DOPING EFFECT OF ZrO₂ ON MICROSTRUCTURAL AND ELECTRICAL PROPERTIES OF ZnO–Pr₆O₁₁-BASED CERAMIC VARISTORS

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ZnO–Pr₆O₁₁–CoO–Cr₂O₃-based ceramic varistors doped with 0–2.0 mol. % ZrO₂ were fabricated via conventional ceramic processing by sintering at 1300°C for 2 h. X-ray diffraction results indicate that the doped ZrO₂ reacted with praseodymium oxides during sintering, resulting in Pr₂Zr₂O₇ phase. Scanning electron microscopy analysis revealed that after the addition of ZrO₂, the growth of ZnO grains was inhibited due to the formation of Pr₂Zr₂O₇. When the amount was less than 0.5 mol. %, ZrO₂ doping was beneficial for increasing the varistor nonlinear exponent. The varistor voltage increased with increasing ZrO₂ contents in the ceramics, but the leakage current also increased with it. In this work, the sample doped with 0.5 mol. % ZrO₂ presented the highest nonlinear exponent (17), and its varistor voltage was 623 V·mm⁻¹. The sample with 2.0 mol. % ZrO₂ presented the highest varistor voltage (1490 V·mm⁻¹), and its nonlinear exponent was 10. The obtained varistor would be very promising in super-high-voltage power transmission systems.

INTRODUCTION

ZnO varistors are electronic ceramic devices produced by sintering ZnO powder with small amounts of various metal oxides, which were announced by Matsuoka in 1969 and are still being actively investigated today [1, 2]. They can be used in AC or DC fields over a wide range of voltages, from a few volts to tens of kilovolts, and a wide range of currents, from microamperes to kiloamperes. Their versatility has made ZnO varistors widely applied both in power industry as well as in semiconductor industry [1, 2].

Today the majority of ZnO varistors are doped with Bi₂O₃ as varistor-forming oxide (VFO), referred as to ZnO–Bi₂O₃-based varistor, which is the commercially commonest composition for ZnO varistor [1]. However, Bi₂O₃ has too much high volatility and reactivity during liquid phase sintering; the former would change the composition ratio of additives and the latter destroy the multilayer structure of chip varistors [3, 4].

To avoid such problems of ZnO–Bi₂O₃-based ceramic varistors, ZnO varistor ceramics containing Pr₆O₁₁ as VFO have been actively and extensively studied [3-12]. It was first reported by Mukae et al. that ZnO ceramics containing Pr₆O₁₁ and Co₂O₃ could exhibit non-ohmic characteristics, referred as to ZnO–Pr₆O₁₁-based ceramic varistors. Such varistors have a simple two-phase microstructure of ZnO grain and a Pr oxide intergranular phase. In comparison with ZnO–Bi₂O₃-based varistors, which have spinel phase that play no significant electrical role, this two-phase microstructure increases the active grain boundary area through which electrical current flows [4, 5]. Since the discovery of ZnO–Pr₆O₁₁ based varistors, a number of papers about ZnO–Pr₆O₁₁ based varistors have been published, in which the doping effects of rare earth metal oxides such as Er₂O₃, Y₂O₃, La₂O₃ and Tb₂O₃ [6-8], or other metal oxides such as Fe₂O₃ [4], SnO₂ [5], Sb₂O₃ [9], and TiO₂ [10], or alkali ions [11, 12] on the microstructural and electrical properties of ZnO–Pr₆O₁₁ based varistors have been well studied, but the breakdown voltages of most varistors reported were about 500 V·mm⁻¹ or below. For super-high-voltage power transmission systems, however, it is known that higher breakdown voltage for varistors is also very important, because the increase of varistor voltage contributes to decrease the size of the varistor bulks, implying the economic use of materials and easy control of the scale of equipments. Therefore, it is not only useful but also necessary to explore ZnO varistors with high breakdown voltage.

For ZnO varistors, the breakdown voltages are directly proportional to the size of ZnO grains. The smaller the ZnO grains, the higher the varistor voltage. The growth of ZnO grains could be effectively controlled by
adjusting the ZrO₂ doping content in ZnO–Bi₂O₃ system, which enabled a wide-range adjustment of varistor voltage [1]. Furthermore, during modern ceramics processing, high energy attrition milling and ZrO₂ grinding media were often applied. As a result, Zr⁴⁺ contamination in ceramic samples is a common phenomenon. However, up to now no literature about the role of Zr⁴⁺ ion (ZrO₂) in ZnO–Pr₆O₁₁-based varistor has been reported. So, the aim of this work is to investigate the doping effect of ZrO₂ on the microstructural and the electrical properties of ZnO–Pr₆O₁₁-based varistor ceramics. It was found that while the nonlinear coefficient can be kept at quite high level, the breakdown voltage of ZnO-Pr₆O₁₁-based varistor ceramics could be greatly increased by doping with an appropriate amount of ZrO₂.

EXPERIMENTAL

Sample preparation

The samples were fabricated using a conventional ceramic processing method [4, 5] with a nominal composition of (98.0-x) mol. % ZnO + 0.5 mol.% Pr₆O₁₁ + + 1.0 mol.% CoO + 0.5 mol.% Cr₂O₃ + x mol. % ZrO₂ (x = 0.0; 0.25; 0.5; 1.0; 2.0). All raw materials are commercial powders of analytical reagent grade. During processing, the sample of each composition, the raw powders were first mixed and ball-milled in deionized water for at least 24 h so that the average grain size of ZnO was no more than 0.3 μm. After milling, the resultant slurries were dried in air at 120°C. After drying, the chunks of powder mixture were crashed into fine powders, and then sieved, resulting in ZnO composite powder with average granular size of no more than 10 μm. After that, discs of 6 mm in diameter and 1.5 mm in thickness were pressed from the prepared composite powders, yielding green bodies with density between 2.5 to 3.5 g·cm⁻³. The samples were then sintered in a muffle oven at 1300°C for 2 h with heating rate of 2°C·min⁻¹ and natural cooling. In order to measure the electrical properties, the sintered samples were coated on both sides with silver pastes and toasted at 500°C.

RESULTS AND DISCUSSION

Sinterability

Figure 1 shows the average linear shrinkages in diameter and bulk densities of the as-prepared varistor ceramics doped with different amounts of ZrO₂. The diameter shrinkage decreased with increasing ZrO₂ doping contents in the varistor ceramics, which implies that the ZrO₂ doping works against the sintering (densification) of the samples. However, the sample density first increased as the doping content of ZrO₂ increased up to 0.5 mol. %, and then decreased with further increasing doping of ZrO₂. The increase of the density might be mainly attributed to the replacement of the lighter Zn atoms by heavier Zr ones; but the decrease of the average size of ZnO grains (see the discussion in next section) might be also a positive factor to certain extent for the densification of the samples [13, 14]. The decrease of the sample density is correlated with the decrease of the sample shrinkage; and the formation of more pores in the microstructures (see next section), due to the worse sinterabilities of the samples doped with more ZrO₂.
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Composition and microstructure

Typical XRD patterns with normalized peak intensity of the as-prepared varistor ceramics doped with different amounts of ZrO₂ are presented in Figure 2. From this figure it can be seen that, without ZrO₂ doping only the phases of ZnO and praseodymium oxides (both cubic Pr₂O₃ and hexagonal Pr₆O₁₁) were identified. The cubic Pr₂O₃ phase was formed due to the decomposition of the applied hexagonal Pr₆O₁₁ at high temperature during sintering. However, after certain amount of ZrO₂ was added, a new phase Pr₂Zr₂O₇ was detected, which is obviously a result of the sintering reaction between ZrO₂ and praseodymium oxides. With the increase of ZrO₂ doping contents in the ceramics, it could be observed that the relative intensity of praseodymium oxide phases decreased and that of Pr₂Zr₂O₇ became much stronger.

In particular, when the ZrO₂ doping content was high enough (1.0 mol. % in this work), the praseodymium oxide phases were almost absent in the XRD patterns. The reason for this phenomenon might be that the...
majority of praseodymium oxides was engaged into the sintering reaction with the doped ZrO\textsubscript{2}, resulting in the above-mentioned Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} phase, which was stable at the high temperature of sintering. In addition, although other dopants of CoO and Cr\textsubscript{2}O\textsubscript{3} were applied, no peaks of them were identified, possibly because their doping amounts were too small, or they were entering into the lattices of ZnO grains after sintering (thus no independent peaks appeared).

Figure 3 displays typical SEM images of the prepared varistor ceramics doped with different amounts of ZrO\textsubscript{2}. It is well known that the microstructure of ZnO–Pr\textsubscript{6}O\textsubscript{11}-based varistor ceramics consists of only two phases, ZnO and intergranular phase. After comparing with the EDS results, one can find from this figure that the doping of ZrO\textsubscript{2} would not change the typical microstructure of ZnO-Pr\textsubscript{6}O\textsubscript{11}-based varistor ceramics. Combined with the results determined by XRD analysis as shown in Figure 2, it can be concluded that the bulk phase in the microstructure of the as-prepared varistor ceramics is ZnO, and the white intergranular phases are praseodymium oxides and Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}. Moreover, from these SEM images, it can be clearly seen that with increasing ZrO\textsubscript{2} contents in the ceramics, the average size of ZnO grains decreases, which is also evident from the calculated average size of ZnO grains as illustrated in Figure 4. The reason for the decrease in ZnO grain size of the as-prepared varistor ceramics may be attributed to the formation of secondary phase Pr\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} during sintering, which would pin at the boundary of ZnO grains, thus hindering the growth of ZnO grains. However, due to the worse sinterability of the samples, more and more pores were clearly observed when too much more ZrO\textsubscript{2} was doped into the ceramics, which is harmful to the densification and electrical properties of the samples.

The C–V characteristics of the as-prepared ZnO–Pr\textsubscript{6}O\textsubscript{11}–CoO–Cr\textsubscript{2}O\textsubscript{3}-based varistors doped with different amounts of ZrO\textsubscript{2} are shown in Figure 5a. The related C–V characteristic parameters of the varistor samples calculated from it including donor density and barrier height were illustrated in Figure 5b. Compared with the sample without ZrO\textsubscript{2}, the donor density of all the samples with ZrO\textsubscript{2} doping, regardless of the ZrO\textsubscript{2} doping contents, all decreased. Thus it is believed that the doped ZrO\textsubscript{2} acted as acceptor in ZnO-Pr\textsubscript{6}O\textsubscript{11} based varistor. Moreover, it was reported that the donor density could directly influence the barrier height of varistors [5]. So, the doping of ZrO\textsubscript{2} could directly change the barrier height of ZnO–Pr\textsubscript{6}O\textsubscript{11}–CoO–Cr\textsubscript{2}O\textsubscript{3}-based varistors. From Figure 5b, it can be seen that the barrier height of the as-prepared ceramic varistors initially increased...
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with small doping content of ZrO$_2$ up to 0.5 mol. %, and then decreased with further increasing ZrO$_2$ doping. In this study the sample doped with 0.5 mol. % ZrO$_2$ presented the largest barrier height. Because the increase of barrier height is in favor of the raise of varistors’ nonlinear coefficient, so it is believed that the samples doped with 0.5 mol. % ZrO$_2$ would possess a relatively high nonlinear coefficient, which is consistent with the results presented in next section.

**E-J characteristics**

The $E$-$J$ characteristics of the as-prepared ZnO–Pr$_6$O$_{11}$–CoO–Cr$_2$O$_3$-based ceramic varistors doped with different amounts of ZrO$_2$ are presented in Figure 6a. Their corresponding electrical parameters calculated from the $E$-$J$ curves are illustrated in Figure 6b.

From Figure 6b, it can be seen that the varistor voltage of the samples increased from 411 to 1490 V·mm$^{-1}$ when the doping content of ZrO$_2$ in them increased from 0.0 to 2.0 mol. %. The increase of varistor voltage can be attributed to the increasing number of grain boundaries owing to the decrease of average ZnO grain size [1,4].

When the doping amount of ZrO$_2$ was no more than 0.5 mol. %, the nonlinear exponent increased with the increase of ZrO$_2$ content in the ceramic varistors; but the nonlinear exponent decreased when more ZrO$_2$ was doped. The increase of the nonlinear exponents might be attributed to the increase of barrier height of the samples, which is consistent with the C–V analysis in the last section that the barrier height increased with the increase of ZrO$_2$ doping contents up to 0.5 mol. %. The decrease of the nonlinear exponents might be correlated to the excessive decrease of the content of praseodymium oxides in the ceramic varistors due to the reaction between praseodymium oxides and ZrO$_2$ into Pr$_2$Zr$_2$O$_7$, consuming out the VFO. This is consistent with results reported by literature that in sintering, praseodymium oxides provided for the formation of insulating boundary layers which controlled the operation of varistors [4, 5]. So, it is believed that the consumption of a large number of praseodymium oxides by such sintering reaction will be adverse to the formation of insulating boundary layers. Furthermore, there would be more pyrochlore phase Pr$_2$Zr$_2$O$_7$ formed when more ZrO$_2$ was doped. The Pr$_2$Zr$_2$O$_7$ phase, which would segregate at grain boundary, might also destroy the insulating boundary layers. Therefore, the consumption of a large number of praseodymium oxides and the mass formation of Pr$_2$Zr$_2$O$_7$ might be the primary cause for the decrease of the nonlinear exponents when the ZrO$_2$ doping amounts were more than 0.5 mol. %.

The leakage currents increased with the increase of ZrO$_2$ doping contents, due to the deteriorating sinterability of the samples after ZrO$_2$ doping, which resulted in continuously increased amount of pores in the ceramics after more and more ZrO$_2$ was doped. This is the decisive factor for the increase in the leakage current of the prepared varistor [1, 15].

The optimum nonlinear electrical properties were obtained in samples doped with about 0.5 mol. % ZrO$_2$, whose varistor voltage and nonlinear coefficient were 623 V·mm$^{-1}$ and 17, respectively. Samples doped with 2.0 mol. % ZrO$_2$ reached the highest varistor voltage in this study, which was about 1490 V·mm$^{-1}$, and its nonlinear exponent was about 10. Such kind of ceramic varistors of high breakdown voltage would be very promising in super-high-voltage power transmission systems.

**CONCLUSIONS**

The microstructure of ZrO$_2$-doped ZnO–Pr$_6$O$_{11}$-based varistor ceramics was composed of two phases, ZnO grain and intergranular phase. The doping of ZrO$_2$...
can inhibit the growth of ZnO grains, due to the formation of Pr$_2$Zr$_2$O$_7$, resulting in greatly increased varistor voltages. Minor doping of ZrO$_2$ up to 0.5 mol. % can improve the nonlinear exponents of the ceramic varistors.

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REFERENCES