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Influence of Ta_2O_5 on the electrical properties of ZnO- and CoO-doped SnO_2 varistors

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Abstract

SnO_2-based varistors doped with 0.5% cobalt, 0.5% zinc and various tantalum amounts were prepared by the solid-state route. Experimental evidence shows that small quantities of Ta_2O_5 improve the nonlinear properties of the samples significantly. It was found that samples doped with 0.05 mol% Ta_2O_5 exhibit the highest density (98.5%), the lowest electric breakdown field ($E_b = 1050$ V/cm) and the highest coefficient of nonlinearity ($\alpha = 11.5$). The effect of Ta_2O_5 dopant could be explained by the substitution of Ta^{5+} by Sn^{4+}.

Keywords: A. Powders: solid state reaction; E. Varistors; Tin dioxide

1. Introduction

Varistors are materials with nonlinear current–voltage characteristics. They are used both as protecting devices against overvoltages in electronic and industrial equipments and as surge arrestors [1]. Commercial varistors used in protection systems are based on SiC (silicon carbide) or ZnO (zinc oxide). SiC-based varistors have low nonlinearity coefficients ($\alpha = 5$) where α is the nonlinearity constant defined by the relation: $I = KV^{\alpha}$, where I is current, V is voltage, and K is a proportionality constant [2]. The ZnO-based varistors have very high nonlinearity coefficients ($\alpha = 50$) and their major phase contains (besides ZnO) small amounts of Bi_2O_3, Sb_2O_3, CoO, MnO_2, and Cr_2O_3 [3,4]. The reaction between the ZnO and the additives at high temperatures leads to the formation of several phases at the ZnO grain boundaries [5,6]. Thus, despite their chemical composition and phases, the processing method as well as the sintering temperature, heating and cooling rates influence the electrical properties of these ceramics fundamentally [7]. In view of this fact, the literature contains extensive reports describing the influence of processing variables on the properties and mechanisms that govern these system properties [8–14]. Other varistor systems based on $SrTiO_3$ [15] or TiO_2 [16–19] have been described in the literature, but the nonlinearity of these systems is around ($2 < \alpha < 12$), which is lower compared to that of the multicomponent ZnO varistors.

Pianaro et al. [20] were the first to present a SnO_2-based system as the main candidate to substitute multicomponent ZnO varistors. Tin dioxide is a n-type semiconductor, its main lattice defects are oxygen vacancies. It exhibits a large band gap (3.5–3.0 eV) and a higher electron mobility than it was found for many other oxides. Because of a relatively high concentration of charge carriers at room temperature [21], tin dioxide has already some conductivity even in the absence of dopants.

Normally, tin dioxide fine powders are relucting to densify during sintering. However, additives such as CoO, MnO_2, and ZnO promote high densification, which makes it possible to define the varistor behavior. A very high nonlinearity coefficient ($\alpha = 41$) was obtained in the SnO_2*CoO*Nb_2O_5 system (1.0 mol% of CoO and 0.05 mol% of Nb_2O_5) when 0.05 mol% Cr_2O_3 were added [22]. The major advantage of this system bases on its single-phase microstructure that leads to a long life-time of the varistors and facilitates the adjustment of its processing parameters. The addition of CoO creates oxygen vacancies and Co'_{Sn} or Co''_{Sn} which can segregate at the grain boundaries [23]. Both defects can help the formation of the Schottky barriers at grain boundaries.

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The function of ZnO is the creation of oxygen vacancies and Zn''_{Sn} defects [24]. The latter are less segregated and contribute to the Schottky barrier formation. However, both additives lead to a highly resistive material. The addition of tantalum oxide creates $Ta^{\circ}_{Sn} + V''''_{Sn}$ defects (donor) that increase the lattice conductivity of SnO_2-based ceramics [23]. Moreover, in small concentrations Ta_2O_5 does not segregate at the grain boundaries resulting in a high grain conductivity. Excess of Ta_2O_5 causes segregation of defects at grain boundaries which decrease both, bulk conductivity and grain size.

In this work, we present results that demonstrate the importance of tantalum addition for the nonlinear behavior of SnO_2-based varistor systems.

2. Experimental

The powder was prepared using the mixed oxide method in alcoholic medium. All the oxides used were analytical grade: SnO_2 (Cesbras-Fine), ZnO (Synth), CoO (Riedel), Ta_2O_5 (Aldrich). The molar composition of the investigated systems was $(99.00 - X)\%$ $SnO_2 + 0.50\%$ CoO $+ 0.50\%$ ZnO $+ X\%$ Ta_2O_5, with X equal to 0.025, 0.050, and 0.075 mol%. The amounts of CoO and ZnO were always kept constant, because this additives were used to facilitate densification during sintering. The powder was pressed into pellets by uniaxial pressing followed by isostatic pressing at 210 MPa. The pellets were sintered at 1400 °C for 2 h in oxygen atmosphere and slowly cooled to room temperature (5 °C/min). Mean grain size was determined by analyzing the SEM micrographies (Topcom Sm-300). To perform the electrical measurements, silver contacts were deposited on the samples surfaces. Current-tension measurements were taken using High Voltage Measure Unit (KEITHLEY Model 237). The breakdown electric field (E_b) was obtained at a current density from 1 mA cm^{-2}. The tetragonal structure (rutile structure) of the SnO_2 starting material was confirmed by X-ray diffraction. The X-ray data were collected with a Rigaku-2000 diffractometer under the following experimental conditions: copper anode, 50 kV, 150 mA, Cu Kα radiation monocromatized by a graphite crystal.

3. Results and discussion

Fig. 1 shows the X-ray diffraction analysis of a SnO_2-based varistor system with a molar concentration of 0.50% CoO + 0.50% ZnO and several amounts of Ta_2O_5. Besides the SnO_2 rutile phase, no secondary phase was observed. A sintering study combined with XRD results indicated that sintering at 1400 °C for 2 h are the optimal conditions to obtain crystalline, dense Ta_2O_5, CoO, and ZnO-doped SnO_2 varistors containing only the expected rutile phase. The amount of additives is too small because of the detection limit of the XRD equipment. All dopants

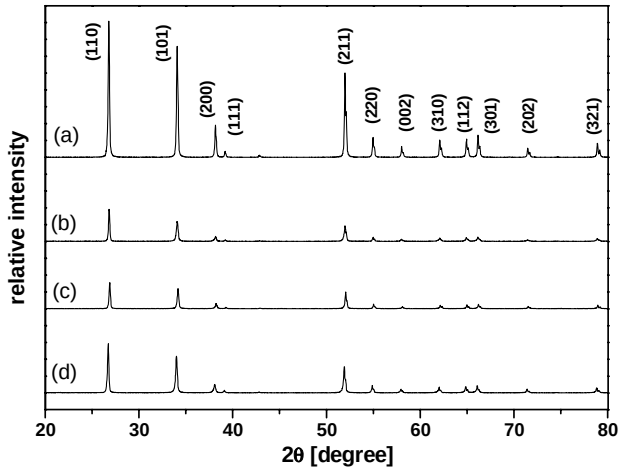

Fig. 1. X-ray diffraction data of the varistor system doped with different tantalum concentrations: (a) without Ta; (b) 0.025 mol%; (c) 0.050 mol%; (d) 0.075 mol%.

introduced in the SnO_2 matrix lead to a stable solid solution according to the Eqs. (1)–(3).

$$\mathrm{ZnO} \xrightarrow{\mathrm{SnO_2}} \mathrm{Zn''_{Sn}} + V_0^{\bullet\bullet} + \mathrm{O}_0^x \quad (1)$$

$$\mathrm{CoO} \xrightarrow{\mathrm{SnO_2}} \mathrm{Co''_{Sn}} + V_0^{\bullet\bullet} + \mathrm{O}_0^x \quad (2)$$

$$2\mathrm{Ta_2O_5} \xrightarrow{\mathrm{SnO_2}} 4\mathrm{Ta_{Sn}}^{\bullet} + V''''_{\mathrm{Sn}} + 10\mathrm{O}_0^x \quad (3)$$

The linear shrinkage rate $(\mathrm{d}(\Delta l/l_0)/\mathrm{d}T)$ and linear variation $\Delta l/l_0$ as a function of temperature for different Ta_2O_5 dopant concentrations are presented in Fig. 2. Here, the maximum shrinkage rate occurred around 1200 °C. The presence of peaks close to 1080 °C indicates the agglomeration during the sintering process (intra- and inter-agglomerates). Another peak close to 1378 °C could arise from defects on the grain boundaries or from a possible SnO_2 evaporation. The increase in tantalum concentration has strong influence on the sintering process of the system. For the highly doped samples, there is a segregation at the grain boundaries shifting the maximum shrinkage temperature to 1300 °C which results to a decrease in grain size. The densities of sintered samples were obtained by the Arquimedes method and are related to the theoretical density of SnO_2 ($\rho_{\mathrm{theoretical}} = 6.95\,\mathrm{g/cm^3}$). The final densities after sintering are higher than 95%, as shown in Table 1. They were only slightly affected by variations of the Ta_2O_5 content, although the average grain size increased significantly with the addition of Ta_2O_5 until 0.050 mol%.

The applied electric field as a function of current density for the different systems is given in Fig. 3. The nonlinear coefficient α was obtained by $\alpha = \log(I_2/I_1)/(V_2/V_1)$ where V_1 and I_1 as well as V_2 and I_2 are corresponding values of voltage and current for two points that can be chosen arbitrarily [25]. The α values were obtained from the curves $E \times J$ for current densities between 1 and 10 mA cm^{-2}. The

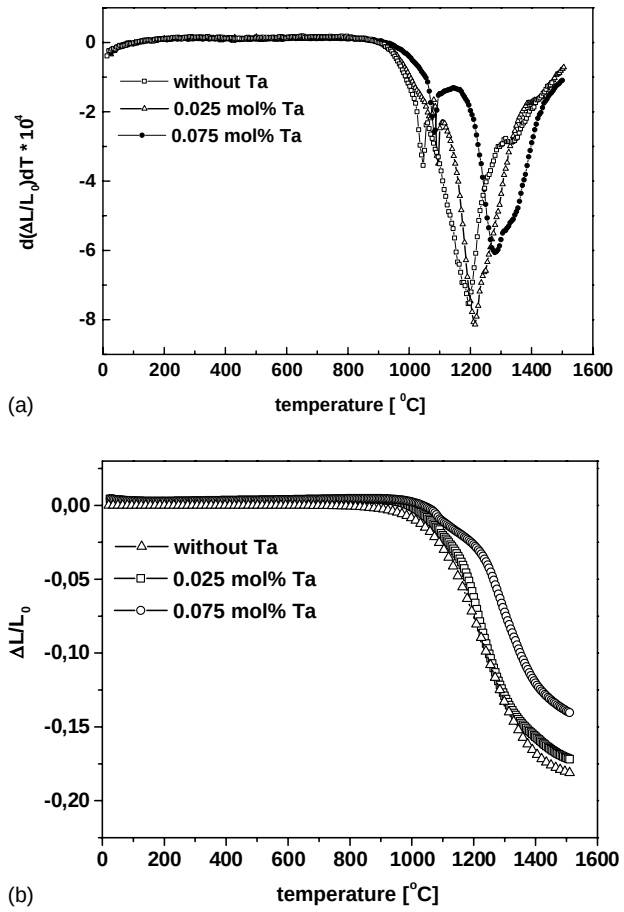

Fig. 2. (a) Linear shrinkage rate. (b) Linear retraction for different dopant concentrations as a function of temperature.

highest nonlinear coefficient ($\alpha = 11.50$) was obtained when molar concentrations of 0.05 mol% Ta_2O_5 were added to SnO_2, presenting an electric breakdown field of 1050 V/cm. For tantalum-free samples, no varistor behavior was found, furthermore the material presented a low conductivity in agreement with low values of current density as shown in Fig. 3a.

It was observed that the addition of Ta_2O_5 in concentrations varying from 0.025 to 0.075 mol% leads to a substantial modification in the electrical behavior of the SnO_2*ZnO*CoO ceramics. The electric behavior of the system without Ta_2O_5, although nonlinear, is highly resistive. The samples containing 0.075 mol% Ta_2O_5 are more resistive (electrical breakdown close to 1900 V/cm) and possess a nonlinear coefficient equal to 9.9. Comparing the results presented in Table 1 and Fig. 3, it can be concluded that the Ta_2O_5 addition until 0.050 mol% to the SnO_2 composition increases the grain size and the nonlinear coefficient thereby reducing the breakdown electric field to 1100 V/cm. Comparing the results obtained for the different compositions (Table 1; Fig. 3), it can be noted that the addition of 0.025 mol% Ta_2O_5 decreases the nonlinear coefficient. This can be explained as follows: The increase in the width of the depletion layer prevents the tunneling of electrons resulting in worse electrical properties. The influence of tantalum oxide on the electric conductivity of CoO-doped SnO_2 ceramics was verified by Dibb et al. [26]. They observed that the electric conductivity of the system increased substantially with Ta_2O_5 doping which was explained by the substitution of Sn^{4+} by Ta^{5+} creating acceptor levels. Recently, Antunes et al. [24] also showed that Ta_2O_5 has the same influence like Nb_2O_5 on SnO_2-based varistor systems without substantial alterations of their electric behavior. This indicates that the importance of this additive arises from its oxidation state (5+).

Table 1 shows the influence of Ta_2O_5 concentration on the average grain size. The mean grain size was obtained by the intercept method. There are significant differences in average grain size with the increase in Ta_2O_5 concentration. The change in grain size could be explained as follows: When low Ta_2O_5 concentrations are introduced to the system, the grain boundary mobility and mass transport are higher and therefore an increase in grain size is observed. For the heavily doped system, the large amount of Ta_2O_5 introduced in the matrix results probably in a segregation at the grain boundaries which might decrease the grain-boundary mobility leading to a decrease in the grain size. These results are in agreement with those of Leite et al. [27] who observed the segregation of Ta_2O_5 in the grain boundaries for the system SnO_2*CoO*Ta_2O_5. From the obtained results one can assume that the addition of tantalum up to 0.05 mol% increases the grain size. Consequently, the Ta_2O_5 concentration deeply influences the morphologic properties of the varistor system. The grains are regularly distributed with an average grain size from 7.0 to 13.45 μm (Table 1).

The mean values of α, E_b and the numbers of effective voltage barriers (V_b) are displayed in Table 1. The effective voltage barriers was determined using the expression: $V_b = E_b \times n$, where n is the number of grains in a line of length L and G is the mean grain size. The V_b can be estimated as $V_b = E_b \times G/L$ [28]. There was a decrease in the number

Table 1
Influence of the Ta_2O_5 on the relative densities, grain sizes and nonlinear coefficients (α) and breakdown fields (E_b) for the SZC system

SnO_2	CoO	ZnO	Ta_2O_5	ρ_r (%)	α	E_b (V/cm)	V_b (V/barrier)	Grain size (μm) ± 1%
99	0.5	0.5	–	97.4	–	–	–	8.5
98.975	0.5	0.5	0.025	96.1	10.9	2440	1.70	7.0
98.95	0.5	0.5	0.050	98.5	11.5	1100	1.49	13.5
98.925	0.5	0.5	0.075	97.4	9.9	1900	1.86	9.8

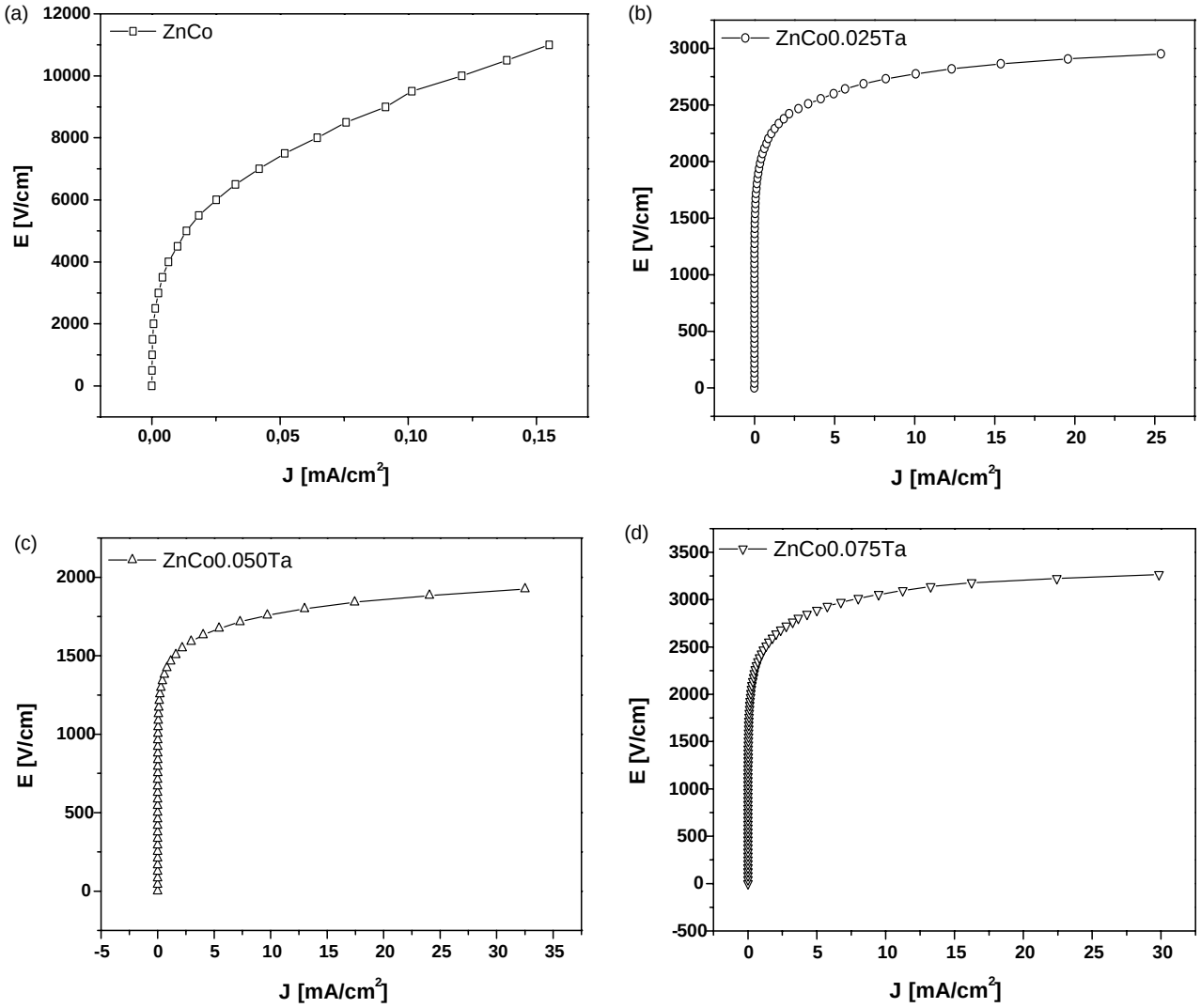

Fig. 3. Applied electric field as a function of current density for the SZC system doped with different tantalum concentrations: (a) without Ta; (b) 0.025 mol%; (c) 0.050 mol%; (d) 0.075 mol%.

of effective barriers of the system doped with 0.050 mol% in Ta_2O_5.

Fig. 4 shows the SEM micrograph of one system considered in this study which confirms a uniform microstructure containing SnO_2 grains free of secondary phases. The relative densities of all samples exceeded 98% of the theoretical density and, according to the XRD analysis no other phases besides SnO_2 rutile were observed.

Considering the microstructure of the SnO_2 varistor, an electric barrier of the Schottky type can be attributed to the SnO_2 grain boundaries. The model presented in Fig. 5 could be proposed basing on the model of Bueno and coworkers [29]. In this model, the donors (positive charges) are distributed on both sides of the grain boundary and are compensated by acceptors (negative charges) at the interface of the grain boundary. Oxygen can be responsible for the formation of a Schottky barrier, provided that it can be adsorbed at the interface and react with the negative defects, according

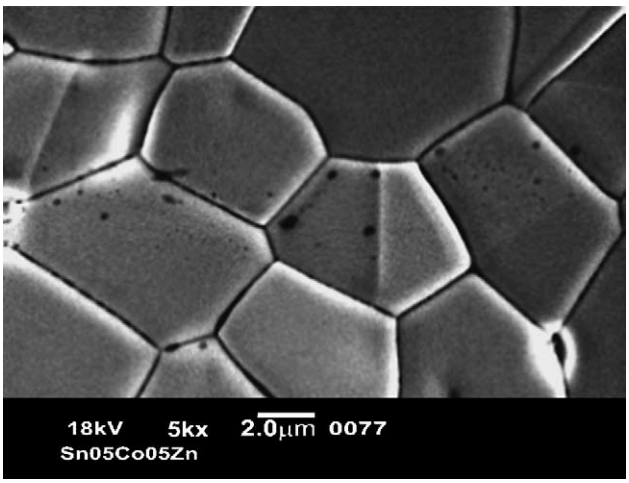

Fig. 4. SEM micrography for SZC system doped with 0.05 mol% of Ta_2O_5.

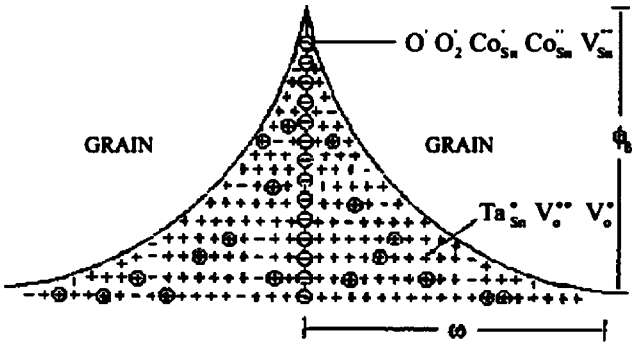

Fig. 5. The grain-boundary defect barrier model for SnO_2*ZnO*CoO*Ta_2O_5 varistors.

to the reactions below:

$$Co'_{Sn} + O_2(ad) \rightarrow O'_2(ad) + Co^x_{Sn} \quad (4)$$

$$Co''_{Sn} + 2O_2(ad) \rightarrow 2O'_2(ad) + Co^x_{Sn} \quad (5)$$

$$Co'_{Sn} + O'_2(ad) \rightarrow 2O'(ad) + Co^x_{Sn} \quad (6)$$

$$Co''_{Sn} + 2O'_2(ad) \rightarrow 4O'(ad) + Co^x_{Sn} \quad (7)$$

These reactions are important to explain the voltage barrier formation at the grain boundaries and therefore a better understanding of the varistor behavior and the mechanisms that lead to this behavior. It can be proposed that the potential barrier is formed by the presence of trap states which are related to oxygen species (O'_2 and O') at the grain-boundary interfaces due to defects such as Co'_{Sn} that transfer electrons to oxide ions.

4. Conclusions

The physical characterization showed that all the systems presented high densifications. The experimental results indicated that α and E_b of the SZC varistor system depend on the Ta_2O_5 concentration. The addition of Ta_2O_5 until 0.05 mol% increases the electric conductivity due to tin vacancy formation. Higher concentrations, however, decrease these properties reducing the number of trap states at the grain boundaries, possibly due to segregation of Ta^{5+} at grain boundaries.

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