

Comparative characteristics of yttrium oxide and yttrium nitric acid doping in ZnO varistor ceramics

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Abstract: The effect of different molar ratios of Y_2O_3 and $Y(NO_3)_3$ on the microstructure and electrical response of ZnO– Bi_2O_3 -based varistor ceramics sintered at 1 000 °C was investigated, and the mechanism by which this doping improves the electrical characteristics of ZnO– Bi_2O_3 -based varistor ceramics was discussed. With increasing amounts of $Y(NO_3)_3$ or Y_2O_3 in the starting composition, Y_2O_3 , Sb_2O_4 and Y-containing Bi-rich phase form, and the average grain size significantly decreases. The average grain size significantly decreases as the contents of rare earth compounds of $Y(NO_3)_3$ or Y_2O_3 increase. The maximum value of the nonlinear coefficient is found at 0.16% $Y(NO_3)_3$ or 0.02% Y_2O_3 (molar fraction) doped varistor ceramics, and there is an increase of 122% or 35% compared with the varistor ceramics without $Y(NO_3)_3$ or Y_2O_3 . The threshold voltage V_T of $Y(NO_3)_3$ and Y_2O_3 reaches at 1 460 V/mm and 1 035 V/mm, respectively. The results also show that varistor sample doped with $Y(NO_3)_3$ has a remarkably more homogeneous and denser microstructure in comparison to the sample doped with Y_2O_3 .

Key words: ceramics; varistor; rare earth; microstructure; electrical properties

1 Introduction

Commercial varistor ceramics are usually made by a solid state process using ZnO particles with dopant oxides, such as Bi_2O_3 , Sb_2O_3 , Co_2O_3 , MnO_2 and Cr_2O_3 . The mixed powder is then pressed and sintered at a high temperature [1–2]. This leads to a final microstructure, which, in the ideal situation, is constituted of a uniform grain size without porosity, segregated at grain boundaries, and homogeneously distributed crystalline secondary phases such as the spinel type $Zn_7Sb_2O_{12}$ and pyrochlore type $Zn_2Bi_3Sb_3O_{14}$ [3–4]. The conducting ZnO is surrounded by Bi_2O_3 phase, that is a result from the liquid phase at the sintering temperature. Therefore,

the kind, the concentration and the distribution of both the dopant and the corresponding created phases on sintering, determine the final microstructure and the electrical properties of the obtained varistor material [5–7].

Recently, it has been confirmed that it is possible to improve the electrical characteristics by the introduction of Y_2O_3 to the varistor ceramics [8–11]. BERNIK et al [12] reported that the microstructural and electrical characteristics of ZnO– Bi_2O_3 -based varistor ceramics doped with Y_2O_3 in the range from 0 to 0.9% (molar fraction) were investigated. LIU et al [13] discussed ZnO– Bi_2O_3 -based varistor ceramics doped with 0–3% Y_2O_3 . XU et al [14] reported Y_2O_3 -doped ZnO– Bi_2O_3 -based varistor ceramics sintered at 1 100 °C. The results

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showed that with the addition of 0.60% Y_2O_3 , the varistor ceramics exhibited comparatively better comprehensive electrical properties, such as the threshold voltage was 482 V/mm, the nonlinear coefficient was 34.8 and the leakage current was 0.17 μA . $Y(NO_3)_3 \cdot 6H_2O$ -doped varistor ceramics sintered at 1 100 °C can be found in our previous research [2]. The results showed that the addition of 0.16% $Y(NO_3)_3 \cdot 6H_2O$ to the ZnO– Bi_2O_3 -based varistor ceramics produced the optimum electrical properties, namely the threshold voltage was 425 V/mm, the nonlinear coefficient was 73.9 and the leakage current was 1.78 μA . In this work, the varistor ceramics were both sintered at 1 100 °C, but the high temperature sintering process had no advantage in both technology and economy.

In this work, the effect of Y_2O_3 and $Y(NO_3)_3$ on the microstructure and electrical response of ZnO– Bi_2O_3 -based varistor ceramics sintered at a lower sintering temperature, such as 1 000 °C, is studied, and the mechanism by which this doping improves the electrical characteristics of ZnO– Bi_2O_3 -based varistor ceramics is discussed.

2 Experimental

Y_2O_3 doped ZnO– Bi_2O_3 -based varistor samples were gained with a composition of (96.5– x)% ZnO, 0.7% Bi_2O_3 , 1.0% Sb_2O_3 , 0.8% Co_2O_3 , 0.5% Cr_2O_3 , 0.5% MnO_2 and x % Y_2O_3 , for $x=0, 0.02, 0.08, 0.20$ and 1.00 (molar fraction, samples labeled as Y0, Y1, Y2, Y3 and Y4, respectively). After milling, the mixture was dried at 70 °C for 24 h, and then the powder was uniaxially pressed into discs of 12 mm in diameter and 2 mm in thickness.

$Y(NO_3)_3$ doped ZnO– Bi_2O_3 -based varistor samples were obtained in the proportions of (96.5– x)% ZnO, 0.7% Bi_2O_3 , 1.0% Sb_2O_3 , 0.8% Co_2O_3 , 0.5% Cr_2O_3 , 0.5% MnO_2 and x % $Y(NO_3)_3 \cdot 6H_2O$, for $x=0, 0.04, 0.16, 0.40$ and 2.00 (samples labeled as YD0, YD1, YD2, YD3 and YD4, respectively). After milling, the mixture was dried at 70 °C for 24 h, and then the powder was calcined at 700 °C for 2 h in air. The calcined powder mixture went through a second milling for 1 h to eliminate large powder lumps. The powders were then dried and pressed into discs of ~12 mm in diameter and 2.0 mm in thickness.

The pressed discs were sintered in air at 1 000 °C (2 h dwell time), using a heating rate of 5 °C/min and then cooled in the furnace. The sintered samples were lapped and polished and then the final samples were about 10 mm in diameter and 1.0 mm in thickness. The bulk density of the samples was measured in terms of their mass and volume [15–16].

For the characterization of DC current–voltage, the

silver paste was coated on both faces of the samples and the silver electrodes formed by heating at 600 °C for 10 min. The electrodes were 5 mm in diameter. The voltage–current (V – I) characteristics were measured using CJP CJ1001. The nominal varistor voltages (V_N) at 0.1 and 1.0 mA were measured, and the threshold voltage V_T ($V_T=V_N/t$; t is the thickness of the sample in mm) and the nonlinear coefficient α ($\alpha=1/\lg(V_{1\text{ mA}}/V_{0.1\text{ mA}})$) were determined. The leakage current (I_L) was measured at $0.75V_N$ [5–6, 8, 17–20]. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2200, Japan) using a $Cu K_\alpha$ radiation. A scanning electron microscope (SEM, FEI QUANTA 400) was used to examine the surface microstructure.

3 Results and discussion

XRD patterns of the samples doped without and with various amounts of $Y(NO_3)_3$ or Y_2O_3 sintered at 1 000 °C for 2 h are shown in Fig. 1. It is well known that ZnO– Bi_2O_3 -based varistor ceramics typically consist of ZnO grain, spinel and intergranular Bi-rich phase. In the sample without $Y(NO_3)_3$ or Y_2O_3 , the ZnO phase, the $Zn_7Sb_2O_{12}$ -type spinel phase, $Bi_3Zn_2Sb_3O_{14}$ and Bi_2O_3

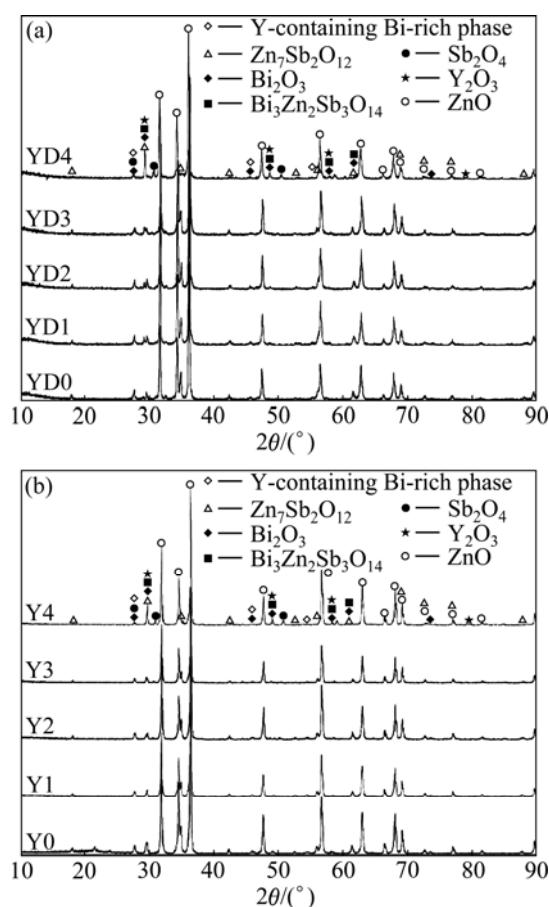


Fig. 1 XRD patterns of ZnO– Bi_2O_3 -based varistor ceramics doped with various amounts of $Y(NO_3)_3$ or Y_2O_3 : (a) $Y(NO_3)_3$; (b) Y_2O_3

phase are identified. However, in samples doped with $Y(NO_3)_3$ or Y_2O_3 , the peak of the $Zn_7Sb_2O_{12}$ -type spinel phase becomes weaker with the addition of $Y(NO_3)_3$ or Y_2O_3 [21], and nearly vanishes when the amount of Y_2O_3 is increased to 1.00%, while that of the Y_2O_3 phase increases at the same time, which agrees with the previous research [13]. With increasing amounts of $Y(NO_3)_3$ or Y_2O_3 in the starting composition, the Y-containing Bi-rich phase ($Bi_{1.9}Y_{0.1}O_3$ phase according to JCPDF 39-0275), the Y_2O_3 phase and the Sb_2O_4 phase are revealed by the XRD analysis. The addition of $Y(NO_3)_3$ or Y_2O_3 affects the time that the mixture is spent in the liquid phase, and since it becomes longer, the vaporization of Bi_2O_3 from the ZnO– Bi_2O_3 -based varistor ceramics becomes significant [5, 17]. In the meantime, the doping with $Y(NO_3)_3$ or Y_2O_3 affects the formation and decomposition of the $Bi_3Zn_2Sb_3O_{14}$ pyrochlore, which promotes the generation of the new phases, such as the Y-containing Bi-rich phase, the Y_2O_3 phase and the Sb_2O_4 phase.

SEM micrographs of the ZnO– Bi_2O_3 -based varistors doped with various amounts of $Y(NO_3)_3$ or Y_2O_3 sintering at 1 000 °C for 2 h are given in Figs. 2 and 3, respectively. The SEM micrographs indicate that the average grain size significantly decreases as the content of $Y(NO_3)_3$ or Y_2O_3 increases. At the same time, the crystallite sizes of the Y_2O_3 phases become smaller but the quantities increase dramatically, and there is little difference from the sample without $Y(NO_3)_3$ or Y_2O_3 doping. The majority of the new phases is much more segregated at the multiple ZnO grain junctions than between two ZnO grains. Since the diameter of the rare-earth cation is larger than that of the Zn^{2+} cation, it is possible that the yttrium cation is not properly dissolved in the ZnO grains. With increasing $Y(NO_3)_3$ or Y_2O_3 content, the Y-rich phase becomes more distributed at the multiple ZnO grain junctions and the Y-rich phase between two ZnO grains is more discontinuously distributed [8, 21–22]. At the same time, the size of the ZnO grains decreases uniformly when the amount of

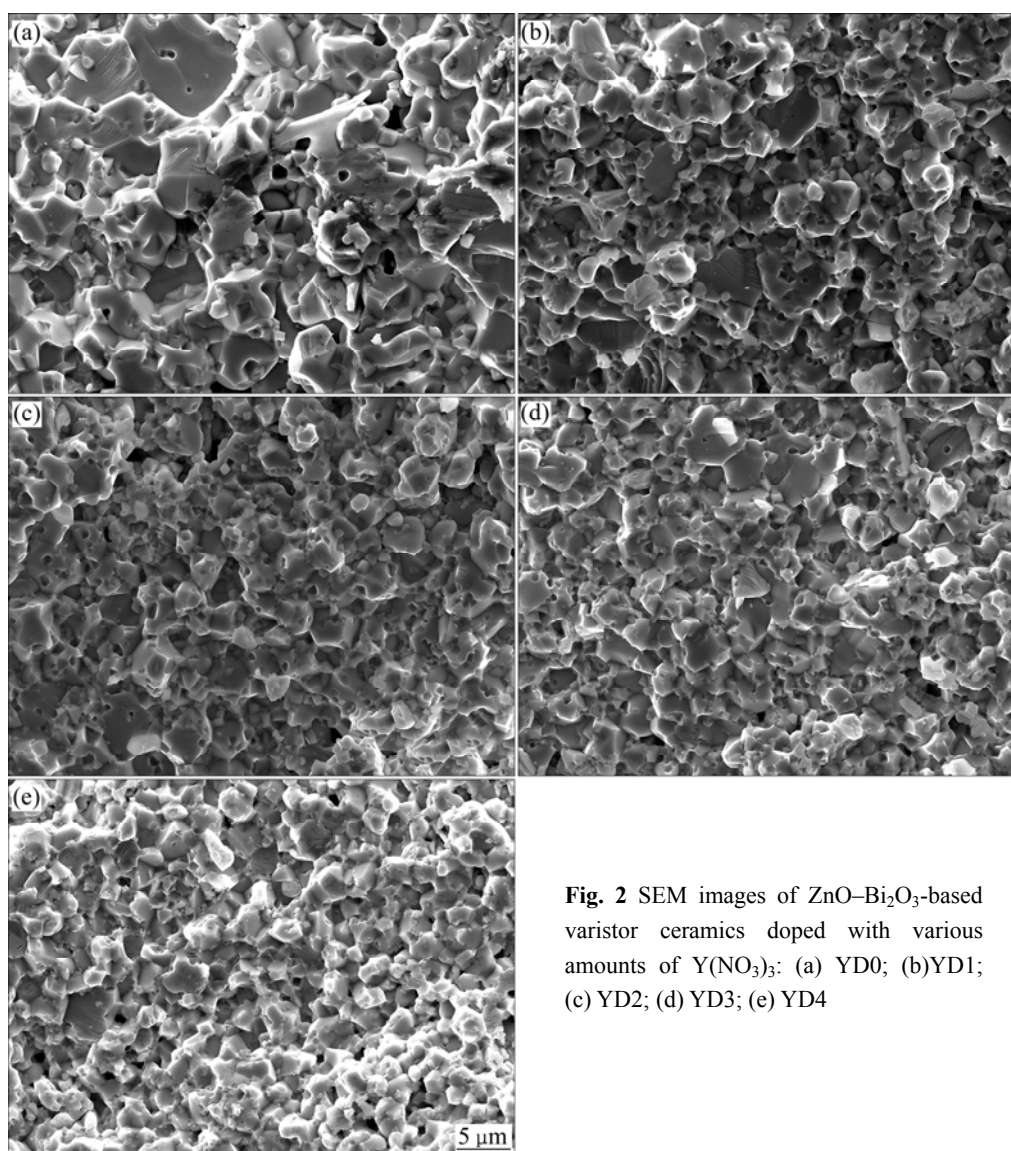


Fig. 2 SEM images of ZnO– Bi_2O_3 -based varistor ceramics doped with various amounts of $Y(NO_3)_3$: (a) YD0; (b) YD1; (c) YD2; (d) YD3; (e) YD4

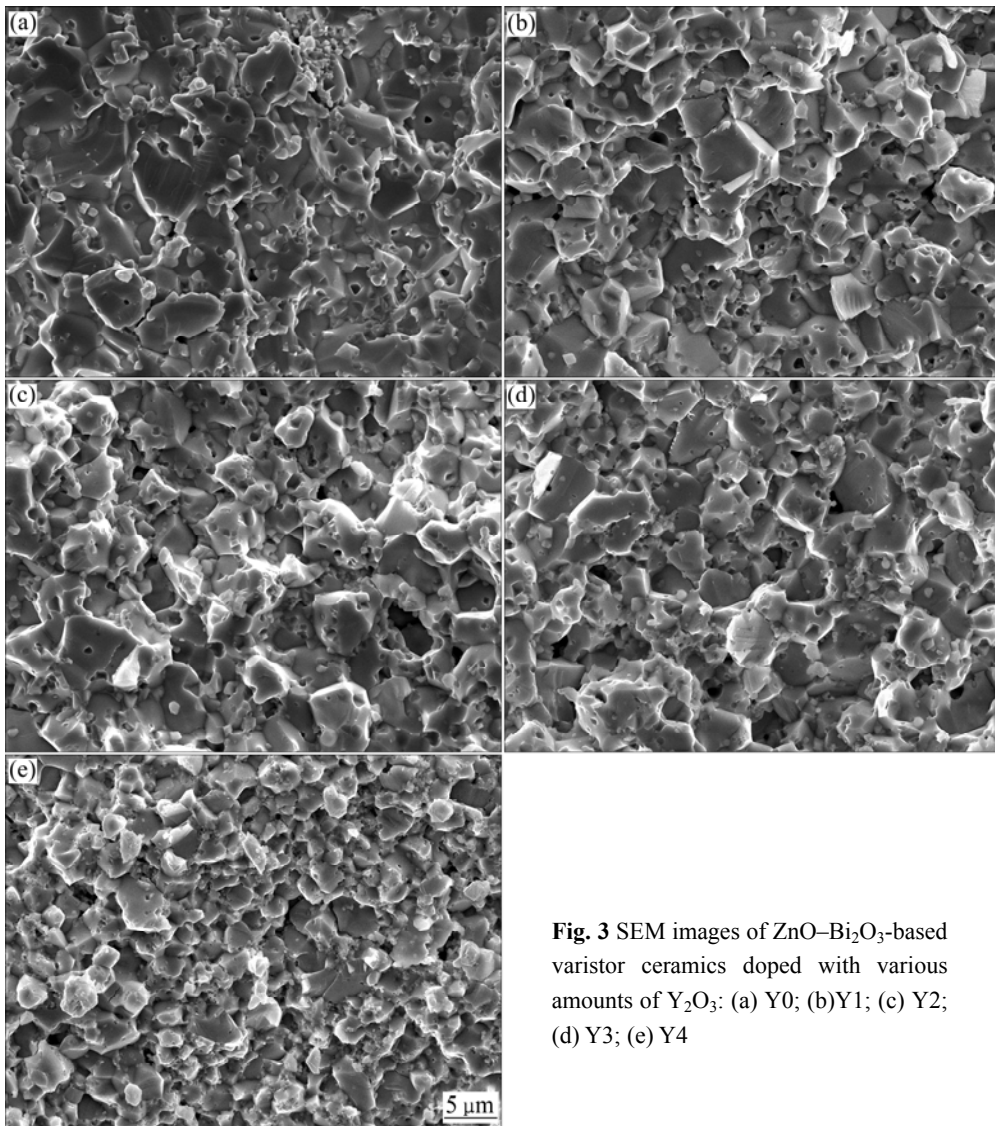


Fig. 3 SEM images of ZnO–Bi₂O₃-based varistor ceramics doped with various amounts of Y₂O₃: (a) Y0; (b) Y1; (c) Y2; (d) Y3; (e) Y4

Y(NO₃)₃ or Y₂O₃ increases, which would have some influence on the electrical properties of varistor ceramics.

The relative density *D* with various amounts of Y(NO₃)₃ or Y₂O₃ doped ZnO–Bi₂O₃-based varistor ceramics sintered at 1 000 °C for 2 h is shown in Fig. 4. The results reveal that doping with Y(NO₃)₃ or Y₂O₃ has a little influence on the relative density of ZnO–Bi₂O₃-based varistor ceramics [2, 14]. With increasing Y(NO₃)₃ or Y₂O₃ content, the relative density changes in the range of 94.1%–97.2%. With increasing the amount of Y(NO₃)₃, the relative density of the Y(NO₃)₃ doped ZnO–Bi₂O₃-based varistor ceramics increases and then decreases. Obviously, in all cases, the extremum of the relative density is reached with 0.08% Y₂O₃.

The threshold voltage *V*_T with various amounts of Y(NO₃)₃ or Y₂O₃ doped ZnO–Bi₂O₃-based varistor ceramics sintered at 1 000 °C for 2 h is shown in Fig. 5. When increasing the Y(NO₃)₃ content, the threshold voltage is markedly increased in the range of 535–

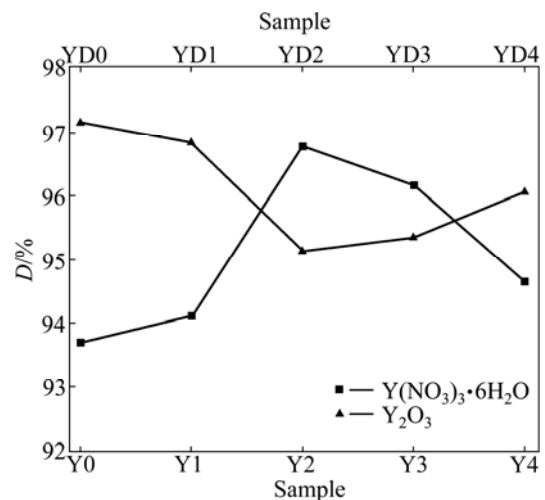


Fig. 4 Density of ZnO–Bi₂O₃-based varistor ceramics doped with various amounts of Y(NO₃)₃ or Y₂O₃

1 460 V/mm along with a decrease in average grain size of ZnO (Fig. 2). When increasing the Y₂O₃ content, the threshold voltage is markedly increased in the range

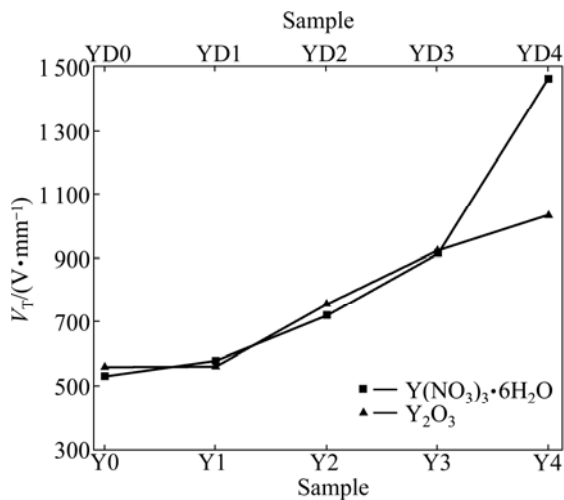


Fig. 5 Threshold voltage of ZnO–Bi₂O₃-based varistor ceramics doped with various amounts of Y(NO₃)₃ or Y₂O₃

of 560–1 035 V/mm along with a decrease in average grain size of ZnO (Fig. 3). At the same time, the breakdown voltages per grain boundary of the samples are all in the range of 2–3 V, according to Refs. [23–24]. The breakdown voltage per grain boundary (V_{gb}) is determined from the expression $V_{gb} = V_{1mA} / n = d \cdot V_T$, where n is the number of grain boundaries arranged as the series between both electrodes and d is the average grain size. The threshold voltage increases as the grain size decreases. The smaller the grains size is, the higher the threshold voltage is.

The nonlinear coefficient α with various amounts of Y(NO₃)₃ or Y₂O₃ of ZnO–Bi₂O₃-based varistor ceramics sintered at 1 000 °C for 2 h is shown in Fig. 6. For Y(NO₃)₃ or Y₂O₃ doped ZnO–Bi₂O₃-based varistor ceramics, the nonlinear coefficient initially increases then decreases with the increase of Y(NO₃)₃ or Y₂O₃ content. The relationship between the nonlinear coefficient and the amount of earth oxide additive reveals an upside-down U-shape curve, which is unsymmetrical. The maximum value of the nonlinear coefficient is obtained in 0.16% Y(NO₃)₃ or 0.02% Y₂O₃ doped varistor ceramics, and it has an increase of 122% or 35% when compared with the varistor ceramics without Y(NO₃)₃ or Y₂O₃, respectively. The significant improvement of the nonlinear coefficient obtained for the varistor ceramics with Y(NO₃)₃ can be accounted for the microstructure uniformity and narrowed grain size distribution.

The leakage current I_L with various amounts of Y(NO₃)₃ or Y₂O₃ of ZnO–Bi₂O₃-based varistor ceramics sintered at 1 000 °C for 2 h is shown in Fig. 7. It is especially meaningful that the leakage current is directly related to degradation and reliability because the leakage current should be as low as possible for various

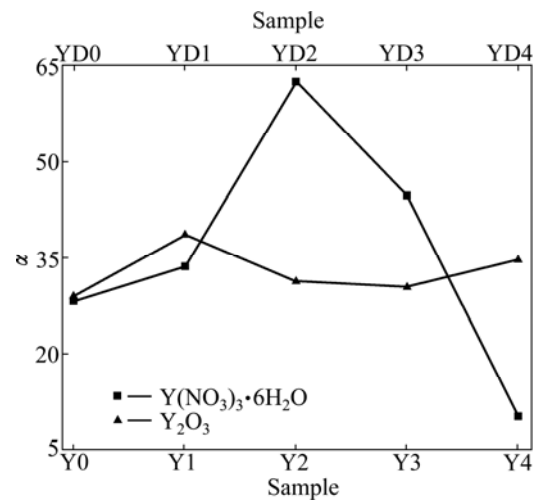


Fig. 6 Nonlinear coefficient of ZnO–Bi₂O₃-based varistor ceramics doped with various amounts of Y(NO₃)₃ or Y₂O₃

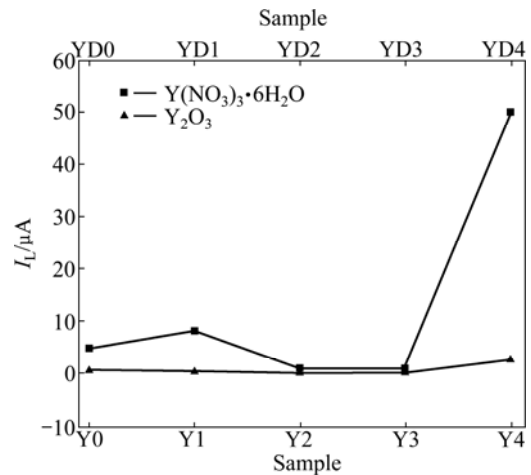


Fig. 7 Leakage current of ZnO–Bi₂O₃-based varistor ceramics doped with various amounts of Y(NO₃)₃ or Y₂O₃

applications [22]. For Y₂O₃ doped ZnO–Bi₂O₃-based varistor ceramics, when the amount of Y₂O₃ increases from 0% to 1.0%, the leakage current is very low and only shows little change. For Y(NO₃)₃ doped ZnO–Bi₂O₃-based varistor ceramics, when the amount of Y(NO₃)₃ is less than 0.40%, the leakage current shows little change, but when the amount of Y(NO₃)₃ is more than 0.40%, the leakage current increases sharply, by up to 50 μA, and the varistor ceramics would not be applied if there is a high leakage current. At the same time, when the ZnO–Bi₂O₃-based varistor ceramics are doped with 2.00% Y(NO₃)₃, there is an increase of amount the second phases, such as Zn₇Sb₂O₁₂-type spinel phase and Bi₃Zn₂Sb₃O₁₄-type pyrochlore phase. When the amount of the second phases is compared with the amount of the ZnO phases, the uniformity of the microstructure would become nonuniform. Consequently, the nonlinear coefficient decreases, and leakage current increases. In general, the variation of the leakage current is opposite to that of the nonlinear coefficient. The leakage current is a

result of most of the electrons passing over the Schottky barrier at grain boundaries. Therefore, the lower the barrier height is, the higher the leakage current becomes, and the lower the nonlinear coefficient is [5, 19, 22, 25–26]. It is believed that the decrease in the leakage current can be attributed to an increase in activation energy (the average energy needed for electrons to overcome the Schottky barrier) and the homogeneous distribution of the limited amount of varistor dopants available in these samples.

Figure 8 shows the electric field–current density (E – J) curves of ZnO–Bi₂O₃-based varistor ceramics with various contents of Y(NO₃)₃ or Y₂O₃. The curves show that the conduction characteristics have divided into two regions: a linear region before the breakdown field and a non-linear region after the breakdown field. The sharper the knee of the curves between the two regions is, the better the non-linear properties are [27]. It is known that the sharper the knee of the curves between the linear region and the breakdown field is, the better the nonlinear characteristic is, in other words, the threshold voltage V_T , the nonlinear coefficient α , and the leakage current I_L are determined by the E – J curves. As can be seen from

Fig. 8(a), the E – J curves show that the nonlinear properties increase in the order of YD4→YD0→YD1→YD3→YD2, and the threshold voltage increases in the order of YD0→YD1→YD2→YD3→YD4. As can be seen from Fig. 8(b), the E – J curves show that the nonlinear properties increase in the order of Y0→Y3→Y2→Y4→Y1, and the threshold voltage increases in the order of Y0→Y1→Y2→Y3→Y4. Narrower grain size distribution indicates more uniform and more homogeneous microstructure, which influences the uniform conducting and increasing number of active grain boundaries. The consequence is an increase of the nonlinearity coefficients and breakdown field. Varistor sample doped with 0.16% Y(NO₃)₃ has a remarkably more homogeneous and denser microstructure in comparison to the sample doped with 0.08% Y₂O₃.

4 Conclusions

1) The minute quantity of rare earth compounds can remarkably develop the properties of ZnO–Bi₂O₃-based varistor ceramics. The average grain size significantly decreases as the content of Y(NO₃)₃ or Y₂O₃ increases. At the same time, the crystallite sizes of the Y₂O₃ phases become smaller but the quantities increase dramatically, and there is little difference from the sample without Y(NO₃)₃ or Y₂O₃ doping.

2) With the increase of the content of Y(NO₃)₃ and Y₂O₃, the threshold voltage is respectively increased in the range of 535–1 460 V/mm and 560–1 035 V/mm along with a decrease in average grain size of ZnO. The maximum value of the nonlinear coefficient is found at 0.16% Y(NO₃)₃ or 0.02% Y₂O₃ doped varistor ceramics, and it has an increase of 122% or 35% compared with the varistor ceramics without Y(NO₃)₃ or Y₂O₃.

3) The leakage current is very low and only shows little change for Y₂O₃ doped ZnO–Bi₂O₃-based varistor ceramics. When the content of Y(NO₃)₃ is less than 0.40%, the leakage current shows little change, but it will change up to 50 μ A when the content of Y(NO₃)₃ is more than 0.40%.

4) Varistor ceramic doped with Y(NO₃)₃ has a remarkably more homogeneous and denser microstructure in comparison to the sample doped with Y₂O₃.

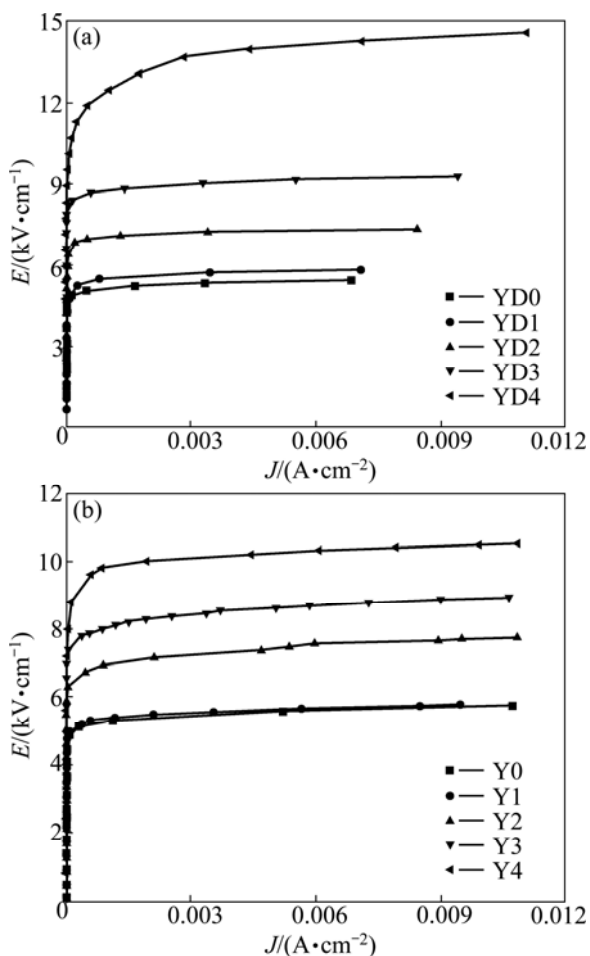


Fig. 8 Electric field–current density (E – J) characteristics of ZnO–Bi₂O₃-based varistor ceramics doped with various amounts of Y(NO₃)₃ or Y₂O₃: (a) Y(NO₃)₃; (b) Y₂O₃

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