TiO_2 Varistors doped with La_2O_3 and Ta_2O_5

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TiO_2 doped with different oxides have been studied to different applications. Dopants like Ta_2O_5 have an especial hole over the barrier formation at the grain boundary in the TiO_2 varistors, increasing the nonlinear coefficient and decreasing the breakdown electric field. In this paper, will presented the microstructural and electrical properties of (Ta, La) doped TiO_2 varistor. The results of the electric characterization associated with the microstructural analysis, clarify and confirm the influence of this dopants over the electronic properties of this systems. It will be demonstrate that some of this systems exhibit electrical properties that possibility their use like low voltage varistors, getting 40 V/ cm of breakdown electric field and low non linear coefficient.

Keywords: varistors, TiO_2, Electrical properties, eletroceramic, ceramic processing.

INTRODUCTION

TiO_2 ceramics doped with different oxides have been studied for a variety of applications, including sensors, photoelectrodes, current-collecting electrodes in Na–S batteries, catalysts and varistors because of their semiconducting and dielectric properties. In the area of varistors, the properties of TiO_2 ceramics render them useful as low voltage varistors. Several studies have concentrated on improving the efficiency of these ceramics by varying the dopants, such as Bi_2O_3, BaO, Nb_2O_5, Ta_2O_5 and Cr_2O_3 and the processing method employed for their preparation.

Reports published in the literature [1] show that dopants with a +5 valence, such as Nb and Ta, readily dissolve in the TiO_2 lattice, reducing its resistivity by donating conductive electrons. Nevertheless, these dopants increase the electrical conductivity of titanium dioxide. The introduction of other additives, such as BaO, MnO_2, SrO, Nb_2O_5, Cr_2O_3, and Bi_2O_3, help densify TiO_2, probably by increasing lattice defects through the formation of a solid solution or of a liquid phase [1- 5].

This paper discusses the microstructural and electrical properties of Ta, Co, and La-doped TiO_2 systems, demonstrating that some of these systems exhibit electrical properties that allow for their use as low voltage varistors.

MATERIALS AND METHODS

Powders were obtained by the conventional oxide mixing method, using the following compounds: TiO_2 (Merck), Ta_2O_5 (Merck), CoO (vetec), Cr_2O_3 (Aldrich) and La_2O_3 (Aldrich). The molar compositions studied were: (TC) 99.98% TiO_2 + 0.02% CoO, (TTC) 99.73% TiO_2 + 0.25% Ta_2O_5 + 0.02% CoO, **(TTCL 1)** 99.71% TiO_2 + 0.25% Ta_2O_5 + 0.02% CoO + 0,025 La_2O_3, **(TTCL 2)** 99.68% TiO_2 + 0.25% Ta_2O_5 + 0.02% CoO+ 0,05 La_2O_3. The material was blended for 6 hours in a ball mill, using isopropyl alcohol as the dispersion medium and butyl polyvinyl alcohol (PVB) as a deflocculant. After it was homogenized, each blend was oven-dried at 60°C for 12 hours, and then deagglomerated in a 200-mesh sieve (with 74 μm openings). The powders thus obtained were isostatically pressed at 150MPa into tablets (10.0 mm diameter by 1mm thickness). These tablets were sintered in a MAITEC furnace at 1400°C for 2 hours, after which they were cooled to room temperature at cooling rates ranging from 5°C °C/minute. The ceramic phases were identified by X-ray diffraction (XRD), using a SIEMENS D - 5000 diffractometer. The microstructure was analyzed through a scanning electron microscope (ZEISS DSM 940A SEM).

To electrically characterize them, the tablets were polished to reduce their thickness to 1mm and then metallized by depositing a silver ink coating on their surfaces. They were then heat-treated at 400°C for 20 minutes to ensure the fixation of the electrodes. Their varistor properties were appraised by analyzing their nonlinear coefficient (α) and breakdown electric field (E_b). The value of α was calculated from the characteristic curve of current density as a function of the applied electric field, and was obtained with a model 237 KEITHELEY high voltage source.

RESULTS AND DISCUSSION

An analysis of the TiO_2 – CoO (TC) binary system's voltage curve as a function of current reveals a resistive behavior. However, Figure 1 and Table I indicate that, after the addition of tantalum oxide (TTC), the system displayed a varistor-like behavior, with a nonlinear coefficient of 6 and a low breakdown electric field (79 V/cm), proving the efficiency of tantalum oxide in the formation of defects. Several studies[2, 6] have found that the substitution of Ta^{+5} for Ti^{4+} promotes the formation of defects (equation 1), creating depletion layers at grain boundaries and leading to the formation of a voltage barrier for the electronic transport, thereby favoring a semiconducting behavior. The decrease in the grain's resistance allows for the formation of barriers at the grain boundary.

The addition of La_2O_3 to the system (TTC) revealed that this dopant decrease the breakdown electric field but wasn´t effective to promove an increase in the nonlinear coefficient, as illustrated in Figure 2 and Table I. In fact, a better response had been expected from the addition of this dopant, such as that observed in SnO_2 varistors doped with this same dopant[7]. The content added here was probably insufficient to create defects at the grain boundaries. It was observed that the addition of La, Ta, and Co oxides did´t have any influence on the density.

An analysis by X-ray diffractometry (Figure 3) indicated the presence of the rutile phase and the absence of any other phases in all the compositions. However, analyses by scanning electron microscopy, X-ray mapping and energy diffraction spectroscopy (Figure 4) allowed for the detection of La precipitated at the grain boundaries.

Conclusions

It was found, therefore, that both Ta_2O_5 and La_2O_3 are dopants that can effectively contribute toward the electrical characteristics of TiO_2-based varistors, increasing their coefficient of nonlinearity and keeping the breakdown voltage below 70 V/cm. Hence, this varistor has the electrical characteristics of a low voltage varistor. Nevertheless, a better understanding is still needed of how the efficiency of these oxides' action can be improved.

Acknowledgments

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FIGURE INDEX

Figure 1. (a) Current as a function of the system's voltage TC - without Ta_2O_5, and Density current as a function of the electric field of TTC systems - with Ta_2O_5.

Figure 2. Effect of lanthanum oxide on the behavior of the curves of current density as a function of the electric field.

Figure 3. X-ray diffraction patterns of the TTCL 1 and TTCL 2 systems.

Figure 4. Microstructure and X-ray mapping of the TiO_2 – Ta_2O_5 – CoO system doped with 0.025 mol% of La_2O_3 (TTCL 1).

TABLE INDEX

Table I. Theoretical densities, Nonlinear coefficients, (α), and breakdown electric field, (E_r), of the TTCL1 and TTCL2 systems sintered for two hours and cooled at a rate of 10°C/min.

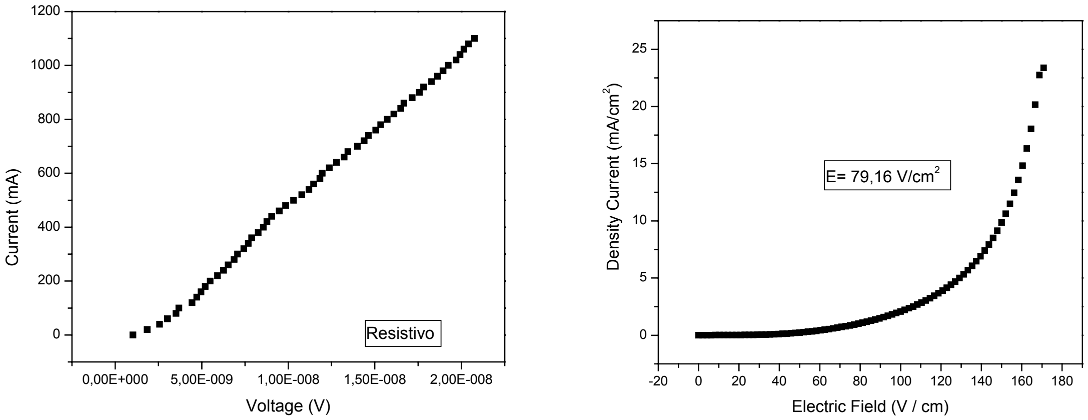

Figure 1

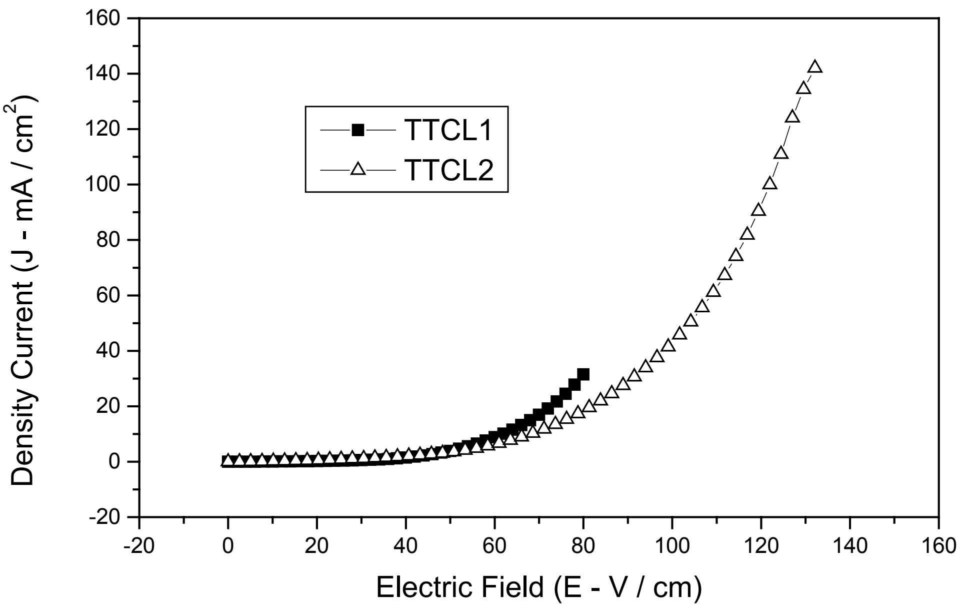

Figure 2.

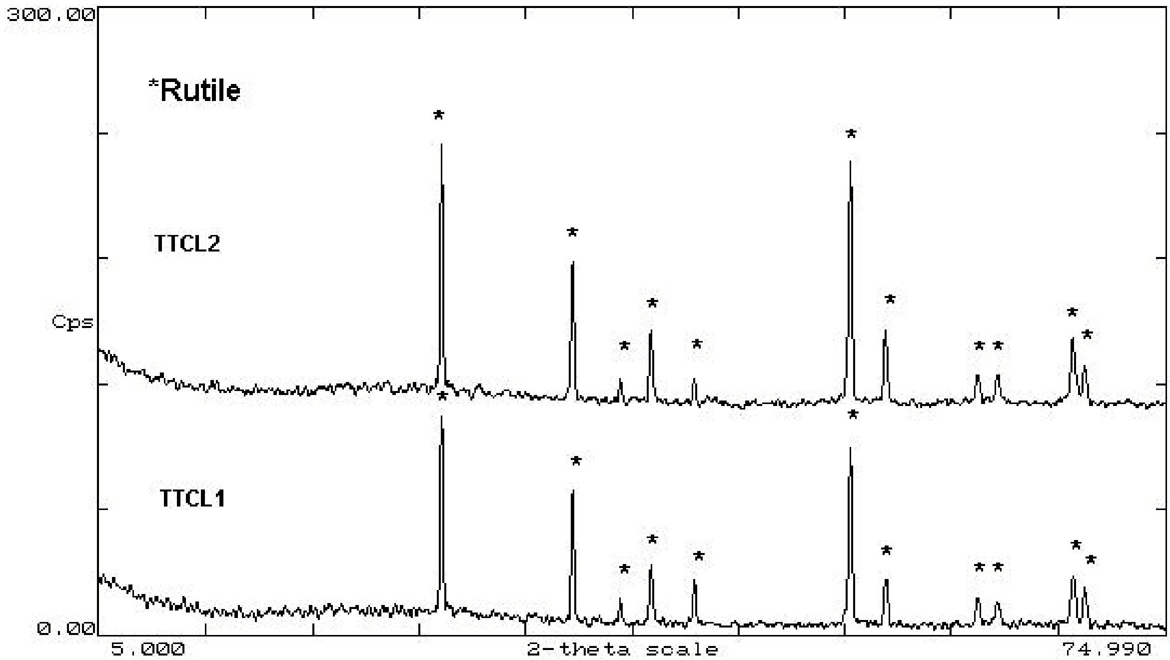

Figure 3

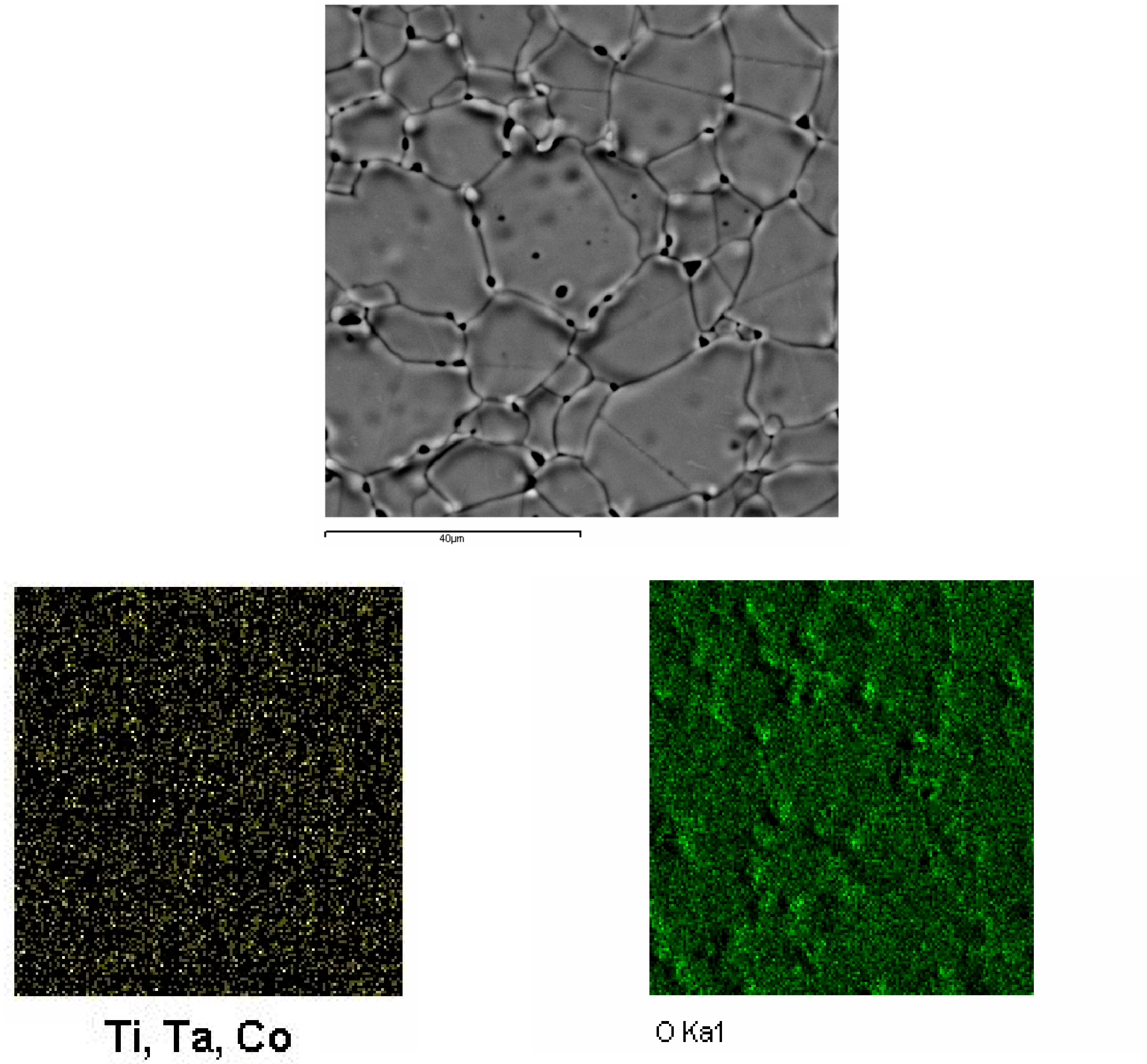

Figure 4

Table I

Sample	**Density (g / cm^3)**	α	**E_B (V / cm)**
TC	97,79	-	-
TTC	97,20	6.1	79
TTCL1	96,92	4,37	36
TTCL2	97,39	4,0	40