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Microstructure and electrical properties of $Y(NO_3)_3{\cdot}6H_2O$-doped $ZnO–Bi_2O_3$-based varistor ceramics

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ABSTRACT

$Y(NO_3)_3{\cdot}6H_2O$-doped $ZnO–Bi_2O_3$-based varistor ceramics were prepared using a solid reaction route. The microstructure, electrical properties, degradation coefficient (D_V), and dielectric characteristics of varistor ceramics were studied in this paper. With increasing amounts of $Y(NO_3)_3{\cdot}6H_2O$ in the starting composition, Y-containing Bi-rich, Y_2O_3, and Sb_2O_4 phases were formed, and the average grain size decreased. Results also showed that with the addition of 0.16 mol% $Y(NO_3)_3{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ -doped ZnO-based varistor ceramics exhibit comparatively better comprehensive electrical properties, such as a threshold voltage of 425 V/mm, a nonlinear coefficient of 73.9, a leakage current of 1.78 μA, and a degradation coefficient of 1.7. The dielectric characteristics and lightning surge test also received the same additional content of $Y(NO_3)_3{\cdot}6H_2O$. The results confirmed that doping with rare earth nitrates instead of rare earth oxides is very promising route in preparing high-performance $ZnO–Bi_2O_3$-based varistor ceramics.

1. Introduction

Varistors can detect and limit high transient voltage surges and can repeatedly endure such surges [1,2]. They are usually used to sense and limit transient voltage surges. ZnO varistor ceramics show a highly nonlinear current–voltage characteristic with a highly resistive state in the pre-breakdown region that has a large non-linear coefficient [1–10]. Zinc oxide-based varistor ceramics are widely used in electronic appliances, such as voltage surge's protection devices, and especially in high-voltage lines. 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 high temperature. This produces a complex microstructure, in which conducting ZnO grains, an electrically insulating secondary spinel phase, and a Bi-rich inter-granular phase, are attained [11–14].

High-voltage varistor ceramics require a fine-grained microstructure and some methods report the development of high-voltage gradient ZnO varistor ceramics. To reduce ZnO varistor size and increase its voltage gradient, different measures are adopted. In the past, one method decreased the sintering temperature of ZnO varistor ceramics to reduce the growing velocity of ZnO grains, and shortened the temperature-keeping time to decrease the growing time of ZnO grains. However, voltage gradient can only be increased a little. Another method added a suitable amount of Sb_2O_3 to inhibit the growth of ZnO grains. The $Zn_7Sb_2O_{12}$ spinel phase generated in the sintering process is distributed around ZnO grains to inhibit their growth because spinels formed in the grain boundary block the motion of the liquid Bi_2O_3 grain boundary by dragging and pinning effect. Recently, the possibility of improving electrical characteristics by introducing Y_2O_3 to varistor ceramics has been confirmed [15–22]. Bernik et al. [15] investigated microstructural and electrical characteristics of $ZnO–Bi_2O_3$-based varistor ceramics doped with 0–0.9 mol% Y_2O_3. The addition of Y_2O_3 results in the formation of a fine-grained Bi–Zn–Sb–Y–O phase along ZnO grain boundaries, which inhibits ZnO grains growth. The average ZnO grain size decreases from 11.3 to 5.4 mm with an increase in the amount of Y_2O_3. Threshold voltage (V_T) of varistor ceramics increases from 150 to 274 V/mm. The nonlinear coefficient (α) is not influenced and remains at approximately 40. The leakage current (I_L) also increases with the addition of Y_2O_3. Liu et al. [23] reported on $ZnO–Bi_2O_3$-based varistor ceramics doped with 0–3 mol% Y_2O_3. The mean grain size of varistor ceramics decreased from about 9.2 to 4.5 μm, with an

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Table 1
Density and electrical properties of $Y(NO_3)_3{\cdot}6H_2O$ doped ZnO–Bi_2O_3-based varistor ceramics.

Sample	D (%)	V_T (V/mm)	d (μm)	V_{gb} (V)	α	I_L (μA)	D_V (%)
YD0	94.5	340	8.00	2.72	27.1	1.60	–
YD1	93.5	339	6.99	2.37	52.8	0.93	3.1
YD2	94.8	425	6. 16	2.62	73.9	1.78	1.7
YD3	94.9	535	4.99	2.67	48.1	2.73	74.0
YD4	93.6	679	3.99	2.71	12.7	25.80	86.1

increase in Y_2O_3 from 0 to 3 mol%. The corresponding varistor's V_T markedly increased from 462 to 2340 V/mm, whereas α decreased from 22.3 to 11.5. However, although some rare earth oxides, such as La_2O_3, Er_2O_3, Lu_2O_3, and Dy_2O_3, were used to improve the electrical characteristics of ZnO–Bi_2O_3-based varistor ceramics, their nonlinearity deteriorated [15,24].

In this paper, the effect of $Y(NO_3)_3{\cdot}6H_2O$ (abbreviated as YN) on the microstructure and the electrical response of ZnO–Bi_2O_3-based varistor ceramics is studied, and the mechanism by which this doping improves the electrical characteristics of ZnO–Bi_2O_3-based varistor ceramics, especially nonlinearity, is discussed.

2. Experimental procedures

Reagent-grade raw materials were used in the proportions (96.5-x) mol% ZnO, 0.7 mol% Bi_2O_3, 1.0 mol% Sb_2O_3, 0.8 mol% Co_2O_3, 0.5 mol% Cr_2O_3, 0.5 mol% MnO_2, and x mol% YN, for x = 0, 0.04, 0.16, 0.40 and 2.00 (samples labeled YD0, YD1, YD2, YD3 and YD4, respectively). After milling, the mixture was dried at 70 °C for 24 h, then the powder was calcined at 700 °C for 2 h in air. The calcined powder mixture was milled again for 1 h to eliminate large powder lumps. The powders were then dried and pressed into discs of ~12 mm diameter and thickness of 2.0 mm. The pressed disks were sintered in air at 1100 °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 weight and volume [25,26].

For the characterization of DC current–voltage, the silver paste was coated on both faces of samples and the silver electrodes were 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 a V–I source/measure unit (CJP CJ1001). The nominal varistor voltages (V_N) at 0.1 and 1.0 mA were measured and the threshold voltage V_T (V/mm) ($V_T = V_N(1\text{ mA})/t$; t is the thickness of the sample in mm) and the nonlinear coefficient α ($\alpha = 1/\log(V_{1\text{ mA}}/V_{0.1\text{ mA}})$) were determined. The leakage current (I_L) was measured at 0.75 V_N (1 mA) [12,13,16,27–31]. The lightning surge test of YN doped ZnO–Bi_2O_3-based varistor ceramics was measured by short duration shocks of 1 kA, 8/20 μs, and the degradation coefficient D_V, $D_V = 100(|V_{sb} - V_{sa}|)/V_{sb}$, where V_{sb} and V_{sa} are the respective threshold voltages before and after degradation by short duration shocks of 1 kA. The dielectric characteristics [32], such as the apparent dielectric constant (ε) and dissipation factor ($\tan\delta$) were measured as a function of frequency (1 kHz to 10 MHz) and at room temperature using an HP4294A impedance analyzer (Agilent).

The surface microstructure was examined by a scanning electron microscope (SEM, FEI QUANTA 400). The average grain size (d) was determined by the linear intercept method, given by $d = 1.56L/MN$, where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of the grain boundaries intercepted by lines. The crystalline phases were identified by an X-ray diffractometry (XRD, Rigaku D/max 2200, Japan) using a Cu Kα radiation.

3. Results and discussion

Crystalline phases identified by powder XRD and spectra of samples doped with and without various amounts of YN, sintered at 1100 °C for 2 h, are shown in Fig. 1. ZnO–Bi_2O_3-based varistor ceramics typically consist of ZnO grains, spinel, and intergranular Bi-rich phase. In the sample without YN, the ZnO, $Zn_7Sb_2O_{12}$-type spinel, the $Bi_3Zn_2Sb_3O_{14}$, and the Bi_2O_3 phases are identified. However, in the samples doped with YN, the peak of the $Zn_7Sb_2O_{12}$-type spinel phase becomes weaker with the addition of YN [24], nearly vanishing when the amount of YN is increased to 2.00 mol%. With an increase in the amounts of YN 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 using XRD analysis. This is so because the addition of YN affects the time that the mixture spends in the liquid phase and, as this becomes longer, the vaporization of Bi_2O_3 from ZnO–Bi_2O_3-based varistor ceramics becomes significant [12,27,33,34]. In the meantime, doping with YN affects the formation and decomposition of $Bi_3Zn_2Sb_3O_{14}$ pyrochlore, which promotes the generation of new phases, such as the Y-containing Bi-rich phase, the Y_2O_3 phase, the Sb_2O_4 phase, and so on.

Figs. 2 and 3 show microstructures of ZnO–Bi_2O_3-based varistor ceramics doped with various amounts of YN. As the concentration of YN increases, average grain size is significantly reduced, from 7.98 to 3.99 μm. At the same time, crystallite sizes of the Y_2O_3 phases become smaller but the quantities increase dramatically, slightly different from the sample without YN doping. Majority of the new phases are much more segregated at multiple ZnO grain junctions than between two ZnO grains. Inasmuch as the diameter of a rare earth cation is larger than that of a Zn^{2+} cation, it is possible that the Yttrium cation was not properly dissolved in the ZnO grains. With an increase in YN content, the Y-rich phase becomes more distributed at multiple ZnO grain junctions, and the Y-rich phase between two ZnO grains is more discontinuously distributed [16,24,35]. At the same time, the size of ZnO grains decreases uniformly when the amount of YN increases, which has some influence on the electrical properties of varistor ceramics. In summary, YN doping can inhibit grain growth, just like rare earth oxides.

The influence of YN concentration on characteristics, including relative density (D), V_T, α, I_L, and degradation coefficient (D_V) of ZnO–Bi_2O_3-based varistor ceramics sintered at 1100 °C for 2 h, is presented in Table 1.

Doping with YN has little influence on the density of ZnO–Bi_2O_3-based varistor ceramics. With an increase in YN concentration, D increases slightly from 93.5% to 94.9%. This trend is similar to D for Y_2O_3-doped ZnO–Bi_2O_3-based varistor ceramics, the difference being that D of Y_2O_3-doped ZnO–Bi_2O_3-based varistor ceramics is higher than D of YN-doped ones [36]. This may be because YN makes the composition more uniform, and the average ZnO grain size becomes very fine. The very fine grain size gives birth to more

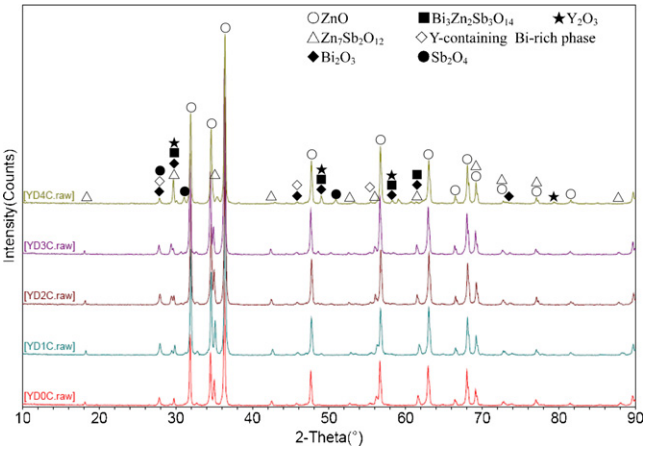

Fig. 1. XRD patterns of ZnO–Bi_2O_3-based varistor ceramics doped with various amounts of $Y(NO_3)_3{\cdot}6H_2O$.