



XIX International Conference on Extractive Metallurgy

*“Recent Developments in Metallurgy,
Materials and Environment”*



PAPER 52

INFLUENCE OF JOULE HEATING ON VARISTOR BEHAVIOR IN $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ CERAMICS

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SALTILLO, COAHUILA, MÉXICO
MAY 18-21, 2010

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ABSTRACT

Current-voltage characteristics of $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ ceramics prepared using planetary milling process are studied in dc, ac and pulse regimes. Although microstructure characterization rather confirms the visible homogeneity of sintered material, quite strong contribution of Joule heating to non-Ohmic behavior was revealed. The quality of the studied $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ ceramics for varistor application is not sufficient. This conclusion contradicts the view in previous publications by other authors.

Keywords: Joule heating, non-Ohmic conduction, tin dioxide, varistor

RESUMEN

Se estudiaron las características corriente-voltaje en los modos ac, dc y de pulso, de cerámicos $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ preparados usando un molino planetario. Aunque la caracterización de la microestructura confirma la homogeneidad visible del material sinterizado, se encontró una contribución fuerte de calentamiento Joule al comportamiento no-Óhmico. La calidad de los cerámicos $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ estudiados no es adecuada para aplicaciones como varistores. Esta conclusión contradice la opinión en algunas publicaciones anteriores de otros autores.

INTRODUCTION

Zinc oxide ceramic varistors are widely used for protection of electrical and electronic equipment against transient surges due to high nonlinearity of current-voltage ($I(U)$) characteristics [1,2]. However, the search of new materials for such devices is continuing. Deviations from Ohm's law were observed in some systems based on other oxides though the nonlinearity of their $I(U)$ characteristics was not high. But it was shown that tin dioxide based $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Bi}_2\text{O}_3\text{-BaO}$ ceramics exhibit $I(U)$ characteristics

with fairly high nonlinearity coefficient $\beta > 20$ [3]. Later simpler $\text{SnO}_2\text{-CoO-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ system was suggested [4,5].

Tin dioxide based ceramic material $\text{SnO}_2\text{-CoO-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ is considered by some authors as suitable for varistor applications [5,6] and they claim that $\text{SnO}_2\text{-CoO-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ ceramics exhibit better pulse properties than ZnO varistors [5,6]. But in SnO_2 ceramics at high current pulses frequently degradation or even electro thermal breakdown occurs [7, 8]. Only recently the resistivity of SnO_2 grains in some SnO_2 varistor sample (about 4 Ohm·cm) was estimated [9] and current-voltage characteristics in the wide current range in some ceramics were reported [6-8,10]. SnO_2 -based varistor ceramics exhibit relatively high grain resistivity (about 4-40 Ohm·cm) [6-11] in comparison with ZnO-based varistor ceramics (about 0.5 Ohm·cm) [2,11-14]. Quite high resistivity of SnO_2 grains is serious disadvantage of SnO_2 varistors because due to that the nonlinearity at high currents is decreased. Therefore, it is possible to conclude that now electrical properties of SnO_2 varistor materials especially at high currents are rather not sufficiently studied.

In some SnO_2 ceramics even at relatively not high currents the Joule micro heating can take place [15]. High resistivity of SnO_2 grains means that in SnO_2 -based varistor ceramics the grains themselves (and not only grain-boundary regions) can be heated in more extent than in ZnO-based varistor ceramics even at not very high current level. Therefore, it can be assumed that Joule heating without proper dissipation of energy can affect the functioning of SnO_2 -based ceramics for varistors.

Then, it would be interesting to examine how strongly the electrical characteristics of SnO_2 varistor can be changed if self heating takes place. With such a purpose in this paper $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ ceramic samples with similar composition to the studied earlier [4-6] were prepared and their microstructure and current-voltage characteristics in different regimes were studied.

EXPERIMENTAL PROCEDURES

Ceramic samples (mol.%) 98.9% SnO_2 -1% Co_3O_4 -0.05% Nb_2O_5 -0.05% Cr_2O_3 were obtained by mixed oxide route. Oxides were mixed during 20 min in planetary mill Retsch PM100 using distilled water (according to [16]), then dried and axially pressed at 40 MPa. Sintering was performed at 1300°C (100 min) in air with a heating rate of 5°C/min and cooling rate of 5°C/min (between 1300 and 800°C) and 2°C/min (between 800 and 200°C). Silver electrodes were obtained at 800°C (10 min), the heating and cooling rate was 2 °C/min.

Current-voltage characteristics were recorded in air by three different ways: manual dc measurement, computer-controlled (automatic) measurement and single pulse measurement. The source-measure unit Keithley 237 was used in the first and the second cases. At computer-controlled process rectangular

unipolar voltage pulses with amplitude increment 2 V, duration of $t_V=100$ ms and pause between pulses $t_P=100$ or $t_P=1000$ ms were used. Current was measured at the end of each voltage pulse.

For the study of high-current $I(U)$ characteristics the single pulse generator [14] was used. In this case preliminary charged capacitor was discharged through the sample using thyatron-based circuit as a key device [14]. Current is increased during some short time about 8 μ s and then gradually decreased. It takes about 20-40 μ s since the start till the drop of current to a half of amplitude. Similar so-called 8/20 μ s single current pulses are used for varistor testing [2]. Time between pulses was not less than 10 min. Storage oscilloscope C8-11 was used to record current pulse. Voltage amplitude was measured by pulse voltmeter B4-17. To plot pulse $I(U)$ characteristic the amplitudes of voltage $u(t)$ and current $i(t)$ curves were used.

The nonlinearity coefficient was estimated as the slope of $I(U)$ curve in double logarithmic scale: $\beta = (U/I)(dI/dU) = d(\log I)/d(\log U)$.

RESULTS AND DISCUSSION

It was found that an application of dc voltage to a sample causes time-dependent current. Therefore, time dependence of current at fixed dc voltage was studied during fixed time (600 s) with subsequent increasing of applied voltage. At low voltage (100 V) current decay is observed (Fig.1). In this case

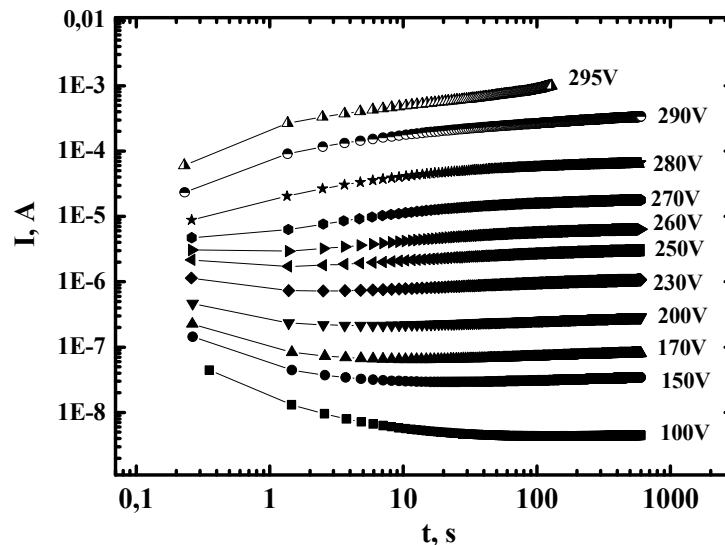


Figure 1. Time dependence of current recorded at different voltages.

the changes in current are quite high (about one decade). This behavior is due to the capture of majority carriers at the grain boundaries. At higher voltages (150-250 V) initial current decay is gradually changed by noticeable

current rise. At voltages higher than about 270 V only increase in current on time takes place (Fig.1). Observed gradual increase in current can be due to the Joule self heating because this effect becomes more pronounced with increase of applied voltage (power dissipated in the sample is strongly increased).

Therefore, current-voltage characteristics can be affected by Joule heating. Indeed, the difference in current-voltage curves obtained at increase and decrease in voltage is detected (Fig.2). For clarity data are presented not only in double logarithmic scale (Fig.2, left) but in linear scale in the narrow range of voltage (Fig.2, right) as well. At high current values current-voltage curve obtained at decrease in voltage is situated higher than curve obtained at increase in voltage because there is not enough time between voltage pulses to cool some micro regions near grain boundaries to ambient temperature (Fig.2, right). At low current values, on the contrary, current-voltage curve obtained at decrease in voltage is situated below than curve obtained at increase in voltage due to the grain-boundary states are already filled by electrons, the grain-boundary barriers are higher and conductance is lower (Fig.2, left). At low currents Joule heating is negligible (temperature of micro regions is practically equal to the ambient temperature).

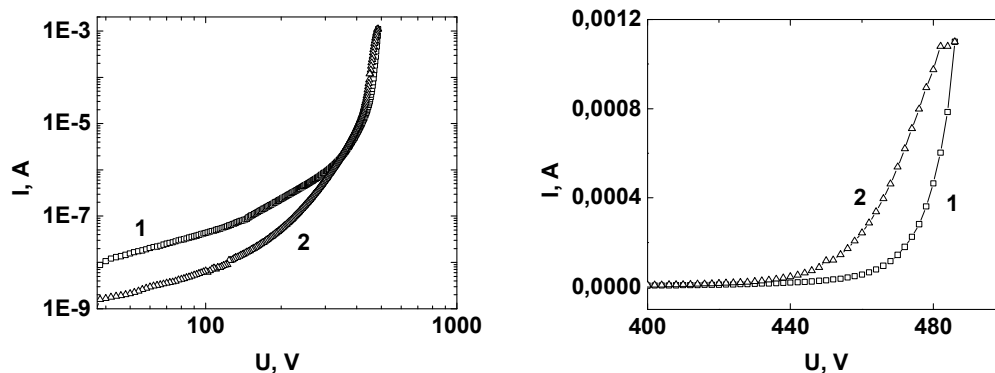


Figure 2. Current-voltage dependence in double logarithmic and linear scale at increase (1) and decrease (2) of voltage. $t_V=100$ ms, $t_P=100$ ms.

Observed hysteresis in Fig.2 can be related to the influence of Joule heating because it is changed if the pause between voltage pulses t_P is varied. If t_P is decreased, the separation between curves “up” and “down” becomes higher. But even if time between voltage pulses is quite high ($t_P=1000$ ms), this hysteresis still exists. Actually the variation of t_V and t_P in automatic measurements gives quite complicated $I(U)$ curves due to not only Joule heating is changed but the filling of the grain-boundary states depends on time. Therefore, automatic measurements rather do not give steady-state values of current.

The distortion of current-voltage curve at relatively high current can be important as far as it can lead to the change in an estimation of the

nonlinearity coefficient. To check this assumption we have compared in Fig.3 the results of $I(U)$ recording obtained by three different ways: manual, automatic ($t_V=100$ ms, $t_P=100$ ms) and single pulse. At manual measurement current was decreased on time up to about $6 \cdot 10^{-7}$ A and started to increase on time at higher currents (it correlates with data in Fig.1). It was rather difficult to read current above about $3 \cdot 10^{-5}$ A at manual measurement. Therefore, there are no “manual” points above this value (Fig.3, left). But automatic measurements gave points up to 1 mA and nonlinearity was quite high (Fig.3, right). At pulse measurements the points in the range about 30 mA-6.6 A (0.1 - 23 A·cm⁻²) were obtained (Fig.3). It is seen that the gap between results of manual and pulse measurements can be interpolated by straight line with some slope though results of automatic measurements in the range of about 10^{-5} - 10^{-3} A give higher nonlinearity (higher slope) clearly visible in Fig.3 (right). This overestimation of the nonlinearity in the case of automatic measurements can be due to the Joule heating. It should be mentioned that in Fig.3 (right) and in Fig.2 the same curves are shown. The conditions for the developing of Joule heating in the studied samples are so favourable that even at relatively short pulses this sample exhibit breakdown at relatively not very high current about 6.6 A (23 A·cm⁻²) (Fig.3).

However, it is necessary to mention that higher nonlinearity obtained by automatic measurements (Fig.3, curve 3) can be due to pure electronic processes (without Joule heating) and the decrease in the nonlinearity seen in pulse data (Fig.3, curve 2) is attributed to high grain resistivity. Further investigations can clarify this problem. But even in this case studied material is not adequate for varistor application because the current range with high nonlinearity is narrow due to high grain resistivity.

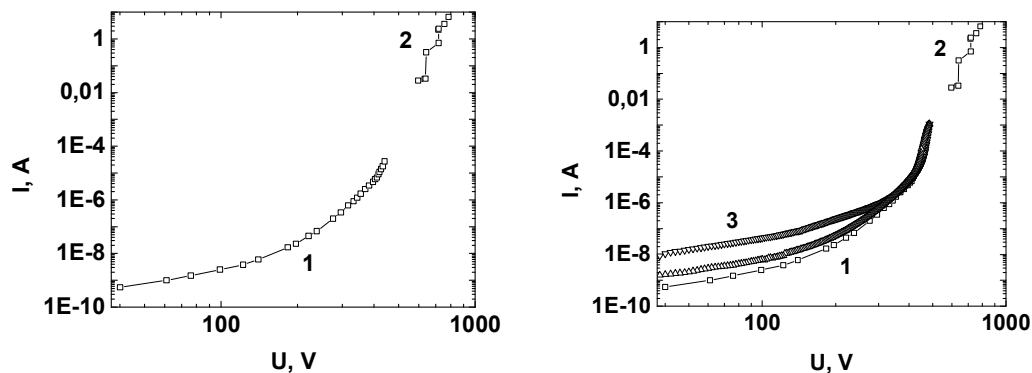


Figure 3. Current-voltage dependences obtained by manual (1), pulse (2) and automatic ($t_V=100$ ms, $t_P=100$ ms) (3) measurements. For clarity data are shown before and after the plotting of curve 3.

All studied samples show practically the same behavior: in the double logarithmic scale the slope of $I(U)$ curve is higher for automatic measurements ($t_V=100$ ms, $t_P=100$ ms) than the slope of straight line interpolating data between manual and single pulse measurements.

Therefore, the value of the nonlinearity coefficient can be overestimated if data are obtained by automatic measurements with frequent voltage application. Additionally, this observation confirms indirectly that studied samples are rather similar in their electrical properties, i.e. used preparation method gives fairly homogeneous oxide mixture.

Earlier it was pointed out that ac (60 Hz) current-voltage characteristics of SnO₂ varistors exhibit some influence of Joule heating because the traces of I(U) dependence for increase and decrease of voltage in the highly nonlinear region are not coincided (i.e. some bifurcation takes place) though in ZnO varistors this effect is less expressed [15]. Therefore, it would be useful to check this feature in the studied samples where Joule heating probably has an influence on non-Ohmic behaviour as it was shown above. With this purpose ac (60 Hz) current-voltage characteristics were studied (Fig.4).

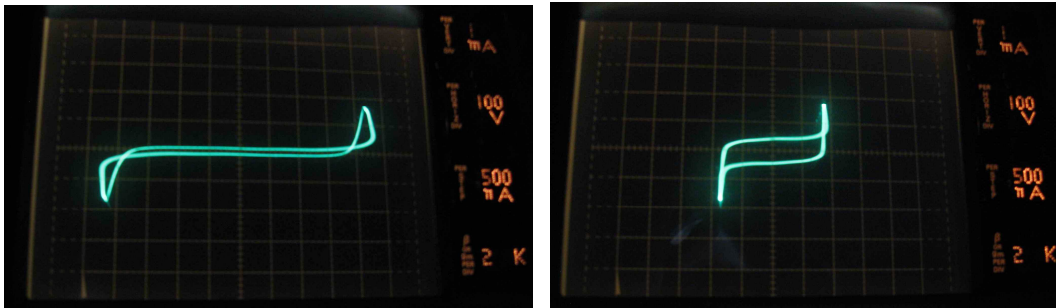


Figure 4. Oscillograms of I(U) characteristics of studied SnO₂ sample (left) and commercial ZnO varistor CH2-1 Positron (right). Horizontal: 100 V/div, vertical: 1 mA/div.

Indeed fairly large loop at ac current-voltage curve of SnO₂ sample takes place (Fig.4, left). Other studied samples demonstrate similar behaviour. For comparison, such effect is practically absent in ZnO varistor (Fig.4, right). It is necessary to stress that in this case mentioned feature in ac current-voltage curve is observed in the samples where Joule heating can have an influence on non-Ohmic behaviour. Therefore, suggested earlier way for simple and quick detection of the Joule heating using ac current-voltage characteristics [15] is useful.

Thus, obtained experimental data show that the Joule heating has significant effect on current-voltage dependence of SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃ ceramics even at relatively low current densities of about 10⁻⁵-10⁻³ A·cm⁻², frequently presented in the published dc data. The reason for an appearance of noticeable effect of the Joule heating can lie in non-homogeneous current distribution in a sample: high local current associated with high voltage drop can cause large local dissipation of energy and subsequent local increase in temperature if heat export is limited.

There are some reasons why non-homogeneous current distribution can take place (spatially non-homogeneous distribution of chemical components, grain size variation throughout the sample if grain boundaries are more resistive than grains, poor sintering resulting in small cross-section of grain boundaries and others). To get more “homogeneous” ceramics (with improved impurity distribution) the planetary milling was used (see section 2 Experimental Details). Additionally, current-voltage characteristics obtained for many samples prepared in this work are quite similar. This means at least that oxide mixture was rather without strong heterogeneities.

For additional verification of microstructural quality of obtained ceramics, the secondary electron images were taken at different regions of the samples. These data are shown in Fig.5. It is seen that the grain size distribution is fairly homogeneous, though, the grains, of course, are not of the same size. It is necessary to point out that microstructure in Fig.5 is similar to the published one [5].

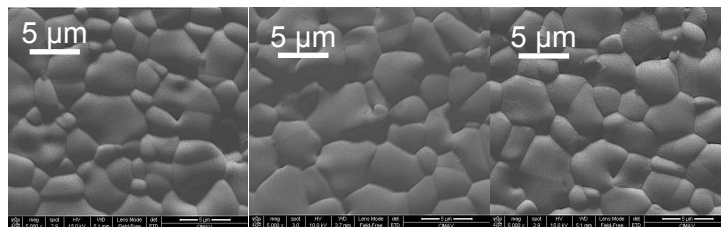


Figure 5. Comparison of the second electron images obtained in three different areas of the same sample. Some variation in the grain size is seen.

The nonlinearity coefficient estimated for studied material on the basis of automatic measurements is in the range of 30-60, which is comparable with published data for $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ ceramics [5]. Why then Joule heating influence is so obvious? It can be assumed that the grain boundaries in this ceramics are not identical or the cross-sections of the grain boundaries are quite small and variable. However, cited authors [5,6], on the contrary, consider that $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ ceramics are quite homogeneous and better than ZnO ceramics. We have some long experience in the study of pulse and other electrical properties of commercial and laboratory-made ZnO and SnO_2 varistors [8-11,13,14] and we would like to mention that SnO_2 varistors (at least ones prepared by ourselves and particularly studied in this work) are inferior to ZnO varistors.

The development of breakdown in time in one of the samples (the same as in Fig.3) is presented in Fig.6. Before thermal breakdown some time delay should take place to heat a region where current occurs. Perhaps this situation is observed experimentally in Fig.6: the current started to drop but

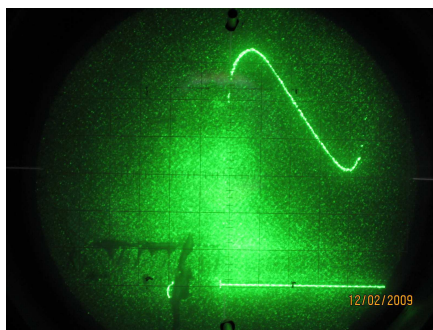


Figure 6. Oscillograms of current vs time dependence for $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$ varistor at initial stage of breakdown. Horizontal: $10 \mu\text{s}/\text{div}$, vertical: $1 \text{ A}/\text{div}$.

after some delay visible increase in current at initial stage of the breakdown takes place. These data prove that observed breakdown is thermal (electro-thermal). This fact indirectly confirms that Joule heating in our samples indeed can take place at lower currents. As a result of the breakdown the resistance of a sample is irreversibly decreased by many decades up to about 1000 Ohm . $I(U)$ characteristic becomes linear. It is necessary to mention that used single pulses actually are wider than “ $8/20 \mu\text{s}$ ” pulses (see Fig.6). This fact contributes to the observation of thermal breakdown.

Some images of an area near the breakdown (puncture) channel at both sides of the sample taken at different magnifications are shown in Fig.7. EDX-spectrum of an area near the breakdown channel shows not only the lines of oxygen and tin but silver as well. It is due to the melted and solidified particles of Ag electrode (ball shaped) are distributed throughout the surface as a result of explosion-like melting at thermal breakdown. These balls are seen in the SEM images (Fig.7). During thermal breakdown melting and evaporation

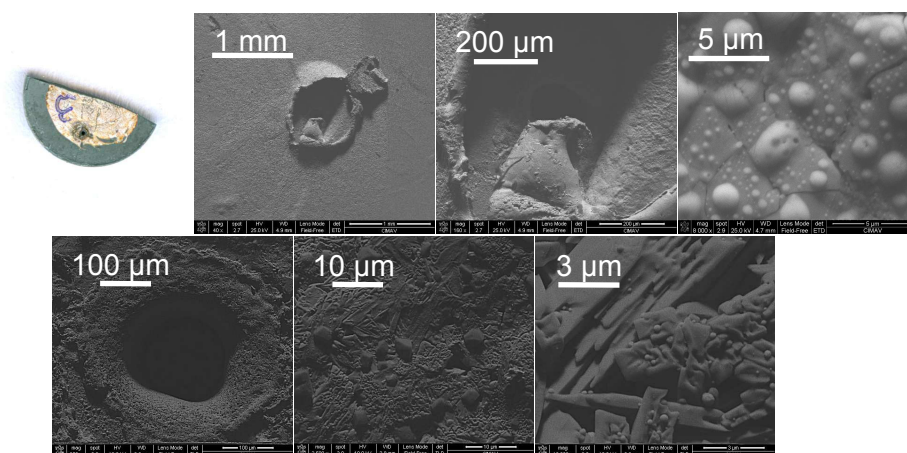


Figure 7. SEM micrographs of the breakdown channel taken at two sides of the sample. Diameter of the sample is about 10 mm . It was broken manually after the breakdown (for research purposes).

of substance in the channel occur. As a result of subsequent condensation and crystallization from vapour phase some microcrystals (probably, SnO₂) appear (Fig.7).

Perhaps SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃ ceramics prepared in this work are not so good as the ones reported in the literature [4-6]. But overall we used similar preparation methods. Unfortunately, we have no samples of SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃ ceramics obtained by cited authors [4-6]. Obtained results make us to have some doubt in the high quality of SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃ ceramics for varistor application, as it is declared by others [5,6]. These results allow us to conclude that the quality of SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃ ceramics studied here is not satisfactory for varistor application. Further study of the preparation route and electrical characterization of these materials especially in respect of a clarification of the role of Joule heating in each case is necessary.

CONCLUSIONS

The manifestation of Joule heating in mainly electronic non-Ohmic conduction in SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃ ceramics is revealed. The overestimations of the nonlinearity coefficient in the published data on SnO₂-based varistor ceramics can take place if the contribution of Joule heating was not analyzed. The quality of studied SnO₂-Co₃O₄-Nb₂O₅-Cr₂O₃ ceramics for varistor application is not adequate. Earlier suggested way for simple and quick detection of the Joule heating based on ac current-voltage characteristics looks useful.

ACKNOWLEDGMENT

This work was performed in part in the frames of the project SEP-2003-C02-42821, CONACYT, México.

REFERENCES

1. M. Matsuoka. Nonohmic Properties of Zinc Oxide Ceramics. *Jpn. J. Appl. Phys.* 10(6) 736-746 (1971).
2. T.K. Gupta. Application of zinc oxide varistors. *J. Am. Ceram. Soc.* 73(7) 1817-1840 (1990).
3. A.B. Glot, A.P. Zlobin. Nonohmic conductivity of tin dioxide ceramics. *Inorg. Mater.* 25(2) 274-276 (1989).
4. S.A. Pianaro, P.R. Bueno, E. Longo, J.A. Varela. A new SnO₂-based varistor system. *J. Mater. Sci. Lett.* 14, 692 (1995).
5. P.R. Bueno, J.A. Varela, E. Longo. SnO₂, ZnO and related polycrystalline compound semiconductors: An overview and review on the voltage-dependent resistance (non-ohmic) feature. *J. Eur. Ceram. Soc.* 28(3), 505 (2008).

6. M. A. Ramirez, W. Bassi, R. Parra, P. R. Bueno, E. Longo, J.A. Varela. Comparative electrical behavior at low and high current of SnO₂-and ZnO-based varistors. *J. Am. Ceram. Soc.* 91 (7) 2402 –2404 (2008).
7. R. Metz, J. Morel, M. Houabes, J. Pansiot, M. Hassanzadeh. High voltage characterization of tin oxide varistors. *J. Mater. Sci.* 42, 10284-10287 (2007).
8. A.V. Gaponov, A.B. Glot, A.I. Ivon, R. Bulpett. Pulse properties of SnO₂-based varistor ceramics, *Phys. Chem. Solid St.* (2009), accepted for publication.
9. A.B. Glot, I.A. Skuratovsky. Non-Ohmic conduction in tin dioxide based varistor ceramics. *Mater. Chem. Phys.* 99(2-3) 487-493 (2006).
10. A.V. Gaponov, A.I. Ivon, A.B. Glot. Effect of Cu₂O additive on the electrical properties of SnO₂-based varistor ceramics. 1st Int. Conf. Electromagnetic compatibility on railway transport, Dniepropetrovsk (Ukraine) 24-26 May 2007, p.19.
11. A.I. Ivon, A.B. Glot, A.V. Gaponov, S.V. Mazurik. Grain resistivity and grain size in non-Ohmic oxide ceramics. *Key Eng. Mater.* 132-136, 1289-1292 (1997).
12. L.M. Levinson, H.R. Philipp. High-frequency and high-current studies of metal oxide varistors. *J. Appl. Phys.* 47(7) 3116-3121 (1976).
13. B.K. Avdeenko, A.B. Glot, A.I. Ivon, I.M. Chernenko, A.I. Schelokov. Thermostimulated conduction of zinc oxide ceramics of different composition. *Inorg. Mater.* 16(7) 1059-1060 (1980).
14. A.I. Ivon. Parameters of ZnO grains in ZnO-based ceramics. *Inorg. Mater.* 36(10) 1074-1077 (2000).
15. A.B. Glot. Non-ohmic Conduction in Oxide Ceramics: Tin Dioxide and Zinc Oxide Varistors. In: *Ceramic Materials Research Trends*, Ed. P.B.Lin, Nova Science Publishers, Inc., 2007, p. 227-273.
16. J. A. Aguilar-Martínez, M. B. Hernández, M. I. Pech-Canul, A. B. Glot, J. Castillo-Torres. A comparative study between the mixed-oxide and high-energy milling planetary method on electrical and microstructural properties for a SnO₂-based ceramic system. *J. Mater. Proces. Technol.* 209, 318-322 (2009).