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Influence of size of seed grains and sintering condition on varistor properties of $ZnO-Bi_2O_3-TiO_2-Sb_2O_3$ ceramics ①

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[Abstract] Varistor ceramics of $ZnO-Bi_2O_3-TiO_2-Sb_2O_3$ system have been fabricated by introducing pre-fabricated ZnO seed grains with different size distributions respectively. The results show that the varistor properties were significantly influenced by the size of introduced seed grains, and introducing larger seed grains is more advantageous to the modification of microstructure and the improvement of varistor properties. The varistor properties were considerably improved with a moderately increased sintering temperature or time, whereas degraded apparently when the sintering temperature or time was excessively increased. Compared with the sintering time, the sintering temperature plays a more critical role in determining the varistor properties. By introducing pre-fabricated ZnO seed grains into the original powders, low-voltage ZnO varistor ceramics possessing the desired electrical properties have been produced with a sintering temperature of about 1210 ℃ and a sintering temperature of 2~ 2.5 h.

[Key words] $ZnO-Bi_2O_3-TiO_2-Sb_2O_3$ ceramics; seed grains; sintering temperature; sintering time; low varistor voltage
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1 INTRODUCTION

Since ZnO varistor ceramics were firstly developed in 1968, significant progresses have been made in investigation and application of the material. As a kind of advanced functional ceramics, ZnO varistor ceramics have been widely used in electronic circuits and electrical power systems. Owing to the widespread use of integrated circuits, recently developed electronic devices and appliances become smaller and are operated at low voltage, which correspondingly requires ZnO ceramics with low varistor voltage as voltage stablizers and sudden surge arresters. ZnO ceramics with low varistor voltages of 4.7~ 22 V as well as those with both low varistor voltages of 22~ 68 V and large surge capabilities exhibit remarkable potential of being extensively applied in computers, domestic electrical appliances, communicating installations and automobiles[1, 2].

An important approach to produce low-voltage ZnO ceramics is to enhance the growth of grains, for which many methods have been used, such as raising sintering temperature[3~ 5], prolonging sintering time[3], adding enhancing additive for grain growth[6, 7] and introducing pre-fabricated ZnO seed grains[3, 8~ 10]. However, it is well known that the varistor properties of ZnO ceramics are affected by many factors, for they are inherently determined by the microstructures and electrical characteristics of both grains and grain boundaries. Hence, it was often found that the varistor voltages could be effectively lowered, whereas the nonlinear coefficients and leakage currents deteriorated simultaneously[4, 5, 10]. Therefore, in order to produce low-voltage ZnO ceramics with desired electrical properties, it is necessary to perform further research to investigate the contributing factors and rules of their influences in detail. In our previous researches, the influences of content of seed grains and annealing condition on varistor properties of $ZnO-Bi_2O_3-TiO_2-Sb_2O_3$ ceramics introduced with pre-fabricated seed grains have been investigated[11, 12]. This study was carried out with the aim at investigating the effects of size of seed grains and sintering condition on varistor properties.

2 EXPERIMENTAL

2.1 Fabrication of ZnO seed grains

ZnO used in this study was obtained from Wuhan Varistor Factory. ZnO was pre-fired at 800 ℃ for 2 h, and then mixed with 0.5% (mole fraction) $BaCO_3$ of chemical purity grade. The mixture was wet ball-milled in a polyethylene bottle with agate balls for 12 h. The milled mixture was calcined at 1 280 ℃ for 5 h, 8 h and 10 h, respectively. The ZnO seed grains were obtained after boiling the calcined mixture in distilled water for 8 h, washing with distilled water for several times and then drying up.

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The seed grains fabricated by sintering at 1 280 ℃ for 5 h, 8 h and 10 h were denoted as seed grains(A), seed grains(B) and seed grains(C), respectively. The size distribution of seed grains was examined by an Mastersize size analyzer (Malvern Instruments Ltd., U.K.)

2.2 Fabrication of ZnO ceramics

ZnO and small amounts of other ingredients with analytical purity grade, such as Bi_2O_3, TiO_2, Sb_2O_3, Co_2O_3, $MnCO_3$ and Cr_2O_3, were weighed respectively according to a designed composition. The original powders were processed by a conventional technique for producing electronic ceramics, including preliminary ball-milling, pre-firing and secondary ball-milling. The three kinds of ZnO seed grains were introduced into the processed original powders, respectively. After being gently mixed in an agate mortar for 1 h and granulated with PVA binder, the mixture was mechanically pressed into tablets of d 13 mm × (1 ~ 2) mm. The green tablets were sintered in air at 1 100~ 1 280 ℃ for 1~ 3.5 h and then furnace-cooled to room temperature.

Ag-Zn ohmic electrodes were coated and fired at 600 ℃ on both surfaces of as-sintered ceramics for electrical measurement. The varistor voltage (V_{1mA}), nonlinear coefficient (α) and leakage current (I_L) were measured at an MY automatic varistor meter. After etching the fractured surfaces of the ceramics in diluted acid, the microstructures of the ceramics were observed with an SX-40 scanning electron microscopy.

3 RESULTS AND DISCUSSION

3.1 Size distribution of seed grains

The size distributions of seed grains are shown in Fig. 1. The sizes of seed grains(A), seed grains(B) and seed grains(C) are mainly in the ranges of 20~ 60 μm, 30~ 80 μm and 40~ 80 μm, respectively, while the average sizes of them are 34.1 μm, 46.7 μm and 52.6 μm, respectively. In addition, it was detected that the specific surface areas of the three kinds seed grains are 5.49×10^2 cm^2/g, 4.02×10^2 cm^2/g and 2.31×10^2 cm^2/g, respectively. The results show that the size of seed grains become larger with increasing sintering time.

3.2 Influence of size of seed grains on varistor properties

The varistor properties of ZnO ceramics introduced with seed grains(A) and seed grains(B) respectively and sintered at 1 210 ℃ for 2 h are shown in Fig. 2. Compared with the ceramics without seed grains, the varistor properties of those introduced with seed grains were improved more or less. Moreover, it can be seen that the improvement of varistor properties in the ceramics introduced with seed grains (B) is more significant. The optimized varistor prop-

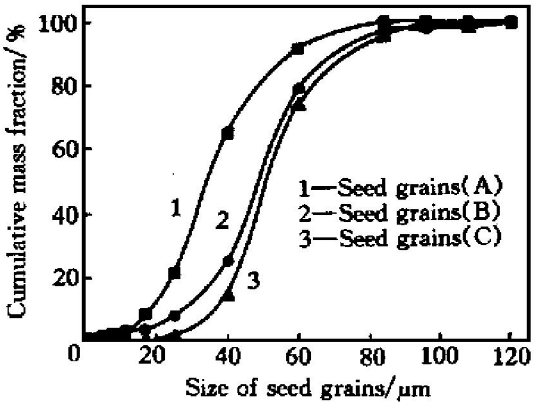

Fig. 1 Cumulative mass fraction as a function of size of seed grains

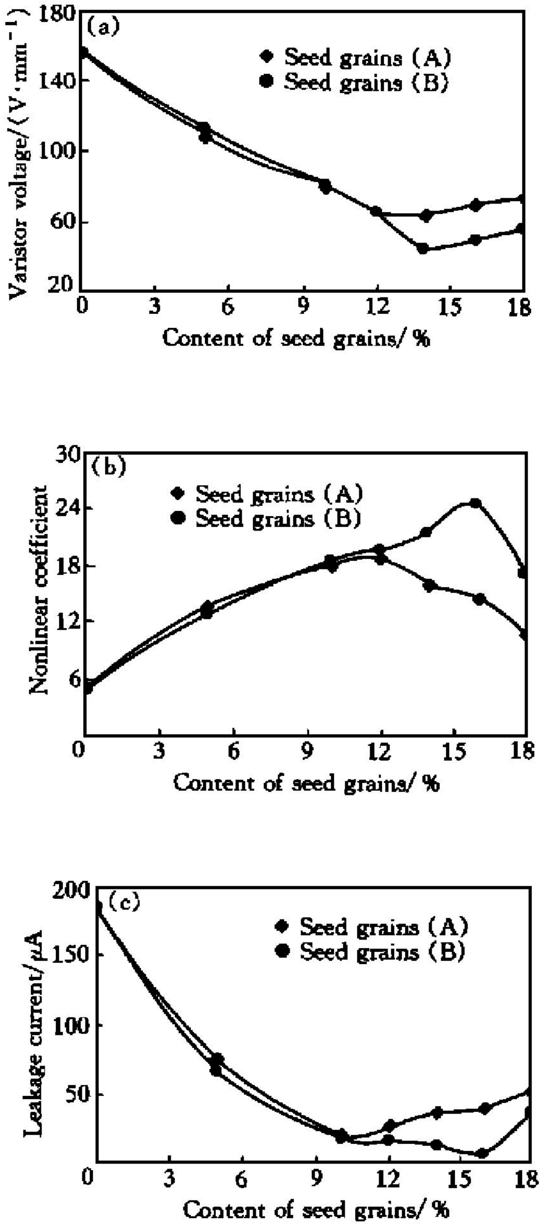

Fig. 2 Varistor properties of ZnO ceramics introduced with different contents of seed grains(A) and seed grains(B) respectively

erties were obtained in the ceramics introduced with 16% (mass fraction) seed grains(B), exhibiting a varistor voltage of 50.5 V/mm, a nonlinear coefficient of 24.2 and a leakage current of 7.5 μA. The varistor properties of ZnO ceramics introduced with different contents of seed grains(C), larger than both seed grains(A) and seed grains(B), have also been investigated in one of our previous researches. The optimized varistor properties were obtained when 10% seed grains(C) were added, which are comparable to those of the ceramics introduced with 16% seed grains(B)[11].

As grains are much larger than milled original powders, seed grains acted as crystal nuclei on sintering, which promoted the dissolution-separation behavior of ZnO fine powders in Bi_2O_3-rich liquid phase. As a result, the homogeneous growth of grain was realized and varistor voltage of the ceramics was correspondingly lowered. Moreover, it was proved[11] that the sufficient dissolution of ZnO fine powders in Bi_2O_3-rich liquid phase accelerated the reaction between TiO_2 and ZnO, forming Zn_2TiO_4 spinel phase at grain boundaries. The nonlinear coefficient and leakage current of the ceramics were thus improved, due to the reduction of the content of Ti^{4+} ions in Bi_2O_3-rich liquid phase. Therefore, it is the homogeneous grain growth enhanced by introducing seed grains that contributed greatly to the modification of microstructure and the improvement of varistor properties[3, 9]. Apparently, the varistor properties of the ceramics are not only affected by the content of introduced seed grains[9~11], but also the size of them. Fig. 3 shows the microstructures of ZnO ceramics introduced with 10% of seed grains(A), seed grains (B) and seed grains(C) respectively and sintered at 1210 ℃ for 2 h. It was found that the homogeneous grain growth was more effectively enhanced when larger seed grains were added, which resulted in larger grains and denser microstructure. The result indicates that it is difficult to achieve the full-grown grains in the ceramics introduced with small seed grains. On the contrary, it is considered that introducing larger seed grains is more advantageous to the modification of microstructure and the improvement of varistor properties.

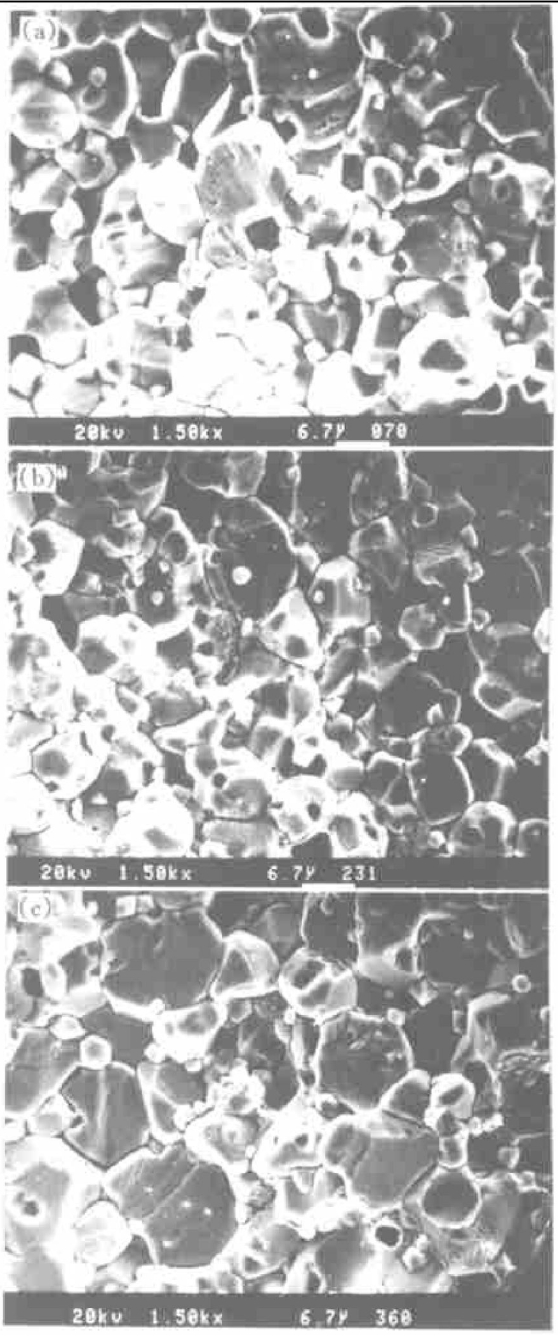

Fig. 3 Microstructures of ZnO ceramics introduced with 10% of (a) seed grains(A), (b) seed grains (B) and (c) seed grains(C) respectively

3.3 Influence of sintering temperature and sintering time on varistor properties

Fig. 4 shows the influence of sintering temperature on varistor properties of ZnO ceramics introduced with 16% seed grains(B) and sintered for 2 h. The nonlinear coefficient increased with increasing sintering temperature in the range of 1100~1210 ℃, while the varistor voltage decreased and the leakage current rose slightly from 5.3 μA to 7.5 μA. Generally speaking, the results illustrate the improvement of electrical properties. However, the nonlinear coefficient decreased rapidly and the leakage current rose abruptly when the sintering temperature was excessively raised, demonstrating the significant degradation of electrical properties. The variation of varistor properties with sintering time in the ceramics introduced with 16% seed grains(B) and sintered at 1210 ℃ manifests a similar tendency, as shown in Fig. 5. The varistor properties were improved with increasing sintering time when it was within 2.5 h, whereas the nonlinear coefficient and leakage current degraded apparently when the sintering time was excessively prolonged.

The above degradation of electrical properties is

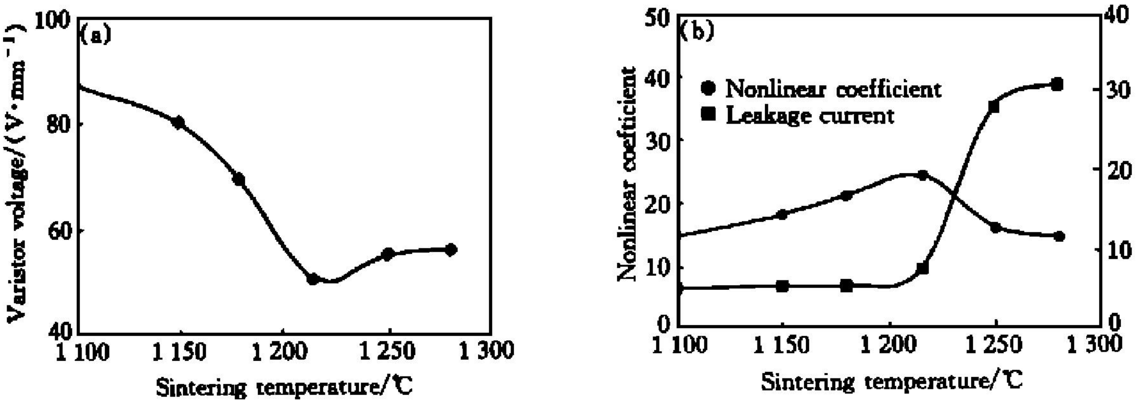

Fig. 4 Influence of sintering temperature on varistor properties of ZnO ceramics

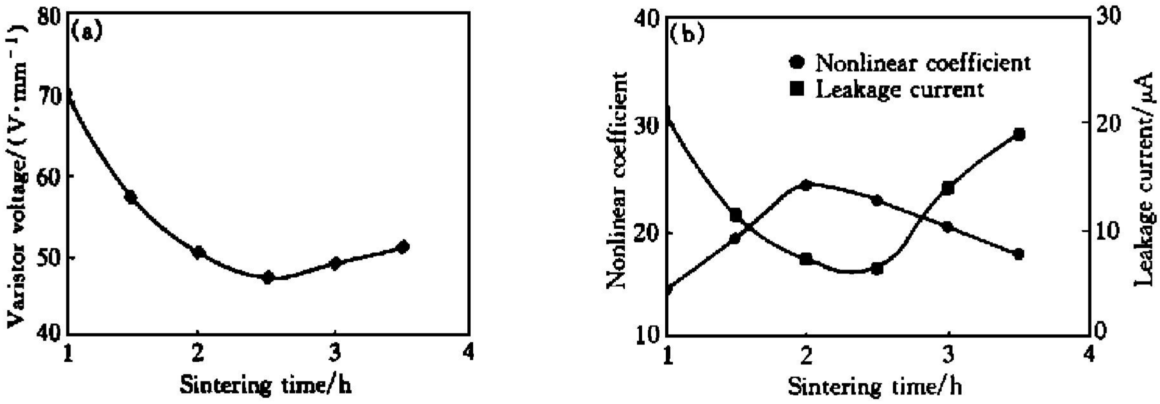

Fig. 5 Influence of sintering time on varistor properties of ZnO ceramics

attributed to the excessive volatilization of Bi_2O_3 on sintering. With a low melting point, Bi_2O_3 contributed greatly to the formation of liquid phase during the sintering course, which promoted the sintering of the ceramics. Moreover, the thin Bi-rich layers between grains in as-sintered ceramics play an important role in the generation of non-ohmic conducting characteristics[13]. It is apparent that when the sintering temperature or time was excessively increased, the volatilization of Bi_2O_3 was accelerated and varistor properties subsequently deteriorated. On one hand, the excessive volatilization of Bi_2O_3 weakened the function of Bi_2O_3-rich liquid phase as a medium of mass transfer during the sintering course and correspondingly restrained the sufficient growth of grains. On the other hand, the excessive volatilization of Bi_2O_3 reduced the content of Bi atoms at grain boundaries, causing the decrease of nonlinear coefficient and the increase of leakage current.

Furthermore, it is notable that the degradation of varistor properties due to the excessively increased sintering temperature is more pronounced. The result reveals that compared with the sintering time, the sintering temperature plays a more critical role in determining varistor properties. In this research, with a sintering temperature of about 1 210 ℃ and a sintering time of 2~ 2. 5 h, low-voltage ZnO ceramics with desired electrical properties have been produced by introducing pre-fabricated seed grains.

4 CONCLUSIONS

1) The varistor properties of ZnO ceramics are significantly influenced by the size of introduced seed grains, and introducing larger seed grains is more beneficial to the modification of microstructure and the improvement of varistor properties.

2) The varistor properties can be improved when the sintering temperature or time is moderately increased, whereas tends to degrade when the sintering temperature or time is excessively increased. Compared with the sintering time, the sintering temperature plays a more critical role in determining varistor properties.

3) With a sintering temperature of about 1 210 ℃ and a sintering time of 2~ 2. 5 h, low-voltage ZnO ceramics with desired electrical properties have been produced by introducing pre-fabricated seed grains.

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