Fabrication and electrical characteristics of flash-sintered SiO$_2$-doped ZnO-Bi$_2$O$_3$-MnO$_2$ varistors

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**Abstract:** The dense ZnO-Bi$_2$O$_3$-MnO$_2$-$\chi$SiO$_2$ (ZBMS) varistors were fabricated by flash sintering method under the low temperature of 850 ℃ within 2 minutes. The phase structure, density, microstructure, and electrical characteristics of the flash-sintered ZBMS varistors with different SiO$_2$ doping content were investigated. According to the XRD analysis, many secondary phases were detected due to the doping of SiO$_2$. Meanwhile, the average grain size decrease with increasing SiO$_2$ doping content. In addition, the electrical properties of all samples were analyzed. The improved nonlinear characteristics were obtained in SiO$_2$ doped samples, which can be attributed to the ion migration and oxygen absorption induced by the doping of SiO$_2$. The flash-sintered ZBMS varistor ceramics exhibited excellent comprehensive electrical properties, with the nonlinear coefficient of 24.5, the threshold voltage and leakage current of 385 V/mm and 11.8 µA, respectively.

**Keywords:** flash sintering; SiO$_2$ additive; ZBMS varistors; electrical properties

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1 Introduction

ZnO varistors have been successfully applied to the surge protector in electrical transmission and transient overvoltage or circuits to prevent lightning strikes due to its excellent nonlinerly electrical characteristics which originated from the grain boundaries.[1] It is generally believed that ZnO varistors are made by mixing zinc oxide powders with various oxide additives, such as Bi$_2$O$_3$[2, 3], Sb$_2$O$_3$[4, 5], Co$_2$O$_3$[6, 7], Sc$_2$O$_3$[8], MnO$_2$[9], Cr$_2$O$_3$[10, 11], and TiO$_2$[12]. In addition, ZnO as the addition can not only shift the tri-critical point to room temperature for the Ba$_{0.85}$Ca$_{0.15}$Ti$_{0.90}$Zr$_{0.10}$O$_3$ ceramics, but also solve evaporation and hygroscopicity problem of K$_2$O in the KNbO$_3$ ceramics.[13,14] At present, most ZnO-based varistors are prepared by conventional sintering method. However, it needs high sintering temperature (~ 1200 °C) and long holding time (~ 2 h), leading to the high energy consumption. In addition, the high sintering temperature may lead to the volatilization of some elements (like Bi), which in turn affect its properties. Thus, it is necessary to find a new sintering method with low sintering temperature and short sintering time.

Recently, a new sintering method, flash sintering (FS), has been reported, which can reduce the furnace temperature required for sintering 3 mol% yttria-stabilized zirconia (3YSZ) from 1450 °C to 850 °C, and greatly shorten the time to around 5s.[15] The combination of temperature and electric field promotes the flash sintering of ceramics. Compared with other sintering methods, the time of flash sintering is extremely short (about few seconds), which is nearly negligible in contrast to the number of hours required by the conventional sintering. Therefore, the flash technology has attracted significant scientific and technical interests. Since its first discovery, the flash sintering method has been widely used in the preparation of a series of ceramics, including ionic conductors (YSZ)[16-18] and (CeO$_2$)[19, 20], electronic conductors (TiO$_2$)[21, 22], ferroelectrics (BaTiO$_3$)[23, 24], semiconductors and varistors (ZnO) [25, 26], perovskites (SrTiO$_3$) [27, 28], insulators (Al$_2$O$_3$) and (Y$_2$O$_3$).[29, 30] The mechanism of the flash sintering has been investigated by many researchers. It is generally believed that the Joule heating caused by flowing current is
the energy source of the flash sintering process[31], which may help to reduce the sintering temperature. In addition, since it is difficult to measure the sample temperature during the flash sintering process, the sample temperature (T, in K) can be estimated by Black Body Radiation model (BBR)[32], and the sample temperature can be calculated by the Eq. (1):

\[ T = \left[ T_0^4 + \frac{W}{A\varepsilon \sigma} \right]^{1/4} \]  

where \( T_0 \) is the onset flash furnace temperature (K), \( W \) is the power dissipation in units of W·m\(^{-3}\), \( A \) is the surface area of the sample (1.429×10\(^4\) m\(^2\)), \( \varepsilon \) is the emissivity, and \( \sigma = 5.67 \times 10^{-8} \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-4} \) is the Stefan-Boltzmann constant.

Based on the above discussion, ZnO varistors can be prepared by flash sintering method. For example, Zhang et al. prepared ZnO specimen by flash sintering method at low furnace temperature (<120 °C).[26] In fact, a series of studies have been conducted on the flash sintering preparation of ZnO.[33,34] However, the current research mainly focuses on the flash sintering of pure zinc oxide, and there are few investigations on ZnO-based varistor. Recently, the ZnO-Bi\(_2\)O\(_3\)-MnO\(_2\) varistors have been fabricated by the flash sintering at a very low sintering temperature of 768~702 °C under an electric field of 200~400 V/cm, which showed an excellent nonlinear properties.[35] The dense ZnO-Bi\(_2\)O\(_3\)-M (M= Cr\(_2\)O\(_3\), MnO\(_2\) or Co\(_2\)O\(_3\)) ceramics were obtained by flash sintering at a low temperature (<750 °C) with the highest nonlinear coefficient of 39.5.[36] In ZnO-Bi\(_2\)O\(_3\)-MnO\(_2\) varistors, Bi\(_2\)O\(_3\) acts as Double Schottky Barrier (DSB) forming in the grain boundary layers, which provides the medium for the liquid phase to wet the grain boundary regions.[37] Meanwhile, the doping of transition metal oxide MnO\(_2\) increases the grain boundary barrier and affects the migration of carriers. The potential barrier is not only related to the ion migration, but also to the oxygen adsorption. It is demonstrated that oxygen can be generated by a chemical defect reaction of silica and zinc oxide.[38] Furthermore, Zn in the ZnO crystal is replaced by Si to form two Si\(^{2+}\), which serves as the center of positively charged to improve the ability of bound electron. The ionic radius of Si is 0.26 Å, Si\(^{4+}\) enters into the continuous path more easily than other transition metal
ions. In addition, the density of traps can be significantly enhanced by SiO$_2$, which may enhance the nonlinear characteristics and flash sintering process.

According to the above discussions, it is very meaningful to explore the effect of different SiO$_2$ content on structure and electrical properties of ZnO-Bi$_2$O$_3$-MnO$_2$-based varistor prepared by flash sintering. In present work, the dense ZnO-Bi$_2$O$_3$-MnO$_2$-xSiO$_2$ varistors were fabricated by the flash sintering method at a temperature of 850 °C within 2 min. The phase transformation and microstructure of the samples were characterized via X-ray diffraction (XRD) and scanning electron microscopy (SEM). Electrical characteristics are measured by a DC parameter meters.

2 Experimental Details

2.1 Preparation of green specimens

ZnO, Bi$_2$O$_3$, MnO$_2$ and SiO$_2$ analytical-grade chemicals were purchased from Sinopharm (Beijing, China) and the materials were used as received. The chemical formula was 98 mol% ZnO + 1.0 mol% Bi$_2$O$_3$ + 1.0 mol% MnO$_2$ + x wt.% SiO$_2$ (x= 0-3 wt.%) and all powders were produced by traditional solid phase reaction method. Firstly, the starting materials were mixed with the right amount of ethanol in a zirconia ball mill. The oxide mixture was subsequently milled for 5 h and then dried at 70 °C for 24 h. Secondly, all powders were mixed 5 wt.% polyvinyl alcohol (PVA) as a binder and after uniaxially pressed in a pellet at ~310Mpa for 3 min. Thereafter, the powders shaped green samples with the dimension of ~7 mm diameter and ~3 mm thickness. Finally, the green sample was calcined at 500 °C for 2 hours to remove the binder, The densities of the green samples were in a range of 55%~57%.

2.2 Flash process

The specimen was placed in a retrofitted tube furnace (OTF-1200X-S, KJ Group, China) with two platinum wires, which were also connected to the electrodes sandwiched between the two sections of the specimen. Subsequently, the specimen was added electric field by a direct-current (DC) (Sorenson DLM-300, Sorensen, CA) and the furnace heating rate at 10 °C·min$^{-1}$ heated to 850 °C. Specifically, due to local sintering in the flash process, a gradient increased current was used in the experiment.
Firstly, the applied electrical field \( (E) \) was 300 V⋅cm\(^{-1}\), and the initial limit current \( (I_0) \) was set to be 1.0 A. Thereafter, when the limit current was reached, the current is maintained for 10 s and then increased to 1.5 A. Similarly until the maximum current \( (I_{\text{max}}) \) was reached to 3.0 A, the flash sintering process continued for 10 s. Finally, the power supply system and the tube furnace were turned off and then the specimen was cooled with the furnace to room temperature. The experimental parameters during flash sintering process were shown in Table 1.

### Table 1. Experimental parameters of flash sintering

| \( x \) (wt.\%) | \( E \) (V⋅cm\(^{-1}\)) | \( I_0 \) (A) | \( I_{\text{max}} \) (A) | FS Condition |
|----------------|--------------------------|--------------|--------------------------|--------------|
| 0 ~ 3          | 300                      | 1.0          | 3.0                      | 0.5A/10s     |

#### 2.3 Characterization

The structure of the flash-sintered specimens was studied by X-ray diffraction (XRD, D8 Advance, Germany). Electron probe micro analyzer (SEM, NANO SEM430, American) was used to observe the sample microstructure. The density of flash-sintered samples was measured and calculated by the Archimedes method. A silver paste was applied as an electrode to the sample surface. The \( I-V \) characteristics of the flash-sintered sample were measured by a digital electrometer (CJ 1001, China) with a DC source. The varistor voltage \( (U_{1\text{mA}}) \) and the leakage current \( (I_L) \) at 75\% \( (U_{1\text{mA}}) \) of ZBMS varistors were measured at room temperature. More generally, the nonlinear coefficient \( (\alpha) \) can be calculated according to the following Eq. (2):

\[
\alpha = \frac{\log(I_{1\text{mA}}/I_{0.1\text{mA}})}{\log(U_{1\text{mA}}/U_{0.1\text{mA}})} = \frac{1}{\log(U_{1\text{mA}}/U_{0.1\text{mA}})}
\]  

(2)

Where \( U_{1\text{mA}} \) and \( U_{0.1\text{mA}} \) are the varistor voltage at 1 and 0.1 mA, respectively. The frequency dependent dielectric properties were characterized via a capacitance meter (Agilent 4294A, American) in the frequency range of \( 10^3 \)-\( 10^6 \) Hz at room temperature.

### 3. Results and Discussion

#### 3.1 Variation of flashing parameters on sintering

The curves of (a) current, (b) voltage, (c) power density and (d) conductivity
versus time during the flash process were shown in Fig. 1. Zero-point is the time when the current reaches a preset value. The current increases from 1.0 A to 3.0 A with a gradient way (see Figure 1(a)). As shown in Fig. 1(b), the voltage drops sharply from 90 V to around 20 V when the current surges to 1.0 A. Thereafter, the voltage tends to be a stable state gradually and then increases with the increasing current. When the current is reached to the maximum value, the voltage is kept at about 63 V. Figure 1(c) highlights the power density as functions of time during the flash sintering process. The power density is calculated according to \( P = \frac{UI}{V} \). Where \( U \) is voltage, \( I \) is the current, and \( V \) is the sample’s volume. Subsequently, the power density curve has the same trend with the variations of current and voltage because the power density is the combination of the voltage and current. Note that the sample in Fig. 1(d), the specimen conductivity increases sharply at the moment of flash. Here, the conductivity can be calculated by the following Eq. (3):

\[
\sigma = \frac{IH}{US}
\]

(3)

Where \( I \) is current, \( H \) is the height of the sample, \( U \) is voltage, \( S \) is the sample’s cross-sectional area. When the current is small, the conductivity increases with the increase of current. When the current is large, the conductivity decreases again because the rate of voltage increase is greater than the current as of the current increases. From the microstructure, it may be due to the formation of grain boundary barrier in high resistance state during sintering, which leads to the decrease of conductivity.
Fig. 1. (a) Current, (b) Voltage, (c) Power density and (d) Conductivity versus time curve during flash sintering.

3.2 Measurements and estimates of the specimen temperature

Figure 2(a) reveals the estimated temperature of \( x = 1 \) wt.\% sample versus time during the flash sintering process, which calculated by the BBR model (Eq. (1)). The specimen temperature is the same as the furnace temperature before the electric field is applied. When the flash is triggered, the peak temperature could reach around 1600 °C. When the voltage control is converted to the current control, the specimen temperature drops to about 1200 °C. [32, 39] The present result shows that the heating rate of temperature is about \( 10^4 \) °C.min\(^{-1}\), and the sample temperature is extremely higher than the furnace temperature. Furthermore, the temperature increases with increasing current. After the current reaches the pre-set value, the current would increase in a gradient manner. In particular, when the current reaches the maximum value, the estimated specimen temperature reaches as high as 1950 °C. At this stage, the average heating rate was about \( 2 \times 10^5 \) °C.min\(^{-1}\). The specimen temperature heating rate greatly decreases after the flash, which
makes the specimen more uniformly during sintering and improves the problem of local sintering. Figure 2(b) depicts the estimated sample temperature and power dissipation as a function of current at $x = 1$ wt.%. Apparently, the estimated specimen temperature and the power dissipation increase linearly with increasing current, and a positive correlation between the estimated specimen temperature and the power dissipation is observed, which indicates that the sintering is strongly dependent on the joule heating generated in the flash process. In addition, the estimated temperature is much higher than the required furnace temperature for conventional solid state sintering, which indicates that high temperature is also an important reason for the rapid densification of ceramics.

![Graph](image)

**Fig. 2.** (a) Estimated sample temperature versus time during flash sintering at $x = 1$ wt.%, (b) Estimating sample temperature and power dissipation as a function of current.

### 3.3 Phase structure, Density and Microstructure

The crystal structures of flash-sintered ZBM-$x$SiO$_2$ ceramics are characterized via XRD, and the results are shown in Fig.3. Obviously, the main phase of all flash-sintered samples is ZnO phase (PDF no.36.1451). In addition to ZnO phase, many extra diffraction peaks were detected which can be identified as Bi$_2$O$_3$ phase (PDF no.41.1449), Bi$_{12}$SiO$_{20}$ glass phase (PDF no.37.0485), and Zn$_2$SiO$_4$ phase (PDF no.37.1485) (see Fig. 3). Since MnO$_2$ and ZnO may form a solid solution, no diffraction peaks related to Mn ions are found. Moreover, the secondary phase type and content are related to the SiO$_2$ doping content. When the doping content is 1 wt.%, the secondary phase is mainly Bi$_{12}$SiO$_{20}$ and Bi$_2$O$_3$. When the doping content increased to 2 wt.%, Bi$_2$O$_3$, Zn$_2$SiO$_4$ and Bi$_{12}$SiO$_{20}$ can be identified in these
compositions. Since the radius of Si ions \((r = 0.26 \, \text{Å})\) is smaller than that of Zn ions \((r = 0.74 \, \text{Å})\), excess Si ions may enter grain boundary and form Zn\(_2\)SiO\(_4\) phase.

**Fig. 3.** XRD pattern of flash-sintered samples with different doping contents of SiO\(_2\).

The relative density of all flash-sintered ZBM-xSiO\(_2\) varistors was measured and listed in Table 2, and the values of the relative density for \(x=0, 1, 2, \) and 3 wt.% samples are 97.8%, 98.4%, 97.1% and 94.3%, respectively. Clearly, the density increases first and then decreases with increasing SiO\(_2\) doping content. It indicated that the proper addition of SiO\(_2\) could form glass phase at the grain boundary, thereby improving the wet ability of the grain boundary, enhancing the surface tension of the Bi-rich liquid phase, accelerating the particle flow rate in the sample, promoting the rearrangement process, and increasing the accumulation density and densification degree of particles in the sample. However, due to the density of SiO\(_2\) \((2.63 \, \text{g/cm}^3)\) is much lower than that of ZnO \((5.67 \, \text{g/cm}^3)\), excessive SiO\(_2\) doping will lead to the decrease of the density.[40]

The microscopic morphology of the flash-sintered ZBM-xSiO\(_2\) ceramics was
shown in Fig. 4. Clearly, the relatively dense ceramics were obtained. Meanwhile, the grain size decreases with increasing SiO$_2$ doping content. The decreased grain size can be attributed to the doping of SiO$_2$, which promotes the formation of glass phase with other additives at high temperature. Then, the Zn$_2$SiO$_4$ spinel phase was condensed in the cooling process, and mainly distributes at grain boundary. Similar to the mechanism of Zn$_7$Sb$_2$O$_{12}$ phase, the Zn$_2$SiO$_4$ phase acts as a nail at the grain boundary, thus hindering grain movement and inhibiting grain growth.[40] In addition, taking the 3wt.% sample as an example, the effect of the electrode on the microstructure was investigated. The microstructures on both sides of the flash-sintered samples electrode were shown in Figure 5. Apparently, the grain size on both sides of the electrode did not change obviously, which is consistent with the previous investigation. [35]

![SEM pattern of flash-sintered samples with different doping contents of SiO$_2$](image)

**Fig. 4.** SEM pattern of flash-sintered samples with different doping contents of SiO$_2$ (a) 0 wt.%, (b) 1 wt.%, (c) 2 wt.%, (d) 3 wt.%.  

3.4 Electrical properties

Figure 6(a) depicted the $E$-$J$ curves of flash-sintered samples doped with different SiO$_2$ contents. Obviously, all samples exhibited nonlinear properties. The variation of nonlinear coefficient ($\alpha$) and threshold voltage ($V_T$) of the ZBM-$x$SiO$_2$ varistors were shown in Fig. 6(b). Meanwhile, electrical properties of flash-sintered samples were evaluated and listed in Table 2. As shown in Figure 6(b), the nonlinear coefficient and threshold voltage of ZBMS varistors were enhanced by doping of SiO$_2$. The optimal nonlinear characteristics are obtained in 2 wt.% sample with a value of 24.5. The threshold voltage increases significantly with increasing SiO$_2$ doping content, and the largest threshold voltage obtained at $x$=3 wt.% with a value of 498 V·mm$^{-1}$. Moreover, the varistor voltage depends on grain size according to the Eq. (4):

$$U_{1mA} = N_{gb}V_{gb}d$$

(4)

Where $N_{gb}$ is the number of grain boundaries, $V_{gb}$ is the breakdown voltage of a single grain boundary barrier, and $d$ is the height of varistor. When the content of SiO$_2$ increases from 1 wt.% to 3 wt.%, the grain size gradually decreases, that is, the number of grain boundaries of per unit thickness increases, and the varistor voltage gradually increases. However, the nonlinear coefficient decreases to 12.2, and the leakage current increases significantly to 58.7 $\mu$A at $x = 3$ wt.%. The deteriorated nonlinear properties at this sample were ascribed to the excess SiO$_2$ doping, which may form a large number of secondary phases. Meanwhile, an increase in leakage
current is attributed to the increased conductivity of the intergranular layer.[41-43] When the specimen is under a low electric field, electrons cross the Schottky Barrier to generate a thermal excitation current, which is related to the electric field as Eq. (5):

$$J_s = A^* \cdot T^2 \cdot \exp \left[ \frac{(\beta E^{3/2} - \varphi_B)}{kT} \right]$$  \hspace{1cm} (5)

Where $A^*$ is the Richardson constant, $\beta$ is related to the width of the Schottky Barrier constant, $E$ is the electric field, $\varphi_B$ is the barrier voltage, and $\beta$ satisfies the Eq. (6):

$$\beta \propto 1/(r \cdot \omega)$$  \hspace{1cm} (6)

Where $r$ is the number of crystals per unit length, $\omega$ is Schottky barrier width. Based on the natural logarithm of Eq. (5), the $\ln J$-$E^{1/2}$ curves of flash-sintered ZBM-xSiO$_2$ ceramics were calculated and displayed in Fig. 6(c). However, after the $E$-$J$ curves were converted to the $\ln J$-$E^{1/2}$ curve, it was found that the curve was not a completely straight line, so a linear fit was performed, and the fitted line extended to $E = 0$. As shown in Fig. 6, the slope of the $\ln J \propto E^{1/2}$ curves is $\beta/kT$, and the intercept is the difference between a constant and the barrier heights.

| $x$ (wt.%) | Relative density | $I_L$ ($\mu A$) | $V_T$ (V·mm$^{-1}$) | $\alpha$ | $\varphi_B$ (eV) |
|-----------|------------------|-----------------|---------------------|--------|-----------------|
| 0         | 97.8%            | 8.48            | 234                 | 20.1   | 0.76            |
| 1         | 98.4%            | 8.43            | 375                 | 22.2   | 0.89            |
| 2         | 97.1%            | 11.8            | 385                 | 24.5   | 0.80            |
| 3         | 94.3%            | 58.7            | 498                 | 12.2   | 0.78            |
Fig. 6. (a) The $E$-$J$ curve of flash-sintered samples with different content SiO$_2$ doped, (b) The variation of nonlinear coefficient and threshold voltage of the flash-sintered ZBM-$x$SiO$_2$ varistors ($x=0-3$ wt.%), (c) The ln$J$-$E^{1/2}$ curves of flash-sintered ZBM-$x$SiO$_2$ ($x = 0-3$ wt.%) varistors.

The values of barrier voltage which fitted by Eq. (5) were listed in Table 2. When the content of SiO$_2$ increases from 0 to 3 wt.%, the barrier voltage is 0.76 eV, 0.89 eV, 0.80 eV and 0.78 eV, respectively. The enhanced barrier voltage can be attributed to the doping of SiO$_2$, which can form glass phase with Bi$_2$O$_3$ at the grain boundary in the flash sintering process. The wetting effect of the liquid phase can be increased at the grain boundary. Moreover, it also affects the segregation concentration of the extrinsic surface impurities on grain surface, which increases the grain boundary barrier. The defect reaction of SiO$_2$ can be represented by Kroger-Vink symbol:

$$SiO_2 \overset{ZnO}{\longrightarrow} Si_i^{x+} + V_z^{x-} + O_2$$

$$SiO_2 \overset{Bi_2O_3}{\longrightarrow} Si^{4+} + 4e + O_2$$

$$O_2 \rightarrow 2O_{ad}$$

$$O_{ad} + e \rightarrow O'_{ad}$$
\[ O_{ad} + 2e \rightarrow O_{ad}^{2-} \]
\[ Zn_i^{+} + O_{ad}^{2-} \rightarrow ZnO \]
\[ Zn_i^{+} + O_{ad}^{2-} \rightarrow ZnO \]

According to the Kroger-Vink symbol, the grain boundary defect structures of the undoped and doped samples were illustrated in Figure 7. When SiO₂ is undoped, the defect structure is mainly composed of MnO₂ related solution diffusion reaction. When the ZnO varistors are doped with SiO₂, oxygen is generated due to the chemical defect reaction between SiO₂, ZnO and Bi₂O₃, resulting in an increase in the adsorbed oxygen content. After that, a large number of free electrons migrate toward the grain boundary, resulting in a significant increase in the width of the depletion layer and a decrease intrinsic donor defects \( Zn_i^{+} \) and \( Zn_i^{2+} \). Furthermore, the Si\(^{4+}\) ion radius (0.26 Å) is smaller than Zn\(^{2+}\) (0.74 Å) and Mn\(^{4+}\) (0.53 Å), which will preferentially diffuse in the ZnO lattice, and may reduce the diffusion rate of Mn\(^{4+}\). As a result, the solid solution reaction on the grain surface were enhanced, the formation of grain boundary state is promoted, the grain boundary barrier is increased and the nonlinear characteristics is improved.[38]

![Fig. 7. Grain boundary defect structure of the flash-sintered sample (a) Undoped, (b) SiO₂ doped.](image)

Figure 8 features the frequency dependent dielectric characteristics of the flash-sintered ZBM-xSiO₂ varistors (x = 0-3 wt.%) at room temperature. As shown in Fig. 8, the doping of SiO₂ leads to a decrease in dielectric constant (\( e' \)) and a increase
in dielectric loss (tanδ) at low frequency. With increasing SiO₂ doping content, the grain size decreases and depletion layer width increases, resulting in a decrease in dielectric constant. Meanwhile, the dielectric constant shows a certain frequency dependence, which decreases with increasing frequency. Especially for x=0 samples, the dielectric constant decreases rapidly at above 10⁵ Hz (see Fig.8(a)). Interestingly, the frequency stability enhanced with increasing doping content. Moreover, the dielectric loss is mainly caused by Joule heating which generated from leakage current and eddy current heat which originated from electric dipole moment rotation.[44] The dielectric loss is high at x = 3 wt.%, which may be attributed to the large leakage current. (Fig.8(b))

![Graph](https://example.com/graph1.png)

Fig. 8. The dielectric properties of the flash-sintered ZBM-xSiO₂ varistors (x = 0-3 wt.%) with frequency (a) Dielectric constant (ε'), (b) Dielectric loss (tan δ).

### 4 Conclusion

The dense ZBM-xSiO₂ varistors were prepared by flash sintering method under low temperature of 850 °C within 2 minutes. The effects of the different SiO₂ content on the structure and properties of ZnO-based varistors were investigated. Except ZnO main phase, some secondary phase containing Si ions were detected with increasing SiO₂ doping content. Meanwhile, the grain size decreased, which can be attributed to the inhibition of grain growth by the secondary phase. The electrical performance analysis of the flash-sintered specimens showed that the electrical properties was improved with doping SiO₂. The improved nonlinear electrical properties can be ascribed to the ion migration and oxygen absorption. The flash-sintered ZBMS
varistors exhibited excellent comprehensive electrical properties at $x=2\text{wt.\%}$, with a nonlinear coefficient of 24.5, a threshold voltage of 385 V/mm, and a leakage current of 11.8 $\mu$A. There is still a lot of work to be done on the preparation of ZnO varistors by flash sintering. Different flash sintering parameters can also be tried to change and explore the flash densification mechanism of rapid densification.

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Table 1 Experimental parameters of flash sintering

Table 2 Electrical properties and relative density of flash-sintered samples with different content SiO\textsubscript{2} doped

Fig. 1 (a) Current, (b) Voltage, (c) Power density and (d) Conductivity versus time curve during flash sintering.

Fig. 2 (a) Estimated sample temperature versus time during flash sintering at x = 1 wt.%, (b) Estimating sample temperature and power dissipation as a function of current.

Fig. 3 XRD pattern of flash-sintered samples with different doping contents of SiO\textsubscript{2}.

Fig. 4 SEM pattern of flash-sintered samples with different doping contents of SiO\textsubscript{2} (a) 0 wt.%, (b) 1 wt.%, (c) 2 wt.%, (d) 3 wt.%. 

Fig. 5 SEM image of the flash-sintered sample on both sides of the electrode (a) Anode (+), (b) Cathode (-) at x = 3 wt.%.

Fig. 6 (a) The $E$-$J$ curve of flash-sintered samples with different content SiO\textsubscript{2} doped, (b) The variation of nonlinear coefficient and threshold voltage of the flash-sintered ZBM-xSiO\textsubscript{2} varistors (x=0-3 wt.%), (c) The ln$J$-$E^{1/2}$ curves of flash-sintered ZBM-xSiO\textsubscript{2} (x = 0-3 wt.%) varistors.

Fig. 7 Grain boundary defect structure of the flash-sintered sample (a) Undoped, (b) SiO\textsubscript{2} doped.

Fig. 8 The dielectric properties of the flash-sintered ZBM-xSiO\textsubscript{2} varistors (x = 0-3 wt.%) with frequency (a) Dielectric constant ($\varepsilon''$), (b) Dielectric loss (tan $\delta$).