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# Sintering behavior and non-linear properties of ZnO varistors processed in microwave electric and magnetic fields at 2.45 GHz

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**Abstract**

A study of the densification behavior and grain growth mechanisms of ZnO-based varistors composed of 98 mol.% ZnO–2 mol.% ($Bi_2O_3$, $Sb_2O_3$, $Co_3O_4$, $MnO_2$) has been carried out. The pressed samples were sintered in microwave electric ($E$) and magnetic ($H$) fields using a single-mode cavity of 2.45 GHz. The effect of the sintering temperature (900–1200 °C), holding time (5–120 min) and sintering mode ($E$, $H$) on the microstructure and electrical properties of the sintered varistor samples were investigated. The grain growth kinetics was studied using the simplified phenomenological equation $G^n = kte^{(-Q/RT)}$. The grain growth exponent ($n$) and apparent activation energy ($Q$) values were estimated for both electric and magnetic heating modes and were found to be $n = 3.06$–$3.27$, $Q = 206$–$214$ kJ mol$^{-1}$, respectively. The lower value of $n$ estimated in the $E$ field was attributed to a volume diffusion mechanism, whereas the higher $n$ value in the $H$ field sintering was correlated mainly to a combined effect of volume and surface diffusion processes. Samples sintered in the $H$ and $E$ fields showed high final densities. Moreover, the ones sintered in the $H$ field presented slightly higher density values and bigger grains for all sintering temperatures than $E$ field heated ones. The optimal sintering conditions were achieved at 1100 °C for a 5 min soaking time for both $H$ and $E$ field processed samples, where respectively densities of $99.2 \pm 0.5\%$ theoretical density (TD) and $98.3 \pm 0.5\%$ TD along with grain size values of $G = 7.2 \pm 0.36$ μm and $G = 6.6 \pm 0.33$ μm were obtained. Regarding the electrical properties, breakdown voltage values as high as 500–570 V mm$^{-1}$ were obtained, together with high non-linear coefficients $\alpha = 29$–$39$ and low leakage currents ($J_1 \approx 5 \times 10^{-3}$ mA cm$^{-2}$), respectively, for $E$ and $H$ field sintered varistor samples. Moreover, samples sintered in an $H$ field systematically exhibited higher breakdown voltage values compared to the ones sintered in the $E$ field. This was attributed to an improved coupling between the $H$ field and the present dopants within the ZnO matrix, this latter being mostly semiconductive, thus leading to an enhanced reactivity and improved properties of the electrostatic barrier.


*Keywords:* Microwave; Varistor; Microstructure; Sintering; Breakdown voltage

## 1. Introduction

Zinc oxide (ZnO) varistors are non-linear, two-terminal, semiconductor voltage-dependent resistors, which are widely used as transient voltage surge suppressors to limit voltage surges in the range from low voltages (5 V) to high voltages (up to 1 MV). The non-linear $J$–$E$ characteristics result from the nature of the grain boundary layer, which mainly consists of ionic additives such as $Bi_2O_3$, $Sb_2O_3$, $Co_3O_4$, etc. Many researchers have reported the sintering behavior of several doped ZnO systems, such as $Bi_2O_3$-doped ZnO [1], $Sb_2O_3$-doped ZnO [2] and $Al_2O_3$-doped ZnO [3]. The electrical properties of ZnO varistors are obviously related to the composition and microstructure, such as grain size, density, morphology and the

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distribution of second phases. As a consequence, the non-ohmic properties of these materials are strongly dependent on the fabrication process, which in turn regulates the defect chemistry in the depletion region and in the vicinity of the grain boundary. It is commonly accepted that the microwave sintering process can densify ceramic materials in a very short time and mostly at lower temperatures than conventional sintering methods. Several authors have reported the non-thermal effects induced by the microwave field ($E$, $H$) [4], acting as an additional driving force (electromigration, ponderomotive force etc.) for diffusion mechanisms. In 1994, Cherradi et al. [5] were the first to notice that the $H$ microwave field can be used for heating semiconducting materials in a single-mode microwave cavity. The basic experimental setup allowed them to correlate the distribution of the $E$ and $H$ fields inside the cavity with the temperature distribution through a CuO bar, this latter being microwave-heated in either an $H$ field or an $E$ field. This $H$ field component has been successfully used when using a specific assembly for heating up semiconducting materials (mainly oxides). Subsequently, a systematic investigation of the heating profile of various materials in $E$ and $H$ field separation was carried out at Penn State University [6,7] in a single-mode microwave cavity at 2.45 GHz. As stated in one of our previous works based on the sintering behavior of pure ZnO in both $E$ and $H$ fields, the material exhibited denser and more homogeneous microstructure during the sintering in the microwave magnetic ($H$) field [8]. This study, which had not been carried out previously, was also applied for the investigation of the sintering behavior of ZnO with several dopants added. Indeed, one could expect the specificities of the electric and magnetic field during the microwave selective sintering of ZnO-based compositions. Due to the high absorption of electromagnetic power and the conductive nature of various dopants in ZnO varistor compositions such as $Bi_2O_3$ [9], $Co_3O_4$ etc., it is expected that the heating will be very high when sintered in a microwave magnetic field.

We report the effect of the sintering temperature and soaking time on the microstructure of ZnO-based ceramics heated in microwave $E$ and $H$ fields. The correlation between the microstructure properties and their $J$–$E$ properties has been also established. For each heating mode, different sintering cycles were used and microstructure and electric characterizations have been carried out. The electrical properties related to the processing conditions are presented and discussed according to the heating conditions.

## 2. Experimental procedure

### 2.1. Powder synthesis, characterization and shaping

High-purity nano-ZnO powder (Nanogard, 99.99% purity, 60 nm mean particle size) and pure grade dopants in the proportion of 98 mol.% ZnO, 0.5 mol.% $Bi_2O_3$, 0.5 mol.% $Sb_2O_3$, 0.5 mol.% $Co_3O_4$ and 0.5 mol.% $MnO_2$ were used for the preparation of ZnO-based varistors. The mixture was ball-milled in an agate mortar using 5 mm diameter zirconia balls in ethanol media. After drying the slurry at 100 °C for 24 h, an organic binder (Rhodoviol 4%, Prolabo) was introduced to the dry mixture to ensure a good cohesion between particles. The latter was thereafter dried under an infrared lamp in order to evacuate the water content of the binder solution. The shaping of the samples was done by uniaxial pressing at 110 MPa using a cylindrical steel die with a diameter of 8 mm, followed by cold isostatic pressing at 300 MPa. The pellets were then calcined in air at 650 °C for 2 h in order to enhance powder reactivity. The crystalline phases were identified by X-ray diffraction (XRD) using Cu $K_\alpha$ radiation (Phillips X'Pert diffractometer). For the microstructural observations, scanning electron microscopy (SEM) observations were made on 1 μm polished and $H_3PO_4$ etched sample surfaces. Bulk densities of the samples were determined using their weights and dimensions. All samples held a green density of 66% of the theoretical density (TD) and weighed ~0.5 g. Based on the accounted absolute errors on the samples dimensions and weights, the overall percentage error on the final densities of the samples was estimated to be ±0.5% of the calculated data.

Grain size measurements were carried out on the micrographs of the etched samples using the following equation:

$$G = 1.56L \quad (1)$$

where $G$ is the average grain size and $L$ is the average grain boundary intercept length of nine random lines on two different micrographs of each sample. Each line accounted for ~30 grain interceptions. The percentage error on the grain size values was estimated to be ±5% of the calculated data.

### 2.2. Microwave furnace

The microwave equipment used in this study consists of a 2 kW, 2.45 GHz magnetron source (Sairem GMP20KSM), a water-cooled aluminum circulator, a rectangular twist and a waveguide (WR340) that conducts the microwaves to a tailor-made TE10p single mode cavity with ports for vacuum and gas feed. The operating modes used in the cavity are TE103 (maximum $E$ field region in the center of the cavity where the $H$ field is minimum) and TE102 (maximum $H$ field region in the center of the cavity where the $E$ field is minimum), and were adjusted by tuning the length between the coupling iris and the short circuit piston from both side ends (Fig. 1).

The sample was placed in an alumina-silicate box Fiberfax (DURABOARD), which is microwave transparent and ensures a homogeneous thermal insulation of the sample by reducing the thermal radiation from the sample surface (Fig. 1b). The box and sample were placed in the middle of the cavity and the cavity length was tuned to either $E$ or $H$ field mode. An infrared pyrometer was placed above the sample and allowed precise optical temperature