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High voltage characterization of tin oxide varistors

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Abstract High current characterization of SnO_2-based varistors have been carried out and the results obtained have been compared with those ZnO-based commercial surge arresters. It is shown that for a high temperature sintering (1350 °C), the leakage current, breakdown voltage and the saturation at high current density are similar between both types of surge arresters. The paper shows, for the first time, that the high breakdown voltage observed with tin dioxide cannot be easily maintained since the saturation of the ceramics is reached for current densities of several amperes per square centimetre.

Introduction

Several varistor systems based on $SrTiO_3$ [1], TiO_2 [2], WO_3 [3], SiC [4] have been described in the literature, but the nonlinearity of these systems is lower ($\alpha < 15$) when compared to that of commercial multicomponent ZnO varistors ($25 < \alpha < 60$).

There is a continuous need to improve the protection level against transient surge voltages i.e. varistors that show reduced residual voltage, better energy capability and lower leakage current. The present research is focused in obtaining more compact ceramics. Varistors based on SnO_2 present several advantages when compared to commercial heterogeneous ZnO-based varistors:

- a simpler ceramic microstruture: single phase versus multiphase-microstructure, which should make it easier for controlling the manufacturing processes of these ceramics [5],
- a higher refractory feature which should minimized the vaporization of oxide out of the ceramics [6],
- the dopant concentration levels are needed in small concentration (10 times less than in ZnO system),
- thermal conductivity of 0.5 WK^{-1} cm^{-1}, two times larger than ZnO-based ceramics, is an advantage when considering thermal runway stability [5],
- a non linear coefficient in the range of ZnO-based varistor measured between 1 mA cm^{-2} and 10 mA cm^{-2},
- high breakdown field, in the range above 1 kV/mm, with sintering cycle of 1350°C for 2 h [7]. This high breakdown field is about 5 times higher than ZnO-based varistors. It is in relation with smaller grain sizes of about 1 μm versus 10 μm.

Tin dioxide might therefore be a serious candidate since for a higher voltage breakdown it is possible to reduce the size of the ceramics. Indeed, to achieve a given breakdown voltage, the varistor thickness is tuned. Since the paper of the SnO_2-based varistor (SnO_2–CoO–Cr_2O_3–Nb_2O_5) by Pianaro et al in 1995 [8], the literature contains extensive reports describing the influence of chemical composition or dopants nature and concentration, on the DC electrical properties. Table 1 reports the main dopants so far investigated. It is worth noticing that all the papers deal with electrical characterization below 100 mA/cm^2 i.e. just after the breakdown voltage. We report in this paper, for the first time, the full electrical J(E) characterization of tin oxide varistors up to the voltage upturn at high currents.

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Table 1 Main dopants investigated in SnO_2 formulations for surge arresters since 1995 (doping elements added as oxides and references)

Co,Ta	[9–11]	Co,Nb,Ce	[12]
Co,Mn	[13]	Co,Nb,Dy	[14]
Co,Sb	[15, 16]	Co,Nb,Cr,Mn	[12]
Co,Nb	[16]	Co,Nb,Zn,Mn	[12]
Nb,Ni	[17]	Co,Cr,Ta	[12, 18]
Nb,Zn	[19]	Co,Cr,Zn,Ta	[20]
Cu,Ta	[21, 22]	Co,Cr,Ta,Sc	[14, 23]
Cu,Nb	[22]	Co,Cr,Nb,La	[24]
Cu,V	[22]	Co,Cr,Mn	[18]
Cu,Sb	[25]	Co,Cr,Ta	[18]
Li,Ta	[26]	Co,Cr,Nb	[12, 27]
Ni,Ta	[28]	Co,Cr,Ta	[29]
Ni,Ta,Cu	[30]	Co,Cr,Bi,B	[31]
Zn,W	[32]	Co,Cr,Nb,La,Pr,Ce	[33]
Co,Nb,Er	[34]	Co,Cr,Zn,W	[7]
Co,Nb,Gd	[35]	Co,Ta,Ba	[36]
Co,Nb,Fe	[37]	Co,Ta,Cu	[38]
Co,Nb,Y	[39]	Co,Ta,Cr	[40]
Co,Nb,Pr	[41]	Co,Ta,Zn	[42]
Co,Nb,In	[43]	Cu,Ta,Ni	[30]
Co,Nb,Bi	[37, 44]	Co,Ta,Gd	[45]
Co,Nb,Ta	[46]	Co,Ta,Er	[47]
Co,Nb,Sc	[48]	Co,Ta,Pr	[35]
Co,Nb,Sr	[49]	Co,Ta,La	[9]
Co,Nb,Ti	[50]	Co,Ta,Sr	[51]
Co,Nb,Al	[12]	Co,Ta,Sc	[22]
Co,Nb,Fe	[52]	Co,Zn,Mn	[34]
Co,Nb,La	[12, 53]	Co,Zn,Cu	[54]
Co,Nb,Ni	[12, 17]	Nb,Zn,Fe	[39, 51]

Experimental procedure

The raw materials used in this work were analytical grade SnO_2 (99.9%), Nb_2O_5 (99.9%), CoO (99.8) and Cr_2O_3 (99.0) supplied by Aldrich. The oxides were mixed and ball-milled in agate bottles for 1 h.

The oxide powders were then mixed with a polyvinyl alcohol binder, granulated and pressed into pellet shapes. The powder was pressed by uniaxial pressing at 7 MPa. The samples were sintered in air at 1250 °C and 1350 °C for 2 h. They were heated at a rate of 120 °C/h to the sintering and room temperature. The non linear coefficient α, for all the samples studied, were estimated between two desired magnitudes of current and corresponding voltage by $\alpha = 1/\log(E_{0.1\mathrm{mA/cm^2}}/E_{1\mathrm{mA/cm^2}})$, where $E_{0.1\mathrm{mA/cm^2}}$ and $E_{1\mathrm{mA/cm^2}}$ are voltage fields at current densities 0.1 $\mathrm{mA/cm^2}$ and 1 $\mathrm{mA/cm^2}$, respectively.

For the electrical measurements, silver contacts were deposited on the cylinder samples surfaces, after which the pellets were heat-treated at 600 °C for several minutes. The electrode area varies from 3.63 cm^2 with a ceramic thickness of 1.97 mm (SnO_2) and 2.26 cm^2 with a ceramic thickness of 3.34 mm (ZnO). The shrinkage after sintering was isotropic: –17.2% for the diameter and –17.6% for the thickness. The densification ($\rho/\rho_{SnO_2-\mathrm{theory}}$ with $\rho_{SnO_2-\mathrm{theory}} = 6.95\ \mathrm{g\ cm^{-3}}$) varies from about 55% before and 98% after sintering. Then, the current-voltage measurements were taken using a high voltage-measuring unit using a current generator which delivers a 8/20 µs impulse current with a peak short-circuit of 6 kA.

At the current density of 1 mA cm^{-2}, the breakdown field, E_b, is measured and at the voltage $U_b/2$ corresponding, the current density is reported as J_L.

Results and discussion

The ceramics where sintered at 1250 °C achieving a breakdown field ($E_{1\ \mathrm{mA}} = 640$ V/mm), which is fairly higher as when compared to commercial varistors. However, the ceramics are saturated at relatively low current density as depicted in Fig. 1. The surface flashover due to the last impulse voltage explains the decrease of the end of the curve. A subsequent shock led to a burst of the device. The empirical surge arrester power law equation:

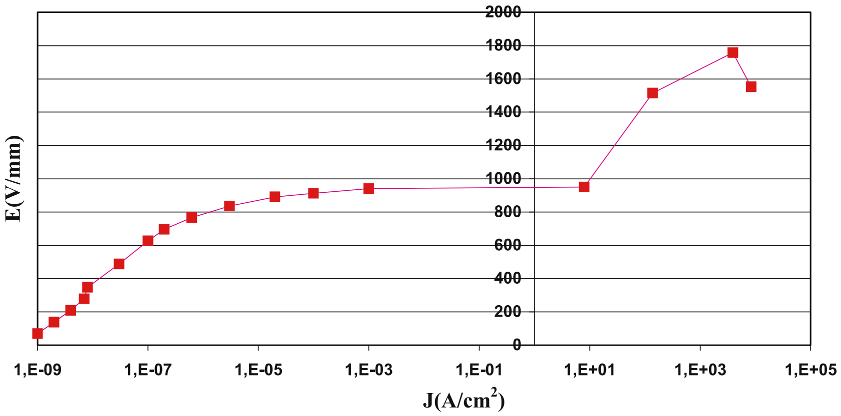
$$J_1/J_2 = [E_1/E_2]^{\alpha} \qquad (1)$$

shows that for an exponent in the range 25–60 the current varies a lot for small changes in the applied field. The current deviation from the power law (i) at high current (around 10 A cm^{-2} in the present case), is due to the intrinsic ohmic bulk resistance of the SnO_2 grains in the varistor. This upturn is obviously an undesirable characteristic that could be improved by proper donor doping of the tin oxide.

Ceramics sintered at higher temperature (1350 °C) show a better characteristic similar to commercial ZnO-based varistors (Fig. 2). There is a large variation in current (a factor of 10^7) for a stable applied voltage field varying in the range of E_b. The curve shows an excellent leakage current in the nA range which corresponds to the transport of very low level currents through the varistor. The breakdown voltage is about 230 V/mm for the present device.

One technical advantage of SnO_2-based surge arrester, the breakdown field, cannot be maintained. The sintering at 1350 °C lead indeed to a dilemma. On one hand, this high temperature leads to a better non linear characterization at high current but on the other hand, the breakdown field is divided by 3. The reason for the difference in behaviour between 1250 and 1350 °C is still not very well understood and will be subject to future work.

Fig. 1 Log-scale plot of applied electrical field versus current densities at 298 K of a tin oxide varistor sintered at 1250 °C



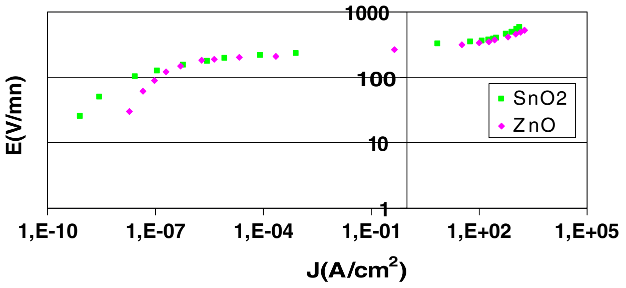


Fig. 2 Log-scale plot of applied electrical field versus current densities at 298 K of a tin oxide varistor sintered at 1350 °C and a commercial ZnO metal oxide varistor

Table 2 presents the α (non linear coefficient), E_b (which was defined as the field applied when current flowing through the arrester is 1 mA/cm^2), densification and J_l (defined as the current density at 0.5 of U_b). As can be seen the value are similar. On one hand, SnO_2 presents a breakdown voltage slightly higher associated with a lower non linear coefficient. However, this coefficient gives only data on the behavior of the varistor effect at low DC current since it is measured in the range: 10^{-4}–10^{-3} A.

Conclusion

In conclusion, we have shown comparative results of electrical properties of commercial ZnO and SnO_2-based varistor. The properties of both of these devices are equivalent even at high current densities. This goal is achieved without any detrimental effect on the mechanical and electrical characteristics. Future works need to be done to show that SnO_2-based arrester can in fact adequately replace ZnO for high field devices with low dimensions.

Table 2 α, E_b, J_L, relative densification for commercial ZnO- and our SnO_2-based varistor system sintered at 1250 °C and 1350 °C, respectively

	α	E_b(V/mm) (1 mA cm^{-2})	J_L (A cm^{-2}) (U_b/2)	densification (%)
ZnO	52	208	$3 \cdot 10^{-7}$	~99
SnO_2 (1350 °C)	33	228	$2 \cdot 10^{-7}$	98
SnO_2 (1250 °C)	63	640	$3 \cdot 10^{-7}$	97

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