Investigación *Revista Mexicana de Física* **40**, *No. 5 (1994) 771–781*

Sintering temperature effects on the performance of ZnO ceramic varistors

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Recibido el 18 de marzo de 1994; aceptado el 16 de junio de 1994

ABSTRACT. Varistor properties of ZnO ceramics with metal oxides were analyzed in relation to sintering and operation temperatures, Sb_2O_3 additive content and grain size.

RESUMEN. El efecto varistor en cerámicas de ZnO con óxidos metálicos se analizó en función de la temperatura de sinterizado y operación, contenido de Sb_2O_3 y tamaño de grano.

PACS: 85.20.E; 81.20.L; 81.60.D

1. INTRODUCTION

Since 1968 non-ohmic zinc oxide (ZnO) ceramics have been widely used as varistor for voltage stabilization or transient surge suppression in electronic circuits and electric power systems [1–4]. The fundamental research of ZnO varistors is usually divided into non-ohmic conduction mechanism and fabrication technology. The studies on the non-ohmic properties are based on the energy band diagram and the conduction process of carriers at grain boundaries of the ceramics [5-7]. Progress in fabrication technology is basically due to novel materials and new ceramic engineering processes [8].

ZnO varistors were used, at first, for the purpose of protection of semiconductor devices against transient surge in TV sets, microwave ovens and other consumer electronic equipment. At the present time, ZnO varistors are one of the most useful devices in automotive, airplane, electric transmission lines and gapless-type Lightning arresters [9].

In this paper, a study is presented in relation with the performance of ZnO ceramic varistors as a function of sintering and operating temperature, Sb_2O_3 additive content and grain size. The aim of this work consists in determine experimentally the optimal conditions in the elaboration process of ZnO ceramic varistors with high performance value for the development of surge protection devices.

2. EXPERIMENTAL

2.1. Sample preparation

A mixture of ZnO (95–70 mol %) with Bi_2O_3 (1.5 mol %), MnO (1.0 mol %), $Co(NO_3)_2$ (0.5 mol %), Cr_2O_3 (1.0 mol %), NiO (0.5 mol %) and Sb_2O_3 (0.5–25.5 mol %) in a

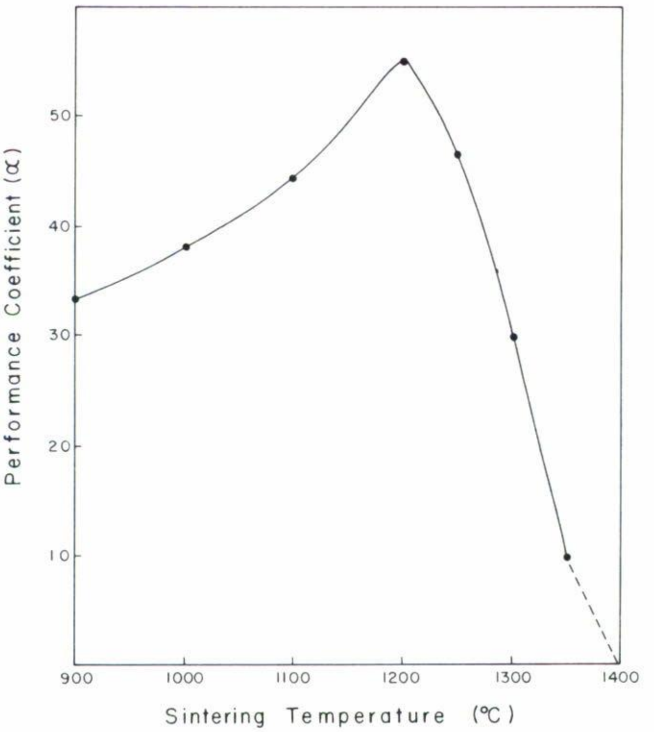

FIGURE 1. Effect of sintering temperature on varistor performance.

chemical reagent grade 99.5% purity was treated with acetone and ultrasonically soaked by 30 min, to homogeneizar the mixture, then dried, pressed into disks 10.0 mm, in diameter and 1.1 to 2.2 mm, in thickness at a pressure of 10 ton/cm^2 and calcined at 750 °C/24 hrs. One set of samples were sintered from 900 to 1400 °C, for 2 hrs, in air and furnace cooled to room temperature, to determine the optimal sintering temperature. At this temperature, other set of samples with different antimony content were sintered. The sintered bodies were lapped with a silicon carbide abrasive of 600 mesh and provided with ohmic electrodes of evaporated silver on both surfaces.

2.2. Analysis of microstructure, additive content and I-V characteristics

The microscopic analysis was carried out by scanning electron microscopy (SEM: JEOL 1200 Ex) and X-ray energy dispersion spectroscopy (EDS.asid-10). The voltage-current characteristics were measured by D.C., and AC., power supply using an electrometer (Keithley 616) and a Philips PM 3055 oscilloscope. The sample temperature was adjusted by a vertical furnace operated in air.

2.3. Definition of non-linear resistance and voltage non-linear exponent

The voltage-current characteristics of ZnO ceramic varistors are expressed by the empirical

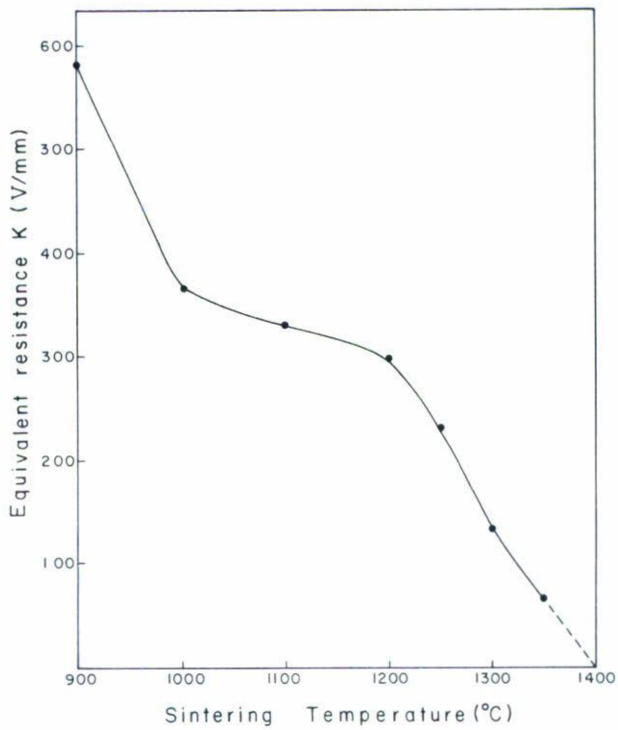

FIGURE 2. Effect of sintering temperature on equivalent ohmic resistance.

equation

$$I = kV^{\alpha}, \tag{1}$$

where k is the constant corresponding to the equivalent resistante of ohmic resistor (V/mm) and α is the exponent defined as the performance of varistor action, which is calculated by the following equation [10]:

$$\alpha = \frac{dI/I}{dV/V} = \frac{d(\log I)}{d(\log V)}. \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. Effect of sintering temperature

Figures 1 and 2 show the effects of sintering temperature on non-ohmic properties of ZnO ceramics. The performance value (α) increase as the sintering temperature rises up to 1200 °C and shows the highest α–value of 55. When sintered above 1200 °C, the α–value decreases steeply with the increasing temperature. At 1400 °C, the ZnO ceramics not have varistor action and are semiconductor disks of low electrical resistivity of about

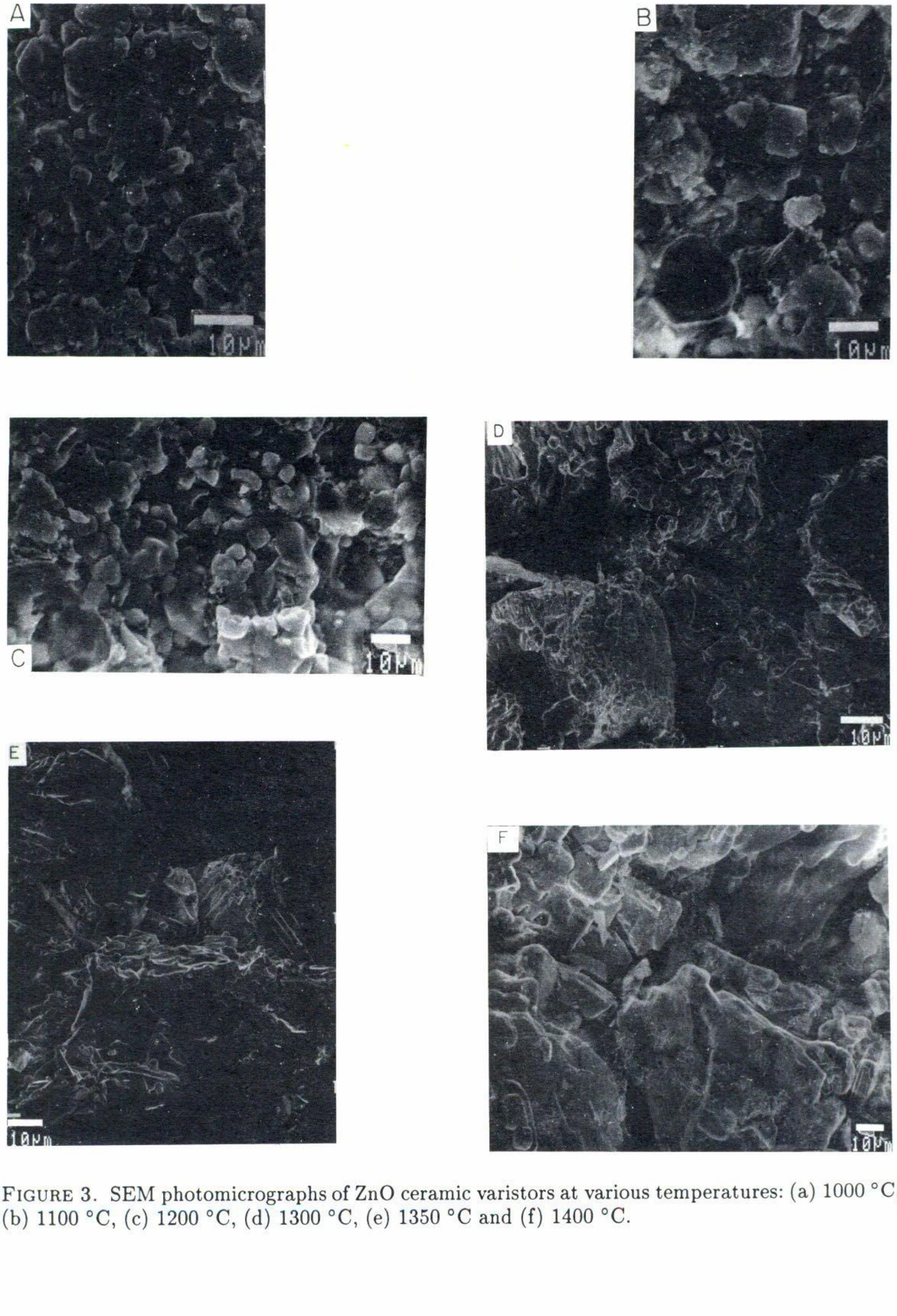

FIGURE 3. SEM photomicrographs of ZnO ceramic varistors at various temperatures: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1350 °C and (f) 1400 °C.

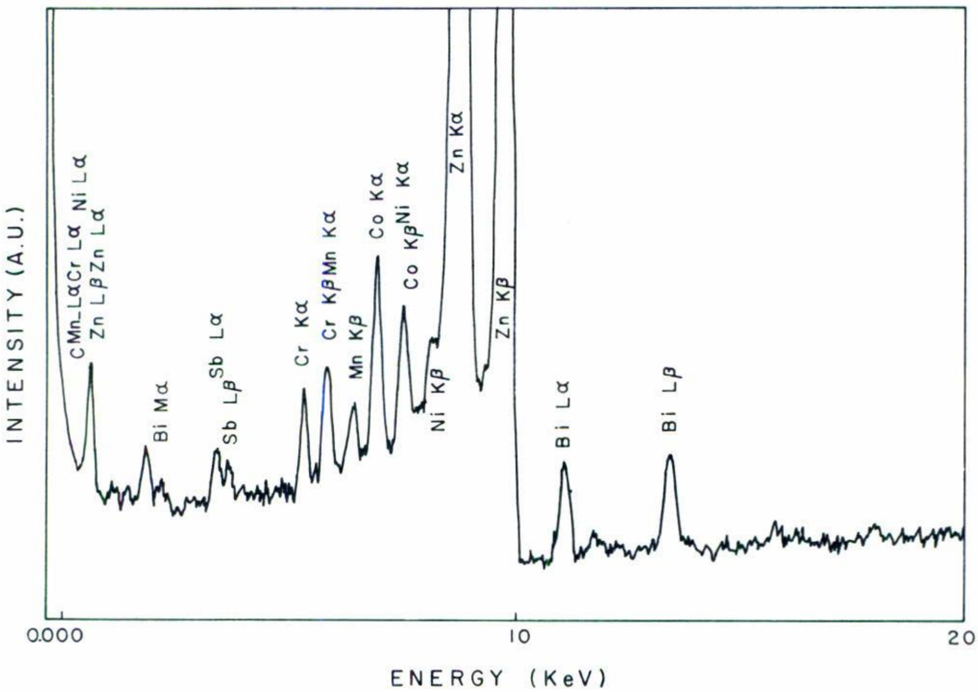

FIGURE 4. EDS X-ray microanalyzer pattern of ZnO ceramic varistor sintered at 1200 °C.

15 ohm-cm. The non-linear resistance (Fig. 2) decrease with an increase in the sintering temperature and becomes ohmic at 1400 °C. Figure 3 shows the SEM photomicrographs of ZnO ceramics sintered at 1000, 1100, 1200, 1300, 1350 and 1400 °C, respectively. It is seen that the grain size increase with an increase in the sintering temperature.

The ZnO ceramics sintered at 1000 °C and 1100 °C show random small average grain size of about 7–10 μm. At 1200 °C, the average grain size is about 16 μm, with a more regular distribution between small and large grains. Above 1200 °C, grain become large ($\sim$ 30–50 μm) with larger porosity, cracked and relatively disordered.

As can be seen, the results indicate that grain size is an important factor that can be adjusted by means of the sintering temperature. A regular distribution of grain size of about 10–20 μm, seems to be optimum respect to varistor action in the samples, because anomalous grain growth at high temperature (1300–1400 °C) induce stress, disorder, porosity and cracking into the grains, which induce the failure in varistor action. A detailed microstructure and anomalous grain growth studies will be reported elsewhere.

Figure 4 is a typical X-ray microanalyzer pattern of ZnO ceramics sintered at 1200 °C. It indicate the differents metallic oxides present in the samples and from the EDS software is obtained their average concentration in percentage value. From 900 to 1200 °C, the EDS average concentration is practically the same that the initial chemical nominal content. At higher temperatures, the Bi_2O_3 and Sb_2O_3 concentrations are less than the

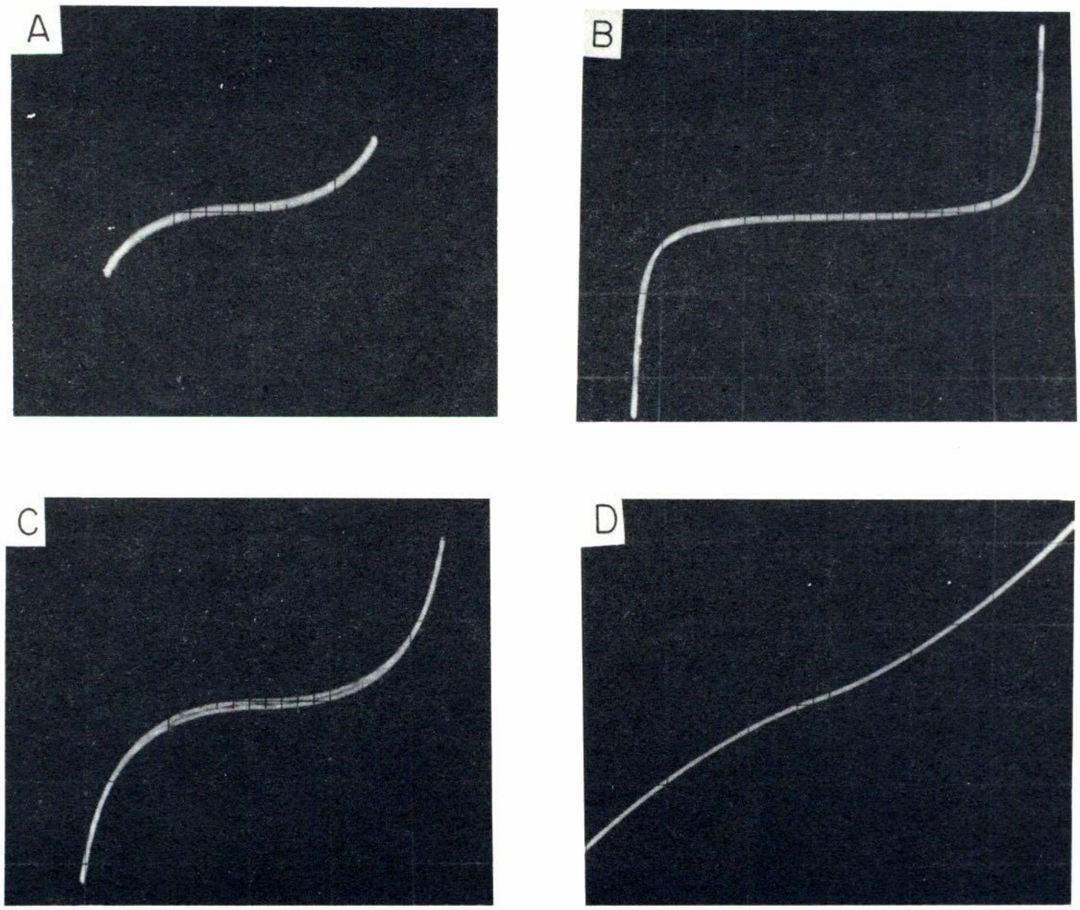

FIGURE 5. AC voltage-current characteristics of ZnO ceramic varistors. (a) 3 mole %, (b) 7 mole %, (c) 15 mole %, and (d) 25.5 mole % of Sb_2O_3 e.h. = 100 volts/square: e.v. = 20 mA/square.

nominal content due to evaporation processes at that temperatures. When ZnO ceramics are sintered at 1350 and 1400 °C, the EDS pattern indicate no existence of Bi_2O_3 and Sb_2O_3 due to complete evaporation.

3.2. Effect of Sb_2O_3 concentration

A set of samples with Sb_2O_3 content of 0.5 to 25.5 mol % were sintered at same time at a temperature in which the highest α–value was obtained (T_s = 1200 °C) with all the others metallic oxides in constant concentration. In Fig. 5 are shown the AC, voltage-current characteristics for the different samples with 3, 7, 15 and 25.5 mol % of Sb_2O_3. It is clear that the performance value change drastically from sample A to sample D, reflecting the Sb_2O_3 content effect onto its non-linear characteristics. At low voltage the grain boundaries that surrounds a more conducting grains, act as an insulating barrier

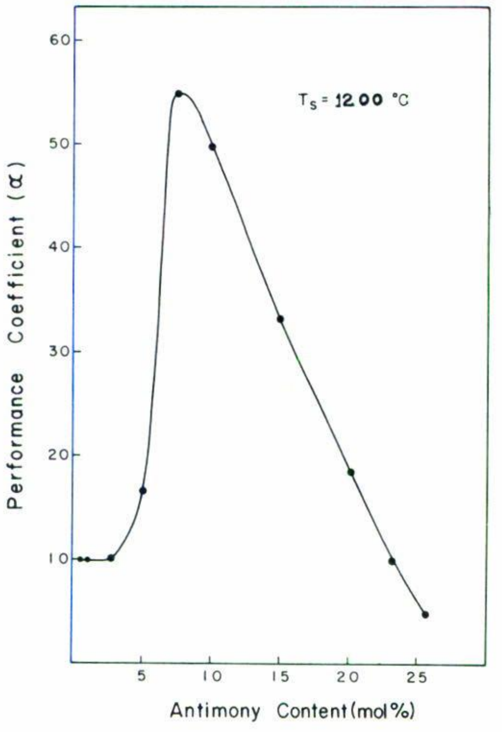

FIGURE 6. Effect of Sb_2O_3 content on the performance of ZnO ceramic varistors sintered at 1200 °C.

to give an equivalent circuit showing high ohmic resistance [9–10]. At higher voltage there is a breakdown effect such that the current increases very rapidly and the barrier resistance is decreased, which leads to a high degree of non linearity, *i.e.*, a large increase in current occurs with a small change in voltage. In order to compare these characteristics, it is calculated the α performance value in each sample and plotted in function of the porcentage of antimony oxide (see Fig. 6). The values obtained indicated that: at low concentration of Sb_2O_3 (≤ 3 mol %), the varistor performance has a low α–value of around 10. Addition of more Sb_2O_3 improves the voltage-current characteristics (see Fig. 5b) due to a further increase in α–value to about 55, that is an ideal value as compared with comercial varistor (α–value in the range 25–50) [11]. Additional content of Sb_2O_3 decreases steeply the α–value, showing that a large increase of Sb_2O_3 results in injuring the performance of the varistor, because the Sb_2O_3 excess became a segregate spinel phase that is a good ionic conductor, which degrade the insulating character of the intergranular layer that is responsible of voltage surge withstand capability of the varistor sample [12–15]. In consecuence, there is an optimum range of Sb_2O_3 concentration of around 6 to 12 mole percent, in which the performance has values adequated to in-line industrial production at a sintering temperature of 1200 °C. The effective operating voltage of the diferent varistors in AC conditions, are in the range 137 to 220 volts, respectively.

TABLE I. Measured properties of ZnO varistors respect to grain size and antimonium content.

Sintering Temperature (°C ± 5)	Grain size (μm)	Performance Coefficient ($\alpha \pm 2$)	Equivalent Resistance (V/mm ± 5)
900		33	584
1000	$\simeq 7 \pm 4$	38	367
1100	$\simeq 10 \pm 5$	44	334
1200	$\simeq 16 \pm 5$	55	300
1250		47	234
1300	$\simeq 30 \pm 12$	30	134
1350	$\simeq 45 \pm 25$	10	67
1400	$\simeq 50 \pm 30$	No varistor effect	

SINTERING TEMPERATURE 1200 °C

Antimonium content (mole %)	$\alpha \pm 2$	V operation (±5 volts)
0.5	10	20
1.0	10	20
3.0	10	65
5.0	17	187
7.0	55	220
10.0	48	195
15.0	34	140
20.0	18	80
23.0	10	20
25.5	5	10

These values are in the range of applicability for electrical comercial lines, so that, the varistors are suitable for surge protection in any comercial electronic system like TV set, PC devices, refrigerators, voltage regulators, etc. The measured properties in function of grain size and antimonium content are given in Table I.

3.3. Temperature effects on ZnO performance

Figure 7 shows the direct current V–I characteristics in a logarithmic plot at various temperatures. Note that the V–I curve presents an ohmic region at low-voltages and a non-ohmic region having high α–value. It is seen that the non-ohmic region becames narrow in the current range as the temperature rises up. The α–value decreases with an increase in the operation temperature as shown in Fig. 8.

The electrical resistance of ohmic region at low voltage decrease with an increase in temperature and the breakdown voltage (operation voltage) becames reduced at the higher current. This last feature make the ZnO varistors an ideal device because it serves an extra purpose in limiting the voltage at higher operating temperatures, that is, there is

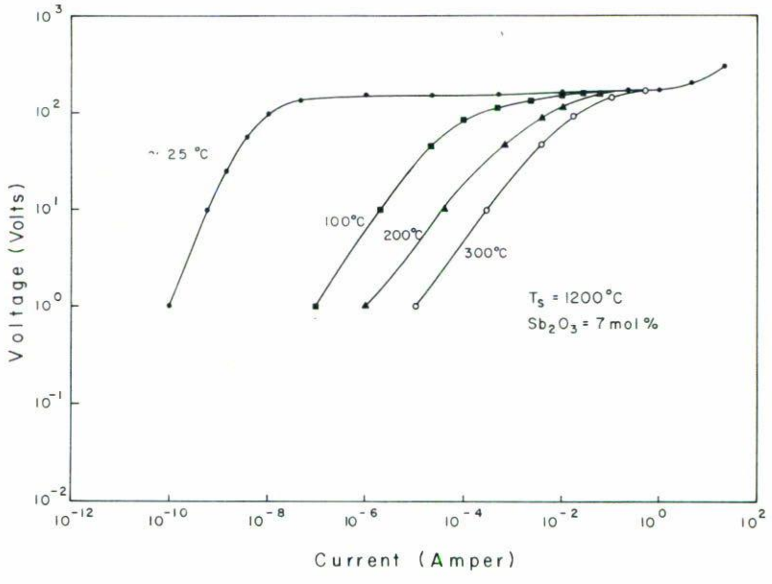

FIGURE 7. Temperature dependence of voltage-current, DC characteristics of ZnO ceramic varistor sintered at 1200 °C, with 7 mole % of Sb_2O_3.

less tendency for thermal runaway under high temperature conditions in real operation under a severe surge in any varistor protected electronic devices.

4. CONCLUSIONS

The ZnO ceramics show a maximum in performance ($\alpha \sim 55$) when sintered at 1200 °C and no varistor action are observed when the ceramics are sintered at 1400 °C. SEM photomicrographs and EDS microanalyzer patterns indicate that the grain size increase with the rise up of sintering temperature and at high temperature ($\geq$ 1300 °C) anomalus large grain size injure the varistor effect. This is probably due to the lost of Sb_2O_3 and Bi_2O_3 by evaporation processes at higher temperatures. Then, controlling grain size of the semiconductive ceramics is an important factor. Upon increase of the grain size, the breakdown voltage decreases and the varistor action becomes worse. The optimum grain size seems to be about 10–20 μm.

The AC voltage-current curves and the α-performance are very dependent on the Sb_2O_3 content at sintering temperature of 1200 °C. This additive is characterized by liquid-phase sintering, which results in the formation of an intergranular layer that improved the non-ohmic properties [10-15]. There is an optimun range of Sb_2O_3 concentration of about 6 to 12 percent in which the α-value has values adequated to industrial production.

An increase in the operating temperature device causes a decrease in the α-values as well as in the ohmic resistance at low voltage and in the breakdown voltage, which is an over protection in real surge varistor operation.

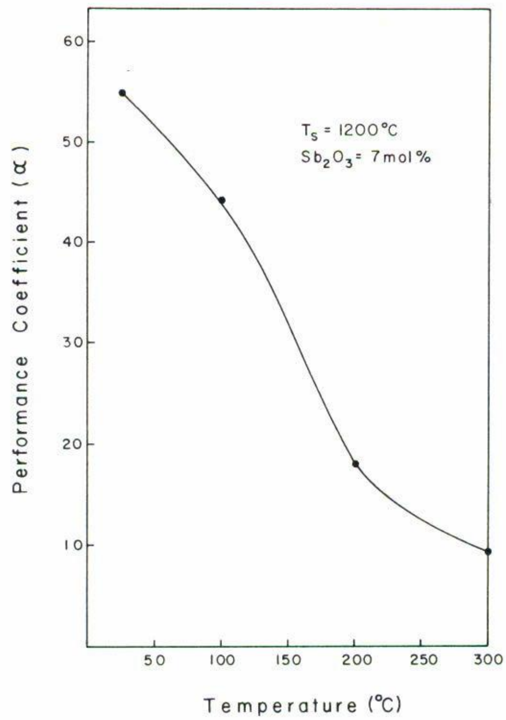

FIGURE 8. Temperature dependence of α performance of ZnO ceramic varistors sintered at 1200 °C with 7 mole % of Sb_2O_3.

In summary, the best quality in varistor behavior was experimentally found at the following conditions: sintering temperature of 1200 °C with Sb_2O_3 content of 7 mol %. Under these optimum determined conditions, it is possible to scale up to in-line industrial production with varistor parameters values in the range of comercial and home electrical lines to surge protection of TV sets, PC devices, voltage regulators, etc.

5. ACKNOWLEDGMENTS

The autor is indebted to Raúl Reyes Ortíz, Eduardo A. Caballero R., José Guzmán Mendoza, Hermilo Zarco and Marco Antonio Leyva R., for their valuable technical assistance.

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