

# NANOSTRUCTURED VARISTOR CERAMICS FOR HIGH VOLTAGE SURGE ARRESTERS<sup>1</sup>

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## Abstract

As the demand for electricity increases, also increases the need to use high and ultra-high voltage surge arresters in the protection of transmission and distribution power lines to prevent failures that can cause damages of the order of billions dollars. In this sense, the technology of surge arresters has sought to use varistors showing high electrothermal performance and thus the way has been found in the search for nanostructured varistor ceramics to reduce the grain size (and thus make possible the increase of the switching voltage), increase the microstructural homogeneity and to maximize the non-ohmic electrical behavior. In accord with these considerations, in the present work, nano-size ceramic powders were used in order to produce varistor ceramics with great electrical protective performance and better electrothermal stability than conventional varistors. Among other conclusions, it was verified that the zinc oxide-based varistor ceramics doped with rare-earth oxides showed less tendency to increase of the leakage current than the conventional varistors and exhibited good electrothermal behavior.

**Key words:** Varistor ceramics; Electroceramics; Nanostructured materials.

## CERÂMICAS VARISTORAS NANOESTRUTURADAS UTILIZADAS EM PÁRA-RAIOS DE ALTA TENSÃO

### Resumo

Com o aumento da demanda por energia também aumenta a necessidade de se utilizar pára-raios de alta e ultra-alta tensão na proteção de linhas de transmissão e de distribuição de energia para evitar falhas que podem causar enormes danos. Neste sentido, a tecnologia de pára-raios tem procurado usar varistores com elevado desempenho eletrotérmico, pesquisando-se varistores nanoestruturados para reduzir o tamanho de grão (e assim tornar possível o aumento da tensão de chaveamento), aumentar a homogeneidade microestrutural e maximizar o comportamento elétrico não-ôhmico. De acordo com estas considerações, no presente trabalho, nano-pós cerâmicos foram utilizados para a produção de varistores cerâmicos com grande desempenho de proteção e maior estabilidade eletrotérmica do que os varistores convencionais. Entre outras conclusões, verificou-se que varistores à base de óxido de zinco dopados com óxidos de terras raras apresentaram menor tendência de aumento da corrente de fuga do que os varistores convencionais e exibiram bom comportamento eletrotérmico.

**Palavras-chave:** Cerâmicas varistoras; Eletrocerâmicas; Materiais nanoestruturados.

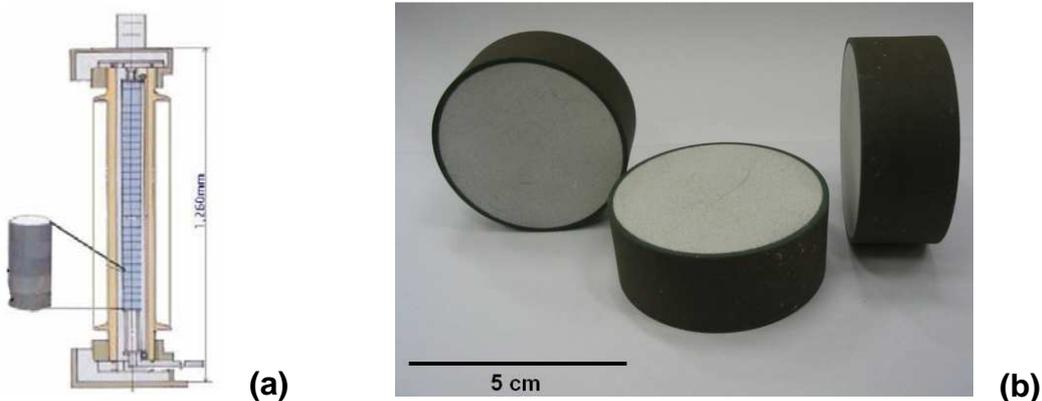
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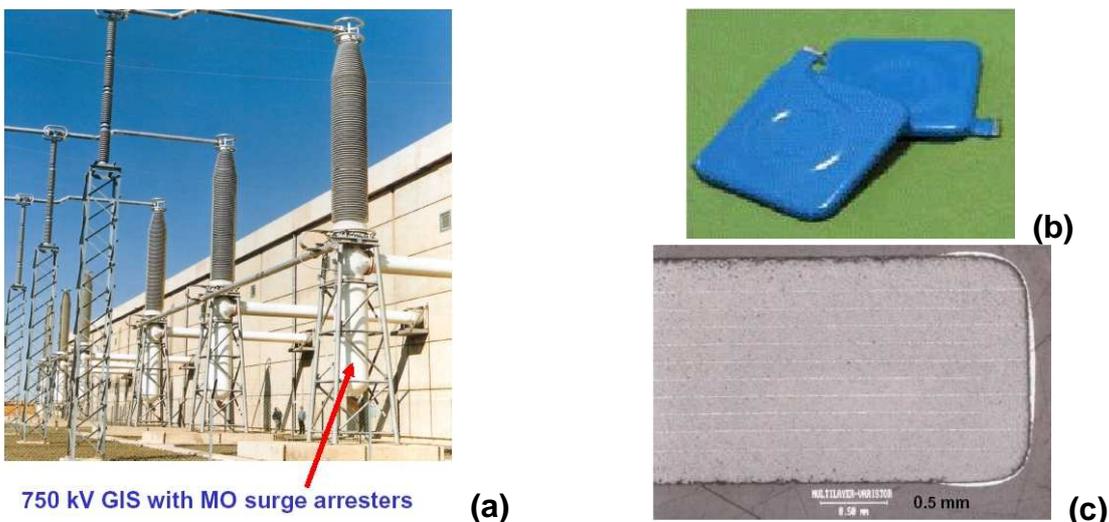
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# 1 INTRODUCTION

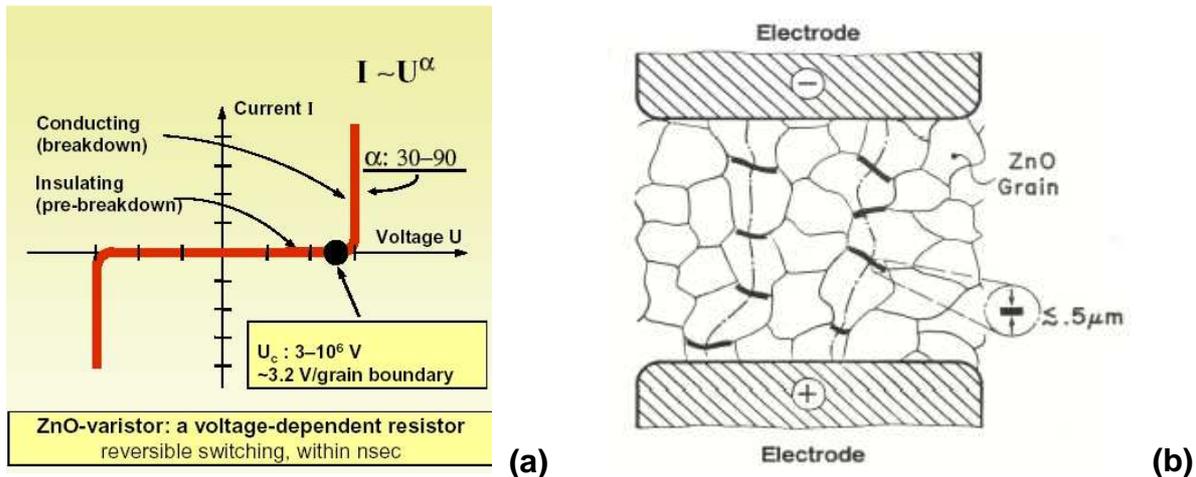
Varistor ceramics are the more common voltage transient suppressors and zinc oxide (ZnO)-based varistor ceramics have been the more used overvoltage protect device since that they were proposed by Matsuoka *et al.*<sup>(1)</sup> in 1969. In high voltage applications, the varistors are ceramic blocks used in surge arresters as shown in Figure 1. However, varistors are extremely versatile and they are used in an ample range of applications, as suggested in the Figure 2. The ZnO varistor exhibits highly non-linear current (I)-voltage (U) characteristics, as shown in Figure 3, owing to electrostatic barriers located at the ZnO grain boundaries. Electrical characteristics such as surge current and transient energy withstanding (energy absorption capability), leakage current, are correlated with distribution of these barriers in the volume of the ceramic and the homogeneity of grain size. The better the homogeneity of barrier distribution, the better the performances of the ZnO varistors. The ideal case corresponds to the localization of a potential barrier for each grain boundary.<sup>(2 3)</sup> For achieving this purpose, the much smaller scale of the preparatory powders, and the more narrow of the three-dimensional distribution are absolutely essential requirements.



**Figure 1.** (a) Cross-section of a 72 kV Toshiba ZnO gapless surge arrester showing the varistor ceramic blocks; (b) varistor ceramic blocks for high voltage applications.



**Figure 2.** The extremes of application of varistor ceramics: (a) 750 kV surge arresters; (b) multilayer varistor (MLV) ceramic devices for electronic applications; (c) structure of a MLV ceramic component showing some active layers.



**Figure 3.** (a) Electrical current (I) versus voltage (U) curve characteristic of a varistor ceramic; (b) schematic microstructure characteristic of a ZnO-based varistor ceramic.

The I-U characteristics of a varistor are altered after some time under electrical bias. This behavior is known as degradation phenomena and manifests itself mainly by alterations in the pre-breakdown and onset of the breakdown regions of the I-U varistor curve.<sup>(4,5)</sup> As a result, the varistors have a tendency of increasing in leakage current, in the pre-breakdown regime, with increasing time and temperature. Thus, the load life of ZnO varistors is restricted by the electrothermal runaway because of the increase of the leakage current under electric load.

Therefore, the reduction of the leakage current is an important problem of the varistor technology<sup>(6,7)</sup> and can be reached by the adequate control of the microstructural parameters, such as grain boundary chemical composition, grain size distribution, densification level, and phase structure.<sup>(8,9)</sup> Thus, in order to enhance the varistor performance and reliability, through to improve homogeneity of the barrier distribution it is believed that, on an atomic scale, powder preparation by chemical methods or high grain size reducing will provide a better homogeneity of additives at the ZnO-ZnO grain boundary and a better grain growth control, as well as the physical-chemical homogeneity and a well defined and uniform grain size.<sup>(9)</sup>

ZnO-based varistor ceramics are divided generally into two categories, called  $\text{Bi}_2\text{O}_3$ -based and  $\text{Pr}_6\text{O}_{11}$ -based varistors, in terms of varistor-forming oxides inducing the nonlinear properties of varistors.<sup>(3)</sup> Most of the commercial ZnO varistors are  $\text{Bi}_2\text{O}_3$ -based varistors, which have been mainly studied in various aspects since ZnO varistors were discovered by Matsuoka *et al.*<sup>(1)</sup> However,  $\text{Bi}_2\text{O}_3$ -based ZnO varistors are not suitable to be used in multilayer chip varistors manufacture, due to  $\text{Bi}_2\text{O}_3$  having a high volatility and reactivity.<sup>(10)</sup> Furthermore, in general,  $\text{Bi}_2\text{O}_3$ -based ZnO varistors possess four phases, namely ZnO grains, Bi-rich intergranular layers, an additional insulating spinel phase, which does not play any role in electrical conduction, and pyrochlore phase. On the other hand, in  $\text{Pr}_6\text{O}_{11}$ -based ZnO varistors only two phases are present in a sintered body, namely, ZnO grains and the intergranular phase composed mainly of praseodymium oxide.<sup>(2,8)</sup> The absence of a spinel phase increases the active grain boundary through which the electrical current flows. Therefore, the effective cross-section area of the element is increased.<sup>(3)</sup> Earlier studies about  $\text{Pr}_6\text{O}_{11}$ -based varistors have been limited to the ternary system ZnO- $\text{Pr}_6\text{O}_{11}$ -CoO and dissimilarities between  $\text{Bi}_2\text{O}_3$ -based and  $\text{Pr}_6\text{O}_{11}$ -based ZnO varistors.<sup>(8-11)</sup> Recently, many works have been made in order to study the influence of other rare-earth oxides (such as  $\text{Y}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ , and  $\text{Dy}_2\text{O}_3$ ) on the



microstructural and electrical properties of the ternary system ZnO-Pr<sub>6</sub>O<sub>11</sub>-CoO.<sup>(2,9)</sup> The varistors produced have exhibited a relatively good electrical performance.

In the present work it was reported considerations and some early results about the application of nanostructured ceramics in order to produce varistor with great electrical protective performance and better electrothermal stability than conventional varistors, within a research line of the CEPEL (Electric Power Research Center, Brazil).

## 2 EXPERIMENTAL

In the present work an evaluation of the microstructural characteristics of the ZnO-based varistor ceramics, whose chemical compositions are shown in Table 1, was made and applied to the understanding of the varistor performance. Appropriate weights of analytical reagent grade powders were used to prepare the ZnO based ceramics. The sample compositions are shown in Table I above. The powders with adequate compositions were ball milled with zirconia balls in isopropyl alcohol media inside of a zirconia jar for 24 h. The resultant mixture was dried at 110°C for 12 h and calcined in air at 750°C for 2 h. The calcined mixture was granulated in a 200 mesh sieve and pressed into discs of 12.4 mm in diameter and 2.1 mm in thickness at a pressure of 80 MPa. The discs were sintered at 1.200–1.350°C in air atmosphere for 1 h. The heating and cooling rates were 5°C/min. The average size of the final samples was 10.2 mm in diameter and 1.1 mm in thickness. The sintered bodies were sanded and polished, silver paste was coated on both faces of the samples and the silver electrode was formed by heating at 600°C for 10 min. The area of the electrodes was approximately 0.212 cm<sup>2</sup>.

**Table 1** - Chemical composition of the varistor ceramic investigated systems

Designation	Chemical composition (mol%)
ZB	96.5·ZnO-0.5·Bi <sub>2</sub> O <sub>3</sub> -1.0·Sb <sub>2</sub> O <sub>3</sub> -1.0·CoO-0.5·MnO-0.5·Cr <sub>2</sub> O <sub>3</sub>
ZP	97.3·ZnO-0.5·Pr <sub>6</sub> O <sub>11</sub> -1.0·Co <sub>3</sub> O <sub>4</sub> -1.0·Nd <sub>2</sub> O <sub>3</sub> -0.2·Cr <sub>2</sub> O <sub>3</sub>

The electrothermal behavior is associated to energy absorption capability (EAC) which were inferred from the dielectric characterization of the varistor ceramic blocks compared to a thermal model considered using a curve tracer source-measurement unit (Tektronix 577). For these measurements, in all the results that follow the EAC average values were obtained from four samples of each system under study.

The sample microstructures were examined by scanning electron microscopy (SEM, ZEISS DSM 960) applied on the polished and 6M-NaOH aqueous solution-etched (5 min) surface of samples, as well as on the fractured surface of the samples, and by transmission electron microscopy (TEM, JEOL 2000 FX). The grain sizes were determined by linear semi-automatic intercept method.<sup>(12,13)</sup> The compositional analysis of the selected areas was determined by an attached X-ray energy dispersive spectroscopy (EDS, Oxford ISIS) system. The crystalline phases were identified by powder X-ray diffraction (XRD, Diano XRD-8545, λCuKα radiation). The density of the varistor ceramics was measured by the Archimedes method and by image analysis techniques.<sup>(14)</sup> The procedures for Image analysis were implemented in Image-Pro Plus 6.0 (Media Cybernetics, 2006) software.

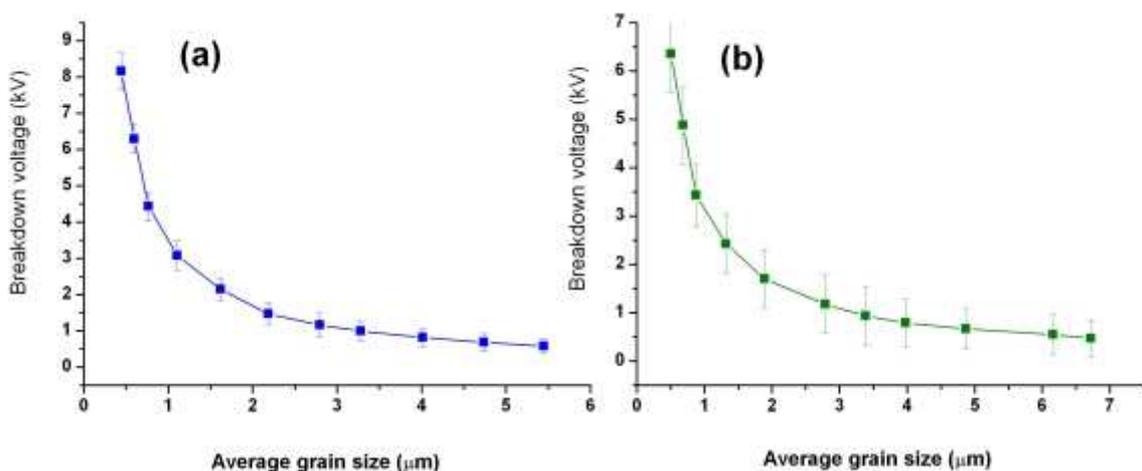
The evolution of the resistive component of the leakage current ( $I_{LR}$ ) with respect to time (at constant temperature of  $100^{\circ}\text{C}$ ) was estimated from the equation:

$$\Delta I_{LR} = I_{LR}(t) - I_{LR}(0) = K_R t^n \quad (1)$$

Where  $\Delta I_{LR}$  is the time-dependent increase in  $I_{LR}$ ,  $K_R$  is an effective rate constant,  $I_{LR}(0)$  is  $I_{LR}$  at time zero, and  $n$  a time exponent that gives a measure of the degree of stability of the device (for the most commercial varistors  $n$  is equal to 0.5).

### 3 RESULTS AND DISCUSSION

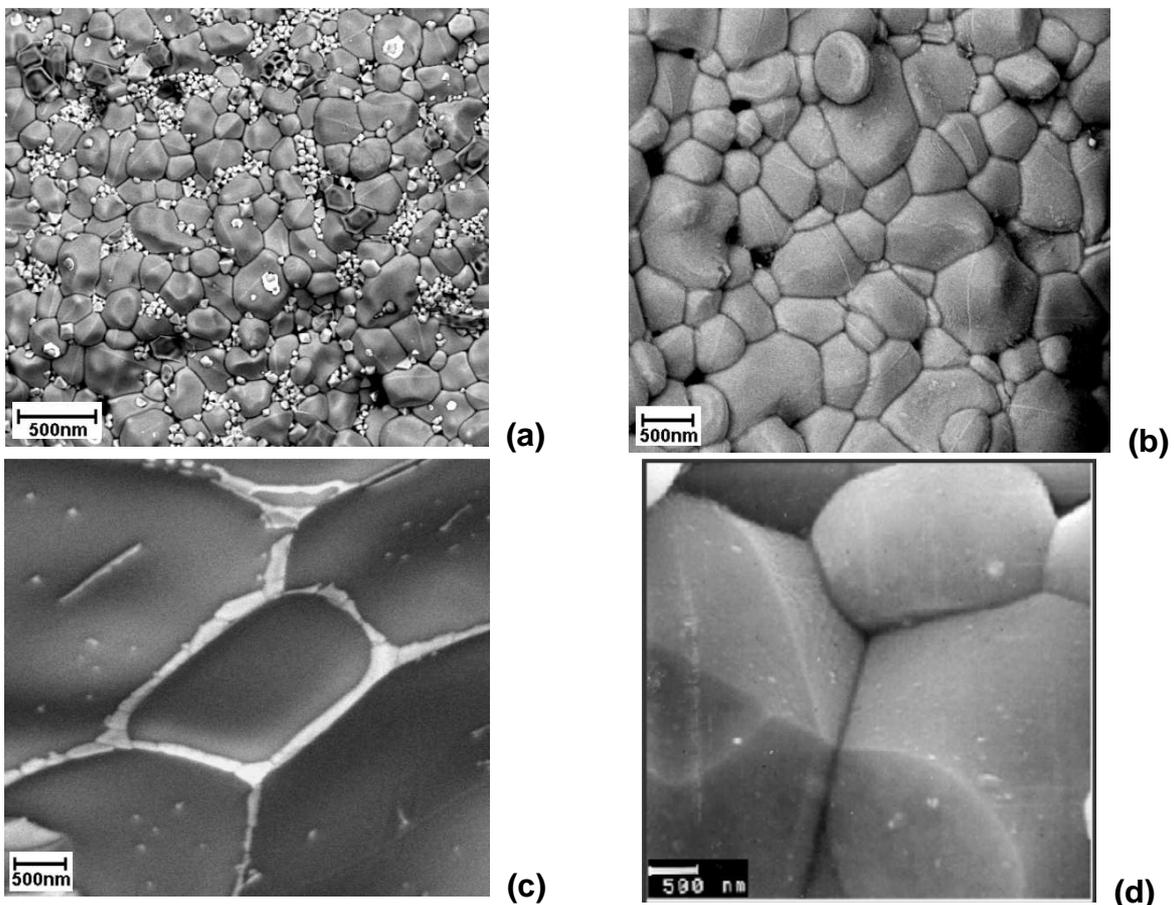
The reduction of grain size is essential for the use of varistors in the high-voltage surge arresters, so that it can achieve high values of breakdown (switching) voltage. Thus, the fabrication of nanostructured ceramics is a major technological trend of production of varistors. In fact, as shown in Figure 4, the relation between the breakdown voltage and the average grain size for a specific ZnO-based varistor ceramic formulations studied in this work. As well as in any varistor ceramics, the global breakdown voltage increases with the decrease of average grain size.<sup>(2,6)</sup> The smaller the average grain size is in ZnO varistor with the same dimension (0.5 cm thickness), the higher the maximum number of grain boundaries between upper and bottom electrodes, and improve the breakdown voltage of these ZnO-based varistors. For average grain size values below  $1 \mu\text{m}$  it was obtained high breakdown voltage for both systems evaluated, which still can be increased by means compositional optimizing (doping) being able to result in adequate varistors for high voltage applications. Additionally it was noted that the maximum breakdown voltage value achieved by the ZP system is about 30% higher than that characteristic of the ZB system, both of which have almost the same average grain size, indicating that the breakdown voltage is not influenced only the grain size, but also by compositional (doping) aspects and other microstructural characteristics.



**Figure 4.** The relationship between the average grain size and the breakdown voltage of the ZnO-based varistor ceramic formulations studied: (a) ZP; (b) ZB.

Indeed, corroborating these observations, the Figure 5 shows microstructural characteristics obtained by scanning electronic microscopy of some varistor ceramic

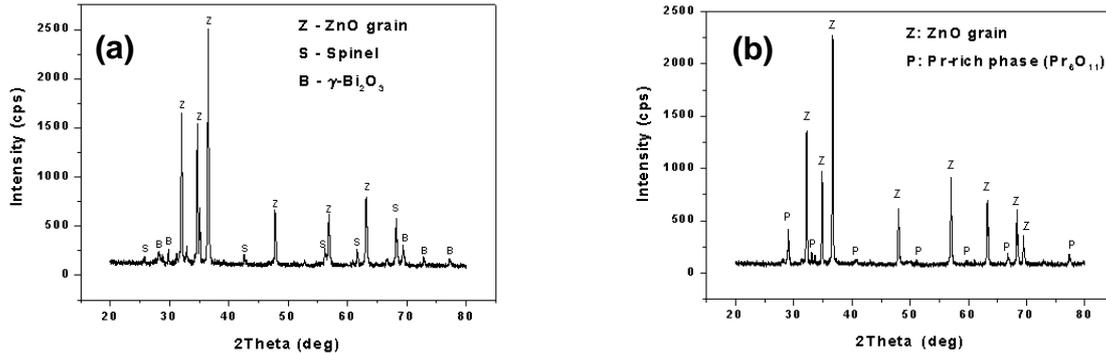
systems studied. The characteristic microstructure of a traditional ZnO-Bi<sub>2</sub>O<sub>3</sub>-based varistor ceramic formulation (ZB), obtained by intensive attrition milling, is shown in Fig. 5(a). In the Figure 5(b) is shown a (ZP) ZnO-Pr<sub>6</sub>O<sub>11</sub>-based chemical (coprecipitated) manufactured full dense nanostructured varistor ceramic. Particularly on the system ZnO-Pr<sub>6</sub>O<sub>11</sub>-based there are several works developed by CEPEL aiming applications in high voltage. Already the Figures 5(c) and 5(d) show microstructural details characteristics of ZP varistor ceramic systems. In the Figure 5(c) it is showed the characteristic of a ZnO-based varistor ceramic obtained by liquid phase sintering, evidencing the intergranular layers, and in the Figure 5(d) it is showed a triple point (or nodal point) characteristic of an ideal varistor ceramic grain boundary region. The fundamental difference between the microstructures shown in Figures 5(a) and 5(b) is the occurrence of phases precipitated heterogeneously distributed in the first case (ZB), while for the system ZP is not the case this situation because there are no precipitates, but only thin intergranular layers as shown in Figure 5(c).



**Figure 5.** Microstructural characteristics of (a) (ZB) ZnO-Bi<sub>2</sub>O<sub>3</sub>-based attrition milled nanostructured varistor ceramic; (b) (ZP) ZnO-Pr<sub>6</sub>O<sub>11</sub>-based chemical manufactured nanostructured varistor ceramic; (c) characteristic of a ZnO-based varistor ceramic obtained by liquid phase sintering (ZP); (d) a triple point characteristic of an ideal varistor ceramic grain boundary region (ZP).

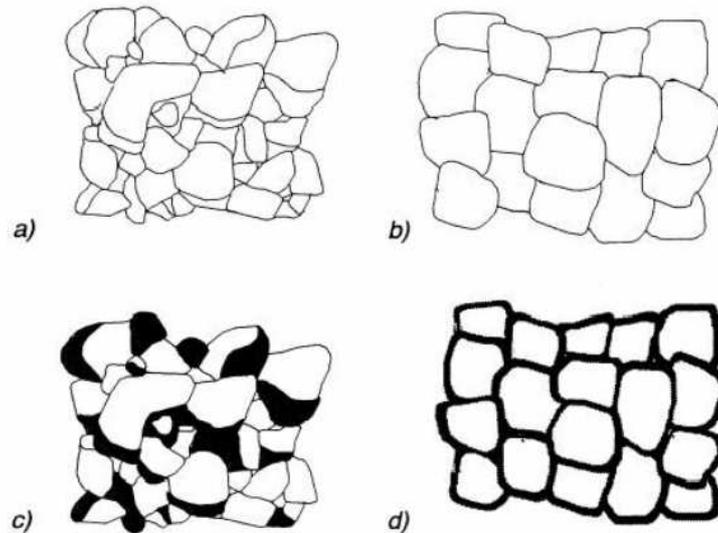
Additionally, and confirming the above observations about the structure phase characteristics of the systems studied, Figure 6 shows the XRD patterns of sintered ZB (evidencing its multiphase structure, including spinel and  $\gamma$ -Bi<sub>2</sub>O<sub>3</sub> phases) and ZP (presents only ZnO and Pr-rich phases) varistor ceramic systems.

The typical microstructural features of ZnO-based varistor ceramics, which, ideally, consists mainly of n-type semiconductor grains and grain boundaries (ZnO homojunctions, cf. Figure 5(d)). However, real microstructures produced by liquid phase sintering processes, as presented in Figures 5(a) and 5(c), results in the formation of intergranular layers and/or secondary precipitate phases depending of the chemical composition. The IGLs (intergranular layers), ideally, must be thin and ceramic microstructure must be full-densified (low porosity), cf. Figure 5(b), for minimize the leakage current.<sup>(2,3)</sup> In fact, the ideal grain boundary junctions behave like “micro-varistors”, therefore already presents a varistor behavior.<sup>(2)</sup>



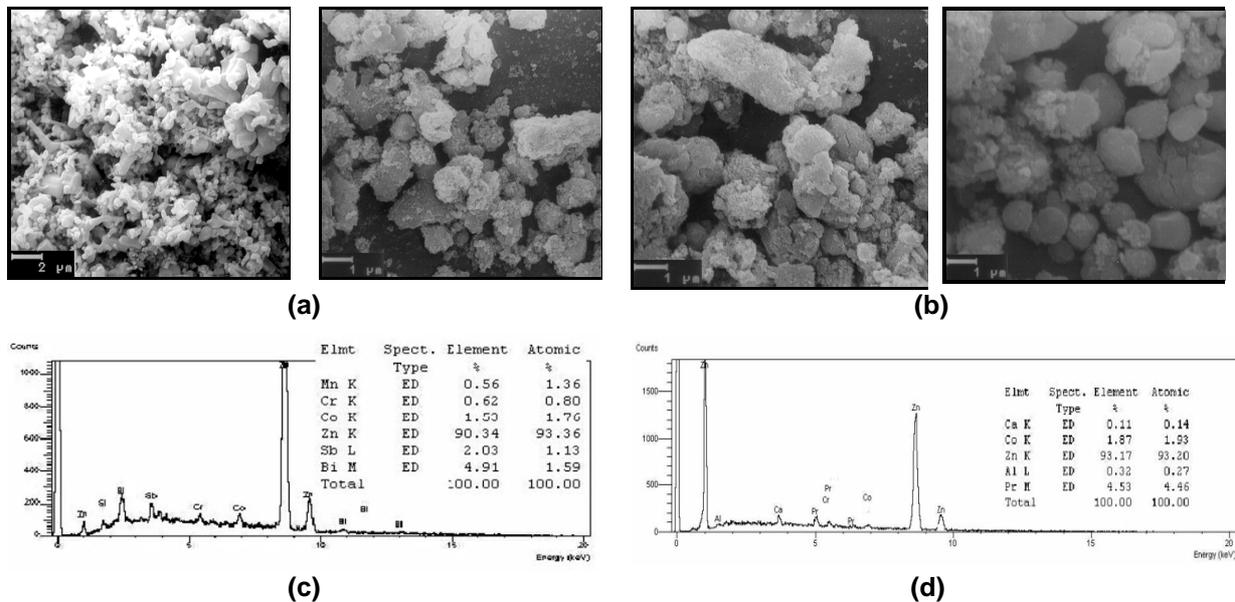
**Figure 6.** X-ray diffraction (XRD) patterns of (a) ZB sintered at 1200<sup>o</sup>C, and (b) ZP sintered at 1300<sup>o</sup>C varistor ceramic systems.

Varistor ceramics can be produced by liquid phase sintering or solid phase sintering processes (depending on the chemical composition). In both cases, the use of the nanoscale powder formulations provide the production of more homogeneity microstructures, in form to prevent the typical (real) microstructure formations showed in Figures 7(a) and 7(c). The ideal microstructures are those shown in the Figures 7(b) and 7(d). Moreover, in conventional varistors, the complex microstructures and the phase transformations that take place along the sintering process can be result in the porosity increase, what will be reflected on the electrical characteristics, mainly on the leakage current. As a matter of fact, the electrothermal runaway of a varistor ceramic is associate with the resistive leakage current increase with respect to time, temperature, and bias cycle, which present greater probability of occurrence in devices characterized by microstructures with lower physical-chemical homogeneity, since that the presence of porosities, phases segregated at the grain boundary region (in high volumes) and phase variability, result in the formation of microstructural zones that present different temperature and current density profiles, in which the degradation process is originated.<sup>(14,15)</sup>



**Figure 7.** Schematic representations about ceramic material microstructures obtained by solid phase sintering (SPS) (a and b) e liquid phase sintering (c e d): (a) “real microstructure” from SPS; (b) “ideal microstructure” from SPS; (c) “real microstructure” from LPS; (d) “ideal microstructure” from LPS.

However, the sinterability of the varistor ceramics strongly depends on the intrinsic characteristics of the precursor powders and the nanostructured varistor research has sought to synthesize ceramic powders at nanometer scale those has high specific surface area in order to increase the densification of the ceramic bodies during the sintering process. Thus the Figure 8 shows the results of the SEM-EDS microstructural analysis of the evaluated powders varistor systems. The Figure 8(d) shows the ceramic powder characteristic of the ZP system, which presents more regular forms and better dispersion condition in connection to its better varistor characteristics and good sinterability.



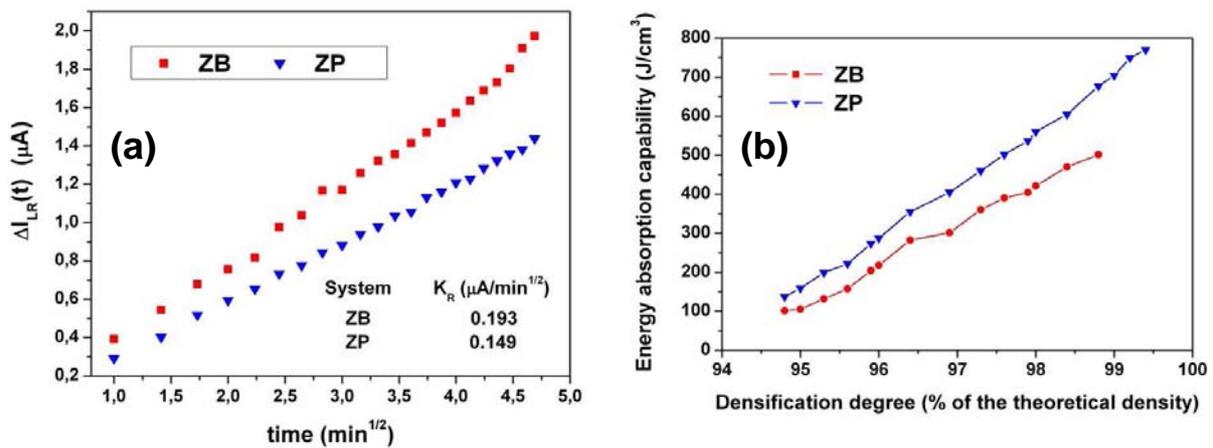
**Figure 8.** SEM-EDS microstructural analysis of the evaluated systems. Photomicrographs of powders: (a) ZB examples; (b) ZP examples. Typical chemical EDS analysis: (c) ZB, (d) ZP.

Quite consistent with the microstrutural analysis above considered are presented in the following figures the results of electrothermal characterization of



such varistor systems. The Figure 9(a) shows the  $\Delta I_{LR}$  time-dependent evolution curves and  $K_R$  ( $I_{LR}$  increment rate) obtained values for each system studied. This results indicates that the studied varistors are in the following descending order of stability: ZP > ZB (in respect to leakage current increasing), which is the same descending order for the EAC (Figure 9(b)), since the ZP system presented the slowest  $I_{LR}$  growth (smaller  $K_R$  values, 0.149 vs. 0.193  $\mu\text{A}/\text{min}^{1/2}$ , about 23% lower), since as much as bigger  $K_R$  value, then greater will be the trend to electrothermal degradation of the device, inasmuch as the  $\Delta I_{LR}$  will grow more quickly.

On the EAC it is verified by analysis of the Figure 9(b) that for the systems studied the EAC increases with the increase of the densification degree. In fact, as shown in the graphs of Figure 9(b), the EAC depends not only on geometric and dimensional factors, but also on chemical composition (ceramic formulation), since the chemical composition influences the grain growth and densification kinetics. Moreover, depending on the chemical composition and on thermal treatments used different phase structures can be generated, as seen by comparing the ZB and rare-earth-based formulation (ZP), since the ZB presents a multiphase structure and the ZP show more simple structure consisting essentially of two phases: ZnO grains (doped with Co) and rare-earth elements (Pr and Nd)-rich phase (doped with Cr and Co) segregated at grain boundaries. In fact, high voltage surge arresters are very susceptible to conditions and voltage surges that result in situations where protective equipment is subjected to large amounts of energy transient. Thus the increase of the EAC and the simultaneous reduction of leakage current are of great technological interest.



**Figure 9.** Electrothermal varistor performance related with its microstructural characteristics for the varistor ceramic systems studied: (a) leakage current increment with respect to time (at constant temperature of  $100^{\circ}\text{C}$ ); (b) energy absorption capability related to densification degree of the varistor block.

#### 4 CONCLUSIONS

The main objective of the research in nanostructured varistor ceramics is to produce more homogeneous and full densified varistor ceramic microstructure, which will result in varistors with better electrical performance and higher electrothermal stability. Additionally, it was verified that the breakdown voltage increases with the decrease of average grain size, and that there are perspectives of production of varistor ceramics for high voltage applications based on nanostructured materials. Based on the studies presented here it was verified that the zinc oxide-based varistor



ceramics doped with rare-earth oxides showed greater energy absorption capability and lower leakage current than the conventional varistors, particularly in densification usual levels the ZP (97.3-ZnO-0.5-Pr<sub>6</sub>O<sub>11</sub>-1.0-Co<sub>3</sub>O<sub>4</sub>-1.0-Nd<sub>2</sub>O<sub>3</sub>-0.2-Cr<sub>2</sub>O<sub>3</sub>, mol%) ceramics exhibited the highest energy absorption capability. Additionally, it was verified that the energy absorption capability depends on chemical composition, which influences the phase structure, although the main dependencies are in relation to densification degree.

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