ABSTRACT

Developments of the modern world depend significantly upon a continuous electric power supply. With growing demand, utilities must provide secure and reliable power delivery by providing protection to the electronics devices and electric power system from both lightning and switching surges. Interruption or failure within these systems may result not only in damage to valuable equipment but can also lead to considerable loss of revenue, particularly for industrial consumers. ZnO varistor are among the key components in the electronics devices and electric power system, essentially required to protect it from the lightning and switching surges. In past few decades, ZnO based varistor have started to gain wide acceptance among power protection utilities worldwide as replacements for the traditional SiC based varistor as it offer many advantages such as high non–linear coefficient, high breakdown field, high energy handling capacity, low leakage current density and low maintenance cost due to gapless protection. Many investigations have been carried out using bismuth and praseodymium based ZnO varistor however there are limited systematic attempt has been made to study the vanadium based ZnO varistor. Therefore, in order to investigate vanadium based ZnO varistor and to explore its scientific importance, structure of the present thesis is divided into the following eight chapters:

Chapter 1: Zinc Oxide Varistor – An Overview:

ZnO varistors are nonlinear devices commonly used for suppression of transient pulses and surges in electronic devices or power lines. $ZnO–V_2O_5$ based varistor ceramics can be well sintered at around 900 °C. This outstanding feature of $ZnO–V_2O_5$ based varistor ceramics makes a potential candidate for the fabrication of multi–layered chip varistor using pure silver as inner electrode instead of the expensive palladium or platinum metals. Present chapter also gives an overview on microstructure of varistor ceramics and its wide engineering applications. This chapter also emphasis on the evolution of overvoltage protection practice, general features of the gapless varistors and varistor application. This chapter also focuses on the conduction mechanism and role of additive in ZnO varistors.

Chapter 2: Literature Review:

The present chapter provides an extensive review of published literature pertaining to the study undertaken. The electrical performances of ZnO varistors critically depend on the

microstructure characteristics, where the electrical characteristics can be controlled by modifying the microstructure at the grain boundary. The nonlinear characteristics are attributed to the formation of double Schottky barriers at the ZnO grain boundaries. Therefore, there are numerous studies addressing the grain boundary phenomena of ZnO–Bi_2O_3 and ZnO–V_2O_5 based ceramic systems. It is vital to understand the mechanism controlling the grain boundary processes of ZnO varistor–based ceramics. It may also facilitate a researcher as well as manufacturer to tailor the grain boundary behaviour of ZnO based varistor ceramics in more efficient manner according to the specific demand of applications. The grain boundary behaviour can be strongly depends on the dopants.

The present chapter briefly reports available literature about the investigations on ZnO varistors describing (i) processing of ZnO varistors by solid state route, (ii) bismuth and vanadium based ZnO varistors systems, their structural, non–linear characteristics and grain boundary behavior and effect of processing parameters on their properties.

Chapter 3: Aims and Objectives of Present Investigations:

The aims and objectives of present investigation are focused on the preparation and characterization of some doped and co–doped varistor material in the ZnO–V_2O_5 varistor ceramic. On the basis of the results of the initial work, a detailed work plan was prepared to explore the optimum composition and processing parameters for development of ZnO–V_2O_5 varistor ceramics with good electrical and electronics properties. The characteristics of materials also depend on doping with suitable dopants and additives as secondary phases. In order to investigate the effect of doping on ZnO–V_2O_5 varistor ceramic, we have selected transition metal oxide i.e. MnO, Nb_2O_5, Cr_2O_3 and ZrO_2. These compositions were processed with optimum sintering schedule to study the effect of doping on electrical and structural behavior. Synthesized specimens were characterized for phase, microstructure, energy dispersive spectroscopy, density and dielectric & impedance spectroscopy.

Chapter 4: Synthesis and Characterization Methods:

This chapter describes (i) synthesis of ZnO based varistor ceramics by using solid state reaction with sintering at 850, 900 and 950 °C in closed atmosphere, (ii) density, XRD, SEM, EDS methods for structural characterizations, (iii) nonlinear characteristics of ZnO based varistor ceramics for varistor properties (iv) measurement and analysis of dielectric properties of ZnO based varistor ceramics and (v) grain boundary studies of ZnO based varistor ceramics using AC impedance spectroscopy (IS). To investigate the effect of doping and sintering temperature, different compositions were prepared using solid state reaction.

i. Synthesis of Nb_2O_5 doped $ZnO–V_2O_5$ ceramics systems
ii. Synthesis of MnO doped $ZnO–V_2O_5–Nb_2O_5$ ceramics systems
iii. Synthesis of ZrO_2 doped $ZnO–V_2O_5–Cr_2O_3$ ceramics systems

All the compositions were sintered at 850 °C, 900 °C and 950 °C to study the effect of composition and sintering temperature on the microstructure and the influence of the grain boundary structure on the electrical properties of ZnO based varistor ceramics in a systematic manner using AC impedance spectroscopy (IS).

Chapter 5: Electrical and structural characterization of Nb_2O_5 doped $ZnO–V_2O_5$– varistor ceramics sintered at different temperatures:

The present chapter addresses the effect of Nb_2O_5 doping on $ZnO–V_2O_5$ based varistor systems. Synthesis of Nb_2O_5 doped $ZnO–V_2O_5$ ceramics systems: Five compositions (99.50 - x) mol% ZnO + 0.5 mol% V_2O_5 + x mol% Nb_2O_5 (where x = 0.00, 0.05, 0.10, 0.25 and 0.50) were prepared using solid state reaction. All the compositions were sintered at 850 °C, 900 °C and 950 °C. The effect of composition and sintering temperature on the microstructure and the influence of the grain boundary structure on the electrical properties of ZnO based varistor ceramics were studied in a systematic manner using AC impedance spectroscopy (IS). Scanning electron micrographs of the etched samples were also taken. The microstructure of the Nb_2O_5 doped $ZnO–V_2O_5$ varistors consisted of ZnO grain as the primary phase and $Zn_3(VO_4)_2$ as the major secondary phases, which acts as liquid–phase sintering promoter and has a significant effect on the sintered density. The average grain size of the Nb_2O_5 doped $ZnO–V_2O_5$ system sintered at 850, 900 and 950°C were found to be increases with sintering temperature. The average grain size of the Nb_2O_5 doped $ZnO–V_2O_5$ system also depend upon the amount of Nb_2O_5 addition. The 0.10 mol% Nb doped $ZnO–V_2O_5$ sample sintered at 900°C exhibited the most optimum grain size. EDS spectra of ZnO grain boundary show V and Nb segregation in the samples. Among all of the samples, the 0.50 mol% Nb–doped sample sintered at 900°C was found to have the highest values of total resistance. The 0.10 mol% Nb–doped system sintered at 900°C exhibited the highest activation energy, highest nonlinear coefficient, highest breakdown field and lowest leakage current density among all of the samples. Conclusively, among all of the Nb doped $ZnO–V_2O_5$ samples, it was found that the 0.10 mol% Nb–doped samples sintered at 900°C is a candidate material for use in chip varistors.

Chapter 6: Electrical and structural characterization of MnO doped $ZnO – V_2O_5 – Nb_2O_5$ varistor ceramics sintered at different temperature:

The present chapter addresses the effect of MnO doping on $ZnO–V_2O_5–Nb_2O_5$ based varistor systems. Synthesis of MnO doped $ZnO–V_2O_5–Nb_2O_5$ ceramics systems: Five compositions (99.4 - x) mol% ZnO + 0.5 mol% V_2O_5 + 0.10 mol% Nb_2O_5 + x mol% MnO/$MnCO_3$ (where x = 0.00, 1.50, 2.00, 2.50 and 3.00) were prepared using solid state reaction. All the compositions were sintered at 850°C, 900°C and 950°C to study the effect of composition and sintering temperature on the microstructure and the influence of the grain boundary structure on the electrical properties of ZnO based varistor ceramics in a systematic manner using AC impedance spectroscopy (IS).

In chapter 5, it was found that the electrical and dielectric properties of liquid–phase sintered $ZnO–V_2O_5$ ceramics doped with Nb_2O_5 critically depend on the grain boundary resistance using impedance spectroscopy (IS). Furthermore Nb_2O_5 doped $ZnO–V_2O_5$ varistor ceramics have a nonlinear coefficient in the range of 4 to 7. Composition with 0.10 mol% Nb_2O_5 sintered at 900°C shows best varistor characteristics among all the composition. To further improve the characteristics above composition i.e. 0.10 mol% Nb_2O_5 varistor system doped with MnO will be essential to be investigated.

The microstructure of the MnO doped $ZnO–V_2O_5–Nb_2O_5$ varistors consisted of ZnO grain as the primary phase, ZnV_2O_4 and $Zn_3(VO_4)_2$ as the major secondary phases, in which $Zn_3(VO_4)_2$ acts as liquid–phase sintering promoter and has a significant effect on the sintered density. The average grain size of the MnO doped $ZnO–V_2O_5–Nb_2O_5$ system sintered at 850 to 950°C were found to be increases with the sintering temperature, which were also depend upon the amount of MnO doping. The MnO doped $ZnO–V_2O_5–Nb_2O_5$ sample sintered at 900 °C exhibited the most optimum grain size. EDS spectra of ZnO grain boundary show V, Nb and Mn segregation in the samples. Among all of the samples, the 0.00 mol% MnO doped sample sintered at 850 °C was found to have the highest values of total resistance. The 2.50 mol% MnO doped $ZnO–V_2O_5– Nb_2O_5$ system sintered at 900 °C exhibited the highest activation energy, the highest nonlinear coefficient, the highest breakdown field value and the lowest leakage current density. The Ɛ' were found to be increases with the sintering temperature. Conclusively, among all of the MnO doped ZnO–V_2O_5– Nb_2O_5 samples, it was found that the 2.50 mol% MnO doped ZnO–V_2O_5– Nb_2O_5 samples sintered at 900 °C is a candidate material for use in chip varistors.

Chapter 7: Electrical and structural characterization of ZrO_2 doped ZnO–V_2O_5–Cr_2O_3 – varistor ceramics sintered at different temperature.

The present chapter addresses the effect of ZrO_2 doping on ZnO–V_2O_5–Cr_2O_3 based varistor systems. Synthesis of ZrO_2 doped ZnO–V_2O_5–Cr_2O_3 ceramics systems*:* Five compositions (96.5 - x) mol% ZnO + 0.5 mol% V_2O_5 + 3.0 mol% Cr_2O_3 + x mol% ZrO_2 (where x = 0.00, 0.10, 0.50, 1.00 and 2.00) were prepared using solid state reaction. All the compositions were sintered at 850 °C, 900 °C and 950 °C to study the effect of composition and sintering temperature on the microstructure and the influence of the grain boundary structure on the electrical properties of ZnO based varistor ceramics in a systematic manner using AC impedance spectroscopy (IS). Scanning electron micrographs of the etched sample were also taken. The microstructure of the samples consists mainly of ZnO grains with $ZnCr_2O_4$ and $Zn_3(VO_4)_2$ as the minority secondary phases, in which $Zn_3(VO_4)_2$ acts as liquid–phase sintering promoter and has a significant effect on the sintered density.The average grain size of ZrO_2 doped samples increase with increases in sintering temperature. EDS spectra of ZnO grain boundary show V, Cr and Zr segregation in the samples. Addition of ZrO_2 along with Cr_2O_3 to the binary ZnO–V_2O_5 system controlled the abnormal ZnO grain growth and produced a more uniform microstructure. The microstructure of the samples consists mainly of ZnO grains with $ZnCr_2O_4$ and $Zn_3(VO_4)_2$ as the minority secondary phases. The non–linear coefficient α increases as the amount of ZrO_2 doping sintered at 900 °C is increased up to 1 mol%. Further increase in ZrO_2 content caused a decrease in α value. A highest non–linear coefficient was obtained for the sample containing 1 mol% ZrO_2 in 3 mol% Cr_2O_3 and 0.5 mol% V_2O_5 doped ZnO varistor.

Chapter 8: Conclusions and Scope for Future Research Work:

This Chapter presents general conclusions based on the findings in this study, and outlines some recommendations for future investigation.

The present thesis reports the successful synthesis of Nb_2O_5 doped ZnO–V_2O_5 varistor ceramics synthesized via solid state reaction technique. Specimens were synthesized by compacting and sintering in closed atmosphere at 850 900 and 950 °C for 3 hrs. $ZnO–V_2O_5$ varistor ceramics specimens shows of ZnO grain as the primary phase, ZnV_2O_4 and $Zn_3(VO_4)_2$ as the major secondary phases, in which $Zn_3(VO_4)_2$ acts as liquid–phase sintering promoter and has a significant effect on the sintered density. The phase formation depends upon the sintering temperature and doping level. The average grain size of the samples increases with the sintering temperature increases. In the next stage of the investigation successful synthesis of MnO doped $ZnO–V_2O_5–Nb_2O_5$ varistor ceramics were carried out by sintering at 850, 900 and 950°C for 3hrs. It was found that the doping of MnO controls the average grain size and makes the grain size more uniform. Properties of MnO doped specimens were found to improve. Activation Energy was found to be high in comparison to $ZnO–V_2O_5–Nb_2O_5$ varistor. Leakage current densities of the specimens were found to be reduced in comparison to the synthesized $ZnO–V_2O_5–Nb_2O_5$ varistor. The last investigation focused on the successful synthesis of ZrO_2 doped $ZnO–V_2O_5–Cr_2O_3$ varistor ceramics were carried out by sintering at 850, 900 and 950 °C for 3hrs. It was found that the doping of ZrO_2 in presence of Cr_2O_3 reduced the average grain size and makes the grain size more uniform. Properties of ZrO_2 doped specimens were found to improve. Specimens showed improved electrical properties. $ZnCr_2O_4$ phases were formed due to the reactive sintering between the ZnO and Cr_2O_3 particles respectively. Activation Energy was found to be higher in comparison $ZnO–V_2O_5–Nb_2O_5$ varistor. Leakage current densities of the specimens were found to be reduced in comparison to the synthesized $ZnO–V_2O_5–Nb_2O_5$ varistor. It is expected that the outcome of the present investigation will be helpful in designing and developing $ZnO–V_2O_5$ varistor ceramics for better protecting devices.

On the basis of above investigations there is an ample amount of scope for further research work for the development of $ZnO–V_2O_5$ varistor ceramics

- Synthesis of few more specimens can be done using different dopants such as Antimony Trioxide and some rare earth oxide etc.
- Lightening testing of the same specimens can be carried out by applying artificial lightening surges.