NANOSTRUCTURED VARISTOR CERAMICS FOR HIGH VOLTAGE APPLICATIONS [1]

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Abstract

Zinc oxide (ZnO) nanostructured material has gained much interest owing to its wide applications for various devices such as solar cells, varistors, transducers, transparent conducting electrodes, sensors, and catalysts. On the other hand, there is an emerging demand for more efficient and reliability electrical protective devices especially for high voltage applications such as transmission and distribution grids and electric power substations. The aim of this work is to present the perspectives on the use of nanostructured varistor ceramics for high voltage applications, as well as some results about this research line at Brazilian Electric Power Research Center (CEPEL).

Keywords: Varistor ceramics; Electroceramics; Nanostructured materials.

CERÂMICAS VARISTORAS NANOESTRUTURADAS PARA APLICAÇÕES EM ALTAS TENSÕES

Resumo

Materiais nanoestruturados à base de óxido de zinco (ZnO) têm recebido grande atenção para aplicações em diversas áreas, tais como células fotovoltaicas, transdutores, varistores, eletrodos transparentes condutores, sensores e catalisadores. Por outro lado, existe uma emergente demanda por dispositivos de proteção de sistemas e equipamentos elétricos mais eficientes e confiáveis, especialmente para aplicações em altas tensões, tais como em linhas de transmissão e distribuição e em subestações de energia. O objetivo deste trabalho é apresentar as perspectivas acerca do uso de cerâmicas varistoras nanoestruturadas para aplicações em altas tensões, bem como alguns resultados desta linha de pesquisa desenvolvida no Centro de Pesquisas de Energia Elétrica (CEPEL).

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

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[1] *Technical contibution to 62nd ABM - International Annual Congress, July 23rd to 27th, 2007, Vitória - ES – Brazil*

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1 INTRODUCTION

Nanoscience and nanotechnology are relatively new subjects and they promise to revolutionize different aspects of the human life. Nanoscience is commonly defined as the study of phenomena and the manipulation of physical systems that produce significant information on a spatial scale known as "nano" (one nanometer is a billionth of a meter), with critical boundaries that do not exceed 100 nm in length at least in one direction.(1) Therefore, nanotechnologies are concerned about the design, characterization, production, and application of nanoscale systems and components. The growing interest in nanostructured materials is the natural consequence of advances and refinements of knowledge about the creative manipulation of materials.(2)

According to Das's work(3) a seminar conducted by Rice University in the USA identified some power-energy nanotechnology challenges, such as: (a) Photovoltaic solar energy – lower cost by ten fold; (b) Achieve commercial photocatalytic reduction of carbon dioxide to hydrocarbons; (c) Creation of a commercial process for direct photo conversion of light and water to produce hydrogen; (d) Lower the cost of fuel cells by tenfold to a hundredfold and create new sturdier materials; (e) Improve the efficiency/storage capacity of batteries and super-capacitors by tenfold to a hundredfold for automotive and distributed generation applications; (f) Create new, lightweight materials for hydrogen storage for pressure tanks and an easily reversible hydrogen chemisorption system; (g) Develop power cables, superconductors or quantum conductors made of new nanomaterials to rewire the electricity grid and enable long-distance, continental, and even international electrical energy transport, and reduce or eliminate thermal sag failures, eddy current losses, and resistive losses by replacing copper and aluminum wires; (h) Enable nanotechnology or nanoelectronics to revolutionize computers, sensors and devices for the electricity grid and other applications; (i) Develop thermo-chemical processes with catalysts to generate hydrogen from water at temperatures lower than 900 degrees Celsius and at commercial costs; (j) Create efficient lighting to replace incandescent and fluorescent lights. In general, nanotechnology can be used to upgrade and increase the protection level of the existing electrical-energy systems in a lot of ways and is going impact power-energy sector. Per example, as the demand for electricity increases, up gradation and continuous protection of existing transmission and distribution lines (to prevent failures that can cause damages of the order of billions dollars) becomes a high priority.

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.(4) 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.(5,6) 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.

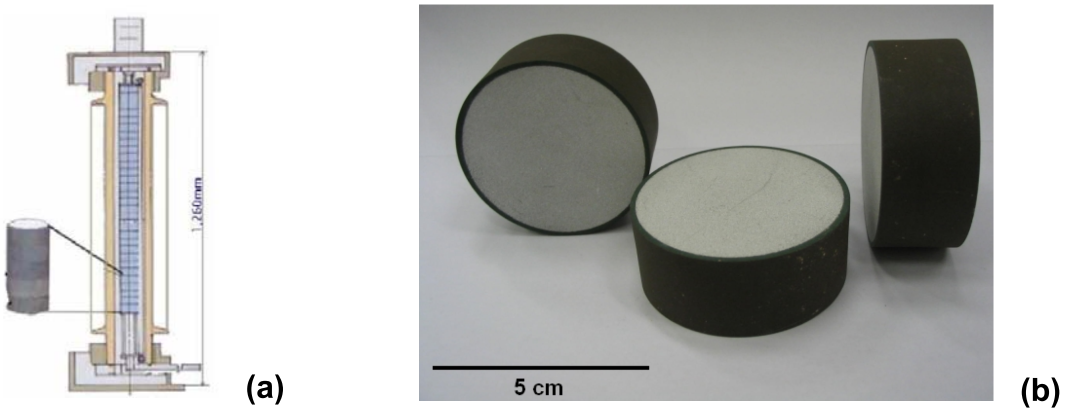


Figure 1. (a) Cross-section of a 72 kV Toshiba gapless surge arrester showing the varistor ceramic blocks; (b) varistor ceramic blocks for high voltage applications.

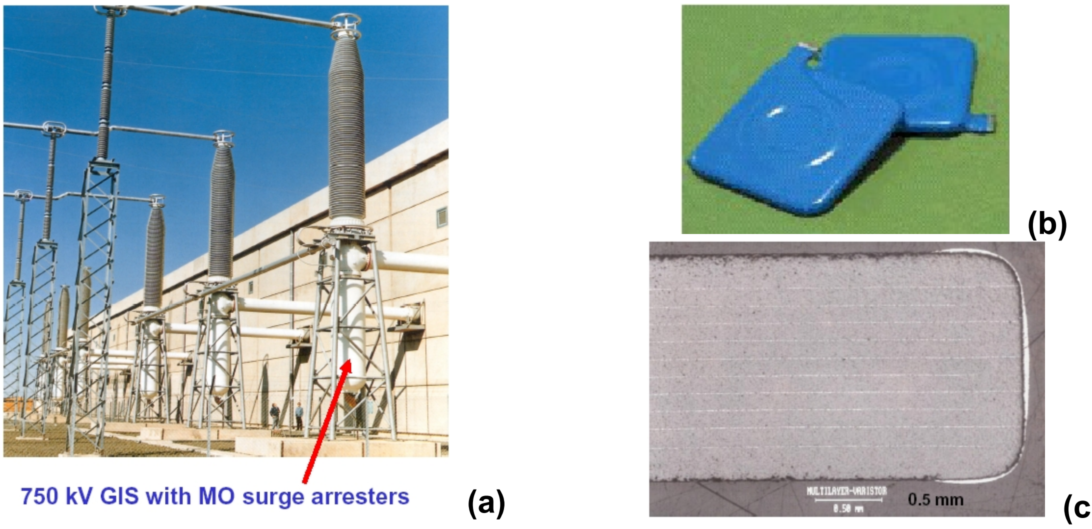


Figure 2. The extremes of application of varistor ceramics: (a) 750 kV surge arresters; (b) multilayer varistor (MLV) ceramic devices for electronic applications; (c) structure of a MLV ceramic component showing some active layers.

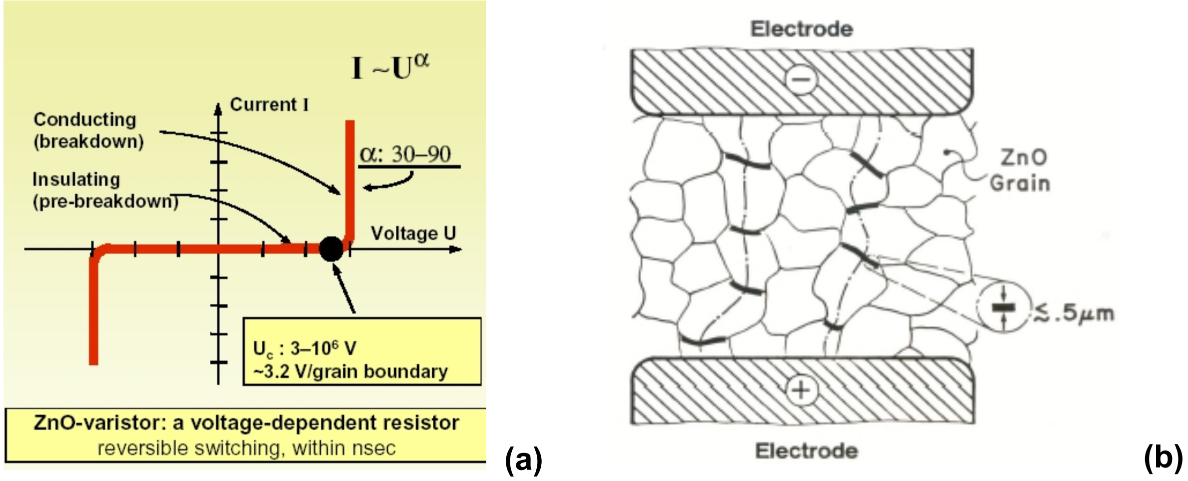


Figure 3. (a) Electrical current versus voltage curve characteristic of a varistor; (b) schematic microstructure characteristic of a ZnO-based varistor ceramic.

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.(7,8) 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(5, 9) 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.(6,10,11) 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.(10) In the present work it was reported considerations and some results about the application of nanoscience and nanotechnology in varistor ceramic research line at CEPEL (Electric Power Research Center, Brazil).

2 RESEARCH LINE DEVELOPMENT

In general, solids used in solid state device technology, as the varistor ceramics, are not single crystalline. Rather, they are made up of an assemblage of crystallites or grains, typically of micrometer dimensions, physical-chemical processed, joined to each other at grain boundaries, resulting in the formation of a polycrystalline solid. In the same way, nanocrystalline materials are polycrystalline solids with a grain size of a few nanometers. Due to the large volume fraction of interfaces between chemically identical and/or chemically different crystallites, the electronic structure of nanocrystalline materials is likely to differ from that of ideal single crystals or from a core of a normal grain, and at small grain sizes space-charge regions at interfaces can occupy a substantial volume fraction of the solid.(11) In varistor technology these considerations are very important, because the varistor behavior exactly has origin in the grain boundary regions. Thus, in a specific material, since such a large fraction of their atoms reside in grain boundaries, these interface structures may play a significant role in affecting the properties of nanostructured or nanophase materials. Thus, there are diverse research and development lines that aim at the production of the nanopowder formulations and the processing of these powders to manufacture of nanostructured varistor ceramics.

Additionally, diverse types of varistor ceramic are produced by liquid phase sintering processes, as schematically represented in Figure 4, resulting in the formation of intergranular layers, which, ideally, must be thin for minimize the leakage current (5, 6). In this way, the use of nanoscale powders, which presents greater specific energy density, provides the production of high densified ceramics by sintering in lower temperature and shorter time than conventional micrometric powders, resulting in a better physical-chemical homogeneity. In general, the main advantages of the use of nanopowders in varistor production are a high degree of homogeneity, chemically pure powders and a well defined and morphological uniform grain size. However, there are disadvantages associated with the more particle aggregation tendency and the high costs of production of these powders, beyond the biggest difficulty of reproducibility. Diverse methods of powder preparation are possible and have been reported in the literature.(12-15) In CEPEL, the mains methods used are chemical coprecipitation, combustion synthesis (also known as self-propagation synthesis), and high energy milling processes.

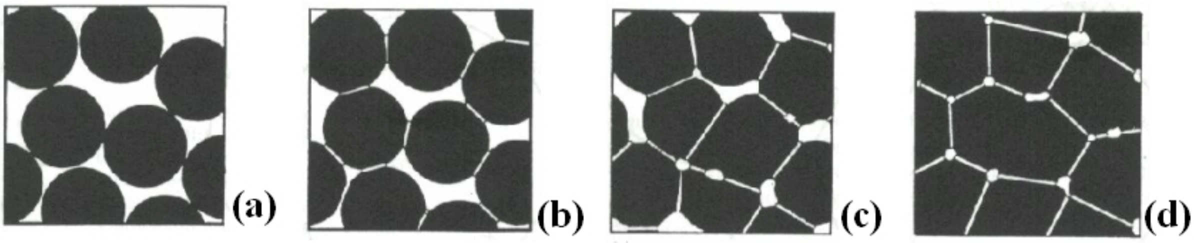


Figure 4. Typical microstructural development of a ceramic obtained by liquid phase sintering: (a) individual original particles; (b) beginning of the sintering (liquid phase) process; (c) microstructure formation; (d) consolidated ceramic microstructure.

The Figure 5 shows the relation between the breakdown voltage and the average grain size for a specific ZnO-based varistor ceramic formulation. As well as in any varistor ceramics, the global breakdown voltage increases with the decrease of average grain size. 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 μm it was obtained high breakdown voltage, which still can be increased by means compositional optimizing (doping) being able to result in adequate varistors for high voltage applications.

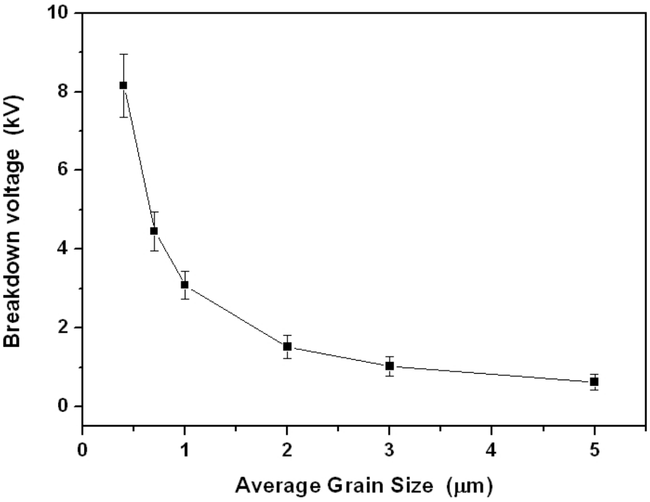
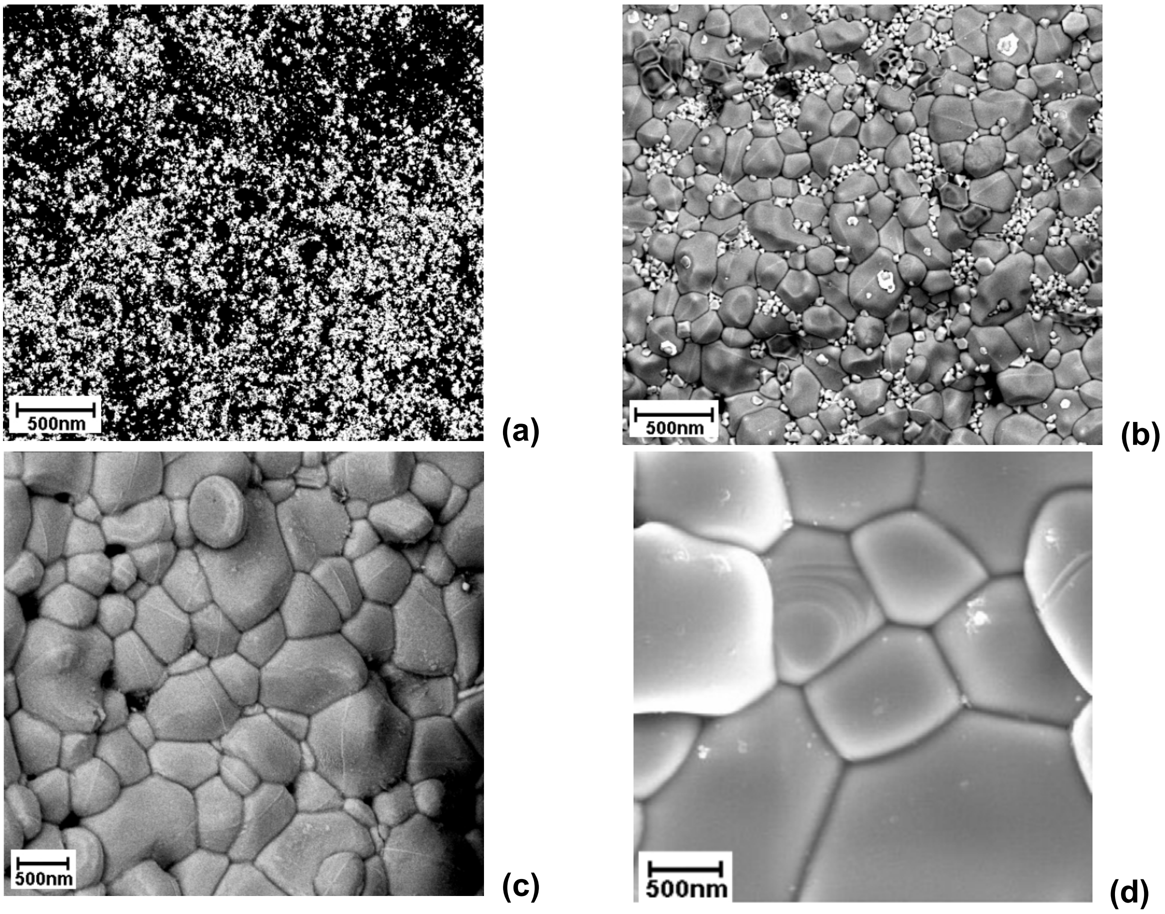


Figure 5. The relationship between the average grain size and the breakdown voltage of a ZnO-based varistor ceramic formulation.

The Figure 6 shows microstructural characteristics obtained by scanning electronic microscopy of some varistor ceramic systems studied. In Figure 6(a) it was showed a zinc oxide-based chemical synthesized (coprecipited) nanopowder formulation. The characteristic microstructure of a traditional ZnO-Bi_2O_3-based varistor ceramic formulation, obtained by intensive attrition milling, is shown in Fig 6(b). In the Figures 6(c) and 6(d) are shown, respectively, a ZnO-Pr_6O_{11}-based and a SnO_2-based chemical (coprecipited) manufactured full dense nanostructured varistor ceramics. Particularly on the system ZnO-Pr_6O_{11}-based there are several works developed by

CEPEL aiming applications in high voltage. Already the Figures 6(e) and 6(f) show microstructural details characteristics of varistor ceramic systems. In the Fig 6(e) it is showed the characteristic of a ZnO-based varistor ceramic obtained by liquid phase sintering, evidencing the intergranular layers, and in the Figure 6(f) it is showed a triple point (or nodal point) characteristic of an ideal varistor ceramic grain boundary region.

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,(5,6,16) 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. (17)



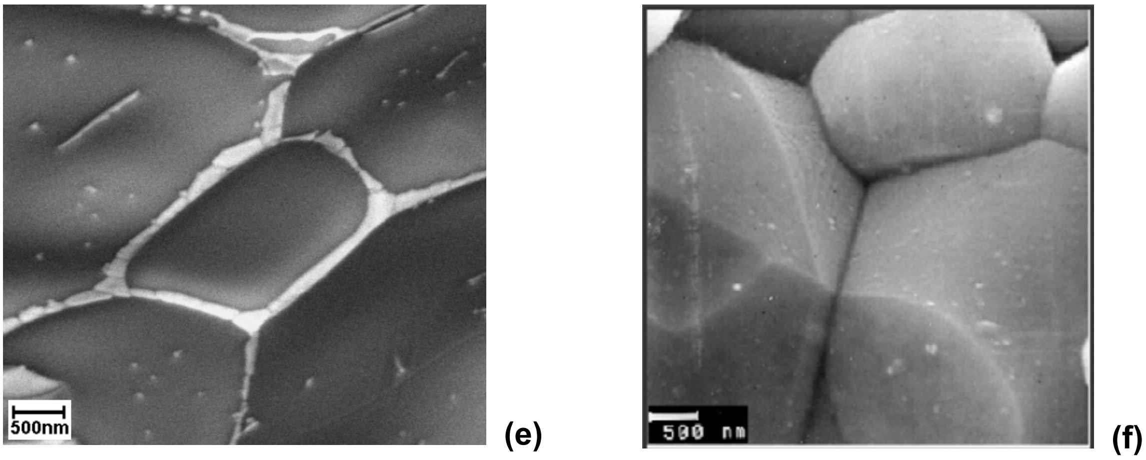


Figure 6. Microstructural characteristics of (a) Zinc oxide-based chemical synthesized nanopowder; (b) ZnO-Bi_2O_3-based attrition milled nanostructured varistor ceramic; (c) ZnO-Pr_6O_{11}-based chemical manufactured nanostructured varistor ceramic; (d) full dense SnO_2-based nanostructured varistor ceramic; (e) characteristic of a ZnO-based varistor ceramic obtained by liquid phase sintering; (f) a triple point characteristic of an ideal varistor ceramic grain boundary region.

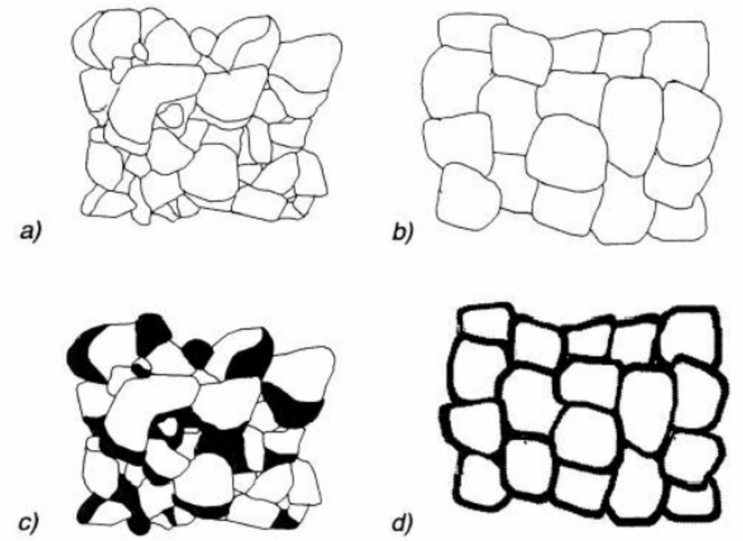


Figure 7. Schematic representations about ceramic material microstructures obtained by solid phase sintering (SPS) (a and b) e liquid phase sintering (c e d): (a) "real microstructure" from SPS; (b) "ideal microstructure" from SPS; (c) "real microstructure" from LPS; (d) "ideal microstructure" from LPS.

3 CONCLUSIONS

An overview of research works, opportunities and challenges of nanotechnology applied to varistor ceramic production and characterization developed at CEPEL was presented. 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.

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