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Influence of intensive milling on the microstructure and electrical properties of ZnO–Bi_2O_3-based varistors

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Abstract

ZnO varistors were synthesized using Pr_6O_{11} doped ZnO–Bi_2O_3 system as raw materials by ball milling. The effects of intensive milling on the microstructure and electrical properties of the varistors were investigated in detail. The results show the intensive milling decreases the particle size and distribution of the powders for ZnO varistors. The optimal samples obtained from the powders milled for 10 h have average crystalline grain size of about 4 μm and the gradient voltage of 565 V/mm, the leakage current of 0.45 μA, and the nonlinear coefficient of 75.

Keywords: A. Milling; C. Electrical properties; D. ZnO; E. Varistors

1. Introduction

ZnO varistor ceramics play a leading role in making surge protection devices, which are commonly used to protect electric power systems from transient voltages [1]. Conventional method of preparation of commercial ZnO–Bi_2O_3 varistors is direct mixing of oxides. However, this method is difficult to precisely control the desirable microstructure and electrical properties [2].

Recently, many researchers have been focusing on the relations between grain size and electrical properties [3,4]. In this study, the effects of milling time on the microstructure and electrical properties of ZnO varistors have been investigated, and the best experimental program has been obtained.

2. Experimental

The ratio (in weight) of raw materials for the present investigation was $85.33ZnO + 2.76Bi_2O_3 + 3.22Sb_2O_3 + 1.28MnCO_3 + 0.84Cr_2O_3 + 0.92Ni_2O_3 + 1.83Co_2O_3 + 0.83SiO_2 + 2.25Pr_6O_{11}$. In addition, 200 ppm $Al(NO_3)_3$, 200 ppm H_3BO_3 and 300 ppm $AgNO_3$ were added, respectively. Except ZnO, all powders were calcinated at 700 °C for 30 min firstly, and then blended with ZnO together with ethanol in nylon vial. After adding 2 wt.% polyvinyl alcohol (PVA), the mixtures were milled at a speed of 800 r/min for 0, 5, 10, 15 and 20 h, respectively. The as-dried powders were then uniaxially pressed into discs of 10 mm in diameter and 2 mm in thickness. The green discs were sintered at 1075 °C for 2 h with a heating rate of 3 °C/min, and then cooled to room temperature in furnace.

The size distribution of the mixture powders was measured by Zetasizer (Nano-ZS, Malvern, UK). The fracture surfaces of the samples were examined by scanning electron microscopy (SEM, JSM-6460, JEOL, Japan) equipped with energy-dispersive spectroscopy (EDS, INCA Energy, Oxford Instruments Inc., UK). The average ZnO diameter (D) was measured for each recognizable grain in polished surface, and the average of 500 grains was calculated without correction factors.

The crystalline phases were identified by an X-ray diffractometry (XRD, D/max-2200/PCX, Rigaku Corporation, Japan) using Cu Kα radiation. The density ρ of samples was measured by the Archimedes method in distilled water.

For DC current–voltage characterization, silver electrodes were painted on both surfaces of the samples and fired at 600 °C for 10 min. *I–V* characteristics were measured by a DC parameter instrument for varistors (Model CJ1001, China). The voltage-gradient ($V_{1\ mA}$) was determined at a current of 1 mA

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and the non-linear coefficient (α) was obtained from the equation $\alpha = 1/\lg(V_{1\ \mathrm{mA}}/V_{0.1\ \mathrm{mA}})$. The leakage current ($I_L$) was measured at 0.75 $V_{1\ \mathrm{mA}}$.

3. Results and discussion

Fig. 1 shows the particle size distributions for the powders that were not subjected to any intensive milling are considerably broad. Upon the powder subjected to 5 h of intensive milling, an apparent reduction in particle size was observed, which may be attributed to the fracture of large particle size and large agglomerates in raw materials. With the increase of milling time to 10 h, smaller reduction in average size occurs, but size distribution is obvious narrower, which means that the milled powders are more uniform. When the powders were further intensively milled over 10 h, very little change in the distribution range occurs, but the average particle size was increased slightly because of the aggregates created.

Fig. 2 shows in addition to the ZnO phase, the $Zn_7Sb_2O_{12}$ spinel phase, and the Bi-rich phase exist in all samples. With increasing the milling time, not any obvious change in phase composition was observed. But the full width at half maximum (FWHM) of the ZnO peaks (at $2\theta = 47$, 63 and 76°) become wider, in combination with Scherrer formulas, which is attributed to the decrease in grain size. The milled powders had high ratio surface area and surface energy and tend to decrease in size with increasing milling time. So the liquid phase of Bi_2O_3 and eutectic phase of Sb_2O_3–Bi_2O_3 can be easy to get and enwrap the surface of ZnO grain at relative low temperature, which inhibit the migration of the grain boundary, as a result, the ZnO grain size decreased in the sintered samples [5].

Fig. 3 shows the SEM and EDS analysis of the ZnO varistor ceramics. It is obvious that the microstructures of the varistor samples prepared from the intensively milled powders appear more homogeneous with a finer distribution of grain size, in comparison to the sample prepared from the un-milled powders. The average grain size decreases from 7.2 to 4.0 μm, and the density increases from 5.28 to 5.71 g/cm^3, when the milling time increased from 0 to 20 h. Fig. 3(f) is the partial enlarged view of Fig. 3 (c). In addition to ZnO grain, other three types of grain in the SEM micrographs have been investigated by EDS (spectrums 1–3). The region of spectrum 1 is mainly consisted of $Zn_7Sb_2O_{12}$ spinel phase with the shape of ball and the color of black, while spectrum 2 is mainly Bi rich phase with the form of ball and the color of bright, and spectrum 3 is mainly Pr rich phase with the form of small rod. These conclusions are well in agreement with that in the previous Ref. [6].

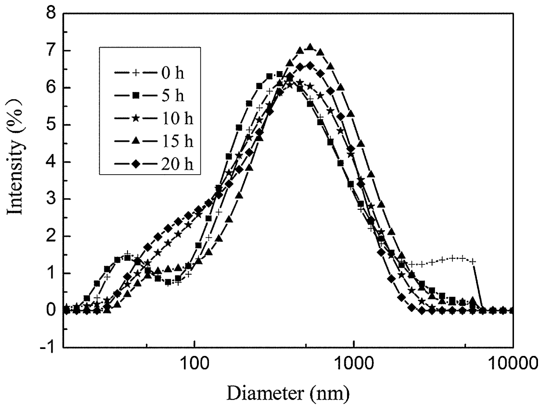


Fig. 1. Size distribution by intensity with different milling times.

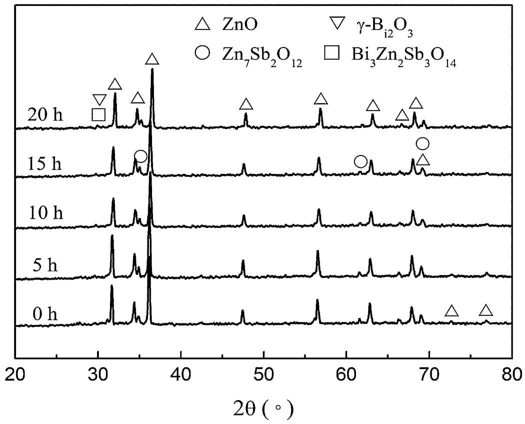
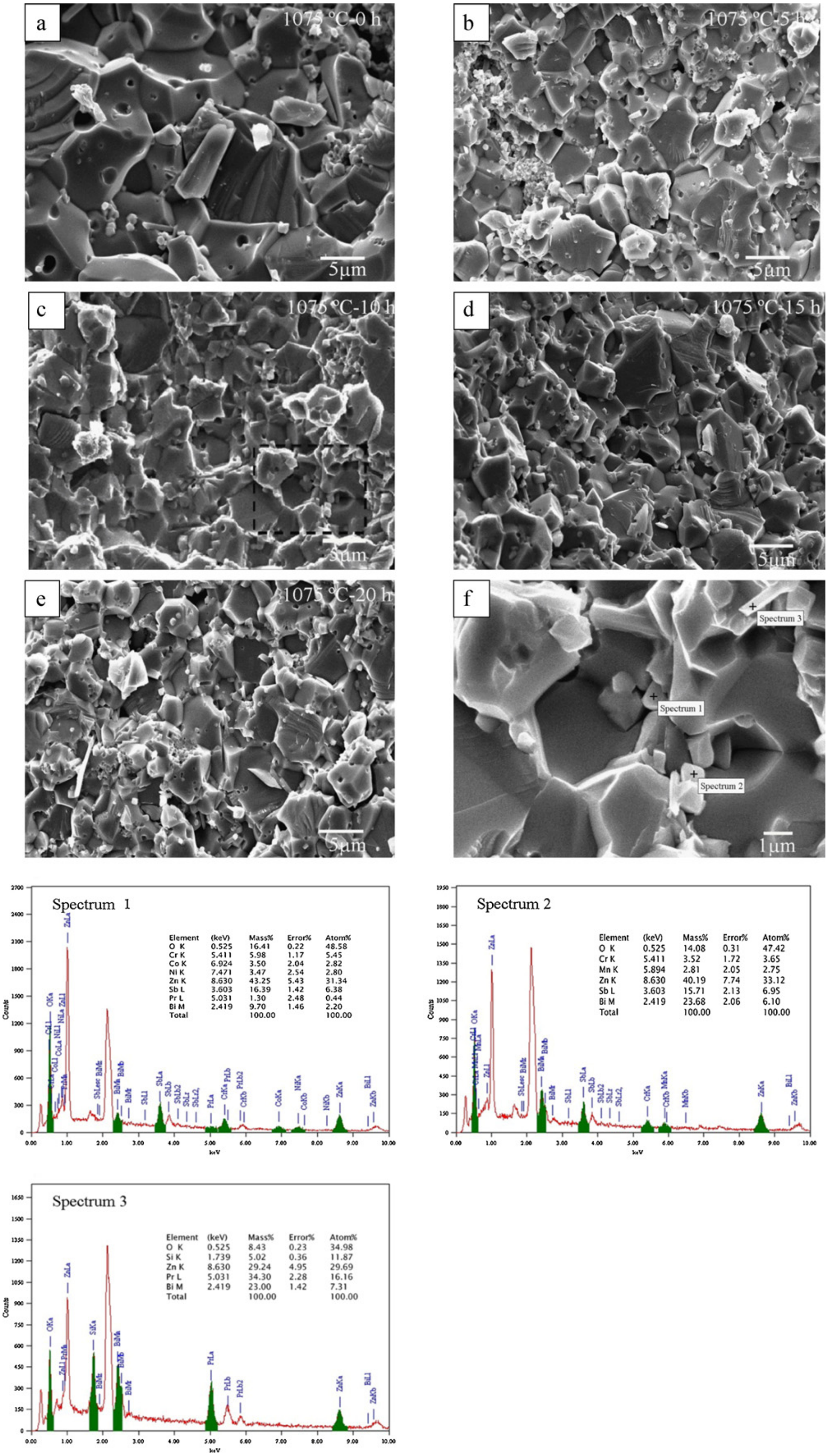


Fig. 2. XRD patterns of ZnO varistor ceramics sintered at 1075 °C for 2 h with different ball milling times.

Based on the microstructure analysis above, it shows that the intensive milling could alter the microstructure of the varistor and decrease the grain size. Firstly, during the process of intensive milling, high strength and high pressure caused by collision between the grinding media and powders make the milled powders have high ratio of surface area and high surface energy. Secondly, the milled particles with refiner and more uniform size distribution obviously lower the sintering temperature of the varistors, which makes the grain grow slowly, and as a result, the as-prepared varistor has small grain size and fine microstructure, which is beneficial for improving the electrical properties of the varistors.

The electrical properties of ZnO varistors were characterized by voltage–current (V–I) in Fig. 4. It shows that the breakdown region of V–I curves is becoming much flatter with the increasing of ball milling time. Table 1 summarizes the corresponding electrical parameters. It shows the varistor voltage increases from 361 to 650 V/mm as the milling time rise from 0 to 20 h. The nonlinear coefficient is improved with the increase of milling time from 0 to 10 h. The appropriate intensive milling remarkably reduces the grain size and improves their uniformity; hence, the nonlinear coefficient has been improved. However, when the milling time continuously increased over 10 h, nonlinear coefficient is slightly decreased, which is attributed to the contamination from the milling medium of steel ball in long time intensive milling. So the optimum value of nonlinear coefficient is 75 when the milling time is 10 h. With the increasing of milling time, the leakage current of all samples decrease firstly, and reach the lowest value when the milling time reaches 10 h. The minimum value of leakage current 0.45 μA is achieved when the milling time is 10 h.



Spectrum 1

Element	(keV)	Mass%	Error%	Atom%
O K	0.525	16.41	0.22	48.58
Cr K	5.411	5.98	1.17	5.45
Co K	6.924	3.50	2.04	2.82
Ni K	7.471	3.47	2.54	2.80
Zn K	8.630	43.25	5.43	31.34
Sb L	3.603	16.39	1.42	6.38
Pr L	5.031	1.30	2.48	0.44
Bi M	2.419	9.70	1.46	2.20
Total		100.00		100.00

Spectrum 2

Element	(keV)	Mass%	Error%	Atom%
O K	0.525	14.08	0.31	47.42
Cr K	5.411	3.52	1.72	3.65
Mn K	5.894	2.81	2.05	2.75
Zn K	8.630	40.19	7.74	33.12
Sb L	3.603	15.71	2.13	6.95
Bi M	2.419	23.68	2.06	6.10
Total		100.00		100.00

Spectrum 3

Element	(keV)	Mass%	Error%	Atom%
O K	0.525	8.43	0.23	34.98
Si K	1.739	5.02	0.36	11.87
Zn K	8.630	29.24	4.95	29.69
Pr L	5.031	34.30	2.28	16.16
Bi M	2.419	23.00	1.42	7.31
Total		100.00		100.00

Fig. 3. SEM/EDS analysis of ZnO varistor ceramics sintered at 1075 °C for 2 h with different milling times: (a) 0 h, (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h, (f) partial enlarged view of (c).

Table 1
Grain sizes and electrical parameters of the sample sintered at 1075 °C for 2 h.

Milling time (h)	Average ZnO grain size (μm)	Gradient voltage, $V_{1\ \mathrm{mA}}$ (V/mm)	Non linear coefficient, α	Leakage current, I_L (μA)
0	7.2	363	67	1.08
5	5.7	514	72	0.86
10	5.1	565	75	0.45
15	4.5	582	73	0.54
20	4.0	650	74	0.58

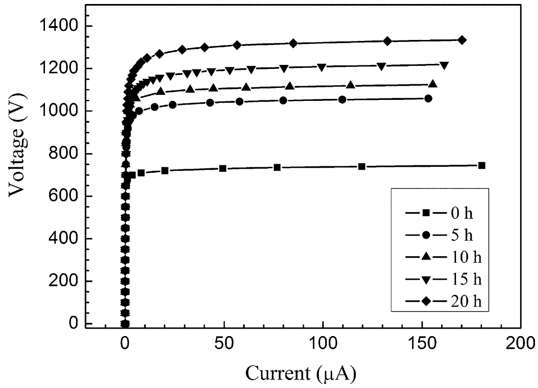


Fig. 4. Current–voltage curves of the varistor samples sintered at 1075 °C for 2 h with different milling times.

4. Conclusions

The intensive milling fined the microstructure of the varistors and optimized the electrical properties. The samples sintered at 1075 °C from the powders milled for 10 h have the best combination of electrical properties: the varistor voltage, nonlinear coefficient, and leakage current are 565 V/mm, 75 and 0.45 μA, respectively.

Acknowledgements

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