

## Thick film ZnO based varistors prepared by screen printing

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### Abstract

Thick film varistors based on the system ZnO–Bi<sub>2</sub>O<sub>3</sub>–Sb<sub>2</sub>O<sub>3</sub> have been prepared by screen printing technology on dense alumina substrates. Different processing strategies have been designed in order to control the excessive volatilization of Bi<sub>2</sub>O<sub>3</sub> in varistor films during the sintering, due to the high area–volume ratio, and as a means to improving their electrical response. Starting powders were selected and pre-treated in different ways to obtain different phases and control the Bi-rich liquid phase formation. Significant differences have been observed in the electrical properties which are related to the selection of the starting powders.

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### 1. Introduction

Zinc-oxide based varistors are multiphase ceramic devices which exhibit highly non-linear current-voltage characteristics.<sup>1</sup> This extensive non-ohmic characteristic results in the widespread application of varistors as voltage surge protectors in electrical circuits.<sup>2</sup>

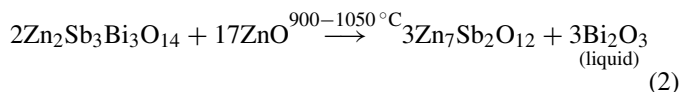
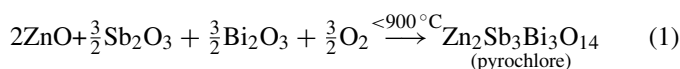
Screen printing has been developed in the fields of micro-electronics for hybrid and integrated circuit manufacture. The advantages of this technology are; low cost, versatility in the design, miniaturization and high reproducibility. One of the main problems, inherent to this technology, is the lack of compaction of the films. In general in this technology to reach a satisfactory level of densification usually involves the addition of a large amount of glass-frit which melts during the firing process. However, in the case of the varistor material, a significant amount of glass-frit will modify the electrical performance of the thick films.

Menil et al.<sup>3</sup> proposed a method to improve the compaction by applying mechanical pressure, either uniaxial or isostatic, to the calcined screen printed samples with composition 95 mol% ZnO–5 mol% additives (CoO, Cr<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>). They obtained nonlinear coefficient values between 17 and 19

for thick films sintered at 1150 °C. Unpressed screen-printed varistors were mostly short-circuited. Tovher et al.<sup>4</sup> prepared thick-film varistors by direct-write techniques in highly integrated, multifunctional electroceramic devices, with chemical composition in mol%: 98.94 ZnO, 0.25 CoO, 0.25 MnO, 0.56 Bi<sub>2</sub>O<sub>3</sub>.

One of the main problems associated with varistor thick film manufacture, as well as the lack of compaction of the films, is the high volatilization of Bi<sub>2</sub>O<sub>3</sub> at the sintering temperatures due to the high area–volume ratio of the thick films. In recent work Peiteado et al.<sup>5</sup> have measured a loss in weight of Bi<sub>2</sub>O<sub>3</sub> up to 60% in bulk varistors with area–volume ratio of 4.1 cm<sup>-1</sup>. De la Rubia et al.<sup>6</sup> reported that the partial volatilization of Bi<sub>2</sub>O<sub>3</sub> limits the highest area–volume ratio in a bulk varistor, exhibiting good varistor behaviour with high and low sintering temperatures to an area–volume ratio of 5 cm<sup>-1</sup>. For higher area–volume ratios than 5 cm<sup>-1</sup>, this volatilization damages the electrical response invalidating its application as a varistor.

Bi<sub>2</sub>O<sub>3</sub> volatilization takes place from the Bi<sub>2</sub>O<sub>3</sub>-rich liquid phase that forms during sintering. Varistor functional microstructure is achieved through the following reactions:



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Appropriate densification of the varistor material is obtained when a  $\text{Bi}_2\text{O}_3$  liquid phase appears leading to liquid phase sintering. However, if the temperature is increased, bismuth volatilization is also increased and has a significant effect on the final electrical properties. Such an effect is even more marked for the thick film geometry, with a very high area–volume ratio (two orders of magnitude higher than for bulk ceramics). Within this framework, a reasonable approach to overcome such difficulties might be based on the formation of the  $\text{Bi}_2\text{O}_3$  rich liquid phase at low temperatures, so that Bi volatilization kinetic is hindered and Bi loss avoided.

The objective of this work is to obtain thick film varistors with good electrical response, controlling the  $\text{Bi}_2\text{O}_3$  volatilization and improving densification. For this purpose, different processing strategies leading to the formation of a  $\text{Bi}_2\text{O}_3$  rich liquid phase at low temperatures have been studied.

## 2. Experimental

### 2.1. Powder preparation

The nominal composition of the varistor powder is 95.5 mol% ZnO, 1.5 mol%  $\text{Sb}_2\text{O}_3$ , 0.5 mol%  $\text{Bi}_2\text{O}_3$ , 0.5 mol%  $\text{Co}_3\text{O}_4$ , 1.25 mol% NiO and 0.75 mol% MnO. Three different processing strategies with this nominal composition have been designed:

- (I) *Batch SCM*: Prepared by a classical mixed-oxide route including ball milling for 2 h in ethanol, calcination treatment at  $950^\circ\text{C}$ –1 h and milling.
- (II) *Batch SP*: Classical mixed-oxide route but replacing the  $\text{Sb}_2\text{O}_3$  by the equivalent amount of a previously synthesized  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  orthorhombic spinel phase.
- (III) *Batch SP + sillenite*: Replacing the  $\text{Sb}_2\text{O}_3$  and the  $\text{Bi}_2\text{O}_3$  by the equivalent amount of a  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  orthorhombic spinel phase and a  $\text{Bi}_{38}\text{ZnO}_{58}$  sillenite phase previously synthesized, respectively.

The average grain size of the starting powders was between 0.7 and  $0.8 \text{ \AA}$ , since the grain size of starting ZnO was around  $1 \mu\text{m}$ . Phase characterization of the starting powders was performed by X-ray diffraction (XRD) in a D5000 Siemens Diffractometer using  $\text{Cu K}\alpha_1$  radiation.

### 2.2. Thick film preparation

The pastes of varistor materials for screen printing were prepared as follow: 60 wt.% of active powder was mixed in an agate mortar with 40 wt.% of organic vehicle, comprising  $\alpha$ -terpineol, ethylcellulose and [2-(2-butoxi-etoxy-ethyl)] acetate. The mixture was homogenized in a three rolls mill. All the pastes show pseudoplastic rheological behaviour which is useful for screen-printing. Prior to deposition of the ZnO pastes onto dense alumina substrates, platinum electrodes were screen-printed onto the substrates and fired at  $1200^\circ\text{C}$ –1 h. After that, six layers of varistor ink were screen-printed, dried in oven at  $150^\circ\text{C}$  after each deposited layer. The organic vehicle was removed by the following calcination cycle: heat to  $425^\circ\text{C}$ –0 h,

with heating–cooling rate of  $0.5^\circ\text{C}/\text{min}$  and soaking times of 30 min at 195, 270 and  $385^\circ\text{C}$ , respectively. The thickness of the calcined green thick films was measured and the surfaces were characterized by optical microscopy. In all cases the thickness of the green films was in the range of  $60$ – $70 \mu\text{m}$ ; after sintering the thickness range was between 30 and  $40 \mu\text{m}$ . Calcined samples were sintered at temperatures between 900 and  $1150^\circ\text{C}$  with different soaking times, varying between 1 and 8 h. Sintered thick films were characterized by SEM and EDS. Finally for electrical characterization, gold top electrodes were deposited by sputtering. V–I measurements were carried out using a DC power multimeter (Keithley 2410).

## 3. Results and discussion

For batch SCM, reaction 2 was partially completed since the calcination step was carried out at  $950^\circ\text{C}$ –1 h, therefore this system initially exhibits  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  spinel phase,  $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$  pyrochlore phase and ZnO. The  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  phase is found in the grain boundaries and triple points and inhibits grain growth, hindering the movement of the grain boundaries.<sup>7</sup> In batch SP, the spinel phase  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  is used as Sb precursor instead of  $\text{Sb}_2\text{O}_3$ , avoiding the reactions 1 and 2. The release of the Bi-rich liquid phase takes place at  $740^\circ\text{C}$  due to the existence of a eutectic reaction in the binary system  $\text{ZnO}$ – $\text{Bi}_2\text{O}_3$ .<sup>8,9</sup> Therefore, the  $\text{Bi}_2\text{O}_3$  phase, as well as being involved in the densification process, providing a liquid medium for sintering, increasing the ZnO grain growth,<sup>10</sup> is also involved in the formation of the potential barriers at the grain boundaries. In batch SP + sillenite, as well as the addition of  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ , the sillenite phase is added as the Bi precursor instead of  $\text{Bi}_2\text{O}_3$ ; therefore no reaction takes place.  $\text{Bi}_{38}\text{ZnO}_{58}$  sillenite phase melts incongruently at  $755^\circ\text{C}$ .<sup>11</sup>

Fig. 1 shows powder XRD of the three starting materials where the main components ZnO,  $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$  pyrochlore phase and  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  spinel phase in batch SCM, ZnO,  $\text{Bi}_2\text{O}_3$  and  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  in batch SP and ZnO,  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$  and the  $\text{Bi}_{38}\text{ZnO}_{58}$  sillenite phase in batch SP + sillenite can be observed.

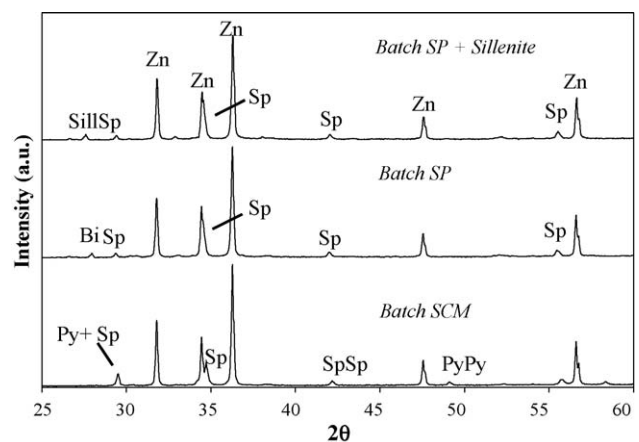


Fig. 1. XRD patterns of the three starting powders before sintering Zn = ZnO, Bi =  $\text{Bi}_2\text{O}_3$ , Sp =  $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ , Py =  $\text{Zn}_2\text{Bi}_3\text{Sb}_3\text{O}_{14}$  and Sill =  $\text{Bi}_{38}\text{ZnO}_{58}$ .

Table 1

Evolution of nonlinear coefficient  $\alpha$  with sintering temperature (soaking time = 1 h)

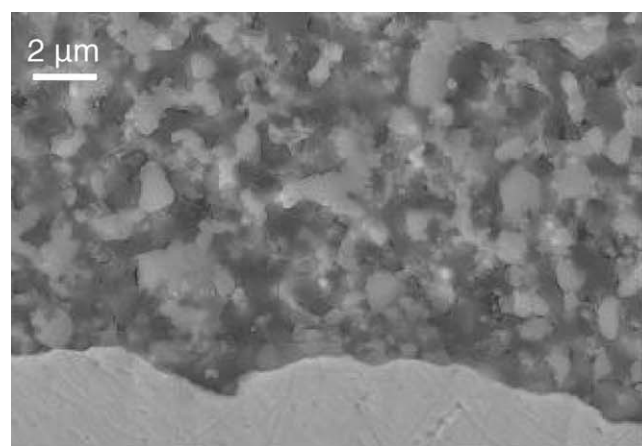
Sintering temperature (°C)	SCM	SP	SP + sillenite
900	No IV	20	18
950	2	15	11
1000	8	10	8
1050	10	9	7
1100	9	7	6
1150	3	6	6

Table 2

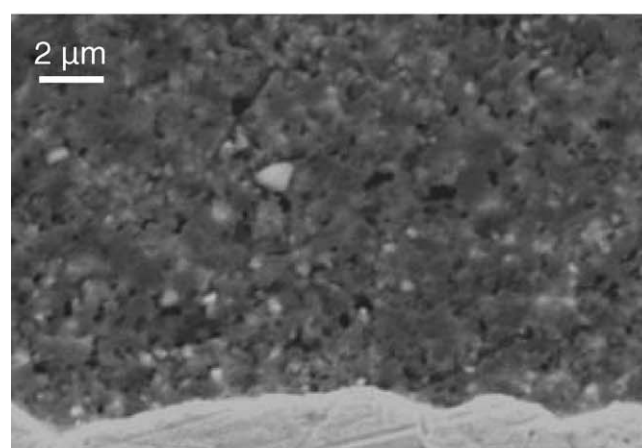
Evolution of nonlinear coefficient  $\alpha$  with sintering time (sintering temperature = 900 °C)

Sintering time (h)	SCM	SP	SP + sillenite
1	No IV	20	18
4	10	8	8
8	8	5	6

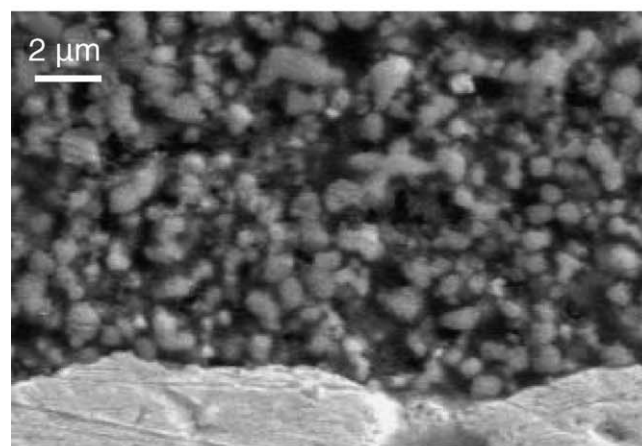
Non-linear coefficient measurements for thick films of each batch, sintered at different temperatures and soaking times, are summarized in Tables 1 and 2, respectively. The results show that batches SP and SP + sillenite exhibit good varistor behaviour for a sintering temperature of 900 °C with soaking time of 1 h, yielding nonlinear coefficients  $\alpha = 20$  and 18, respectively. Both strategies were designed to allow significant densification and control the  $\text{Bi}_2\text{O}_3$  volatilization. Consequently it is possible to prepare thick film varistors with good electrical response. As the sintering temperatures increase above 900 °C, with soaking time of 1 h, a substantial volatilization of Bi occurs for batches SP and SP + sillenite; therefore the non-linear coefficient decreases significantly. A probable mechanism for the decrease in  $\alpha$  is that the Bi is being removed from the varistor microstructure vigorously with the increase of the sintering temperature due to the high  $A/V$  ratio ( $335 \text{ cm}^{-1}$ ). In Batch SCM at lower sintering temperatures, like 900 °C, all the  $\text{Bi}_2\text{O}_3$  is included in the  $\text{Bi}_3\text{Zn}_2\text{SbO}_{14}$  pyrochlore phase (reaction 1) since at this temperature the pyrochlore decomposition does not take place (reaction 2). Therefore, the  $\text{Bi}_2\text{O}_3$  is not free and the thick film does not densify during the sintering treatment. Fig. 2 shows SEM micrographs of the different thick films sintered at 900 °C–1 h. Micrographs of batches SP and SP + sillenite exhibit higher density than batch SCM, as a result of the processing strategies designed to control the volatilization of  $\text{Bi}_2\text{O}_3$  that prevents the necessary reactions taking place during sintering. Therefore, in batches SP and SP + sillenite the presence of liquid phases develop at 740 °C or 755 °C, while the system SCM follows the reaction path previously indicated and, at this temperature, the liquid phase does not form. As a consequence of this microstructure, the thick films of batch SCM sintered at lower temperatures do not exhibit useful varistor behaviour. At higher sintering temperatures than 950 °C with a soaking time of 1h, thick films of batch SCM exhibit limited varistor behaviour. This is a consequence of the release of  $\text{Bi}_2\text{O}_3$  since reaction 2 takes place but at the same time the volatilization of  $\text{Bi}_2\text{O}_3$  is more noticeable. The nonlinear coef-



(a)



(b)



(c)

Fig. 2. SEM micrographs of thick films sintered at 900 °C–1 h: (a) batch SP; (b) batch SP + sillenite and (c) batch SCM.

ficients ( $\alpha$ ) are clearly lower than the values obtained for thick films sintered at 900 °C for the strategies SP and SP + sillenite. Therefore, it is possible to prepare a thick film with good varistor behaviour avoiding excessive volatilization of  $\text{Bi}_2\text{O}_3$  with the processing strategies of batches SP and SP + sillenite and decreasing the sintering temperature to 900 °C. The change of the soaking time (4–8 h) at 900 °C produces a decrease in the

nonlinear coefficient in batches SP and SP + sillenite until the values are rather low, approximately 5–8, due to the substantial volatilization of  $\text{Bi}_2\text{O}_3$  from the extended soaking time. For the same sintering conditions ( $900^\circ\text{C}$ –4/8 h) batch SCM does not

present varistor behaviour due to the pyrochlore decomposition reaction (reaction 2), which takes place at higher temperatures ( $900$ – $1050^\circ\text{C}$ ). Consequently there is no free  $\text{Bi}_2\text{O}_3$  and thus the thick films do not densify to provide the necessary connectivity between Bi-rich grain boundaries.

Fig. 3 shows SEM micrographs of different thick films sintered at  $1050^\circ\text{C}$ –1 h where the microstructure of all the samples is very similar since the  $\text{Bi}_2\text{O}_3$  has been released completely in all the batches and excessive volatilization has taken place. As a consequence all the thick films sintered at this temperature present similar varistor behaviour (Table 1).

#### 4. Conclusions

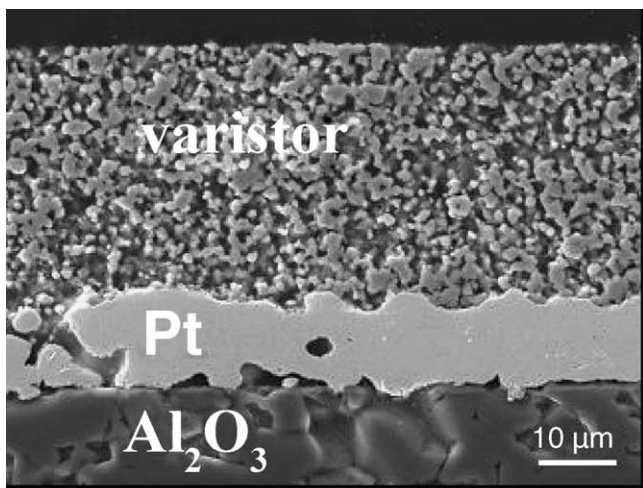
By means of different processing strategies, thick films of ZnO-based varistors have been prepared with  $\alpha$  values as high as 20. Between the strategies suggested, the incorporation of the previously synthesized spinel phase allows for a lower sintering temperature,  $900^\circ\text{C}$ , and so prevents excessive  $\text{Bi}_2\text{O}_3$  volatilization, which due to the extremely high area–volume ratio of the films represents the major challenge in manufacturing these devices. Together with the incorporation of the spinel phase the substitution of bismuth oxide by the  $\text{Bi}_{38}\text{ZnO}_{58}$  sillenite type phase also yields good varistor behaviour at low temperature; as yet, no important differences between the strategies have been found. On the other hand the system with calcinated varistor powders does not release the  $\text{Bi}_2\text{O}_3$  at low temperature, so that it does not exhibit varistor behaviour and moreover exhibits poor density. Sintering at higher temperatures produces a nonlinear response in this system, but never as high as that of the two other systems because of the vigorous volatilization of  $\text{Bi}_2\text{O}_3$ . The best strategies yield thick films exhibiting nonlinear behaviour similar to that for films prepared by routes including a uniaxial-isostatic pressing step.

#### Acknowledgements

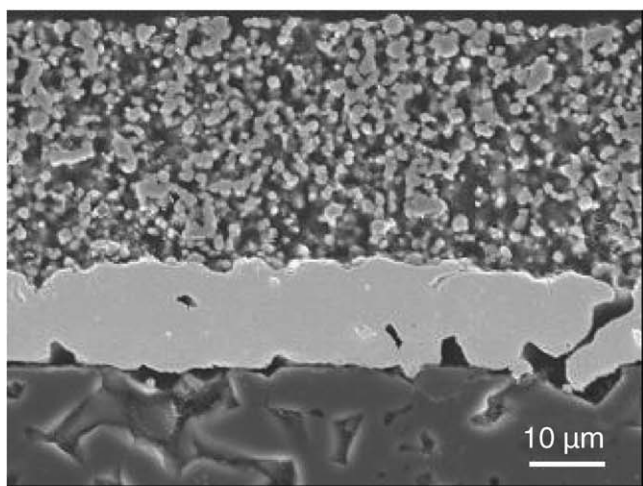
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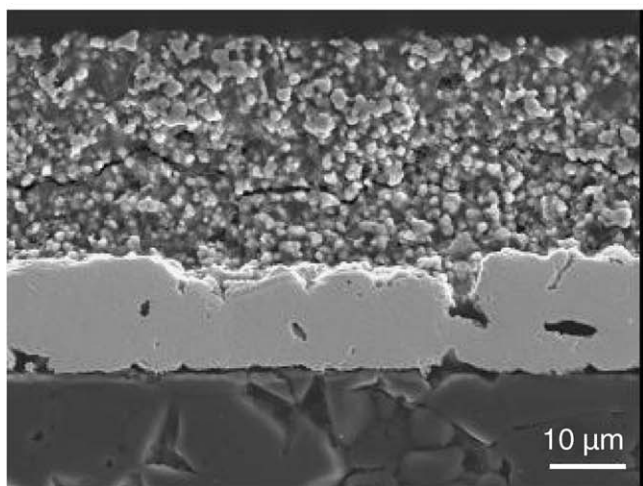
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(a)



(b)



(c)

Fig. 3. SEM micrographs of thick films sintered at  $1050^\circ\text{C}$ –1 h: (a) batch SP; (b) batch SP + sillenite and (c) batch SCM.

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