We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

4,400 Open access books available
117,000 International authors and editors
130M Downloads

154 Countries delivered to
TOP 1% Our authors are among the
most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Abstract

Breakdown characteristics are of great importance for varistor ceramics, which largely depend on Schottky barriers at grain boundaries. In order to enhance breakdown performance for meeting the requirement of device miniaturization, different doping methods are introduced to not only restrict grain size from additional phase but also manipulate defect structure of Schottky barrier at grain boundaries from substitution. Distribution of barriers is another key point affecting breakdown characteristics in varistor ceramics. Dimensional effect, which is detected in not only ZnO ceramics but also CaCu$_3$Ti$_4$O$_{12}$ ceramics, is practically and theoretically found to be closely correlated with uniformity of grains. As a result, breakdown characteristics of varistors are dominated by combination effect of single barrier performance and spatial barrier distribution. In this chapter, enhanced breakdown field in Ca$_{x}$Sr$_{1-x}$Cu$_3$Ti$_4$O$_{12}$ ceramics, in situ synthesized CaCu$_3$Ti$_4$O$_{12}$-CuAl$_2$O$_4$ ceramics, and CaCu$_3$Ti$_4$O$_{12}$-Y$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ composite ceramics are investigated from the aspect of Schottky barriers at grain boundaries. In addition, dimensional effect is found in both ZnO and CaCu$_3$Ti$_4$O$_{12}$ ceramics, which are investigated from grain size distribution through theoretical and experimental analysis.

Keywords: breakdown characteristics, varistor ceramics, Schottky barrier, CaCu$_3$Ti$_4$O$_{12}$ ceramics, ZnO ceramics

1. Introduction

Varistor ceramics exhibit excellent nonlinear current-voltage ($I$-$V$) characteristics that they are widely employed for overvoltage protection in power system and electronic circuits. Zinc oxide (ZnO) varistor ceramics is one typical varistor ceramics, which has been for decades widely employed in arrestors [1]. The breakdown field of commercial ZnO varistor ceramics is commonly 200–300 V/mm and the nonlinear coefficient is ~50. Besides, perovskite CaCu$_3$Ti$_4$O$_{12}$ (CCTO) ceramics exhibit giant permittivity and nonlinear characteristics that...
made them potential candidates for application in surge absorption [2, 3]. Varistor ceramics consist of grains and grain boundaries, and it is grain boundary which manipulates the breakdown field. Breakdown field is commonly suggested to be dominated by single grain boundary and the amount of grain boundaries along electric field direction. The single grain boundary electrical performance is determined by Schottky barriers which are primarily comprised of positively charged depletion layers and negatively charged interface states [4]. Meanwhile, the amount of grain boundaries is decided by grain size. With the progress of device miniaturization, the demand for varistor ceramics with high breakdown field and high-energy absorption capability needs to be fulfilled. In order to enhance breakdown characteristics, microstructure of varistor ceramics should be improved which can be summarized into decreasing grain sizes on one hand and enhancing single barrier performance on the other hand. Two major ways of achieving greater breakdown characteristics are (1) improving preparation method and (2) finding a better recipe which might contain additives [5–10]. For improved preparation process, lots of methods like nano-sized particles and spark plasma sintering (SPS) techniques are induced to reduce the grain sizes [11, 12]. Doping is another typical topic in enhancing breakdown performance in varistor ceramics. As is known in ZnO varistor ceramics, nonlinear properties do not exist until Bi$_2$O$_3$ is added which forms an intergranular layer and manipulates defect structure to form better Schottky barriers at grain boundaries. Later on, Sb$_2$O$_3$, Co$_2$O$_3$, Mn$_2$O$_3$, etc. are added to further enhance breakdown field and improve nonlinear performance. As for CCTO varistor ceramics, several doping methods were introduced which have different effects on microstructure. Firstly, the doping ions are able to substitute ions in CCTO lattice (Ca$^{2+}$, Cu$^{2+}$) and form a relatively homogeneous structure [5]. This method dominantly manipulates Schottky barrier structure at grain boundaries. Secondly, another phase is formed besides CCTO phase resulting in heterogeneous structure, like SrTiO$_3$, TiO$_2$, CuAl$_2$O$_4$, etc. [6–8]. The additional phases mainly restrict the growth of grains and control the grain size to produce more grain boundaries. Thirdly, to form another CCTO-like phase with CCTO phase, like Y$_{2/3}$Cu$_3$Ti$_4$O$_{12}$ [9], is also suggested. This method not only introduces heterogeneous structure which restricts grain growth but also induces more defects at grain boundaries to enhance Schottky barriers. In summary, these three methods of doping result in diverse improvement of electrical characteristics due to various effects on microstructure of varistor ceramics. In the main text, these three kinds of doping methods are, respectively, introduced in detail.

Besides methods of enhancing breakdown characteristics, a non-negligible phenomenon that electrical performance is not uniform in the bulk of the ceramics should be taken into consideration for design and practical application. The inhomogeneous electrical properties at the cross section have been widely reported. About 5–11% of cross-section region in varistor ceramics was found to exhibit lower breakdown voltage than the rest of the regions [13]. This further results in current localization, which causes electrical puncture, thermal cracking, or even thermal runaway [14]. In addition, dimensional effect, which exhibits as the thickness dependence of breakdown field, is found in not only ZnO ceramics but also CCTO ceramics [15–17]. It is found that breakdown field and nonlinear coefficient are significantly decreased below a critical thickness, which brings much trouble in designing. The spatial electrical nonuniformity was widely attributed to inhomogeneous grain size distribution and grain
boundary characteristics. Electrical measurements using microcontact on single grain boundary suggested that 50% grain boundaries can be defined as “good,” 30% are “bad,” and the rest are ineffective [18]. At the same time, reports from luminescence created by electrical breakdown also provide support for uneven grain boundaries [19]. In this work, the structural origin of dimensional effect in varistor ceramics is investigated through experiment and simulation, which suggested that wide grain size distribution should be responsible. After careful processing of controlling grain sizes into narrower distribution, dimensional effect is diminished, which, to some extent, proves the responsibility of grain size distribution.

2. Enhancement of electrical breakdown field in varistor ceramics

2.1. Enhanced breakdown field in Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ ceramics via tailoring donor density

2.1.1. Phase composition and surface morphology

X-ray diffraction (XRD) patterns of Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ ceramics are presented in Figure 1. Main perovskite phase of CCTO is detected with small amount of impurity phase of CuO and SrTiO$_3$ in Figure 1(a). In the enlarged view of (220) peak in Figure 1(b), the peak gradually moves to a lower angle with the increase of Sr/Ca ratio, indicating increased lattice constant as a result of Ca$^{2+}$ (0.99 Å) with smaller radius being substituted by Sr$^{2+}$ (1.26 Å).

SEM images and corresponding grain size distribution are shown in Figure 2. Grain size of the samples is smaller than that in CCTO ceramics (>8 μm), while it changes little on the ratio of Sr/Ca (2.4–2.8 μm). Energy dispersive X-ray spectroscopy (EDS) is further measured at the marked regions in Figure 2 with the results listed in Table 1. No pure CaCu$_3$Ti$_4$O$_{12}$ or SrCu$_3$Ti$_4$O$_{12}$ is detected, indicating solid solution systems. Major discrepancy for those large

![Figure 1. XRD patterns of Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ varistor ceramics.](image)
grains (A1, B2, C2, D1) and small grains (A2, B3, C3, D2) is found to be Sr/Ca ratio. The higher Sr/Ca ratio in larger grains indicates Sr$^{2+}$ might have benefit for grain growth in relatively low temperatures.

2.1.2. Enhanced breakdown field and complex impedance spectra

Figure 3 is current density-electric field ($J$-$E$) curves of Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ ceramics. The breakdown field $E_{1mA}$ and nonlinear coefficient $\alpha$ are calculated:

Figure 2. Backscattering SEM pictures of Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ ceramic samples. (a) Sr0.2-Ca0.8, (b) Sr0.4-Ca0.6, (c) Sr0.6-Ca0.4 and (d) Sr0.8-Ca0.2. (usage permitted by Elsevier).

<table>
<thead>
<tr>
<th>Atom (%)</th>
<th>Sr0.2-Ca0.8</th>
<th>Sr0.4-Ca0.6</th>
<th>Sr0.6-Ca0.4</th>
<th>Sr0.8-Ca0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>66.68</td>
<td>70.31</td>
<td>62.31</td>
<td>68.99</td>
</tr>
<tr>
<td>Ti K</td>
<td>17.14</td>
<td>15.49</td>
<td>0.86</td>
<td>16.20</td>
</tr>
<tr>
<td>Cu K</td>
<td>11.94</td>
<td>10.64</td>
<td>36.82</td>
<td>10.74</td>
</tr>
<tr>
<td>Sr L</td>
<td>0.85</td>
<td>0.28</td>
<td>1.69</td>
<td>1.14</td>
</tr>
<tr>
<td>Ca K</td>
<td>3.39</td>
<td>3.27</td>
<td>0.71</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 1. EDS results for marked points in Figure 2 (usage permitted by Elsevier).

Figure 3. Current-voltage ($J$-$E$) characteristics (a) and impedance spectra (b) of Ca$_{1-x}$Sr$_x$Cu$_3$Ti$_4$O$_{12}$ ceramics at room temperature.
where $U_{1mA}$ and $U_{0.1mA}$ are the voltage under current density of 1 and 0.1 mA/cm$^2$, respectively, and $d$ is the sample thickness. The corresponding $\alpha$ and $E_{1mA}$ are listed in Table 2. Enhanced $E_{1mA}$ are observed in Ca$_{1-x}$Sr$_x$Cu$_4$Ti$_4$O$_{12}$ especially for samples with Sr/Ca ratio of 0.4/0.6. It increased remarkably to 24.52 kV/cm, which is as twice as that of CCTO. Elevated $E_{1mA}$ can be partially ascribed to decreased grain size. However, greatly varied $E_{1mA}$ are found in samples with similar grain size of $\approx$2.5 $\mu$m in Figure 2, indicating grain size is not decisive. Series connected RC units are widely employed for characterizing properties of grains and grain boundaries based on the fact that CCTO ceramics consist semiconducting grains and insulating grain boundaries [2, 20]. The complex impedance $Z^*$ can be expressed as:

$$Z^* = Z' - iZ'' = \frac{R_{gb}}{1 + i\omega R_{gb}C_{gb}} + \frac{R_g}{1 + i\omega R_gC_g},$$

where $R_{gb}$ and $C_{gb}$ are resistance and capacitance of grain boundaries while $R_g$ and $C_g$ are resistance and capacitance of grains. $R_g$ and $R_{gb}$ can be thus obtained as intercepts in complex impedance spectra in Figure 4. In addition, resistance activation energies of grain ($E_g$) and grain boundary ($E_{gb}$) are calculated via the Arrhenius equation. As shown in Table 2, $R_g$ and $E_g$ remain constant to $\approx$225 $\Omega$ and $\approx$0.13 eV, while $R_{gb}$ and $E_{gb}$ vary significantly. Highest $R_{gb}$ and $E_{gb}$ of 9900 M$\Omega$ and 1.03 eV are obtained for samples with Sr/Ca ratio of 0.4/0.6, which is in accordance with breakdown field in Figure 3(a). Consequently, it is reasonable to deduce that modified grain boundary characteristics that are crucial for the improved breakdown field.

2.1.3. Tailoring of donor density

Back-to-back Schottky barrier at grain boundary is crucial for the nonlinearity of varistors. Generally, the barrier height $\phi_0$ depends on the depletion layer width $x_d$, interface state density $N_s$, and donor concentration $N_d$:

$$\phi_0 \propto \frac{1}{x_d} + \frac{N_s}{x_d} + \frac{N_d}{x_d}.$$

Breakdown Characteristics of Varistor Ceramics

Table 2. Parameters for electrical nonlinearity and inhomogeneity of grain and grain boundary of Ca$_{1-x}$Sr$_x$Cu$_4$Ti$_4$O$_{12}$ varistor ceramics.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sr0.2-Ca0.8</th>
<th>Sr0.4-Ca0.6</th>
<th>Sr0.6-Ca0.4</th>
<th>Sr0.8-Ca0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>6.83</td>
<td>8.11</td>
<td>8.24</td>
<td>8.32</td>
</tr>
<tr>
<td>$E_{1mA}$ (kV/cm)</td>
<td>15.88</td>
<td>24.52</td>
<td>7.28</td>
<td>6.15</td>
</tr>
<tr>
<td>$R_g$ ($\Omega$)</td>
<td>221</td>
<td>221</td>
<td>234</td>
<td>233</td>
</tr>
<tr>
<td>$R_{gb}$ (M$\Omega$)</td>
<td>640</td>
<td>9900</td>
<td>270</td>
<td>12</td>
</tr>
<tr>
<td>$E_g$ (eV)</td>
<td>0.14</td>
<td>0.13</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>$E_{gb}$ (eV)</td>
<td>1.01</td>
<td>1.03</td>
<td>0.86</td>
<td>0.71</td>
</tr>
</tbody>
</table>
\[ \phi_0 = \frac{eN_d^2}{8\varepsilon\varepsilon_0 N_d}. \] (4)

For single grain boundary, the grain boundary capacitance of unit area \( C_0 \) under zero biased voltage is \( C_0 = [\varepsilon\varepsilon_0 N_d/(8\phi_0)]^{1/2} \), while the capacitance \( C \) under a bias voltage \( U \) is as follows [21]:

\[ \left( \frac{1}{C} - \frac{1}{2C_0} \right)^2 = \frac{2(\phi_0 + U)}{\varepsilon\varepsilon_0 N_d}. \] (5)

Dependence of \((C^{-1} - 1/2C_0^{-1})\) on \( U \) is plotted in Figure 4, showing good nonlinearity. Barrier parameter is calculated and listed in Table 3. \( N_d \) for all the samples is almost constant, while \( N_s \) varies remarkably from \( 3.3 \times 10^{13} \) cm\(^{-3}\) for Sr0.4-Ca0.6 to \( 15.6 \times 10^{13} \) cm\(^{-3}\) for Sr0.8-Ca0.2. Consequently, the highest barrier height is obtained in Sr0.4-Ca0.6 and lowest in Sr0.8-Ca0.2, which matches the results of \( E_{gb} \) from impedance spectra.

Oxygen vacancy is considered as origin of electron formation due to weak cation–O bonds. Space of \( A \) site in CCTO is rather rigid as the observed Ca–O distance is 2.61 Å, while the

![Figure 4. C-V characteristics of Ca\(_{1-x}\)Sr\(_x\)Cu\(_3\)Ti\(_4\)O\(_{12}\) varistor ceramics.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Sr0.2-Ca0.8</th>
<th>Sr0.4-Ca0.6</th>
<th>Sr0.6-Ca0.4</th>
<th>Sr0.8-Ca0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_0 ) (eV)</td>
<td>1.11</td>
<td>1.17</td>
<td>0.96</td>
<td>0.40</td>
</tr>
<tr>
<td>( x_d ) (nm)</td>
<td>630</td>
<td>880</td>
<td>460</td>
<td>240</td>
</tr>
<tr>
<td>( N_s ) (10(^9) cm(^{-3}))</td>
<td>7.73</td>
<td>5.90</td>
<td>9.20</td>
<td>7.53</td>
</tr>
<tr>
<td>( N_d ) (10(^{13}) cm(^{-3}))</td>
<td>6.11</td>
<td>3.34</td>
<td>9.99</td>
<td>15.67</td>
</tr>
</tbody>
</table>

Table 3. Parameters of Schottky barrier of Ca\(_{1-x}\)Sr\(_x\)Cu\(_3\)Ti\(_4\)O\(_{12}\) varistor ceramics (usage permitted by Elsevier).
Radius of Sr is much larger than that of Ca so that Sr–O bonds are extremely over bonded. In increasing the ratio of Sr/Ca, larger Sr stretches the Ti–O bonds, leading to enhanced polarizability of the tilted TiO$_6$ octahedra and possible breaking of the balance of Cu–O plane. Therefore, oxygen vacancy is much easier to be produced as well as segregated Cu-rich secondary phase, shown in Figure 1 [23].

On the contrary, oxygen vacancy may be inhibited due to solid solution effect between SCTO and CCTO. Taking Sr$^{2+}$ in CCTO as an example, besides Sr$_{Ca}$, Sr exists as Sr$_{Cu}$ and Sr$_{i}$ as Cu$^{2+}$ is easily loss in CCTO. Sr-Cu distortion is likely formed due to the same valence of Sr, Ca, and Cu ions. Increased A site ions can coordinate with the O$^{2-}$ in TiO$_6$ octahedron. Moreover, Sr$_{i}$ can compensate the electrons generated by oxygen vacancies. As a result, declined donor density is thus formed, which can result from Ca in SCTO as well. Maximum integrated action of strong solid solution effect and weak Sr stretching effect is achieved when Sr/Ca ratio is 40/60, which leads to greatly elevated potential barrier height more than 1.0 eV and enhanced breakdown field consequently.

2.2. In situ synthesized CCTO-xCuAl$_2$O$_4$ varistor ceramics

2.2.1. Preparation and characterization of in situ synthesized CCTO-xCuAl$_2$O$_4$ samples

CCTO powders are prepared via traditional solid-state reaction method and suspended in Al(NO$_3$)$_3$ aqueous solution. Subsequently, the suspension was quantitatively titrated with NH$_4$OH to make Al(OH)$_3$ precipitate on the surface of CCTO particles. After drying, the powders are calcined at 950°C for 4 h to dehydrate Al(OH)$_3$ into Al$_2$O$_3$. Finally, they were pressed into pellets and sintered in air at 1100°C for 4 h.

XRD patterns are presented in Figure 5(a). Only single phase of CCTO can be detected when x = 0. With increased precipitation of Al$^{3+}$, another spinel phase CuAl$_2$O$_4$ is found. Backscattering
SEM picture of CCTO-0.4CuAl$_2$O$_4$ sample is further taken as shown in Figure 5(b), in which three typical regions, A, B, and C, can be observed. According to EDS results presented in Table 4, element distribution of the gray grains (A, 15–20 µm in size) is similar to CCTO with a little Al. The black grains (B1, B2, and B3, 1–4 µm in size) are found to be the secondary phase, while the bright region of C is Cu-rich intergranular phase. It is proposed that Cu$_2$O and CuO are easily precipitated over 1000°C as Cu-rich phase, which is the main source for CuAl$_2$O$_4$. The involved chemical reactions can be expressed as:

\[
\begin{align*}
2\text{Al(OH)}_3 & = \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \uparrow \\
\text{CuO} + \text{Al}_2\text{O}_3 & = \text{CuAl}_2\text{O}_4 \\
\text{Cu}_2\text{O} + 2\text{Al}_2\text{O}_3 + \frac{1}{2}\text{O}_2 & = 2\text{CuAl}_2\text{O}_4.
\end{align*}
\]

(6)

Surface morphology of the samples is characterized by SEM as shown in Figure 6. For CCTO ceramics, little secondary phase is found, and the average grain size is 19.1 µm as shown in Figure 6(a). As to samples with $x = 0.4$ found in Figure 6(b), numbers of small particles appear in interior and intergranular region of CCTO grains, and the average grain size is 18.8 µm. When $x$ increases to 0.5 and 0.65, average grain sizes decrease notably to about 1.6 µm. It is proposed that reduction of grain size may arise from the depleted Cu-rich phases, which assists grain growth in forming CuAl$_2$O$_4$ according to Eq. (4). Pinning effect of CuAl$_2$O$_4$ phase could further inhibit the grain growth, which generally obeys the Zener model:

![Table 4. EDS results of in situ synthesized CCTO-0.4CuAl$_2$O$_4$ sample in Figure 5(b) (usage permitted by IOP Publishing).](image)

![Figure 6. SEM images of CCTO-xCuAl$_2$O$_4$ ceramic samples: (a) $x = 0$, (b) $x = 0.4$, (c) $x = 0.5$, and (d) $x = 0.65$ (usage permitted by Elsevier).](image)
where $G$ is the limit size of the matrix grain and $r$ and $f$ are particle diameter and volume fraction of the secondary phase, respectively. The grain size of the secondary phase decreases, and the volume fraction of the secondary phase increases; the matrix grain size apparently declines. Therefore, the best pining effect is achieved in the sample with $x = 0.5$ for relatively small grain size and high volume fraction of the spinel phase.

2.2.2. Enhanced breakdown field in CCTO-$x$CuAl$_2$O$_4$ ceramic samples

$J$-$E$ characteristics of in situ synthesized CCTO-$x$CuAl$_2$O$_4$ ceramics are plotted in Figure 7, and the corresponding $E_{1mA}$ and $\alpha$ are plotted in the inset. It is clear that $E_{1mA}$ of samples with $x = 0.5$ increased sharply to about 21 kV/cm with reduced grain size. On this basis, it is proposed that aggregation of CuAl$_2$O$_4$ and the inhibiting of grain growth should take responsibility for the greatly enhanced $E_{1mA}$. Although $E_{1mA} = 4.3$ kV/cm is found in $x = 0.65$ samples with similar grain size of $\sim 1.6 \mu m$, it can be ascribed to abnormally large grains as presented in Figure 6(d).

For comparison, CuAl$_2$O$_4$ is directly introduced into CCTO by solid-state reaction method following the same sintering condition. Dependence of $\alpha$ and $E_{1mA}$ on addition of the secondary phase is plotted in Figure 7(b). Similar to the in situ synthesized samples, the highest $E_{1mA}$ is achieved when $x = 0.5$. However, its highest $E_{1mA}$ is only about 15 kV/cm. This suggests that enhanced $E_{1mA}$ in directly induced samples mainly arise from pinning effect while additional depletion of Cu-rich phase should be also considered for in situ synthesized samples.

2.2.3. Complex impedance analysis for CCTO-$x$CuAl$_2$O$_4$ samples

Figure 8(a) is complex impedance spectra of CCTO-$x$CuAl$_2$O$_4$ samples at 393 K. $R_{gb}$ increases greatly from 0.37 to 13.55 MΩ with increased Al. Based on the dominant effect of $R_{gb}$ to the overall resistance, DC conductivity can approximate to conductivity of grain boundary. Activation energy of DC conductivity can be thus calculated via the Arrhenius equation, as shown
Highest energy of 0.81 eV is found for samples with $x = 0.5$, indicating inhibited hopping conduction process in them. Thus, it is suggested that the new formation of insulating phase CuAl$_2$O$_4$ may modify the electronic structure of grain boundaries and improve the electrical properties of CCTO ceramics. The enhanced $R_{gb}$ can be attributed to higher activation energy required for hopping conduction at grain boundary.

2.3. CCTO-YCTO composite ceramics with enhanced nonlinearity

2.3.1. Phase composition and surface morphology

$(1 - \chi)\text{CaCu}_3\text{T}_4\text{O}_{12} - \chi\text{Y}_2\text{Cu}_3\text{T}_4\text{O}_{12}$ [(1 - $\chi$)CCTO-$\chi$YCTO] ceramics were prepared via solid-state reaction method. They were sintered in air at 1100 °C for 10 h. XRD patterns are shown in Figure 9(a), in which the main phase of perovskite phase and small amount of CuO, TiO$_2$, and Y$_2$Ti$_2$O$_7$ are detected. With increased Y$^{3+}$, (200) peak moves to lower angle. However, it is hard to identify CCTO with YCTO phase due to similar lattice structure. Therefore, EDS is conducted (Figure 9(b) and Table 5). Element distribution of the large gains (4–6 μm) is close to YCTO, while small grains (1–2 μm) are close to CCTO although solid solution is found.
SEM pictures were taken, as shown in Figure 9. Large grains are formed in pure CCTO and YCTO ceramics with Cu-rich phase segregated in the intergranular region marked by red circles as shown in Figure 10(a) and (d). Discontinuous distribution of grain size is finally formed in CCTO samples. Stripy grains in pure YCTO ceramics suggest that sintering temperature is so high that grains could not hold the hexagonal shape. Meanwhile, two kinds of grains, with grain sizes of 4–6 μm and 1–2 μm, respectively, were found uniformly distributed in composite ceramics. Average grain size is reduced, which indicates that grain growth of CCTO and YCTO was suppressed by each other in the form of pinning effect.

2.3.2. Enhanced electrical nonlinearity

J–E characteristics at room temperature are presented in Figure 11. $E_{1mA}$ of 0.5CCTO-0.5YCTO and 0.2CCTO-0.8YCTO are enhanced to 10.17 and 11.24 kV/cm, respectively, which are approximately 10 times of that 1.24 kV/cm of CCTO sample. $\alpha$ is improved to 9.57 and 9.88, respectively. Although extremely high $\alpha$ is reported in some reports, they are hard to be repeated. $\alpha$ largely depends on the current range used for calculation in Eq. (2) and the measuring method. As shown in Figure 11(b), some reports of high $\alpha$ are actually ~5 in the current range 0.1–1 mA/cm in lnJ–lnE plots [24–26]. The reported high $\alpha$ might also originate from positive feedback of heat generated from thermal emission process at grain boundary.

Complex impedence spectroscopy at room temperature is plotted in Figure 12. $R_g$ is close to 20–40 Ω, and $R_{gb}$ varies significantly up to 1200 MΩ in samples with $x = 0.8$, while it is 55.5 MΩ in pure CCTO. To further explore the carriers’ migration across barrier, $E_g$ and $E_{gb}$ are calculated in Table 6. Similar to other reports, $E_g$ is constant while $E_{gb}$ differs significantly, inferring crucial role of grain boundary on carrier transport. $E_{gb}$ gradually increases with increased $x$, suggesting gradually developed Schottky barrier with the addition of YCTO. The barrier

<table>
<thead>
<tr>
<th>Atom (%)</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>B1</th>
<th>B2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y K</td>
<td>4.00</td>
<td>4.6</td>
<td>4.56</td>
<td>0.89</td>
<td>0.83</td>
</tr>
<tr>
<td>Ca K</td>
<td>0.87</td>
<td>0.61</td>
<td>0.94</td>
<td>4.90</td>
<td>4.76</td>
</tr>
<tr>
<td>Cu K</td>
<td>9.08</td>
<td>8.29</td>
<td>7.98</td>
<td>9.15</td>
<td>10.34</td>
</tr>
<tr>
<td>Ti K</td>
<td>20.49</td>
<td>19.41</td>
<td>19.89</td>
<td>20.77</td>
<td>21.77</td>
</tr>
<tr>
<td>O K</td>
<td>64.86</td>
<td>66.09</td>
<td>65.62</td>
<td>64.29</td>
<td>61.89</td>
</tr>
</tbody>
</table>

Table 5. EDS results of 0.2CCTO-0.8YCTO sample in Figure 9(b) (usage permitted by Elsevier).

Figure 10. Surface morphology of (1 − $x$)CCTO-$x$YCTO ceramics: (a) $x = 0$, (b) $x = 0.5$, (c) $x = 0.8$, and (d) $x = 1.0$. 

SEM pictures were taken, as shown in Figure 9. Large grains are formed in pure CCTO and YCTO ceramics with Cu-rich phase segregated in the intergranular region marked by red circles as shown in Figure 10(a) and (d). Discontinuous distribution of grain size is finally formed in CCTO samples. Stripy grains in pure YCTO ceramics suggest that sintering temperature is so high that grains could not hold the hexagonal shape. Meanwhile, two kinds of grains, with grain sizes of 4–6 μm and 1–2 μm, respectively, were found uniformly distributed in composite ceramics. Average grain size is reduced, which indicates that grain growth of CCTO and YCTO was suppressed by each other in the form of pinning effect.
height of sample with $x = 0.8$ reaches a maximum of 1.50 eV, which is twice higher than 0.69 eV of CCTO. The high barrier height leads to high nonlinear coefficient, which is consistent with results of $J-E$ performance shown in Figure 11(a).

<table>
<thead>
<tr>
<th>Energies</th>
<th>CCTO</th>
<th>0.5CCTO-0.5YCTO</th>
<th>0.8CCTO-0.2YCTO</th>
<th>YCTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$ (eV)</td>
<td>0.10</td>
<td>0.09</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>$E_{gb}$ (eV)</td>
<td>0.69</td>
<td>1.11</td>
<td>1.50</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 6. Activation energies of grain and grain boundary resistance of (1 – x)CCTO-xYCTO samples.
Grain boundary resistance dominates the conduction process. So the hopping conduction is deduced, inhibiting improved grain boundary resistance and activation energy in composite ceramics. This inhibition may arise from increased number of grain boundaries or enhanced blocking effect of single barrier. There are three types of grain boundaries: CCTO/YCTO, CCTO/CCTO, and YCTO/YCTO. $E_{gb}$ of 0.2CCTO-0.8YCTO samples (1.43 eV) is higher than that 1.11 eV of 0.5CCTO-0.5YCTO samples, indicating effect of grain boundary type is more important. Assuming both CCTO and YCTO grains are cubic, its surface area ratio can be simply written as:

$$A_{CCTO} / A_{YCTO} = \frac{r_{CCTO}^2 \times (Vol\%_{CCTO}/Vol_{CCTO})}{r_{YCTO}^2 \times (Vol\%_{YCTO}/Vol_{YCTO})} = \frac{r_{CCTO} \times Vol\%_{CCTO}}{r_{YCTO} \times Vol\%_{YCTO}}.$$  

where $A$ is surface area of grains, $r$ is grain size, Vol is single grain volume, and Vol\% is volume fraction. Densities of CCTO and YCTO are 5.05 and 5.20 g/cm$^3$, respectively. The average grain sizes for CCTO and YCTO are 1.24 and 4.57 μm according to results found in Figure 10(b and c). On this basis, it can be obtained that $A_{CCTO}/A_{YCTO}$ for 0.5CCTO-0.5YCTO is 0.38, while it is 0.95 for 0.2CCTO-0.8YCTO. In other words, the number of CCTO/YCTO interfaces reaches maximum in 0.2CCTO-0.8YCTO sample. On one hand, solid solution between $Y^{3+}$ and $Ca^{2+}$ could inhibit generation of donors, leading to thicker depletion layers. On the other hand, more interface states are produced at the YCTO/CCTO heterojunction. As a result, barrier height is improved so that more energy is needed for carriers to migrate across barriers.

3. Dimensional effect of varistor ceramics

3.1. Phenomenon of dimensional effect

Thickness dependence of $E_{1mA}$ and $\alpha$ of ZnO ceramics with low, medium, and high potential gradients is plotted in Figure 13(a). Similar phenomenon is also found in CCTO ceramics in Figure 13(b). Every curve exhibits a turning point corresponding to sample thickness $d$. Critical thickness $d_c$, critical breakdown field $E_c$, and critical nonlinear coefficient $\alpha_c$ are determined by each curve. Such behavior can be empirically represented as:

$$E_{1mA} \propto e^{bd},$$  

where the exponent $b$ represents the transitional behavior for the entire curve. Let this exponent in $d < d_c$ domain be denoted as $b_1$ while it is denoted as $b_2$ in the $d > d_c$ domain, i.e.: 

$$\ln E_{1mA} = a_1 + b_1d \ (d < d_c),$$  

$$\ln E_{1mA} = a_2 + b_2d \ (d > d_c).$$  

The summary of the parameters $b_1$, $b_2$, $d_c$, and $E_c$ in Figure 13 is listed in Table 7. $d_c$ significantly decreases with increased $E_{1mA}$ and $E_c$ which indicate that those who exhibit higher $E_{1mA}$ exhibit less severe dimensional effect. At the same time, $b_2$ slightly decreases with
increased $E_{1mA}$, suggesting more stable $E_{1mA}$ with variation of thickness. However, no matter what varistors are used in high-voltage or low-voltage situations, dimensional effect undoubtedly exists, which brings much trouble for practical application and design. Therefore, further investigation of dimensional effect is needed for stable electrical performance.

### 3.2. Simulation of dimensional effect

Breakdown voltage of single grain boundary is acknowledged to be nearly constant (~3 V), indicating other factors should be responsible for dimensional effect. To understand the structural origin of dimensional effect, a model based on the network of grains and grain boundaries is proposed. Grain sizes in varistor ceramics fit the normal distribution, in which the probability density $f(l)$ can be expressed as:

$$f(l) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(l - \mu)^2}{2\sigma^2}\right],$$  \hspace{1cm} (12)$$

where $l$ is the average grain size, $\sigma$ is the standard deviation, and $\mu$ is the mathematical expectation. For ceramics with diameter of $D$ and thickness of $d$, it is assumed that all grains are cubic with length of $m$; the number of grains on the cross-section $N$ is thus calculated as:

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|}
\hline
Samples & $b_1$ & $b_2$ & $d_c$ (mm) & $E_c$ (V/mm) \\
\hline
ZnO ceramics & High & 9.4 & 0.21 & 0.19 & 185 \\
 & Medium & 18.6 & 0.31 & 0.28 & 110 \\
 & Low & 6.0 & 0.36 & 0.98 & 33 \\
CaCu$_3$Ti$_4$O$_{12}$ ceramics & & 0.278 & 0.087 & 0.90 & 53 \\
\hline
\end{tabular}
\caption{The exponents $b_1$ and $b_2$, critical thickness $d_c$, and the transitional breakdown field $E_c$ of ZnO ceramics and CCTO ceramics in Figure 12.}
\end{table}
\[ N = \frac{\pi D^2}{4 \mu^2}. \]  

(13)

It is assumed that these \( N \) grains on the cross section lead to \( N \) grain chains along thickness direction. Since \( l \) also fits normal distribution, the average grain number should be \( \bar{d}/m \), and the variance of the average grain size should be \( \sigma^2/(d/m) \); therefore:

\[
f(l) = \frac{1}{\sqrt{2\pi \frac{d}{\mu}}} \exp \left[ -\left( \frac{l - \mu}{\frac{d}{\mu}} \right)^2 \right].
\]

(14)

The amount of chains with grain sizes from \( \bar{l} \) to \( \bar{l} + \Delta l \) fits:

\[
\Delta n(\bar{l}) = N f(\bar{l}) \Delta l.
\]

(15)

Another assumption is that the current that went through one grain chain is independent on other chains. On this basis, the relationship between the voltage and the current in one grain chain can be expressed as:

\[
V = \frac{d}{l} V_B + I_i(\bar{l}) \frac{d}{\Delta n(\bar{l}) \mu^2} \rho_g
\]

(16)

where \( V_B \) is the breakdown voltage of single grain boundary and \( \rho_g \) is the electrical resistivity of grain. Consequently, the total current in this piece of ceramics should be the sum of current flowing in \( N \) grain chains:

\[
I = \sum I_i(\bar{l}).
\]

(17)

Based on the model above, \( J-E \) characteristic under a fixed thickness can be acquired with increased applied voltage \( V \), and the \( E_{1mA} \) is able to be calculated. With variance of \( d \) in Eq. (12), a series of \( J-E \) curves are acquired, and \( E_{1mA} \) corresponding to different thicknesses are therefore known. According to grain size distribution of the measured ZnO varistor samples with high and medium \( E_{1mA} \) found in Figure 13(a), average grain size \( m \) and variance \( \sigma^2 \) are calculated and taken into the model. Hence, the thickness dependences of \( E_{1mA} \) are plotted in Figure 14. The \( d_c \) of high-voltage varistors is \(~0.2 \) mm, whereas it is \(~0.3 \) mm for medium-voltage varistors. Both \( d_c \) and \( E_c \) from simulation fit the experimental results in Figure 13(a) well, proving the effectiveness of the proposed model.

In addition, if the average grain size is fixed, sample thickness \( d \) is reversely proportional to the variance of the average grain size. The maximum of the probability density \( f(\mu) \) fits:

\[
f(\mu) = \frac{1}{\sqrt{2\pi \frac{d}{\mu}}}.
\]

(18)

With increased \( d \), \( f(m) \) increases, indicating a narrower grain size distribution. Therefore, dimensional effect of varistor ceramics originated from the thickness dependence of grain size variance.
As for CCTO ceramics which also exhibits dimensional effect shown in Figure 13(b), SEM images and grain size distribution on longitudinal section morphologies are investigated, as shown in Figure 15. Grains are smaller near the surface, whereas they are larger and denser in the interior. Quantitative analysis shows that grain sizes are more uniform near the surface while the size distribution is wider in the interior. The average grain size increased from 20.23 μm near the surface to 23.94 μm in the interior, while the porosity decreased from 4.95% near the surface to 0.33% in the interior. Although the grains with size below 30 μm are dominant in number, they contribute less to the section area. It can be seen in Figure 15(b), (d), and (f) that although grains with size below 15 μm contribute to more than 50% of grains, the sum of their occupied area is less than 10%. Despite small increase of average grain size from the surface to interior part, the major grain size that contributed to section areas is significantly different. On the surface, amount of the grains between 20 and 40 μm is most, while grains between 40 and 60 μm dominate the section area. Especially, the grain size range extends to 50–90 μm in the interior. From this point, it can be deduced that nonuniform distribution of grain size indeed contributed to dimensional effect in varistor ceramics, which is in accordance with simulation discussed above.

3.3. Elimination of dimensional effect

In not only ZnO varistor ceramics but also CCTO ceramics, dimensional effect exists because of nonuniform grain size distribution, which restricts its practical application. Therefore, in order to diminish or to attenuate dimensional effect, it is important to make grain size distribution more uniform. Despite the traditional processed ZnO varistor ceramics (Tr), another amine processed (Am) samples are prepared. At first, ZnO is dissolved in NH₄(OH) and NH₄(HCO₃)
solution with other additives in solutions, which is consequently heated to 110°C. After careful monitoring and controlling the pH of this mixed solution to 8–9, the precipitations are separated from the solution by filtration and washed with diethylamine solution to remove all chloride ions. When the solution is dried, the remained powders are calcined at 500°C, and then traditional processes are followed.
SEM photos of traditional processed (Tr) and amine processed (Am) ZnO samples are shown in Figure 16(a) and (b), respectively. Lots of small grains are scattered between compactly aligned big grains in Tr samples, as shown in Figure 16(a). However, no such small grains are seen in Am samples. The grains in Am samples are more uniform than those in Tr samples. Lots of grains with size below 3 μm exist in Tr samples, while the grains are compact with almost no grains with size below 3 μm.

Thickness dependence of $E_{1mA}$ of Tr and Am samples are depicted in Figure 17. Tr samples exhibit distinct dimensional effect with $d_c$ of 0.28 mm. Notably, the Am samples show lower...
$E_{1mA}$ but exhibit no distinct dimensional effect. The decreased $E_{1mA}$ might be attributed to larger average grain size in Am samples than that in Tr samples. What is evident is that uniform grain sizes are obtained, which could effectively eliminate dimensional effect.

4. Conclusion

Breakdown characteristics in varistor ceramics are investigated from grain boundary characteristics based on single barrier performance and barrier distribution. On one hand, different methods of doping including substitution and additional phase result in not only restriction on grain sizes but also manipulation of defects in Schottky barriers of varistor ceramics to enhance breakdown field to meet the requirement of device miniaturization. In addition, restriction on further decreased thickness of varistor ceramics is found as dimensional effect in not only ZnO ceramics but also CaCu$_3$Ti$_4$O$_{12}$ ceramics. From theoretical analysis and experimental results, the dimensional effect is found closely related with the uniformity of grain sizes, which influence the distribution of grain boundaries quite well. Consequently, the breakdown characteristics in varistor ceramics are understood from the aspect of single barrier performance and spatial distribution of barriers.

Author details

Jianying Li*, Kangning Wu and Yuwei Huang

*Address all correspondence to: lijy@xjtu.edu.cn

State Key Laboratory of Electrical Insulation and Power Equipment, Xi’an Jiaotong University, Xi’an, China

References


[22] Li J, Subramanian MA, Rosenfeld HD, Jones CY, Toby BH, Sleight AW. Clues to the giant dielectric constant of CaCu$_3$Ti$_4$O$_{12}$ in the defect structure of “SrCu$_3$Ti$_4$O$_{12}” “. Chemistry of Materials. 2004;16:5223-5225. DOI: 10.1021/cm048345u


