

## Electrical properties of varistors in relation to their true bismuth composition after sintering

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### Abstract

New varistors compositions are often directly evaluated in relation to varistor electrical characteristics. The compositions are well known since it is easy to weigh with accuracy the single oxides raw materials. However, this paper emphasizes the fact that the compositions of ceramics used to carry out electrical measurements differ from green ceramics. For instance and depending on the conditions, it is shown that bismuth can be either vaporized or can diffuse inside the substrate during the sintering. To reduce the loss of material we suggested using a new route where ceramics are produced by mixture from pre-synthesized spinel and pyrochlore phases with the other classical single oxides additives such as Co, Mn, Cr, Ni, etc. ©2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Varistors; Sintering; Bismuth

### 1. Introduction

Since the seventies ZnO varistors ceramics have been produced in large quantities. Despite many improvements the production of electronic components made of ceramics remains an industrial challenge. For instance in 1994, about 5 to 10% of sintered pieces were still withdrawn from commercialization when though specifications were requested such as a narrow statistical spread of breakdown voltages [1]. Many sources of problems may arise in a ceramic process due to the number of industrial operations that need specific care: quality control of raw materials, slip homogeneity, spraying, pressing operations, etc. Among these operations, the composition after sintering is difficult to handle because several oxides with high vapor pressure are used in typical ZnO varistor formulation used as arresters in power transmission. The composition is likely to change after sintering because of component vaporization. Beyond the control of electrical properties of varistors there is also the problems in production of furnace life-expectancy and toxicity of vaporized oxide such as antimony and bismuth in the expanding atmosphere.

### 2. Bismuth and antimony oxide as powder materials

Bismuth oxide has at least four polymorphs ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ). There are very different from the point of view of the structure [2] or the stability [3]. Monoclinic form  $\alpha$  is stable at room temperature up to 730°C where it is transformed to  $\delta$ -Bi<sub>2</sub>O<sub>3</sub>. This structure can be retained at room temperature by quenching. It is stable between 730°C until the oxide fusion at 825°C. This high temperature form consists of a Bi<sub>4</sub>O<sub>6</sub> molecule in a cubic unit cell, so that Bi component can be easily vaporized as Bi<sub>4</sub>O<sub>6</sub>(g) species. Hence, although the vapor species for low O<sub>2</sub> pressures over Bi<sub>2</sub>O<sub>3</sub>(s) have vapor pressure decreasing, respectively, such as Bi(g), Bi<sub>4</sub>O<sub>6</sub>(g) and Bi<sub>2</sub>O<sub>3</sub>(g), the Bi<sub>4</sub>O<sub>6</sub>(g) is considered as being the principal species in air [4]. The  $\beta$  and  $\gamma$  forms are known as metastable polymorphs resulting from cooling from high temperature to 650 and 639°C, respectively. Both phases are subsequently transferred to  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub> around 500°C.

Antimony exists with several oxidation states ranging from III to V: Sb<sub>2</sub><sup>3+</sup>O<sub>3</sub><sup>2-</sup>, Sb<sup>3+</sup>Sb<sup>5+</sup>O<sub>4</sub><sup>2-</sup> and Sb<sub>2</sub><sup>5+</sup>O<sub>5</sub><sup>2-</sup>. The sesquioxide form has two polymorphs:  $\alpha$  which is stable at room temperature until 570 or 605°C depending on the authors [5–6] and  $\beta$  which is the high temperature form which melt at 655°C. Its vapor pressure is about 4 kPa at 655°C. Sb<sub>2</sub>O<sub>4</sub> has also two polymorphs. The low temperature  $\alpha$  and the high temperature  $\beta$  appearing above 933°C [7] in air and melt at 1145°C [5]. Sb<sub>2</sub>O<sub>4</sub> would decompose in air at 1100°C [8] under a total vapor pressure of 4.3 kPa

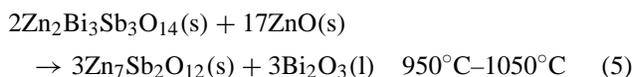
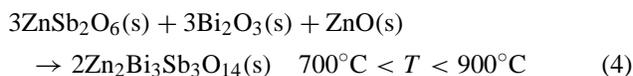
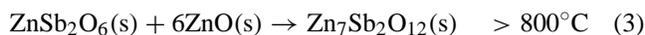
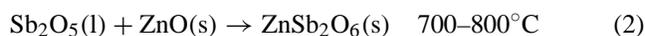
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( $P(\text{Sb}_4\text{O}_6) + P(\text{O}_2)$ ) and eventually  $\text{Sb}_2\text{O}_5$  is decomposed to  $\text{Sb}_2\text{O}_4$  at  $400^\circ\text{C}$  under an oxygen pressure  $P(\text{O}_2) = 6 \text{ kPa}$ .

### 3. Bismuth and antimony oxides in varistor ceramic microstructure

In the case of ZnO ceramic varistors, two oxides are found in the microstructure  $\alpha$  and the high temperature polymorph  $\delta$  [9]. This last polymorph would be retained at room temperature, suggesting that either the  $\delta$  to  $\alpha$  transition is rather sluggish and does not keep pace with the rate of cooling from the sintering to room temperature or that only  $\alpha$  part of  $\text{Bi}_2\text{O}_3$  is transferring to  $\delta$  during heating. However, the presence of these phases is controversial because significant amounts of additives such as Co, Mn, Cr, Ni, etc., have to be taken into account since they can disrupt the polymorphism transformation of bismuth oxide during cooling. Indeed it is known that polymorphs can be both stabilized by specific thermal treatment or by additives. For instance  $\delta$  and  $\gamma$   $\text{Bi}_2\text{O}_3$  can be formed in the system  $\text{Bi}_2\text{O}_3\text{--SiO}_2$  [10]. Then several authors have identified by X-ray diffraction only one  $\beta$  phase [11,12], only one  $\alpha$  [13,14] phase, a mixture of two phases such as  $\beta$  and  $\delta$  phases [15,16] or still a mixture of  $\gamma$  and  $\delta$  phases [17]. Nevertheless most of the authors agree that an annealing between  $600$  and  $800^\circ\text{C}$  leads to the phase  $\gamma$  which can be stabilized at room temperature by slow cooling.

Differential thermal and high temperature X-ray analysis have recently suggested [18] the following reactions for the microstructure development of ZnO varistor during reactive liquid phase sintering in the temperature range  $500\text{--}1050^\circ\text{C}$ :



At the first stage of sintering, after the formation of, first, spinel ( $\text{ZnSb}_2\text{O}_6$ ) and, second, pyrochlore ( $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$ ) phases by reactions (1)–(4), pyrochlore reacts with ZnO to lead to the appearance of a liquid bismuth oxide phase according to reaction (5). This liquid oxide might dissolve adjacent solid ZnO phases generating an eutectic liquid rich in bismuth [19].

In the case of nonohmic ceramics ( $\text{ZnO--Bi}_2\text{O}_3\text{--CoO}$ ), it has been shown that fast cooling from the sintering temperature leads to freeze  $\text{Bi}_2\text{O}_3(\text{l})$  in at the grain boundaries [20].

These results have been correlated with the wetting properties of the bismuth rich phase on ZnO grain boundaries at high temperature. Slow cooling from the sintering allows the  $\text{Bi}_2\text{O}_3$  phase to recede from the grain boundaries, leaving behind ZnO–ZnO homo-junctions. A high leakage current and low  $\alpha$  value are obtained for samples with the most grain-boundary wetting, demonstrating that simply coating the ZnO grains with Bi-rich phase is not sufficient to produce good varistor electrical properties, and may even be detrimental.

Pyrochlore phase plays, therefore, a key role since microstructural evolution and grain growth is controlled from about  $700^\circ\text{C}$  by its formation and decomposition. It, thus, promotes densification by a mechanism involving simultaneously the above chemical reaction and the classical diffusion mechanism of sintering also referred as liquid sintering [20–22]. However the presence of pyrochlore in varistor ceramics after sintering is not desirable. Indeed quenched samples show no varistor effect but present large amount of pyrochlore phase. This observation led Olson et al. [9] to believe that pyrochlore has a detrimental effect on the ability of an interface to act as electrical barrier. Based on the above reaction, two cases are possible. If bismuth oxide get lost by vaporization the reaction (5) suggests that samples sintered at high temperature during long dwell should present few amounts of pyrochlore. This seems to be the case. Specimens sintered for 4 h contained about half the pyrochlore than that which was sintered for 0 h [9]. On the contrary if no loss of bismuth oxide occurs spinel phase can be decomposed by dilution in the bismuth liquid and lead to the precipitation of pyrochlore by the reaction (5) which is reversed on slow cooling: pyrochlore is found in the microstructure at room temperature.

Several authors have pointed out that bismuth oxide was lost at high temperature during the sintering without quantifying it. Chiang et al. [23] have reported a considerable loss of bismuth. Indeed starting with a composition: 0.5 mol%  $\text{Bi}_2\text{O}_3$  and 0.5 mol%  $\text{Co}_2\text{O}_3$  before the sintering operation, the ceramic after sintering at  $1150^\circ\text{C}$  for 90 min and cooled at a rate of  $150^\circ\text{C h}^{-1}$  end with a bismuth content measured by emission spectroscopy of 0.81% Bi. This means that about 19 wt.% have been lost.

This paper is, therefore, devoted to the correlation of electrical properties of varistors ceramics in relation with the true bismuth oxide present in the ceramics after sintering.

### 4. Techniques

Thermogravimetry were carried out by means of a Linseis L81 apparatus. An air flow of  $0.2 \text{ dm}^3 \text{ min}^{-1}$  was used to maintain a permanent excess of oxygen and to exhaust the products out of the thermobalance. All the experiments were carried out at atmospheric pressure:  $P(\text{O}_2) \sim 20 \text{ kPa}$ .

Electrical measurements were carried out at 25°C using a multimeter. Samples were prepared by depositing a silver paste on opposite faces of the disc samples.

## 5. Experiments and results

### 5.1. Varistors elaboration

Small amounts of several oxide additives must be used to reach satisfactory electrical properties. New compositions are often directly evaluated in relation to varistor characteristics. To control the composition of sintered ceramics several empirical techniques have been used such as covering the furnace walls with a slip of bismuth and antimony in order to create an equilibrium between the vapor pressure and the solid. Another technique which has been developed is the use of mixed oxide as starting materials. In this case pyrochlore and spinel are mechanically mixed with ZnO. This approach has several advantages such as to bypass the reactions (1)–(4). Antimony oxide is already in the oxidation state V ( $\text{Zn}_7^{2+}\text{Sb}_2^{5+}\text{O}_{12}^{2-}$ ). This allows a better control of the complex liquid-sintering process and a technological advantage based on a reduced furnace cycle since a dwell at about 700°C is not anymore compulsory to let pyrochlore and spinel phases appear from the starting single oxides:  $\text{Bi}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$  and ZnO. Since pyrochlore and spinel phases are already present in our green ceramics a dwell is no more necessary.

The rate of heating is increased by a factor of about 33%. The sintering time of the whole profile is reduced by about 40%. In the classical case a dwell at 800°C of 5 h is useful for the appearance of the spinel and pyrochlore phases according to the reactions (1)–(4).

In order to study the vaporization of  $\text{Bi}_2\text{O}_3$  a reference composition has been chosen. The reference varistor composition was: 97 mol% ZnO, 0.5 mol%  $\text{Bi}_2\text{O}_3$ , 1 mol%  $\text{Sb}_2\text{O}_3$ , 0.5 mol%  $\text{MnO}_2$ , 0.5 mol%  $\text{Co}_3\text{O}_4$ , 0.5 mol%  $\text{Cr}_2\text{O}_3$  [25]. Pyrochlore ( $\text{Bi}_3\text{Zn}_2\text{Sb}_3\text{O}_{14}$ ) and spinel ( $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ ) phases

Table 1  
Raw materials used in the present paper.

Mixture	ZnO	Py	Sp	$\text{Mn}_2\text{O}_3$	$\text{Co}_3\text{O}_4$	$\text{Cr}_2\text{O}_3$
(mol%)	92.83	0.33	0.5	0.25	0.5	0.5
(wt.%)	86.97	5.17	5.14	0.454	1.386	0.875

were used in the corresponding proportions (Table 1). Both pyrochlore and spinel phases have been synthesized by direct oxidation of a precursor alloy (DOPA) [26,27]. The principle consists of having the oxygen acts on a homogeneous alloy powder which contain the metallic constituents zinc, antimony or bismuth in stoichiometric proportions. Oxidation of the powder was done in an oxidizing atmosphere of air, water-saturated at 20°C which circulates inside the furnace at a pressure of 95 kPa with a flow of  $0.2 \text{ dm}^3 \text{ min}^{-1}$  in order to maintain a permanent excess of oxygen. The pyrochlore and spinel powders were then annealed at 1100°C in air for 1 h and at 1200°C in air for 4 h, respectively.

To obtain well densified ceramics, the previous oxide powders were first pressed into disc (12 mm diameter, about 1.2 mm thickness and an average weight of 0.6 g) under 7 kbar. The green discs had an average density of  $4.2 \text{ g cm}^{-3}$  i.e. 75% of the theoretical density of ZnO.

Then the green discs were fired at 1250°C for 1 h. After the sintering the samples were cooled at a rate of  $180^\circ\text{C h}^{-1}$  up to 1100°C,  $420^\circ\text{C h}^{-1}$  up to 900°C and eventually  $180^\circ\text{C h}^{-1}$  up to 700°C. The final cooling was a quench in air.

## 6. Characterization

### 6.1. Vaporization from single oxides powders

In order to study the bismuth vaporization several procedures were carried out. First of all we study the vaporization from single oxides powder. A Bismuth oxide powder specimen of 121 mg is introduced in a platinum crucible

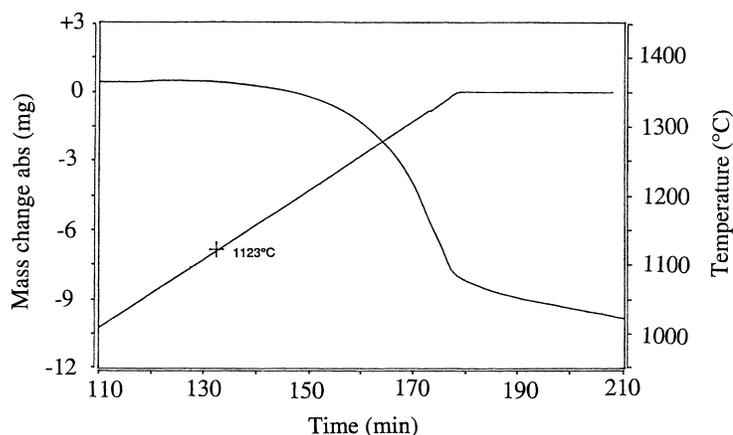


Fig. 1. Thermogram of the decomposition of  $\alpha$  bismuth oxide powder specimen.

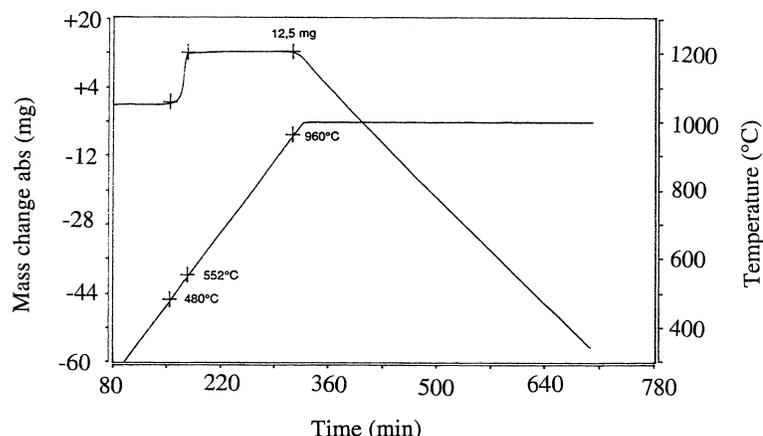


Fig. 2. Thermogram of the decomposition of an antimony oxide powder specimen.

and heated to 1350°C with a heating rate of 5°C min<sup>-1</sup>. The first loss is detected around 1123°C (Fig. 1). The kinetic of bismuth loss is increased up to 1350°C to reach a rate of -0.05 mg min<sup>-1</sup>. A similar experiment is carried out with an antimony oxide powder specimen of 266 mg (Fig. 2). The specimen transforms from 480°C to Sb<sub>2</sub>O<sub>4</sub> which is the product of partial oxidation of Sb<sub>2</sub>O<sub>3</sub>: half of SbIII are converted into SbV in order to reach the oxide Sb<sup>3+</sup>Sb<sup>5+</sup>O<sub>4</sub><sup>2-</sup>. At 960°C Sb<sub>2</sub>O<sub>4</sub> is vaporized. In our analysis conditions where an air flow sweep over the sample the solid-gas equilibrium conditions are never reached and Sb<sub>2</sub>O<sub>4</sub> is entirely lost by vaporization. It is worth noticing that the starting of this reaction seems to be delayed with the presence of dopants in varistor ceramics since this reaction was known to start in varistor microstructure at only about 600°C [24]. However, in our elaboration conditions where the whole antimony is contained in the mixed raw material oxide (Zn<sub>7</sub>Sb<sub>2</sub>O<sub>12</sub>) there is no longer vaporization of antimony oxide from ceramics since Sb is stabilized to the oxidation state V.

## 6.2. Vaporization from varistor ceramic

We have then studied the vaporization of bismuth from our ceramics by following the loss of weight observed during sintering at 1100°C. Several procedures have been carried out. In the first one, the ceramics are deposited on an alumina substrate. Second, a batch of ceramics is put on a platinum foil and eventually ceramics are introduced in a platinum crucible which is kept closed by a platinum foil.

On alumina substrate ceramics have kept only 5 wt.% of the initially Bi<sub>2</sub>O<sub>3</sub> introduced favor the pyrochlore oxide (Bi<sub>3</sub>Zn<sub>2</sub>Sb<sub>3</sub>O<sub>14</sub>) decomposition. The whole loss of bismuth is found inside the substrate. This suggests that the liquid bismuth oxide phase was transferred by superficial tensile. The second batch, sintered in a platinum crucible, shows a loss of 50 wt.%. In this case the loss has been achieved by vaporization since no weight gain was identified on the

platinum crucible. The last run was carried out in a closed platinum environment. The vapor was kept around the ceramic. 15 wt.% of the bismuth oxide is found after cooling on the walls of the crucible. The weight gain observed on the closed crucible is assumed to be representative of the bismuth vapor in equilibrium with the liquid oxide. Fig. 3 reports the true bismuth content after sintering at 1100 and 1250°C. (It is worth noticing that in the case where the ceramics are sintered on an alumina substrate:

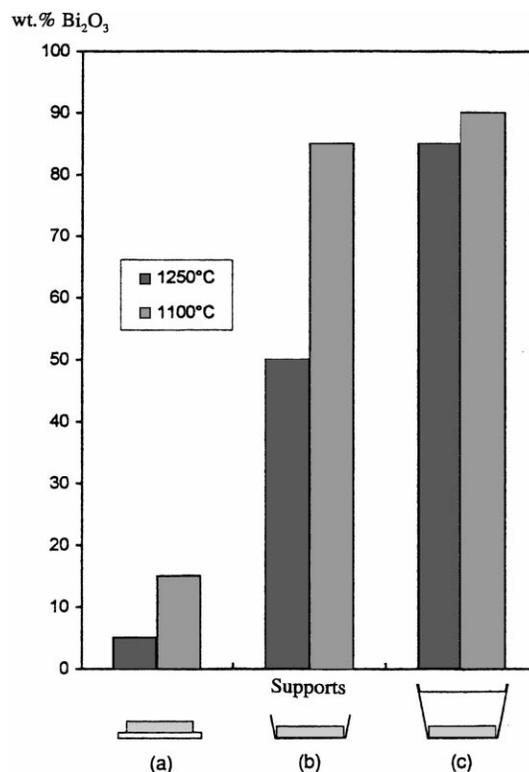


Fig. 3. Amount of bismuth oxide left in the ceramics after sintering with several substrates. Sintered at 1100 and 1250°C on alumina substrate (a), platinum substrate (b), and closed platinum substrate (c).

Table 2  
Apparent density of sintered ceramics relative to the substrate

Substrate	Sintering temperature 1100°C		Sintering temperature 1250°C	
	wt.% Bi <sub>2</sub> O <sub>3</sub> kept inside the ceramic	Apparent density	wt.% Bi <sub>2</sub> O <sub>3</sub> kept inside the ceramic	Apparent density
Alumina	15	5.0	5	4.9
Platinum foil	85	5.3	50	5.2
Closed platinum foil	90	5.5	85	5.4

the final bismuth oxide composition is about: 0.027 wt.%, 0.05 wt.% = 0.0013 wt.%.)

Apparent density is directly linked to the Bi<sub>2</sub>O<sub>3</sub> kept inside the ceramic (Table 2). Indeed it can be noted that variations in density follow variations in bismuth content rather than variation in sintering temperature. This is not surprising since density of a single Bi<sub>2</sub>O<sub>3</sub> is closed to 9 g cm<sup>-3</sup> and a loss of this component leads to a drastic decrease of the total density of the sintered ceramic.

It appears that the increase of sintering temperature does not lead to a better densification. This suggests that the loss of bismuth oxide has a detrimental effect on the sintering.

### 6.3. X-ray diffraction

In the limit detection of about several percent, only Bi<sub>2</sub>O<sub>3</sub>, ZnO and a spinel phase of formula Zn<sub>7-x</sub>Co<sub>x</sub>Sb<sub>2</sub>O<sub>12</sub> has been detected by X-ray diffraction. This suggests that the pyrochlore phase has entirely reacted to free Bi<sub>2</sub>O<sub>3</sub>(l) according to the reaction (4) and that reaction (5) has not been reversed on cooling.

### 6.4. Electrical characterization

Table 3 depicts the nonlinear coefficient and the breakdown voltage  $V_s$  versus the wt.% of Bi<sub>2</sub>O<sub>3</sub> kept inside ceramics after sintering at room temperature.  $\alpha$  coefficient were comprised between 35 and 45 for all ceramics. However, ceramics with low bismuth oxide contents had the highest  $\alpha$  coefficient. Electrical measurements show also that the breakdown voltage is diminished when the sintering temperature is increased when also the bismuth content after sintering is high. In both cases the breakdown voltage decrease has to be linked to an increase of the grain size and concomitant decrease of the grain boundaries surface density [28].

Table 3

Breakdown voltage and nonlinear coefficient  $\alpha$  versus sintering temperature and true amount of bismuth oxide in ceramics after sintering. Ceramics were prepared from mixture of pre-synthesized spinel phase, pre-synthesized pyrochlore phase, single manganese, cobalt and chromium oxide. Sintered on alumina substrate at 1100°C (ti) and sintered on platinum substrate at 1100°C (tii) and sintered on alumina substrate at 1250°C (tiii) and sintered on platinum substrate at 1250°C (tiv)

	Sintering temperature (°C)	wt.% Bi <sub>2</sub> O <sub>3</sub> kept inside varistor microstructure	$\alpha$	Breakdown voltage $V_s$ (V mm <sup>-1</sup> )	Average grain size ( $\mu$ m)
ti	1100	15	41	480	–
tii	1100	85	35	410	–
tiii	1250	5	45	335	10
tiv	1250	85	35	250	14

### 6.5. Scanning electron microscopy

We have observed by scanning electron microscopy of the (tiii) and (tiv) ceramics which compositions are depicted in Table 3. In all cases ZnO grain size were of the order of 10–15  $\mu$ m. Spinel phases (1–4  $\mu$ m in size) were usually located in clusters and occasionally singly between ZnO grains or more often at triple junction. However, if large amounts of bismuth oxide have been retained in the microstructure after sintering (specimen (tiv)) most of the ZnO–ZnO grain boundaries contained a continuous intergranular ( $\sim$ 0.5  $\mu$ m) bismuth-rich material. This suggested that Bi<sub>2</sub>O<sub>3</sub> liquid phase resulting from pyrochlore decomposition at high temperatures has wetted the ZnO grains and had been frozen in at room temperature. On the contrary, in the case of ceramics with few bismuth oxide contents (specimen (tiii)) no segregated bismuth oxide intergranular phase was detected. ZnO–ZnO homo-junctions were observed with the most relative frequency of occurrence.

## 7. Conclusion

Olsson showed that the continuous network of Bi-rich phase along multiple ZnO grain junctions can provide an additional current path which is of significance in the breakdown region of the current/voltage characteristics [29]. This leads to a high leakage current which is obviously not desirable on stand-by conditions. The present work lets us suggest that there is an optimum Bi<sub>2</sub>O<sub>3</sub> concentration and that very few Bi<sub>2</sub>O<sub>3</sub> amounts are requested to produce a good varistor effect. Indeed ceramics with the highest loss of bismuth, i.e. with the lowest final concentration or lowest true composition, present the highest  $\alpha$  coefficient.

Production of varistors by mechanical mixing of pre-synthesized spinel and pyrochlore phases with other

classical single oxide additives ( $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{MnO}_2$ ,  $\text{Cr}_2\text{O}_3$ , etc.) allows to simplify the complex reactive liquid sintering process. It, thus, might be an interesting route for varistors production by shortening the sintering profile and avoiding departure of antimony from ceramics.

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