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Synthesis of Zinc Oxide Varistors Through Microwave-Derived Precursor

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Abstract: A rapid microwave decomposition method has been reported for the preparation of ZnO varistor precursors which on subsequent heat treatment for short period results in non-ohmic properties. Thus a mixture of nitrates of zinc and praseodymium along with minor additives such as cobalt, chromium and potassium when subjected to microwaves of 2·45 GHz in a domestic oven for 8 min, resulted in the decomposition of nitrates and formation of the precursor oxide mixtures. The precursor powder consists of easily friable agglomerates of size about 5 μm, having the major phase as ZnO. Such powder on further compaction at about 150 MPa and sintering in the range of 1200–1350°C, resulted in high density (> 95%) varistors. The electrical measurements of the varistor sample showed nonlinearity coefficient ($\propto$) above 30. Electrical field (E) vs current density (J) measurements showed breakdown fields of 135 V/mm for Pr_2O_3-doped varistors. The fractograph of the sintered varistor sample indicates an average grain size of 6–8 μm.

INTRODUCTION

Suitably doped ZnO has shown non-ohmic properties and such materials, usually known as varistors or non-ohmic resistors, are used widely in electronic and electrical applications as voltage control and surge protective devices.[1,2] The non-ohmic behaviour is a grain boundary phenomenon in which n-type ZnO grains are surrounded by insulating grain boundary or charge depletion layers (known as Schottky barriers). At low voltages these grain boundaries act as barriers for any current to pass through the device but when the field is increased, the varistor starts conducting. This condition can be expressed empirically by the equation $J = KE^{\propto}$, where J and E are current density and electric field, respectively, K is a constant and $\propto$ is the nonlinearity coefficient. Good varistors have high resistance at low fields and large conductance at high fields. The grain-to-grain conduction takes place through the grain boundary and the average voltage drop per grain boundary for ZnO varistors is around 2–4 V/gb when operated in the nonlinear region.[3] The important aspects of varistor formulations are (1) size and distribution of ZnO grain and (2) nature and extent of distribution of dopants and reduction in the processing time at high temperature. So, the uniform microstructure of sintered ZnO has a key role in deciding the breakdown field characteristics. Usually the ZnO varistors are made by mixing the constituent oxides by ball milling, followed by compaction and sintering.

Oxides of bismuth are widely used as the varistor formers. Minor additives such as cobalt oxide, manganese oxide and chromium oxide are also added to influence the nonlinearity coefficient. Other oxides such as praseodymium oxide and strontium oxide are also reported to introduce nonlinearity in ZnO varistors. The specific significance of doping with Pr_2O_3 appears to be the formation of a two-phase microstructure involving absence of the spinel phase, which is found in the usual bismuth-doped varistors. They are also reported to have improved I–V characteristics.[4,5] The preparative technique is generally selected in

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order to achieve reactive precursor powders and with short sintering time to result in well-distributed microstructure for ZnO varistors. The present authors reported a solid-state flash combustion method involving metal nitrates–urea mixtures for easy preparation of rare earth oxide doped ZnO.[6] For varistors with low breakdown voltage, large ZnO grains are required and, therefore, preferential grain growth procedures involving addition of BaO have been reported.[7]

The present work describes a simple and novel method based on microwave heating of zinc nitrate and additives for the preparation of precursors for varistor formulations. The electrical properties and microstructural features of ZnO varistors thus prepared are presented.

EXPERIMENTAL

The varistor compositions selected in the present experiment contain, ZnO 96·7, Pr_2O_3 2, CoO 0·5, Cr_2O_3 0·5, and K_2O 0·3 mol%. Stoichiometric quantities of nitrates of the constituent cations were mixed in an agate mortar in presence of *n*-hexane to a paste. The paste was transferred into an alumina crucible and the crucible introduced into a domestic microwave oven having frequency of 2·45 GHz and power of 600 W and exposed to microwaves for 8 min. The mixture first melted into a clear solution and then foamed into a voluminous mass which further converts to a porous solid mass with the evolution of gases of oxides of nitrogen. The above solid was crushed to a fine powder in an agate mortar and was made into 1-mm thick circular pellets of 10 mm dia. by uniaxial pressing at 150 MPa in a stainless steel die. Sintering was carried out at three different temperatures, 1200, 1250 and 1350°C, at the rate of 10°C/min with a soaking at the maximum temperature for a period of 2 h. The sintered samples were polished to maintain planar, parallel surfaces. These surfaces were first given a thin electroless coating of silver, followed by low-temperature silver paste, to ensure ohmic contacts, by further observing the linear nature of resistance with thickness of sintered pellets. Current (I)–Voltage (V) characteristics of the electroded samples were determined with the aid of an adjustable DC power supply up to 200 V/mm. To prevent overheating at higher currents an impulse technique was employed. The current waveform was 8 × 20 μs (i.e. it took 8 μs to reach the peak current and 20 μs to reach half peak current on the falling part of the waveform) was used and observed in a Techtronix curve tracer. The sintered microstructure was observed in a JEOL 35C Scanning Electron Microscope using fractured samples.

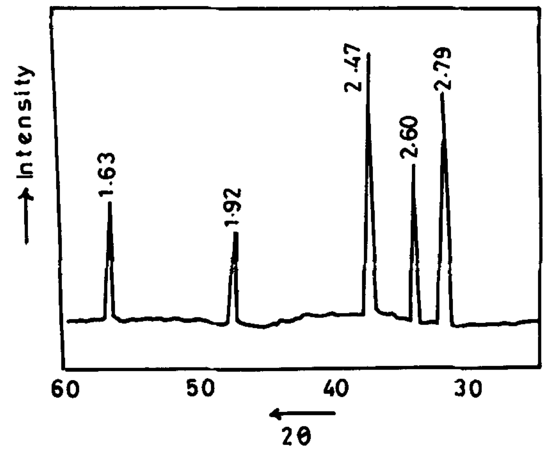

Fig. 1. X-ray diffraction pattern of microwave-exposed Pr_2O_3-doped varistor precursor powders.

RESULTS AND DISCUSSION

Microwave heating of inorganic materials has given encouraging results in ceramic technology,[8] such as drying, binder-burnout, formation of precursors, and even in sintering. This technique has recently been extended to the preparation of high Tc superconductors.[9] Microwaves couple effectively with various materials generating heat within the substance.

Material–microwave interaction has been recently reviewed by Newnham.[10] Like many ceramic materials, ZnO or its salts are found to be good microwave absorbers[11] and a temperature as high as 600°C is reached within a short period of time when exposed to microwaves. The intimately mixed nitrates of the constituents of ZnO varistors when exposed to microwaves of 2·45 GHz, first form a melt and then foam up to fill the container, become red-hot accompanied by decomposition of the nitrates, visible in the form of brown nitrogen peroxide fumes. The reaction is

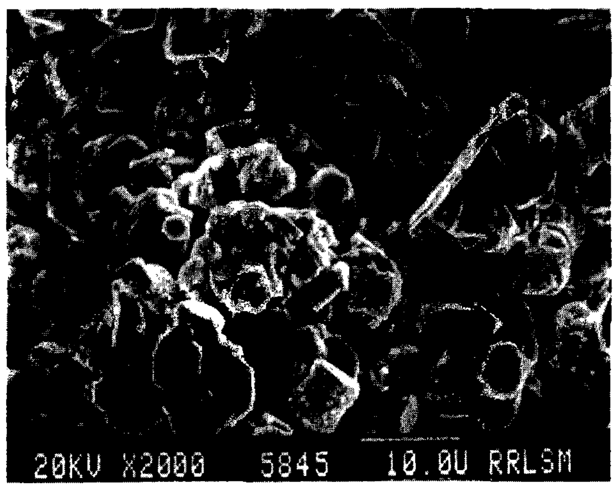

Fig. 2. SEM micrograph of as-prepared Pr_2O_3-doped varistor precursor powders.

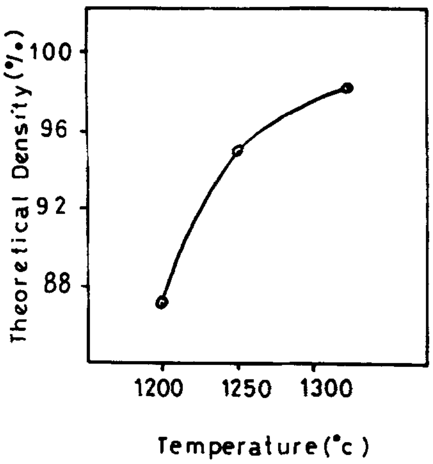

Fig. 3. Sintering characteristics of Pr_2O_3-doped varistors with different temperature.

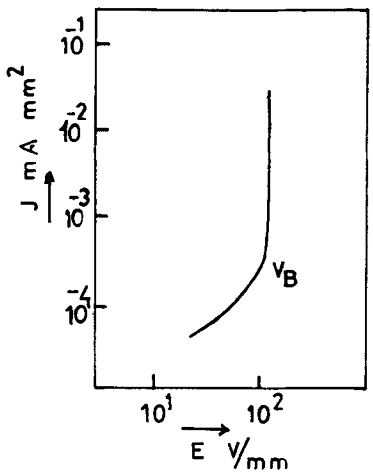

Fig. 5 Electric field vs current density behaviour of Pr_2O_3-doped varistor samples.

complete when the evolution of the gases stops. The resultant oxide mixture is easily friable. Figure 1 shows the XRD pattern of the microwave-exposed Pr_2O_3-containing varistor precursor powders, which is characteristic of ZnO. The major phase is zincite, which shows the complete decomposition of zinc nitrate to zinc oxide. It is extremely interesting that the mixture of nitrates has completely decomposed to the precursor oxides under the microwaves in such a short time. Figure 2 shows the SEM picture of the as-prepared Pr_2O_3-doped zinc oxide precursor powder having an agglomerated particle size of 6–8 μm with narrow size distribution. However, due to the evolution of the gases during decomposition of the salts, these agglomerates are weak and friable and simple grinding can break them down to very fine powders which can be compacted to densities as high as 55% under a uniaxial pressure of about 150 MPa. Figure 3 indicates the densification characteristics of the varistor compacts in the range of 1200–1300°C when maximum densities above 95% are obtained at less than 2 h soaking. There is a total diametrical shrinkage of about 16% which is quite uniform. The optimum sintering temperature is 1250°C. Figure 4 shows the SEM fractograph of the Pr_2O_3-doped samples sintered at 1250°C. Average grain size of the Pr_2O_3-doped samples is 7–8 μm. The fracture appears to be of intragranular nature in Pr_2O_3 samples indicating enhanced liquid phase formation. It is important to note that samples show narrow grain size distribution which is desired for varistors. Figure 5 gives the electrical field vs current density of the varistor samples. The higher breakdown field is due to larger grain boundary area in the case of Pr_2O_3-doped samples. The nonlinearity coefficient ($\propto$) was calculated as approx. 30 for Pr_2O_3-doped varistors.

Fig. 4. SEM micrograph of Pr_2O_3-doped varistor samples at 1250°C.

CONCLUSION

A novel microwave decomposition method as applied to zinc oxide varistors is reported for the first time. A uniform mixing of constituent oxides was achieved during the melting and subsequent rapid combustion of the mixed nitrate gel. The powder obtained could be sintered to high densities. The sintered grain size was 7–8 μm for the varistor doped with Pr_2O_3. This study reveals the possibility of preparing doped ZnO varistors employing microwave reactive precursors. Such powders can further be sintered to higher density varistors having desirable non-ohmic properties and microstructure.

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