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Effect of CaO on the microstructure and non-ohmic properties of (Co,Sb)-doped SnO_2 varistors

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The effect of CaO through additions of $CaCO_3$ on the physical characteristics, microstructure, and current-voltage properties of (Co-Sb)-doped SnO_2 varistors was investigated. SnO_2-Co_3O_4-Sb_2O_5 ceramics with additions of 0.1, 0.5 and 1 mol % CaO were sintered at 1450°C under oxidizing atmosphere and characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD). Results show that, at low and intermediate CaO levels, density is not significantly influenced, whilst at the highest level, density decreases substantially. The nonlinear coefficient and the breakdown voltage behave similarly in one sense because both present a maximum, and because at the highest CaO level, both response variables show the lowest values. The nonlinear coefficient presents a maximum of 12.9 at 0.1 mol % CaO, while the same maximum for the breakdown voltage occurs at 0.5 mol % CaO. At 1 mol % CaO, the breakdown voltage is 288 Vcm^{-1}.

Keywords: Varistors; breakdown voltage; nonlinearity.

Se investigó el efecto del CaO a través de adiciones de $CaCO_3$ sobre las características físicas, la microestructura y las propiedades corriente-voltaje de varistores de SnO_2 dopados con Co y Sb. Los cerámicos SnO_2-Co_3O_4-Sb_2O_5 dopados con 0.1, 0.5 y 1% molar de CaO fueron sinterizados a 1450 °C bajo condiciones oxidantes y caracterizados por microscopía electrónica de barrido (MEB), espectroscopía por energía dispersiva de rayos X (EDX) y por difracción de rayos X (DRX). Los resultados muestran que, a niveles bajo e intermedio de CaO, la densidad no se ve afectada significativamente mientras que al nivel más alto, la densidad disminuye sustancialmente. El coeficiente de no linealidad y el voltaje de ruptura se comportan en un sentido de manera similar, porque ambos presentan un máximo y porque al nivel más alto de CaO ambos presentan los valores más bajos. El coeficiente de no linealidad presenta un máximo de 12.9 a 0.1% molar de CaO, mientras que el máximo correspondiente para el voltaje de ruptura ocurre a 0.5% molar de CaO. A 1% molar de CaO, el voltaje de ruptura es de 288 V cm^{-1}.

Descriptores: Varistores; voltaje de ruptura; no linealidad.

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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 main feature used to describe the varistor's non-ohmic behavior is the nonlinearity coefficient α defined by the following equation:

$$J = kE^{\alpha}, \tag{1}$$

where J is the current density, E is the applied electric field, and k is a constant related to the material's microstructure. Since it was introduced by Matsuoka back in 1971, zinc oxide (ZnO) has been the most extensively studied material (as the base for ceramic systems), and thus became the most important ceramic for the commercial production of varistors [4,6]. Because of the need for better properties, there has recently been an increase in interest in other ceramic materials such as TiO_2[7], $SrTiO_3$[8] and SnO_2[9]. Tin dioxide (SnO_2) is an n-type semiconductor with a rutile-type structure and space group D_{4h}^{14} $[P4_2/\mathrm{mnm}]$ [10]. As the base for ceramic systems, it has been considered a promising material for varistor applications [9], and specifically SnO_2-based ceramics havefound great acceptance as gas sensors [11,12]. Tin dioxide has a low densification rate and limited sinterability. Densification of SnO_2-based ceramics is enhanced by adding dopants such as Co_3O_4 or MnO_2[13], which allow values close to that of the theoretical density to be achieved. Dense SnO_2 ceramics could find a different application in electronic devices, for example, as varistors [9,14]. It has been reported that, besides acting as a densifier for SnO_2-based systems, the Co dopant atoms benefit the interaction of oxygen species with the oxide surface [15]. Specifically, Co_3O_4 induces changes in the oxygen vacancy concentration and promotes an increase in density. The purpose of the present work is to analyze the influence of CaO on the electrical properties and on the microstructure of the ternary system SnO_2-Co_3O_4-Sb_2O_5. The effect of inhomogeneities on the microstructure is also addressed.

2. Experimental procedure

Analytical grade SnO_2 (Aldrich), Co_3O_4 (Aldrich), Sb_2O_5 (Aldrich) and $CaCO_3$ (Baker) were used as the raw chemicals in this work. The molar composition of the systems investigated was (98.95-X)% SnO_2-1% Co_3O_4-0.05% Sb_2O_5-X% $CaCO_3$, where X = 0.0, 0.1, 0.5 and 1%. The powders were processed by a non-conventional mixing method, through high-energy milling performed in a Restch PM-100 planetary ball-mill using vials and balls of agate for 20 minutes. The resulting powders were uniaxially pressed in the form of tablets (10.0 mm diameter and about 1.2 mm thickness) at 230 MPa and using no binder. The tablets were sintered in ambient atmosphere at 1450°C for 1 hour with a heating and cooling rate of 6°C/min in a tube furnace (Lindberg/Blue STF55433C-1). For electrical characterization, silver electrodes were placed on both faces of the ceramic sintered samples followed by thermal treatment at 800°C for 6 minutes. Current-voltage measurements were taken using a High Voltage Measure Unit (Keithley 237). The nonlinear coefficient α was evaluated in terms of the relation:

$$\alpha = \frac{\log (J_2/J_1)}{\log (E_2/E_1)}, \tag{2}$$

where E_1 and E_2 are the applied electric fields corresponding to the current densities J_1 and J_2, respectively. The breakdown voltage E_B was measured at 1 mA cm^{-1}. J and E can be calculated by means of i/s and V/t, where i is the electric current, s is the area of the silver electrode, and t is the thickness of the tested sample. The values of linear shrinkage γ were obtained according to the expression:

$$\gamma = \frac{D_O - D}{D_O}, \tag{3}$$

where D_0 and D stand for the sample diameter before and after sintering, respectively. Density measurements of the sintered samples were made using Archimedes' method and related to the theoretical density of SnO_2: 6.95 g/cm^3. Microstructure characterization of the sintered specimens was carried out by X-ray diffraction ($Cu_{K\alpha}$ radiation in a Philips 3040 X-ray diffractometer), by scanning electron microscopy (SEM) (Philips XL30 ESEM), and by energy dispersive X-ray spectroscopy (EDX). The mean grain size was determined from SEM micrographs, using an Image Analysis Software (Image-Pro Plus), according to standard procedures, ASTM-E112.

3. Results and discussion

Introducing Co_3O_4 into the SnO_2 lattice leads to the formation of vacancies by substituting tin atoms, thus providing an increase in the diffusion coefficient of ions. This ion diffusion promotes the SnO_2sintering, and therefore, an increase in its density. These changes can be explained with the aid of replacement equations representing phenomena occurring in the tin dioxide lattice. Possible substitution equations, using the Kröger-Vink standard notation, are as follows:

$$Co_3O_4 \rightarrow CoO + Co_2O_3 \tag{4}$$

$$CoO \xrightarrow{SnO_2} Co''_{Sn} + V_O^{\bullet\bullet} + O_O^x \tag{5}$$

$$CoO \xrightarrow{SnO_2} Co''_{Sn} + 2V_O^{\bullet} + \tfrac{1}{2}O_2 \tag{6}$$

$$Co_2O_3 \xrightarrow{SnO_2} 2Co'_{Sn} + V_O^{\bullet\bullet} + 3O_O^x \tag{7}$$

$$Co_2O_3 \xrightarrow{SnO_2} 2Co'_{Sn} + 2V_O^{\bullet} + 2O_O^x + O_2 \tag{8}$$

$$V_O^{\bullet\bullet} + e' \rightarrow V_O^{\bullet}. \tag{9}$$

The addition of Sb_2O_5 to the SnO_2 ceramics may cause the reaction:

$$Sb_2O_5 \xrightarrow{SnO_2} 2Sb_{Sn}^{\bullet} + 2e' + 4O_O^x + \tfrac{1}{2}O_2(g), \tag{10}$$

where e is an electron activated from donor Sb in the SnO_2 lattice. As the current carrier, the electrons cause an increase in the electrical conductivity of the grain. Thus resistivity of SnO_2 grains is decreased. Please note that calcium carbonate decomposes thermally into calcium oxide and carbon dioxide, according to

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}. \tag{11}$$

At ambient pressure, there is previously a transition from aragonite to calcite at 457°C, and the most important weight loss occurs between 650-730°C [16,17]. It is therefore more correct to focus our discussion on the effect of CaO (instead of $CaCO_3$) on the microstructure and electrical properties of the SnO_2-based ceramics. Moreover, due to the stoichiometry of reaction in Eq. (11), it is safe to consider that CaO also varied at the levels 0.1, 0.5 and 1 mol %. Therefore, the addition of CaO to the SnO_2 ceramics may cause the following reaction:

$$CaO \xrightarrow{SnO_2} Ca''_{Sn} + V_O^{\bullet\bullet} + O_O^x, \tag{12}$$

where the dissolution of CaO into SnO_2 grains creates an oxygen vacancy and a negatively charged defect (Ca''_{Sn}) [see Eq. (11)]. Because of its large ionic radius, Ca has low solubility in the SnO_2 grains. Table I shows the values of relative density, shrinkage, grain size, nonlinearity coefficient, and breakdown voltage of the samples doped with different contents of $CaCO_3$. So, it can be seen that the relative density of the samples was unchanged by the addition of CaO to the ternary system, except for that with the highest $CaCO_3$ content, namely 1 mol %. It can also be seen that the grain size decreases when the ceramic is doped with CaO and that the grain size gradually decreases if the CaO content in the (Co, Sb)-doped SnO_2 varistors increases. The increase in CaO content inhibits the grain growth because only a little Ca very likely dissolves in the SnO_2 grains, while most of the Ca segregates preferentially at the SnO_2 grain boundaries due to its low solubility, which might decrease the grain boundary mobility, leading to a decrease in the grain size. According to Fig. 1, there is a very similar behavior of current-voltage

TABLE I. Characteristics of the samples doped with different contents of CaO.

$CaCO_3$ (mol %)	Density (g/cm^3)	Relative density* (%)	Grain size (μm)	Shrinkage (%)	α	E_B (V/cm)
0.00	6.71 ± 0.06	96.40	14.53	13.1	10.6	378
0.1	6.68 ± 0.03	96.11	12.32	12.8	12.9	376
0.5	6.72 ± 0.05	96.69	12.66	12.9	12.5	446
1	6.59 ± 0.08	94.82	10.23	13.3	9.1	288

*Theoretical density of SnO_2 is 6.95 g/cm^3.

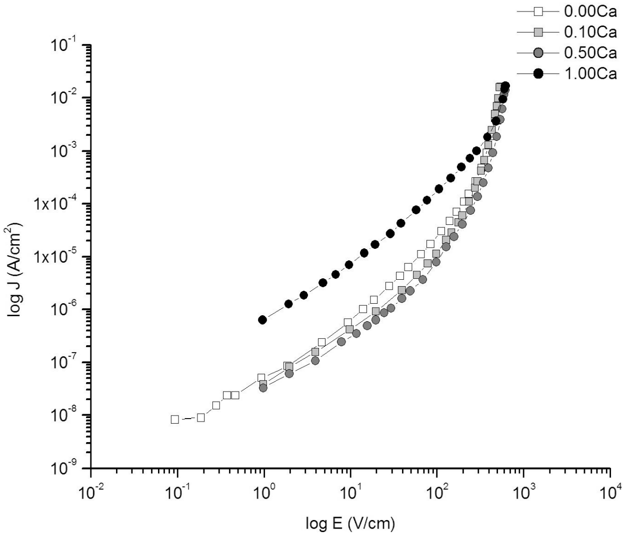

FIGURE 1. Current–voltage logarithmic plots for all samples: (a) 0.0, (b) 0.1, (c) 0.5, and (d) 1 % Ca.

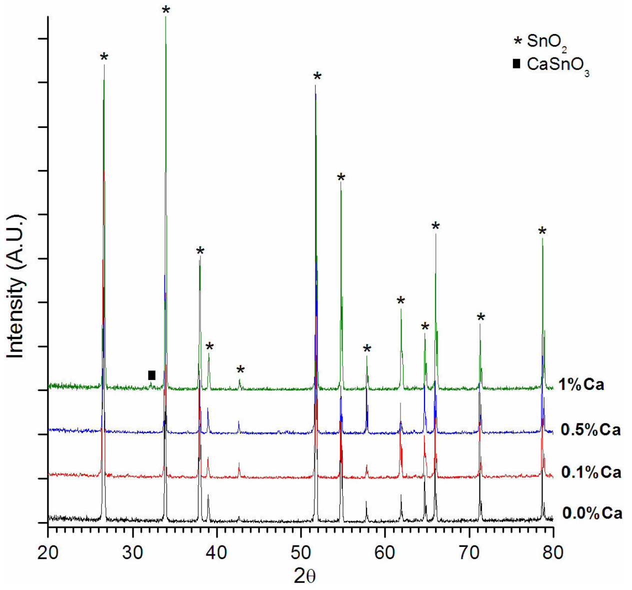

FIGURE 2. XRD patterns of the varistors for different calcium contents.

characteristics in samples doped with 0, 0.1, and 0.5 mol% CaO. The highest α value was obtained when the molar concentration of CaO was 0.1 mol%, while the lowest α and E_B values were found in the composition doped with 1.0 mol % CaO. Traditionally, the following equation should explain the breakdown voltage measurements:

$$E_B = nV_b, \tag{13}$$

where E_B is the breakdown voltage, n is the number of grains per unit length, and V_b is the rupture voltage for a grain boundary. This Eq. (13) implies that the smaller the grain size, the greater the number in potential barriers and the larger the breakdown voltage, if rupture voltage per grain unit is constant at only one sintering temperature. However, as can be seen in Table I, Eq. (13) is not able to describe our results because the smaller grain size corresponds to the lowest breakdown voltage. The reason for this behavior is that only a small quantity of the CaO added dissolves in the SnO_2 grains, which promotes a modification in the rupture voltage V_b of the grains. As a consequence, V_b is no longer constant in Eq. (13), and therefore the highest breakdown voltage in our ceramic does not necessarily correspond to the lowest grain size. Figure 2 shows the X-ray diffraction analysis of an SnO_2 based varistor system with a molar concentration of 1% Co_3O_4-0.05% Sb_2O_5 for different amounts of CaO. Besides the SnO_2 rutile phase, no secondary phase is observed in the samples doped with a molar concentration of 0.0, 0.1, and 0.5% CaO. However, in the sample doped with 1% of CaO, the presence of a $CaSnO_3$ spinel phase is observed. This spinel phase might be the reason why the breakdown voltage behavior of our samples deviates from Eq. (13), that is, the rupture voltage V_b of the grains is modified by the presence of the spinel phase. Meanwhile, Fig. 3 shows SEM photomicrographs of specimens with 0.0 (a), 0.1 (b), 0.5 (c), and 1.0 (d) mol % CaO, respectively. In all cases, a good bonding between the grains exists, and it appears geometrically well-defined. Apparently, the increase in CaO addition causes no change in the ceramic microstructure at 1450°C. However, there is a particular characteristic that can only be noticed when comparing with the microstructure of a specimen sintered at 1350°C. A discussion of the effect of both temperature and CaO additions on the microstructure and electrical behavior is not dealt with in this paper; nonetheless, it will be reported elsewhere. Figure 4 shows photomicrographs representing the microstructure of specimens sintered at 1350°C with 0.0 (a) and 0.1 (b) mol % CaO. Apparently addition CaO at 1350°C promotes densification but, in turn, limits grain growth. By contrast, important grain growth is observed at 1450°C. A detailed comparison of the

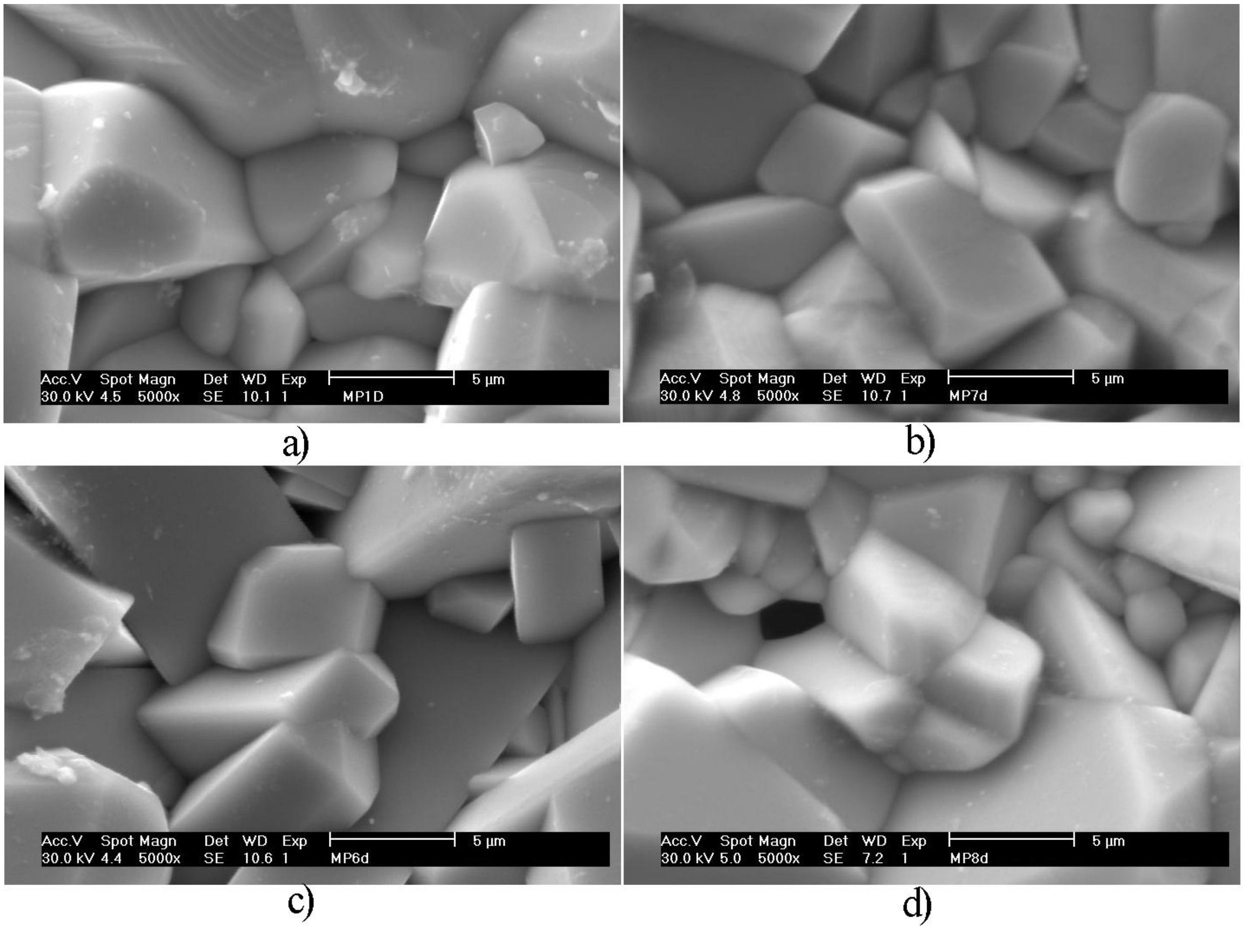

FIGURE 3. SEM micrographs of samples sintered at 1450°C for 1 hour: (a) 0.0, (b) 0.1, (c) 0.5, and (d) 1 % Ca.

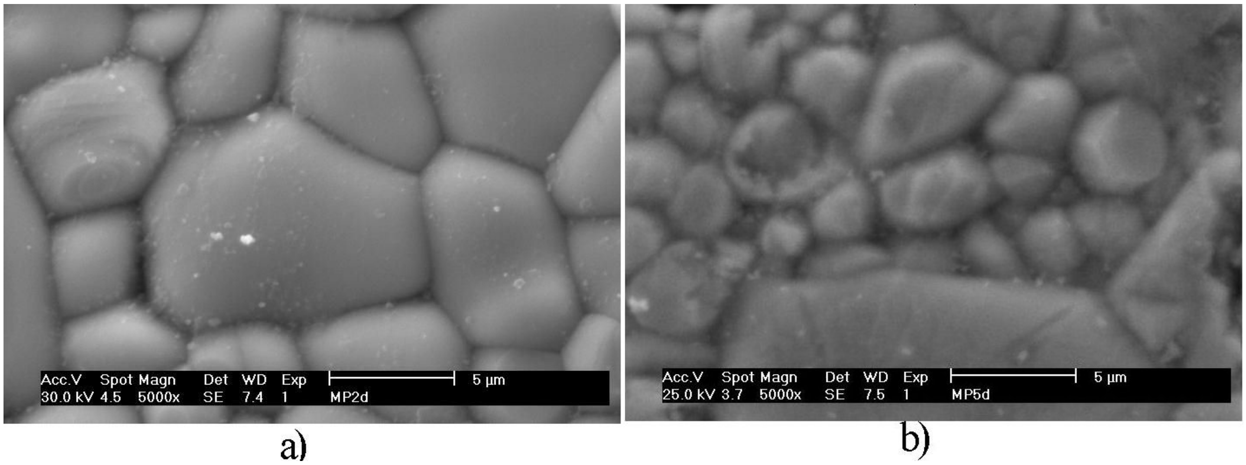

FIGURE 4. SEM micrographs of samples sintered at 1350°C for 1 hour: (a) 0.0 and (b) 0.1 % Ca.

microstructures shown in Fig. 2 and 3 suggests that, during sintering at 1450°C, the grains not only bond together but also obstruct each other in such a way that exaggerated grain growth occurs towards free surfaces.

4. Conclusions

In this work, the effect of CaO through the addition of $CaCO_3$ on the microstructure and electrical properties of SnO_2-Co_3O_4-Sb_2O_5 ceramic mix was investigated. Apparently density is not significantly influenced by addition of CaO at low and intermediate levels. However, it is strongly influenced by the highest level of $CaCO_3$ addition, namely

1 mol %. With the addition of CaO to the raw mix, an increment in the nonlinear coefficient α is obtained, and a slight decrease on going from 0.1 to 0.5 mol % $CaCO_3$ is also observed. However, a noticeable decrease with the highest carbonate addition is determined. The breakdown voltage on the other hand behaves differently, because there is a maximum at 0.5 mol % $CaCO_3$. Both α and E_B are minimal at the highest $CaCO_3$ (1 mol %).

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