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Characterisation of SnO_2–CoO–MnO–Nb_2O_5 ceramics

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Abstract

Varistors based on SnO_2 have attracted increasing interest in recent years. However, the combined effect of CoO–MnO on SnO_2 ceramics is still unclear. In this study, the non-Ohmic behaviour of the 98.95 mol%SnO_2–0.5 mol%CoO–0.5 mol%MnO–0.05 mol%Nb_2O_5 system, the microstructures and the influence of sintering temperature were investigated. The samples were prepared by the mixed oxide route, and were sintered at temperatures in the range 1250–1450 °C. SEM observation and EDS analysis revealed that the ceramics have a two-phase microstructure comprising SnO_2 primary grains and a Mn, Co rich secondary phase of small particles. The sintered density of the samples increased with the increase in sintering temperature. The maximum non-linear coefficient ($\alpha = 10$) was obtained at a sintering temperature of 1350 °C.

Keywords: SnO_2 varistor; CoO–MnO doping; Non-linearity; Microstructure; Second phase

1. Introduction

SnO_2 varistors ceramics are new type of varistor material developed since middle 1990s, firstly reported by Pianaro et al.[1–3] SnO_2 is an n-type semiconductor with a crystalline structure of the rutile type. It exhibits low densification (about 50% theoretical density), which is related to the dominance of mechanisms for mass transport such as evaporation–condensation.[2–4] The level of densification of SnO_2 ceramics can be improved by introducing dopants, such as CoO, MnO, ZnO, NiO, CuO and Bi_2O_3.[2–6] Among these, the dopants CoO, MnO and ZnO are the most effective, achieving densities in SnO_2 ceramics >95% theoretical by the addition of any of these dopants at 0.5–1 mol% levels.[3]

If doping with the combinational divalent and quinquevalent metal oxides (such as Nb_2O_5), the dense SnO_2 ceramics will have non-Ohmic characteristics. Pianaro et al.[1] were the first to report that the SnO_2–CoO (1 mol%)–Nb_2O_5 (0.05 mol%) ceramics have a non-linearity coefficient (α) of 8, and a breakdown electric field (E_b) of about 1870 V/cm. Bueno et al.[6] reported that the α value of dense SnO_2–MnO (0.5 mol%)–Nb_2O_5 (0.25 mol%) ceramics can be as high as 17, but the E_b reaches 12650 V/cm. Varela et al.[7] and Cerri et al.[4] proposed that the sintering of SnO_2 doped with CoO or MnO is controlled by grain boundary diffusion with no liquid phase during the sintering process. The high densification of SnO_2 based ceramics makes it possible to define the varistors' behaviour after the addition of Nb_2O_5; Bueno et al.[8] demonstrated the effect of Nb as a donor in SnO_2 polycrystalline semiconductor. Bueno et al.[6] noted that the main microstructure of SnO_2–CoO based ceramics is more homogeneous than that of SnO_2–MnO based ceramics, in which the presence of a precipitate phase, mainly at triple points, is easily visible. Therefore the solubility of Mn^{2+} atoms appears to be lower than that of Co^{2+} in the SnO_2 matrix. The formation of Mn_2SnO_4 and $MnSnO_3$ in the grain boundary region has been reported.[4,6] However, the combined effect of CoO–MnO doping on the sintering properties and electrical characteristics of SnO_2 based ceramics is still unclear. The purpose of the present work is to investigate the combined effects of CoO and MnO additions on the sintering properties and electrical characteristics of SnO_2 based ceramics.

2. Experimental methods

The ceramic samples used in this study were based on the two compositions: 99 mol% SnO_2 + 0.5 mol% CoO + 0.5 mol% MnO (designated as SCM) and 98.95 mol% SnO_2 + 0.5 mol% CoO + 0.5 mol% MnO + 0.05 mol% Nb_2O_5 (designated as SCMN). All oxides were analytic grade from Aldrich. They were mixed in deionized water with zirconia balls for 20 h ball

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milling. After drying, granules were obtained by passing the dried powders through a screen having an aperture mesh of nominally 0.3 mm. The small disc shape samples (12 mm in diameter and 2.5 mm thickness) were pressed by a uniaxial press at 80 MPa. The samples were sintered at 1250, 1300, 1350, 1400 and 1450 °C for 1 h in air, with heating and cooling rates of 3 °C/min.

The sintered densities of the samples were determined using the Archimedes method. The reference theoretical density was taken to be 6.95 g/cm^3, that of pure SnO_2. The phases present were identified by X-ray diffraction (XRD) techniques (Philips X'Pert system) using Cu Kα radiation. Morphologies and microstructures were examined by scanning electron microscopy (SEM) using a Philips EX-30 equipped with energy dispersive spectrometer (EDAX), and a JEOL 6300.

Before electrical measurements, sliver electrodes were applied to both sides of the samples. The current–voltage (I–V) characteristics of the samples were measured at room temperature using a variable d.c. power supply (Bradenburg 475R). The non-linearity coefficients (α) and the breakdown electric field (E_b) were determined from the I–V data.

3. Results and discussion

Fig. 1 shows the densities of SCM and SCMN samples as a function of the sintering temperature. It can be seen that the combined addition of 0.5 mol% CoO and 0.5 mol% MnO effectively improved the densification of SnO_2 ceramics to above 97.5% theoretical even at the low sintering temperature 1250 °C. The sintered densities for both sample increased as sintering temperature increased. However, the sintered densities of SCMN samples are slightly lower than those of SCM samples at a constant sintering temperature; this could be related to the addition of Nb_2O_5. The sole addition of Nb_2O_5 did not benefit the densification of pure SnO_2 ceramics.

Typical micrographs of SCM and SCMN samples are shown in Fig. 2. It is interesting to see that triangle or trapezium shape second phase particles were visible on the sintered surfaces (Fig. 2a–c) and inside the body (Fig. 2d) for both types of samples at the full range of sintering temperatures. This type of small particles was rarely found in the SnO_2–CoO ceramics, although

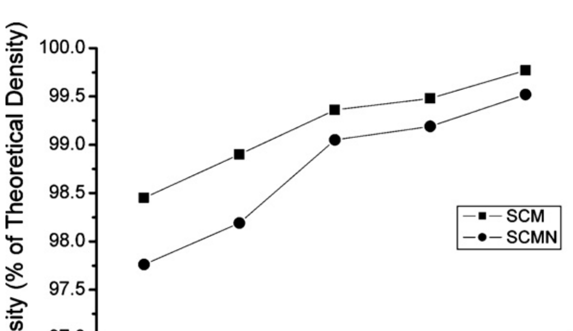

Fig. 1. Sintered density of SCM and SCMN samples as a function of sintering temperature.

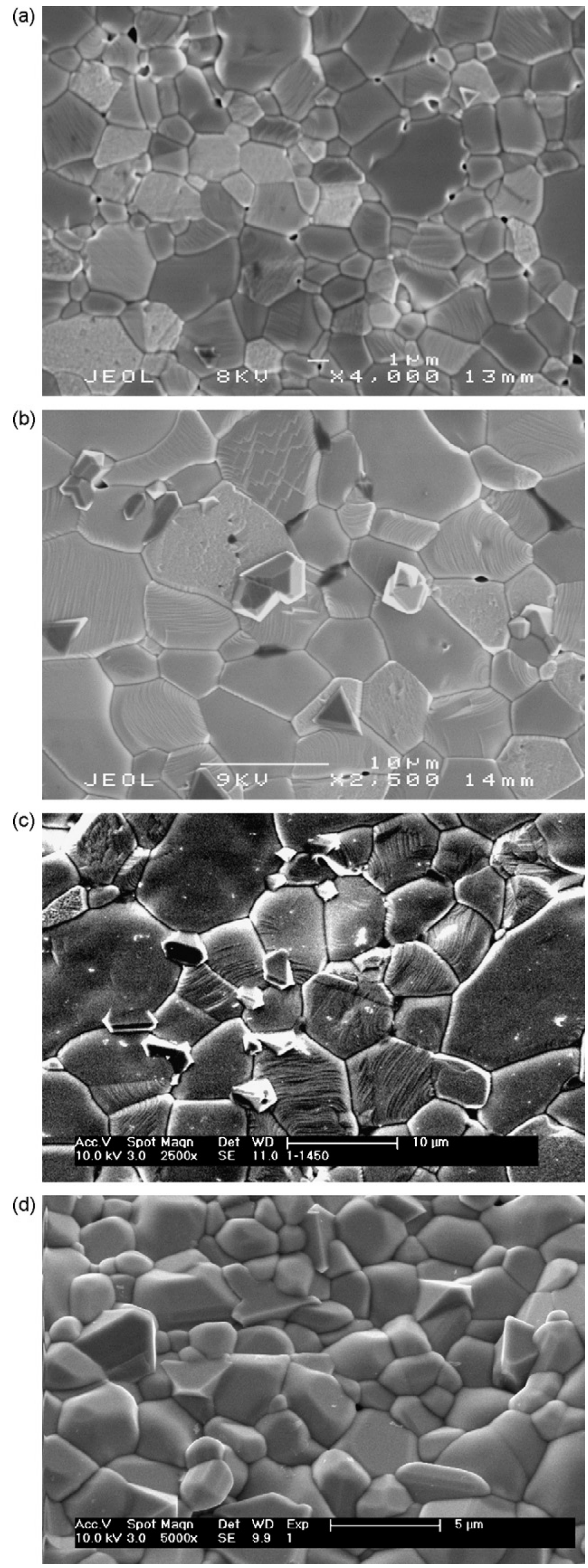

Fig. 2. The SEM micrographs of SCM and SCMN samples; the triangle or trapezium shape second phase particles can be clearly seen: (a) the surface of SCM sample sintered at 1300 °C; (b) the surface of SCMN sample sintered at 1400 °C; (c) the surface of SCM sample sintered at 1450 °C; (d) the fracture surface of SCMN samples sintered at 1350 °C.

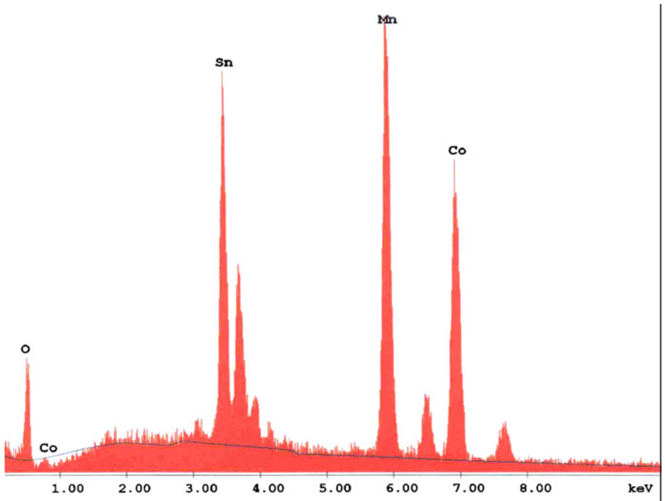

Fig. 3. EDAX spectrum for the second phase particle.

Varela et al.[7] reported much smaller precipitates in ceramics of the system SnO_2–CoO by using TEM. However, the small particles, with a similar size, were observed in the SnO_2 ceramics merely doped with different manganese oxides, no matter how fine the MnO or MnO_2 powders.

An EDAX spectrum, shown in Fig. 3, confirms that these second phase particles are Mn and Co rich containing Sn. The normalized element analysis indicates that: Mn: 31.2 ± 1.1 wt%, Co: 32.1 ± 0.2 wt%, Sn: 30.7 ± 1.4 wt% and O: 6.1 ± 0.5 wt%. The weight percent ratios of Mn, Co, and Sn are quite similar to those of Mn_2SnO_4 and Co_2SnO_4 that were found within SnO_2–MnO and SnO_2–CoO ceramics, except for the weight percent of oxygen.[4,7] Due to low doping levels (both MnO and CoO are 0.5 mol%), the presence of this phase could not be confirmed by X-ray diffraction.

The SCM samples sintered at temperature in the range of 1250–1450 °C have quite high resistivities, so that their *I–V* characteristics could not be determined using standard facilities. For a similar reason the *I–V* characteristics of the SCMN samples sintered at low temperatures (1250–1300 °C), could not be obtained. Fig. 4 shows the *I–V* characteristics of SCMN samples sintered at higher temperatures (1350–1450 °C); the

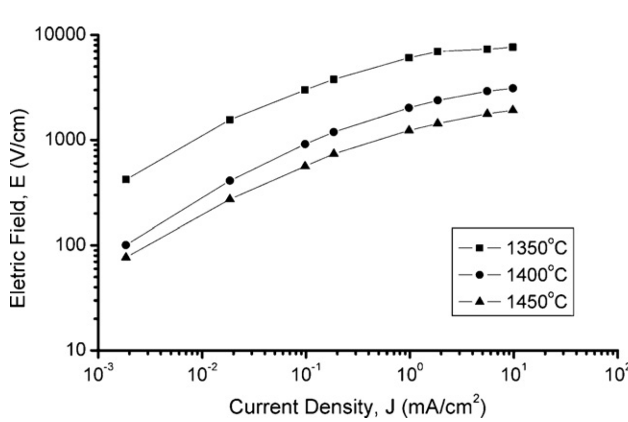

Fig. 4. The *I–V* characteristics of SCMN samples sintered at 1350, 1400 and 1450 °C.

Table 1
The non-linearity coefficient and breakdown electric field for SCMN samples.

Sintered temperature (°C)	1350	1400	1450
Non-linearity Coefficient, α	10	5	3
Breakdown electric field, E_b (V/cm)	6070	2030	1235

non-linearity coefficients and breakdown electric fields are shown in Table 1.

Bueno et al.[9] proposed that the nature of the Schottky-like double potential barriers existing at grain boundaries characterized the SnO_2 based varistors. The chemical origin of these double Schottky barriers is likely to be related to the degree of enrichment of grain boundaries with oxygen. Doping materials to generate p-type semiconductor oxides, such as CoO and MnO, increases the amount of oxygen species in the region of the grain boundary in comparison to the bulk, exhibiting n-type features. For varistor ceramics, it is usually the case that the higher the barrier, the better the non-linearity. The non-linearity coefficients of SCMN samples decreased with increasing sintering temperature; this could be due to the decrease in the amount of oxygen species at the grain boundaries in samples sintered at higher temperatures and the resultant lower barrier heights.

4. Conclusions

(1) The combined addition of CoO and MnO can significantly improve the densification of SnO_2 based ceramics. The sintered density can be higher than 97.5% theoretical for samples sintered in the range of 1250–1450 °C. The sintered density increased as sintering temperature increased.
(2) SEM observations and EDAX analysis revealed that both SCM and SCMN samples have a two-phase microstructure comprising SnO_2 grains and a small particulate second phase. EDAX analysis revealed that the triangle or trapezium-shaped second phase particles are Mn and Co rich containing Sn.
(3) SCM samples have high resistivities. With addition of Nb_2O_5 (0.05 mol%), the SnO_2 ceramics doped with both CoO and MnO (SCMN samples) have a non-linearity coefficient of 10 when sintered at 1350 °C for 1 h. The non-linearity coefficients of SCMN samples decreased with increase of sintering temperature.

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