinel.

Further increase of temperature causes the saturation and penetration of ZnO–ZnO grain borders by Bi-rich liquid and appearance of the non-ohmic property in ceramics. The origin of nonohmic behaviour in composition added with $BaBiO_{2.77}$ takes place at a lower temperature: 1150 instead of 1250°C. The other components, besides Bi, constituting an intergranular layer are Ba, Cr, Ti and Sb. The large amount of $BaCr_2O_4$, $BaTiO_3$ and $Zn_7(Sb,Ti)_2O_{12}$ phases on varistor surfaces gives evidence that they are dissolved in Bi_2O_3, which is essential for ceramics varistor behaviour. Phases dissolved in Bi_2O_3 condense on ZnO particle surfaces while the Bi_2O_3 volatilizes.

Compared to traditional additives, $BaBiO_{2.77}$ addition benefits varistor ceramics in uniform distribution of Bi, limitation of inactive electrically intergranular regions and improvement of varistor electrical properties.

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