

PREPARATION OF ZnO CERAMIC POWDER BY SOL-GEL METHOD AND ITS VOLTAGE SENSITIVE PROPERTIES^①

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ABSTRACT The method of preparing large grain ZnO powder by sol-gel method for making low voltage sensitive ZnO ceramics were put forward. The ceramics have been made from this ZnO powder. XRD, IR, DTA, SEM, TEM were used to study the mechanisms of sol-gel method by using ZnSO₄ as the primary material, Na₂CO₃ as the precipitating agent. The voltage sensitive properties of the ceramics were determined. The results showed that it is feasible to prepare large grain ZnO powder by using the properties of hard agglomerate that easily occurs in the course of dehydrating. The ZnO powder prepared by this method not only has a high sintering activity, but also easily, efficiently reaches the goal of lowering the breakdown voltage.

Key words sol-gel large grain ZnO powder voltage sensitive ceramic voltage sensitive properties

1 INTRODUCTION

At present, the studies for preparation of voltage sensitive ZnO ceramics tend to lower the breakdown voltage (V_B). There are two ways in these studies. One is changing the prescription of other oxides^[1], the other is adding the ZnO seed grains^[2-4]. The latter has been studied more. The ceramics made from this ZnO powder, which is an *n*-type semiconductor, have the voltage sensitive property because of the other additives including Bi₂O₃, Sb₂O₃, MnO₂, Cr₂O₃, Co₂O₃ etc, and forming the grain boundary layer between ZnO grains. These active grain boundaries act as microvaristors with breakdown voltages (V_g) generally estimated to be 3 to 4 V^[5,6] and are the key part to produce the nonlinear I-V property. The ceramic macroscopic breakdown voltage V_B can be calculated as following:

$$V_B = nV_g = DV_g/d \quad (1)$$

where n is the number of ZnO grains between two electrodes, d is the average grain diameter

of ZnO grains and D is the thickness of ceramics.

According to Eqn. (1), decreasing the number of ZnO grains or the thickness of ceramics (D) can lower the macroscopic breakdown voltage. Because it is limited to reduce the thickness of ceramics, increasing the diameter of the ZnO grain is mainly chosen to lower the breakdown voltage.

At present, the technology of adding large ZnO seed grain to the starting powders has been developed to prepare the low voltage sensitive ceramics, which can effectively prevent the growth of single large grains and will make the ZnO seed grains annex the small ZnO grains, produce even sintered ceramics and decrease the number of ZnO grains. Although it can efficiently decrease the breakdown voltage, there are two defects in this method: (1) The process of producing ZnO seed grain is very complex, it needs high temperature (1400 °C) sintering for a long time (10 h) and the productivity is low; (2) The rate of ZnO seed grains annexing small ZnO grains is slow.

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It is well known that sol-gel technology has been used to prepare the ultrafine powders^[7,8]. Because the sol particles are very small and have a very high surface activity, the agglomerating structure is formed easily. So, the agglomeration between particles must be avoided when the ultrafine powders are prepared by sol-gel method.

On the contrary, if the property of agglomeration between particles is made use of and the favorable conditions are controlled, the large size ZnO grains will be prepared easily. In this paper, the large size ZnO powders have been prepared by sol-gel method, the voltage sensitive properties of the ceramics made from this large size ZnO powder have been determined also.

2 EXPERIMENTAL

2.1 Sol preparation and determination

The samples were prepared by adding the 5.0% Na₂CO₃ aqueous solution into the 0.1 mol/L ZnSO₄ aqueous solution. The mixed solution fully reacted at different temperature with stirring. Then, the sol solution was filtered, washed by water and alcohol, dried at 110~120 °C. The properties of the sol samples were determined by X-ray diffraction, IR, TEM, SEM.

2.2 Preparation and properties of voltage sensitive ceramics

The ZnO powder was prepared by the fol-

lowing processes: the dry gel precipitated at room temperature was ground into 0.1~0.3 mm, then roasted at 550±10 °C in air. The proportion of other additive oxides was as the following (mass fraction): ZnO 86.96%, Bi₂O₃ 5.96%, Sb₂O₃ 3.49%, Co₂O₃ 0.546%, MnO₂ 0.698%, Cr₂O₃ 0.895%, NiO 0.94%, In₂O₃ 0.50%. The additive oxide powders were mixed with a mortar and pestle, then fully mixed with the above ZnO powder. The mixed powders were pressed (20 MPa) into disks (1.527 cm in diameter by 2.0 mm thick). The specimens were subsequently sintered at 1000~1200 °C for 3 h, then cooled. After polished with emery paper, the ceramics disks were sintered at 550~600 °C for 20 min in air, and then Pt electrodes were welded on for electrical measurement.

3 RESULTS AND DISCUSSION

3.1 Properties of dry gel

The sol particle produced by mixing ZnSO₄ and Na₂CO₃ aqueous solutions, did not precipitate for a long time. After filtered, washed and dried at 110~120 °C in air, the hard agglomerates were formed. All filtered cakes solidified into solid porcelain. The SEM and EDAX photograph of the fracture surface are illustrated in Fig. 1.

Fig. 1 shows that the dry gel is very compact and a small amount of gas pores exist in the

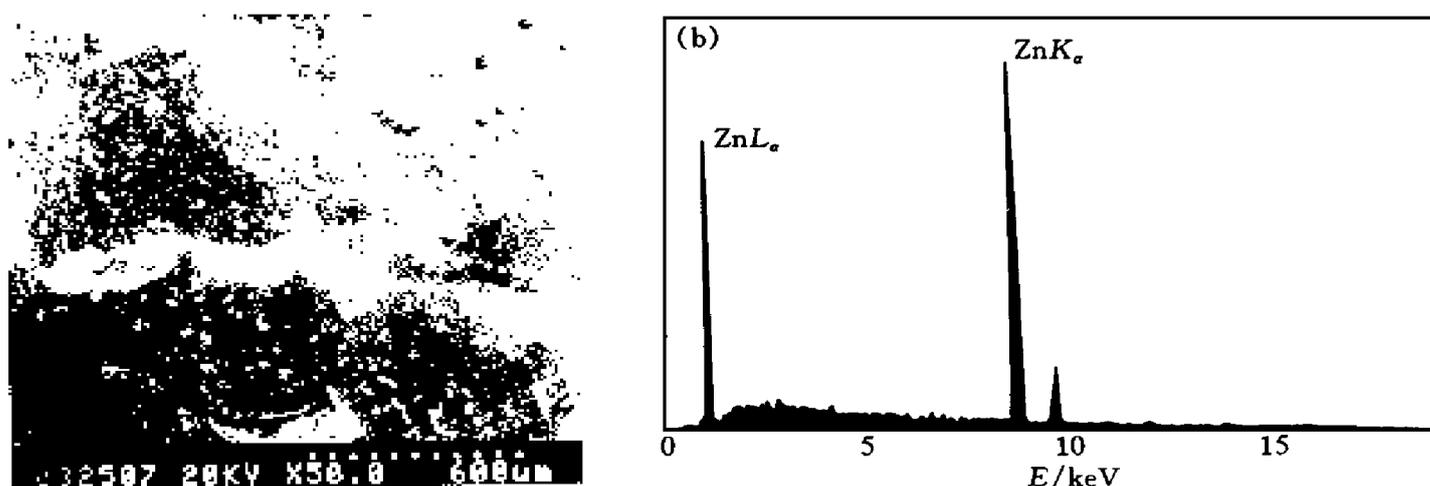


Fig. 1 SEM photograph (a) and EDAX spectrum (b) of dry gel

gel body. Other metal elements are not found except zinc element. It can be known from our previous work^[9] that the gel is zinc carbonate hydroxide hydrate ($\text{Zn}_4\text{CO}_3(\text{OH})_6 \cdot \text{H}_2\text{O}$), its decomposition process is simple and the range of the decomposition temperature is 156~ 297 °C.

Fig. 2 is the SEM photograph of ZnO powders roasted at 550 ± 10 °C. It can be seen that the ZnO grain size is about 90~ 100 μm.



Fig. 2 SEM photograph of ZnO powders roasted at 550 °C

3.2 Mechanism of sol-gel formation

There exist two processes, namely, homogeneous nucleation and growth, when the sol is produced in the aqueous solution. The diameter of the sol particles normally ranges from 1 nm to 100 nm, the sol can exist steadily for a long time in the aqueous solution because of the high activity of small particles. In order to form high stable sol, the following two conditions are required:

- (1) The solubility of sol particles is negligible (it is one of the essential conditions).
- (2) The concentration of reactant must be dilute, so the conditions for the particle growth do not exist.

Fig. 3 shows the IR spectrum of gel powders produced at different temperatures. Fig. 4 is the TEM photograph.

To avoid the formation of hard agglomerate during the dehydrate of sol and truthfully reflect

the morphotropy of sol particle, the sol was washed using alcohol when filtering.

Fig. 3 shows that the powders produced at different temperatures are the same material.

Fig. 4(a) is the TEM photograph of gel powders prepared at 25 °C. From this picture, it can be seen that the particle is basically spherical. All particles attract together because the particle size is very small.

It can be seen from Fig. 4(b), (c) and (d) that the sol particles gradually grow and form into filamentary structure with the increase of reaction temperature.

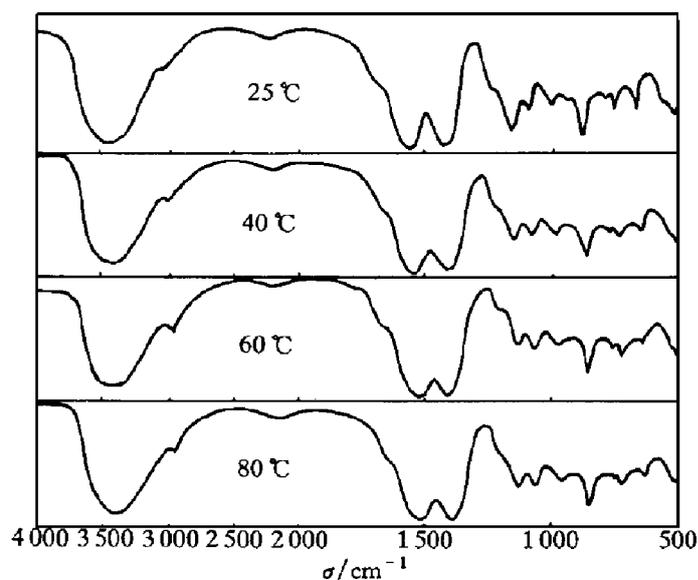


Fig. 3 IR spectrum of gel powders produced at different temperatures

The sol particle produced at room temperature is superfine particle with great surface area. Therefore, it shows an abnormal surface and volume effect and is in non-steady state. It will not precipitate for a long time in the aqueous solution due to the same electric charge adsorbed. When the reaction conditions are changed (for example, increasing the reaction temperature), the growth of sol particles in the aqueous solution will result in the energy and the activity decreasing. Because the stability of the sol is destroyed, the sol particle will precipitate speedily due to gravity. The particles will close together and form into hard compact gel body through the

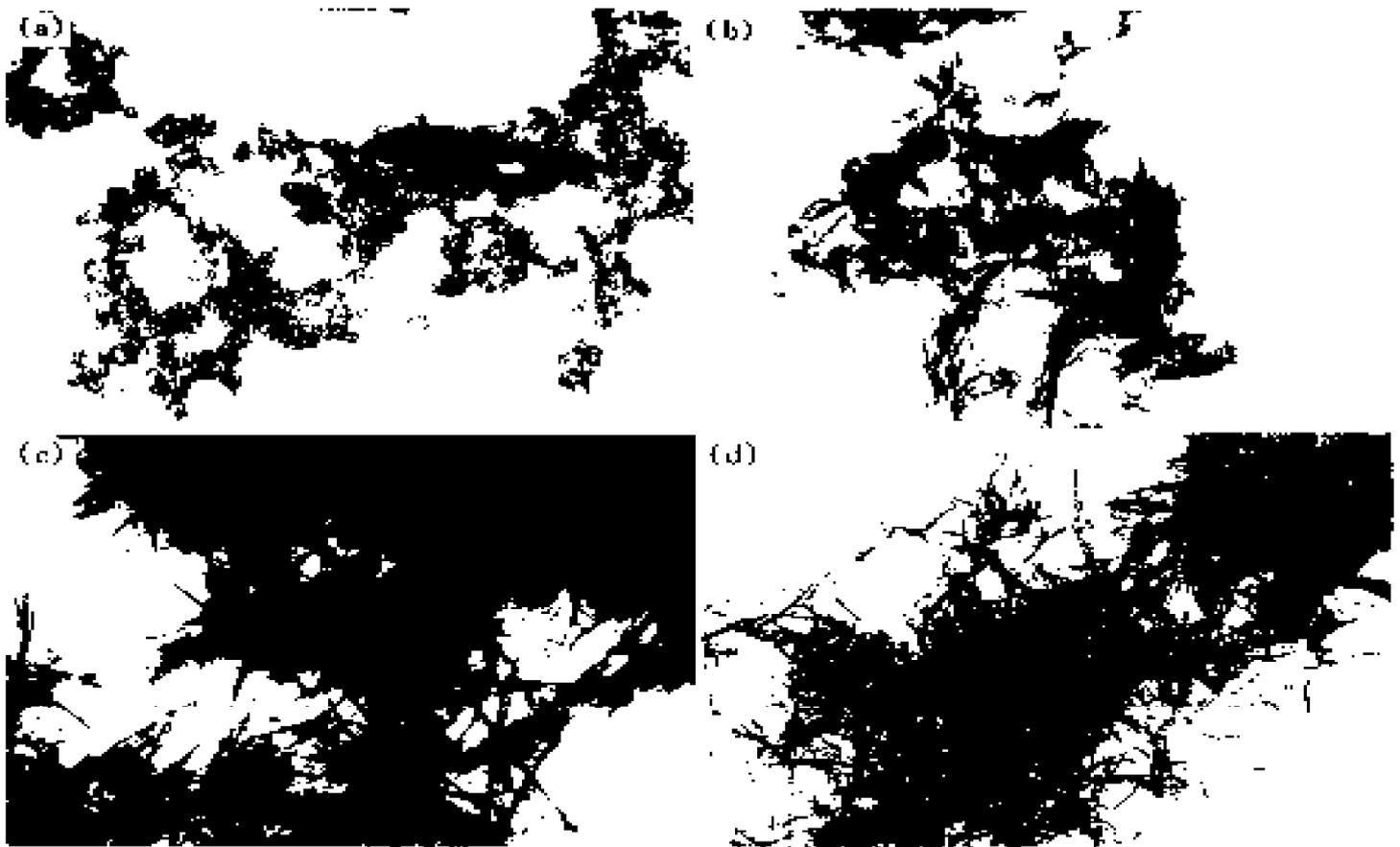


Fig. 4 TEM photographs of gel powders produced at different temperatures
(a) $-25\text{ }^{\circ}\text{C}$; (b) $-40\text{ }^{\circ}\text{C}$; (c) $-60\text{ }^{\circ}\text{C}$; (d) $-80\text{ }^{\circ}\text{C}$

hard agglomeration during dehydrating.

3.3 Characteristics of ceramic

The sintering densities of the ceramics are illustrated in Table 1.

Table 1 Densities of ceramics sintered at different temperatures

$t/ ^{\circ}\text{C}$	1000	1100	1150	1200
$\rho/ (\text{g}\cdot\text{cm}^{-3})$	5.62	5.5	5.4	5.3

Generally, the smaller the particle size, the bigger the sintering motive force, and the more compact the sintered ceramics. But in this study, the sintering densities of the ceramics prepared by the large size ZnO powders are also high (The general densities are $5.35 \sim 5.5 \text{ g/cm}^3$)^[10]. In the bellet, the ZnO grains are wrapped by the doping oxides (containing

Bi_2O_3), and the molten Bi_2O_3 at a lower sintering temperature can form liquid phase during sintering. The formation of liquid phase promote the sintering process and make the ceramics have higher sintering density.

The voltage-current curves of the ceramics made from this ZnO powders are illustrated in Fig. 5. From Fig. 5, the breakdown voltage (V_B) at different sintering temperatures can be obtained. The α value can be determined by following equation:

$$\alpha = \frac{\lg(I_2/I_1)}{\lg(V_2/V_1)} \quad (2)$$

where I_2 and I_1 are the current corresponding to V_2 and V_1 . The calculated results are shown in Table 2.

From Table 1, 2 and Fig. 5, it can be concluded that the V_B of the ceramics produced by using this ZnO powders decreases with the increasing of the sintering temperature. For the

decreasing of α value with the decreasing of V_B , the Ohm resistance of ZnO grains play an important role when uses the large size ZnO powder is used. In order to lower the V_B value and at the same time increase the α value, the electric conductivity of this ZnO grain must be increased.

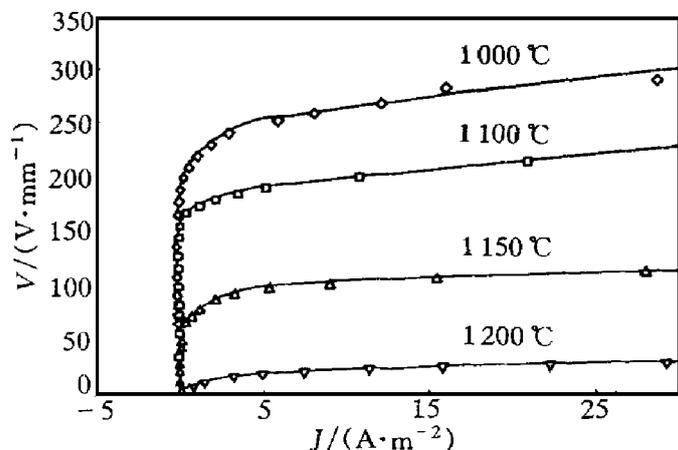


Fig. 5 Voltage-current characteristics of ceramics sintered at different temperatures

Table 2 Electronic properties of ceramics

$t/^\circ\text{C}$	1000	1100	1150	1200
V_B/V	225	190	92	17
α	9.5	13.8	11.0	3.0

4 CONCLUSIONS

(1) The large compact particle ZnO pow-

ders were produced by using hard agglomerates formed in the sol particle dehydration with ZnSO_4 as the starting material, Na_2CO_3 as the precipitating agent. Increasing the reaction temperature resulted in the sol particles growing and decreased the sol stability when other conditions were fixed.

(2) The V_B of the ceramics made from this larger particle size ZnO powders decreased with increasing sintering temperature.

REFERENCES

- 1 Zhou Yadong and Yang Yanmei. Journal of Beijing Polytechnic University, (in Chinese), 1994, 20(1): 111.
- 2 Zhou Dongxiang. Semiconductor and Application, (in Chinese). Wuchang: Hua Zhong University of Sci & Tech Press, 1991: 198.
- 3 Zhang Yunbao. Advanced Ceramics, 1996, 1: 27.
- 4 Gao Jiming, Du Haiqing and Tang Shaoqiu. Journal of Inorganic Materials, 1996, 11(3): 476.
- 5 Detlev F K *et al.* J Am Ceram Soc, 1990, 73(3): 645.
- 6 Schwing U and Hoffmann B. J Appl Phys, 1985, 57: 5372.
- 7 Ramaurthi S D, Xu Zhengkui and Payne D A. J Am Ceram Soc, 1990, 73: 2760.
- 8 Ding Zishang and Weng Wenjian. Journal of the Chinese Ceramic Society, 1993, 21(5): 443.
- 9 Chen Jianxun, Zhao Ruirong, Jiang Hanying *et al.* Trans Nonferrous Met Soc China. 1998, 8(1): 149.
- 10 Yao Yao *et al.* Journal of Inorganic Materials, 1989, 4(1): 53.

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