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Preparation of ZnO crystal by sol-gel method①

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[Abstract] A new method to prepare ZnO crystal was put forward. The preparation process was studied and the mechanism of this method was also discussed. The results show that the sol particles will aggregate when being dehydrated and will form into hard compact gel body through the hard agglomeration between particles. This dry gel is a hard compact agglomeration composed of the first sol particles. At high sintering temperature, the small compacted particles will easily grow up and form a fine ZnO crystal.

[Key words] ZnO; sensitive ceramics; crystal; sol-gel
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1 INTRODUCTION

The ZnO voltage sensitive ceramics (or varistor) has been widely used for its excellent nonlinearity and a large surge-energy absorption capability[1~3]. At present, with the fast development of household appliances of electronic device, computer and communication technology, the low-voltage varistors are in great need[4]. Therefore, the present tendency in this field is to decrease the breakdown voltage. The breakdown voltage of ZnO varistor is controlled by the voltage of grain layer, therefore, the key problem is how to decrease the number of ZnO grains between two electrodes by means of controlling the technological condition so as to decrease the breakdown voltage. Crystal technology is one of the most effective methods to obtain low-voltage ZnO varistors[5, 6].

However, there are some defects in the course of the preparation of ZnO crystal. For example, the process to produce ZnO crystal is very complex and needs sintering at a very high temperature (1 400 ℃) for a long time (10 h) which will affect the application prospect. Therefore, at the present paper, the new method to prepare ZnO crystal by using sol-gel technology has been developed and its mechanism is discussed.

2 EXPERIMENTAL

The materials used in this experiment were $ZnSO_4 \cdot H_2O$(AR), Na_2CO_3(AR) and $BaCl_2$(AR).

The samples were prepared by adding 0.1 mol/L Na_2CO_3 aqueous solution into 0.1 mol/L $ZnSO_4$ aqueous solution. The mixed solution fully reacted at room temperature with stirring. After reaction, the sol solution was filtered, washed by distilled water and the wet gel was obtained. The sol particles for the morphology determination was got from the reaction solution and observed at once by using H800 TEM. The wet gel was dried at 110~ 120 ℃ for 10 h and then the dried gel was sintered at different temperatures of 600, 800, 1 000 and 1 200 ℃ respectively to prepare different ZnO crystal. The morphologies of ZnO crystal were observed under JSM-35C Scanning Electron Microscope.

3 RESULTS AND DISCUSSION

3.1 Formation process of sol

Sol-gel method is a technique used in ceramic industry since the 1960s. Dishch[7] prepared the block glass in 1971. Since then, studies in this field have developed very fast. It is a powder preparation method by means of sol dispersive system. Usually, the sol particles are all in the range of 1~ 100 nm, and among the particles is the molecular cluster with high decentralization. It is an unstable multiphase system in thermodynamics but stable in dynamics. Therefore, the sol is very stable with metal ions in solution. After dehydration, the sol becomes gel. After Na_2CO_3 solution is mixed with Zn^{2+} solution, Zn^{2+} ion forms insoluble Zn_2CO_3 particle due to the very small K_{sp} (1.4×10^{-11}). The newly formed Zn_2CO_3 particle is very fine, then, this precipitate also hydrolyzes and transforms into zinc carbonate hydroxide hydrate ($x ZnCO_3 \cdot y Zn(OH)_2 \cdot z H_2O$), where, the value of x, y, z depends on the different conditions. The reacting process is

$$Zn^{2+} + CO_3^{2-} + H_2O \longrightarrow x ZnCO_3 \cdot y Zn(OH)_2 \cdot z H_2O$$

Fig. 1 is the TEM photograph of sol particles

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getting from the reacting process directly. In this figure, we can find that the sol particle is very small with a diameter of about 0.025 μm. Sol particles agglomerate each other and form a web structure due to their large surface area and high activity.

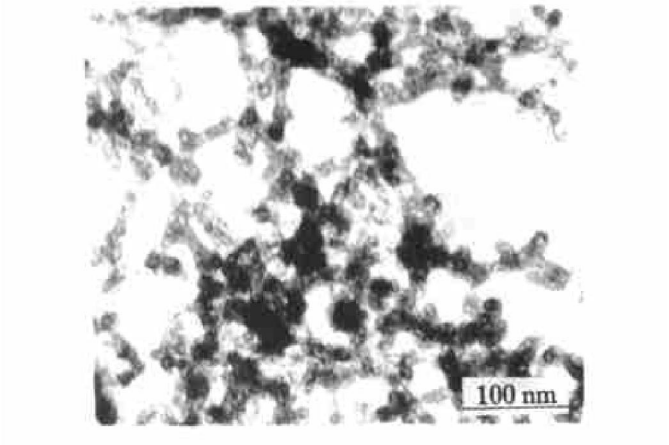

Fig. 1 TEM photograph of sol particles

3.2 Formation process

At room temperature, $ZnSO_4$ reacts with Na_2CO_3 and forms sol. This sol can not precipitate in aqueous solution. The sol particles will bond together and form the hard compact agglomeration during dehydrating.

The dry gel is very compact, and with a small amount of gas pores existing in the gel body, nevertheless, we can also find that the dry gel is the solid block formed by very small compact particles. It can be concluded that the sol particle is superfine with great surface area[8]. Therefore, it shows an abnormal surface and volume effect.

The particles in the wet gel were bonded by water moleculars. The water moleculars include hydroxyl water (– OH), structure water, coordinate water and absorption water, and it is the reason for hard agglomeration.

When the wet sol was dried, the water in the sol will be vaporized, and the distance between the particles is shortened. Owing to the great deal of – OH existing on the particles surface, the – OH will dehydrate and produce Zn-O-Zn bond when the wet water and absorption water were dehydrated. These actions make the particles contact together and agglomerate. The above reaction is very fast in dynamics, even if at room temperature. As has been reported before[9], the smaller the particle size, the more compact the agglomeration. Therefore, to get the compact agglomeration, the growth of the new formed sol particles in the aqueous must be avoided. The chemical composition of this dry gel is $Zn_4CO_3(OH)_6H_2O$[10]. The decomposition temperature of the dry gel is among 157 ℃ to 297 ℃.

3.3 Microstructure of ZnO crystal

The dry gel were calcined at the same heating rate and different temperatures of 600, 800, 1 000, 1 200 ℃ for 20 min, then quenched in the air.

Fig. 2 is the microstructure of ZnO crystal calcined at 600 ℃. It shows that the milled and calcined product is not regular, with a diameter of over 100 μm. Fig. 3(a) shows the surface state of ZnO crystal calcined at 600 ℃. Which indicates that fine ZnO particles still can be seen, with a diameter of about 0.3 μm.

Fig. 2 Morphology of ZnO crystal

Fig. 3(c) and (d) are ZnO micrographs calcined at 800 and 1 000 ℃. These results show that with the increasing of calcined temperature, the seed grains made up of ZnO crystals become bigger and bigger, but fine grains still existed. When the calcined temperature is higher (1200 ℃), not only is the ZnO seed grain bigger than that at lower temperature, but also are the grains more compact. The ZnO varistor made by this ZnO crystal shows a low voltage[9].

In fact, the dry gel after dehydration is the agglomeration of the first sol grain through the band of O-Zn-O. This agglomeration contains very high energy, and is metastable. It has a tendency to lose energy and become stable. In the course of calcine, with the increasing of sintering temperature, the first grain will overcome the energy obstacle and become bigger, which makes the ZnO crystal more compact. The finer the sol particle size formed in solution, resulting in the more compact the dry gel, the higher the energy of the grain, and the bigger the sintering drive of the primary grain.

4 CONCLUSIONS

1) The dry gel can be made by using $ZnSO_4$ as the start material, Na_2CO_3 as the precipitator. The result shows that the sol particle structure is the web one.

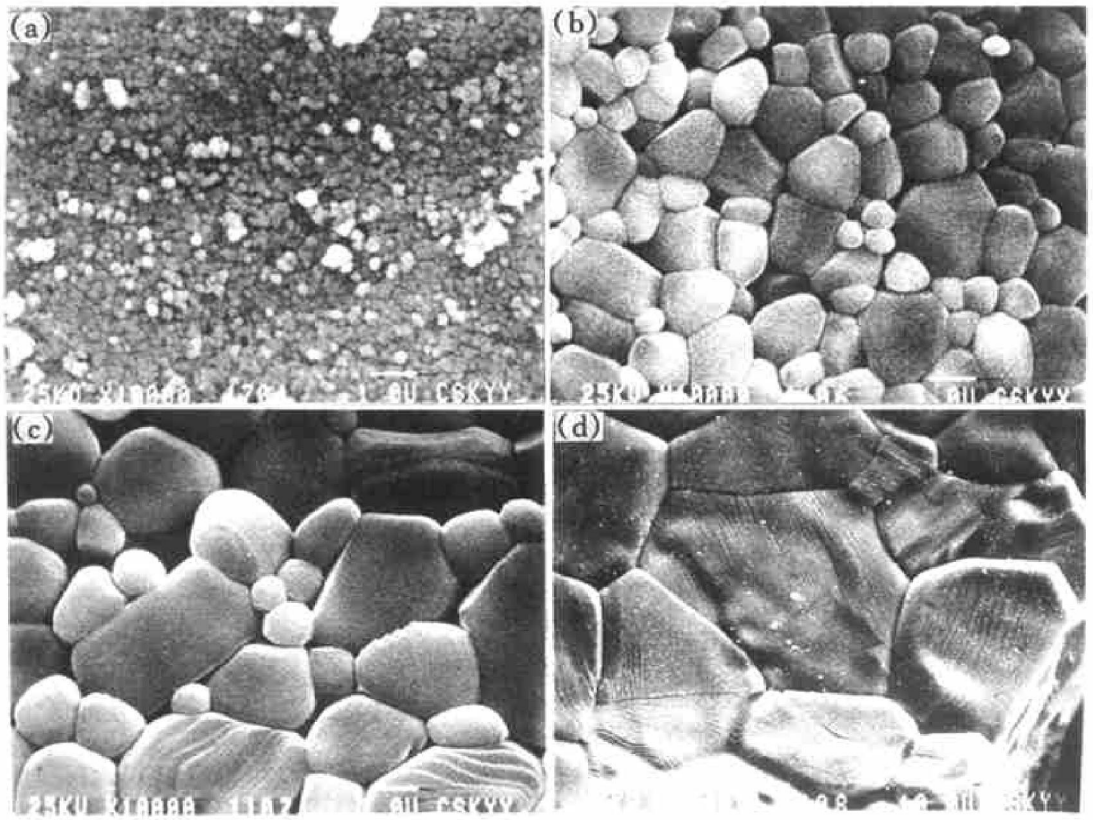

Fig. 3 Surface morphologies of ZnO crystal at different calcined temperatures
(a) —Calcined at 600 ℃; (b) —Calcined at 800 ℃; (d) —Calcined at 1 000 ℃; (d) —Calcined at 1 200 ℃

2) The dry gel is a very compact agglomeration made up of the first fine grains. In the course of sintering and decomposing, with the increasing of sintering temperature, the fine grain existing in ZnO crystal will become bigger and more compact.

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