Preparation of ZnO-Varistors

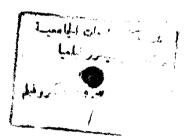
presented by

USAMA AMINE DESOUKY

Make mouse

B.Sc. Chemistry (very good)

May 1987



TO

CHEMISTRY DEPARTMENT FACULTY OF SCIENCE AIN SHAMS UNIVERSITY 51111

in partial fulfillment of requirement for the degree of master of science (chemistry)

346.6

THESIS ADVISOR



prof. Dr. MOHAMED F. EL-SHAHAT

prof. of analytical and inorganic chemistry, faculty of science, Ain Shams University

prof. Dr. DOREYA M. IBRAHIM

prof. of Ceramics, Department of Ceramics, National Research Centre, Cairo

prof. Dr. ESSAM M. H. SALLAM

prof. of ceramics, department of ceramics National Research Centre, Cairo



1994

"سُبُحَانَكُ لاَ عِلْمَ لَنَا إِلاَّ مَا عَلَمْتَنَا إِلَّكَ أَنْتَ الْسَبُحَانَكُ لاَ عِلْمَ لَنَا إِلاَّ مَا عَلَمْتَنَا إِلْكَ أَنْتَ الْعَلِيمُ الْحَكِيمُ"



PREPARATION OF ZnO-VARISTORS

Thesis Advisor

Prof. Dr. M.F. Elshahat

Prof. Dr. Doreya M. Ibrahim

Prof.. Dr. Essam H. Sallam

Approved Labort

Prof. Dr. Fareuk Fahmy

Head of Chemistry department

A-F-H-tahmy

Faculty of Science Ain Shams University

NOTES

Beside the work carried out in this thesis, the candidate had attended one year post graduated courses on analytical and inorganic chemistry covering the following topics:-

- Advanced Electro Analytical Chemistry.
- Advanced Instrumental Chemical Analysis.
- Inorganic Reaction Mechanism.
- Group Theory and Computer Application in Chemistry.
- Molecular Spectroscopy.
- Organometalic Chemistry.
- Advanced Chromatographical and Seperation Techniques.

He has successfully passed a written examination in this topics

Prof. Dr. Farmuk Fahmy

Head of Chemistry Department, Faculty of Science, Ain Shams University

ACKNOWLEDGMENT

The author is deeply grateful to *Prof. Dr. M.F. El-Shahat*, Prof. of inorganic and analytical chemistry, Faculty of Science, Ain Shams University, for his supervision, active support, guidance, valuable advices and encouragement during the entire course of this study.

The author wishes to express his deep gratitude to *Prof. Dr. Doreya M. Ibrahim*, prof. of ceramics, Department of Ceramics, National Research Centre, Cairo, for her scientific supervision, valuable advice, planning of study, fruitful discussions, valuable assistance and continuous encouragement, her help will always be remembered and not forgotten.

Thanks and gratitude also go to *Prof. Dr. Essam M. H. Sallam*, Prof. of Ceramics, Department of Ceramics, National Research Centre, Cairo, for his supervision, help guidance and encouragement.

Thanks and gratitude also go to *Prof. Dr. Fadel Elkassabghy*, prof. of physics, Department of Physics, American University in Cairo, for his help, guidance and encouragement.

Last but not least, to all the members of the Department of Ceramics, National Research Centre, thanks and gratitude for the help, encouragement and facilities offered to the author through out entire course of this work.

CONTENTS

	page
AIM OF THE WORK	
ABSTRACT	1
I- INTRODUCTION	3
structure of ZnO	8
Effect of Additives on the characteristics of ZnO-varistors	14
Microstructure of ZnO-varistors	22
Electrical Properties	24
II-MATERIALS AND METHODS	28
2.1.1. Raw Materials	28
2.2.1. Mix Composition	28
2.2.2. Processing	28
2.3. Methods of testing	29
2.3.1. Grain size Distribution (by sedimentation)	29
2.3.2 Physical Properties	30
2.3.3. XRD Analysis	32
2.3.4. Electric Properties	32
2.3.5. Micro-structure (SEM)	35
III- RESULTS	37
3.1. starting ZnO	
3.1.1. Grain Size Cistribution	
3.2.2 Physical Properties of Mixes	
3.3. Results of XRD	57
3.4. Results of Microstructure	64
3.5. Results of Electric properties	77
IV- DISCUSSION	86
V - CONCLUSION	95
VI- SUMMARY	96
VII- REFERENCES	97
VIII- ARABIC SUMMARY	

LIST OF TABLES

No.	page
1. Composition of different Mixes mol.% and Wt%	29
2. Firing shrinkage percentage of different mixes	38
3. Bulk density of different mixes (g/cm ³)	42
4. Water absorption of different mixes	45
5. Apparent porosity of different mixes	48
6. Specific gravity of different mixes	55
7. Degree of densification samples	56
8. Electric properties of group I	79
9. Electric properties of group II	80

LIST OF FIGURES

No.	page
1. Energy bands in semiconductors	4
2. Schematic representation of energy levels in excess semiconductor such as $Zn_{1+X}O$	9
3. V-I static characteristics of ZnO varistor	11
4. Principle of connection of varistor	12
5. Shows silver paint on the samples	33
6. Shows the position of varistor sample in electric circle	34
7. Grain size distribution of ZnO used	3 .7
8. Firing shrinkage % of group I	40
9. Firing shrinkage % of group II	4 t
10.Bulk density of group I	43
11.Bulk density of group II	44
12. Water absorption % of group I	46
13. Water absorption % of group II	47
14.Apparent porosity of group I	49
15.Apparent porosity of group II	50
16.Bulk density of group I at different temperatures	5.1
17.Bulk density of group II at different temperatures	5 2
18. Water absorption of group I at different temperatures	53
19. Water absorption of group II at different temperatures	54
20.XRD patterns of startung calcined oxides	58
21.XRD patterns of 1mol% ZnO+1mol% Ce ₂ O ₃	59
22.XRD patterns of group I	60
23.XRD patterns of group II	61
24. Show displacement of XRD patterns of group I	
25 Displacement of XRD patterns of group II	

26.SEM of mix M _O group (I), growth in preferred orientation in ZnO grain	65
27.SEM of mix Mo group (I), the parallel cleavage planes (inverse twin planes) in ZnO grain, indicating grain growth in preffered orientation	66
28.SEM of mix M2 of group (I), polished thermally etched surface, x7500. showing crystal growth of ZnO grains represented by annular epitaxial tiny exsolution of Ce rich particles lying interagranular and along the growth rings	6 7
29.SEM map analysis for the distribution of Ce of the above image. Ce is uniform distributed in ZnO grain, but concentrated in the interagranular accumulations	
30.SEM of mix M3 group (I) growthof ZnO, the exsolution of Ce rich granules along the growth ring, in various sizes	6 8
31.SEM of mix M3 of group (I), growth of ZnO grain in preffered orientation parallel rings. exsolution of Ce rich phase along the rings and interagranular	63
32.SEM of mix Zo of group (II) ZnO-ZnO grain boundaries smooth	69
33.SEM of mix Zo of group (II), preffered orientation in ZnO grain	69
34.SEM of mix Z ₃ group (II), accumulation of Ce rich phase intragranular at the	
corners of the grains.	7◊
35.SEM map analysis showing Ce distribution of the above image	70
36.SEM mix Z ₃ of group (II) intragranular Ce rich phase	71
37.SEM showing line profile for Ce distribution of the above image. Ce is concentrated in the intragranular accumulation	71
38.SEM mix Z ₃ of group (II), growth of ZnO grains showed annular and Ce rich	
phase at the grain corners and along the growth rings	72
39.SEM map analysis for Ce of the above image. Ce concentrated in the regions of accumulation at the grain corners	f 72
40.SEM mix Z ₃ group (II), growth rings in a ZnO grain and exsolution of the Ce	
rich phase along the prephery of plates in the stock	73
41. Shows the concentration of Ce ₂ O ₃ with ZnO in ZnO grain in mix Z ₃	
group (II)	74
42.EDAX shows the concentration of Ce ₂ O ₃ with ZnO and CoO in	
intragranular accumulation	75
43.SEM of mix M1 group I showing ZnO and accumulated phase of the triple point	

44.SEM of mix M1 group (I), distribution of Ce concentrated along grain boundary	
of the above image	76
45. Current density versus applied field for the different mixes	8.1
46. Current density versus applied field for the different mixes (on log paper)	82
47. Current density versus applied field for the different mixes (on semi log paper)	83
48. Resistivity versus applied field for the different mixes	84
49.mol % of Ce2O3 versus resistivity for the different mixes (at 200 volt)	85

AIM OF THE WORK

Aim of the work

The present study comprises the following:

- 1-Preparation of ZnO-varistors by conventional method using oxides as precursors.
- 2-Study the addition of Ce₂O₃ in the range of (2-6) mole % to ZnO standard mix containing 0.25 CoO, 0.25 Cr₂O₃.
- 3-Determination of physical properties (densification) and electrical properties.
- 4- Study of microstructure developed by SEM & EDAX.

I-INTRODUCTION

ABSTRACT

Early work on ZnO based varistor was largly limited to binary systems comprising ZnO and few mole percent of a second insulating oxide components. This leads to materials with a moderate degree of non-ohmicity, typical values for exponent of non-linearly, α -defined by $I\alpha V^{\alpha}$, lie in the region $2<\alpha<6$.

The superior electric properties were developed by Matsuoko in multicomponent ZnO-varistors, where α ranged between (30< α <50). A typical multicomponent varistor has a composition 97% mol ZnO, 1% Sb₂O₃, 0.5 Bi₂O₃, 0.5 CoO, 0.5 MnO₂ and 0.5 Cr₂O₃.

The field of application of ZnO varistor in low voltage was extended to high voltage electric power stations by the addition of Pr_2O_3 substituting Bi_2O_3 . The merits of the addition of rare earth oxides beside extending the field of application to high voltage is directly related to the microstructure based on two phase model. As this structure increases the active grain boundary area through which electric current flows.

The effect of addition of Ce_2O_3 on microstructure, electric properties was the subject of the present study. The results achieved showed that Ce_2O_3 could be used to improve the varistor properties in the presence of their oxides as Cr_2O_3 and CoO. Low additions of Ce_2O_3 entered into solid solution with ZnO therby rendering the material totally conductive and shows nearly ohmic relation. High addition on the other hand, showed signs non-linearty as proved from electrical properties measured. Microstructure of the product revealed the presence of two

1