Effect of Cr_2O_3 on the microstructure and non-ohmic properties of (Co, Sb)-doped SnO_2 varistors

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The effect of Cr_2O_3 addition 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 0.0, 0.03, 0.05 and 0.07 mol % Cr_2O_3 were sintered at 1350 ^{o}C under ambient atmosphere and characterized microstructurally and electrically. The characterization by XRD and SEM show that the microstructure remains as a single phase material with multimodal size distribution of SnO_2grains. The greatest effect of Cr_2O_3additions is manifested in the electric breakdown field. Additions of high levels (0.07 and 0.05 %) of this oxide promote an increase of approximately 55% in this parameter compared to the Cr_2O_3-free sample. Another physical property is affected: the measured density values decreases as the Cr_2O_3 content increases. A change in the nonlinearity coefficient value is produced only at the highest Cr_2O_3 content while at intermediate levels there is not change at all. Consequently, when seeking high nonlinearity coefficients, intermediate levels of Cr_2O_3 are not recommended.

Keywords: Varistor; breakdown voltage; nonlinearity.

Se investigó el efecto de adición de Cr_2O_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 0.0, 0.03, 0.05 y 0.07 % molar de Cr_2O_3 fueron sinterizados a 1350°C a medio ambiente y caracterizados microestructuralmente y eléctricamente. Los resultados de la caracterización por DRX y MEB muestran que la microestructura del material permanece como una sola fase con una distribución multimodal de tamaño de grano del SnO_2. El mayor efecto de la adición de Cr_2O_3 se manifiesta en el campo eléctrico de ruptura. A altos niveles (0.07 y 0.05%) de adición de éste óxido se promueve un incremento de aproximadamente 55% de este parámetro comparado con el de la muestra libre de Cr_2O_3. Otra propiedad física que es afectada son los valores de la densidad medida ya que disminuye cuando se incrementa el contenido de Cr_2O_3. Un cambio en el valor del coeficiente de no-linealidad se produce solamente en el mayor contenido de Cr_2O_3 mientras que en los niveles intermedios no existe cambio alguno. Por lo tanto, cuando se busquen altos coeficientes de no-linealidad, los niveles intermedios de adición no son recomendables.

Descriptores: Varistores; voltaje de ruptura; no linealidad.

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1. Introduction

The continuous growth in the production of household appliances and electronic components has stimulated the development of a large number of ceramic materials for the fabrication of electronic devices, including varistors. Varistors are variable resistors, in which the electrical resistivity is a function of the applied voltage [1]. These components 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, defined by the following equation:

$$J = kE^{\alpha}, \quad (1)$$

where J is the current density, E is the applied electric field, and k is a constant related to the material's microstructure. Ever since its introduction by Matsuoka early in the 1970s, zinc oxide (ZnO) has been by far the most important ceramic material (as the base for ceramic systems) for the commercial production of varistors [4,6]. Recently, from the materials science and engineering viewpoint, the development of a wide variety of ceramic systems for varistor applications has undergone a remarkable expansion. The new or alternative ceramic systems include TiO_2 [7], $SrTiO_3$[8], WO_3 [9], CeO_2 [10] and SnO_2 [11], amongst others. Owing to its attractive properties, the latter, tin dioxide, has received special attention by many researchers. Tin dioxide (SnO_2) is an n-type semiconductor with a rutile-type structure and space group $D^{14}_{4h}\,[P4_2/mnm]$ [12]. Because of its poor densification attributes during sintering, it has been generally used in porous materials, specifically for gas sensors [13,14]. However, densification of SnO_2-based ceramics can be enhanced by using hot isostatic pressing [15] and by adding dopants such as Co_3O_4 or MnO_2 [16], which allow achieving values close to that of the theoretical density. Moreover, certain oxides have been used not only for improving densification/sintering characteristics, but also for enhancing non-ohmic properties [17]. Antimony pentoxide (Sb_2O_5) for instance, has been tested previously in compositions intended for low-voltage SnO_2-based varistors [11].

Another important oxide lately regarded for the enhancement of the non-ohmic properties of SnO_2-based varistors is chromium oxide (Cr_2O_3). Its presence has been correlated with modifications in the density and nonlinear properties of SnO_2-based ceramics. According to Filho and co-workers [18], in addition to influencing density, Cr_2O_3 causes a significant decrease in the average grain size while increasing both, the nonlinear coefficient and the electric breakdown field. Piannaro ascribed this effect to the inhibition of grain growth during sintering [19,20]. On the other hand, by testing levels of Cr_2O_3 up to 0.05 %, Bueno and co-workers suggested that formation of $CoCr_2O_4$ at the grain boundaries make the ceramic lose its nonlinearity [21].

In view of the variety of outcomes reported so far as regards to the use of $Cr_2O_3$and of the need for understanding the correlation *processing → microstructure → properties*, the authors have conducted a study on the influence of Cr_2O_3 on the microstructure and electrical properties of the ternary system SnO_2-Co_3O_4-Sb_2O_5. Assessment of other physical properties resulting from the processing conditions, like shrinkage and average grain size is also carried out.

2. Experimental procedures

Analytical grade SnO_2 (Baker), Co_3O_4 (Baker) and Sb_2O_5 (Aldrich) were used as the raw chemicals in this work. The molar composition of the investigated systems was (98.95-X) % SnO_2-1 % Co_3O_4-0.05 % Sb_2O_5-X % Cr_2O_3, where X = 0.0, 0.03, 0.05 and 0.07 %. The powders were processed by a non conventional method of mixture, through high-energy milling performed in a planetary ball-mill Pulverisette P7/2 (Fristsh GmbH, Germany) using vials and balls of agate for 20 minutes. The so-called non conventional mixing method has important advantages on the material's microstructure and electrical behavior, as compared to the traditional mortar and pestle route [22]. The resulting powders were uniaxially pressed in the form of tablets (10.0 mm in diameter and about 1.2 mm thick) at 230 MPa and using no binder. The tablets were sintered in ambient atmosphere at 1350°C for 1 hour with heating and cooling rates of 6°C/min in a tube furnace (Lindberg/Blue STF55433C-1). For electrical characterization, silver electrodes were place 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 mAcm^{-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 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 the 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), scanning electron microscopy (SEM) (Philips XL30 ESEM). The mean grain size was determined from SEM micrographs, using an Image Analysis Software (Image-Pro Plus), according to the ASTM-E112 standard procedures.

3. Results and discussion

Results from the analysis by X-ray diffraction in Fig. 1 show no apparent second phases but only tin dioxide (SnO_2, JCPDS No. 77-0447). It is also to be noted that the concentrations of dopants added (Co, Sb and Cr) are too small to be detected by X-rays. It also can be seen that X-ray patterns of samples doped with Cr show higher refraction intensities than samples without Cr due to a enhanced crystallization of the Cr-containing samples. Microstructure characterization

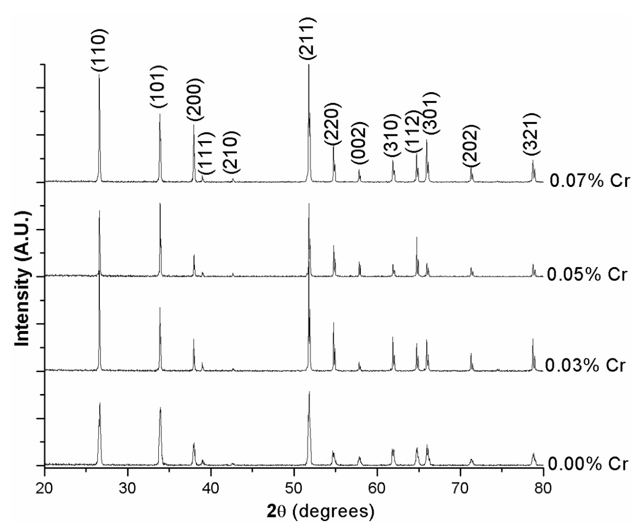

FIGURE 1. XRD patterns of SnO_2 ceramics with different chromium oxide contents. It should be noted that tin dioxide is present as a single phase.

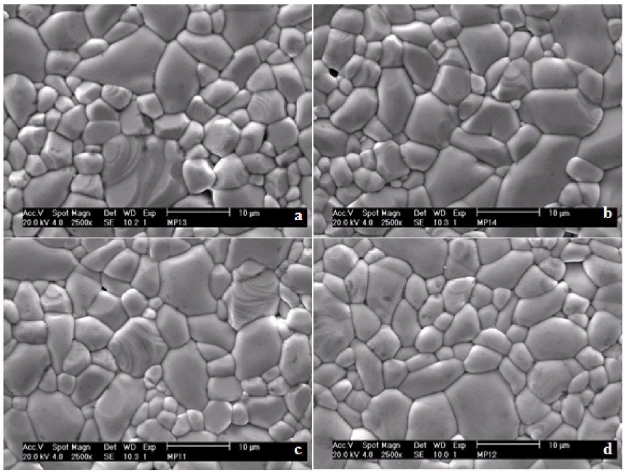

FIGURE 2. SEM micrographs of samples sintered at 1350°C for 1 hour: (a) 0.00, (b) 0.03, (c) 0.05, and (d) 0.07 % Cr_2O_3.

by SEM suggests a good densification process with an apparent multimodal grain size. This multimodal feature however, cannot be attributed to Cr_2O_3 additions because the reference specimen also does have the same appearance. Figure 2 shows representative SEM photomicrographs of all four specimens taken at the same magnification for comparison purposes. An important effect associated to the sintering process is the shrinkage undergone by the specimens. The magnitudes of density, relative density, grain size and shrinkage are all summarized in Table I. Notably, the highest level of Cr_2O_3 in the SnO_2 ceramic prevents the specimen from shrinking substantially in contrast with the effect of the intermediate and low levels. Most likely this outcome is associated to mass transfer phenomena and mass buildup at the grain boundaries, and is by no means trivial because dimensional stability is an important parameter for design purposes.

It is also clear that small additions of Cr_2O_3 induce a significant augment in density and relative density and that both properties tend to decrease with increment in chromium oxide. Densification is on the other hand, aided by the effect of other constituents in the ceramic mix. 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_2 sintering, and therefore, an increase in its density.

TABLE I. Shrinkage (γ), measured density (ρ), relative theoretical density (ρ_{tr}), mean grain size (l_g), nonlinearity coefficient (α) and electric field at fixed current density (E_1) of the samples doped with different contents of Cr_2O_3.

Cr_2O_3 (mol%)	γ (%)	ρ (g/cm^3)	$^a\rho_{\text{tr}}$ (%)	l_g (μm)	α	E_B (V/cm)
0.00	13.0	6.76	97.26	13.99	7.89	542
0.03	13.1	6.94	99.85	12.82	9.65	759
0.05	13.5	6.85	98.56	13.72	9.65	829
0.07	12.6	6.43	92.51	13.27	10.42	972

[a]Theoretical density of SnO_2 is 6.95 g/cm^3.

These changes can be explained with the aid of replacement equations representing phenomena occurring in the tin dioxide lattice. Possible substitution equations, by the Kröger-Vink standard notation are as follows:

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

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

$$Co_2O_3 \xrightarrow{SnO_2} 2Co'_{Sn} + V_O^{\bullet\bullet} + 3O_O^x, \tag{6}$$

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

$$Sb_2O_5 \xrightarrow{SnO_2} 2Sb_{Sn}^{\bullet} + 2e' + 4O_O^x + \frac{1}{2}O_2(g), \tag{7}$$

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.

Figure 3 shows plots of current density as a function of electric potential for all specimens with different Cr_2O_3 additions and for the reference specimen. The magnitudes of α and E_B parameters for all test specimens are also summarized in Table I. As regards to previous reports, in the case of the nonlinearity coefficient such increment is not as significant as that observed by others; addition of 0.07 % Cr_2O_3 induces an increment of 32 %. The enhancement in E_B is even better because the corresponding increment is nearly 45 %. It is clear that intermediate levels of Cr_2O_3 do not significantly influence the magnitude of α. This is because the varistor behavior depends strongly on the number of oxygen defects (O' and O") at the grain boundaries. According to previous studies using several SnO_2-based systems with various dopants (ZnO, CoO and Ta_2O_5, Nb_2O_5, MnO_2) [18,23-27], since Cr_2O_3 is more susceptible to oxygen, increasing the amount of oxygen in the grain boundary region may improve the system's nonohmic properties [27]. Thus, when Cr_2O_3

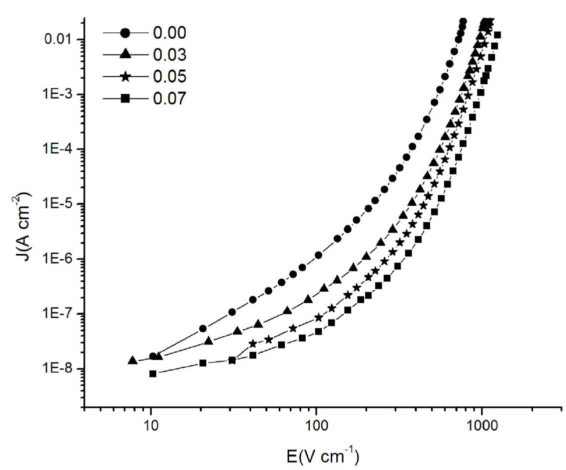

FIGURE 3. Current–voltage logarithmic plots for all samples: (a) 0.00, (b) 0.03, (c) 0.05, and (d) 0.07 % Cr_2O_3.

concentration is increased to 0.07 mol%, dopant segregation and/or solid solution formation at the grain boundaries promote the formation of electrical barriers which improve the varistor behavior. However, according to Piannaro *et al*, an excess of Cr_2O_3 leads to porous ceramics, destroying the material's electrical characteristics probably due to precipitation of second phase of $CoCr_2O_4$ [25]. This porosity and alteration of the microstructure quite often makes it difficult correlating a change in the grain size with increasing the Cr_2O_3 content, as has been suggested by some authors [23,26].

4. Summary and conclusions

Results from the characterization by XRD and SEM show that the microstructure remains as a single phase material - essentially of SnO_2-, but with an apparent multimodal size distribution of grains. This feature is not however promoted by the Cr_2O_3 additions because the reference sample has the same appearance. Results suggest that α is not as sensitive as E_B is to Cr_2O_3 concentration changes. In pursuing high nonlinearity coefficients, intermediate levels of Cr_2O_3 are not recommended because α is not significantly influenced. Rather, high levels of Cr_2O_3 are required in order to increase oxygen defects at the grain boundaries, and thus, enhance the system's nonohmic properties.

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