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Microstructural analysis of varistors prepared from nanosize ZnO

S. C. Pillai, J. M. Kelly, D. E. McCormack and R. Ramesh

ZnO nanoparticles were prepared by a solid state pyrolysis reaction of zinc acetate dihydrate and oxalic acid dihydrate at 500°C. The course of reaction at various temperatures was followed by XRD. Subsequently varistors were fabricated from this nano-ZnO material by solid state mixing with various oxide additives and sintering to 1050°C. The microstructure of the sintered material was studied using XRD, field emission SEM (FESEM), and EDX, and ZnO grains, bismuth rich regions and spinel phases were identified. Discs made from oxide doped nano-ZnO show considerably higher breakdown voltage (656 ± 30 V mm^{-1}) compared to those prepared from micrometre sized ZnO (410 ± 30 V mm^{-1}) and commercial varistors (454 ± 30 V mm^{-1}). However, varistors made from the nano-ZnO show very low densification and high leakage current, making them unsuitable for device fabrication.   MST/6097

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Introduction

ZnO varistors are well known electroceramic devices, which have voltage dependent switching capabilities.[1-4] Varistors are usually connected across the power line in parallel with the instrument to be protected from overvoltage surges.[3] These devices are highly resistive up to a certain field (breakdown voltage, V_c), above which they become highly conducting. When the voltage exceeds V_c, the varistor starts conducting and draws current through it. At present, varistors are used for overvoltage protection in many electrical and electronic networks at voltages ranging from 12 V to over 10^6 V.[5] As a result of the demand for miniaturised devices, it is essential to provide voltage surge absorbers of a similar scale.[6] It should be noted that careful control of the microstructure is required to produce varistors with a high breakdown voltage as V_c is proportional to the number of active grain boundaries in the sintered body.[1,3,6,7] In principle, it should be possible, through nanostructuring, to produce ZnO varistors with a high V_c by controlling the grain size and hence the increased number of active grain boundaries per unit volume in the material. Nano-ZnO prepared through different routes including sol–gel,[6-9] precipitation,[10,11] microemulsion[12] and plasma synthesis[13] were some of the early methods attempted to make materials for varistor applications. It has recently been observed that nano-ZnO material,[6] prepared from zinc acetate and oxalic acid through a multistep solution route, can be used to produce varistor materials with markedly improved breakdown voltage. The aim of this work was to prepare nano-ZnO in an environmentally friendly (solvent free) fashion and to prepare the varistors by sintering at a low temperature. Recently nano-ZnO has been successfully prepared by solid state pyrolysis[14,15] and used for making a gas sensor[14] and UV emitter.[15] In this paper nano-ZnO has been prepared by the previously reported solid state pyrolysis procedure[14] and varistors have been fabricated by incorporating various additives, and sintering at 1050°C. These samples are compared to others prepared from micrometre sized ZnO.

Experimental

MATERIALS

Zinc acetate dihydrate (Riedel-de Haen, 99·5%) and oxalic acid dihydrate (Aldrich, 99%) are used as received. Micron sized ZnO (Grillo), Bi_2O_3 (Ferro corporation), Sb_2O_3 (Cookson), CoO (Outokumpu), MnO (Campbell Chemicals), NiO (Campbell Chemicals), Cr_2O_3 (Merck), Al_2O_3 (Merck) (all reagent grade) and commercial varistor powder were supplied by Littelfuse Ltd, Dundalk.

PREPARATION OF NANO-ZnO

Zinc oxide nanoparticles were prepared by a solid state pyrolysis technique using zinc acetate and oxalic acid.[14,15] In a typical experiment 10·98 g (50 mmol) zinc acetate dihydrate and 12·6 g (100 mmol) oxalic acid dihydrate were mixed in an agate mortar for 3 min. This mixture was then calcined by heating from room temperature to 500°C using a ramp rate of 3 K min^{-1} and held at this temperature for 2 h in a chamber furnace to yield nanosized particles of ZnO (nano-ZnO).

ADDITION OF DOPANTS TO NANO-ZnO

ZnO was mixed with commercial oxide additives by a solid state mixing technique. In a typical experiment nano-ZnO (2·000 g, 24·500 mmol) calcined at 500°C was added to Bi_2O_3 (0·060 g, 0·1300 mmol), Sb_2O_3 (0·0940 g, 0·3200 mmol), MnO (0·0220 g, 0·2500 mmol), NiO (0·0120 g, 0·1600 mmol), CoO (0·021 g, 0·280 mmol), Cr_2O_3 (0·0196 g, 0·130 mmol) and Al_2O_3 (0·0005 g, 0·0047 mmol) and mixed in an agate mortar for 5 min. This mixture was plastified by mixing with one drop each of 10% aqueous solution of poly(vinyl alcohol), poly(ethylene glycol) and 0·015 g of gum arabic. The material was then dried, pelletised and sintered at 1050°C for 2 h. Varistors were also made by mixing micrometre sized ZnO (micron-ZnO) with oxide additives in a similar way. Solid
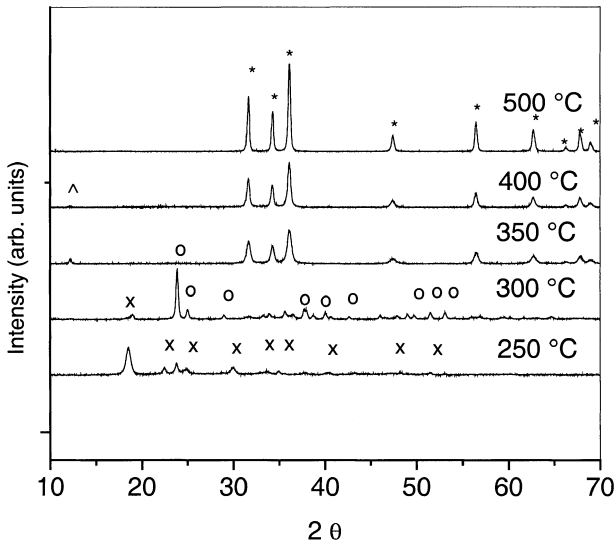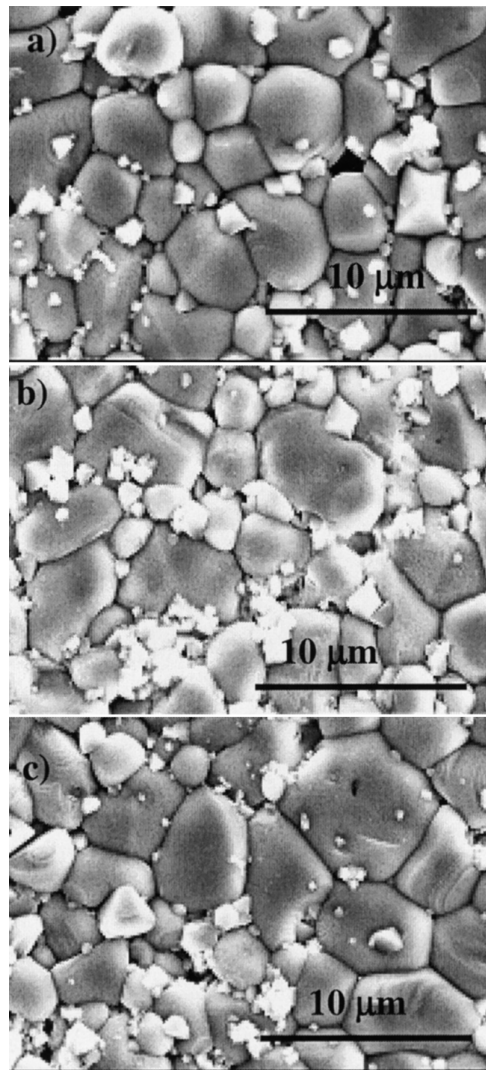
1 XRD pattern of ZnO precursors calcined at various temperatures: (x zinc oxalate dihydrate; o anhydrous zinc oxalate, $^\wedge$ unidentified phase; * ZnO)
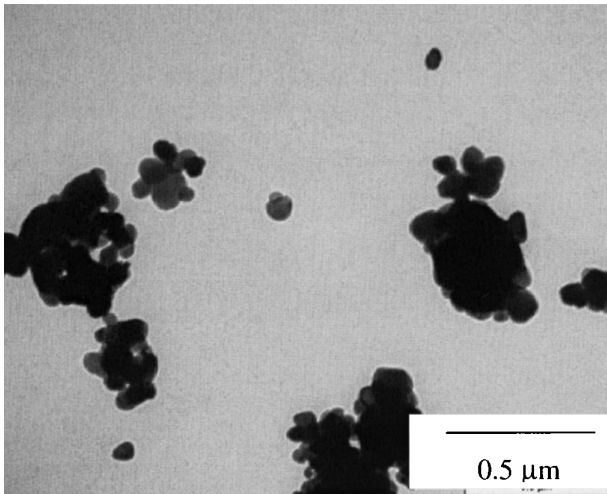
2 TEM image of nano-ZnO sample calcined at 500°C
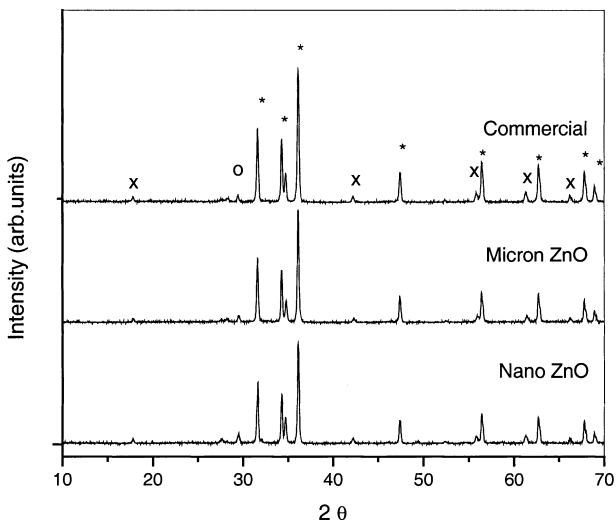
3 XRD pattern of sintered (1050°C) varistor samples (* ZnO; x $Zn_7Sb_2O_{12}$; o Bi_2O_3)

a prepared from nano-ZnO; *b* prepared from micrometre-ZnO; *c* commercial varistor

4 FESEM images of sintered surface (not etched) at 1050°C of differently prepared varistors

state pyrolysis reaction, calcination, and sintering were performed in a Nabertherm S-27, chamber furnace.

INSTRUMENTATION

Samples for powder X-ray diffraction (XRD) were prepared by making a thin layer of the powder with acetone on a glass plate and the measurements were performed with a Siemens D 500 X-ray diffractometer. The particle size was calculated by applying the Scherrer equation[16]

$$\text{crystalline size} = \frac{0 \cdot 9\lambda}{B \cos \theta} \qquad \ldots \ldots \ldots \ldots \quad (1)$$

where λ = X-ray wavelength, θ = Bragg angle, B = line broadening. The line broadening B is measured from the increased peak width at half the peak height and is obtained from the Warren formula $B^2 = B_M^2 - B_S^2$ where B_M is the measured peak width and B_S is the corresponding width of a peak of a standard material (commercial ZnO) whose particle size is greater than 200 nm.

$I - V$ characteristics from $0 \cdot 1$ µA to 1 mA were measured using a Keithley Instruments (Model 2410, Sourcemeter). The breakdown voltage V_c is given as the nominal voltage at a current of 1 mA.
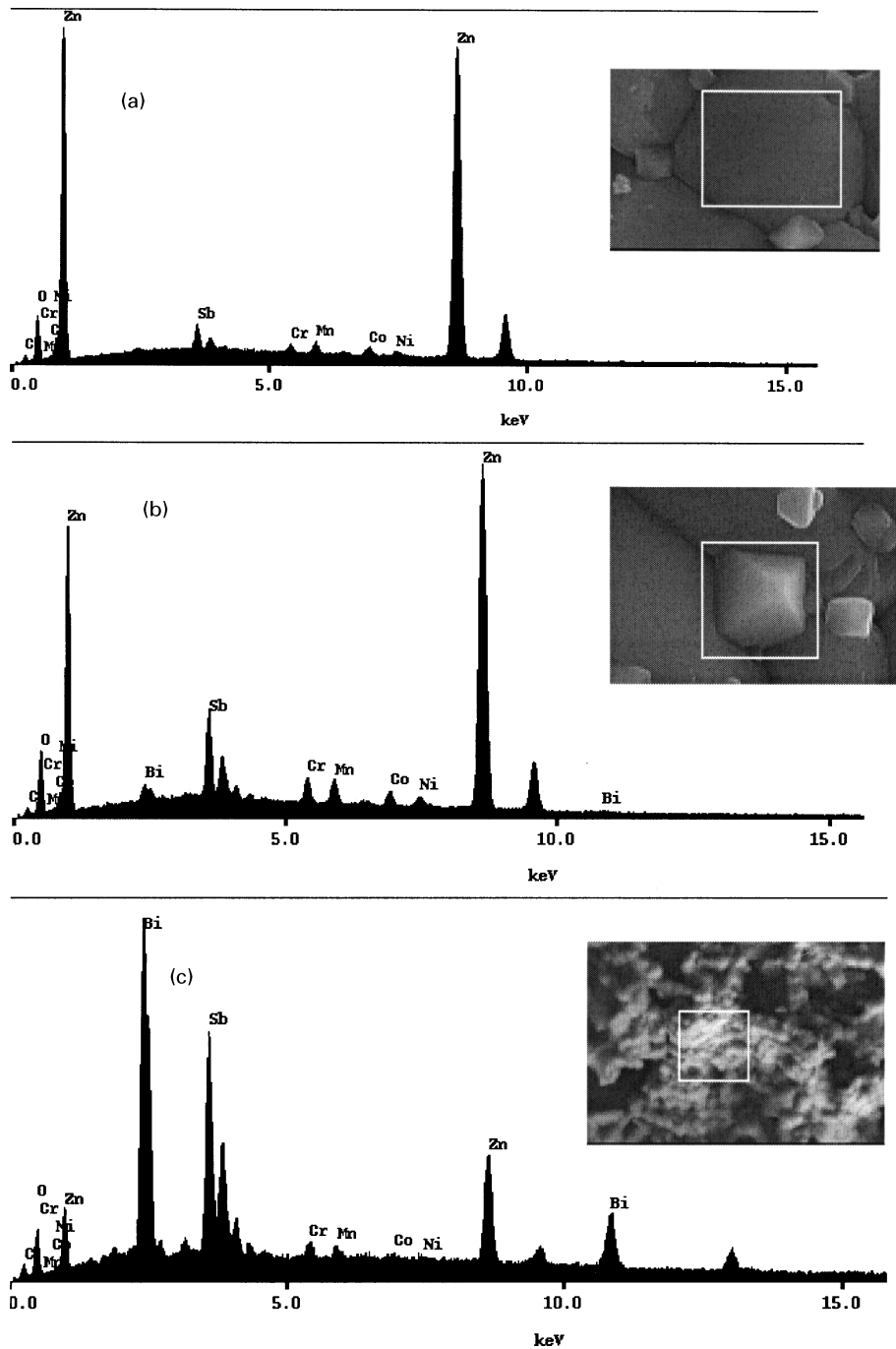
a ZnO grain; *b* spinel phase; *c* bismuth rich area

5 EDX analysis of varistor prepared from nano-ZnO (sintered at 1050°C)

Transmission electron microscopy (TEM) was performed using a Hitachi 7000 TEM instrument. 300 mesh copper grids coated with formvar were used to prepare the samples.

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) studies were carried out by field emission scanning electron microscopy (FESEM, Hitachi S-4300), which was operated at 5 or 20 kV. Samples for analysis were mounted on aluminium stubs and were coated with graphite.

Results and discussion

PREPARATION AND CHARACTERISATION OF NANO-ZnO

Zinc oxide nanoparticles were prepared by mixing zinc acetate dihydrate and oxalic acid dihydrate and heating to 500°C.[14]

Using thermogravimetric analysis (TGA) Shen *et al.*[14] proposed that in this reaction the ZnO is formed via zinc oxalate hydrate. XRD analysis was carried out at various stages of the reaction at different temperatures starting from 250°C. The XRD pattern (Fig. 1) of the precursor powder calcined at 250°C showed that zinc oxalate dihydrate (Joint Committee on Powder Diffraction Standard (JCPDS) card no. 25-1029) is the predominant phase with traces of anhydrous zinc oxalate (JCPDS card no. 37-0718).[6,17] The pattern at 300°C matches the JCPDS data of anhydrous zinc oxalate with a very weak peak of zinc oxalate dihydrate.[6,17] These results are similar to earlier observations[6] with a ZnO sample prepared through a solution route, except that anhydrous zinc oxalate was already formed at 250°C. ZnO is formed at 350°C with a very small percentage of impurity (unidentified phase) and this has fully vanished in samples calcined at 500°C.
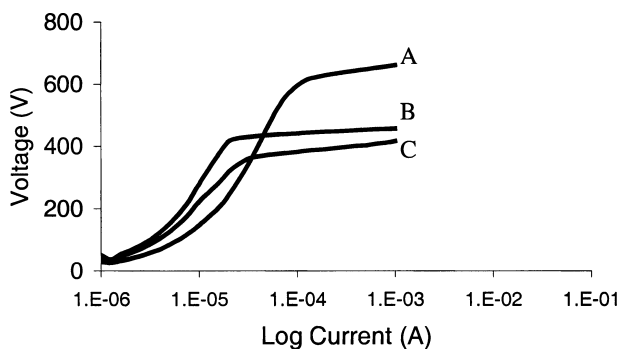
A: varistors prepared from nano-ZnO; B: commercial varistor supplied by Littelfuse Ireland Ltd; C: varistors prepared from micrometre-ZnO

6 *I–V* curve of varistor samples sintered at 1050°C for 2 h

Broadening of the larger XRD intensity peak (101, $2\theta = 36\cdot2°$) of the sample at 500°C shows this nano-ZnO sample has an average particle size of 40 ± 8 nm and this is reasonably consistent with TEM analysis (Fig. 2) which gives an average diameter of 61 ± 10 nm.

VARISTOR PREPARATION AND MICROSTRUCTURE ANALYSIS

Nano-ZnO was mixed with commercial oxide additives (Bi_2O_3, Sb_2O_3, CoO, MnO, NiO, Cr_2O_3 and Al_2O_3) by solid state mixing. The mixture was then plastified and pelletised. Analogous preparations were made with micrometre sized ($\sim 0\cdot5$ μm) ZnO. Each of these samples and a commercial varistor mixture were then sintered at 1050°C for 2 h.

XRD measurements (Fig. 3) carried out on each of the samples sintered at 1050°C revealed the presence of spinel ($Zn_7Sb_2O_{12}$), bismuth rich (Bi_2O_3) and zinc oxide phases. FESEM studies of the sintered samples (Fig. 4) indicate a smaller average grain size (~ 2 μm) in the material derived from nano-ZnO compared to the samples made from micrometre sized material (~ 3 μm) and to the commercial sample (~ 3 μm). EDX analysis (Fig. 5) revealed that three different phases could be readily identified in the microstructure of the material derived from nano-ZnO. A ZnO phase was the most abundant which appeared as spherical or polygonal grains and contained a small amount of other dopants such as Sb, Cr, Mn, Co and Ni. A second phase present mainly at the triple points was also seen in the microstructure. EDX revealed that this phase contains a significant amount of Zn and Sb along with a small amount of Cr, Mn, Bi, Co and Ni and this is attributed to a $Zn_7Sb_2O_{12}$ phase.[1,3,6,18–21] The white section observed in the microstructure near the intergranular region contains a large amount of Bi, which is identified as the Bi_2O_3. These findings are consistent with previous literature reports,[3,18–21] as it is known that above 650°C ZnO, Bi_2O_3 and Sb_2O_3 form a pyrochlore ($Zn_2Bi_3Sb_3O_{14}$) phase. This then changes into the spinel ($Zn_7Sb_2O_{12}$) phase (equation (2)). The presence of spinel and bismuth rich phases are reported to play a significant role in the formation of varistors.[18–20]

$$2Zn_2Bi_3Sb_3O_{14} + 17ZnO \xrightarrow{950-1050°C} 3Zn_7Sb_2O_{12} + 3Bi_2O_3 \quad (2)$$
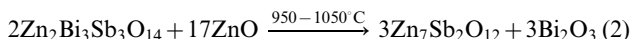
A significant difference between the samples was revealed by density measurements of the sintered bodies. Thus while the commercial sample showed 96% densification, and the sample prepared from micrometre sized ZnO 94%, the material originating from nano-ZnO had achieved only 91%. This is also apparent from the number of voids observable by FESEM. This is a notable disadvantage of this method compared with our earlier core–shell method,[6]

where 97% densification was obtained. It can also be seen from the microstructure (Fig. 4) that the final grain size of the sintered varistors made from nano-ZnO is only slightly smaller than in the other two samples, despite the fact that the reactant ZnO particles are about 10 times smaller. The grain growth in varistor ceramics is usually accompanied by the formation of $ZnO–Bi_2O_3$ binary system during the liquid phase sintering.[22,23] Bismuth oxide has a lower melting point (656°C) and it is reported that the eutectic liquid temperature for $ZnO–Bi_2O_3$ binary system is 740°C. A significant enhancement of grain growth is expected above this temperature compared with the grain growth of pure ZnO.[24,25] This is reported as due to the formation of a bismuth rich liquid phase along the grain boundaries, which increases the grain boundary mobility and thus facilitates the grain growth.[24] This demonstrates that controlling the grain size during sintering at high temperature remains a real challenge.[12,13,25] It is possible that other sintering procedures such as step sintering[26,27] or microwave assisted sintering[28] might be applied to obtain a fully sintered varistor disc at a lower temperature.

BREAKDOWN VOLTAGE

The breakdown voltages of the sintered materials were measured at 1 mA. These results (Fig. 6) show a breakdown voltage of 454 ± 30 V mm^{-1} for commercial samples and 410 ± 30 V mm^{-1} for varistors made from micrometre sized samples. Considerably higher breakdown voltage (656 ± 30 V mm^{-1}) was obtained with varistors made from nano-ZnO. These results point towards the formation of more grain boundaries by nanostructuring.[6,9,10,12] However, the sample derived from this nano-ZnO shows a disappointingly high leakage current, making it quite unsuitable for further industrial exploitation. A more favourable approach is to prepare varistors using ZnO made by a sol–gel route and adding the dopants using a solution technique to prepare core–shell type materials.[6]

Conclusions

Nano-ZnO has been produced by a solid state pyrolysis reaction and the precursors formed at various temperatures have been characterised by XRD. These results are consistent with the formation of anhydrous zinc oxalate as an intermediate. Considerably higher breakdown voltages were observed for varistors prepared from nano-ZnO, which indicates a larger number of grain boundaries per unit area. Microstructural analysis revealed the presence of ZnO, spinel and bismuth rich phases. Varistor samples prepared from the nano-ZnO sintered at 1050°C have a smaller grain size. Unfortunately the material has a low density and high leakage current compared to other novel samples prepared by our group.

Acknowledgements

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