Densification and Grain Growth in BaO.Bi$_2$O$_3$.ZnO Varistor Ceramics

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Abstract

The effect of barium addition on the densification and grain growth of ZnO-based ceramics was investigated. ZnO-based varistors have been employed as surge arresters to prevent damages from voltage surges in electrical or energy-related equipments such as transformer and consumer products. These devices have been commercially incorporated into energy-supplying grids. The selected composition was ZnO + 0.0025Bi$_2$O$_3$ + (x) BaCO$_3$ where x = 0 and 0.005. Both solid-state processing and precipitation method were investigated. It was shown that the amount of Bi addition was too low to be effective for improving grain growth; however, it was sufficient to enhance densification. When barium was further added, the averaged grain size was more than doubled, possibly due to liquid-phase sintering. This result suggests the possibility of BaO-containing liquid-phase formation along grain boundaries. However, the main drawbacks of barium addition were a slight decrease in density, which was presumed to be caused by closed pores trapped in the grain interior during the sintering process, and a reduction in the threshold voltage.

Key words: Grain growth, Varistor, Zinc oxide, Doping

Introduction

ZnO-based ceramics have been widely used in varistor application due to their suitable electrical properties. The highly nonlinear current-voltage characteristics and high current handling capability enables them to be efficient overvoltage protectors in electronic circuits, electric power system and equipment for power transmission.$^{(1-5)}$ Different oxide compounds are usually added during the processing to tune various electrical characteristics such as non-linearity and breakdown voltage. Bi$_2$O$_3$ is always included in the composition as its derivatives have been reported to be responsible for the non-ohmic properties. Other well-known dopants and additives include CoO, Nb$_2$O$_5$, Cr$_2$O$_3$, MnO and Sb$_2$O$_3$. Among various microstructural aspects, the grain size appears to frequently dictate the breakdown voltage. Several reports have found that high thresholds tend to be associated with small-grained varistor samples.$^{(6-7, 9-10)}$ Control of grain growth is one major subject of research, and wet chemical route has appeared to be one potential solution to tailor the final grain size in the varistor piece.$^{(11-14)}$ Since grain growth is a complex process and can be affected by different dopants and additives in the system, it would be interesting to investigate these compounds in detail. This study examined the influence of barium addition (at 0.5 mol%) on densification and grain growth in ZnO-based varistor ceramics. The starting precursors were prepared from both solid-state processing and chemical precipitation method in order to investigate the effect of the processing condition on the final microstructure.

Materials and Experimental Procedures

The chemicals for the solid-state processing were reagent-grade ZnO, Bi$_2$O$_3$ and BaCO$_3$. They were weighed according to the composition: ZnO + 0.0025Bi$_2$O$_3$ + (x) BaCO$_3$ where x = 0 and 0.005. The mechanical mixture was ball-milled with alumina balls in ethanol for 24 hours. For the precipitation method, reagent-grade ZnCl$_2$, Bi(NO$_3$)$_3$.5H$_2$O and C$_6$H$_5$BaO$_4$ were dissolved in distilled water (1M). The pH of the system, using a 1M NaOH solution, was adjusted to be 14. After one-hour of continuous stirring, the solutions were dried at 120°C and washed thoroughly to remove chloride ions. Thermogravimetric analysis (TGA, 7 Perkin-Elemer) was employed to determine the
calcination temperature. The precipitates were calcined at 400°C for 6 hours to remove inorganics. The morphology of the nanosized powders was examined through Transmission Electron Microscope (TEM, Philips EM201C). The powders were pressed into disks with a diameter of 8 mm and a thickness of ~2 mm. These disks were sintered in air for 6 hours at 900, 1000, 1100, 1200, 1300 and 1400°C, with heating and cooling rates of 5°C/min. Sinterability was characterized by the geometric (bulk) density measurement. Scanning electron microscopy (SEM, Hitachi S-3000N) was used to examine the microstructure. The averaged grain size was calculated by the line-intercept method. Phase formation was confirmed by X-rays diffraction (XRD, D/MAX 2000 Rigaku). The non-linear response was measured by a simple variac and multimeters.

Results and Discussion

The XRD patterns of the calcined nanopowders are shown in Figure 1. TGA showed complete decomposition of organic residues at 400°C (data not shown) which was chosen to be the calcination temperature. No impurity peaks were present within the detection limit of XRD. The averaged crystallite sizes calculated by the Scherrer’s formula are approximately in between 45 and 50 nm for both x = 0.00 and x = 0.005 samples. No preferential orientation was observed, and all major peaks can be indexed as a zincite phase according to the JCPDS database (75-0576). The morphology of the crystals (Figure 2) displays both equiaxed and slightly elongated character. The latter might be yielded from the hexagonal structure of ZnO. Agglomeration of the particles is clearly seen as evidenced by high specific surface area and grain coalescence at the calcination temperature of 400°C.

Figure 1. XRD patterns of the ZnO nanopowders (undoped and doped) calcined at 400°C for 6 hours.

Figure 2. TEM image of the ZnO nanoparticles calcined at 400°C for 6 hours.

Figure 3 shows the relationship between bulk density and sintering temperature of all samples. Similar densities were obtained from both solid-state processing and precipitation method. The undoped pellets display a continuous increase in density from 66% (900°C) to the maximum of 94% (1300°C) where as the density values of the (Ba,Bi)-doped pellets never exceeded 90%. In fact, they fluctuate in the range between 84% and 90%. The greatest improvement in sintering was observed in the samples of Bi-doped compositions among which a relative density of 94% was readily acquired at 1100°C.

Figure 3. Relationship between density and sintering temperature of the undoped, Bi-doped and (Ba,Bi)-doped samples. Similar trends were observed for both solid-state processed and precipitated samples.

The sintered samples were crushed and x-rayed to examine phase purity. Figure 4 shows the XRD pattern of the (Ba,Bi)-doped sample (x = 0.005) sintered at 1300°C for 6 hours. The major peaks belong to a zincite phase with very small traces of secondary peaks. The intensities of these peaks are comparable to the undoped sample.
minor peaks are too low to accurately determine their corresponding phases.

![Figure 4](image.png)

**Figure 4.** XRD pattern of the (Ba,Bi)-doped sample (x = 0.005) sintered at 1300°C. The impurity peaks are denoted as asterisks.

The microstructures of the sintered samples (1300°C, 6 hours) were shown in Figures 5 and 6. Most grains appeared to be equiaxed with some being a little elongated. There seemed to be no significant intergranular pores. The averaged grain sizes of the undoped and Bi-doped samples are 4.0 μm for solid state processing and 15.9 μm for precipitation. A dramatic change in grain size, however, was observed in the (Ba,Bi)-doped sample (10.5 μm for solid-state processing and 6.6 μm for precipitation). Note that different trends in grain size upon addition of barium were obtained: an increase in the solid-state processing but a decrease in the precipitation method. Figure 6 also displays a number of small pores trapped within these large (Ba,Bi)-doped grain; these intragranular pores could be responsible for a lower density in this (Ba,Bi)-doped sample. Also, the Bi-doped precipitated sample (Figure 5(b)) displays small, discrete grains of approximately 1 to 2 μm along grain boundaries.

![Figure 5](image.png)

**Figure 5.** SEM image of the Bi-doped sample sintered at 1300°C for 6 hours. (a) Solid-state processing. (b) Precipitation method.

![Figure 6](image.png)

**Figure 6.** SEM image of the (Ba,Bi)-doped sample sintered at 1300°C for 6 hours. (a) Solid-state processing. (b) Precipitation method.

Figure 7 shows the microstructures of the (Ba,Bi)-doped precipitated sample sintered at 1300°C for 6 hours at different magnifications. A great degree of porosity can be seen with sizes varying from approximately 5 to 20 μm. Accumulation of pores to form macroscopic voids (larger than 50 μm) occurred extensively, confirming sluggish sinterability as evidenced by the density data in Figure 3. Hence, the (Ba,Bi)-doping tended to yield both intergranular and intragranular pores. Figure 7(b) also shows a microstructure at a higher magnification. It is very interesting to see smaller grains trapped within a large grain (in the middle of the figure). This type of grain entrapment was observed locating randomly throughout the sample. It is believed that such occurrence might be caused by abnormal grain growth typically associated with multicomponent systems within which additives possessing low melting temperatures or are capable of inducing formation of a liquid phase with other oxides.

![Figure 7](image.png)

**Figure 7.** SEM image of the (Ba,Bi)-doped precipitated sample sintered at 1300°C for 6 hours at different magnifications.

Increases in both density and grain growth at the temperatures higher than 1200°C for both Bi-and (Ba,Bi)-doped samples could likely be explained by liquid phase formation; different systems would yield different mechanisms of such formation. Addition of Bi2O3 has been reported to result in drastic improvement in densification and grain growth kinetics. The sintering temperatures between 1100°C and 1300°C were much higher than the eutectic temperature (~750°C) for the ZnO-Bi2O3 system.1, 3 The formed liquid phase...
enhances diffusion during sintering. Nevertheless, this study shows that there was virtually no difference in grain size between the undoped and Bi-doped samples. Such finding could likely be explained by the amount of Bi addition which was very low in this study. Previous studies usually employed Bi addition of more than 0.5 mol%. In addition, a very small amount of Bi2O3 (0.04 mol%) has been stated to yield microstructural inhomogeneity with noticeable porosity. Hence, there seemed to exist a critical amount of Bi addition beyond which significant grain growth could occur.

Similarly, the increase in grain size of more than two-fold in the (Ba,Bi)-doped solid-state sample should not be correlated to Bi addition alone. Nevertheless, the theory of liquid phase sintering could still be valid in spite of the absence of observable intergranular liquid films in Figure 6. The larger ionic radius of Ba2+ (0.134 nm) would likely segregate along grain boundaries due to its insolubility with the smaller Zn2+ ion (0.074 nm). The BaO liquid phase, along with possible Ba-Zn-O compounds, was reported to help enhance grain growth rate.

A typical I-V characteristic is shown in Figure 8 for (Ba,Bi)-doped solid-state sample sintered at 1300°C for 6 hours. Other samples displayed similar I-V format. No significant difference in the threshold voltage was obtained between the solid-state and precipitated samples. The threshold voltages at 0.1 mA/cm² are approximately 120 V/cm for the Bi-doped samples and 90 V/cm for the (Ba,Bi)-doped samples. These relatively low values of the threshold voltage might be explained by ineffective barrier along the grain boundary due to inefficient amount of bismuth-containing liquid phase.

Conclusions

The undoped pellets display a continuous increase in density to the maximum of 94% (1300°C). On the contrary, the density values of the (Ba,Bi)-doped pellets only fluctuated in the range between 84% and 90%. The best sinterability was observed in the Bi-doped samples with a relative density of 94% readily obtained at 1100°C. The averaged grain sizes were found to be similar between the undoped and Bi-doped samples. An increase of more than two-fold in grain size was observed in the (Ba,Bi)-doped sample. Differences in both densification and grain growth could be explained by the mechanism of liquid phase formation as well as possible inhomogeneous distribution of additives. The amount of Bi-addition of only 0.5 mol% in this study was sufficient to greatly improve sintering but did not seem to be high enough to produce a required amount of liquid phase. Ba addition, however, yielded possibly a different liquid phase compound which was effective for enhancing grain growth but not for eradication of porosity nor improvement in the non-linear response.

References


