Short Communication

Improved Direct-Current Aging Stability and Suppressed Leakage Current of Zinc Oxide Varistors by Co-doping with Boron, Gallium, and Yttrium

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Abstract

The effect of B³⁺, Ga³⁺ and Y³⁺ co-doping on the microscopic and electrical properties of ZnO varistors is studied. Co-doping with multiple ions greatly improves the comprehensive performance of the ZnO varistors. The doped Ga³⁺ increases the acceptor concentration, raises the barrier height, and inhibits the increase of leakage current. Y³⁺ increases the voltage gradient by limiting the growth of grains. B³⁺ improves the resistance of ZnO varistors to direct-current aging. The varistor with a B³⁺ content of 0.2 mol% achieves a voltage gradient of 450 V/mm, leakage current of 0.54 A/cm², and a nonlinear coefficient of 79. Accelerated aging experiments carried out for 1 000 h at 0.9 U₁mA and 115 °C give an aging coefficient of 0.027. This research illustrates the ability of cation co-doping to improve the protection effect of metal oxide arrestors and the stability of power systems that operate at ±1100 kV.

Keywords: Ceramic, varistor, electrical properties, DC aging, aging coefficient

I. Introduction

With the development of economic globalization, the demand for electricity is rapidly increasing. However, the uneven distribution of the world’s energy generation and use requires ultra-high voltage (UHV) direct-current (DC) technology for long-distance and large-capacity transmission across regions and countries. The construction of ±1100-kV UHV DC technology raises the requirements for the safe and stable operation of power grids. The arrester plays an irreplaceable role in the safe and stable operation of a power grid, especially in the suppression of operating and lightning overvoltages. The varistor is an important part of the arrester that determines the protection performance of arresters. Because of their high non-linearity and energy absorption capacity, zinc oxide (ZnO) varistors are used extensively as surge protectors in power systems. In DC power systems, the arrester is constantly subjected to DC bias, which accelerates the aging process of ZnO varistors and seriously lowers their protection performance, posing a severe potential risk to the safe and stable operation of power grids. Therefore, it is particularly important to improve the aging stability of DC ZnO varistors. The leakage current of the ZnO varistor directly affects the service life of the arrester, which has potential risks for the safe and stable operation of the power system. Rare earth elements can be introduced to improve the other properties of arrestors, but it is necessary to restrain the increase of leakage current. Doping a ZnO varistor with boron oxide (B₂O₃) improved its stability and suppressed leakage current. However, the co-doping of ZnO varistors with boron (B³⁺), gallium (Ga³⁺), and yttrium (Y³⁺) has not been investigated. In this study, the effects of B³⁺, Ga³⁺, and Y³⁺ co-doping on the electrical properties of ZnO varistors are studied in detail.

II. Experimental Procedure

High-performance DC ZnO varistor samples were prepared using the following raw materials: (94-x) mol% ZnO, 1.0 mol% Bi₂O₃, 0.75 mol% MnO₂, 1.0 mol% Co₂O₃, 0.5 mol% Cr₂O₃, 1.0 mol% Sb₂O₃, 1.2 mol% SiO₂, 0.45 mol% Y₂O₃, 0.1 mol% Ga₂O₃, and x mol% B₂O₃ (x = 0.1, 0.2, 0.3, or 0.4 mol%). The mixed raw materials and an appropriate amount of deionized water were placed in a micro-nanopowder dispersion mill to give a ratio of raw materials to water of 2:3. Polyvinyl alcohol (400 mL) and dispersant (150 g) were added and then ball milling was carried out for 11 – 12 h to uniformly disperse the raw materials. The resulting slurry was spray granulated and then the powder was pressed at 400 MPa to form a disk with a diameter of 30 mm and thickness of 2.0 mm. The disks were heated at a rate of 5 °K/min to 1200 °C,
sintered for 3 h in a furnace (Nabertherm LH60/14, Germany), and then cooled in air at a rate of 2 °K/min. The surfaces of the sintered varistors were polished, coated with silver paste, and then sintered at 550 °C for 2 h to obtain an electrode. Scanning electron microscopy (SEM; Hitachi 8010, Japan) was used to observe the surface microstructure of the samples. A source meter (Keithley 2410, USA) was used to measure the electric field–current density (E–J) relationship of the sample in the pre-breakdown region. The breakdown electric field ($E_{1mA}$) was measured at $J = 1.0 \text{ mA/cm}^2$ and the leakage current density ($J_L$) was measured at a breakdown electric field of 0.75 $E_{1mA}$. The following formula was used to calculate the non-linear coefficient $\alpha$: $\alpha = \frac{\log I_2 - \log I_1}{\log E_2 - \log E_1}$. A broadband dielectric device (Novocontrol Concept 80, Germany) was used to measure the capacitance–voltage (C–V) characteristics of the varistors at 1 kHz. X-ray diffraction (XRD; Rigaku H/max 2500, Japan) was used to analyze the crystal phase composition of the varistors.

### III. Results and Discussion

Fig. 1 shows an SEM image of varistors with $\text{B}_2\text{O}_3$ content of 0.1 – 0.4 mol%. The average particle diameter ($d$) of the ZnO varistors doped with different concentrations of $\text{B}^{3+}$ was measured with the linear intercept method and the results are listed in Table 1. With increasing $\text{B}^{3+}$ concentration, $d$ decreased only slightly, indicating that the $\text{B}^{3+}$ doping concentration had little effect on the grain size of ZnO.

![Fig. 1: Scanning electron microscopy images of ZnO varistors prepared with various concentrations of B: (a) 0.1, (b) 0.2, (c) 0.3, and (d) 0.4 mol%.

<table>
<thead>
<tr>
<th>$\text{B}_2\text{O}_3$ concentration (mol%)</th>
<th>$d$ (µm)</th>
<th>$N_d$ ($\times 10^{23}$ m$^{-3}$)</th>
<th>$\varphi_b$ (eV)</th>
<th>$N_i$ ($\times 10^{16}$ m$^{-2}$)</th>
<th>$E_{1mA}$ (V/mm)</th>
<th>$J_L$ (µA/cm$^2$)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>6.7</td>
<td>1.5</td>
<td>2.05</td>
<td>1.7</td>
<td>410</td>
<td>1.2</td>
<td>66</td>
</tr>
<tr>
<td>0.2</td>
<td>6.5</td>
<td>2.1</td>
<td>2.79</td>
<td>2.4</td>
<td>450</td>
<td>0.54</td>
<td>79</td>
</tr>
<tr>
<td>0.3</td>
<td>6.3</td>
<td>1.9</td>
<td>2.38</td>
<td>2.0</td>
<td>438</td>
<td>0.68</td>
<td>73</td>
</tr>
<tr>
<td>0.4</td>
<td>6.1</td>
<td>1.6</td>
<td>2.14</td>
<td>1.8</td>
<td>425</td>
<td>0.86</td>
<td>69</td>
</tr>
</tbody>
</table>
The $E$-$J$ characteristics of the ZnO varistors are shown in Fig. 2. The parameters calculated from the $E$-$J$ curves, such as $E_{1\text{mA}}/J$, and $\alpha$, are summarized in Table 1. Within the $\text{B}_2\text{O}_3$ range of 0.1 to 0.4 mol%, as the $\text{B}^3+$ doping concentration increased, $E_{1\text{mA}}$ and $\alpha$ first increased and then decreased, whereas $J_{1\text{mA}}$ showed the opposite behavior. When the $\text{B}_2\text{O}_3$ doping content was 0.2 mol%, the maximum $E_{1\text{mA}}$ of the samples of 450 V/mm was obtained, along with an $\alpha$ of 79 and $J_{1\text{mA}}$ of 0.54 $\mu$A/cm$^2$. An $E_{1\text{mA}}$ value of 450 V/mm is suitable for ±1100-kV UHV power systems and will allow the size of the arrester to be substantially reduced and its internal structure to be optimized to make the potential distribution more uniform. Suppressing leakage current helps to improve the long-term stability of ZnO arresters. The $J_{1\text{mA}}$ is lower than that of 1 $\mu$A/cm$^2$, which is even lower than that of 1 $\mu$A/cm$^2$, which improved the stability of arrestors greatly, and consequently the operation stability of ±1 100-kV UHV power systems.

To investigate the Schottky barrier in the ZnO varistors, the voltage dependence of the measured capacitance was measured; the results are shown in Fig. 3. The donor concentration $N_d$, barrier height $\varphi_b$, and interface state concentration $N_i$, calculated from the C-V curves are summarized in Table 1. These parameters were calculated from the C-V equation:

$$\varphi_b = eN_i^2/2N_d\varepsilon\varepsilon_0$$  \hspace{1cm}(1)

Eq. (1) shows that the Schottky barrier is a comprehensive result of the interaction between $N_i$ and $N_d$ at the ZnO grain interface. The maximum potential voltage of 2.79 V was obtained for the ZnO varistor with 0.2 mol% $\text{B}^3+$. At finite $\varphi_b$, the higher the potential barrier of the ZnO varistor, the greater the $E_{1\text{mA}}$.

It is noteworthy that the trend of $\varphi_b$ is consistent with that of $\alpha$, which is opposite to the trend of $J_{1\text{mA}}$ in Table 1. In the $\text{Ga}^3+$ doping range of 0.1 to 0.2 mol%, rare-earth $\text{Ga}^3+$ behaves as a donor ion and affects both $N_i$ and $N_d$, but the increase of $N_i$ is much larger than that of $N_d$. Eq. (1) reveals that $\text{Ga}^3+$ doping increases $\varphi_b$ of the varistor.

The liquid-phase sintering time of the ZnO-$\text{Bi}_2\text{O}_3$ system can be prolonged by the low melting point of $\text{Bi}_2\text{O}_3$ ($450$ °C) 9, which promotes ion exchange between ZnO grains and other additives at grain boundaries, allowing more $\text{Ga}^3+$ to enter the grains and further raise $\varphi_b$. The increase of $\varphi_b$ inhibits the increase of leakage current. The nonlinear effect of ZnO varistors is controlled by the $\varphi_b$. Therefore, an increase in $\varphi_b$ contributes to an increase of $\alpha$. The increase of $\alpha$ is beneficial to improve the protection properties of arrestors under all kinds of impulse current, so the operational stability of the grid is improved. Within the $\text{B}^3+$ concentration range of 0.2 to 0.4 mol%, $\alpha$ and $E_{1\text{mA}}$ decreased with increasing $\text{B}_2\text{O}_3$ content, as shown in Table 1. Rare-earth $\text{Y}^3+$ mainly existed at grain boundaries to form the spinel phase, which limited the growth of ZnO grains through pinning effect and enhanced $E_{1\text{mA}}$. Meanwhile, the effect of $\text{Y}^3+$ on $N_d$ is greater than that on $N_i$, which can decrease the $\varphi_i$ and increase $J_{1\text{mA}}$. With increasing $\text{B}_2\text{O}_3$ content of the raw materials, the liquid-assisted sintering process became more effective. Because the $\text{Y}^3+$ doping content was higher than that of $\text{Ga}^3+$, more $\text{Y}^3+$ than $\text{Ga}^3+$ can dissolve into the ZnO particles, which decreases the thickness of the barrier layer. The decrease of $\varphi_b$ leads to decreases of $E_{1\text{mA}}$ and $\alpha$ and the increase of $J_{1\text{mA}}$.

To determine the stability of the co-doped ZnO varistors in a UHV DC transmission system, an accelerated aging test for 1000 h at 0.9 $E_{1\text{mA}}$ and 115 °C was used to verify the DC anti-aging performance of the varistor doped with 0.2 mol% $\text{B}^3+$. The results of the aging test are shown in Fig. 4. The DC accelerated aging curve rapidly increased to the maximum power loss and then slowly decreased. After a DC voltage had been applied for about 45 h, the curve began to flatten. The gentle aging curve indicated that the power loss of the sample was stable. The sample operated for a long time without thermal collapse at a working voltage of 0.9 $E_{1\text{mA}}$. In an evaluation of the aging properties of varistors, the degradation rate coefficient ($K_t$) is usually determined using the following equation:

$$K_t = \frac{I_t - I_{10}}{\sqrt{t}}$$  \hspace{1cm}(2)
where $I_{L0}$ is the leakage current at $T = 0$. A lower $K_t$ indicates a varistor has higher stability. $K_t$ calculated for the ZnO varistor doped with 0.2 mol% B$^{3+}$ is 0.027. This value indicated that B$^{3+}$ doping greatly improved the aging resistance of DC ZnO varistors. Because the ionic radius of B$^{3+}$ is 0.027 nm smaller than that of a zinc ion (Zn$^{2+}$; 0.074 nm), a small amount of B$^{3+}$ can penetrate into the ZnO grains and occupy the interstitial position, which reduces the concentration of interstitial Zn$^{2+}$ 20,21. B$^{3+}$ doped into the ZnO crystals during the high-temperature sintering process formed a glass phase at the grain boundary, which decreased the content of grain boundary defects, effectively inhibiting the migration of interstitial Zn ions and suppressing the distortion of the Schottky barrier 22. The prepared samples can further lower the Zn$^{2+}$ concentration in the gap by means of high-temperature heat treatment 20. The defect reactions can be expressed by the following equations 20:

$$V_O^X + O = O_O^-$$ (3)

$$O_O^X + V_Zn = O_O^X + V_Zn^-$$ (4)

$$Zn^{2+} + V_Zn = V_Zn^- + Zn^{2+}$$ (5)

$$Zn^{2+} + O^O = ZnO$$ (6)

The XRD patterns of ZnO varistor samples doped with different B$^{3+}$ content are shown in Fig.5. The patterns indicated that the varistors mainly contained ZnO, spinel, willemite, Bi$_2$O$_3$, and BiO$_2$ phases. Only a small amount of willemite ($b = 56.004, d = 1.6406$ nm) was observed in the XRD patterns. No new phases were observed, and the peak intensity was low because of the small amount of B$^{3+}$ doped in the samples.

### IV. Conclusions

DC ZnO varistors with co-doped B$^{3+}$, Ga$^{3+}$, and Y$^{3+}$ were fabricated. These varistors displayed a high gradient, low leakage, and strong DC aging resistance. The ZnO varistor with a B$^{3+}$ content of 0.2 mol% displayed the highest performance of the varistors studied, with an $E_{1mA}$ of 450 V/mm, $\alpha$ of 79, $J_L$ of 0.54 A/cm$^2$, and $K_t$ of 0.027. The high $E_{1mA}$, small $J_L$, high non-linearity, and stable aging performance of the DC ZnO varistor studied in this paper is of great significance for the safe and stable operation of ±1100-kV UHV power systems.

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### References


