

Study on ZnO Varistors Doped with Y₂O₃ by Microwave Two-step Sintering

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Abstract. The zinc oxide varistor prepared in this paper is mainly composed of submicron zinc oxide powder and dopants, and is prepared by two-step sintering method, which is in contrast with traditional sintering method and ordinary microwave sintering method. The effects of microwave sintering temperature and holding time on the microstructure and electrical properties of ZnO varistors were investigated. The results show that the potential gradient of microwave sintering is higher than that of traditional sintering, but the leakage current also increases. Compared with ordinary microwave sintering, the two-step sintering can further effectively reduce the grain size, enhance densification, not only improve the potential gradient, but also reduce leakage current. In two-step sintering, increasing sintering temperature can effectively reduce leakage current and non-linear coefficient, but the potential gradient is also greatly reduced. When the holding time is more than 1 hour, there is little difference in electrical performance. When the holding time is too small, its electrical performance is weak overall.

Keywords: Two-step sintering; ZnO varistors; Dielectric relaxation; Electrical performance; Microstructure.

1. Introduction

Sintering, as the last step in the preparation of ceramic materials, is the most important and critical step. In traditional sintering, heat diffuses from the surface to the inside through radiation, while microwave energy absorbed by the material during microwave sintering is converted into kinetic energy and potential energy of molecules inside the material, heating has integrity and uniformity, temperature gradient inside the material is very small, and heating and sintering speed are very fast. Under the action of microwave electromagnetic energy, the kinetic energy of molecules or ions in the material increases and the diffusion coefficient increases, so that low-temperature rapid sintering can be realized, sintering can be completed before crystal grains can grow up, and the performance of ceramic materials is obviously improved ^[1-4].

Using microwave sintering and nano-sized zinc oxide powder to produce varistor has very high density and high potential gradient, but leakage current is also very large ^[5-7]. The two-step sintering process was first proposed by Chen et al. in 2000 and applied to the densification of Y₂O₃ ceramics. The densification of ceramics and the inhibition of grain growth can be achieved at a lower sintering



temperature by exploring the difference in activation energy required for grain boundary migration or grain boundary migration^[8]. At present, there is little research on the performance of ZnO varistors produced by two- step sintering of micron-sized zinc oxide powder, and there is little discussion on the influence of two-step sintering temperature and holding time.

2. Test Sample Preparation and Sintering Methods

Sub-micro varistor powder is prepared with analytically pure materials in the following molar ratio by normal solid phase reaction technology:

95.09mol% ZnO+0.8mol% Bi₂O₃+0.8mol% Sb₂O₃+1.0mol% Co₂O₃+0.8mol% MnO₂+0.6mol% NiO+0.2mol% SiO₂+0.4mol% Y₂O₃+0.3mol% Cr₂O₃+0.01mol% Al (NO₃)₃·9H₂O.

Grinding in a high-speed ball mill for 3 hours and carrying out centrifugal spray granulation to obtain varistor powder, and pressing into a disc under 200 MPa. The organic binder (polyvinyl alcohol) added to the mixture was removed at 600°C. After sintering, the upper and lower polished surfaces of varistor samples were covered with silver paste, and then the samples were heated in air at 600°C for 10 minutes to form electrodes. The final disc has a diameter of 30mm and a thickness of 4mm.

The schematic diagram of the two-step sintering is shown as follows: firstly, the sintering temperature t_1 is increased at v_1 heating rate for a duration T_1 , and then the sintering temperature t_2 is decreased at v_2 cooling rate for a duration T_2 .

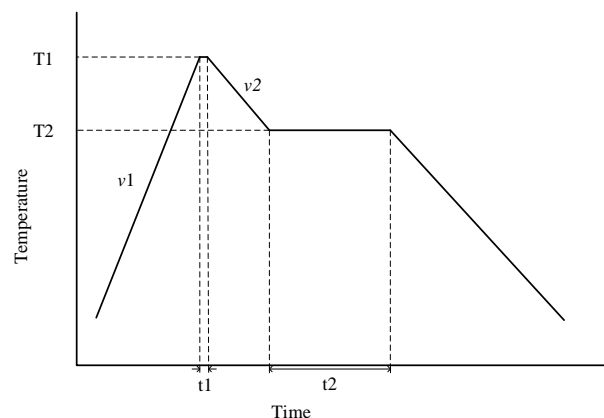


Figure1. Schematic Diagram of Microwave Two-step Sintering

3. Result and Analysis

3.1 Influence of Sintering Temperature on Varistor Performance

T_1 is set to 850, 950, 1050°C, v_1 is 10°C/min, t_1 is 5 min; T_2 is 800°C, v_2 is 5°C/min, t_2 is 240min. The measured electrical performance parameters are shown in the following table, and the microstructure is shown in the following figure:

Table 1 Comparison of Non-linearity Coefficient, Leakage Current and Voltage-sensitive Voltage at Different Sintering Temperatures

$T_1/^\circ\text{C}$	α	$J_L/(\mu\text{A}\cdot\text{cm}^{-2})$	$V_{1\text{mA}}/(\text{V}\cdot\text{mm}^{-1})$
850	16.8	18.3	733

950	31.0	13.0	435
1050	48.0	2.11	303

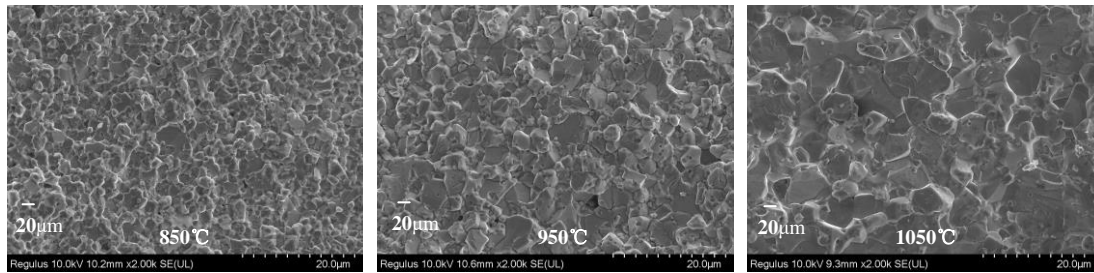


Figure2. SEM photos of samples at different sintering temperatures

From the above figure, it can be seen that the crystal grain grows continuously with the increase of T1, the porosity decreases, the density increases, the nonlinear performance improves, and the leakage current decreases. At the same time, since the voltage-sensitive potential depends on the number of grains per unit length, the voltage-sensitive voltage decreases as T1 increases.

3.2 Influence of Holding Time on Varistor Performance

T1 is 1025°C, v_1 is 10°C/min, t_1 is 5 min; T2 is 800°C, v_2 is 5°C/min, t_2 is set to 60, 120 and 240min respectively. The measured electrical performance parameters are as follows:

Table 2 Comparison of Non-linearity Coefficient, Leakage Current and Voltage-sensitive Voltage under Different Insulation Time

t_2/min	α	$J_L/(\mu\text{A}\cdot\text{cm}^{-2})$	$V_{1\text{mA}}/(\text{V}\cdot\text{mm}^{-1})$
30	41.9	3.71	286
60	53.8	1.69	342
120	46.8	1.62	361
240	47.5	1.60	345

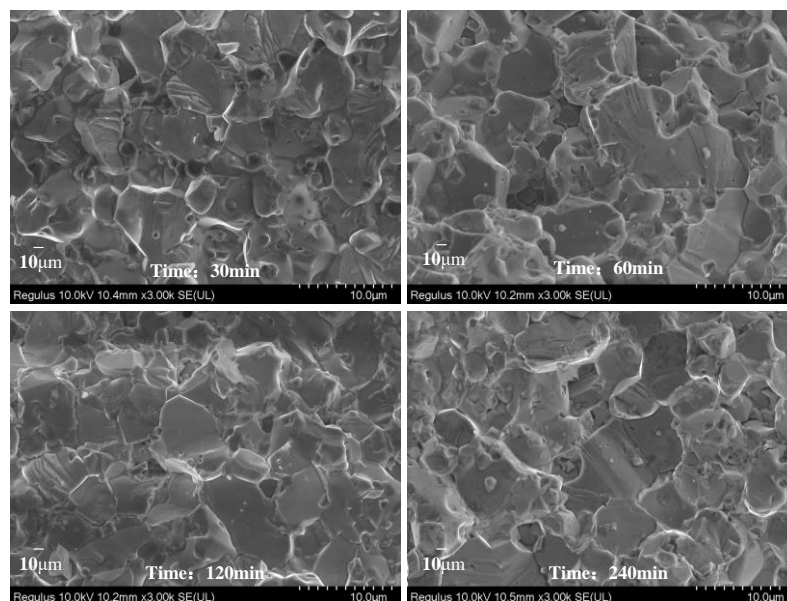


Figure3. SEM photos of samples at different holding times

As can be seen from the above figure, when the holding time is increased from 30min to 60min, the grain size slightly increases and the densification further increases. When the holding time is further prolonged, the porosity tends to be saturated and the properties tend to be stable.

3.3 Influence of Sintering Methods on Varistor Performance

Comparison of two-step sintering with traditional sintering and microwave One-step sintering is as follows:

Table 3 Comparison of Sex Coefficient, Leakage Current and Voltage-sensitive Voltage under Three Sintering Non-linear Conditions

Sintered Powder	T/°C	t/min	α	$J_L / (\mu A \cdot cm^{-2})$	$V_{1mA} / (V \cdot mm^{-1})$
One-step Sintering	1050	240	42.2	5.05	203
Two-step Sintering	1050	240	48.0	2.11	303
Ordinary Sintering	1050	240	40.7	1.71	266

As can be seen from the above table, compared with traditional sintering, the potential gradient of wave sintering is increased, but the leakage current also increases. Compared with ordinary microwave sintering, the two-step sintering can further effectively reduce the grain size, enhance densification, not only improve the potential gradient, but also reduce leakage current.

4. Conclusion

In this paper, submicron zinc oxide powder varistor was prepared by two-step sintering. The effects of microwave sintering temperature and holding time on the microstructure and electrical properties of zinc oxide varistor were investigated and compared with traditional sintering method and ordinary microwave sintering. The conclusions are as follows:

- 1) Compared with traditional sintering, microwave sintering has higher potential gradient, but leakage current also increases;
- 2) Compared with ordinary microwave sintering, the two-step sintering can further effectively reduce the grain size, enhance densification, not only improve the potential gradient, but also reduce leakage current;
- 3) In two-step sintering, increasing the sintering temperature can effectively reduce leakage current and nonlinear coefficient, but the potential gradient is also greatly reduced. When the holding time is more than 1 hour, there is little difference in electrical performance. When the holding time is too small, its electrical performance is generally weak.

5. References

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