Electrical Behavior against Current Impulse in ZnO Varistor Ceramics with SiO$_2$ Addition

Bowen Wang$^1$, Zhen Fang$^1$, Zhiyao Fu$^2$ and Yongjing Peng$^1$

$^1$State Key Laboratory of Disaster Prevention & Reduction for Power Grid Transmission and Distribution Equipment, State Grid Hunan Electric Power Company Disaster Prevention and Reduction Center, Changsha 410129, China.

$^2$State Key Laboratory of Advanced Electromagnetic Engineering and Technology, Huazhong University of Science and Technology, Wuhan 430074, Hubei, China

Email: bowen_wm@163.com

Abstract. SiO$_2$ addition effect on electrical behaviour against current impulse in the ZnO varistors was investigated. SiO$_2$ acts as a controller in ZnO grain growth, decreasing the grain size of ZnO from 8.87 to 5.86 μm, which in turn results in an increase in breakdown voltage $E_{1mA}$ from 192.77 to 252.57 V/mm. SiO$_2$ has a significant influence on the current energy withstand capability and impulse aging characteristics. The results indicated that the SiO$_2$ content was optimized at 1.5 mol%, exhibiting the best energy withstand capability of 332.03 J/cm$^3$ and clamping ratio of 1.71.

1. Introduction
Zinc oxide resistors are widely used as key components in the power systems to limit overvoltage and absorb energy owing to their high nonlinearity and rapid response to transient pulses or lightning strikes [1]. In varistor applications, surge current characteristic is one of the most important factors to consider in an application. The lifetime of zinc oxide varistor for lightning protection of power systems generally requires more than 10 years. However, after many lightning strikes, its lifetime will be significantly reduced, affecting the line lightning protection [2]. At the same time, the varistor need to withstand a large amount of energy under lighting strikes, and the energy handling capability of the varistor is also related to its protective effect on the line [3]. Therefore, the electrical stability against surge impulse and energy handling ability are technologically very important characteristics of ZnO varistors. The energy handling capability is usually referred to the permitted energy absorbed by a varistor under different impulses, measured in J/cm$^3$. In this work, Electrical behavior against current impulse in ZnO varistor ceramics with with SiO$_2$ content was investigated.

2. Experimental Procedures

2.1. Sample Preparation
Preparation of submicron varistor powder using analytically pure materials by conventional solid state reaction techniques in the following molar ratios: (96.09% - x) ZnO, 1.0% Bi$_2$O$_3$, 1.0% Sb$_2$O$_3$, 0.8% Co$_2$O$_3$, 0.35% Cr$_2$O$_3$, 0.75% MnO$_2$, x % SiO$_2$, 0.01% Al(NO)$_3$$\cdot$9H$_2$O. After grinding in a high speed ball mill for 3 hours with deionized water, the slurry mixture was converted to a dry powder by and centrifugal spray drying. The powders were compacted into disks at 80 MPa. And the organic binder (PVA) added to the mixtures was removed at 600 °C. The compacts were sintered at 1150 ºC and then cooled with a cooling rate of 2 °C /min to 850 °C. Then naturally cooled in the furnace to room
temperature. The surface electrodes are aluminum electrode sprayed up. The final discs were with a diameter of 30 mm and a thickness of 20 mm. The average grain size \((d)\) was determined by the lineal intercept method, given by 
\[ d = 1.56L/MN, \]
where \(L\) is the random line length on the micrograph, \(M\) is the magnification of the micrograph, and \(N\) is the number of the grain boundaries intercepted by the lines [4]. The sintered density \((r)\) of ceramics was measured by the Archimedes method.

2.2. Electrical Measurement

The electric field–current density \((E–J)\) characteristics were measured using a V–I source. \(u_{\text{bma}}\) defined as the breakdown voltage is the voltage of the varistor when the current is 1.0 mA. The \(E_{\text{bma}}\) defined as the breakdown field was the breakdown voltage at a unit height measured when the current density is 1.0 mA and the leakage current density \((J_{l})\) was measured when the voltage is 0.75 \(u_{\text{bma}}\). In addition, the nonlinear coefficient \((\alpha)\) is defined by follows

\[
\alpha = \frac{\log J_{2} - \log J_{1}}{\log u_{2} - \log u_{1}} \tag{1}
\]

where \(u_{1}\) and \(u_{2}\) are the electric fields when the current density is \(J_{1}=0.1\) mA/cm\(^2\) and \(J_{2}=1\) mA/cm\(^2\), respectively. The clamping voltage \((u_{c})\) was measured at a single pulse current of 5000 A with 8/20 \(\mu\)s waveform. The clamp voltage ratio is defined by the ratio of clamping voltage to breakdown voltage.

\[
K = \frac{u_{c}}{u_{\text{bma}}} \tag{2}
\]

2.3. Impulse Stress Test

The impulse aging stress test was performed under the current value of 2000, 5000, 10000 A with the 8/20 \(\mu\)s current waveform, which generating from impulse current generator. Each pulse current with continuously 3 times is applied to the samples. The interval of each impulse is 2 min. The V–I characteristics were measured at room temperature after the impulse stress test. The experiment of single-impulse is carried out to acquire the energy handling capability of varistor. The waveform is 2ms square wave, which is the standard current for the varistor applying to Power system [5]. The failure criterion is shown in reference [6]. The impulse failure energies \(J_{f}\) \((\text{J/cm}^2)\) is acquired under different SiO\(_2\) content.

3. Results and Discussion

![Figure 1. SEM images of polished and etched fracture surfaces for all the samples. The diagrams of grain size distribution are in left-upper insets.](image-url)
Fig. 1 shows SEM micrographs of the samples for different ZnO contents. The average grain size \((d)\) decreased with increasing SiO\(_2\) content. The sintered density \((r)\) for the samples decreased in the order of 5.50, 5.48, 5.46, 5.44, 5.42 g/cm\(^3\) (theoretical density 5.78 g/cm\(^3\) for ZnO). Therefore, the SiO\(_2\) content in the study for this composition significantly modified the densification process.

The most important electrical parameters obtained from the E–J characteristics, including breakdown field \((E_{\text{imp}})\), leakage current \((I_l)\), and nonlinear coefficient \((\alpha)\), are summarized in Table 1. When the SiO\(_2\) range from 0.2 mol% to 2.0 mol%, the breakdown voltage \(E_{\text{imp}}\) from 192.77 to 252.57 V/mm, the leakage current and nonlinear did not show linear changes with the SiO\(_2\) content, which ranged from 1.43 \(\mu\)A/cm\(^2\) to 2.95 \(\mu\)A/cm\(^2\) and from 41.20 to 29.40 respectively. The impulse failure energies \(J_f\) decreased from 332.03J/cm\(^2\) to 244.21 J/cm\(^2\). The clamp voltage ratio \(K\) is range from 1.80 to 1.71. The experimental results indicate that the energy handling capability of varistors doped with 1.5 mol% SiO\(_2\) is the largest. While, the varistors doped with 0.5 mol% SiO\(_2\) has the minimum energy tolerance.

### Table 1. Microstructure and E–J parameters of the samples for different amounts of SiO\(_2\)

| Sample | \(d(\mu m)\) | \(r(\text{g/cm}^3)\) | \(V_{\text{imp}}(V)\) | \(J_l(\mu\text{A/cm}^2)\) | \(\alpha\) | \(J_f (\text{J/cm}^2)\) | \(K\) |
|--------|-------------|----------------|----------------|----------------|-------|----------------|-----|
| 0.2mol% | 8.87        | 5.50           | 192.77         | 2.49           | 36.98 | 319.68         | 1.80 |
| 0.5mol% | 7.79        | 5.48           | 219.33         | 1.43           | 41.20 | 244.21         | 1.75 |
| 1.0mol% | 7.45        | 5.46           | 246.77         | 2.95           | 29.40 | 304.80         | 1.76 |
| 1.5mol% | 6.69        | 5.44           | 252.57         | 2.11           | 38.70 | 332.03         | 1.71 |
| 2.0mol% | 5.86        | 5.42           | 250.84         | 3.05           | 34.30 | 294.17         | 1.73 |

**Figure 2.** E–J characteristics of the samples with different SiO\(_2\) contents before and after applying the higher current impulses

Fig. 2 shows E–J characteristics before and after applying the higher current impulses of 2000 A, 5000 A, 10000A for the varistors doped with different SiO\(_2\). When a current impulse ranges from 2000 A to 10000A, the varistor doped with 1.0 mol% SiO\(_2\) exhibited a smaller E–J characteristic variation than that of the varistor doped with other SiO\(_2\) content. The largest E–J characteristic variation under current impulse is the varistor doped with 0.5 mol%. Table 2 shows E–J characteristic variation after applying the current impulses of 2000 A, 5000 A and 10000A.
Table 2. Variations of Breakdown Field ($E_{inA}$), Nonlinear Coefficient ($\alpha$), and Leakage Current Density ($J_L$) after Applying the Impulse Stress (2000–10000A)

| Sample | current (A) | $E_{inA}$(V) | %Δ$E_{inA}$ | $J_L$(μA/cm$^2$) | %Δ$J_L$ | $\alpha$ | %Δ$\alpha$ |
|--------|-------------|--------------|-------------|-----------------|----------|---------|------------|
|        | Initial     | 192.77       | -           | 2.49            | -        | 36.98   | -          |
| 0.2mol%| 2000        | 181.23       | -5.99       | 4.02            | 61.45    | 21.00   | -43.21     |
|        | 5000        | 166.55       | -13.60      | 4.99            | 100.40   | 16.50   | -55.38     |
|        | 10000       | 150.15       | -22.11      | 6.93            | 178.31   | 14.16   | -61.71     |
|        | Initial     | 219.33       | -           | 1.43            | -        | 41.2    | -          |
| 0.5mol%| 2000        | 199.05       | -9.25       | 2.77            | 93.71    | 22.9    | -44.42     |
|        | 5000        | 184.32       | -15.96      | 4.44            | 210.49   | 17      | -58.74     |
|        | 10000       | 159.19       | -27.42      | 6.10            | 326.57   | 13.9    | -66.26     |
|        | Initial     | 246.77       | -           | 2.95            | -        | 29.40   | -          |
| 1.0mol%| 2000        | 232.31       | -5.86       | 4.72            | 60.00    | 20.70   | -29.59     |
|        | 5000        | 205.41       | -16.76      | 5.13            | 73.90    | 16.35   | -44.39     |
|        | 10000       | 206.32       | -16.39      | 6.80            | 130.51   | 15.55   | -47.11     |
|        | Initial     | 252.57       | -           | 2.11            | -        | 38.70   | -          |
| 1.5mol%| 2000        | 219.4        | -13.13      | 3.74            | 77.25    | 17.70   | -54.26     |
|        | 5000        | 211.60       | -16.22      | 5.69            | 169.67   | 15.65   | -59.56     |
|        | 10000       | 201.57       | -20.19      | 8.18            | 287.68   | 14.2    | -63.31     |
|        | Initial     | 250.84       | -           | 3.05            | -        | 34.3    | -          |
| 2.0mol%| 2000        | 225.33       | -10.17      | 3.47            | 13.77%   | 22      | -35.86     |
|        | 5000        | 202.65       | -19.21      | 3.74            | 22.62%   | 17.7    | -48.40     |
|        | 10000       | 197.54       | -21.25      | 5.13            | 68.20%   | 16.3    | -52.48     |

4. Conclusion
SiO₂ did have a significant effect on electrical behavior against current impulse. The best stability was obtained from the varistors doped with 1.0 mol% SiO₂, with %Δ$E_{inA}$= 16.39%, %Δ$J_L$=130.51, and %Δ$\alpha$=47.11 after applying the impulse stress of 10000 A. On the other hand, the varistors doped with 1.5 mol% SiO₂ exhibited the best energy withstand capability of 332.03J/cm³ and best clamping characteristics. Conclusively, SiO₂ content was optimized at 1.5 mol% in terms of the energy withstand capability and impulse aging characteristics.

5. Acknowledgements
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6. References
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