

Experimental Study about the Concentration of Cr₂O₃ and MnO₂ inside a New Metal Oxide Varistor Material

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Abstract

Metal Oxide Varistors are, from the chemical point of view, ceramics, acting as n – semiconductors and having a polycrystalline and complex structure. The main application of these power electronic devices is for construction of overvoltage protection equipment (for every voltage level), because of some advantages like: an increased level of non-linearity between the resulting current and the voltage characteristic, a high energy adsorption capacity and an excellent fast response time, which make them ideal for protecting other sensible electronic devices and circuits. This paper presents a new material and some manufacturing technology aspects for a Metal Oxide Varistor based on a new mixture of oxides used in order to obtain a new ceramic with higher non-linear electric properties. The two oxides involved are Cr₂O₃ and MnO₂ as dopants or additives. All measurements of the electrical performances will be carried out in relation with an existing 5 dopants material (three +these two).

1. Introduction

Metal Oxide Varistors (also known as ZnO varistors, due to their most important component, the Zinc Oxide, having, at least, more than 60%) are applied for manufacturing the most performant surge arresters for all voltage levels, from domestic low voltage consumers and networks, up to high voltage power lines. Their main goal is to protect any piece of sensitive electronic equipment against all types of over voltage which occurs on the power supplying network (technical incident, induced overvoltage or lightning stroke) [1].

They are the best technical solution for many modern surge arresters technologies due to some important issues like: a high level of non-linearity for the current-voltage characteristic, a relatively high energy (heat) absorption capacity and an excellent (nanoseconds) response time. They are ceramic materials having a poly-crystalline structure and acting as n – semiconductors. These ceramics are made of a mixture of several metal oxides such ZnO (starting from 60 molar % up to more than 80-90 molar %), Sb₂O₃, MnO₂, Bi₂O₃, Cr₂O₃, Co₃O₄ and many others [2]. Depending on their application domain, not all the ingredients (dopants, additives) presented below are necessary or mandatory. This paper will partially confirm this.

The varistance principle (or effect) consists in a highly non-linear (non-ohmic) relation between the resulting current (in fact the crossing current density, a material parameter) and the voltage applied (the electric field intensity, when speaking about the material). In practice, for voltages lower than the nominal one, the varistor acts as an insulator and when exposed at higher

voltages, it acts like a normal conductor material, offering a parallel leakage way for any overvoltage.

This property makes him ideal for any protective device made for voltage suppression (surge arresters).

Two of the most important additives, Cr₂O₃ and MnO₂, are introduced in the initial composition, in order to obtain different crystal structural phases during the whole elaboration process. By consequent, the amount of Cr₂O₃ and MnO₂ used during the manufacturing period has a high influence over all electrical, mechanical and thermal proprieties of that new manufactured varistor [2].

The main objective of this paper is to determine the influence of the concentration of Cr₂O₃ and MnO₂ (and of other dopants, too), over the electrical properties (non-linearity, electric field intensity and current density) of that varistor, as well as to find a new and easy to made material, suitable for low voltage (domestic) lines and consumers.

2. New Varistor Material and the Manufacturing Process

In practice, all physical proprieties of the varistor material are highly depending of the initial chemical composition. First of all, weighing all ingredients (after establishing a certain composition plan) is an important manufacturing operation, when speaking of weights having more than 0.1 mg in precision. This manufacturing operation is relatively simple, because, for this first step, all the ingredients required are delivered as powders, having, by factory specifications a very uniform and well determined granulation [5].

The team of authors has developed, during their research stages at the LAPLACE Laboratory from the PAUL SABATIER University of Toulouse, in France, a new varistor material based only on the variation of 2 additive oxides MnO₂ and Cr₂O₃, one by one.

The initial classic chemical composition [6] was, (in molar percentage and mass for 500 grams of mixture): ZnO (87.45 %, 437.25g), MnO₂ (1.843 %, 9.215g), Cr₂O₃ (1.515 %, 7.575g). Of course there were other at least 3 additives, less important from the electrical point of view.

The roles of these two main oxides are [4]:

- Cr₂O₃ is used mostly for grain growth limitation, as well as doping;
- MnO₂ is used only as a doping element.

After this initial precision weighing, all these ingredients have to be carefully mixed together by using a standard mixing ball machine. The mixing operation can last for more than 32 hours, in order to obtain a very homogeneous powder, which could be pressed in molds after.

As we mentioned before, the other three oxides will be slightly decomposed after passing through all the phases of the manufacturing process. Only traces of them could be found inside when finishing [5].

At the end, the resulting piece of semiconductor material will be carefully put to some specific mechanical tests and electrical measurements in order to determine all its main parameters. We will not insist on the manufacturing phases, but on testing these resulting varistors.

3. Experimental Measurements

For this set of comparative measurements we used some simple 20 mm diameter 3 mm height varistors, made with 3 different concentrations of 2 that additives (new material). The concentrations were 0.5, 1 and 1,5 molar percentage for each additive. When one of the dopants has a bigger concentration, the other was diminished consequently.

Because the response current of the varistor is highly influenced by temperature, measurements are performed inside a thermal insulated chamber.

The measurements performed were:

- Current density versus field intensity for each concentration of the dopants (main electric characteristic);
- Non-linearity coefficient, for each concentration of the dopants;
- Opening voltage (field intensity) for each concentration of the dopants.

All the experiments were also carried out at the LAPLACE Laboratory, from the Paul Sabatier University in Toulouse, France, by using a dedicated DC measuring facility, presented in Figure 1a and 1b. For a certain imposed voltage, provided by the programmable DC source, current could be measured with a high precision, using that microampermeter. All of te measurements are performed in DC regime, as required by regular procedures for overvoltage protections.

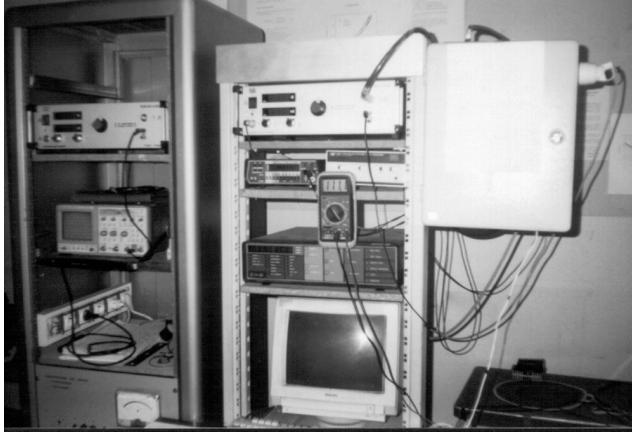


Fig. 1a. The testing facility for low voltage varistors

Temperature inside the measuring box must be kept constant, around 20 degrees Celsius.

Environmental temperature is also important, because current inside a varistor is thermal activated, so we have to maintain same conditions for all tests.

The shock wave tests were not performed because in this case they are not relevant for the material pure electric behavior.

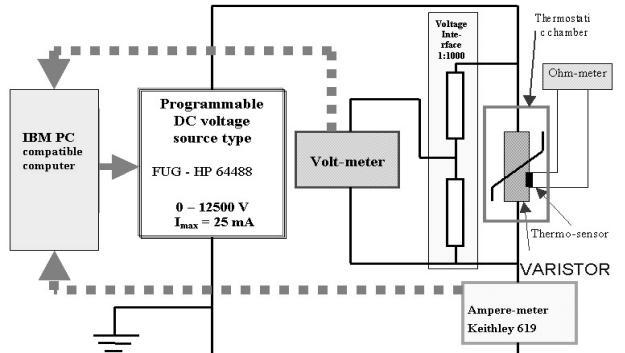


Fig. 1b. The electric shema of the testing facility for low voltage varistors

The relation between current and voltage is non-linear and the non-linearity coefficient α is given by [2]:

$$\alpha = \frac{\ln(I_2) - \ln(I_1)}{\ln(U_2) - \ln(U_1)} = \frac{\ln \frac{I_2}{I_1}}{\ln \frac{U_2}{U_1}} = \frac{d \ln(I)}{d \ln(U)} \quad . \quad (1)$$

Where I_1 , I_2 are two consecutive values of the current obtained for two consecutive voltages U_1 and U_2 .

Current density [A/mm^2] and field intensity [V/m] are two essential material parameters which are obtained by dividing the value of the crossing current with the section of that 20 mm varistor and by dividing the opening voltage by the 3 mm height of the varistor. Only the characterization of the material will be taken into account, disregarding the geometrical dimensions of the varistors (these dimensions were removed by dividing current with the cross-sectional area equal to 706.5 mm^2 and with the height of $d = 3 \text{ mm}$). The resulting values are specific for that material, not for a certain varistor that has a given geometry and is made of that material.

Figure 2 and Figure 3 show the influence of the concentration of each dopant (Cr_2O_3 and MnO_2) when assessing the electrical characteristic of the material (current density versus field intensity).

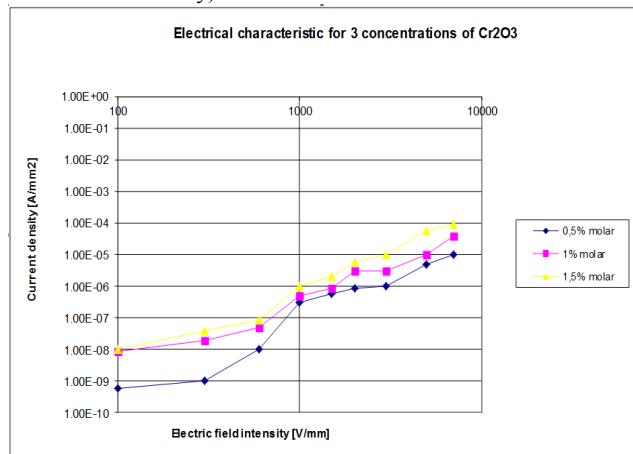


Fig. 2. Electric characteristics for 3 different Cr_2O_3 concentrations

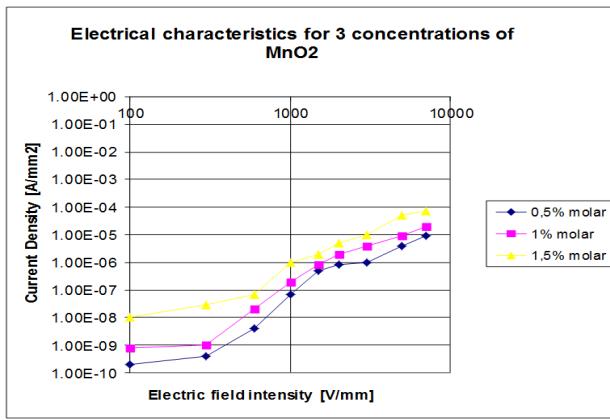


Fig. 3. Electric characteristics for 3 different MnO₂ concentrations

We notice that by modifying these concentrations, current density increases each time when one of the dopants has a concentration higher than 1.5 molar percentage. The resulting characteristics are very closed each other. It means that this small modification in concentration does not affect very much the whole assembly. Practically, for the final result, we have to modify only one concentration, because effects are mostly the same.

The electrical characteristic of these materials is not very influenced by those concentrations. It maintains almost the same shape and numeric range for each set of tests. All dopants are acting almost the same no matter their type and concentrations. The results are similar from the electric point of view, when talking about the integrator of such a varistor made from this material.

A complete evaluation of the material could be realized only by measuring the non-linearity coefficient as well as the opening field intensity, in order to provide a new technical solution.

Figure 4 and Figure 5 will present the values of the non-linearity coefficient function of the same concentrations of the dopants.

All measurements were taken around the value of 350 V for the applied voltage, corresponding mostly with the opening voltage of that varistor. The principle of this experiment is very simple. It means that for a certain imposed voltage, provided by the programmable DC source, current could be measured with a high precision, using a microampermeter.

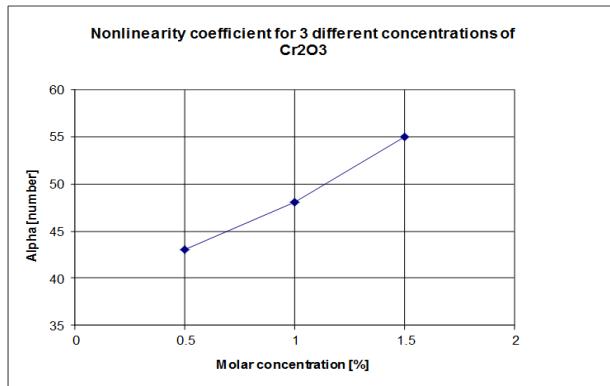


Fig. 4. Non-linearity coefficient for 3 different Cr₂O₃ concentrations

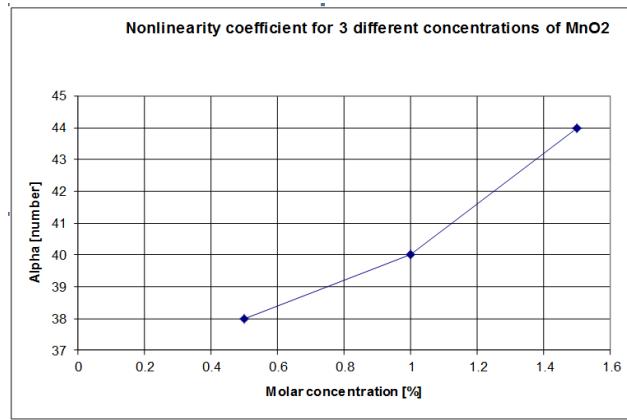


Fig. 5. Non-linearity coefficient for 3 different MnO₂ concentrations

On these graphs we can observe that the non-linearity coefficient has a peak value around 55 for Cr₂O₃ and around 44 for MnO₂, increasing with the molar concentration. It means that by increasing the concentration of Cr₂O₃ we can obtain significant changes.

Figure 6 and Figure 7 will present the values of electric field opening intensity as function of the same concentrations of the dopants.

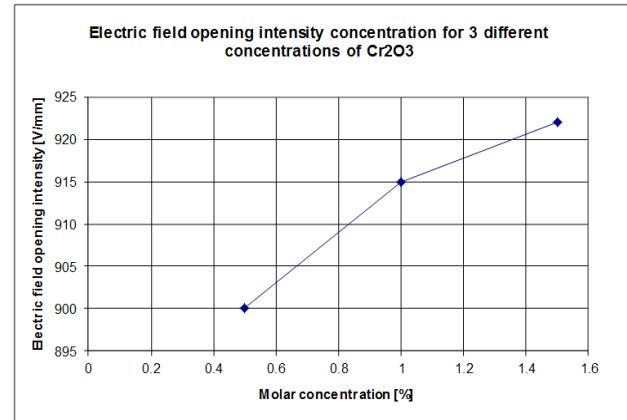


Fig. 6. Opening electric field intensity for 3 different Cr₂O₃ concentrations

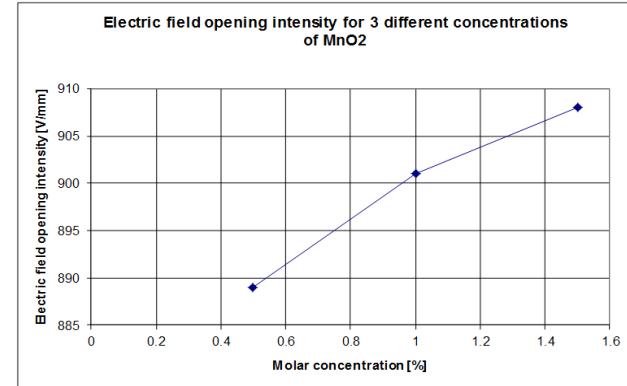


Fig. 7. Opening electric field intensity for 3 different MnO₂ concentrations

If, in the situation of the electrical characteristics both dopants are acting almost in the same mode, here we can say that Cr_2O_3 must have a higher concentration, corresponding to the previous situation too.

By analyzing all 3 concentrations, we easily notice that values are almost the same for the two dopants, increasing with the concentration of each one. We can admit that Cr_2O_3 is the most interesting dopant, taking in consideration the results discussed before. Any new receipt for manufacturing of high quality varistors must take in consideration this important dopant and its concentration.

4. Conclusions

This is an experimental procedure which could be used for the assessment of varistor materials, in order to obtain better compositions and manufacturing parameters.

The materials involved are new ones, not tested before.

In all cases materials are performing almost similar, exception in the situation of the non-linearity coefficient, where Cr_2O_3 acts a little bit better, obtaining a higher value. The main conclusion of this paper is that we can increase its molar concentration up to a level of 1.5%, positively influencing the other material parameters too.

This is an important conclusion which could be taken in consideration by manufacturers, in order to verify the influence of all dopants.

Future studies could be completed with the influence of the other dopants on the electrical behavior.

5. References

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