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Compact shape as a relevant parameter for sintering ZnO–Bi_2O_3 based varistors

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Abstract

Ceramic varistors based on the ZnO–Bi_2O_3–Sb_2O_3 system, are usually sintered at 1150–1200 °C in the presence of a Bi-rich liquid phase that forms at 700–800 °C. Bismuth is critical for the formation of electrically active grain boundaries, and the Bi-rich liquid phase plays a major role in the grain growth kinetics. Therefore, uncontrolled bismuth oxide vaporization during sintering can heavily deteriorate the electrical response of the varistor, and the area–volume ratio of the green compact becomes a relevant parameter, along with the sintering temperature and soaking time. In the present work, we have studied the microstructure and the current–voltage characteristics of ceramic varistors with different area–volume ratios and sintering cycles. We find that, depending on the sintering cycle, there exists a value for the area–volume ratio that leads to a strong deterioration of the varistor electrical properties.
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1. Introduction

Ceramic varistors based on the ZnO–Bi_2O_3–Sb_2O_3 system show a characteristic nonlinear current-voltage response. This is a consequence of their microstructure and electronic structure:[1,2] non-ohmic behaviour is due to the presence of electrically active grain boundaries, formed by an intergranular Bi_2O_3-rich phase that separates the semiconducting ZnO grains.[3,4] Besides Bi_2O_3, other oxides enter in minor proportions into the varistor composition (Sb_2O_3, CoO, MnO_2 and Cr_2O_3): their role is to improve the electrical response. The main reactions that, during sintering, lead to the final microstructure, are:[5,6]

$$4\ ZnO + 3\ Bi_2O_3 + Sb_2O_3 + O_2 \rightarrow 3\ Bi_2(Zn_{4/3}Sb_{2/3})O_6 \quad (1)$$

$$Bi_2(Zn_{4/3}Sb_{2/3})O_6 + 3\ ZnO \rightarrow Zn_7Sb_2O_{12} + Bi_2O_3(liq) \quad (2)$$

According to the literature the formation of the spinel phase also occurs through the direct reaction between Sb_2O_3 and ZnO in excess to the Bi_2O_3.[7–9]

$$ZnO + Sb_2O_3 + O_2 \rightarrow ZnSb_2O_6 \quad (3)$$

$$ZnSb_2O_6 + 6\ ZnO \rightarrow Zn_7Sb_2O_{12} \quad (4)$$

The spinel phase is important for grain growth control according to the generally accepted model of grain growth inhibition.[1] The Bi_2O_3-rich phase wets the grain boundaries,[10] forming intergranular layers that during cooling recede to the pockets created by grain packing.[1,9] It has been shown that oxygen excess at the grain boundaries is necessary to develop electrically active junctions.[11] Moreover, the formation of the spinel phase occurs through Sb oxidation. Consequently the Bi-rich skeleton plays a predominant role in oxygen transport.[12] Recently, uncontrolled Bi vaporization has been reported to take place at sintering temperatures usually needed for densification of ZnO–Bi_2O_3 based varistors.[8,13] This can contribute to changing relevant features of the functional microstructure in severals ways: (1) compositional changes of the liquid phase can modify the diffusion kinetics and therefore the grain growth rate and oxygen transport, (2) bismuth defficiency may decrease the density of electrically active boundarie and/or decrease

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Table 1
Area–volume ratio measured on green compacts

Sample	A	B	C	D	E
Height (cm)	0.33	0.67	1.03	1.38	1.72
Weight (g)	2.0	4.0	6.0	8.0	10.0
A/V ratio (cm^{-1})	8.67	5.64	4.60	4.11	3.83

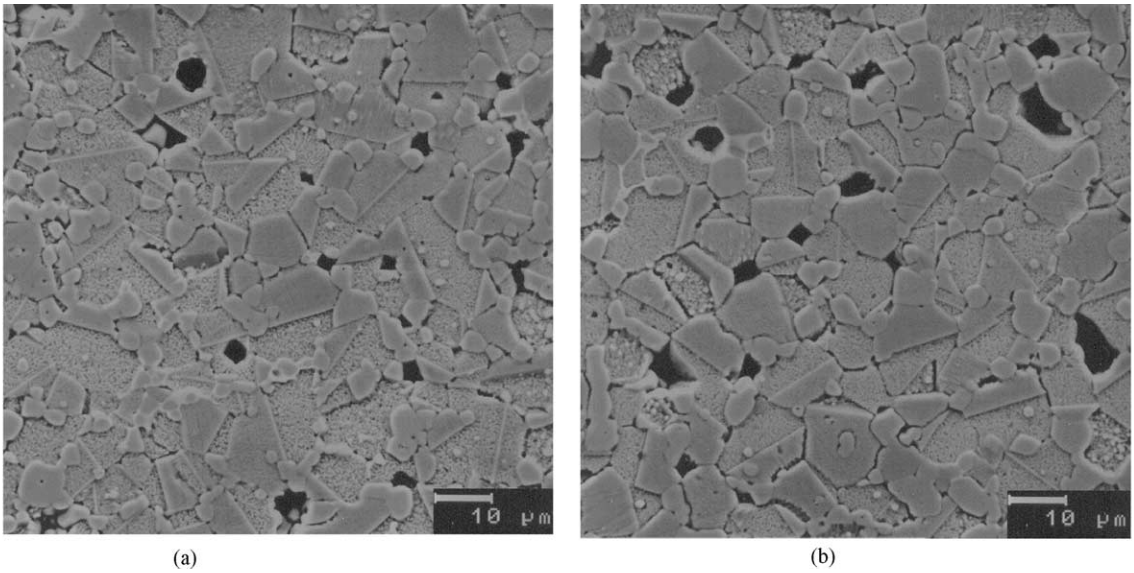
the potential barrier height.[9] Bismuth loss depends on the surface area in direct contact with the reaction atmosphere: a greater surface can lead to a better oxygenation, but can also increase Bi loss. Hence, there should be an optimum area–volume ratio that balances both effects. In this work, we study the microstructure and the electrical response of varistor samples sintered at different temperatures and with different area–volume ratios.

2. Experimental procedure

We have used a well known varistor composition, commonly reported in the literature:[5,8] 97.2% mol ZnO, 0.5% Bi_2O_3, 1% Sb_2O_3, 0.5% MnO_2, 0.5% Cr_2O_3 y 0.3% CoO. High purity raw materials (above 99.9%) were used. Oxides were mixed by ball-milling (ZrO_2 balls) in ethanol medium. Powder was oven dried at 60 °C and sieved below 100 μm. The mixed powders were calcined at 900 °C 2 h and then attrition milled (ZrO_2 balls) in ethanol medium. An organic mixture of Polivinyl Alcohol and Etilen Glycol were added to the milled powders to favour pressing of the compacts. Green cylindric compacts were uniaxially pressed at 78 MPa, with a constant 15 mm-diameter and a variable height. Green density was geometrically measured and always kept between 3.1 and 3.2 g/cm^3. The organic was slowly burnt out at 500 °C. The sintering temperatures used in this study were 1160 and 1200 °C for 2 h. The mass losses by vaporization during sintering, was determined by weighing samples before and after sintering. The density of sintered ceramics was determined by Arquimedes method. The obtained density always reach values of 5.62 ± 0.02 g/cm^3. The microstructure of the samples was observed by Scanning Electronic Microscopy (SEM) in a Zeiss DSM 950 microscope on polished and chemically etched surfaces. Average grain size was determined by the interception method, using at least 300 grains. Electrical characterization was carried out on sliced discs from the centre of the sample of 1.5 milimeter thick with silver electrodes. The current–voltage response in DC was measured by using a Keithley multimeter, equipped with a voltage source of 1100 V. In order to compare the varistor characteristics the following set of parameters were evaluated: the field E_{eff} that produces a 5 mA/cm^2 current density through the sample (usually called switching field); the leakage current density J_{MCOV}, measured at 85% of E_{eff}; and, finally, the non-linearity coefficient, α, estimated between 5 mA/cm^2 and 20 mA/cm^2 through $V = kI^{\alpha}$.

3. Results and discussion

Table 1 shows the values of mass, height and area–volume ratio that characterize the green compacts. The samples were labeled with a capital letter from A having the highest A/V ratio of 8.67 cm^{-1} to E with less than a half A/V ratio of 3.81 cm^{-1} that corresponds to a five times thicker green compacts. The average grain size was



(a) (b)

Fig. 1. SEM micrographs of sample C sintered at: (a) at 1160 °C; (b) at 1200 °C.

found to depend only with the sintering temperature, and not with the area–volume ratio (see Fig. 1, corresponding to sample C).The average grain size was 8±0.5 μm for samples sintered at 1160 °C and 10±0.5 μm for samples sintered at 1200 °C. This indicates, that the diffusion processes responsible for the grain growth control is independent with the area-volume ratio for a given sintering temperature, as it was expected.

Figs. 2 and 3 show the current-voltage response of sintered samples. Tables 2 and 3 summarize the corresponding electrical parameters. Note that, as a consequence of a smaller grain size, the switching field is higher for the samples sintered at 1160 °C than for those sintered at 1200 °C. It can be seen that samples sintered at 1160 °C, and with area–volume ratio below 5.64 cm^{-1}, exhibit quite close electrical responses; however, the sample A with a greater area–volume ratio exhibits reduced non-linearity, increased leakage current and higher switching field, when compared with the others. These effects can be explained through a decrease in the intergranular electrostatic barrier height (which accounts for reduced non-linearity and higher leakage), along with an increase in the percentage of electrically active junctions, which accounts for the increased switching field.[1,4] Regarding the samples sintered at 1200 °C, a greater dispersion can be observed in their current–voltage behaviour. Notwithstanding, the sample with the higher area–volume ratio is again clearly distinguished from the others: non-linearity coefficient and switching field are reduced, while leakage current is increased for this sample. This result can be explained through a notorious reduction in the barrier height. Therefore, we see that samples with greater area–volume ratios present poorer varistor behaviour, even when the opposite effect could be expected from the corresponding improvement in sample oxygenation. This result can be due to bismuth oxide vaporization during sintering, at both sintering temperatures. Such an effect shifts the Bi content in the sintered material, changing the actual composition of the varistor.[8]

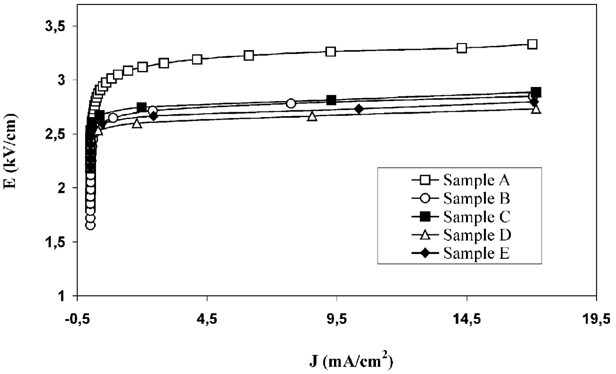


Fig. 2. Current–voltage response for samples sintered at 1160 °C.

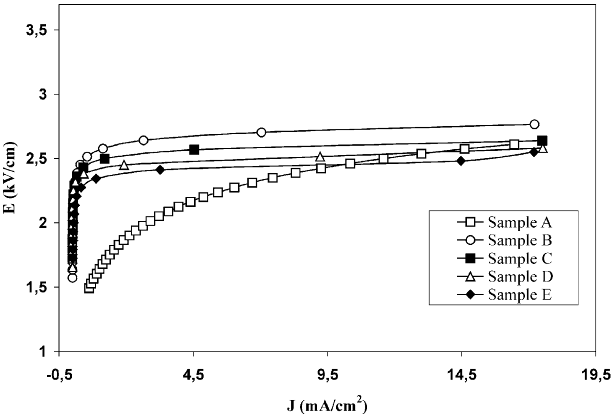


Fig. 3. Current–voltage response for samples sintered at 1200 °C.

For the sample B (A/V ratio 5.64 cm^{-1}) it is possible to obtain good varistor behaviour lowering the sintering temperature, however its behaviour is slightly worse than expected according to the C, D and E samples. It seems that the critical A/V ratio is very close to that of the sample B.

In the case of sample A, it is not possible to obtain good varistors properties, therefore Bi_2O_3 loss increased because of the high surface area and cannot be controlled within these sintering conditions.

Table 4 shows the measured weight losses for samples A and D sintered at 1160 and 1200 °C during different sintering times. If we assume as a rough approach, that all weight losses are due to Bi_2O_3 vaporization, at the beginning of sintering at 1160 °C about half the initial Bi_2O_3 in sample A has been lost by vaporization

Table 2
Area–volume ratio vs. electrical response for samples sintered at 1160 °C

1160 °C	E_{eff} (kV/cm)	J_{MOCV} (mA/cm^2)	α
A	3.21	0.186	37
B	2.76	0.052	50
C	2.79	0.003	54
D	2.64	0.001	52
E	2.70	0.002	57

Table 3
Area–volume ratio vs. electrical response for samples sintered at 1200 °C

1200 °C	E_{eff} (kV/cm)	J_{MOCV} (mA/cm^2)	α
A	2.20	1.92	7
B	2.68	0.064	44
C	2.57	0.025	53
D	2.48	0.007	57
E	2.43	0.040	52

Table 4
Bi_2O_3 loss as function of the sintering time at 1160 and 1200 °C for samples A and D

SAMPLE	% Losses	Sintering at 1160 °C		Sintering at 1200 °C	
		1 min	6 h	1 min	6 h
A	Weight loss (%) ± 0.05	1.5	2.1	2.1	2.3
	Bi_2O_3 loss (%) ± 0.05	55.6	77.8	77.8	87.0
D	Weight loss (%) ± 0.05	0.5	1.3	0.7	1.4
	Bi_2O_3 loss (%) ± 0.05	21.6	51.6	30.1	55.5

whereas in sample D this loss is reached after 6 h at sintering temperature. At higher sintering temperatures the increase of the kinetics of the vaporization process is more acute for samples with the highest A/V ratio. Nevertheless a higher sintering temperature produces a deterioration of the electrical response for all the A/V ratios as can be observed in the samples sintered at 1200 °C.

An important point for defining sintering strategies is that sintering time has a less marked effect on the Bi_2O_3 losses than the sintering temperature. Bi_2O_3 vaporization seems to occur more efficiently during heating and most of the losses have taken place just when sintering temperature is reached.

4. Conclusions

Area–volume ratio in green compacts is a critical parameter to obtain ceramic varistors based on the system ZnO–Bi_2O_3. The potential barriers formed at grain boundaries depend on the amount of Bi^{3+} and oxygen present in each sample. The maximum area–volume ratio is limited by partial bismuth oxide vaporization rendering the material useless as a varistor device.

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