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Elaboration and characterization of zinc oxide varistors

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Abstract

ZnO-based varistors were fabricated by sintering zinc oxide micro crystals with several additives of metal Oxides. The effect of sintering temperature on varistor properties of (Bi, Co, Cr, Mn, Sb, Al)-doped ZnO ceramics was investigated in the range of 1280–1350 °C. The average grain size increased to 5.13 to 7.88 µm with the increase of sintering temperature. However, the nonlinear coefficient of this system was nearly constant in the range of sintering temperature. The highest breakdown voltage was 1143.4 v / cm for the varistor sintered at 1350 °C the sample C sintered exhibited the best electrical properties.
Keywords: *ZnO; Microstructure; Electrical properties; Varistors*

1. Introduction:

ZnO varistors have been widely used as surge protection devices due to their highly nonlinear current–voltage (I–V) characteristics in the normal case, varistors are subjected to a voltage below their characteristic breakdown and pass only a leakage current. When the voltage exceeds the breakdown voltage during voltage fluctuations, the varistor becomes highly conducting and draws current through it, usually to ground. When the voltage returns to normal, the varistor returns to its highly resistive state. [1] Zinc oxide (ZnO) varistors are formed by sintering mixture of ZnO powders with small amounts of other oxides, such as Bi_2O_3, Sb_2O_3, Al_2O_3, MnO_2, Cr_2O_3, etc., the relationship between the voltage across the terminal, V, and the current in the devices, I, is typically expressed by $I = kV^{\alpha}$. The term α in the equation is a nonlinear coefficient, inherent parameter of varistors representing the degree of nonlinearity of conduction. It is very important to comprehend the influence of the sintering process on varistor properties. The influence of sintering temperature on varistor properties is different with existing compositions of ceramics. [2]

The purposes of the present study are to develop the ZnO-based ceramic varistors. In this work, ZnO-based ceramic varistors with more than five additives of metal oxides have been fabricated. The microstructure of the varistors were studied using scanning electron microscopy (SEM) and X-ray diffraction(XRD) analysis and the properties of the ZnO based ceramic for use as varistors were discussed on the basis of the measurements of V(I) and C(V) characteristics.

2. Experimental procedure

2.1. Sample preparation

ZnO– Bi_2O_3-based varistor samples with a nominal composition of 97.2 mol.% ZnO, 0.5 mol.% Bi_2O_3, 1.0 mol.% Sb_2O_3, 0.3 mol.% Al2O3, 0.5 mol.% Cr_2O_3, and 0.5 mol.% MnO_2 were used, samples (B). Reagent-grade raw materials were pulverized by an agate mortar/pestle for 1h. Reagent-grade raw materials were used for preparing the varistor (C) of 98 mol.% ZnO, 0.5 mol.% Bi_2O_3, 1.0 mol.% Sb_2O_3, 0.5 mol.% Cr_2O_3, Reagent-grade raw materials were mixed and homogenized in absolute ethanol media in a polyethylene bowl with zirconia balls for 24 h. After milling, the mixture was calcined in air at 750 °C for 2 h. [3] The calcined powders were pressed into discs of 13 mm in diameter and 1 mm thickness at a pressure of 1000 kg/cm2. The discs were sintered at four fixed sintering temperatures 1280 °C, 1300 °C, 1320 °C, and 1350°C in air for 1 h in a furnace (Nabertherm, MORE THAN HEAT 30-3000 °C), at a heating rate of 5 °C/min and then cooled in the furnace. Finally, the surfaces of the sintered Samples were grinded and covered with silver paste to obtain electrodes. [4]

2.2. Characterization

The microstructure was examined by a scanning electron microscope PHILIPS (XL 30). The average grain size (d) of the ceramics was determined by the linear intercept method , given by d = 1.56L/MN,[5] 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. [6] The crystalline phases were identified by an X-ray diffractometry (BRUKER - AXS type D8) with CuKα radiation. The electric field–current density (E–J) characteristics were measured using a V–I source (TEKTRONIX 370) The breakdown field ($E_{1mA/cm2}$) was measured at 1.0mA/cm^2 and the leakage current density (J_L) was measured at 0.8 $E_{1mA/cm2}$ In addition, the nonlinear coefficient (α) is defined by the empirical law, $J = CE^{\alpha}$ where J is the current density, E is the applied electric field, and C is the constant. ˛ was determined in the current density range of 1mA/cm^2 to 10mA/cm^2, where$\propto = 1/(logE_2 - Elog_1)$, and E_1 and E_2 are the electric fields corresponding to 1.0mA/cm^2 and10mA/cm^2, respectively. The capacitance–voltage (C–V) characteristics were measured at 1 MHz as test frequency using an RLC meter (KEITHLE 590). The donor concentration (N_d) and the barrier height (Φ_b) were determined by the equation $(1/C_b - 1/2C_{b0})^2 = 2(\varphi_b + V_{gb})/q\varepsilon N_d$ where C_b is the capacitance per unit area of a grain boundary, C_{bo} is the value of C_b when V_{gb}=0, V_{gb} is the applied voltage per grain boundary, q is the electronic charge, ε is the permittivity of ZnO (ε=8.5εo). [7]

3. Results and discussion

Fig. 1 shows XRD patterns to the samples for different sintering temperatures. In all cases diffraction peaks corresponding to the major ZnO hexagonal phase are obtained (JCPDS card no 36-1451), together with some secondary peaks attributed to the Zn7Sb2O12 spinel and the Bi2O3 phases (JCPDS cards no 36-1445 and no 41-1449, respectively). The spinel phase plays an important role as the grain growth inhibitor during the sintering process of the varistor sample. Actually, this is the characteristic distribution of crystalline phases for a varistor formulation based in the ZBS ternary system. [8][9] For all temperatures a shift in the peaks positions to the right was observed with increase of sintering temperature.

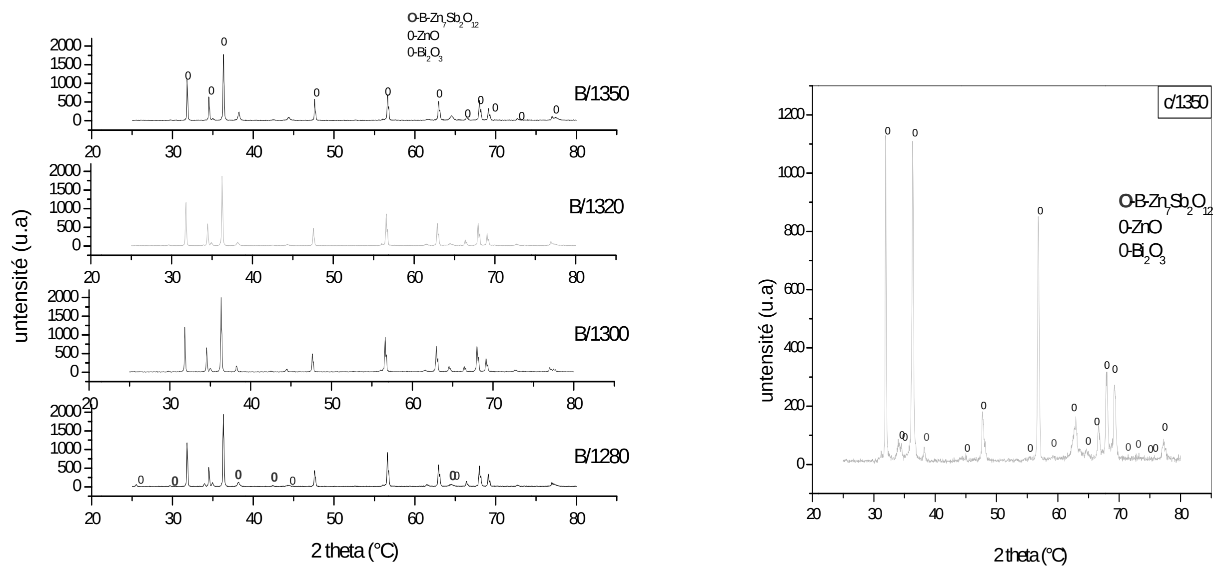

Fig. 1 XRD patterns of the samples for different sintering temperatures

Table 1:Microstructure and E_J characteristic parameters of the samples for various sintering temperatures

Sintering temperature (°C)	d(µm)	E(v/cm)	α	J_L (µA/cm^2)	N_d(10^{18}cm^{-3})	φ_b(ev)
B/1280	4.54	31.34	1.64	62.5	0.0043	1.21
B/1300	5.14	36.59	1.47	93.3	1.01	0.77
B/1320	5.81	6.35	1.04	77.6	1.93	0.30
B/1350	6.06	13.79	1.42	79.4	0.55	0.29

The SEM micrographs of the varistor samples for various sintering temperatures are shown in Fig. 2. There is no remarkable difference in the phases, which consisted of ZnO grains and intergranular layers in accordance with sintering temperatures. The average grain size (d) greatly increased from 4.54 to 7.88 µm in accordance with increasing sintering temperatures. The detailed microstructure parameters are summarized in Table 1.

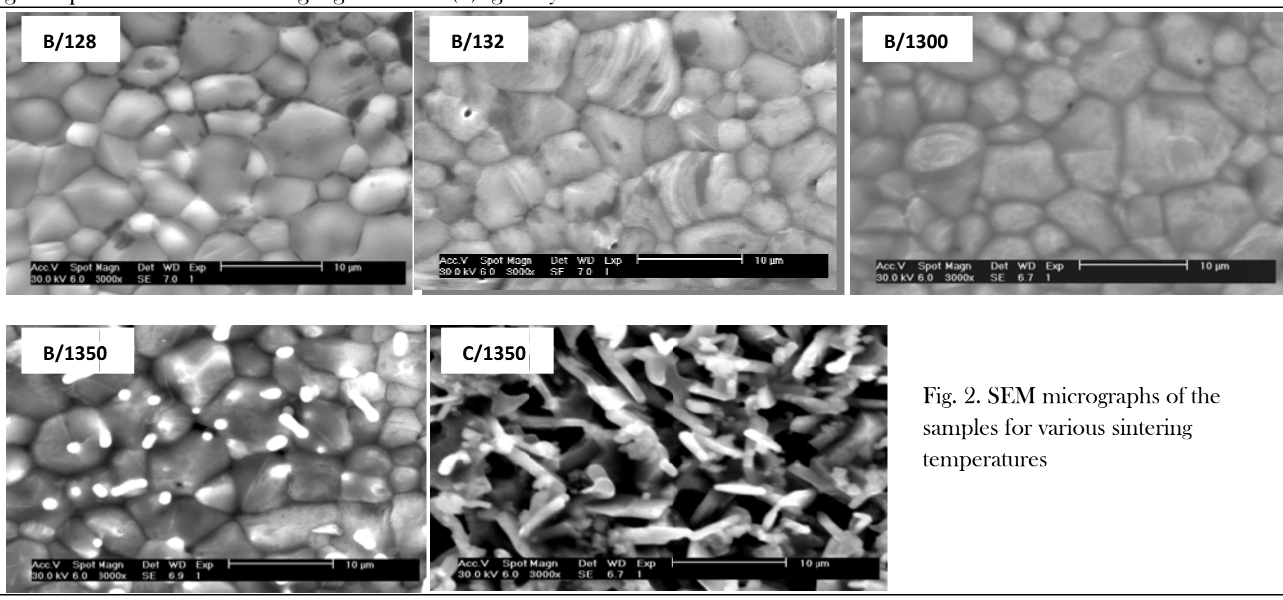

Fig. 2. SEM micrographs of the samples for various sintering temperatures

Fig. 3 shows the E–J characteristics of the samples for different sintering temperatures. The conduction characteristics of varistors are divided into a linear region with much higher. impedance before breakdown field and a nonlinear region with much lower impedance after breakdown field. The E–J characteristic parameters calculated from Fig. 3 are summarized in Table 1. Results showed that sample (C) sintered at 1350°C had the best nonlinear electrical property since it had the largest nonlinear coefficient of 3.39. The minimum J_L value (59.06 μA/cm^2) was obtained in that sample (C) sintered at 1350°C . The nonlinear coefficient (α) decreased slightly with the increase of sintering temperature. [1] The variation of J_L, on the whole, was opposite to that of nonlinear coefficient. The breakdown field (E) decreased with the increase of sintering temperature. This is attributed to the decrease in the number of grain boundaries caused by the increase in the ZnO grain size.

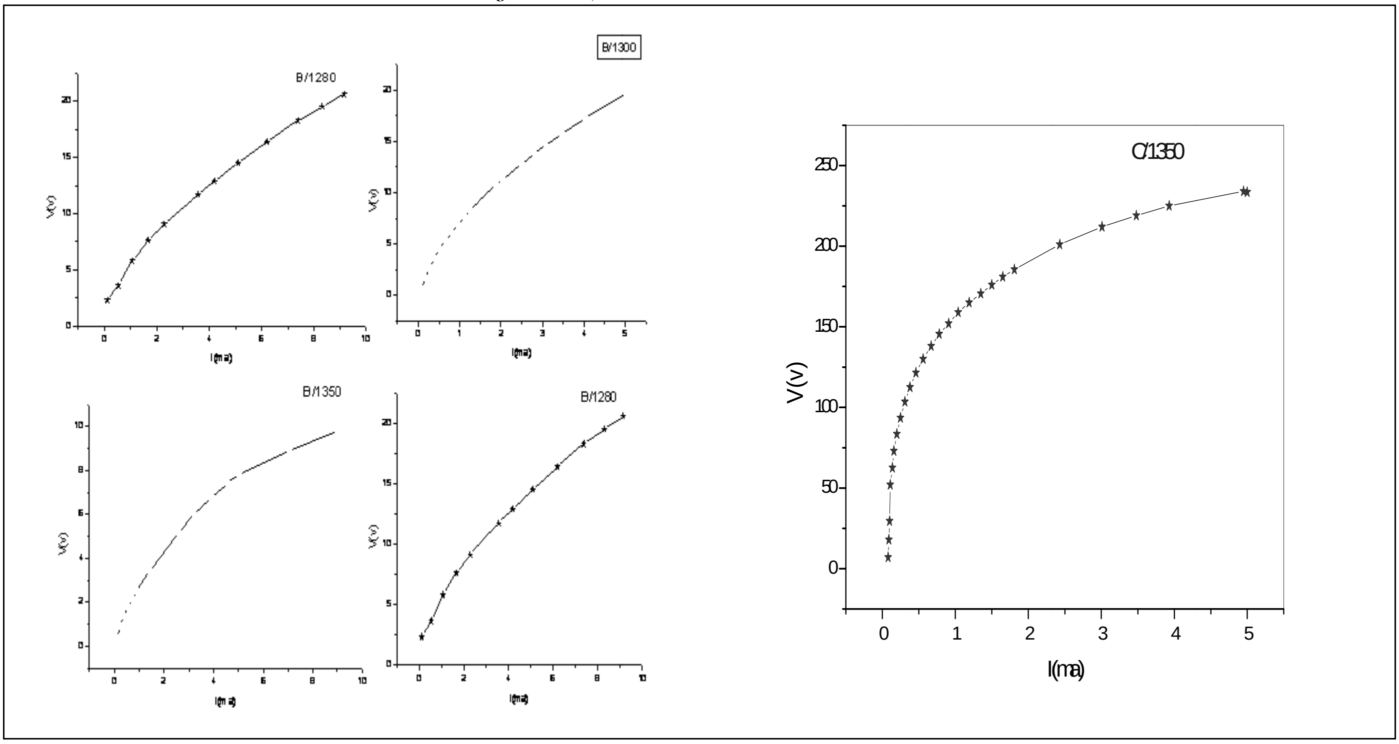

Fig. 3. I_V characteristics of the samples for various sintering temperatures

The *C–V* characteristics of the samples for different sintering temperatures are shown in Fig. 4. Modified C-V curves gradually shifted upward with decreasing sintering temperatures . The detailed *C–V* characteristic parameters are summarized in Table 1. the donor concentration (N_d) and barrier height ($φ_b$) are calculated by the modified C-V equation. The N_d value decreased slightly from 2.8* 10^{18} to 0.39* 10^{18} cm^{-3} with the increase of sintering temperature. The decrease of the N_d value is assumed to be due to an increase of oxygen. The barrier height ($φ_b$) at the grain boundaries decreased from 1.21 ev to 0.29eV with the increase of sintering temperatures. This coincides with the variation of the α in the E_J characteristics.

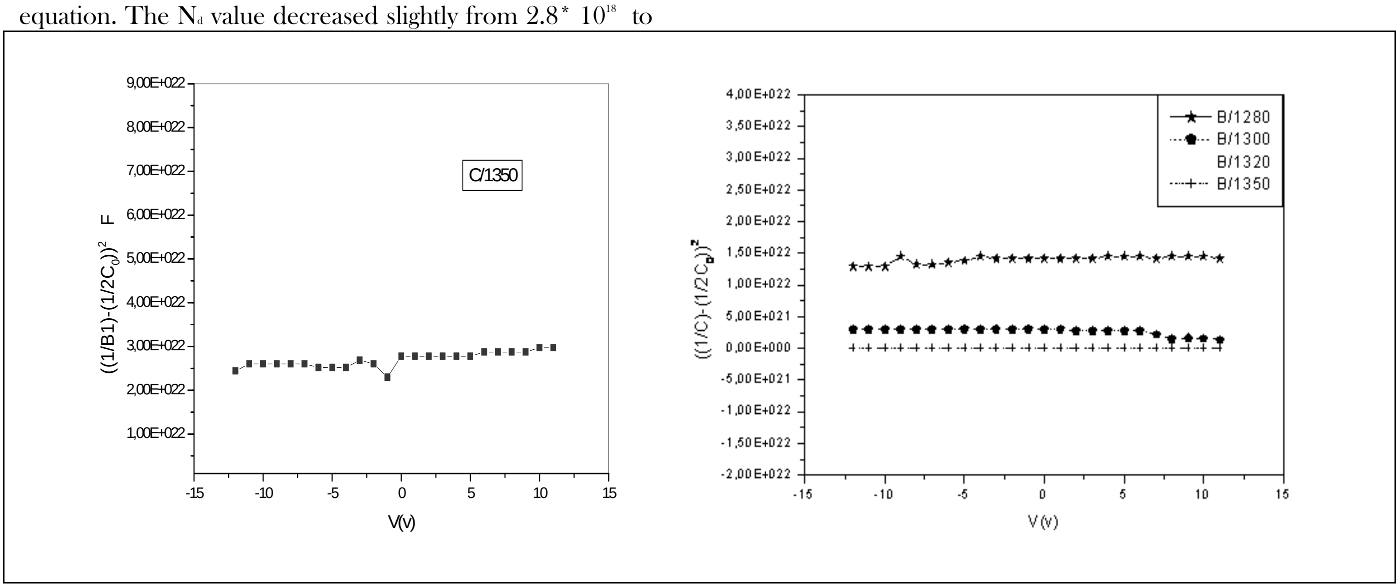

Fig. 4. C_V characteristics of the samples for various sintering temperatures.

4. Conclusions

The dependence of the microstructure and electrical propertie of Zn–Bi-Sb-Al-Mn-based varistors on the sintering temperatures was investigated. The average grain size greatly increased with the increase of sintering temperature. The breakdown field decreased due to the increase of ZnO grain size and the decrease of the breakdown voltage per grain boundary. A maximum value (3.39) of the nonlinear coefficient was obtained for the sample (C) sintered at 1350°C. Conclusively, this system provides the advantage of applications because it exhibits a nearly constant nonlinear coefficient.

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