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The effect of Ta_2O_5 and Cr_2O_3 on the electrical properties of TiO_2 varistors

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Abstract

An investigation was made of low voltage TiO_2 varistors doped with Ta_2O_5, MnO_2 and Cr_2O_3. Our findings revealed that the addition of 0.25 mol% of Ta_2O_5 improved the varistors' characteristics. The addition of Cr_2O_3 increased the nonlinear coefficient (from 2.6 to 8), thereby producing low voltage varistors ($E_r = 34$ V/cm). Thermal treatment in an oxidizing atmosphere improved the nonlinear coefficient and increased the breakdown electric field of the composition under study.

Keywords: Cr_2O_3; Electrical properties; Ta_2O_5; TiO_2; Varistors

1. Introduction

Varistors exhibit highly nonlinear voltage–current characteristics and are used as surge protection devices in power systems and in electronic circuits. Ceramics such as SiC, ZnO, TiO_2 and SnO_2 are some of the varistors studied. Actually, the recent trend in electrical appliance design, however, requires varistors with different functions and relatively low breakdown voltage.

TiO_2 varistor has been studied since 1982 by Yan and Rhodes[1] who reported that (Nb, Ba)-doped TiO_2 ceramic have useful varistors properties, with low non-linearity coefficients of $\alpha = 3-4$, and that an oxidizing atmosphere during cooling would be necessary.[1] Pennewiss and Hoffmann[2] studied the effect of an oxidizing atmosphere on the electrical properties of TiO_2 doped with Al. The best nonlinear coefficient ($\alpha = 7$) was obtained when voltage- dependent resistivity was caused by opposite surface oxidation layers of the pellets, rather than grain boundary effects within the pellets. Many other additives over the TiO_2 varistors was studied, Wu et al.[3] investigated the effect of PbO on Nb doped TiO_2 varistors. It was observed that existed an optimal range of PbO starting from 0.25 to 1 mol% for the nonlinear I–V characteristics of the 0.25 at% Nb- doped TiO_2 ceramics. Within this PbO range, an effective boundary energy barrier of about 0.70 eV was created which yielded nonlinear I–V characteristics with $\alpha = 7.6$. Yang et al.[4,5] and Cheng et al.[6] studied the effect of Nb_2O_5 in (Ba, Bi, Nb) added TiO_2 ceramics varistor. They also investigated the influence of the temperature atmosphere compensation and time. The results showed that varied atmosphere compensation had only a little influence on grain growth and microstructure in the interior of the sintered samples, although the varistor properties were affected greatly. They observed that sintering at 1350 °C, samples compensated with Ba promote the formation of a more effective boundary barrier layer as contrasted with that compensation with Bi only. Additionally the sample compensated with both Ba and Bi has a more effective boundary layer than that compensated with Ba only. It was observed that Ba dominates the varistor action not Bi, and thus is the most effective contributor to boundary barrier layer.[5] At 1350 °C, the addition of both Ba and Bi on the Nb-doped TiO_2 ceramics creates the most efficient boundary barrier layer, with $\alpha = 9.5$, Vgb = 0.8 V, $E = 0.42$ eV. The single addition of either Ba or Bi produces samples that lack an efficient boundary barrier layer, with $\alpha = 1.7$, Vgb = 0.04 V and $E_r = 0.2$ eV.

Bueno et al.[7] studied the effect of Cr_2O_3 in the varistor behavior of TiO_2. The best non- linear coefficient ($\alpha = 12$) was obtained when molar concentration of 0.05% Cr_2O_3 and Nb_2O_5 were added to TiO_2. A concentration greater

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than 0.05% Cr_2O_3 did not lead to varistor behavior of the 99.95% TiO_2 + 0.05% Nb_2O_5 like as SnO_2 based varistor system.[8] They observed by impedance spectra measured that the Cr_2O_3 act in the boundary.

Recently Cheng et al.[6] investigated the addition of the (Ba, Bi, Nb) added TiO_2 ceramics prepared by the sol precipitation method. From this study they suggested that Mn ions substitute Ti sites and dissolve homogeneously into the lattice of TiO_2 rutile phase and Mn forms interface states at grain boundaries. They observed that 0.02%cat% of Mn followed by sintering at 1350 °C, leads to an improvement of varistor characteristics, an enhanced α of 17 and a breakdown voltage of 3.2 V per grain boundary.

In this article we will investigate the effect of Ta_2O_5 (in the place of Nb_2O_5) and Cr_2O_3 on the electric properties of TiO_2 varistor. We intend to determinate how this additives acts over this new system.

2. Materials and methods

Appropriate molar reagent grades of TiO_2 (Merck), Ta_2O_5 (Merck) and MnO_2 (Merck) powders were used to prepare the TiO_2 based ceramic. The following compositions (in mol%) were prepared using the above oxides: (TTM1) 99.93 TiO_2 + 0.05 Ta_2O_5 + 0.02 MnO_2, (TTM2) 99.73 TiO_2 + 0.25 Ta_2O_5 + 0.02 MnO_2, (TTMC1) 99.71 TiO_2 + 0.25 Ta_2O_5 + 0.02 MnO_2 + 0.025 Cr_2O_3 and (TTMC2) 99.68 TiO_2 + 0.25 Ta_2O_5 + 0.02 MnO_2 + 0.050 Cr_2O_3.

The powders with the above compositions were ball milled with zirconia balls in isopropyl alcohol media inside of a polypropylene jar during 6 h. Then the powder was dried, inside an oven, at 60 °C during 12 h. The resulting powders were granulated in a 200 mesh sieve and isostatically pressed at 150 MPa into pellet shapes (10.0 mm diameter by 1 mm in height). Samples were sintering in air in a furnace (MAITEC) at 1400 °C for 2 h and slowly cooled to room temperature at 10 °C min^{-1}. To analyze the sintering, other pellets were sintering in a dilatometer (model 402E Netzsch). The microstructures of the thermally etched (1350 °C/15 min) samples were analyzed by scanning electron microscopy (SEM)(ZEISS DSM 940 A). Mean grain size, D, was determined by using the equation proposed by Mendelson,[9] $D = 1.558\ L$, where L is the average intercept number between a series of random lines, drawn in the micrograph, with the grain boundaries. The ceramic phases were observed by X-ray diffraction using a Siemens D-5000 apparatus. A stabilized voltage source (Keithley Model 23) was used for electrical characterization of the samples. The sintered pellets were sand grinded before reaching 1 mm thickness and silver electrodes were deposited in both faces followed by heat treatment at 400 °C during 20 min. The heat treatment is made to eliminate the organics compounds of the solvent and to promote a better contact between the electrodes and the ceramic. Current–tension measurements were taken using high voltage measure unit (KEITHLEY Model 237). The pellets were put into a sample holder attached to a furnace (EDG model EDGCON 3P) and current voltage curves were determined for different temperatures. The nonlinear coefficient α was obtained by linear regression of points on a logarithmic scale of around 1 mA cm^{-2} and the breakdown electric field (E_r) was obtained at this current density.

The samples were subjected to treatment in O_2 (under a flux of 4l/min) atmospheres at 800 °C for 1 h. The electric behavior was checked throughout the above-mentioned procedures and after each treatment.

3. Results and discussion

Table 1 presents the results of the powders and the surface area calculated by BET. As can be seen, the surface area remained constant while particle size increased with the addition of Ta_2O_5; however, the addition of Cr_2O_3 caused the reverse effect, i.e. higher levels of Cr_2O_3 led to decreased particle sizes.

Fig. 1 shows the X-ray diffraction diagrams of the $TiO_2{\cdot}Ta_2O_5{\cdot}MnO_2$ and $TiO_2{\cdot}Ta_2O_5{\cdot}MnO_2Cr_2O_3$-based varistor systems sintered at 1400 °C with molar concentrations of 0.25% Ta_2O_3, and 0.02% MnO_2 and different amounts of Cr_2O_3. No secondary phase, except the crystalline TiO_2 rutile phase, was revealed by any of the curves.

Fig. 2 presents the linear shrinkage rate ($d(\Delta L/L_o)/dT$) as a function of temperature for different Cr_2O_3 dopant concentrations. As shown in the figure, the maximum shrinkage rate occurred at 900 °C in all samples, and the increased concentration of Cr_2O_3 gave rise to an increase in the maximum shrinkage rate temperature (TM) (Table 2). The XRD results and sintering study indicated that sinterization at 1400 °C for 2 h is the optimal condition under which to obtain crystalline, dense Ta_2O_5, MnO_2 and Cr_2O_3-doped TiO_2 varistors containing only the expected rutile phases that, according to the literature, are naturally present at that temperature.

The final relative densities of samples sintered in a dilatometer at a constant heating rate of 10 °C/min and at temperatures of up to 1400C are higher than 95%, as

Table 1
Characteristics of stoichiometric powders

Composition	As (m^2/g)	D_{BET} (nm)
TTM1	11.0	128.9
TTM2	9.2	154.7
TTMC1	9.5	148.1
TTMC2	10.6	134.2

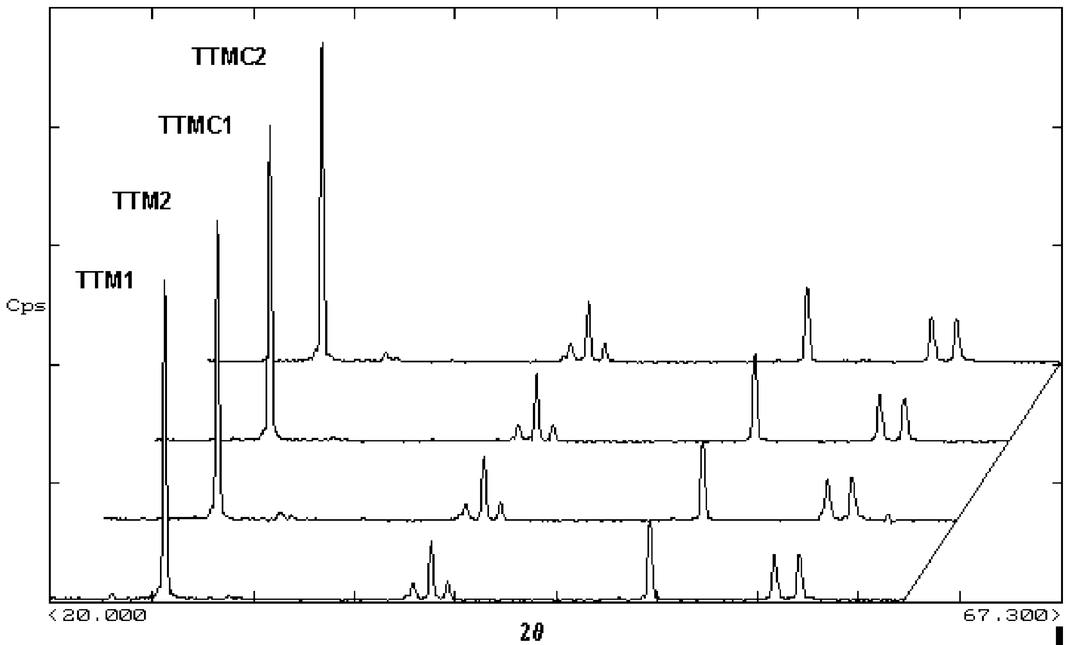

Fig. 1. Diffractogram of the TTM1 and TTM2 varistors with 0.05 and 0.25 mol% of Ta_2O_5 and $TiO_2 \cdot Ta_2O_5 \cdot MnO_2Cr_2O_3$ varistors with 0.025 mol% and 0.050 mol% of Cr_2O_3.

Table 2
Influence of the Cr_2O_3 over the relative density, grain size and maximum shrinkage rate temperature (T_M) of the $TiO_2 \cdot Ta_2O_5 \cdot MnO_2$ varistor

Composition	Relative density (%)	Grain size (μm)	T_M (°C)
TTM1	95.02	8.31	940
TTM2	95.62	8.0	1079
TTMC1	96.04	4.67	1284
TTMC2	94.13	4.5	1329

Table 3
Influence of the thermal treatment in atmosphere of O_2 on the nonlinear coefficient (α) and breakdown electric field (E_r)

Samples	Without treatment		Treatment O_2	
	α	E_r (V/cm)	α	E_r (V/cm)
TTM2	2.6	60	4.23	95
TTMC1	8.23	34	11	110
TTMC2	2.5	19	3.3	15

shown in Table 2. It should be noted that these dopants may promote densification of TiO_2, similarly to the influence of CoO and MnO_2 over the SnO_2 varistor.[10]

These results demonstrate that the concentration of MnO_2 and Cr_2O_3 dopants in TiO_2 systems exert an influence on sintering. Table 2 reveals that the apparent density was only slightly affected by variations in the Ta_2O_5 and Cr_2O_3 content, although the average grain size decreased with the addition of Cr_2O_3. This result is similar to the findings of Yang and Wu[4] on the addition of Nb_2O_5.

Fig. 3 plots the applied electric field as a function of current density, while Table 3 presents the nonlinear coefficient and breakdown electric field for the different systems studied. The best nonlinear coefficient ($\alpha = 8$) was obtained when molar concentrations of 0.25% Ta_2O_5 and 0.25% Cr_2O_3 were added to TiO_2, presenting a low breakdown electric field (34 V/cm). It was observed that increasing the Ta_2O_5 concentration from 0.05 to 0.25 mol% leads to a substantial modification in the electrical behavior of $TiO_2 \cdot Ta_2O_5 \cdot MnO_2$ ceramics. The samples proved highly resistive with 0.05 mol% Ta_2O_5 (TTM1), but an increase in the concentration of Ta_2O_5 led to a low nonlinear coefficient ($\alpha < 3$) in the varistor. After the addition of Cr_2O_3 (0.25%), the α value increased ($\alpha = 8$), showing a low voltage (≈30). This result is very important for applications that require low voltages. Comparing the results presented in Table 2 with Table 3 and Fig. 3, it can be observed that the Cr_2O_3 addition to the TTM2 composition decreases the grain size and breakdown electric field but increases the non- linear coefficient. The decrease in the E_r in the samples without Cr_2O_3 can be explained by the decrease in the effective barrier. Otherwise, another explanation is that the Cr_2O_3 decreases the height of the barrier. Comparing the results obtained with the TTMC1 and TTMC2 compositions (Table 3 and Fig. 3), it can be noted a decrease in the non- linear coefficient after the addition of 0.05 mol% of Cr_2O_3 (TTMC2). It can be explained, by the increase in the width of the depletion layer, as it will be published in another article, preventing the tunneling of electrons, therefore causing a deterioration in the electrical properties.

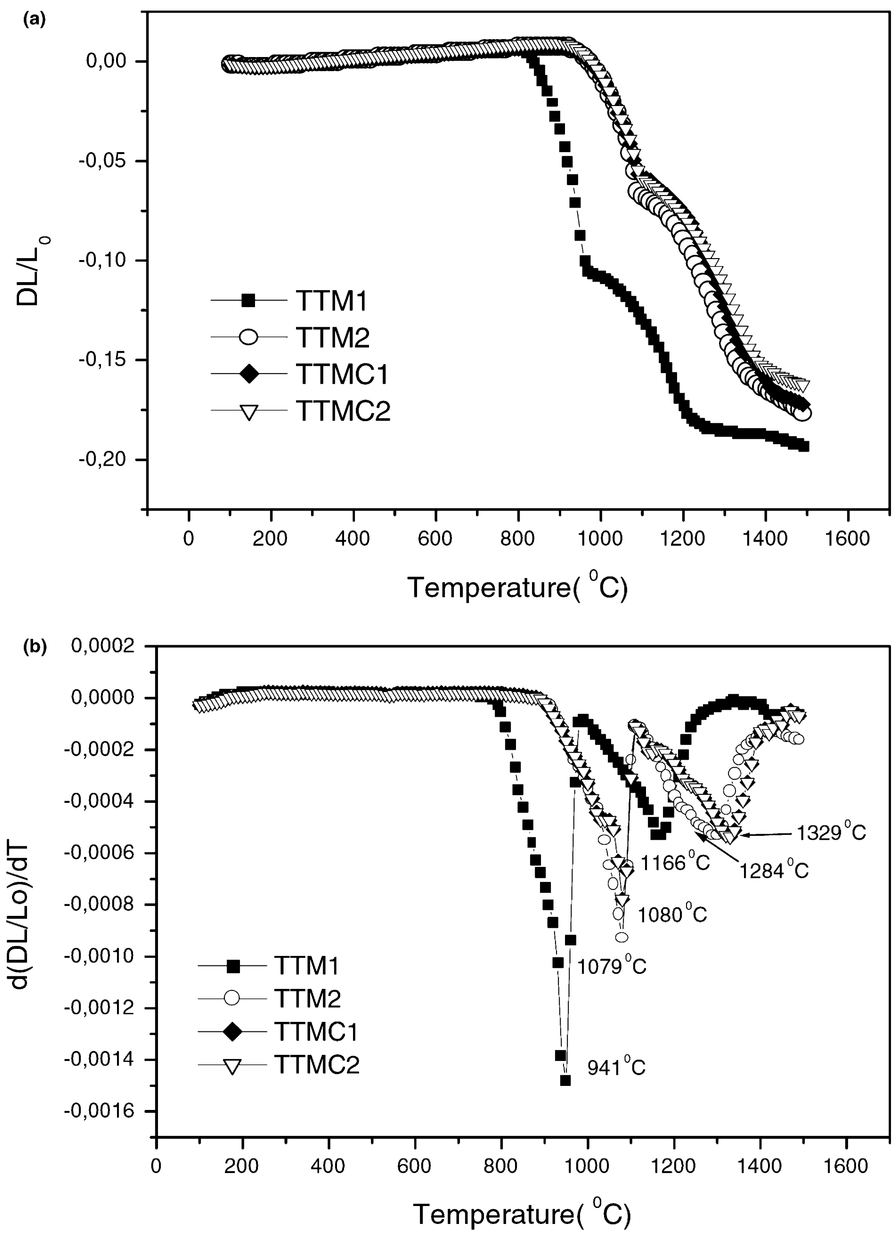

Fig. 2. Linear retraction as a function of the temperature for the $TiO_2{\cdot}Ta_2O_5{\cdot}MnO_2$ and $TiO_2{\cdot}Ta_2O_5{\cdot}MnO_2Cr_2O_3$ varistors with 0.025 mo% and 0.050 mol% of Cr_2O_3 sintered up 1500 °C at a heating and cooling rate of 10 °C/min.

Based on previous studies of the beneficial effect of thermal treatment in an oxidizing atmosphere on the non-ohmic properties of ZnO[11] and SnO_2[12] varistors, an investigation was made of the influence of thermal treatments in an oxidizing atmosphere on the ohmic properties of TiO_2 varistors doped with Ta_2O_5, MnO_2 and Cr_2O_3. For this purpose, the TTM2, TTMC1 and TTMC2 systems were subjected to treatment in an O_2 atmosphere at 800 °C for 1 h (Table 3), and the O_2 atmosphere was found to increase the α value and the breakdown electric field in all the compositions studied.

Fig. 4 and Table 4 present the results of applied electric field versus current density for the $TiO_2{\cdot}Ta_2O_5{\cdot}MnO_2$ system doped with 0.025 mol% Cr_2O_3 (TTMC1) measured at different temperatures. The leakage current was found to increase while the nonlinear coefficient and breakdown electric field (E_r) decreased with increasing testing temperature. The varistor's electrical behavior is governed by the presence of electrical barriers at the grain boundaries of the ceramic material. Thus, the breakdown electric field, E_r, depends both on the average number of electrical barriers formed per unit length during sintering (n) and on the voltage barrier (υ_b).

Fig. 5 illustrates the microstructure of the samples sintered at 1400 °C. This figure shows a uniform microstructure containing TiO_2 grains. X-ray dispersion

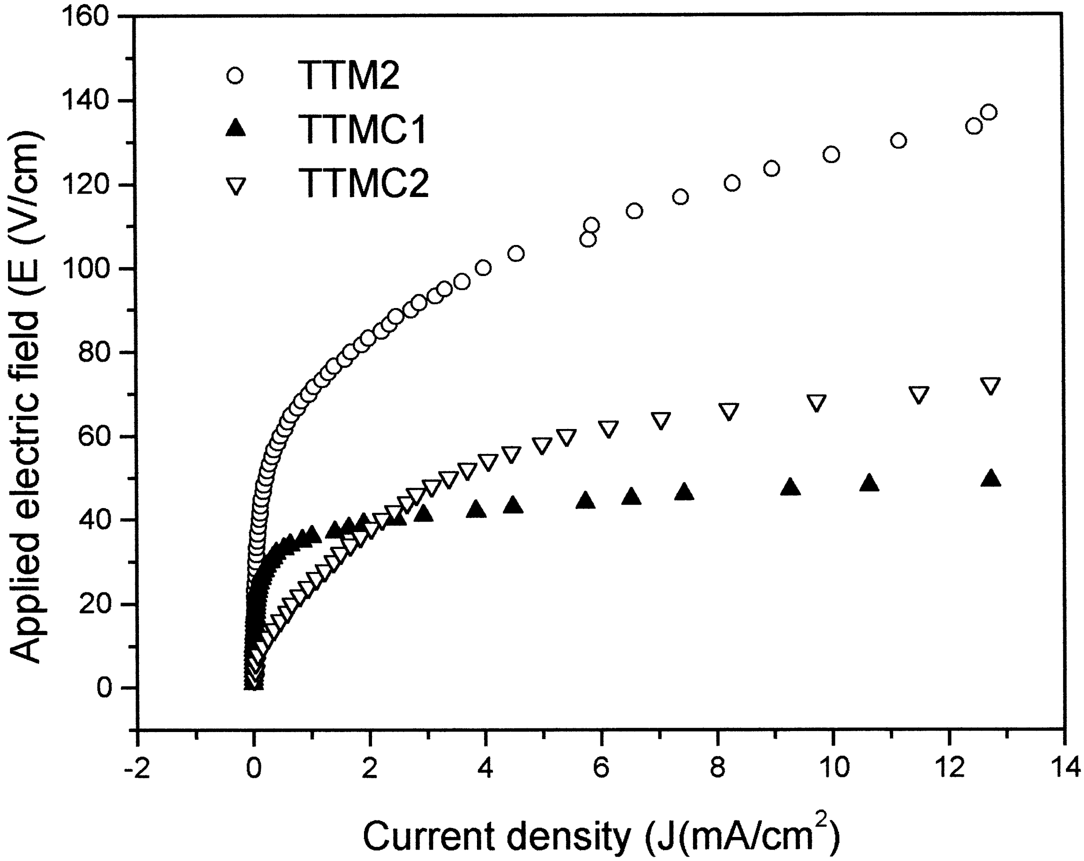

Fig. 3. Current density as a function of the electric field of the TTM2 ($TiO_2 \cdot Ta_2O_5 \cdot MnO_2$ with 0.25 mol% of Ta_2O_5), TTMC1 and TTMC2 (TiO_2 $Ta_2O_5 \cdot MnO_2Cr_2O_3$ with 0.025 mo% and 0.050 mol% of Cr_2O_3) varistors.

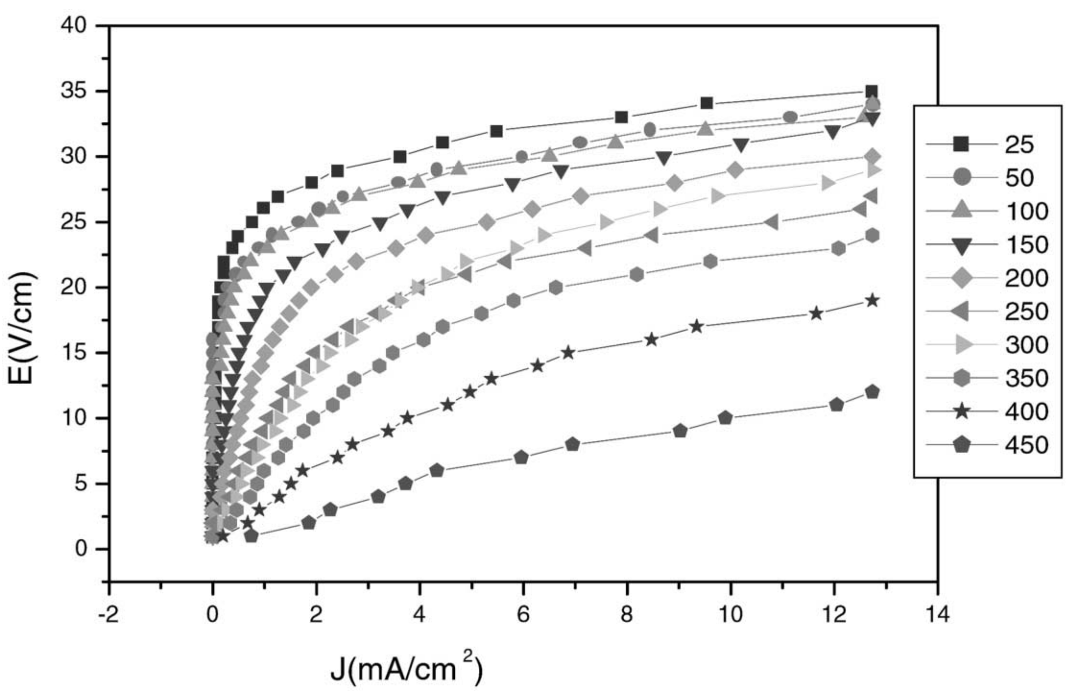

Fig. 4. Influence of the temperature over the nonlinear coefficient, breakdown electric field and leakage of the system with a molar concentration of $TiO_2 + 0.25\%\ Ta_2O_5 + 0.02\%\ MnO_2$ and 0.025% Cr_2O_3.

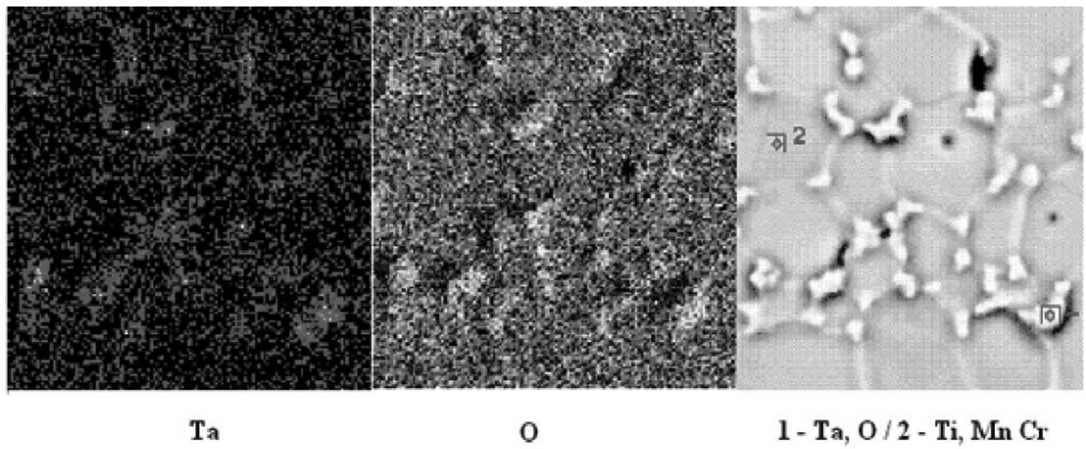

Fig. 5. SEM—microstructure of the system with a molar concentration of 99.71 TiO_2 + 0.25% Ta_2O_5 + 0.02% MnO_2 and 0.025% Cr_2O_3 (TTMC1).

Table 4
Influence of the temperature on the nonlinear coefficient (α) and breakdown electric field (E_r) of the system with a molar concentration of TiO_2 + 0.25% Ta_2O_5 + 0.02% MnO_2 and 0.025% Cr_2O_3

Temperature (°C)	α	E_r (V/cm)
25	8.68	27
50	6.92	24
100	6.69	23
150	5.44	20
200	3.74	15
250	2.60	10
300	2.04	9
350	1.85	7
400	1.49	4
450	1.15	3

spectroscopy and X-ray mapping revealed the presence of Ta_2O_5 precipitated in the grain boundary and MnO_2 and Cr_2O_3 diffused throughout the whole compact. The added manganese dissolved into the TiO_2 grains without precipitating, forming secondary phases, as proposed by Cheng and Wu[6] in their report on their studies of the effect of Mn on the microstructure of (Ba, Bi, Nb) doped TiO_2 ceramics. These results indicate that there are at least one kind of adsorbed species of O_2 at the grain boundary region. The influence of Cr'_{Ti} is to increase the O' and O'_2 adsorption at the grain boundary interface and to promote a decrease in the conductivity by donating electrons to O_2 adsorbed at the grain boundary. An atomic defect model for the TiO_2 varistor based system can be proposed considering the grain boundary concentration of negative charge defects (O'_2, O') stabilized by charge defects (Ta°_{Ti}), $V^{\bullet\bullet}_{\bullet}$, $V^{\bullet}_{\bullet}$). The barrier is formed by the presence of negative defects in the grain boundary region. These defects are mainly O'_2 and $O^{\bullet}$.[13]

4. Conclusion

Low voltage varistors can be produced by the addition of Ta_2O_5 (0.25 mol%), but the best low voltage varistor characteristics (34 V/cm) were observed to result from the addition of Cr_2O_3 (0.025%). Increasing the added Cr to up to 0.025 mol% decreases the nonlinear coefficient. Thermal treatments in an oxidizing atmosphere increase the nonlinear coefficient ($\alpha = 11$) and the breakdown electric field ($E_r = 110$ V/cm).

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References

1. Yan, J. F. and Rhodes, W. W., Preparation and properties of TiO_2 varistors. *Appl. Phys. Lett.*, 1982, **40**, 536.
2. Pennewiss, J. and Hoffmann, B., Varistors made from TiO_2—practicability and limits. *Mater. Lett., 1990, 219.*
3. Wu, J. M. and Lai, C. H., Effect of lead oxide on niobium-doped titania varistors. *J. Am. Ceram. Soc.*, 1991, **74**(n.12), 3112–3117.
4. Yang, S. L. and Wu, J. M., Effects of Nb_2O_5 in (Ba, Bi, Nb)-added TiO_2 ceramic varistors. *J. Mater. Res.*, 1995, **10**, 345–352.
5. Yang, S. L. and Wu, J. M., Varied atmosphere compensation-exploring the roles of barium and bismuth in (Ba, Bi, Nb)-doped TiO_2 varistors. *J. Am. Ceram. Soc.*, 1995, **78**(8), 2203–2208.
6. Cheng, J. J. and Wu, J. M., Effect of Mn on the electrical properties of (Ba, Bi, Nb)-added TiO_2 ceramics prepared by the sol-precipitation method. *Mater. Chem. Phys.*, 1997, **48**(2), 129–135.
7. Bueno, P. R., Camargo, E. and Longo, E. *et al.*, Effect of Cr_2O_3 in the varistor behaviour of TiO_2. *J. Mat. Sci. Lett.*, 1996, **15**, 2048– 2050.
8. Pianaro, E., Bueno, P. R., Longo, E. and Varela, J. A., A new SnO_2-based varistor system. *J. Mater Sci Lett*, 1995, **14**, 692–694.

9. Mendelson, M. I., Average grain size in polycrystalline ceramics. *J. Am. Ceram. Soc.*, 1969, **8**, 52, 443, 1969.
10. Cerri, J. A., Leite, E. R., Gouvêa, D., Longo, E. and Varela, J. A., Effect of cobalt (II) oxide and manganese (IV) oxide on sintering of tin (IV) oxide. *J. Am. Ceram. Soc.*, 1996, **79**(3), 799.
11. Leite, E. R., Longo, E. and Varela, J. A., A new interpretation for the degradation phenomenon of ZnO varistors. *J. Mater. Sci.*, 1992, **27**, 5325.
12. Santos, M. R. C., Bueno, P. R., Longo, E. and Varela, J. A., Effect of oxidizing and reducing atmospheres on the electrical properties of dense SnO_2 based varistor, accepted. *J. Eur. Ceram. Soc.*).
13. Bueno, P. R., Pianaro, S. A., Pereira, E. C., Bulhões, L. O. S., Longo, E. and Varela, J. A., Investigation of the electrical properties of SnO_2 varistor system using impedance spectroscopy. *J. Appl. Phys.*, 1998, **84**, 7–16.