



Influence of the preparation process on the electrical properties of high-field co-doped zinc oxide varistors

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Abstract

High-field ZnO/Bi₂O₃ varistors co-doped with Mn and Co were synthesized using a two-step co-precipitating process. A Zn²⁺ solution containing the Mn and Co doping elements was first precipitated into hydroxides, further converted into oxalates and finally calcined to create the doped ZnO phase. Bi³⁺ precipitated at the grain boundaries thanks to an HNO₃ treatment of the ZnO grains. The influence of the precursor type (nitrates or chlorides) and the calcination temperature on the properties of the powders and ceramics were investigated. ICP-AES, microstructural analysis and non-linear voltage measurements were used to characterize the samples. The type of precursor solution was found to have a strong influence on the electrical properties. Furthermore, the calcination temperature modified the microstructure of the powder and consequently also that of the varistor.

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1. Introduction

ZnO-like varistors were introduced more than forty years ago by Matsuoka [1]. Also known as voltage-dependant resistors, they have been widely studied because of their high and reversible non-linear I - V behavior [2–5]. Typically resistive at low voltages, they become conductive above a breakdown voltage. Their main characteristic is the breakdown field $E_{1.0A}$ taken at 1 A [6]. They are mainly used as transient surge suppressors or voltage regulators, and are especially useful for high voltage applications because of their tremendous surge energy absorption.

At the breakdown field, the I - V characteristic can be simulated by a power law given by the following equation:

$$I = KE^\alpha \quad (1)$$

where K is a proportional factor, α is the non-linearity coefficient, I is the current and E is the electric field. The higher the value of α , the greater is the non-linearity.

Varistors are generally composed of zinc oxide which is a nonstoichiometric n-type semiconductor with linear characteristics, and an additive considered as a varistor former (e.g. Bi₂O₃, Pr₂O₃, and Sb₂O₃) [7–10] added in quantities generally lower than 1 mol%. This varistor former is responsible for the non-linear effect and it is well accepted in the literature that it creates a highly resistive depletion layer at the grain boundaries, considered as a double Schottky barrier [11,12]. Different doping elements of the ZnO phase such as MnO₂, CoO, BaO, NiO or Al₂O₃ were studied in order to modify the non-linear characteristics [13–15] or improve the stability of the system [16–18].

These ceramics are usually prepared using an oxide mixing route, resulting in chemical inhomogeneities, strong dependence toward the characteristics of the raw materials (purity/granulometry), coarse microstructures and high sintering temperatures. Another drawback of this oxide mixing route is the insufficient homogeneity and stability of the grain boundaries.

During the course of this study, we elaborated ZnO/Bi₂O₃ sub-micrometric homogeneous varistor powders co-doped with Mn and Co using a soft chemistry process. We studied the

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influence of two critical parameters of this process on the powders and the properties of the ceramics.

First, as the electrical properties of ZnO varistors are recognized to be very dependent of the content of impurities, we determined the influence of the precursor type (nitrate or chloride). Secondly, as it is well known that the physico-chemical properties of the final powder rely strongly on the decomposition temperature (modification of the specific surface area), its influence was also investigated.

2. Experimental procedure

The varistor powders had the following composition: 98.94 mol% ZnO, 0.25 mol% CoO, 0.25 mol% MnO and 0.56 mol% Bi₂O₃. Starting from Zn²⁺, Mn²⁺ and Co²⁺ nitrates or chlorides (reagent grade), various aqueous solutions of precursor were prepared and titrated. The process was divided into two steps and conducted in the same manner for both precursor types. Zn²⁺, Co²⁺ and Mn²⁺ salts were first mixed and homogenized according to the final composition. A saturated NaOH solution was added to simultaneously precipitate the Zn, Co and Mn hydroxides. After a period of vigorous mixing, a saturated oxalic acid solution was added to the reactor to convert the hydroxides into their corresponding oxalates. The resulting white precipitate was filtered, washed, dried, and calcined at 500 or 600 °C to obtain the combined ZnO powder. In a second step, the powder was mixed with an acidic aqueous Bi(NO₃)₃ solution. The mixture was again filtered, washed and dried before a second calcination step at 400 °C to decompose the bismuth nitrate.

Herein, the samples obtained from nitrates and chlorides are referred to as Ntr and Chl, respectively. The calcination temperature (500 °C or 600 °C) is also included to the sample references (e.g., Ntr-500 °C for the varistor prepared with nitrate and calcined at 500 °C).

Different analyses were carried out in order to characterize the powders, such as inductively coupled plasma-atomic emission spectrometry (ICP-AES, HORIBA Activa), servocoulometric analysis for the determination of the content of chloride species, combustion analysis for the determination of N, O (LEICO TC-600) and H contents (HORIBA EMGA-621 W), X-ray diffraction (PANAnalytical X'Pert Pro with K_α(1) copper radiation) for phase identification, laser granulometry (Cilas granulometer), specific surface area measurements (Asap 2010 Micromeritics), thermogravimetric analysis (TGA, Setaram TAG 24) and scanning electron microscopy (SEM, ZEISS ULTRA Plus).

The powders were isostatically pressed at 100 MPa. The resultant slugs were sintered at 730 °C for 16 h—a temperature close to the theoretical eutectic temperature of the ZnO–Bi₂O₃ mixture [19]. This sintering temperature was chosen because a low temperature limits the grain growth and ensures that the breakdown field remains high. The relative densities of the slugs were measured using the Archimedes method, taking into account a theoretical density of 5.67 g/cm³ for ZnO. Finally, the microstructures of the sintered compacts were examined using SEM.

Cylindrical pellets were cut into slugs. An Ag paste was deposited on both ends of the samples which were then calcined at 600 °C. A minimum of two varistors were tested for each composition.

3. Results

TGA measurements were carried out on the oxalate powders to ensure that their decomposition was complete for the two selected calcination temperatures. As shown in Fig. 1, the weight loss was identical for the samples prepared with nitrate and chloride. The decomposition was divided into two steps. First, the samples lost around 19% of their weight between 100 and 200 °C. This is typical of residual water desorption. Subsequently, the samples lost around 36% of their weight between 350 and 420 °C. A simple calculation led us to explain this weight loss as the oxalate decomposing into the corresponding oxide (e.g., ZnC₂O₄ into ZnO). These TGA analyses thus confirmed that the chosen firing temperatures of 500 and 600 °C led to a complete decomposition.

The purity of the final powders was determined using ICP-AES and combustion analysis (Table 1). The theoretical composition was respected for all the samples since the Zn,

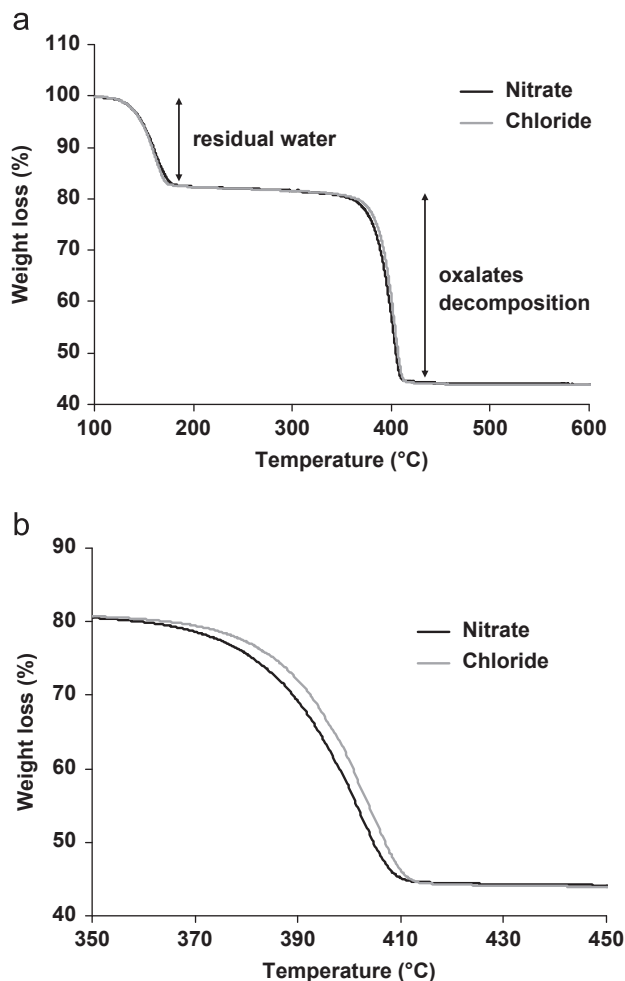


Fig. 1. (a) TGA analysis of nitrate and chloride prepared oxalates and (b) detail of the 350–450 °C range.

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