Abstract

Zinc oxide (ZnO) based ceramic sensor belongs to a new class of electronic materials, based on grain boundary properties. Its primary function is to sense and limit transient voltage surges and to do so repeatedly without being destroyed. In particular, sintered zinc oxide ceramics containing a variety of selective additives (dopants such as bismuth oxide and other transition metal oxides) have shown excellent nonlinear current voltage (I-V) characteristics. These unique electrical properties make them suitable for use as surge arrestors and voltage limitors in electrical/electronic devices. It has been reported from the earlier studies that zinc oxide (ZnO) varistor consists of electrically conducting zinc oxide grains surrounded by electrically insulating barriers at the grain boundaries. These barriers are formed by the addition of bismuth oxide and other transition metal oxides so as to improve the performance properties. The electrical properties of these devices are determined by their detailed "functional microstructure", which develops during the synthesis. Two important performance parameters are, (i) nonlinear coefficient (?) and; (ii) breakdown electric field (Eb), generally specified at a current density of 1mA/cm2 . The value of breakdown electric field can be achieved by either optimising the varistor thickness and the grain size related microstructure of the dense compacts. At present ZnO varistors are dominating large segment of surge protection market, including consumer, military electronics, power transmission and distribution, data processing, communication and variety of industrial systems. The increased application range of ZnO varistors is reflected by high level of world research and development activities. The intense interest in this electronic ceramics is an indication of the growing range of applications and importance of ZnO varistor technology. It appears that usages of the material will grow and the applications will broaden as the technology continues to mature. The work incorporated in the thesis is an attempt to develop simple varistor comprising of 97 mol% ZnO and 1 mol% each of Bi2O3, CO2O3 and MnO2, their synthesis and characterizations etc. Series of experiments were carried out to modify the basic varistor composition with 10 mol% MgO as a grain growth inhibitor. These varistor systems were abbreviated as ZBCM and ZBCM-l0MgO. After the confirmation of the varistor properties, MgO concentration was changed from 5,15 and 20 mol% to see the effect of MgO on the performance properties of the modified varistors. These varistor systems were abbreviated as ZBCM-5MgO, ZBCM-15MgO and ZBCM-20MgO respectively. The varistors were synthesized using conventional solid state (chemical) ceramic route. From the very extensive experimental work done, and its subsequent analysis, important processing parameters such as chemical composition, particle size and its distribution, binder removal and its burnout effect, sintering temperature - time correlationship, electrical contents have been meticulously identified and optimised. During the synthesis, active powders were characterized at various stages such as after mixing, pressing and sintering etc. The current-voltage (I-V) characteristics of these varistor systems were measured at room temperature as a function of sintering temperature and data was plotted in a log-log scale. The values of nonlinearity coefficient and breakdown electric field were calculated using the empirical equation, J = (E/C)?

Where, J = current density, E = electric field, C = constant and ? = nonlinearity coefficient. It was seen from the results of Eb and ? that a varistor system modified with 10 mol% MgO gives the higher breakdown electric field with almost same nonlinear coefficient (e.g. Eb(ZBCM) 282V/mm , ?(ZBCM) 36 and Eb(ZBCM-10MgO) 1000 V/mm, ?(ZBCM-10MgO) 29) for the Pellets sintered at 1050 ?C/ 1hr. The

improvement in Eb and ? are most likely due to the improvement in the functional microstructure achieved by controlling the processing parameters. It was predicted that higher values can be obtained by increasing the number of grain boundaries and reducing the grain size. There exist two possibilities for the improvement in the microstructure (i) due to addition of MgO, the grain growth of the dense compacts of highly conducting grains is inhibited which helps in increasing the number of barriers per unit thickness in the sintered compacts and; (ii) the composition may correspond to two phase system containing zincite and a mixture of ZnO and magnesia (ZnO-MgO) which is highly insulating. To understand the relative contributions from these two pathways, extensive physicochemical characterization of the sintered compacts/powders of ZBCM and ZBCM-l0MgO varistor systems were carried out using density, XRD, SEM, XPS and AC impedance analysis techniques. Density analysis of these systems have shown that density increases with the increase of sintering temperature over the temperature 900-1300 ?C and it is maximum when sintered at 1050?C. Thus 1050?C is an optimum temperature at which varistor pellets have shown the high degree of compactness and high values of ?. Beyond 1050?C, between 1100-1300?C the density decreases with increase of sintering temperature due to evaporation of Bi_2O_3 and the weight loss of the pellets. At these sintering temperatures, pellets have shown poor I-V performance characteristics. X-ray diffractogram studies of these systems have shown the similar behaviour e.g. in both the cases, all ZnO characteristic lines are present in physical mixture and powders sintered between 900-1300?C. X-ray diffractograms of physical mixture have shown the visible characteristic lines of ?-Bi_2O_3 (monoclinic) and ?-Bi_2O_3 when sintered at 900?C. This shows that Bi_2O_3 phase transformation has taken place. In both the Xray diffractograms, ?-Bi_2O_3 characteristic lines are visible upto 1050?C and thereafter they start disappearing slowly at higher sintering temperatures (1150-1300?C). This indicates that the evaporation of Bi_2O_3 is taking place at higher sintering temperatures. This supports the earlier observation about the decrease in density and poor (I-V) performance at higher sintering temperatures. However, there is no indication of any separate (mixed phase) characteristic lines of MgO (2? 42.9, 63.3) in the powder X-ray diffractogram of ZBCM-l0MgO varistor, which shows that MgO forms a solid solution (ZnO-MgO) with ZnO during sintering. In other words, all characteristic lines of these two phase system (ZnO and ZnO-MgO) are overlapping with each other. We did not attempt to resolve these superimposed pattern to derive finite changes in the lattice parameters of ZnO-MgO solid solutions. This confirms the postulates that the formation of two phase system within the detection limit of powder XRD data. SEM photomicrographs of these systems have shown that the grain size increases with the increase of sintering temperature. However, in case of ZBCM varistor system the grain size is very high, grains are not closely packed and uniformly distributed. The average grain size for the pellet sintered at 900? is 2 ?m and it increased to 47.5 ?m when sintered at 1300?C. However, in case of ZBCM-l0MgO varistor system the average grain size is small, grains are closely packed and uniformly distributed. The average grain size for the pellet sintered at 900?C is 1.5 ?m and it increased to 20.0 ?m when sintered at 1300 ?C. The microstructure of these varistors shows that ZnO grains are isolated from each other by a continuous network of Bi_2O_3 segregation/intergranular layer with some voids and pores. The pellets of ZBCM-l0MgO varistor sintered at 1050?C have shown the difference in microstructure as compared to ZBCM varistor. In case of ZBCM, average grain size is 5.3 ?m and grains are not uniformly distributed. However, in ZBCM-l0MgO, average grain size is 4 ?m and grains are uniformly distributed and closely packed. This increases the number of grains and grain boundaries in a modified varistors with 10mol% MgO, showing that MgO acted as a grain growth inhibitor. Consequently, all these changes in microstructure resulted in different current carrying pathways with different breakdown voltage for each pathways. As the number of current carrying pathways are increased in ZBCM-l0MgO varistor microstructure, this leads to the increase of breakdown electric field and the performance, as evident from the I-V, XRD and density results. The XPS spectra of these varistors have shown that the Bi2O3 migrates with the increase in sintering temperature from the ZnO grain surface. However, XPS spectra of ZBCM-l0MgO varistor system do not show any visible intensity peaks of MgO states. This is mainly because MgO is not migrating on the ZnO grain surface but dissolves during liquid phase sintering and forms ZnO-MgO solid solution with ZnO as predicted from XRD studies. To find the role of breakdown electric field per barrier, electric field versus the reciprocal of grain size was plotted. It is found that breakdown voltage per barrier for ZBCM is Vg(ZBCM) 1.16 V/barrier and for ZBCM-l0MgO, Vg(ZBCM-10Mg0) 3.0 V/barrier. This shows that the breakdown voltage per barrier in the modified varistor (with 10 mol% MgO) has increased almost three times than the basic ZBCM varistor system. The above results show that addition of 10 mol% MgO have improved the functional microstructure under controlled processing conditions. However, XRD and XPS studies on this composition have not shown the presence of any other additional complex (bulk) phases formed during sintering. To resolve this dilemma and to differentiate between varying contributions from grains, grain boundaries/intergranular layers and electrode interfaces, AC impedance spectroscopy was used as an important tool due to high sensitivity microstructural changes. The technique is used successfully over the frequency range of 1Hz-10MHz in the temperature range of 25-250?C. From the complex impedance plots the performance was modeled in a electrical equivalent circuit which leads to the different network elements. To understand the electrical conduction across the grain, grain boundaries and grain interfaces in terms of RC network elements, activation energies associated with these processes were calculated from the Arrhenious plots. The values of activation energies across the network elements RZnO, Rgb, and Rgi were found in the range of 0.10, 0.88 and 0.61 eV for ZBCM and 0.11, 0.14 and 0.34 eV for ZBCM-l0MgO varistors. The noticeable feature is the appreciable reduction in the activation energies related to the lumped parameters Rgb and Rgi for ZBCM-l0MgO varistor. It is confirmed on the basis of the conduction model proposed by Greuter and Blatter that lowering of activation energies across Rgb and Rgi components in case of ZBCM-l0MgO varistor from 0.88 eV to 0.14 eV and 0.61 eV to 0.34 eV are due to the improved electrical microstructure i.e., the width of the grain boundary is relatively reduced and at the same time, the number of grain boundaries interlinking grain boundaries have considerably increased which affects indirectly the interfacial charge transport. This is again proved on the basis of grain/conduction model proposed by Burton. All these changes in the microstructure lead to the improvement in the performance parameters of ZBCM-10MgO varistor in comparison with ZBCM varistor. It is hoped that in the coming years the research efforts in this area are likely to have a path breaking impacts in the design and development of better devices produced by controlling structure-property correlationships, so as to make them most cost effective and challenging in the field of SMART sensor technology.