



# Modified Citrate Gel Techniques to Produce ZnO-Based Varistors (Part II—Electrical Characterisation)

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Submitted April 20, 2000; Revised June 30, 2000 Accepted September 12, 2000

**Abstract.** The electrical characteristics of doped ZnO pellets prepared by novel, modified citrate gel routes and the conventional mixed oxide route were compared. The mixed oxide route produced rather inhomogeneous materials at the sintering temperatures employed in this study (970 °C and 1000 °C). In contrast, the modified citrate gel routes enabled some control over the location of the minority components incorporated into the ZnO. By positioning these components according to their function, varistor pellets with higher nonlinearity coefficients, higher characteristic voltages and slightly higher energy absorption abilities than those of the conventional mixed-oxide route were prepared. Differences in the electrical characteristics of varistors prepared by different routes but with apparently similar microstructures was taken to indicate successful control over the compositional homogeneity.

**Keywords:** ZnO-based varistors, citrate gel process, nonlinearity coefficient, breakdown voltage, energy absorption

## 1. Introduction

Two novel synthetic methods were employed to prepare dense ceramic pellets of doped ZnO [1]. Route 1 involved precipitation and calcination of a layer of dopants (Co, Mn, Al, Ni, Cr) onto a pure ZnO powder, followed by precipitation and calcination of an additive layer (Bi, Sb, Ba, B, Si). Route 2 involved co-precipitation of Zn salts with the dopant salts followed by calcination to leave a doped ZnO powder which was then coated with a layer of additives. The powders produced from these routes were compared with those from the conventional mixed-oxide route, denoted route 0. In each case the nominal composition of the materials was the same.

The doped ZnO powders were mixed with binder and pressed into pellets. The pellets were heated to 400 °C to remove the binder and leave green bodies with approximately 50–60% of their maximum theoretical densities.

In the first part of this work [1] it was found that

after sintering at 1000 °C dense ceramic pellets were formed. The microstructure of the pellets prepared by the novel routes was more homogeneous than that of the conventional route, the average grain sizes were lower and the intergranular phases more evenly distributed.

Various electrical characteristics (breakdown voltage, nonlinearity coefficient, energy handling capability) are often used to characterise varistors. In order to verify that the microstructural improvements observed previously, for the modified citrate routes, would translate into improved varistor performance the electrical characteristics of samples from the three routes were examined.

## 2. Experimental Procedure

Doped ZnO pellets with similar nominal compositions were prepared by the three synthetic routes outlined in Part 1 [1]. In addition to the sintering procedure described before (1000 °C for 90 min) a further set of pellets were sintered at 970 °C for 90 minutes for com-

parison. A  $3\text{ }^{\circ}\text{C min}^{-1}$  heating rate and  $1\text{ }^{\circ}\text{C min}^{-1}$  cooling rate were implemented in both regimes. In order to make electrical measurements varistor samples were polished and contacted on both opposing faces with fired-on silver paste received from Siemens-Matsushita. The geometric area of each contact was  $20\text{ mm}^2$ .

The voltage-current ( $V$ - $I$ ) characteristics were measured at five different currents ( $1\text{ }\mu\text{A}$ ,  $10\text{ }\mu\text{A}$ ,  $100\text{ }\mu\text{A}$ ,  $1\text{ mA}$ , and  $10\text{ A}$ ). The  $V$ - $I$  characteristics in the range of  $1\text{ }\mu\text{A}$  to  $1\text{ mA}$  were measured in a continuous d.c. mode. In order to avoid excessive heating of the sample at  $10\text{ A}$  a pulse of  $8 \times 20\text{ }\mu\text{s}$  shape ( $8\text{ }\mu\text{s}$  rise time,  $20\text{ }\mu\text{s}$  total time to return to 50% of the maximum current) was used when measuring the voltage.

Two different nonlinear coefficients  $a1$  and  $a2$  were evaluated by the relationship given in Eqn. 1.

$$a = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \quad (1)$$

where  $V_1$  and  $V_2$  are the voltages corresponding to the currents  $I_1$  and  $I_2$  respectively. The nonlinearity coefficient,  $a1$  was calculated using Eqn. 1 with  $V_1$  measured when the current was  $10\text{ }\mu\text{A}$  and  $V_2$  with a current of  $1\text{ mA}$ .  $a2$  was calculated when  $I_1 = 1\text{ mA}$  and  $I_2 = 10\text{ A}$ .

All five of the voltage measurements were used to verify the monotonicity of the  $V$ - $I$  curve and hence that the electrical contacts were good and the pellets unbroken.

ZnO-based varistors are often characterised by a breakdown voltage that marks the transition from the linear pre-breakdown region to the non-linear region. However, as is commonly found, it was difficult to determine the exact location of this breakdown voltage because of the lack of sharpness of the transition in the  $V$ - $I$  curve. Therefore, we have chosen to compare the characteristic voltages ( $E_v$ ) at a current of  $1\text{ mA}$ , which, from experience, generally lie in the break-

down region and are therefore close in value to the breakdown voltage.

The energy absorption characteristics were also measured by subjecting five pellets prepared by the three routes ( $970\text{ }^{\circ}\text{C}$  sintering temperature) to  $8 \times 20\text{ }\mu\text{s}$  pulses of increasing magnitude. Pellet failure was defined as a change in  $E_v$  (at  $1\text{ mA}$ ) of more than 10% from the initial value. The energy absorption  $W$  was calculated using Eqn 2:

$$W = \int_{t_0}^{t_1} V(t) \cdot i(t) dt \quad (2)$$

where  $t_0$  and  $t_1$  were the times at which the pulse started and finished, respectively.

### 3. Results and Discussion

The values of the characteristic voltages and first non-linear coefficients ( $a1$ ) for the samples sintered at  $970$  and  $1000\text{ }^{\circ}\text{C}$  are listed in Table 1. From which it may be noted that the  $a1$  and  $E_v$  values for the samples prepared by routes 1 and 2 are higher than those previously reported from the citrate gel route [2] ( $E_v = 443\text{ V mm}^{-1}$ ,  $a = 27.8$ ), possibly due to the lower sintering temperatures employed in this work ( $970\text{ }^{\circ}\text{C}$  and  $1000\text{ }^{\circ}\text{C}$  as compared with  $1200\text{ }^{\circ}\text{C}$ ).

A relation between the microstructure and the d.c. breakdown voltage  $V$  per unit thickness (which is numerically close to  $E_v$ ) is given by:

$$V = V_{gb} N_g \quad (3)$$

where  $V_{gb}$  is the voltage per barrier,  $N_g$  the number of active grain boundaries per unit thickness.

The value of  $V_{gb}$  is typically  $3.0$ – $3.6\text{ V}$  [3] and varies little with the type and concentration of dopants (although there is a temperature dependence). Hence, at a given sample thickness the breakdown voltage  $V$

Table 1. Characteristic voltage and the first non-linear coefficient of samples prepared by routes 0, 1 and 2 and sintered at  $970\text{ }^{\circ}\text{C}$  and  $1000\text{ }^{\circ}\text{C}$ .

Synthetic method	Characteristic voltage $E_v$ / $\text{V mm}^{-1}$		Non-linearity coefficient $a1$	
	$970\text{ }^{\circ}\text{C}$	$1000\text{ }^{\circ}\text{C}$	$970\text{ }^{\circ}\text{C}$	$1000\text{ }^{\circ}\text{C}$
Route 0, mixed oxide	$490 \pm 25$	$380 \pm 20$	$47 \pm 4$	$47 \pm 4$
Route 1, precipitation	$560 \pm 30$	$480 \pm 25$	$104 \pm 20$	$70 \pm 9$
Route 2, co-precipitation	$710 \pm 35$	$560 \pm 30$	$75 \pm 11$	$45 \pm 4$

and the closely related characteristic voltage  $E_V$  only depend on the number of active grains between the electrodes.

The value of  $N_g$  reflects the largest grains in the pellet, because two single large grains would have a much lower breakdown voltage than a parallel route of the same length containing many smaller grains. Therefore, the conduction pathways are formed by larger than average particles [4,5]. Hence, a characteristic grain size,  $d_g$ , may be defined (Eqn. 4) which has a value between the average and maximum grain sizes.

$$d_g = \frac{V_{gb}}{V} \quad (4)$$

By making the approximations that  $V_{gb} = 3.3$  V and that  $V = E_V$ , from Eqn. 4, the values of  $d_g$  for the 1000 °C samples were found to decrease in the order route 0 > route 1 > route 2, Table 2. This order is in agreement with the SEM observations from the first part of this work. The values of  $d_g$  were higher than the average values measured from the micrographs, by 5–20%, as was anticipated above. However, the grain size values for the route 2 material estimated by the two techniques showed the least difference (5%). This may imply that current paths in the route 2 sintered bodies were less dominated by anomalously large particles than for the route 0 or route 1 materials. Alternatively  $V_{gb}$  may vary slightly among the samples due to differences in the barrier composition.

The values of  $d_g$  calculated for a pellet prepared by a given route and sintered at 970 °C were smaller than for those sintered at 1000 °C, Table 2. This indicates that growth of the ZnO grains continued for each sample over the temperature range 970–1000 °C.

The nonlinear coefficients  $a1$  of the samples are also shown in Table 1.  $a1$  typically describes the non-linear behaviour around the breakdown region. A high  $a1$  value represents a small voltage change with increasing current in the non-linear region. An ideal

varistor would have an infinite  $a1$  value, and an ohmic resistor an  $a1$  value of unity. The value of  $a1$  for a real varistor is dependent on the homogeneity of the microstructure as well as the type and concentration of additives [6].

Experimentally the  $a1$  values were found to be lowest for the conventional route 0 materials and highest for those prepared by route 1. Also after sintering at 1000 °C the  $a1$  values were lower than those after 970 °C sintering. The values found for the route 0 samples and the 1000 °C route 2 sample ( $a1 = 45 - 47$ ) are typical of commercial varistors [7–9]. The route 1 and 970 °C route 2 samples had unusually high values ( $a1 = 70 - 104$ ).

The routes 1 and 2 pellets after sintering at a given temperature had similar characteristic grain sizes, microstructures and nominal chemical compositions [1]. However, the value of  $a1$  for route 1 was significantly higher than route 2 (Table 1). The only major difference between the pellets was the method by which the dopants were incorporated: in route 1 the dopants were precipitated onto pure ZnO powder, in route 2 zinc salts were co-precipitated with the dopants. Previously this difference was found to affect the number of distinct densification stages (one for route 1, two for route 2) [1]. The difference in  $a1$  is evidence that the fashion in which the dopants are incorporated in ZnO ceramics can influence the varistor characteristics.

It was postulated previously [1] that the dopants in the route 1 material were not homogeneously distributed throughout the ZnO grains in the green bodies but retained some ‘memory’ of their initial location. As the dopants were originally deposited on the surface of the ZnO grains under route 1 it was concluded that the concentration of dopants at the surface of the ZnO grains in the green bodies was higher for route 1 than route 2. However, no suggestion was made as to the distribution of dopants in the sintered pellets. From the

Table 2. Characteristic grain sizes for varistor pellets prepared by the three routes as determined from scanning electron micrographs [1] (marked as \*) or electrical measurements. Note that the limits represent the errors in the characteristic grain sizes and not standard deviations of the readings.

Synthetic method	Characteristic grain size / $\mu\text{m}$	
	1000 °C sintering temperature	970 °C sintering temperature
Route 0, mixed oxide	$7.4 \pm 0.7^*$	$8.8 \pm 0.4$
Route 1, precipitation	$5.9 \pm 0.5^*$	$6.9 \pm 0.3$
Route 2, co-precipitation	$5.6 \pm 0.5^*$	$5.9 \pm 0.3$

difference in  $\alpha_1$  values it is apparent that the dopant distribution in the green bodies also affected the distribution in the sintered bodies, Fig. 1.

Because the route 1 materials had higher  $\alpha_1$  values and presumably higher surface dopant concentrations it may be reasoned that one or more of the species which were originally considered to simply increase grain conductivity (the dopants: Co, Mn, Al, Ni, Cr) acted beneficially in forming the intergranular layers (an 'additive' property). In other words, the wetting of the grains and the composition of the intergranular regions may have differed between routes 1 and 2 as a consequence of the different initial distribution of the dopant species. Some evidence that the 'additives' could act as 'dopants' was observed previously from studies of the densification of green bodies during sintering [1], where it was found that powders from routes 1 and 2 densified at different temperatures.

That the route 0 pellets did not have similarly high values of  $\alpha_1$  to the route 1 materials, even though little positional distinction was made between the dopant and additives under either regimes, may simply be a consequence of the distinctly different microstructures. It would also be expected that the route 0 material possessed a wide range of dopant concentrations near the grain boundaries. Different  $\alpha$  values have been observed even between grains of the same pellet, prepared by a conventional mixed-oxide synthesis [10]. These variations in  $\alpha$  values may be indicative of compositional variations and structural differences at the grain boundaries. However, no comparable single grain boundaries data is available for the route 1 or route 2 materials.

The decrease in  $\alpha_1$  for the routes 1 and 2 materials after 1000 °C rather than 970 °C sintering could be a consequence of changes in the number or composition

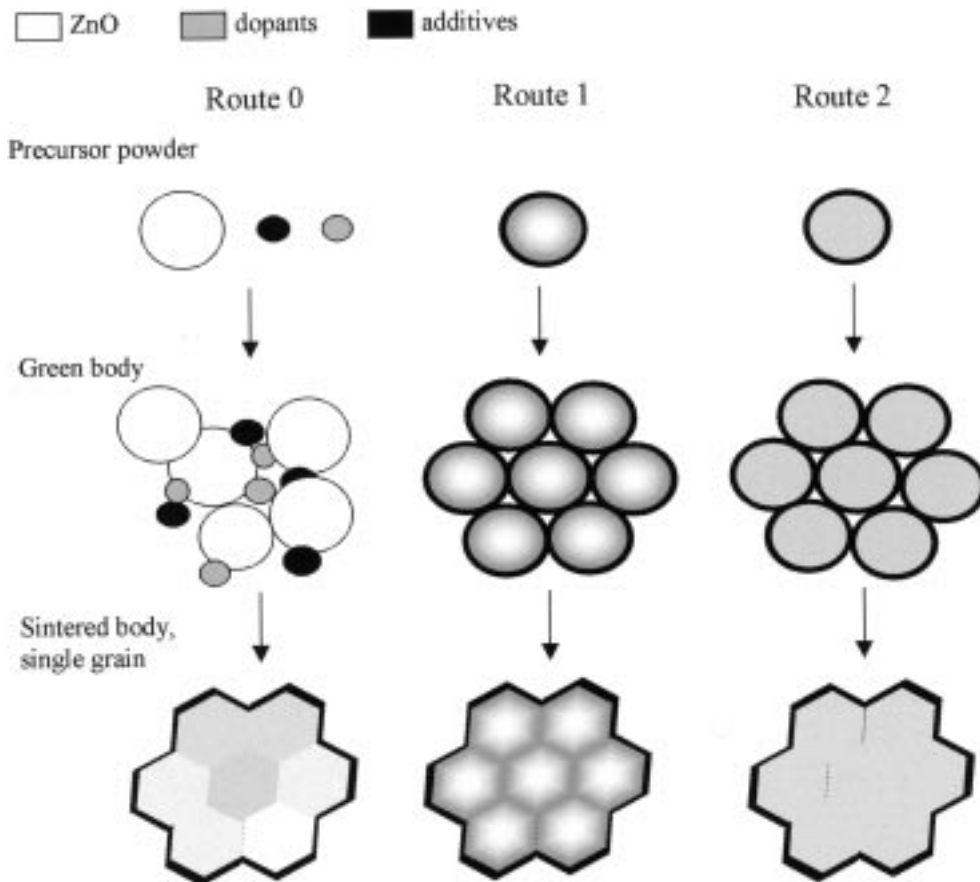


Fig. 1. Schematic representation of the distribution of additive and dopant species in the precursor powders, green bodies and sintered bodies under routes 0, 1 and 2. Note that the depth of grey shading indicates the concentration of dopants.

of active grain boundaries. It would be expected that the spinel grain size would be larger after the higher temperature sintering [11], possibly restricting the number of current conduction paths. However, it may be noted that sintering at sufficiently high temperatures above 1000 °C (or with sufficiently long sintering times) may increase the extent of diffusion of dopants and additives such that similar materials would be produced regardless of the powder synthesis route.

Systematically replacing the ‘additives’ with ‘dopants’ in the route 2 synthesis should enable the function of the minor components to be clarified. In this sense route 2, although giving lower  $a_1$  and  $E_v$  values in this study, offers distinct advantages in terms of flexibility over both routes 0 and 1.

The  $a_2$  values may be taken as a rough indication of the extent of the non-linear region; higher values of  $a_2$  indicating non-linearity extending to higher currents. The values of  $a_2$  obtained for all of the varistor pellets lay in the range 34–36, implying that the voltage up-turn regions commenced at similar currents.  $a_2$  may be expected to vary with the chemical composition of the intergranular boundaries and the proportion of the boundaries which are active in a given pellet. As the  $a_2$  values are similar for each pellet it may be assumed that either there was little variation in the proportion and composition of active grain boundaries or that the two factors varied in a complimentary fashion.

The energy absorption ability,  $W$ , was measured for the pellets sintered at 970 °C. Two values are given for  $W$  (Table 3) corresponding to the minimum energy required to cause one out of the five pellets to fail and for all of the pellets to fail.

As can be seen from Table 3 the range of  $W$  was very small for each route, especially noting that the experimental accuracy was typically  $\pm 25 \text{ J cm}^{-3}$ . The small variation in  $W$  between the highest and lowest values for any given route indicates that pellets had

similar, reproducible microstructure and compositions. It may also be noted that the values for the route 2 pellets were within experimental error of those from route 0 and that the route 1 pellets had typically 50  $\text{J cm}^{-3}$  higher values.

$W$  is a complex function of the electrical characteristics of the individual grains and grain boundaries and of the number of conduction pathways. Clearly the highest energy absorption abilities will be observed for pellets in which the current is uniformly distributed across the whole of any given cross-section perpendicular to the current path. Such a pellet may be expected to have a uniform microstructure with homogeneous, good-quality grain boundaries. As there is little variation in the range of  $W$  values among the three routes it may be assumed that the number and quality of active grain boundaries also varied little (as was supposed from the small variation in  $a_2$  values). However, the slightly higher value of  $W$  for the route 1 than route 2 pellet indicates that more grain boundaries may have been active in the route 1 pellet or that the energy handling capabilities of the individual grain boundaries were higher.

#### 4. Conclusions

ZnO-based varistors prepared by a modified citrate gel route show higher values of characteristic voltages ( $E_v$ , up to  $710 \text{ V mm}^{-1}$ ) and non-linear coefficients ( $a_1 > 70$ ) when compared with varistor ceramics produced by the mixed-oxide route ( $E_v = 380 - 490 \text{ V mm}^{-1}$ ,  $a = 47$ ).

These improvements and differences in the electrical properties are due to a more homogeneous and finer-grained microstructure and a more controlled distribution of the dopants and additives obtained in the citrate gel precipitation processes.

However, differences were also observed in the non-linearity and maximum energy absorption of pellets with similar microstructures prepared by the two modified citrate gel routes. These differences were attributed to the appropriate location of the minority components in the ZnO grains or grain boundaries according to their function as ‘dopants’ or ‘additives’. Tailored differences in compositional homogeneity of the initial powders appeared to be retained, to some extent, in the final bodies after sintering at 970 or 1000 °C.

Table 3. Energy absorption abilities until the first pellet failed and all of the pellets failed for samples prepared by the three routes. Note experimental accuracy  $\pm 25 \text{ J cm}^{-3}$ .

Synthetic method	Energy absorption ability $W / \text{J cm}^{-3}$	
	First pellet	All pellets
Route 0, mixed oxide	610	660
Route 1, precipitation	700	700
Route 2, co-precipitation	640	650

## Acknowledgments

We thank Siemens-Matsushita, Deutschlandsberg (now EPCOS) for providing materials and performing electrical measurements. Discussion with J. Schoonman are gratefully acknowledged.

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