Novel Ultrahigh-Performance ZnO-Based Varistor Ceramics

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ABSTRACT: The nonlinear response of a material to an external stimulus is vital in fundamental science and technical applications. The power-law current–voltage relationship of a varistor is one such example. An excellent example of such behavior is the power-law current–voltage relationship exhibited by Bi$_2$O$_3$-doped ZnO varistor ceramics, which are the cornerstone of commercial varistor materials for overvoltage protection. Here, we report on a sustainable, ZnO-based varistor ceramic, without the volatile Bi$_2$O$_3$, that is based on Cr$_2$O$_3$ as the varistor former and oxides of Ca, Co, and Sb as the performance enhancers. The material has an ultrahigh $\alpha$ of up to 219, a low $I_L$ of less than 0.2 $\mu$A/cm$^2$, and a high $E_b$ of up to 925 V/mm, making it superior to state-of-the-art varistor ceramics. The results provide insights into the design of materials with specific characteristics by tailoring states at the grain boundaries. The discovery of this ZnO-Cr$_2$O$_3$-type varistor ceramic represents a major breakthrough in the world market for overvoltage protection.

KEYWORDS: ZnO, Cr$_2$O$_3$, varistor ceramics, double-Schottky barriers, microstructure, $I$–$V$ characteristics

INTRODUCTION

Varistors, better described as variable resistors, are used in billions of low-power electronic devices and heavy-duty electrical-energy-distribution systems to protect circuits from transient voltage surges by means of their nonlinear current–voltage ($I$–$V$) characteristics.\(^1\)-\(^3\) Specifically, a varistor is highly resistive at a low applied voltage but becomes conductive very quickly when the applied voltage exceeds a material-specific threshold known as the breakdown voltage $E_b$. Above $E_b$, the nonlinear $I$–$V$ characteristics are empirically described by a power-law function $I = bV^\alpha$, where $b$ is a constant and $\alpha$ is a nonlinear coefficient. The value of $\alpha$ is thus a gauge of how responsive the varistor is to the transient voltage surge. As illustrated in Figure 1a, the value of $\alpha$ is physically governed by the height of the double-Schottky barrier (DSB), $\varphi_B$, at the grain boundary (GB);\(^4\)-\(^6\) $\varphi_B = E_{FB} - E_{FG}$, where $E_{FB}$ and $E_{FG}$ are the Fermi levels in the GB and the grain, respectively. Besides the high $\alpha$ value, a high-performance varistor entails a small leakage current ($I_L$), which is the current at $0.75 \times E_b$. Low values of $I_L$ ensure a low chance of thermal runaway, good stability and aging behavior, and also a low power consumption.\(^6\)

Among the metal–oxide varistors (MOVs) that are the state-of-the-art varistors, ZnO-based varistors have the highest DSB heights $\varphi_B$ and superior nonlinear properties (high $\alpha$ values and low $I_L$ values).\(^6\) Note that pristine ZnO displays a very weak, nonlinear $I$–$V$ characteristic, reflecting $E_{FB}$ and $E_{FG}$ that are nearly equal. It takes varistor former(s), also known as varistor activator(s), to create defect complexes at the GB, which shift the $E_{FB}$ to a deeper position in the band gap, and the resulting $\varphi_B$ gives rise to the DSB and in turn elicits nonlinear $I$–$V$ characteristics in the ZnO.\(^5\) In parallel with the varistor former(s) implemented at the GB, performance enhancer(s) can be doped into the grains to actively raise the $E_{FG}$ and thus increase $\varphi_B$ to higher $\alpha$ and smaller $I_L$ values.\(^6\)-\(^8\)

Other than $\alpha$ and $I_L$, a high $E_b$ value is desired for surge protection and a reduction of device size in high-voltage dc power transmission and heavy-duty power-supply systems, thereby broadening the scope of applications. However, the increase of $E_b$ tends to worsen $\alpha$ and $I_L$ simultaneously.\(^3\)-\(^9\) As a result, the state-of-the-art ZnO-based varistors, with varistor formers such as Bi$_2$O$_3$, Pr$_6$O$_{11}$, and V$_2$O$_3$ along with their corresponding performance enhancers, such as Sb, Co, Mn, Ni, and Cr, typically achieve an $\alpha$ value of less than 60, an $I_L$ values higher than 1 $\mu$A/cm$^2$, and an $E_b$ value in the range 200–500 V/mm.\(^3\)-\(^5\)

After exploring a large phase space (Supporting Information), here we report on a novel ZnO-based varistor ceramic that uses Cr as the varistor former and Ca, Co, and Sb as the performance enhancers. These ceramics have record-high nonlinear characteristics, manifested in an ultrahigh $\alpha$ value up to 219, a very low $I_L$ value of less than 0.2 $\mu$A/cm$^2$, and a high $E_b$ value of 925 V/mm, making them superior to today’s
varistor ceramics. For conciseness, we only list the performance of ZnO-based varistors for comparison in Figure 1b. Moreover, the materials sustainability (volatility and toxicity) of these ultrahigh-performance varistors is significantly improved. Specifically, the compositions avoid the use of highly volatile bismuth oxide, expensive rare earths like praseodymium, or the toxic vanadium oxide.

**EXPERIMENTAL SECTION**

**Sample Preparation.** Reagent-grade powders of ZnO, Cr$_2$O$_3$, CaCO$_3$, Co$_3$O$_4$, and Sb$_2$O$_3$ were used for preparation of the materials. Cr-added ZnO with nominal compositions of $(1-x)$ mol ZnO- $x$ mol Cr$_2$O$_3$ (x = 0.05%, 0.1%, 0.2%, 0.3%, and 0.4%, namely, ZnO-xCr$_2$O$_3$), Ca-doped ZnO-0.1% Cr$_2$O$_3$ (Zn$_{0.997}$Ca$_{0.002}$Cr$_{0.001}$O$_{1.002}$), aka 97.9 mol % ZnO + 0.1 mol % Cr$_2$O$_3$ + 2 mol % CaCO$_3$ in raw materials), (Co, Ca)-codoped ZnO-0.1% Cr$_2$O$_3$ (Zn$_{0.997}$Ca$_{0.002}$Ca$_{0.001}$Co$_{0.003}$O$_{1.017}$), aka 97.4 mol % ZnO + 0.1 mol % Cr$_2$O$_3$ + 2 mol % CaCO$_3$ + 0.5 mol % Co$_3$O$_4$ in raw materials), (Co, Ca, Sb)-doped ZnO-0.1% Cr$_2$O$_3$ (Zn$_{0.997}$Ca$_{0.002}$Ca$_{0.001}$Co$_{0.003}$Sb$_{0.003}$O$_{1.02}$), aka 97.25 mol % ZnO + 0.1 mol % Cr$_2$O$_3$ + 2 mol % CaCO$_3$ + 0.5 mol % Co$_3$O$_4$ + 0.15 mol % Sb$_2$O$_3$ in raw materials), and (Co, Ca)-codoped ZnO (Zn$_{0.997}$Ca$_{0.002}$Ca$_{0.001}$Co$_{0.003}$O$_{1.017}$), aka 97.5% mol ZnO + 2 mol % CaCO$_3$ + 0.5 mol % Co$_3$O$_4$ in raw materials) ceramics were synthesized by a conventional solid-state technique. We used CaCO$_3$ instead of CaO because CaO is not stable in air. At high temperatures, CaCO$_3$ was decomposed to CaO and CO$_2$ gas and then Ca is doped into ZnO. The starting powders were wet mixed by ball milling for 8 h, followed by drying at about 120 °C for 5 h, and then cold pressed as pellets with a diameter of 12 mm and thickness of 1 mm. Finally, the pellets were sintered at 1200 °C for 3 h. Silver pastes were covered on the sample’s opposite surfaces and then dried at 560 °C for 15 min as electrodes.

**Characterization.** X-ray diffraction using Cu Kα radiation (D/max 2550 V, Rigaku, Tokyo, Japan) was used to analyze the phase
 purity. Microstructural observations were carried out on the polished surfaces using a field-emission scanning electron microscope (Magellan 400, FEI Co., USA). Energy-dispersive X-ray spectroscopy (Oxford Instrument, UK) was performed to detect elements and distributions. Spherical aberration-corrected transmission electron microscopy (HF 5000, Hitachi, Japan) with energy-dispersive X-ray spectroscopy (Oxford X-Max 100TLE, UK) and transmission electron microscopy (Tecnai-F20, FEI Co., USA) were used to observe the microstructures and compositions of the grain boundaries (GBs). The micro-Raman spectra were recorded with a Renishaw InVia Confocal micro-Raman system using the 532 nm line as an excitation source. Micro-Raman spectra were recorded with a Renishaw InVia Confocal microscopy (Tecnai-F20, FEI Co., USA) were used to observe the microstructures and compositions of the grain boundaries (GBs). The micro-Raman spectra were recorded with a Renishaw InVia Confocal microscopy (HF 5000, Hitachi, Japan) with energy-dispersive X-ray (Oxford Instrument, UK) was performed to detect elements and compositions Zn1-xCr0.75O nanocrystallites and compositions of the grain boundaries (GBs). The micro-Raman spectra were recorded with a Renishaw InVia Confocal microscopy (HF 5000, Hitachi, Japan) with energy-dispersive X-ray (Oxford Instrument, UK) was performed to detect elements and compositions Zn1-xCr0.75O nanocrystallites and compositions of the grain boundaries (GBs).

RESULTS AND DISCUSSION

Unlike previous reports, Cr is, in this work, found to be a varistor former rather than a performance enhancer for ZnO-based varistors. Cr was thought to be a performance enhancer and, in this role, together with other performance enhancers (i.e., Sb, Co, Mn, Ni, etc.) was added to ZnO along with the well-established varistor formers such as Bi and Pr.17,19 To verify whether Cr is a varistor former at the GB or a varistor former to shift the band structure and the added performance enhancers (Figure 2c).

The varistor former Cr elicits nonlinear I–V characteristics in ZnO, but the α value is only about 2 in the ZnO-0.1% Cr2O3 sample (Figure 2c). Introducing performance enhancers is thus a must to enlarge the difference between $E_{FB}$ and $E_{FG}$ i.e., $\eta_{FB}$. To this end, the results of our study show that codoping with Ca, Co, and Sb acts as an effective performance enhancer in the presence of the varistor former Cr. Figure S4a, which shows elemental mapping, indicates that Ca, Co, and Sb are homogeneously distributed in the grains in the absence of Cr within the EDS detection limit. Hereafter, the chemical formula (Ca, Co, Sb)-doped ZnO with a varistor former derived from x% Cr2O3 will be written in the form (Ca, Co, Sb)-doped ZnO-x% Cr2O3.

Figure 2c shows that the nonlinear current density vs. electric field (J–E) characteristics are observed in all of the Cr-added ZnO ceramics, but the α values vary by several orders of magnitude with the specific compositions of the performance enhancers (Table 1). The detailed electrical properties (JL, $E_b$, shown in Tables S1–S3) of the ZnO ceramics with various Ca, Co, and Cr-doping ratios are presented in the Supporting Information. In the following, we will focus on the samples with 0.1 mol % Cr2O3, 2 mol % CaCO3, 0.5 mol % CoO4, and 0.15 mol % Sb2O3 ratios as an illustration and for conciseness. As shown in Figure 2d and Table 1, the α value increases from about 2 for ZnO-0.1% Cr2O3 to 27 for Ca-doped ZnO-0.1% Cr2O3, to 73 for (Ca, Co)-codoped ZnO-0.1% Cr2O3 and finally to an exceptional value of 219 in (Ca, Co, Sb)-codoped ZnO-0.1% Cr2O3. It is not rare to observe increased α values with an increasing number of enhancers (dopants),29 however, the magnitude of the improvement attained here is unprecedented (Figure 2d).

Table 1. Electrical properties of Cr-added ZnO varistor ceramics with different performance enhancements

| Sample | α | JL (μA/cm²) | E_b (V/mm) |
|--------|---|-------------|------------|
| ZnO-0.1%Cr2O3 | 2 | - | - |
| Ca-ZnO-0.1%Cr2O3 | 27 | 8.6 | 424 |
| (Ca,Co)-ZnO-0.1%Cr2O3 | 73 | <0.2 | 394 |
| (Ca,Co,Sb)-ZnO-0.1%Cr2O3 | 219 | <0.2 | 925 |

Furthermore, a high $E_b$ of 925 V/mm is obtained in the (Ca, Co, Sb)-doped ZnO-0.1% Cr2O3 ceramic due to the greatly decreased grain size (Figure S5). The very low JL and greatly decreased grain size suggest a high GB resistance. This argument is corroborated by the results of impedance spectroscopy. As shown in Figure S6, the resistances of the GBs are much larger than those of the grain in all of the Cr-containing ZnO ceramics. In particular, the (Ca, Co, Sb)-doped ZnO-0.1% Cr2O3 ceramic shows an extremely high resistance at the GBs, an indication of the as-formed DSB.

The record-high varistor performance in 0.2% Cr-added (Co, Ca, Sb)-doped ZnO ceramics with a high α value, a very low JL value, and a high $E_b$ value needs to be related to the band structure and the added performance enhancers (Figure 3a). As discussed above, $E_{FB}$ is close to $E_{FG}$ in the pristine and 0.2% Cr-added ZnO ceramics, yielding small α values. When...
adding the performance enhancers in ZnO, shallow donor levels form near the bottom of the conduction band of the grains, thus raising $E_{\text{FG}}$, $\phi_B$, and $\alpha$.

To probe the shallow donor levels in the grains, we performed temperature-dependent dc conductivity measurements. The activation energy ($E_a$) is estimated by fitting the experimental data for the dc conductivity to the Arrhenius relation $\sigma(T) = \sigma_0 e^{-E_a/kT}$, where $\sigma_0$ is a constant, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. As shown in Figure 3b and Figure S7, the high-temperature $\sigma$ data (373–473 K) and the low-temperature $\sigma$ data (below 253 K) point toward two distinct $E_a$ values, hereafter termed $E_{aL}$ and $E_{aH}$ respectively. With the composition varying from ZnO-0.1% Cr$_2$O$_3$ to Ca-doped ZnO-0.1% Cr$_2$O$_3$, to (Ca, Co)-doped ZnO-0.1% Cr$_2$O$_3$, and finally to (Ca, Co, Sb)-doped ZnO-0.1% Cr$_2$O$_3$, $E_{aL}$ and $E_{aH}$ evolve with opposite trends: $E_{aH}$ systematically increases (cf. Figure 3b), whereas $E_{aL}$ systematically decreases (Figure S7b). The decreasing $E_{aL}$ indicates that the donor level becomes shallower in the band gap. Notably, the dc conductivities are nearly temperature independent at $T < 253$ K for (Co, Ca)-ZnO-0.1% Cr$_2$O$_3$ and (Co, Ca, Sb)-ZnO-0.1% Cr$_2$O$_3$, suggesting that the Fermi levels of the grain $E_{\text{FG}}$ in these two compositions shift into the conduction band with practically zero activation energy. The $E_{\text{FG}}$ value is enhanced with an increasing number of dopants (enhancers). The increasing $E_{\text{FG}}$ value helps increase the $\phi_B$ and $\alpha$ values (Figure 2d) and substantiates the band-structure diagram plotted in Figure 3a. More supporting evidence will be provided in the following.

The high-temperature dc conductivities are known to be sensitive to $\phi_B$.34 The results, including the fitted high-temperature activation energy $E_{aH}$, are presented in Figure 3b. The $E_{aH}$ value is proportional to $\phi_B$, i.e., $|E_{\text{FG}} - E_{\text{BL}}|$34. The $E_{aH}$ value of the (Co, Ca)-codoped ZnO ceramic is found to be 0.14 eV, similar to that of pristine ZnO, as shown in Figure S8. This implies that the $E_{\text{FG}}$ and $E_{aH}$ values are close, giving rise to a very weakly nonlinear $I$–$V$ behavior (Figure S9). These results also indicate that Ca and Co are not effective varistor formers. In contrast, the $E_{aH}$ value for the ZnO-1% Cr$_2$O$_3$ ceramic is 0.43 eV, significantly higher than that of ZnO and (Co, Ca)-doped ZnO. Thus, Cr is an effective varistor former. The $E_{aH}$ value is further increased to 0.82 eV in Co-ZnO-0.1% Cr$_2$O$_3$, to 0.93 eV in (Co, Ca)-ZnO-0.1% Cr$_2$O$_3$, and to 0.95 eV in (Co, Ca, Sb)-ZnO-0.1% Cr$_2$O$_3$. The $E_{aH}$ value can also be cross-checked by decomposing the high-temperature complex impedance $Z^*$ into the grain resistance $R_g$ and the GB resistance $R_b$ and fitting the temperature dependence of $R_b$ into the Arrhenius model (Figure S10). As shown in Figure 3c, the $E_{aH}$ values derived from the high-temperature dc conductivities and high-temperature impedance spectra agree well with each other.

All of the results presented and discussed in the last two paragraphs thus support the schematic diagram shown in Figure 3a, in which $\phi_B$ is significantly enhanced with an increasing number of dopants (enhancers). The systematically enhanced Schottky barrier height is further confirmed by the results from scanning Kelvin probe microscopy (Figure 3d and Figure S11). The surface potential across the GBs in ZnO-0.1% Cr$_2$O$_3$ is low and under the detection limit, but it quickly

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Figure 3. Evolution of the band structure, double-Schottky barrier height, high-temperature excitation energy, and surface potential of ZnO-based varisters with former Cr and enhancers Ca, Co, and Sb. (a) Schematic diagram of the DSB and band structure. (b) High-temperature dc conductivities vs. temperature. Solid lines are the fit to the Arrhenius model. Derived high-temperature activation energy $E_{aH}$ values are labeled. (c) $E_{aH}$ derived from the dc electrical conductivities (purple) and GB resistances (green). (d) Surface potentials. (Inset) Line-scan profile of the surface potential of (Co, Ca)-ZnO-0.1% Cr$_2$O$_3$. The results, including the fitted high-temperature activation energy $E_{aH}$, are presented in Figure 3b. The $E_{aH}$ value is proportional to $\phi_B$, i.e., $|E_{\text{FG}} - E_{\text{BL}}|$34. The $E_{aH}$ value of the (Co, Ca)-codoped ZnO ceramic is found to be 0.14 eV, similar to that of pristine ZnO, as shown in Figure S8. This implies that the $E_{\text{FG}}$ and $E_{aH}$ values are close, giving rise to a very weakly nonlinear $I$–$V$ behavior (Figure S9). These results also indicate that Ca and Co are not effective varistor formers. In contrast, the $E_{aH}$ value for the ZnO-1% Cr$_2$O$_3$ ceramic is 0.43 eV, significantly higher than that of ZnO and (Co, Ca)-doped ZnO. Thus, Cr is an effective varistor former. The $E_{aH}$ value is further increased to 0.82 eV in Co-ZnO-0.1% Cr$_2$O$_3$, to 0.93 eV in (Co, Ca)-ZnO-0.1% Cr$_2$O$_3$, and to 0.95 eV in (Co, Ca, Sb)-ZnO-0.1% Cr$_2$O$_3$. The $E_{aH}$ value can also be cross-checked by decomposing the high-temperature complex impedance $Z^*$ into the grain resistance $R_g$ and the GB resistance $R_b$ and fitting the temperature dependence of $R_b$ into the Arrhenius model (Figure S10). As shown in Figure 3c, the $E_{aH}$ values derived from the high-temperature dc conductivities and high-temperature impedance spectra agree well with each other.

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increases to about 5 mV in Ca-doped ZnO-0.1% Cr2O3, to 14 mV in (Co, Ca)-doped ZnO-0.1% Cr2O3, and finally to 35 mV in (Co, Ca, Sb)-ZnO-0.1% Cr2O3, consistent with the trend in the variation of $E_{\text{av}}$.

**CONCLUSIONS**

A novel type of ZnO-based varistor ceramic with Cr as the varistor former and Ca, Co, and Sb as performance enhancers was discovered with simultaneously an ultrahigh nonlinear coefficient, a high breakdown voltage, and a low leakage current, superior to all of the state-of-the-art varistor ceramics, including the existing ZnO-based ones. The breakthrough is not only in the varistor’s performance but also in terms of the materials sustainability in terms of chemical stability, being environmental friendly, and having low cost. Specifically, the element Cr at the GBs as a varistor former and the proper performance enhancers (Ca, Co, Sb) doped in the grain work in tandem to yield a record-high varistor performance for the novel ZnO-Cr2O3 type of varistor ceramics.

The discovery of a novel ZnO-Cr2O3-type varistor ceramic represents the first such major breakthrough in the field of overvoltage protection after several decades that were dominated by the ZnO-Bi2O3-based ceramics. The results also provide insights into the design of the material and the development of nonlinear varistor ceramics with enhanced performance.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c07735.

Additional characterization of Zn$_{1-x}$Cr$_x$O$_{1.525}$, (Co, Ca, Sb)-ZnO-0.1% Cr$_2$O$_3$, and (Co, Ca)-ZnO-0.1% Cr$_2$O$_3$; additional electrical properties of ZnO-0.1% Cr$_2$O$_3$, Ca-ZnO-0.1% Cr$_2$O$_3$, (Co, Ca)-ZnO-0.1% Cr$_2$O$_3$, (Co, Ca, Sb)-ZnO-0.1% Cr$_2$O$_3$, Cr$_2$O$_3$, ZnO, and (Co, Ca)-ZnO; surface potential images by AFM for (Co, Ca)-ZnO-0.1% Cr$_2$O$_3$, (Co, Ca)-ZnO, and ZnO-Cr$_2$O$_3$ ceramics (PDF).

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**AUTHOR CONTRIBUTIONS**

G.L. supervised the research. X.S. analyzed the data and participated in the manuscript preparation. S.B. designed the experiments. T.T. conducted the experiments, interpreted data, and wrote the manuscript. L.Z. assisted in analyzing the data. M.P. and X.R. assisted in synthesizing the samples. H.Z. and K.X. characterized and analyzed the surface potential data. All authors reviewed and commented on the manuscript.

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**REFERENCES**

(1) Wang, Z.; Nelson, J. K.; Hillborg, H.; Zhao, S.; Schadler, L. S. Graphene Oxide Filled Nanocomposite with Novel Electrical and Dielectric Properties. *Adv. Mater.* 2012, 24, 3134–3137.

(2) Guo, J.; Zhao, X.; Herisson De Beauvoir, T.; Seo, J.-H.; Berbano, S. S.; Baker, A. L.; Azina, C.; Randall, C. A. Recent Progress in Applications of the Cold Sintering Process for Ceramic-Polymer Composites. *Adv. Funct. Mater.* 2018, 28, 1801724.

(3) Macary, L. S.; Kain, M. L.; Estournès, C.; Fau, P.; Trémouilles, D.; Bafleur, M.; Renaud, P.; Chaudret, B. Size Effect on Properties of Varistors Made From Zinc Oxide Nanoparticles Through Low Temperature Spark Plasma Sintering. *Adv. Funct. Mater.* 2009, 19, 1775.

(4) Raidl, N.; Supancic, P.; Danzer, R.; Hofstatter, M. Piezotronically Modified Double Schottky Barriers in ZnO Varistors. *Adv. Mater.* 2015, 27, 2031–2035.

(5) Chung, S. Y.; Kim, J. D.; Kang, S. J. Strong Nonlinear Current-Voltage Behaviour in Perovskite-Derivative Calcium Copper Titanate. *Nat. Mater.* 2004, 3, 774–778.

(6) Clarke, D. R. Varistor Ceramics. *J. Am. Ceram. Soc.* 1999, 82, 485–502.

(7) Zhao, H.; He, J.; Hu, J.; Chen, S.; Xie, Q. High Nonlinearity and Low Residual-Voltage ZnO Varistor Ceramics by Synchronously Doping Ga$_2$O$_3$ and Al$_2$O$_3$. *Mater. Lett.* 2016, 164, 80–83.
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(8) Ma, S.; Xu, Z.; Chu, R.; Hao, J.; Liu, M.; Cheng, L.; Li, G. Influence of Cr$_2$O$_3$ on ZnO-Bi$_2$O$_3$-MnO$_2$-Based Varistor Ceramics. *Ceram. Int.* 2014, 40 (7), 10149–10152.

(9) Beynet, Y.; Izoulet, A.; Guillemet-Fritsch, S.; Chevallier, G.; Bley, V.; Pérèl, T.; Malprice, F.; Morel, J.; Estournès, C. ZnO-Based Varistors Prepared by Spark Plasma Sintering. *J. Eur. Ceram. Soc.* 2015, 35, 1199–1208.

(10) Badev, A.; Mariné, S.; Heuguet, R.; Savary, E.; Agraydaw, D. Sintering Behavior and Non-linear Properties of ZnO Varistors Processed in Microwave Electric and Magnetic Fields at 2.45 GHz. *Acta Mater.* 2013, 61, 7849–7858.

(11) Nahm, C. W.; Park, C. H. Effect of Er$_2$O$_3$ Addition on the Microstructure, Electrical Properties, and Stability of Pr$_2$O$_3$-Based ZnO Ceramic Varistors. *J. Mater. Sci.* 2001, 36, 1671–1679.

(12) Nahm, C. W. Microstructure and Electrical Properties of ZnO–V$_2$O$_5$–MnO$_2$–Co$_2$O$_3$–Dy$_2$O$_3$–Nb$_2$O$_5$-Based Varistors. *J. Alloys Compd.* 2010, 490, L52–L54.

(13) Xu, D.; Cheng, X.-n.; Yan, X.-h.; Xu, H.-x.; Shi, L.-y.T. Sintering Process as Relevant Parameter for Bi$_2$O$_3$ Vaporization from ZnO–Bi$_2$O$_3$-Based Varistor Ceramics. *Trans. Nonferrous Met. Soc. China* 2009, 19, 1526–1532.

(14) Xu, D.; Cheng, X.; Yuan, H.; Yang, J.; Lin, Y. Microstructure and Electrical Properties of Y(NO$_3$)$_3$·6H$_2$O-Doped ZnO–Bi$_2$O$_3$-Based Varistor Ceramics. *J. Alloys Compd.* 2011, 509, 9312–9317.

(15) Izoulet, A.; Guillemet-Fritsch, S.; Estournès, C.; Morel, J. Microstructure Control to Reduce Leakage Current of Medium and High Voltage Ceramic Varistors Based on Doped ZnO. *J. Eur. Ceram. Soc.* 2014, 34, 3707–3714.

(16) Zhao, H.; Hu, J.; Chen, S.; Xie, Q.; He, J. Tailoring the High-Impulse Current Discharge Capability of ZnO Varistor Ceramics by Doping with Ga$_2$O$_3$. *Ceram. Int.* 2016, 42, 5582–5586.

(17) Xiao, X. K.; Zheng, L. Y.; Cheng, L. H.; Tian, T.; Ruan, X. Z.; Li, G. R. Effect of Cr$_2$O$_3$ on the Property and Microstructure of ZnO–Bi$_2$O$_3$ Varistor Ceramics in Different Sintering Temperature. *Ceram. Int.* 2015, 41, 5557–5562.

(18) Long, W.; Hu, J.; Liu, J.; He, J. Effects of Cobalt Doping on the Electrical Characteristics of Al-Doped ZnO Varistors. *Mater. Lett.* 2010, 64, 1081–1084.

(19) Park, J.-A. Effect of Al$_2$O$_3$ on the Electrical Properties of ZnO–Pr$_2$O$_3$-Based Varistor Ceramics. *Phys. B* 2008, 463, 639–643.

(20) Feng, H.; Peng, Z.; Fu, X.; Fu, Z.; Wang, C.; Qi, L.; Miao, H. Effect of SnO$_2$ Doping on Microstructural and Electrical Properties of ZnO–Pr$_2$O$_3$-Based Varistor Ceramics. *J. Alloys Compd.* 2011, 509, 7175–7180.

(21) Feng, H.; Peng, Z.; Fu, X.; Fu, Z.; Wang, C.; Qi, L.; Miao, H. Effect of TiO$_2$ Doping on Microstructural and Electrical Properties of ZnO–Pr$_2$O$_3$-Based Varistor Ceramics. *J. Alloys Compd.* 2010, 497, 304–307.

(22) Peng, Z.; Fu, X.; Zang, Y.; Fu, Z.; Wang, C.; Qi, L.; Miao, H. Influence of Fe$_2$O$_3$ Doping on Microstructural and Electrical Properties of ZnO–Pr$_2$O$_3$-Based Varistor Ceramic Materials. *J. Alloys Compd.* 2010, 508, 494–499.

(23) Pandey, S.; Kumar, D.; Parkash, O. Electrical Impedance Spectroscopy and Structural Characterization of Liquid-Phase Sintered ZnO–V$_2$O$_5$–Nb$_2$O$_5$ Varistor Ceramics Doped with MnO. *Ceram. Int.* 2016, 42, 9686–9696.

(24) Hng, H. H.; Chan, P. L. Cr$_2$O$_3$ Doping in ZnO–0.5 mol% V$_2$O$_5$ Varistor Ceramics. *Ceram. Int.* 2009, 35, 409–413.

(25) Hng, H. H.; Chan, P. L. Microstructure and Current–Voltage Characteristics of ZnO–V$_2$O$_5$–MnO$_2$ Varistor System. *Ceram. Int.* 2004, 30, 1647–1653.

(26) Kumar, S.; Tiwari, N.; Jha, S. N.; Chatterjee, S.; Bhattacharyya, D.; Ghosh, A. K. Structural and Optical Properties of Sol–Gel Derived Co-Doped ZnO Diluted Magnetic Semiconducting Nanocrystals: An EXAFS Study to Relate the Local Structure. *RSC Adv.* 2016, 6, 107816–107828.

(27) Carlsson, J.; Domingos, H.; Bristow, P.; Hellsing, B. An Interfacial Complex in ZnO and Its Influence on Charge Transport. *Phys. Rev. Lett.* 2003, 91, 165506.