ARTÍCULO 15

EFFECT OF Sb_2O_5 DOPING AND SINTERING TEMPERATURE ON VARISTOR PROPERTIES OF SnO_2 -Co3O_4- BASED CERAMICS

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Effect of Sb_2O_5 doping and sintering temperature on varistor properties of SnO_2 -Co_3O_4-based ceramics

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RESUMEN

En el presente trabajo se realizó un estudio del efecto del contenido de Sb_2O_5 y de la temperatura de sinterización sobre las propiedades varistoras de cerámicas a base de SnO_2–Co_3O_4. Los materiales cerámicos fueron preparados mediante mezclado convencional variando los contenidos de Sb_2O_5 en cinco niveles (0.1, 0.2, 0.3, 0.4 y 0.5 % molar) y la temperatura a dos niveles (1350 y 1450 °C). Los resultados muestran que la temperatura de sinterización afecta significativamente el valor del voltaje de ruptura, siendo dicho efecto más marcado en el cerámico con 0.3 % mol Sb_2O_5. Además, se produce un crecimiento de grano notable pero sin una densificación total aparente. A 1450 °C, la temperatura de sinterización óptima para lograr los voltajes de ruptura más bajos, adiciones de Sb_2O_5 confieren un efecto benéfico pero sólo hasta 0.3 % mol. El coeficiente de no-linealidad también se ve afectado por la temperatura de sinterización, pero de manera opuesta, pues con la misma composición (0.3 mol % Sb_2O_5) el coeficiente de no linealidad óptimo se obtiene a 1350 °C y el mejor voltaje de ruptura a 1450 °C.

ABSTRACT

In this work, the effect of Sb_2O_5 content and sintering temperature on varistor properties of SnO_2–Co_3O_4 based ceramics was investigated. The ceramic materials were prepared by conventional mixing varying the amounts of Sb_2O_5 in five levels (0.1, 0.2, 0.3, 0.4 and 0.5 mol %) and the sintering temperature in two levels (1350 and 1450 °C). Results show that sintering temperature significantly affects the breakdown voltage, being the effect more prominent in the ceramic with 0.3 mol % Sb_2O_5. Moreover, an evident grain growth was produced but without any apparent total densification. At 1450 °C, the optimum sintering temperature to achieve the lowest breakdown voltages, Sb_2O_5 additions confer a beneficial effect but only up to 0.3 mol %. The nonlinearity coefficient is also affected by sintering temperature but in an opposite manner because, at the same composition (0.3 mol %), while the optimum nonlinearity coefficient is achieved at 1350 °C, the best breakdown voltage is obtained at 1450 °C.

1. Introduction

Varistors are polycrystalline ceramic materials characterized by a high non-ohmic current-voltage behavior [1]. These materials are commonly used as over-voltage and surge absorbers in electronic circuits and electrical systems [2-5]. The foremost parameter used to describe the varistor's non-ohmic behavior is the nonlinearity coefficient (α), defined by the following equation [6]:

$$I = kV^{\alpha} \qquad (1)$$

where I is the current, V is the voltage, k is a constant related to the material's microstructure. The current-voltage behavior of a varistor - as represented schematically in Fig. 1- usually displays three regions. The first one is known as the low-current linear region due to the linear response between current and voltage. The current voltage characteristics of this region are controlled by the resistance of the grain boundary. The intermediate nonlinear region is considered the heart of the varistor. In this region the device conducts an increasingly large amount of current for a small increase in voltage [7]. The transition value between the linear and nonlinear regions is known as the breakdown voltage (U_B) (or breakdown field (E_B)) and defines the varistor's operation range. Finally, in the last region (the high-current region) characterized by grain control, the current-voltage characteristics are linear again as the first region.

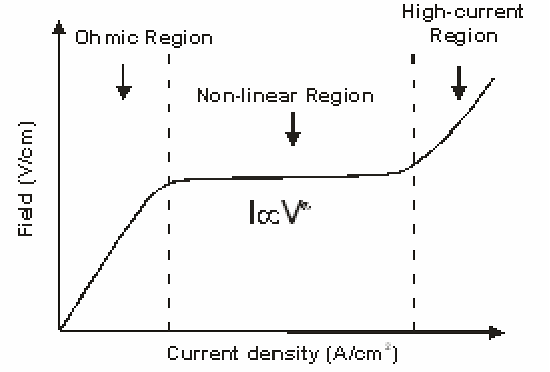

Fig.1 Schematic plot of nonlinear current -voltage characteristics of a ceramic varistor.

Since it was introduced by Matsuoka back in 1971, zinc oxide (ZnO) has been the most extensively studied material (as the base for a ceramic system) and consequently became the most important ceramic for the commercial production of varistors [4, 8]. Due to the need for better properties, recently there has been increased interest in other ceramic materials like TiO_2 [9], $SrTiO_3$ [10] and SnO_2 [11].

Tin oxide (SnO_2) is n-type semiconductor with a rutile-type structure and space group D_{4h}^{14} $[P4_2/mnm]$[12]. As the base for a ceramic system, it has been considered as a promising material for varistor applications [11] and specifically, SnO_2-based ceramics have found great acceptance as gas sensors [13,14]. SnO_2 has low densification rate and limited sinterability [16]. Densification of SnO_2-based ceramics may be enhanced by the addition of dopants such as Co_3O_4 and MnO_2, which allow achieving values close to that of the theoretical density. Highly dense SnO_2 ceramics could found a different application in electronic devices, for example, as varistors [11,15]. It has been reported that in addition to acting as a densifier for SnO_2-based systems, the Co dopant atoms favor the interaction of oxygen species with the oxide surface [16]. More specifically, Co_3O_4 induces modifications in the oxygen vacancy concentration and promotes increase in density. These changes can be explained with the aid of replacement equations representing phenomena occurring in the tin oxide lattice. Possible substitution equations, in terms of the Kröger-Vink standard notation are as follows:

$$Co_3O_4 \rightarrow CoO + Co_2O_3$$

$$CoO \xrightarrow{SnO_2} Co_{Sn}'' + V_O^{\bullet\bullet} + O_O^x$$

$$CoO \xrightarrow{SnO_2} Co_{Sn}'' + 2V_O^{\bullet} + \tfrac{1}{2}O_2$$

$$Co_2O_3 \rightarrow 2Co_{Sn}' + V_O^{\bullet\bullet} + 3O_O^x$$

$$Co_2O_3 \rightarrow 2Co_{Sn}' + 2V_O^{\bullet} + 2O_O^x + O_2$$

$$V_O^{\bullet\bullet} + e' \rightarrow V_O^{\bullet}$$

It is worth noting that although the majority of dopants are added to enhance the electrical nonlinearity and/or stability, some of them are used specifically to either enhance or limit grain growth. Since both, the breakdown voltage and the energy handling capability increase with the number of grains (per unit distance) between the electrodes, the grain size is an important process parameter in the manufacture of both high- and low-voltage varistors. As with many other ceramics, grain growth control can be brought about by changing both the defect structure and particle pinning of grain boundaries. Antimony has been reported as one of the most effective dopants [17]. In the case of ZnO-based ceramics, it readily forms both the spinel (nominally $Zn_7Sb_2O_{12}$) and the pyrochlore (nominally Zn_2Bi_2 Sb_3O_{14}) phases that primarily form at the grain boundaries [2-4]. In spite of the numerous investigations devoted to studying the effect of dopants on the nonlinear electrical characteristics of ceramic based materials (mainly on SiC and ZnO) the related literature shows that the use of Sb_2O_5 has not been considered until now.

Antimony pentoxide Sb_2O_5 can be used in compositions for low-voltage SnO_2-based varistors [11]. Therefore, the present work is an effort to develop a SnO_2-based varistor in a system SnO_2-Co_3O_4-Sb_2O_5 with low breakdown voltage. The effect of Sb_2O_5 doping and the variation of sintering temperature on varistor properties in the binary system SnO_2+5mol % Co_3O_4 was investigated.

2. Experimental Procedure

Analytical grade of SnO_2 (Baker), Co_3O_4 (Baker) and Sb_2O_5 (Aldrich) powders were used as raw starting materials for the preparation of a series of mixtures with compositions given by (95-x) % SnO_2 + 5% Co_3O_4 + x% Sb_2O_5, being x equal to 0.1, 0.2, 0.3, 0.4 and 0.5 (mol. %). The powders were thoroughly mixed in an agate mortar using distilled water as milling media for 1 hour and dried in an oven at 125°C for 2 hours. Then the resulting mixtures were compacted axially in tablets (10.0 mm in diameter x 1.2 mm height) at a pressure of 230 MPa.

Sintering was carried out in a tube furnace (Lindberg/Blue STF55433C-1), heating the tablets at a rate of 6 °C/min up to the test temperature (1350 or 1450 °C), holding for 1 hr at this temperature and then cooling down to room temperature at 6 °C/min. After reaching room temperature, the specimens were removed from the furnace for physical and electrical characterization, using a scanning electron microscope (JEOL JSM 6300) and a High Voltage Measure Unit (Keithley 237). Density evaluation of the sintered specimens was carried out using Archimedes' principle. In preparation for the electrical characterization, silver electrodes were placed on both faces of the sintered specimens followed by a thermal treatment at 800°C for 6 minutes. Current-voltage measurements were taken using the aforementioned apparatus and the non-linear coefficient α was evaluated according to the following relationship:

$$\alpha = \frac{\log(J_2 / J_1)}{\log(E_2 / E_1)} \qquad (1)$$

where E_1 and E_2 are the applied electric fields corresponding to the current densities $J_1 = 0.2\ mA \cdot cm^{-2}$ and $J_1 = 2\ mA \cdot cm^{-2}$, respectively. The breakdown field (E_B) was determined using a current density of 1mA/cm^2. *J* and *E* were calculated through *I/s* and *V/t*, where *s* is the area of the silver electrode and *t is* the thickness of the specimen tested.

3. Results and discussion

Figures 1 (a) and (b) are plots of electric field *vs*. current density for all compositions at 1350 and 1450 °C, respectively. These plots clearly show the nonlinear behavior of $J - E$ - characteristic and the effect of sintering temperature on the variation of the breakdown field.

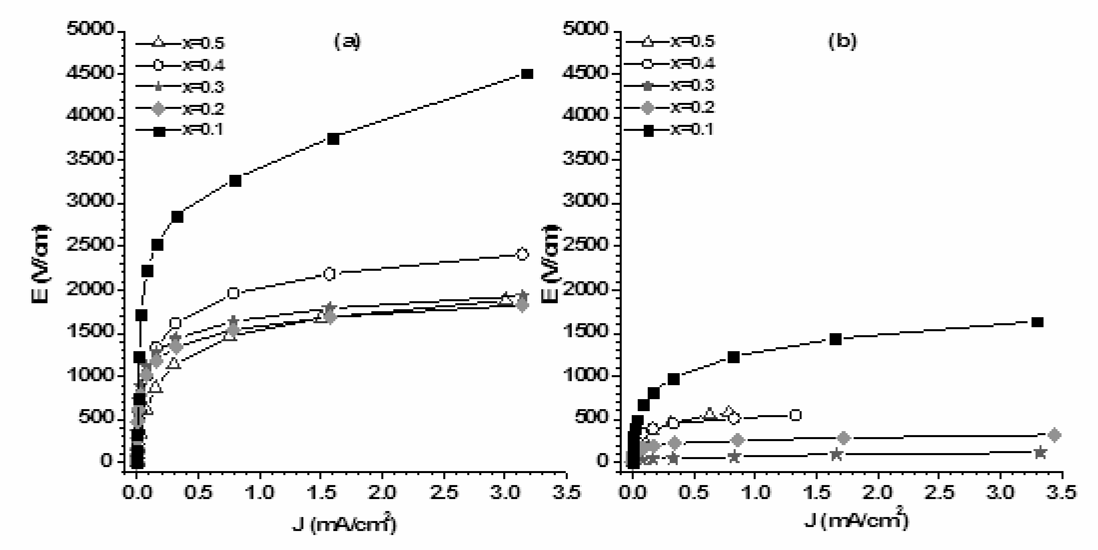

Figure 1 *J* vs. *E* curves for ceramics with variation in composition according to *(95-x)%* SnO_2 + *5%* Co_3O_4 + *x%* Sb_2O_5, (x = 0.1, 0.2, 0.3, 0.4 and 0.5) for specimens sintered for 1h at: (a) 1350 °C and (b) 1450 °C.

The effect of composition and sintering temperature on the magnitude of breakdown voltage can be seen more clearly in Fig. 2 and although at both temperatures the curves feature a minimum and a maximum, the effect is more evident at 1350 ^{o}C. Furthermore, the lowest values of E_B are obtained at 1450 ^{o}C, being 0.3 mol % the optimum Sb_2O_5 content.

Figure 3 shows plots of nonlinearity coefficient vs composition at both sintering temperatures. At 1350 ^{o}C an increase in the nonlinearity coefficient is observed up to 0.3 mol % Sb_2O_5, after which α drops off. At 1450 ^{o}C two maximum and one minimum are observed. Although this behavior had been observed previously by others, no explanation has been given up to now [18,19]. However, the optimum Sb_2O_5 content is 0.3 mol % and the most favorable temperature is 1350 ^{o}C.

The observed behavior can be directly related with the microstructure. Figure 4 shows SEM photomicrographs of specimens with 0.4 mol % Sb_2O_5 sintered at 1350 and 1450 ^{o}C. Although grain size is augmented with increase in sintering temperature, not much improvement is obtained with regard to densification, because a considerable amount of porosity still remains.

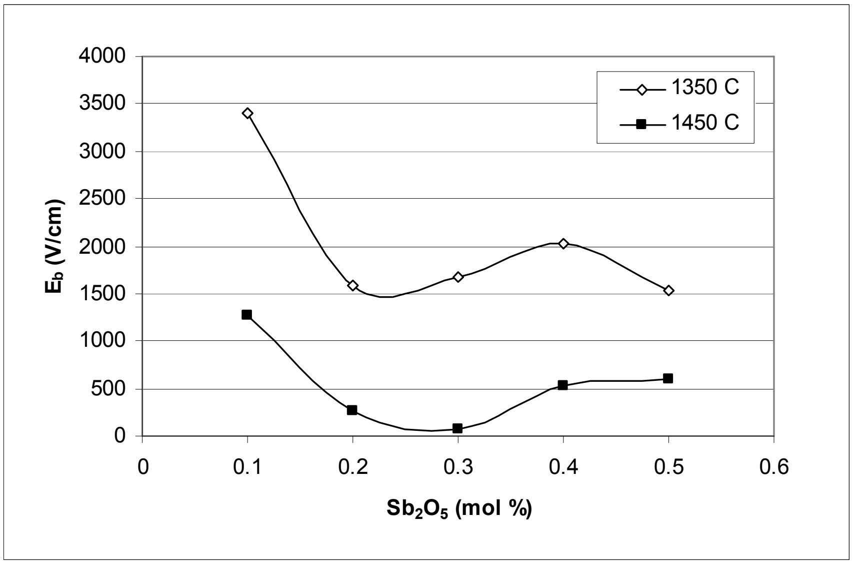

Figure 2 Effect of variation in composition ((95-x)% SnO_2 + 5% Co_3O_4 + x% Sb_2O_5, (x = 0.1, 0.2, 0.3, 0.4 and 0.5) and sintering temperature on the magnitude of the breakdown voltage E_b.

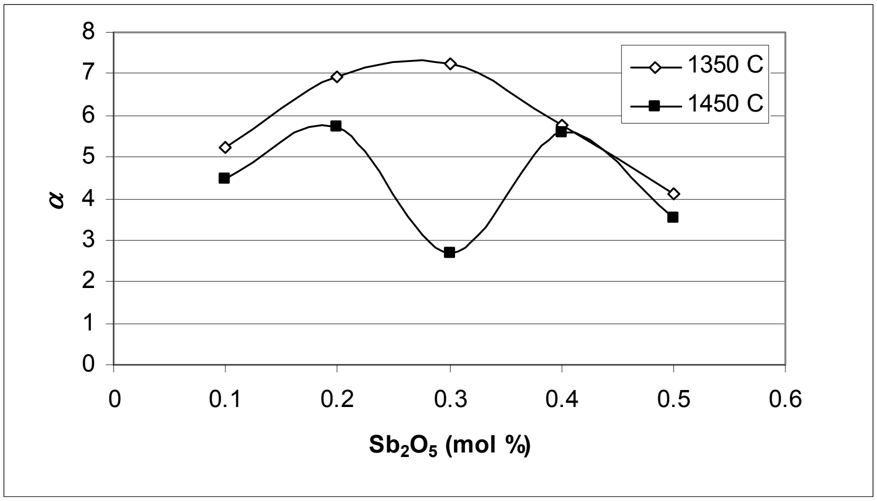

Figure 3 Effect of variation in composition (*(95-x)%* SnO_2 *+ 5%* Co_3O_4 *+ x%* Sb_2O_5, (x = 0.1, 0.2, 0.3, 0.4 and 0.5) and sintering temperature on the magnitude of the nonlinearity coefficient *α*.

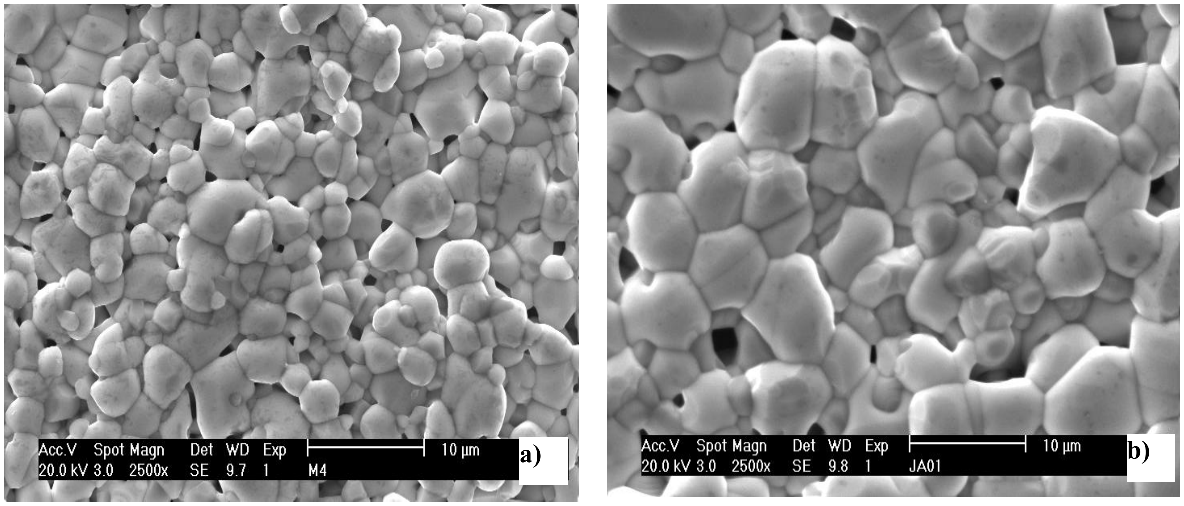

Figure 4 SEM photomicrographs of specimens with the composition SnO_2+5%Co_3O_4+0.4%Sb_2O_5 sintered at (a) 1350 °C and (b) 1450 °C.

Although the behavior of the magnitude of the breakdown voltage with variation in the amount of Sb_2O_5 is quite complex, comparing both temperatures, it is evident that E_B decreases significantly when the amount of Sb_2O_5 is increased from 0.1 mol% to any of the other levels tested (Fig.2). It can be related to the variation of microstructure (mainly, through the variation of the grain size) and to the decrease of the grain resistivity due to a doping by Sb. An increase of electronic conductivity in the SnO_2 lattice is attributed by the substitution of Sn^{4+} by Sb^{5+}, according to the next scheme:

$$Sb_2O_5 \xrightarrow{SnO_2} 2Sb_{Sn}^{\bullet} + 2e' + 4O_O^x + \tfrac{1}{2}O_2(g)$$

It has been recognized that cobalt ions in the SnO_2-based ceramics play a crucial role in densification, although no relevant improvements are attained in terms of electrical properties [20]. Cobalt ions bring about an increase in the oxygen vacancies concentration allowing solid state diffusion and material densification. To illustrate this additionally, in Fig. 5 a SEM photomicrograph of a SnO_2 specimen doped only with 5 mol % Co_3O_4 and sintered at 1350 °C is shown. Although the beneficial effect on densification during sintering was obvious, the specimen turned out to exhibit poor electrical properties for varistor applications.

Table 1 summarizes the processing conditions as well as the values of physical and electrical parameters of the varistor systems studied. The best nonlinearity coefficient (α = 7.2) was obtained when the molar concentration of Sb_2O_5 was 0.3 mol %., at the sintering temperature of 1350 °C.

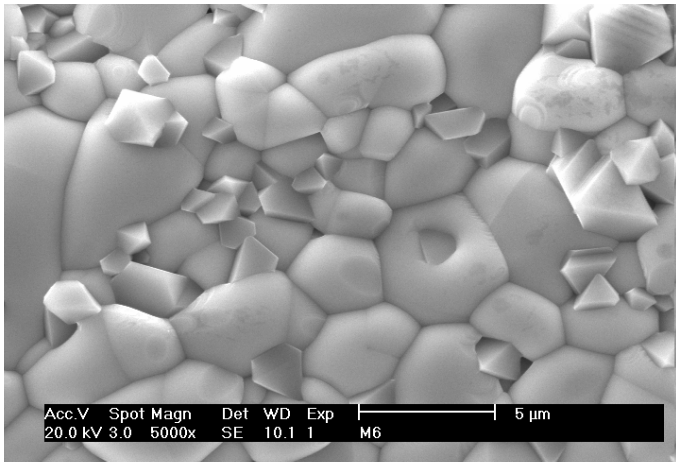

Figure 5. SEM photomicrograph of a ceramic sample with composition 95%SnO_2-5%Co_3O_4, sintered at 1350 °C.

Table 1 Physical and electrical parameters of the ceramic-mix systems investigated.

Sb_2O_5 (%mol)	Temperature (°C)	ρ (g/cm^3)	Relative density (%)	α	E_B (V/cm)
0.1	1350	5.74	82.58	5.2	3408
	1450	5.96	85.75	4.5	1275
0.2	1350	5.68	81.75	6.9	1580
	1450	5.84	84.02	5.7	264
0.3	1350	5.88	84.64	7.2	1682
	1450	6.29	90.58	2.7	72
0.4	1350	6.07	87.35	5.8	2022
	1450	6.10	87.79	5.6	527
0.5	1350	5.76	83.00	4.1	1533
	1450	5.86	84.33	3.5	600

SnO_2 theoretical density: 6.95 g/cm^3

CONCLUSIONS

Results from this investigation show that sintering temperature significantly affects the breakdown voltage. At the lowest sintering temperature, additions of Sb_2O_5 from 0.1 to 0.3 mol% induce a decrease in E_B. Particularly for the ceramic with 0.3 mol % Sb_2O_5, the value of E_B lowers dramatically by a factor of about 1/23 when sintering temperature increases from 1350 °C to 1450 °C. The best nonlinearity coefficient is obtained in the specimen with 0.3 mol% at 1350 °C.

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