Dependence of the properties of CoO-doped ZnO-Bi_2O_3 varistors on heating and cooling rates during ceramic processing

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Varistors are voltage dependant resistors which are used widely in current-over-surge protection circuits [1–3]. The ceramics are highly resistive below a certain threshold field, but become conducting when this field is exceeded. The threshold or switching field is usually referred to as the breakdown field, E_b. Immediately above E_b, the relation between current and field may be expressed in terms of a power-law, $J \propto E^{\alpha}$, where J is current density and E the applied field [4]. The parameter α, is referred to as the nonlinearity exponent [4].

Varistor properties are dependent on dopant type and concentration, grain size, composition and distribution of intergranular phases, and ceramic processing conditions [5–7]. The ability to control E_b and α are both important for device applications [4, 8, 9]. Usually ZnO varistors contain a small amount of added Bi_2O_3 and a combination of numerous dopants, one of which is often CoO. This communication reports the effects of heating and cooling rates on the current voltage response of ZnO-Bi_2O_3 (0.5 mol%) ceramics doped only with CoO (0.75 mol%). In all experiments a constant sintering temperature of 1000 °C, and dwell time of 4 hrs were adopted. Densities were measured by geometric measurements; microstructures were examined using backscattered scanning electron microscopy (SEM) and SEM-EDX chemical analysis. Average grain sizes were measured by a linear intercept method. Values of E_b were determined from the field at which $J = 1$ mA/cm^2; current densities, J, in the range 1–10 mA/cm^2 were used to calculate α values.

Plots of current density versus electric field for different heating and cooling rates are shown in Fig. 1a and 1b respectively. Values of E_b and α are plotted against ramp rates in Fig. 2. For a constant cooling rate of 5 °C/min, changes to the heating rates from 1 to 5 °C/min produced similar J-E responses, with E_b values of ∼750–800 V/cm. However there was a significant jump in breakdown field, to 910 V/cm for samples fabricated by more rapid heating at 10 °C/min, Fig. 2a. For different cooling rates (with a constant heating rate of 5 °C/min) E_b decreased progressively, from 925 to 755 V/cm, as cooling rates were increased from 1 to 2 °C/min to 5 °C/min, Fig. 2b. However a further increase in cooling rate to 10 °C/min produced an opposite trend, with E_b increasing to 870 V/cm.

There was a corresponding decrease in α values, from 25 to 19, as cooling rates increased from 1–5 °C/min, but the fastest cooling rate, 10 °C/min, produced an increase in α to 25, Fig. 2b. Heating rates which were faster than 2 °C/min resulted in reduced α values; the lowest α value of any of the conditions studied occurred for a heating rate of 10 °C/min, producing an α value of only 15, Fig. 2b. Table I summarizes the various values of E_b and α.

In any project designed to examine heating and cooling rates it is necessary to consider the effects of possible differences in thermal input, as this would alter sintering conditions and, in the present system, could also lead to variations in the amount of bismuth oxide lost by volatilization at high temperatures. However, by considering the results of samples processed using reversed combinations of heating and cooling rates, for example by comparing a sample heated at 1 °C/min and cooled at 5 °C/min with a sample heated at 5 °C/min and cooled at 1 °C/min, it is possible to assess the effects of variable ramp rates for similar total thermal inputs (i.e., area under the time-temperature heating profile). The differences in electrical properties of these samples, Table I and Fig. 3, illustrate that the properties were indeed directly affected by combined differences in heating and cooling rates.

A typical microstructure is shown Fig. 4a. The regions of lightest contrast in the backscattered SEM image correspond to a Bi-rich intergranular phase derived from a liquid phase formed during sintering (the eutectic temperature of the ZnO-Bi_2O_3 system is ∼750 °C [10]). The combination of the doped semiconducting ZnO matrix grains (medium contrast in Fig. 4a), and the Bi_2O_3 based intergranular phase is the key to developing varistor behavior; an electrostatic barrier is formed at the grain boundaries preventing electronic conduction below the breakdown field [4, 11]. SEM-EDX analysis confirmed the Bi-rich nature of the intergranular phase, Fig. 4b; it also revealed that Co was present in the ZnO matrix grains, Fig. 4c, but no Co was detected in the intergranular phase. The matrix EDX analysis is therefore consistent with a ZnO-CoO solid solution being formed; low levels of Zn detected by EDX in the intergranular phase may have been due to beam overlap. However, it may be a genuine result as there are reports of compound formation in the ZnO-Bi_2O_3 system [12]; it is also possible that a limited solid solution

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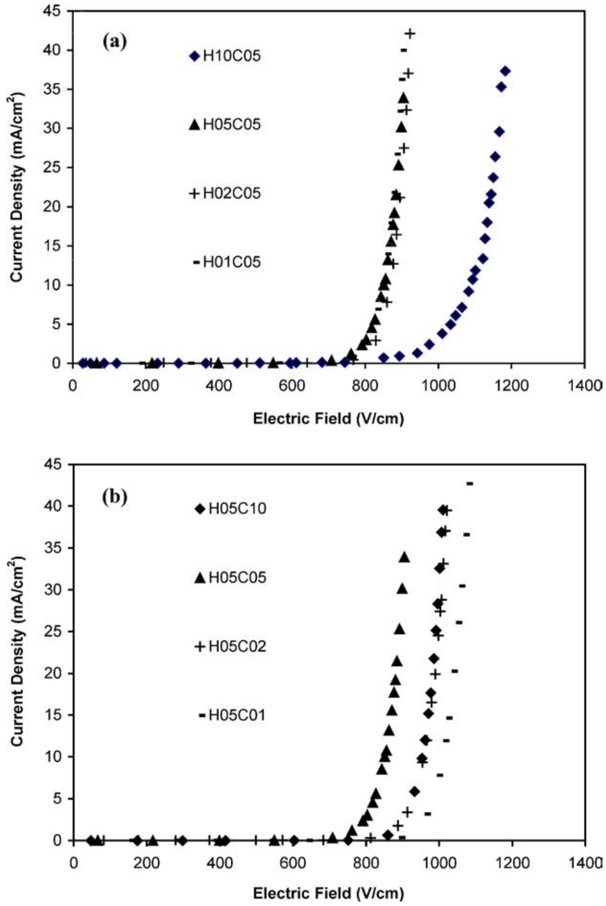

Figure 1 I-V characteristics of samples sintered using: (a) cooling rate of 5 °C/min and heating rates 1, 2, 5 and 10 °C /min; (b) heating rate of 5 °C/min and cooling rates of 1, 2, 5 and 10 °C /min. Key: H10C05 = heating rate 10 °C/min, cooling rate 5 °C/min, etc.

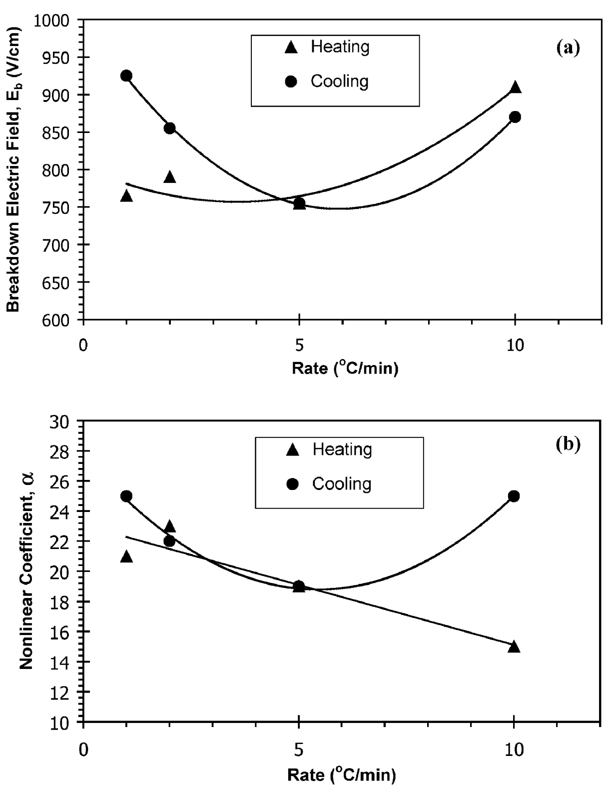

Figure 2 Plots of (a) breakdown field, E_b, versus heating and cooling rate; (b) nonlinearity coefficient, α, versus heating and cooling rate.

TABLE I Summary of values of breakdown field, E_b, nonlinearity coefficient, α, and average grain size

Heating rate (°C/min)	Cooling rate (°C/min)	E_b (V/cm)	α	Average grain size (μm)
1	5	765	21	23
2	5	790	23	23
10	5	910	15	16
5	5	755	19	21
5	10	870	25	22
5	2	855	22	24
5	1	925	25	22

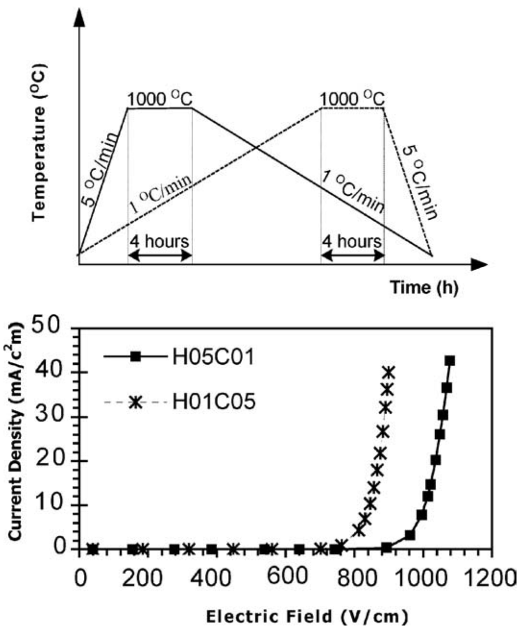

Figure 3 Temperature–time profiles and J-E values of samples processed using similar total thermal inputs achieved by using different combinations of heating and cooling rates as indicated. Key: H05C01 = heating rate 5 °C/min, cooling rate = 1 °C/min; H01C05 = heating rate 1 °C/min, cooling rate = 5 °C/min.

is formed between Bi_2O_3 and ZnO. X-ray diffraction indicated that on cooling, the liquid phase had crystallised to β-Bi_2O_3, [13]; although it is possible that lesser amounts of other crystalline phases were present at levels below the XRD detection limit, amorphous regions may also have been present. No differences in EDX and XRD results were observed for different ramp rates. Similarly, there was no difference in measured density in the different samples, with all samples having a density of ~5.36 g/cm^3.

For heating rates up to 5 °C/min there was no significant microstructural change, with average grain sizes as measured by the linear intercept method, of 21–23 μm; however grain size decreased to ~16 μm for the fastest heating rate studied, 10 °C/min, Fig. 4 and Table I. Varistor properties are known to depend on grain size, breakdown fields decreasing with increasing grain size [2, 13]. In a study in this laboratory, sintering temperatures were varied to induce changes in grain size for the same CoO doped ZnO-Bi_2O_3 composition; the resulting plot of average grain size versus breakdown field showed a linear correlation [13]. The graphical relationship between grain size and E_b obtained

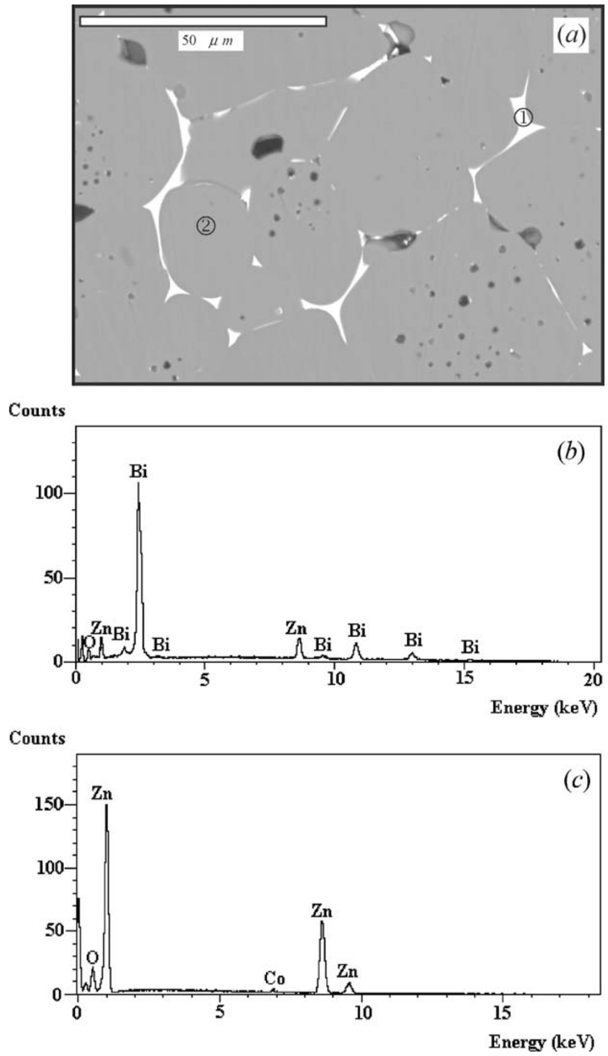

Figure 4 (a) Backscattered SEM image; (b) EDX data from intergranular region labeled "1" in Fig. a; (c) EDX data from matrix grain labeled "2" in Fig. (a).

from that study was used to predict values of E_b for the grain sizes obtained here, using different heating rates. For grain sizes of 21–23 μm (heating rate 1–5 °C/min) and 16 μm (heating rate 10 °C/min), the extrapolated values were 770–720 and 900 V/cm respectively [13], which compare to experimentally determined values of 790–755 and 910 V/cm, Table I. This close agreement is a strong indication that the heating rate effect observed in the present work was directly attributable to the reduced grain growth using the 10 °C/min heating rate cycle.

Cooling rates produced no significant change in microstructure, with average grain sizes of 21–24 μm, Table I. It is speculated that the changes in the J-E response for the different cooling rates may have been due to grain boundary conductivity changes caused by subtle changes to the phase content of the intergranular regions. The β tetragonal polymorph of Bi_2O_3 is often reported in varistor compositions [10, 13, 14], but there are reports of various phase combinations, including the stable monoclinic α low-temperature polymorph and a metastable cubic γ form [15–17]. Changes to cooling rate could possibly change the type and proportion of intergranular phases which are formed as the liquid crystallises on cooling from sintering temperatures, which in turn would be expected to alter the electrical properties of the grain-grain boundary interfaces. XRD peaks from the intergranular phase were very faint in all samples and small differences in phase content in the 1 °C/min sample would not have been detected. Alternatively, it has been suggested that cooling rate could influence the wetting properties of the intergranular liquid and so affect the physical distribution of the Bi-rich phase at the grain boundaries and triple points, thereby affecting varistor response [4]. Oxygen diffusion along grain boundaries may be another factor to consider, as would changes in oxidation state of matrix and grain boundary ions.

In summary, for this CoO doped ZnO-Bi_2O_3 varistor composition, the current-voltage characteristics were manipulated by changing heating and/or cooling rates. In this series of experiments, at a sintering temperature of 1000 °C, the highest breakdown fields, E_b, were obtained by using heating rates of 10 °C/min and/or slow cooling rates, 1 °C/min. A reduced grain size was responsible for the heating rate effect. The value of exponent of nonlinearity had a maximum value of 25, with a minimum value of 15 recorded for the fastest heating rate.

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