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Evaluation of Rare Earth Oxides doping $SnO_2.(Co_{1/4},Mn_{3/4})O$-based Varistor System

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The present paper aims to verify the influence of rare earth oxide such as lanthanum (La_2O_3) and neodymium (Nd_2O_3) doping SnO_2 + 0.25%CoO + 0.75%MnO_2 + 0.05%Ta_2O_5 system. The analysis focus on microstructural influence on electrical properties. Microstructural analysis were made by using Transmission Electron Microscopy (TEM) at different regions of the samples. From such analysis it was found that La_2O_3 and Nd_2O_3 oxides cause heterogeneous segregation and precipitation at grain boundary concerning cobalt and manganese, decreasing the nonohmic electrical properties, as discussed, likely due to the increasing of grain boundary non-active potential barriers.

Keywords: *ceramic, varistor, tin dioxide, rare earth oxides*

1. Introduction

Tin dioxide is an *n*-type semiconductor with rutile structure that present low densification after sintering[1]. However, SnO_2 can be densified by its doping with specific oxides such as CoO and MnO_2[2–4]. The effects of CoO and MnO_2 doping on the sintering of SnO_2 were studied by Cerri et al.[2]. It was also reported that manganese and cobalt oxides are sensitive to temperature and oxygen partial pressure, changing its valence state with temperature. For instance, at higher temperatures (temperatures higher than 950 °C for cobalt and 1100 °C for manganese) both oxides present +2 valences. The densification of SnO_2 ceramics has been attributed to the effect of cobalt and manganese in the surface of the SnO_2 grains by replacing of Sn^{+4} by Co^{+2} and/or Mn^{+2} leading to the formation of oxygen vacancies. It is believed that such a picture increases oxygen diffusion at grain boundary, promoting densification.

Although the CoO and MnO_2 are extremely active in the promotion of the SnO_2 densification, these binary ceramic compounds are highly electronically resistive. Therefore, other additives are needed to improve electrical conduction. Pianaro et al.[3] added 0.05 mol% of Nb_2O_5 to SnO_2 + 1.0%CoO system obtaining a varistor behavior with nonlinear coeffient (α) about 8 and electric breakdown field (E_b) of 1800 $V.cm^{-1}$. In a later study, Antunes et al.[4] substituted the Nb_2O_5 by Ta_2O_5 also obtaining varistor behavior with α about 13 and E_b about 2940 $V.cm^{-1}$. Therefore, dopants of valence (+5), such as Nb^{+5} or Ta^{+5}, when added in small amounts to SnO_2-based ceramics are capable of leading to an increasing of electronic conductivity which assists the nonohmic behavior performance.

The non-ohmic behavior is dependent of the dopants added to SnO_2 and the sintering conditions as temperature and atmosphere. During the sintering and cooling processes the diffusion of molecular oxygen throughout grain boundary may occur, promoting reactions responsible for potential barrier voltage formation[5]. The effect of partial substitution of CoO by MnO_2 in the (98.95)%SnO_2 + x%CoO + (1-x)%MnO_2 + 0.05%Ta_2O_5 system was studied[6,7] using x = 0.25 and 0.50 mol%. However, for x = 0.25 better nonlinear characteristics were found: $\alpha \sim 54$ and $E_b \sim 8500$ $V.cm^{-1}$ [7].

The main goal of the present paper is to evaluate the influence of small addition of La_2O_3 and Nd_2O_3 (both in 0.05 mol%) to SnO_2 + 0.25%CoO + 0.75%MnO_2 + 0.05%Ta_2O_5 system[8] concerning microstructural characteristics and electrical properties.

2. Experimental Procedure

The oxides used to prepare the ceramic systems were SnO_2 (Aldrich), CoO (Sigma), MnO_2 (Sigma), Ta_2O_5 (Sigma), La_2O_3 (Sigma) and Nd_2O_3 (Sigma). The powder were prepared by mechanical mixing in isopropyl alcohol, using polypropylene jars with yttrium stabilized zirconium balls to aid the mixing process. After drying, the powders were pressed into pellets (11.0 mm x 1.0 mm) by uniaxial pressing, followed by isostatic pressing. The pellets were then sintered at 1300 °C (heating rate of 10 °C / min) for 1 hour and cooled (cooling rate of 5 °C / min) to room temperature. The grain size was determined by SEM (Scanning Electron Microscopy) micrographic analysis (obtained with a TOPCON SM 300) (ASTM-112 norm). The relative densities of the samples were measured using the Archimedes method. The presence of a solid solution phase was determined by X ray diffraction patterns (obtained with a SIEMENS diffractometer, model D-5000, CuKα radiation). In order to take the electrical measurements, silver contacts were painted on the samples' surfaces, after which the pellets were treated at 400 °C for 30 min. Current-voltage plots were obtained by measurements using High Voltage Unit Source (KEITHLEY Model 237). The microstructural analyses were also obtained by Transmission Electron Microscope (TEM) PHILIPS CM 200 equipped with an X ray Energy Dispersive (EDS) unit. To better description of the samples we adopt the following nomenclature: SnO_2 + 0.25%CoO + 0.75%MnO_2 + 0.05%Ta_2O_5 were named as S2C7MT and the same composition doped with La_2O_5 and Nd_2O_5 were named respectively as S2C7MTL and S2C7MTN.

3. Results and Discussion

The Figure 1 illustrates the microstructure obtained by SEM for (a) S2C7MT, (b) S2C7MTL and (c) S2C7MTN systems. From this figure it cannot be observed any segregation or precipitation. However, the addition of rare earth oxides promote a decrease in the average grain size, according to the results presented in Table 1.

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The relative density values are not influenced substantially. The rare earth oxides led a similar behavior to that cause by the addition of the Cr_2O_3 in SnO_2-based varistor systems[3,4,9]. Besides, segregated at grain boundary are causing changes on potential barrier height so that modifying the electrical properties. As shall be showed latter herein by means of TEM analysis, the observed behavior are being caused by precipitation and segregation at grain boundary region.

The nonohmic electric features of the sample are presented in Table 1. The plots of electric field versus current density of the systems are shown in Figure 2.

A large decrease of breakdown voltage (E_b) and nonlinear coeffcient α occurs due to the addition of rare earth oxides. The observed effect can be explained by the fact that the addition of the rare earth oxides cause a decrease on the amount of Co and Mn atoms segregation at grain boundary during sintering, leading to formation of higher amount of non-active potential barrier since the mean grain size are also decreasing. Accordingly, in addition, there are also grain boundary heterogeneities as will be better discussed further when TEM micrographs of the systems were introduced. From electrical point of view, these microstructural feature is reflected on the amount of effective potential barrier throughout microstructure[10,11]. The phenomenology discussed in these two papers[10,11] also applies here and the discussion on results validates the phenomenology that relates excess of precipitates to higher amount of non-active potential barriers.

Indeed, Figure 3 illustrates the microstructure obtained by TEM and EDS spectra for S2C7MT system. Table 2 presents the results from EDS analysis. The microstructure indicates that cobalt and manganese are found segregated and eventually precipitated at grains boundary region. In average, concerning bulk region it was found that SnO_2 and Ta_2O_5 are homogeneously distributed as expected[5] albeit sometimes Ta_2O_5 are found in higher concentration in the precipitates. The manganese and cobalt elements are also found to be homogeneously distributed in bulk regions. The Figure 3 also shows that near precipitates these elements are absent (below sensitivity detection of the equipment) which is in agreement to what was proposed in reference 11. These results are also in agreement with those reported in literature concerning the presence of a secondary phase of Co_2SnO_4 composition precipitated at SnO_2.CoO-based system grain boundaries[12]. In addition, it was already showed that grain boundaries are rich in cobalt and/or manganese and that these elements are important in modelling the nonohmic properties[5]. However, an excess of precipitate can deteriorate the grain boundary electrical properties due to heterogeneous precipitation and/or segregation at grain boundaries as discussed in reference 11 which appear to be the specific role of rare earth doping SnO_2.$(Co_{1/4},Mn_{3/4})O$-based varistor system concerning its influence on microstructural and electrical properties.

Figure 4 illustrates the microstructure obtained by TEM and EDS spectra for S2C7MTN system. As can be seen from this illustrative TEM image of the system, the microstructure is more heterogeneous compared to that of S2C7MT system. In average, similarly to S2C7MT bulk region, the S2C7MTN bulk region contains SnO_2 and Ta_2O_5 homogeneously distributed. There are also regions where cobalt and manganese were found precipitated, specially at triple grain junctions. Such regions are more abundant in S2C7MTN than in S2C7MT system. Besides, cobalt and manganese elements at grain boundaries were, in average, detected in lower amounts compared to S2C7MT system. The higher heterogeneity of S2C7MTN compared to S2C7MT is indicated by the analysis of larger precipitates containing cobalt and manganese in higher amount, where neodymium was found absent. Otherwise, in precipitates containing neodymium, cobalt is absent and manganese are found in higher amounts.

Table 1. Relative density (ρ/ρ*t*), grain size values (*d*), mean values of the nonlinear coeffcient (α), breakdown electric field (E_b) and current leakage (I_l) obtained for the varistor ceramic systems.

System	ρ/ρ*t* (%)	d (μm)	α	E_b (V.cm^{-1})	I_l (mA)
S2C7MT	98	5.3	32	8500	0.206
S2C7MTL	95	2.4	20	5400	0.207
S2C7MTN	98	3.3	15	5950	0.344

Table 2. EDS mapping of some precipitate regions and adjacent bulk region. These maps are just illustrative and must be considered qualitatively.

system	region	Sn	Mn	Co	Ta	La	Nd
S2C7MT	a	71.40	18.79	0.43	-	-	-
	b	98.40	1.32	0.28	-	-	-
	c	100.00	-	-	-	-	-
S2C7MTL	a	52.70	0.70	-	45.02	1.58	-
	b	70.50	17.45	12.05	-	-	-
	c	100.00	-	-	-	-	-
S2C7MTN	a	48.81	-	-	44.70	-	6.49
	b	59.87	26.85	13.28	-	-	-
	c	100.00	-	-	-	-	-

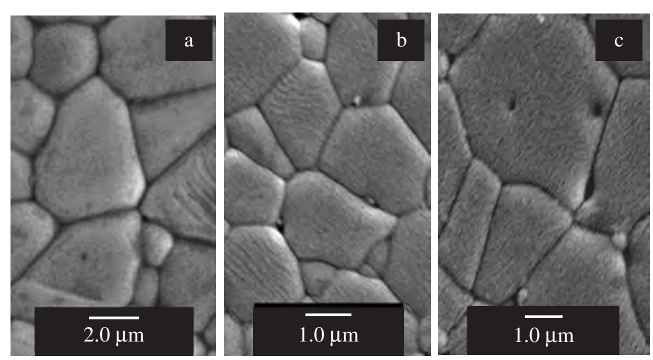

Figure 1. Microstructure of the varistor systems studied: a) S2C7MT; b) S2C7MTL; c) S2C7MTN.

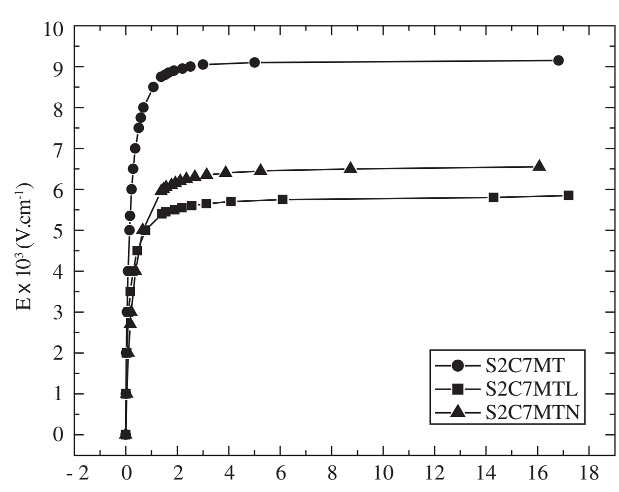

Figure 2. Electric field *vs.* current density curves (*V-I* characteristics) behavior of SnO_2.$(Co_{1/4},Mn_{3/4})O$-based varistor systems studied.

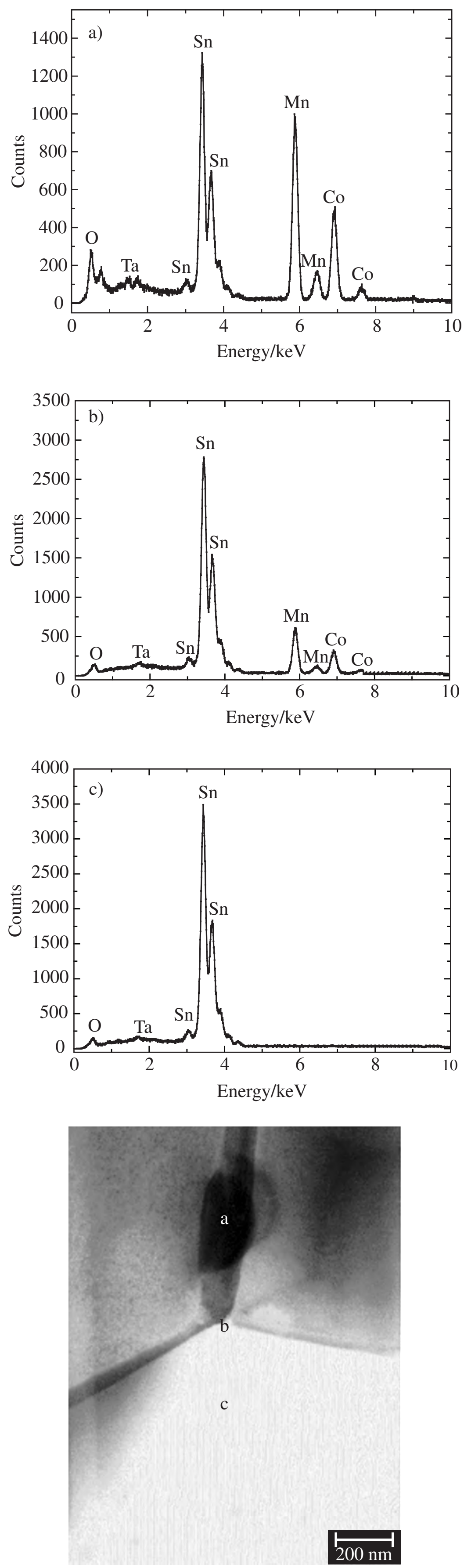

Figure 3. TEM and EDS spectra of the S2C7MT system.

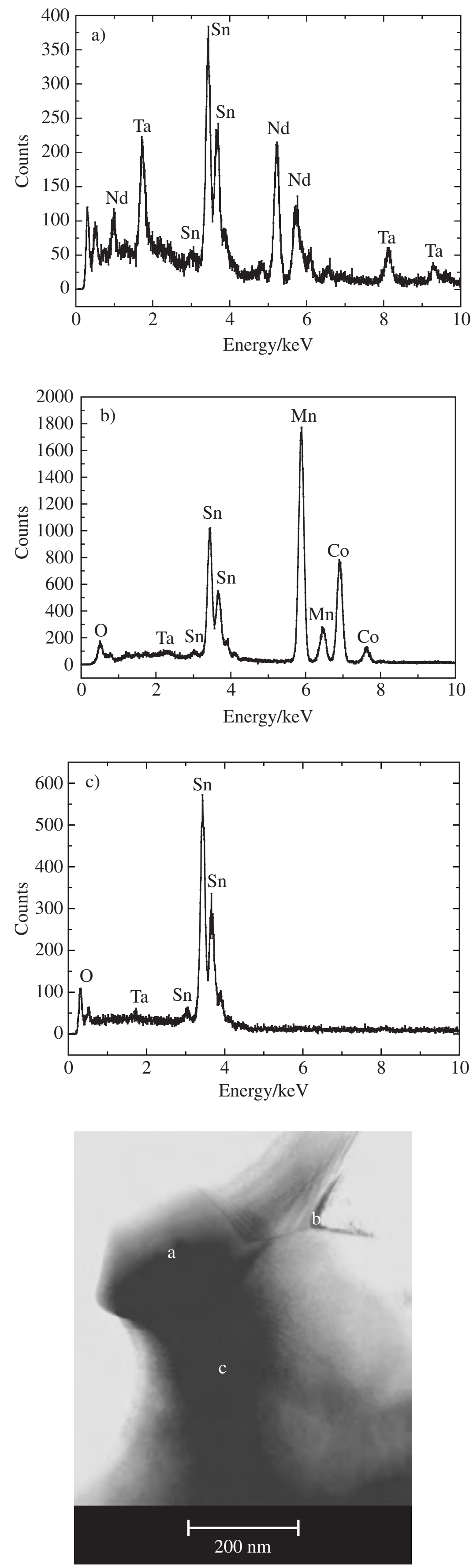

Figure 4. TEM and EDS spectra of the S2C7MTN system.

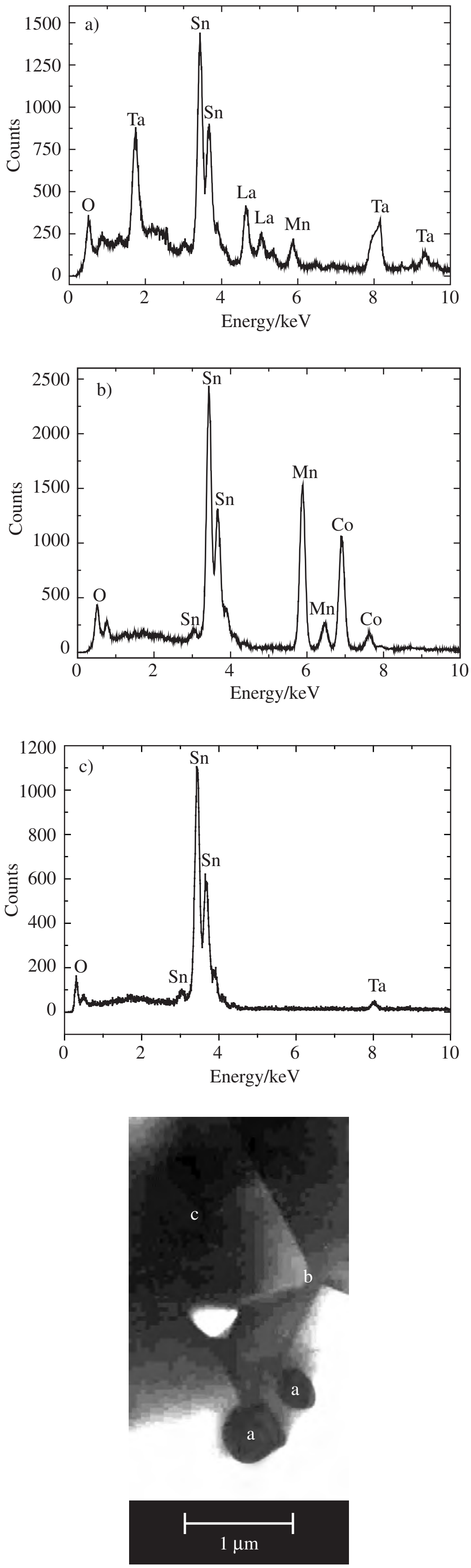

Figure 5. TEM and EDS spectra of the S2C7MTL system.

Figure 5 illustrates the microstructure obtained by TEM and EDS spectra for S2C7MTL system. The S2C7MTL system, in average, showed highly homogeneity of grains concerning amounts of tin, tantalum, cobalt and manganese elements, similarly to what was observed to S2C7MT and S2C7MTN systems. It was found higher amount of precipitates at triple points compared to S2C7MT. At grains boundaries double junctions these elements were found to be lower than those found in the S2C7MT and comparable to those found S2C7MTN systems. This behavior occurs in S2C7MTL and S2C7MTN likely because precipitates richer in Co and Mn at triple grain boundaries when are been formed consume the amount of Co and Mn elements adjacent to these regions[11]. Besides, it was observed from microstructure analysis that lanthanum presents an irregular distribution in the sample. In the precipitate points were lanthanum was found, cobalt was absent or in lower quantities compared to the points were lanthanum was not found. Similar features were found in neodymium containing systems.

In the specific case of $SnO_2.(Co_{1/4},Mn_{3/4})O$-based varistor composition in which there are two dopants used to improve densification, CoO and MnO, the addition of rare earth dopants can cause deleterious precipitation leading to lower nonohmic properties. In the case of $SnO_2.MnO$, according to what was discussed in the literature[10,13], the nonohmic properties are controlled by the distribution of different junctions which is formed depending on the dopant and thermal treatment features. It was already showed that the $SnO_2.MnO$ system consists of two phases, SnO_2 grains and Mn_2SnO_4, precipitated along multiple grain junctions[10] and two types of SnO_2-SnO_2 grain boundaries were identified one rich in Mn and other poor in Mn element. It was concluded from reference 10 that the changes in the concentration of Mn along the grain boundary are associated not only to grain misorientation but also to Mn diffusity along the grain boundary, which controls the junctions' heterogeneities. Therefore, in other words, SnO_2-based systems doped with MnO tending to cause a more heterogeneous microstructure which does not favor the nonohmic electrical properties since $SnO_2.CoO$-based system when appropriated doped with La_2O_3 presents a homogeneous microstructure accompanied by high electrical nonohmic properties[14]. From this aspect, it is important to note that the deleterious effect of neodymium and lanthanum oxides observed in this work is an armful indirect effect which explain just the properties when MnO is present.

4. Conclusion

The addition of rare earth oxides in $SnO_2.(Co_{1/4},Mn_{3/4})O$-based result in a deleterious effect over nonohmic electrical properties due to heterogeneous precipitation of metal elements at grain double and triple junctions. This effect on the microstructure results in a heterogeneous active junctions distribution throughout device, resulting in the decreasing of the nonohmic electrical properties.

Acknowledgments

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