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ScienceDirect

Ceramics International 41 (2015) S557–S562

CERAMICS INTERNATIONAL

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Effect of Cr_2O_3 on the property and microstructure of ZnO–Bi_2O_3 varistor ceramics in different sintering temperature

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Received 26 October 2014; accepted 19 March 2015
Available online 30 March 2015

Abstract

The electrical property, phase transformation, and microstructure of Cr_2O_3 doped ZnO–Bi_2O_3–Sb_2O_3–Co_2O_3–MnO_2 (ZBSCM)-based varistors were investigated for different sintering temperature. The structure and morphological modifications were analyzed by X-ray diffraction and scanning electron microscopy (SEM), respectively. Doping Cr_2O_3 could lower the decomposition temperature of the pyrochlore phase $Zn_2Bi_3Sb_3O_{14}$, resulting in more Bi_2O_3 rich liquid phase and spinel phase $Zn_7Sb_2O_2$. The results indicated that Cr_2O_3 played multiple roles in the grain growth and microstructure. Cr_2O_3 which acted as an indirect sintering aid to promote the grain growth was an effective additive which contributed to lower sintering temperature of ZnO varistors.

Keywords: C. Electrical properties; D. ZnO; E. Varistor; Microstructure

1. Introduction

ZnO-based varistor have a highly nonlinear I–V performance because of the electrostatic barriers at individual ZnO grain boundaries [1–3]. The properties of varistor ceramics are modified by various dopants. The chemical compositions of traditional dopants consist of several metal oxides[4], such as Bi_2O_3 [5–9], Sb_2O_3 [10–15], Co_2O_3 [14,16–19], MnO_2 [14,20–22] and Cr_2O_3 [23–26]. During the sintering process, these oxides react with ZnO to form different phases. These phases are the spinel phase $Zn_7Sb_2O_2$, the pyrochlore phase $Zn_2Bi_3Sb_3O_{14}$ and the Bi_2O_3 rich liquid phase. The pyrochlore phase forms at 750–850 °C and with temperature increasing it decomposes into spinel and Bi_2O_3 rich liquid phase at 950–1050 °C [27]. As the temperature decreases, the reaction reverses. The reversible reaction can be described as Eq. (1) [28].

$$2Zn_2Bi_3Sb_3O_{14}(s) + 17ZnO(s) \leftrightarrow 3Zn_7Sb_2O_{12}(s) + 3Bi_2O_3 \quad (1)$$

The spinel phase [28,29] and the Bi_2O_3 rich phase [30,31] are known to influence grain-growth. The spinel phase can inhibit the grain growth due to the pinning effects [29]. According to the reports by Senda [32] and Day [5] in ZnO ceramics, the grain-growth process is enhanced by the phase boundary dissolution–precipitation reaction of the ZnO with the Bi_2O_3-rich liquid at lower addition of Bi_2O_3 up to about 0.5 mol%. While at higher additions above 1 mol% grain growth is slowed by diffusion of ZnO within the thicker layer of the Bi_2O_3-rich liquid phase.

With the development of the electronic devices, the multilayer devices are the trend of the ZnO varistor. ZnO–Bi_2O_3–Sb_2O_3–Co_2O_3–MnO_2 (ZBSCM)-based varistor has been widely studied due to its high performance. However, the sintering temperature is still too high (> 950 °C) to use Ag as an internal electrode in multilayer devices. Therefore, in order to co-fire with Ag electrode and avoid Bi loss, it is important to lower the sintering temperature below 950 °C. Liquid-phase sintering is known to be a most effective way to achieve high-density and large-grain-size

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http://dx.doi.org/10.1016/j.ceramint.2015.03.137
0272-8842/

sintered ceramics at low sintering temperatures [33,34]. However, at low temperature, the liquid phase would be decreased and density of the ceramics sintered usually is low. Thus, Grain size control in ZnO varistor ceramics is quite challenging, especially at low sintering temperature.

The additive Cr_2O_3 attracts much attention because it markedly influences the reaction (1) and consequently the phase and microstructure of ceramics [25,35,36]. Several studies on the microstructure properties related to additive Cr_2O_3 have been published. Inada [35,37] reported that from XRD analysis, the Bi_2O_3 rich phase containing the Cr_2O_3 was observed only at a comparatively wide grain boundary and Cr_2O_3 played an important role in forming the spinel particles. Cho [26] reported that the doping Cr_2O_3 reduced grain size in ZnO–Bi_2O_3–Sb_2O_3-based varistors by changing the nature of liquid phase during Sintering. Recently, Ma [38] reported that the varistor low breakdown voltages with low current leakage obtain by controlling the amount of Cr_2O_3. However, the previous studies only reported influence of Cr_2O_3 on the formation of pyrochlore and spinel phase and no investigations about how the Cr_2O_3 the influences the interaction between pyrochlore and spinel phase are preformed [25,28,35,37]. What is more, in these studies, only the grain growth behavior in the high sintering temperature about 1200 °C was discussed. The analysis of grain growth in the sintering temperature, below 1000 °C is still currently absent.

The purpose of this work is to analysis how the Cr_2O_3 influences the interaction between pyrochlore and spinel phase and lowers the sintering temperature. In this paper, we carried out a detailed study on the ZBSCMCr and ZBSCM system from low sintering temperature 920 °C to high sintering temperature 1150 °C. The results indicated that chromium oxide not only played important roles in the reaction of pyrochlore phase, Bi_2O_3 rich phase and spinel phase, but also influenced the grain growth and subsequent microstructure. At the low sintering temperature below 985 °C, the addition of Cr_2O_3 promoted the grain growth, while it inhibited the grain growth at higher sintering temperature.

2. Experimental procedure

ZnO–Bi_2O_3-based varistor samples with the following chemical compositions: $(98.75-x)$ mol% ZnO + 0.40 mol% Bi_2O_3 + 1.25 mol% $(Sb_2O_3+Co_2O_3+MnO_2)$ + x mol% Cr_2O_3 with x=0 and 0.1 were prepared using the conventional solid-state reaction technique. In order to simplify the notation, the varistor systems would be called ZBSCMCr and ZBSCM. The powder mixtures of reagent-grade raw materials and de-ionized water were milled for 8 h in a planetary mill. The dried powder was granulated and uniaxially pressed with a pressure of 200 MPa into disks. After burning out the organic binder (PVA) at 600 °C, the disks were sintered in air at 920, 930, 940, 950, 985, 970, 1000, 1025, 1050, 1150 °C (2.5 h) respectively. The final size of the samples was a diameter from 3 mm to 11 mm and a thickness of about 1.0 mm. Silver paste was applied to the sample surfaces to serve as electrodes with an area of about 0.64 cm^2 after sintering at 500 °C for 15 min.

X-ray diffraction patterns of the ceramic samples were obtained using Cu-Kα radiation (XRD, D/max 2550 V, Rigaku, and Tokyo, Japan). Microstructures in the cross-section direction of the sintered samples were prepared by grinding and polishing. Half of each microstructure was etched in dilute hydrochloric acid to reveal the grains. The microstructure was examined using a scanning electron microscope (SEM, JSM-5800F, JEOL Co., Tokyo, Japan). The grain sizes (d) of the ZnO are measured using the linear intercept method. The breakdown voltage field (E_b) was measured at a current of 1.0 mA/cm^2 and the leakage current density (I_L) was measured at 0.75 E_b (75% of the breakdown voltage). The nonlinear coefficient (α) was determined using the following equation:

$$\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \quad (2)$$

where V_1 and V_2 are the voltages corresponding to I_1=0.1 mA/cm^2 and I_2=1.0 mA/cm^2, respectively.

3. Results and discussion

3.1. Electrical properties

The breakdown voltage (E_b), electrical nonlinearity (α), leakage current (I_L) and grain size (d) were summarized in Table 1. In Fig. 1 the influence of the Cr_2O_3 on electrical parameters of the ceramic sintered at the temperature from 920 to 1150 °C was graphically presented. It indicated that the E_b of the ZBSCMCr samples was lower than that of the ZBSCM samples sintered at low temperature (below 985 °C). However, the E_b of the ZBSCMCr samples became larger when the

Table 1
Grain Size (d), Breakdown Voltage (E_b), Electrical Nonlinearity (α) and Leakage Current (I_L), in ZBSCMCr and ZBSCM systems with different sintering temperature.

Samples	T(°C)	920	930	940	950	970	985	1000	1025	1050	1150
ZBSCMCr	E_b (v/mm)	380	379	359	351	330	328	319	269	246	162
ZBSCMCr	α	45	38	30	32	33	31	29	18	45	38
ZBSCMCr	I_l (μA/cm^2)	11.4	2.27	1.93	0.37	0.01	0.01	0.1	0.01	0.3	4.3
ZBSCMCr	d(μm)	6.7	6.9	7.3	7.5	7.5	7.8	8.2	8.8	10.7	11.2
ZBSCM	E_b (v/mm)	452	463	440	388	358	285	274	250	244	148
ZBSCM	α	30	33	39	35	35	33	38	23	30	33
ZBSCM	I_l (μA)	11	0.42	0.17	0.23	0.2	0.1	0.17	0.1	0.23	1.6
ZBSCM	d(μm)	3.7	4.1	5.5	7	7.7	8.3	8.5	9	10.5	11.4