Effect of Pr$_6$O$_{11}$ doping in electrical and microstructural properties of SnO$_2$-based varistors

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ABSTRACT. The influence of the dopant Pr$_6$O$_{11}$ was investigated with regard to the electrical and microstructural properties of the system (98.95-x)%SnO$_2$.1.0%CoO.0.05%Ta$_2$O$_5$.x%Pr$_6$O$_{11}$, where x = 0.05%, 0.10%, 0.30% and 0.50% in mol. Pr$_6$O$_{11}$ doping modifies the electrical behavior of the ceramics. The electrical parameters were: $\alpha = 8.0$, $E_b = 319$ V cm$^{-1}$ and $V_b = 0.66$ V barrier$^{-1}$ for the system without Pr$_6$O$_{11}$ and $\alpha = 17.0$, $E_b = 853$ V cm$^{-1}$ and $V_b = 1.15$ V barrier$^{-1}$ with the addition of 0.10% in mol Pr$_6$O$_{11}$. The system with 0.05% in mol Pr$_6$O$_{11}$ had the same non-linearity coefficient $\alpha$ as the system with 0.10% in mol. However, breakdown electrical field and voltage per barrier rates were lower ($E_b = 708$ V cm$^{-1}$ and $V_b = 0.98$ V barrier$^{-1}$). The low rates in the breakdown electrical field enabled the varistor systems under study to be used in protection systems for low-voltage energy grids. In the case of Pr$_6$O$_{11}$ concentrations above 0.10% in mol, the presence of the dopant became deleterious to the varistor’s electrical characteristics. This effect was due to an increase in praseodymium stannate (Pr$_2$Sn$_2$O$_7$) secondary phase. The crystalline phase coupled to the cassiterite (SnO$_2$) phase was found with XRD and SEM/EDS and quantified by Rietveld’s refining method.

Keywords: characterization, tin dioxide, praseodymium oxide, tantalum oxide.

Efeito da dopagem com Pr$_6$O$_{11}$ nas propriedades elétricas e microestruturais de varistores a base de SnO$_2$

RESUMO. Neste trabalho foi investigada a influência do dopante Pr$_6$O$_{11}$ nas propriedades elétricas e microestruturais do sistema (98,95-x)%SnO$_2$.1,0%CoO.0,05%Ta$_2$O$_5$.x%Pr$_6$O$_{11}$, em que x = 0,05, 0,10, 0,30 e 0,50% em mol. A dopagem com Pr$_6$O$_{11}$ modifica o comportamento elétrico das cerâmicas. Os parâmetros elétricos encontrados foram: $\alpha = 8,0$, $E_b = 319$ V cm$^{-1}$ e $V_b = 0,66$ V barreira$^{-1}$ para o sistema ternário sem Pr$_6$O$_{11}$ e $\alpha = 17,0$, $E_b = 853$ V cm$^{-1}$ e $V_b = 1,15$ V barreira$^{-1}$ para o sistema contendo 0,10% de Pr$_6$O$_{11}$. O sistema contendo 0,05% de Pr$_6$O$_{11}$ apresentou o mesmo coeficiente não linear $\alpha$ que o sistema com 0,10%. Talvez, os valores obtidos de campo elétrico de ruptura e tensão, por barreira, foram menores ($E_b = 708$ V cm$^{-1}$ e $V_b = 0,98$ V barreira$^{-1}$). Os baixos valores de campo elétrico de ruptura possibilitam o uso destes varistores para proteção em redes elétricas de baixa tensão. Para concentrações de Pr$_6$O$_{11}$ acima de 0,10% em mol, a dopagem se torna deletério às propriedades elétricas do varistor. Tal efeito se deve ao aumento da concentração da fase estanato de praseódímio (Pr$_2$Sn$_2$O$_7$). Esta fase cristalina, juntamente com a fase cassiterita (SnO$_2$), foram encontradas por DRX e MEV/EDS e quantificadas por refinamento pelo método de Rietveld.

Palavras-chave: caracterização, dióxido de estanho, óxido de praseódímio, óxido de tantalo.

Introduction

Varistor ceramics are polycrystalline materials that present non-ohmic properties at certain working electric voltage range. They protect electrical circuits against over-voltages without being destroyed.

The quality of the protection offered by the varistor is given by the non-linearity coefficient ($\alpha$) defined by the relation $I = c.V^\alpha$, where $I$ is the current, $V$ is the voltage and $c$ is a proportionality constant.

The varistor ceramics present a semi-insulating characteristic (ohmic resistor) up to a certain voltage, called breakdown electric field ($E_b$), and start acting as an electrical conductor from this threshold. The breakdown electric field rate determines the use of a varistor ceramic in either high or low-voltage energy grids (MENEGOTTO et al., 2002).

SnO$_2$ is one of the frequently studied materials as a varistor ceramic since it provides monophasic varistors, unlike the ZnO polyphasic varistors.
Although pure SnO₂ presents intrinsic non-ohmic behavior and low densification, it may be used to produce a varistor system when properly doped.

Research works have been found in the literature in which dopants such as CoO and MnO densify SnO₂, while dopants such as Nb₂O₅ and Ta₂O₅ promote the electrical conductivity of SnO₂ (BUENO et al., 2004; MENEGOTTO et al., 2002; VARELA et al., 1999).

Specific literature (MENEGOTTO et al., 2002) shows that the addition of Cr₂O₃ to SnO₂-CoO-Ta₂O₅-based varistor increases the non-linear coefficient. The authors suggest that the effect of Cr₂O₃ is to produce higher and wider potential barriers at the SnO₂ grain boundaries. Other dopants with 3+ charges, such as Pr₂O₃, may be used to promote the formation of potential barrier in SnO₂-based varistor.

In current analysis the addition of Pr₆O₁₁ to the ternary system SnO₂-CoO-Ta₂O₅ verified the influence of this oxide in potential barrier formation and in microstructure modifications.

Material and methods

Current analysis verified the influence of the Pr₆O₁₁ dopant on the SnO₂-CoO-Ta₂O₅ ternary system. Pr₆O₁₁ concentrations were 0.05, 0.10, 0.30 and 0.50 mol %, with concentration constants of CoO in 1.0 mol % and Ta₂O₅ in 0.05 mol %. The oxides employed were SnO₂ (CESBRA), Co₃O₄ (VETEC), Ta₂O₅ (ALDRICH), Pr₆O₁₁ (ALDRICH) featuring analytical grade (purity ≥ 99.5 %).

Table 1 shows the compositions of the systems analyzed.

<table>
<thead>
<tr>
<th>Varistor Systems</th>
<th>SnO₂ (mol %)</th>
<th>Co₃O₄ (mol %)</th>
<th>Ta₂O₅ (mol %)</th>
<th>Pr₆O₁₁ (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr₀</td>
<td>99.62</td>
<td>0.33</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>Pr₀.05</td>
<td>99.57</td>
<td>0.33</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Pr₀.10</td>
<td>99.52</td>
<td>0.33</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>Pr₀.30</td>
<td>99.32</td>
<td>0.33</td>
<td>0.05</td>
<td>0.30</td>
</tr>
<tr>
<td>Pr₀.50</td>
<td>99.12</td>
<td>0.33</td>
<td>0.05</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The systems were prepared by the conventional oxide mixture in Ball Mill, using zirconia balls as milling elements and isopropyl alcohol for wet homogenization. After milling, the powders were dried in an oven at 100°C 12h⁻¹ and de-agglomerated in a 149 μm sieve (# 100 mesh). Samples were pressed to form pellets in an isostatic press at 50 MPa, with 10 mm diameter metallic molds. Samples were sintered at 1350°C 2h⁻¹ at air atmosphere, with 10°C min⁻¹ heating rate and 5°C min⁻¹ cooling rate.

Samples sintered were analyzed through X-ray diffraction with phase quantification by Rietveld method. An X-ray diffractometer SHIMADZU XRD 6000 was used for this analysis, at 0-20 configuration; KCuα tube operating in 40.0 kV and 30.0 mA; range 20° ≥ 20 ≥ 120°; step 0.02°; integration time of 4s step⁻¹; divergence slit 0.5°; scatter slit 0.5°; receiving slit 0.15 mm. Data were refined by Rietveld method.

Microstructural characterization was performed by scanning electron microscopy (SEM/EDS SHIMADZU SSX 550). The samples were ground, polished and thermally etched at 1300°C for 15 min. to reveal the microstructure. The mean grain size was measured following method by (MENDELSON, 1969).

For electrical characterization, a regulated voltage source was used (TECTRON TCH 3000-2) and the voltage (V) and current (I) readings carried out in digital multimeters (FLUKE 8050 A). The electrical measurements (I versus V) were performed in continuous current (CC) at various temperatures and normalized to J (density of current, mA cm⁻²) x E (electric field, V cm⁻¹). The breakdown electric field (Eₜ) was determined at current density of 1 mA cm⁻² and the leakage current (Iₜ) was determined at an electric field of 200 V cm⁻¹. The non-linearity coefficient α was obtained from the points in Log E as a function of Log J curve, for J values between 1 and 10 mA cm⁻².

Results and discussion

Figure 1 presents the XRD diffractograms of the non-doped SnO₂, Pr₀ ternary system and Pr₀.05, Pr₀.10, Pr₀.30, Pr₀.50 quaternary systems, with different Pr₆O₁₁ concentrations. As may be observed, only the diffraction peaks that refer to the cassiterite phase (JCPDF 41-1445) were identified for the ternary system Pr₀. However, the existence of a spinel phase Co₂SnO₄ (cobalt stannate) in this system, at small concentrations non-detectable by XRD, already observed by other authors (MOREIRA et al., 2006; OLIVEIRA et al., 2003), cannot be ignored. The Pr₆O₁₁ doped quaternary systems comprise two ceramic phases. As Figure 1 shows, the increase in the praseodymium oxide concentration in the composition was followed by an increase in the intensity of peaks (2θ = 29 and 49°) related to the Pr₆SnO₁₄ pyrochlore phase (praseodymium stannate - JCPDF 13-0184). Phase Pr₆SnO₁₄ has also been cited in literature for SnO₂-based varistors doped with CoO, Nb₂O₅ or Ta₂O₅.
SnO₂ based varistor with Pr₆O₁₁ doping (OLIVEIRA et al., 2003; SAFAEE et al., 2011; WANG et al., 2005).

Cell parameters could be determined and the phases present could be identified and quantified from XRD refinement by the Rietveld method.

Table 2 shows results of the quantification of phases characterized by XRD by Rietveld method, cell parameters and Rietveld statistic indicators.

Through an increase in the compositions Pr₆O₁₁ concentration, a decrease in the cassiterite phase (SnO₂) and an increase in the Pr₂Sn₂O₇ pyrochlore phase occurred. Table 2 reveals that a 10 times increase of Pr₆O₁₁ concentration, from 0.05 % (Pr₀.05) to 0.50 % in mol of Pr₆O₁₁ (Pr₀.50), a tenfold increase in the Pr₂Sn₂O₇ pyrochlore phase occurred, namely from 0.7 to 7.0%. The above indicated that nearly all the Pr₆O₁₁ added to the composition was consumed in the formation of the pyrochlore phase.

The cell volume in the Pr₀.05 system increased in relation to the Pr₀ system. An increase in Pr₆O₁₁ (Pr₀.10 to Pr₀.30) concentration caused a decrease in the cell volume. This was due to the release of Sn⁴⁺ ions from the cell interior to form the Pr₂Sn₂O₇ secondary phase.

Statistical indicators evaluated the quality of XRD data refinement by the Rietveld Method. The S = Rwp/Rexp index must be a rate close to 1.0 so that the refinement may be considered good. The Bragg R factor, Rb, is related to the calculated structural model, indicating whether the model chosen represented well the real crystalline structure. Rates obtained in current research were relatively high due to the difficulty to model the structural disorder, microdeformations and the crystal size anisotropy, caused by the release of Sn⁴⁺ ions from the SnO₂ crystalline reticulum to form the Pr₂Sn₂O₇ secondary phase.

So that the morphology, distribution and chemical elements’ distribution in the varistor ceramic microstructures could be characterized, SEM/EDS analyses were carried out. Figure 2a shows the micrography of the ternary system Pr₀. The ternary system microstructure shows pores trapped inside the grains, few pores located in the grain boundaries, and the absence of precipitates related to the secondary phase Pr₂Sn₂O₇. Figure 2b registers the micrograph of the quaternary system Pr₀.50. Drastic reduction in the average grain size is seen with the addition of Pr₆O₁₁. The presence of pores in the sintered systems may also be observed by the micrographs.

Figure 3 shows enlarged micrographs of the quaternary system Pr₀.05, revealing the presence of precipitates in the triple junctions of the microstructure and inside the grains. These precipitates were ascribed to the Pr₂Sn₂O₇ secondary phase. Precipitate analysis by SEM/EDS chemical analysis identified grains with high concentration of Sn and Pr with regard to the Pr₂Sn₂O₇ phase. The above was identified by XRD as well as grains with high concentration of Sn and Co that might be related to the solid solution between cobalt and tin oxides or, with the spinel Co₂SnO₄ (cobalt stannate) phase, which, although not identified by XRD in current analysis, were probably present in small amounts in the microstructure, as pointed out by other authors (MOREIRA et al., 2006; OLIVEIRA et al., 2003; VARELA et al., 1999).

Table 2. Rietveld quantification of phases characterized by XRD.

<table>
<thead>
<tr>
<th>Varistor Systems</th>
<th>Quantified Phases</th>
<th>Cell Parameters</th>
<th>Rietveld Statistic Indicators</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>Pr₀</td>
<td>100 % SnO₂</td>
<td>4.73758(5)</td>
<td>3.18647(5)</td>
</tr>
<tr>
<td>Pr₀.05</td>
<td>99.3 % SnO₂ + 0.7 Pr₂Sn₂O₇</td>
<td>4.73762(3)</td>
<td>3.18664(3)</td>
</tr>
<tr>
<td>Pr₀.10</td>
<td>98.6 % SnO₂ + 1.4 Pr₂Sn₂O₇</td>
<td>4.73748(3)</td>
<td>3.18644(3)</td>
</tr>
<tr>
<td>Pr₀.30</td>
<td>96.0 % SnO₂ + 4.0 Pr₂Sn₂O₇</td>
<td>4.73719(3)</td>
<td>3.18642(3)</td>
</tr>
<tr>
<td>Pr₀.50</td>
<td>93.0 % SnO₂ + 7.0 Pr₂Sn₂O₇</td>
<td>4.73707(3)</td>
<td>3.1864(3)</td>
</tr>
</tbody>
</table>
Precipitates of Pr$_2$Sn$_2$O$_7$ phase in the grain boundaries caused grain growth inhibition by pinning process leading to a decrease in average grain size.

Figure 2. SEM-obtained micrographs of the compact ceramic systems (a) Pr0 and (b) Pr0.50, sintered at 1350°C 2h$^{-1}$. Magnified 1000 X.

Figure 3. SEM-obtained micrographs of the quaternary ceramic systems Pr0.05, sintered at 1350°C 2h$^{-1}$. Magnified 5000 X.

Table 3. Average grain size obtained for the systems.

<table>
<thead>
<tr>
<th>Varistor Systems</th>
<th>Average Grain Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr0</td>
<td>20.8</td>
</tr>
<tr>
<td>Pr0.05</td>
<td>13.9</td>
</tr>
<tr>
<td>Pr0.10</td>
<td>13.4</td>
</tr>
<tr>
<td>Pr0.30</td>
<td>5.8</td>
</tr>
<tr>
<td>Pr0.50</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Average grain sizes were calculated by Equation (1), in which \(d\) is the average grain size; \(n\) is the number of grains intercepted by a test line with known \(L\) (µm) length (MENDELSON, 1969).

\[
d = 1.558 \frac{L}{n}
\]  \(\text{(1)}\)

Table 3 shows average grain size obtained by the systems. Data analysis reveals the drastic reduction in the average grain size, from 20.8 µm in the ternary system Pr0 to 4.3 µm, when Pr$_6$O$_{11}$ concentration reached 0.50% (in mol) in the Pr0.50 system. The presence of precipitates of the secondary phase Pr$_2$Sn$_2$O$_7$ led to a maximum decrease of 5 times the average grain size when compared to that of the ternary system. Reduction effect in the average grain size due to the Pr$_6$O$_{11}$doping has also been verified by other authors in the literature (OLIVEIRA et al., 2003; SAFAEE et al., 2011; SIMÕES et al., 2003; WANG et al., 2005; ZHANG et al., 2007) and is also related with the grain growth inhibition caused by the presence of secondary phase precipitates in the grain boundaries.

The average grain size rates obtained in current research were three times larger than those reported in the literature for similar systems (SIMÕES et al., 2003). This was due to the higher sintering temperature in the assay. Equation (2) demonstrates that larger grain sizes (\(d\)) lead to a decrease in the number of effective barriers (\(N_b\)) present in the varistor ceramics, considering a fixed thickness (\(t\)) of the sample, for example, 1mm. Equation (3) reveals that the reduction in the number of effective barriers (\(N_b\)) leads to a decrease in its breakdown electric field (\(E_b\)), favoring the use of such varistors in low-voltage energy grids.

\[
N_b = \frac{t}{d}
\]  \(\text{(2)}\)

The accumulation of positive punctual defects in the grain boundaries region and negative defects in the grain-grain interface leads to the formation of the potential barrier responsible for the varistor effect in SnO$_2$-based ceramics. The varistor effect of such ceramics may be verified by performing electric measurements in continuous current.

In Figure 4, the characteristic curves (E versus J) of the systems, measured at room temperature, are...
SnO₂ based varistor with Pr₆O₁₁ doping

It is known that the electrical properties of varistors are strongly influenced by the temperature and the presence of applied electrical field. In Figure 5, the Ln E versus Ln J characteristic curves carried out at different temperatures for the quaternary system Pr₀.05 are presented. In Figure 5, strong influence of temperature on the varistor properties may be observed, indicating Schottky-type thermally activated electrical conduction. The same behavior was observed in other systems under analysis.

The values of electrical (E_b, α, I_L) and potential barrier (V_b, φ_b, β) parameters are given in Table 4. The V_b values were obtained from Equation (3).

\[ V_b = \frac{E_b}{N_b} \]  \hspace{1cm} (3)

where \( V_b \) is the voltage per barrier at the grain boundary, \( E_b \) is the breakdown electrical field and \( N_b \) is the number of effective barriers (Equation 2).

Height and width of potential barrier may be determined from electrical measurements (I x V) at several temperatures (Figure 5) and taking into consideration the Schottky-type conduction model (Equations 4 and 5). Using the linear region of graphs ln J as a function of \( \sqrt{E} \), the β (related to the potential barrier width – Equation 5) rate is obtained and from the slope of graphs ln J as a function of 1/T, the \( \phi_b \) (potential barrier height – Equation 4) rates are obtained. Height \( \phi_b \) and parameter β potential barrier for the systems Pr₀-Pr₀.10, which presented a good varistor behavior, are shown in Table 4.

\[ J_s = A^* T^2 e^{-\left(\phi_b - \frac{\phi_b}{\sqrt{E}}\right)} \]  \hspace{1cm} (4)

where: \( A^* \) is the Richardson constant, \( T \) is the absolute temperature, \( \phi_b \) the potential barrier height, \( E \) is the applied electrical field, and \( k \) is the Boltzmann constant. Parameter β is inversely proportional to the square root of the potential barrier width (\( \phi_b \)).

\[ \beta = \left[ \frac{1}{N_b \phi_b} \left( \frac{e^3}{4\pi \varepsilon_0 \varepsilon_r} \right) \right]^{1/2} \]  \hspace{1cm} (5)

Table 4. Electrical and potential barrier parameters obtained for the systems.

<table>
<thead>
<tr>
<th>Varistor Systems</th>
<th>( E_b ) (V cm⁻¹)</th>
<th>( \alpha )</th>
<th>( I_L ) (A)</th>
<th>( V_b ) (V barrier⁻¹)</th>
<th>( \phi_b ) (eV)</th>
<th>( \beta ) (V¹/² cm¹/²) x 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr₀</td>
<td>319</td>
<td>8.0</td>
<td>1.55 x 10⁴</td>
<td>0.66</td>
<td>0.27</td>
<td>15.57</td>
</tr>
<tr>
<td>Pr₀.05</td>
<td>708</td>
<td>17.0</td>
<td>7.11 x 10⁴</td>
<td>0.98</td>
<td>0.69</td>
<td>9.64</td>
</tr>
<tr>
<td>Pr₀.10</td>
<td>853</td>
<td>17.0</td>
<td>7.11 x 10⁵</td>
<td>1.15</td>
<td>0.75</td>
<td>8.52</td>
</tr>
<tr>
<td>Pr₀.30</td>
<td>1608</td>
<td>8.6</td>
<td>6.92 x 10⁵</td>
<td>0.92</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pr₀.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

† \( I_L \) at 200 V cm⁻¹.

There is an increase in the breakdown electric field value (E_b) with an increase in the Pr₆O₁₁ concentration. The E_b value increased almost 5 times with the increase in Pr₆O₁₁ from Pr₀ to Pr₀.30 systems. System Pr₀.50 presented a linear
electrical behavior in the range of current and voltage studied. Such increase in $E_b$ is related in Equations (2 and 3) with the reduction in the average grain size $(d)$ verified through the SEM microstructural characterizations (Figure 2 and Table 3). For constant values of $V_b$ and sample thickness $(t)$, a reduction in the average grain size $(d)$ leads to an increase in the number of effective barrier $(N_s)$ present in grain boundaries, with a consequent increase in $E_b$ value. However, $E_0$ rates obtained in this work for systems Pr0.05 and Pr0.10 are about 7 times lower than those reported in the literature for similar systems (SIMÕES et al., 2003), favoring the use of such ceramics in low-voltage energy grids.

A significant reduction in the leakage current $(I_L)$ with an increase in Pr$_6$O$_{11}$ concentration was also observed. The leakage current reduction is due to the higher resistivity caused by reduction in average grain size (Table 3) with an increase in Pr$_6$O$_{11}$ concentration.

The increase in the Pr$_6$O$_{11}$ concentration also leads to an increase in the non-linearity coefficient from $\alpha = 8.0$ in the ternary system Pr0 to $\alpha = 17.0$ in the quaternary systems Pr0.05 and Pr0.10. These results show that Pr$_6$O$_{11}$ promoted the varistor effect in these ceramics. For the system Pr0.30, the non-linearity coefficient rate was drastically reduced and for the system Pr0.50, the $E$ versus $J$ response was linear in the range of current and voltage studied, which did not correspond to a varistor behavior. Thus, a maximum limit value of 0.10 % in mol of Pr$_6$O$_{11}$ may be considered the limit value for the systems under analysis. Above this concentration, their effect becomes deleterious for varistor characteristics. This limit is related to Pr$_6$O$_{11}$ solubility in the SnO$_2$ matrix, where the increase in the concentration above 0.10% in mol Pr$_6$O$_{11}$ leads to the formation of great amounts of the secondary phase Pr$_5$Sn$_2$O$_7$.

The $V_b$ value increased in relation to the ternary system Pr0. This indicated that Pr$_6$O$_{11}$ contributed to the formation of potential barriers at the grain boundaries, similarly to Cr$_2$O$_3$, as described by (MENEGOTTO et al., 2002). The $V_b$ values obtained for the Pr$_6$O$_{11}$ doped systems Pr0.05, Pr0.10 and Pr0.30 were nearly the same, even with the increase in the dopant concentration. This indicated that the $E_b$ increase in relation to system Pr0 was mainly due to the effect of the reduction in the average grain size caused by the increase in the dopant Pr$_6$O$_{11}$ content, as discussed above.

Table 4 shows an increase in the potential barrier height $\phi_b$, and a decrease in the $\beta$ parameter, which represents increase in the potential barrier width with Pr$_6$O$_{11}$ addition to the ternary system Pr0. This fact is in accordance with results obtained in the electrical characterization, where increase in $E_b$ and $\alpha$ is observed (Table 4), since such electrical properties are affected by the potential barrier present in the grain boundaries.

Changes in the potential barrier may be explained by the segregation in the region of grain boundaries of point defects due to the Pr$_6$O$_{11}$ solid solution formation, in addition to the solid solution formed with Ta$_2$O$_5$ and CoO/Co$_2$O$_3$ in SnO$_2$, according to the equations:

$$\begin{align*}
\text{Pr}_2\text{O}_3 + \text{SnO}_2 &\rightarrow 2 \text{Pr}_\text{Sn}’’ + \text{V}_0’’ + 3 \text{O}_0’’^+ \quad (6) \\
2 \text{Ta}_2\text{O}_5 + \text{SnO}_2 &\rightarrow 2 \text{Ta}_\text{Sn}’’ + \text{V}_\text{Sn}’’ + 10 \text{O}_0’’^+ \quad (7) \\
\text{CoO} + \text{SnO}_2 &\rightarrow \text{Co}_\text{Sn}’’ + \text{V}_0’’ + \text{O}_0’’^+ \quad (8) \\
\text{Co}_2\text{O}_3 + \text{SnO}_2 &\rightarrow 2 \text{Co}_\text{Sn}’’ + \text{V}_0’’ + 3 \text{O}_0’’^+ \quad (9)
\end{align*}$$

The increase in the potential barrier may also be associated with the increase in effective surface states $(N_s)$, according to the following equation:

$$\phi_b = \frac{\varepsilon^2 N_s^2}{2\varepsilon_0 \varepsilon_r N_d} \quad (10)$$

Increase in the potential barrier height and width are then associated with the increase in both $N_s$ and $N_d$ (density of donors) due to the segregation of Pr$_6$O$_{11}$ next to the grain boundaries as well as to the creation of positive defects $(\text{V}_0’’^+)$ in the depletion layer and negative defects at the grain-grain interface (Pr$_{\text{Sn}’’}$). After the adsorption of oxygen from atmosphere at the grain-grain interface and the transfer of negative charges from (Pr$_{\text{Sn}’’}$) and other negative species to the adsorbed oxygen, which increases $N_c$, a Schottky-type electrical barrier may be ascribed as the most likely barrier at the SnO$_2$ grain boundary, since no inter-granular insulating layer separating two SnO$_2$ grains was observed in SEM. The negative surface charge at the grain boundary interface is compensated by the positive charge in the depletion layer in the grain on both sides of the grain-grain interface (GUPTA; CARLSON, 1985) developed a grain boundary defect model comprising the Schottky barrier.
In an attempt to explain the grain boundary barrier formation in a SnO₂ varistor, an analogy to this model may be considered, as Figure 6 demonstrates. In this model, the intrinsic SnO₂ defects \(V_{\text{Sn}}^{\cdot}\), \(V_{\text{O}}^{-}\) and extrinsic defects created by the dopants CoO/Co₂O₃; Ta₂O₅ and Pr₆O₁₁ could be responsible for the grain boundary electrical barrier formation. These dopants form a solid solution with the SnO₂ at high temperatures and create defects near the grain boundary, according to Equations 6 to 9.

\[
\text{Pr}_{\text{Sn}}^x + O_{2 \text{(ads)}} \rightarrow \text{Pr}_{\text{Sn}}^{x+} + 2O_{\text{ads}}^\cdot
\]  

(17)

The absorbed oxygen at the grain boundary captures electrons from negatively charged defects at the grain boundary and remains at the grain-grain interface, modifying the potential barrier and consequently the electrical properties of varistor systems.

**Conclusion**

The detection of a secondary phase \(\text{Pr}_6\text{Sn}_2\text{O}_{17}\), present in all quaternary systems was possible by XRD and SEM/EDS techniques. The reduction in grain average size was due to the growth inhibition process caused by the precipitates of \(\text{Pr}_6\text{Sn}_2\text{O}_{17}\) in the grain boundaries. All compositions under study, except that containing 0.50% in mol \(\text{Pr}_6\text{O}_{11}\), presented non-linear electrical behavior, with significant decrease in the leakage current and increase in the breakdown electrical field. The breakdown electric field rates obtained indicated that varistor systems were suitable for the protection of low-voltage energy grids.

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