STRUCTURAL, MICROSTRUCTURAL AND NON - OHMIC BEHAVIOUR OF ZnO BASED VARISTORS WITH FIVE ADDITIVE OXIDES

Pwint Yi Thein[1], Thandar Win[2], Yin Yin Swe[3] and Mar Mar Myint[4]

Abstract

ZnO based varistors with 5 additive oxides Bi_2O_3, Cr_2O_3, Co_3O_4, MnO_2 and Sb_2O_3 are prepared and characterized in this research work. Standard varistor processes, known as weighting, ball milling, mixing with distilled water, pre heat treatment, secondary ball milling, seiving, sintering, pressing into circular shape disc, electroding and reheating processes are carried out to obtain the varistors with desired stoichiometric compositions. XRD technique is used to examine the structural features of prepared varistors. It is obvious that a little change of lattice dimensions is obtained. But there are no significant change of hexagonal, wurtzite ZnO structure after addition of additive oxides. Microstructural features of prepared varistors are characterized with the help of SEM. From the SEM images, it is noticed that irregular micro grains are uniformly distributed and there are no cracks. Further, average grain size slightly increases with increasing composition " x " in prepared varistors. Non - ohmic behaviour of prepared varistors are studied by using the high voltage DC power supply. From the ln V vs. ln I variations, non linearity factor, threshold voltage and leakage current are estimated. It is observed that non linearity factor slightly increases as composition " x " increases, on the other hand, threshold voltage and leakage current decrease when the composition " x " is raised. The transition metal oxides are involved in formation of interface states and deep traps in host matrix ZnO and both of which are contributed to high - non ohmic behaviour. Additive oxides, used in this study are known to be non - linearity enhancers and inducers. Threshold voltage is affected by the numbers of grain boundaries across the series between the two electrodes and inversely proportional to grain size. In this study, average grain size slightly increases with composition " x " in prepared varistors and that leads to lower the threshold voltage. The higher the non - linearity factor affects the lower the leakage current and the better the performance of varistor. It can be concluded that, prepared varistors can be used as transient surge voltage protection device.

Keywords: varistor, additive oxides, XRD, SEM, non - ohmic behaviour.

Introduction

Research activity in the area of ZnO based ceramics has been traditionally fueled by the need for ideal candidate as intrinsic voltage regulator in the context of circuit protection. Consequently the wide range of doped ZnO based systems have been studied. It is well known that the ZnO varistor is controlled essentially by the dopant additives, usually metal oxides and the dopants are responsible for the formation of varistor behavior. It is believed that, the dopants play an important role to modify the defect concentration at the ZnO grain and / or of grain boundary where the performance of ZnO is sensitive to the some additives even when the amount is very small [Levinson L. M. and Phillip H. R. 1975].

The structure of metal oxide varistor (MOV) consists of a matrix of conductive ZnO grains separated by the grain boundaries providing P - N junction semiconductor characteristics. These boundaries are responsible for blocking conduction at low voltages and are the source of the non - linear electrical conduction at high voltages.

Varistors are inherently polycrystalline, multi junction grain boundary devices, that can absorb transient surge voltage and serve to protect electronic and electrical circuit components. The voltage surges are induced by power switching and electromagnetic pulses. Varistors are ceramic elements whose I - V characteristics is highly non - linear [Bialek T., 1999]. The varistors are usually manufactured in the ceramic process, in which pressed zinc oxide with admixture of

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other metallic oxides is sintered. A matrix made of ZnO grains enclosed by an intergranular layer composed of dissolved oxides admixtures form the obtained microstructure [Emtage P. R., 1977; Mah an G. D., 1983 ; Cao Z. C. et al., 1994 ; Sun H. T. et al., 1993].

The primary constituent of varistor is ZnO, typically 80 mol % or more. In addition to ZnO, varistor contains the smaller amounts of a numbers of other additive oxides. A typical composition contains 97 mol % ZnO, 1 mol % Sb_2O_3, and 1/2 mol % each Bi_2O_3, CoO, MnO and Cr_2O_3 [Masuoka M. et al., 1969; Masuoka M., 1971].

In this research work, ZnO based varistors with 5 additive oxides Bi_2O_3, Cr_2O_3, Co_3O_4, MnO_2 and Sb_2O_3 are prepared by solid state sintering. X - rays diffraction studies are used to examine the structural features of prepared varistors. Microstructural properties of prepared varistors are investigated with the help of SEM technique. Non – ohmic behaviour of prepared varistors are characterized by using high voltage DC power supply.

Experimental Detail

In this study, analar grade II - VI compound semiconductor ZnO and five additive oxides, Bi_2O_3, MnO_2, Co_3O_4, Cr_2O_3 and Sb_2O_3 were chosen as starting precursors. Bi_2O_3 play the essential role on varistor effect by providing the high non - linearity of current - voltage characteristics. It is also reported that Bi is located between ZnO electrically conductive granules, ensuring electrical insulation. Co_2O_3 are oxides indispensable for obtaining the strong non - linear characteristics. The role of MnO_2 and Cr_2O_3 is to dope ZnO granules and thus to remove the Fermi level and modify the ZnO structure of space load and facilitating the reduction of potential barrier height. Sb_2O_3 has a role of fixing Bi_2O_3 at high temperature and thus limit the size of ZnO granules [Frigura - Llisa F. M. et al., 2019]. In this way, the threshold voltage is set for certain height of barrier pocket. Starting precursors, ZnO and 5 additive oxides were weighted by the following stoichiometric compositions:

$$(1 - x)\ ZnO + (2.x)\ Bi_2O_3 + (2.x)\ MnO_2 + (2.x)\ Co_3O_4 + (2.x)\ Cr_2O_3 + (2.x)\ Sb_2O_3,$$

where x = 0.01, 0.02, 0.03, 0.04 and 0.05 respectively. Precursor weighting was performed with an electronic balance, which can accurately weigh more than 0.01 milligram. The weighting operation was relatively simple because of all oxides were delivered in the form of powders, for which granulometry was well determined. Homogenization of mixture of oxides, milling was necessary to facilitate. After weighting, the oxides were milled in ball milling process for each 5 hrs. The mixing operation was made much easier in liquid phase by addition of distilled water.

The resulting materials in previous step were viscous and dried over the heated plate (~ 200^{o}C) for each 3 hrs. This step was carried out with the help of thermostatic oven. After this operation, the resulting powder had a non - uniform grain size. Therefore it must be milled again by ball milling process for each 5 hrs. Ball milling process had led to acceptable granulation and sieving with 400 mesh sieve, was carried out in order to separate the granules from the powder with the size greater than 200 μm. After that, sintering process (at 1100^{o}C) was carried out to all samples for each 5 hrs.

Then a slow cooling down to ambient temperature occurred. At this high temperature, the physicochemical knowledge of processes inside the varistor was still imperfect. The variator' s heating was obviously uneven, being more important at the surface than in the center. Regardless the chemical composition of the varistors, in the industry thermal cycle parameters were the same.

After the samples were sintered, the powder samples were pressed with the 20 - tons press into circular shape disc with 20 cm in diameter and 3.5 mm in thickness. A conductive pastes, based on Ag were deposited onto both surface of the circular shape discs, where the cross sectional

area of electrode was A = 7.0695 mm^2. Cu electrodes were attached to those surfaces and the varistors were reheating at 600^oC for each 3 hrs, known as varistor reheating process. At this stage, removal of the solvent and polymerization on the surface of the electrodes were carried out.

X - rays diffraction studies were used to determine the prepared powdered samples (varistors) with the help of Rigaku Multiflux x - ray diffractometer with Cu K_α (λ = 1.5418 Å) monochromatic radiation. The powdered samples were scanned from 10° to 70° with a scanned speed of 0.01°/sec. Applied voltage and current of the x - ray diffractometer were set to be 50 kV and 40 mA. XRD is a rapid analytical technique primarily used for phase identification of crystalline material and can provide information on unit cell dimensions. X - rays diffraction is now commonly technique for the study the crystal structures and atomic spacing. It is based on constructive interference of monochromatic x - rays and a crystalline sample. These x - rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's law. This law relates the wavelength of electromagnetic radiation to the diffracted angle and the lattice spacing in the crystalline sample. These diffracted x- rays are then detected, processed and counted. By the scanning the sample through a range of 2 θ angle, all possible directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffracted peaks to d - spacings allows identification of the powdered mineral because each mineral has a set of unique - spacings. This is achieved by comparison of d - spacings with standard reference patterns. From the x - ray diffraction spectra of powdered materials / samples, unit cell dimensions, such as lattice parameters, lattice distortion, unit cell volume, crystalline size.

Microstructural features of powdered samples (varistors) were characterized with the assistance of (JEOL, Model No. JSM- 5610 LV). Applied voltage and current of SEM were set to be 15 kV and 68 uA, and 4000 magnification. The SEM uses a focused beam of high - energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron - sample interactions reveal information about the sample including external morphology (texture), chemical composition, crystalline structure and orientation of materials making up the samples. Data are collected over a selected area of the surface of the sample and a 2 - dimensional image is generated that displays spatial variations in these properties. Area ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM technique. The SEM is also capable of performing analyses of selected point locations on the samples; this approach is especially useful in qualitatively determining chemical composition, crystalline structure and crystal orientation. From the SEM images, surface morphology of the powdered samples such as average grain size and grain growth situation were examined and lattice micro strain were studied.

Electrical characteristics, known as I vs. V variations, of prepared varistors were carried out by using (Gwinstek PFR 100 M) high voltage DC power supply. To eliminate the transient response, I -V measurements were done with the step voltage 0.5 V and delay time 1 minute in the DC voltage range from 0 V to 250 V. From the ln V vs. ln I plots, important parameters of varistor, known as non - linearity factor, threshold voltage and leakage current were examined. ZnO based variators with 5 additive oxides were listed in table 1.

Table 1 ZnO based varistors with 5 additive oxides

Sample Name	Stoichiometric composition
Sample 1	0.99(ZnO) +(0.002) Bi_2O_{3+} (0.002) MnO_2 + (0.002) Co_3O_4 + (0.002) Cr_2O_3 + (0.002) Sb_2O_3
Sample 2	0.98(ZnO) +(0.004) Bi_2O_{3+} (0.004) MnO_2 + (0.004) Co_3O_4 + (0.004) Cr_2O_3 + (0.004) Sb_2O_3
Sample 3	0.97(ZnO) +(0.006) Bi_2O_{3+} (0.006) MnO_2 + (0.002) Co_3O_4 + (0.006) Cr_2O_3 + (0.006) Sb_2O_3
Sample 4	0.96(ZnO) +(0.008)6Bi_2O_{3+} (0.008) Mn_2 + (0.008) Co_3O_4 + (0.008) Cr_2O_3 + (0.008) Sb_2O_3
Sample 5	0.95(ZnO) +(0.01) Bi_2O_{3+} (0.01) MnO_2 + (0.01) Co_3O_4 + (0.01) Cr_2O_3 + (0.01) Sb_2O_3

Flow diagram of experimental detail was presented in figure 1.

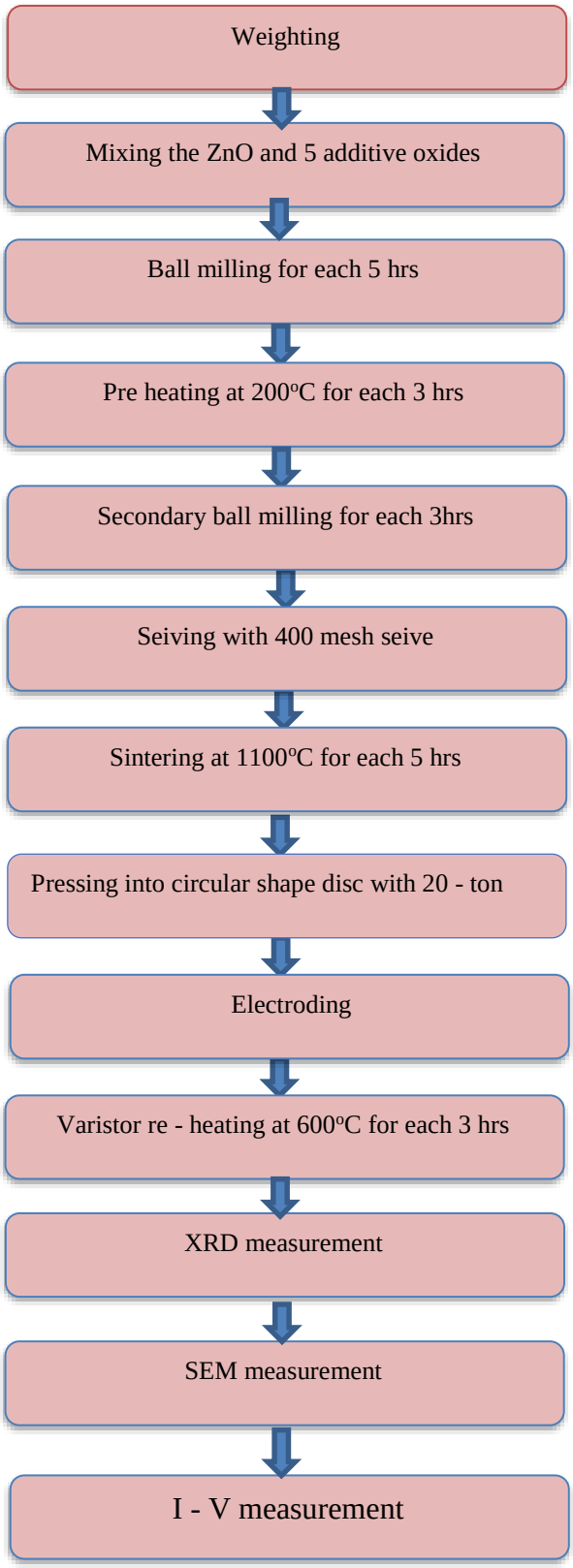

Figure 1 Flow diagram of experimental.

Results & Discussion

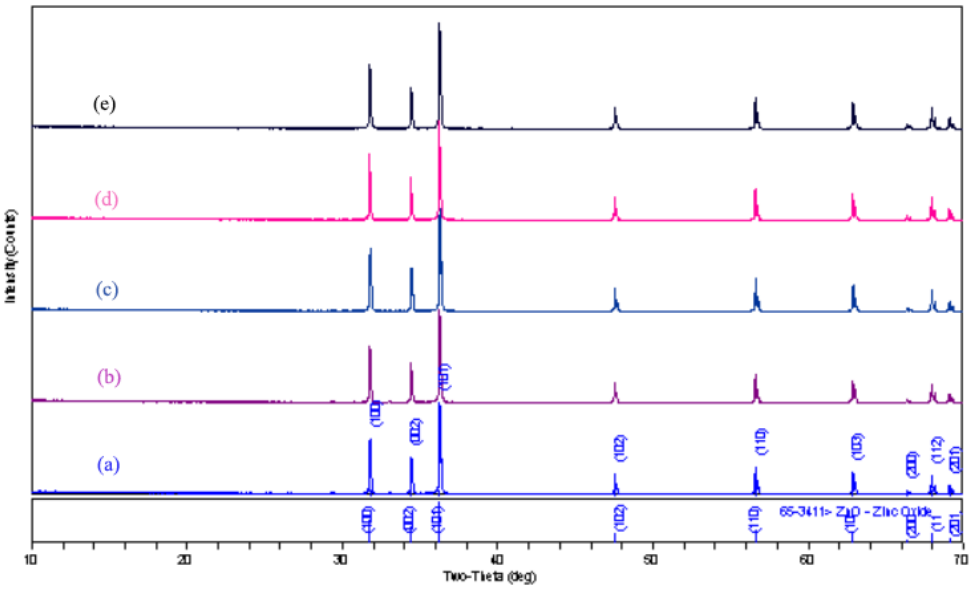

Figure 2 XRD spectra of ZnO with five additive oxides (composition 'x'= 1 mol%, 2 mol%,3 mol%,4 mol% and 5 mol%).

Figure 2 depicts the x - rays diffraction spectra of ZnO based varistors with 5 additive oxides. Peak search algorithm, known as Jade software is used to identify the unknown peaks in this study. Only x - rays diffraction peaks from single phase, hexagonal, wurtzite ZnO structures with reference (66 - 3411 > JCPDF file no.) are observed. Further, (101) peak is the most intense peak and a little shift of (101) peak, in terms of 2 - θ value is noticed in all spectra. These results indicate that, Bi, Mn, Co, Cr and Sb ions are partially occupied into Zn site in the crystal of ZnO lattice. Lattice dimensions, known as lattice constants " a " and " c " are evaluated by substituting the interplanar spacing " d " values from (101) and (110) planes in the following equation (1):

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (1)$$

d = interplanar spacing

h, k, l = miller indices

a, c = lattice parameters

Unit cell volume of ZnO based powdered samples are estimated by using the following equation (2):

$$V = \frac{\sqrt{3}}{4}a^2 \times 6 \times c \qquad (2)$$

V = cell volume

Lattice constants, lattice distortion and unit cell volume of ZnO based powdered samples are collected in table (2).

Table 2 List of lattice constants, lattice distortion and unit cell volume of ZnO based powdered samples.

Sample	lattice parameter "a(Å)"	Lattice parameter "c(Å)"	lattice distortion	Cell Volume $\times 10^{-30}$ (m^3)
1	3.235	5.243	1.621	142.570
2	3.238	5.241	1.618	142.761
3	3.241	5.239	1.616	142.933
4	3.244	5.236	1.614	143.147
5	3.249	5.234	1.611	143.496

Crystalline size and lattice micro strain of ZnO based powdered samples are examined by using the following Debye - Scherrer equations (3) and (4).

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad (3)$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \qquad (4)$$

Crystallite size, lattice micro strain and full width at half maximum (FWHM) of the most intense (101) peak are listed in table (3)

Table 3 List of crystallite size, lattice micro strain and FWHM of (101) peak of ZnO based powdered samples.

Sample	crystallize size (nm)	micro strain	β $\times 10^{-3}$ rad
1	31.46	3.567	4.635
2	31.15	3.602	4.681
3	30.87	3.635	4.724
4	30.64	3.662	4.759
5	30.39	3.692	4.798

Figure (3) depicts the variation of composition " x " with the lattice constants of ZnO structure. It is noticed that lattice constant " a " increases with decreasing lattice constant " c " when composition " x " is raised.

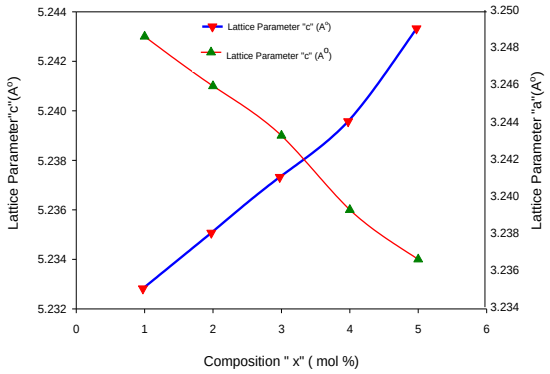

Figure 3 Variation of composition " x " (mol %) with the lattice constants of ZnO structure.

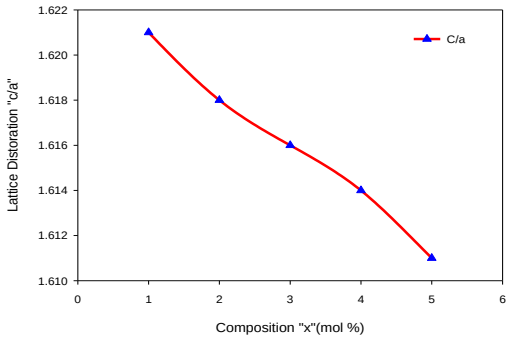

Figure 4 Influence of composition " x "(mol %) on lattice distortion " c/a " of ZnO structure.

Figure (4) shows the influence of composition " x " on lattice distortion " c/a " of ZnO structure. It is examined that lattice distortion " c/a " decreases with increasing composition " x ".

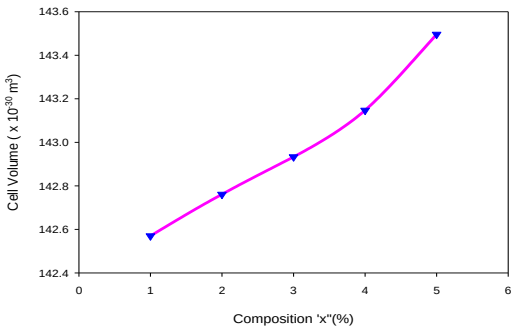

Figure 5 Effect of composition " x "(mol %) on unit cell volume of ZnO structure.

Figure (5) illustrates the effect of composition " x " on unit cell volume of ZnO structure. It is found that, unit cell volume slightly increases when composition " x " is raised.

It is believed that, there will be compress stress during the sintering process. Further, additional additive oxides create the dislocations, defects and vacancies in host ZnO structure. Those facts cause a little change of unit cell dimensions of ZnO structure and appearance of lattice micro strain. But there are no significant change of hexagonal, wurtzite ZnO structure.

Microstructural features of prepared varistors are studied with the help of SEM technique. It is found that all SEM images are not remarkly different and irregular micro grains are uniformly

distributed in all SEM images. Agglomerations of grains are formed on all images and average grain sizes are in micron scale. Further, there are crack free and no pin - hole arrangement in all images. Average grain sizes are found to be 2.8 μm, 3.32 μm, 4.16 μm, 4.6 μm and 5.2 μm respectively. It is also noticed that average grain size slightly increases as composition " x " increases in prepared varistors. Average grain sizes are found to be 2.8 μm, 3.32 μm, 4.16 μm, 4.6 μm and 5.2 μm respectively, as seen in figure (6).

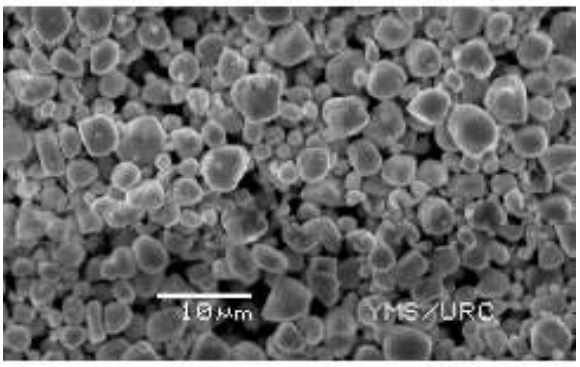

Figure 6(a) The SEM Images of ZnO based Varistor with five additive oxide (composition x = 0.01)

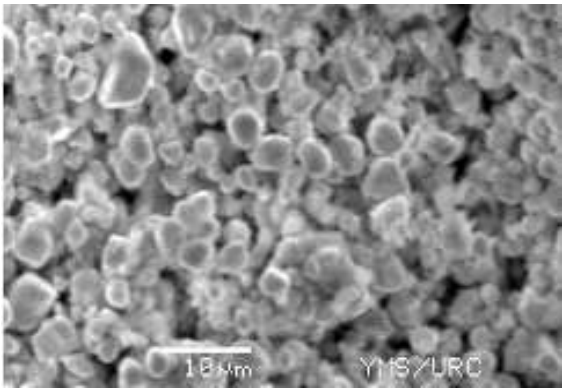

Figure 6(b) The SEM Images of ZnO based Varistor with five additive oxide (composition x = 0.02)

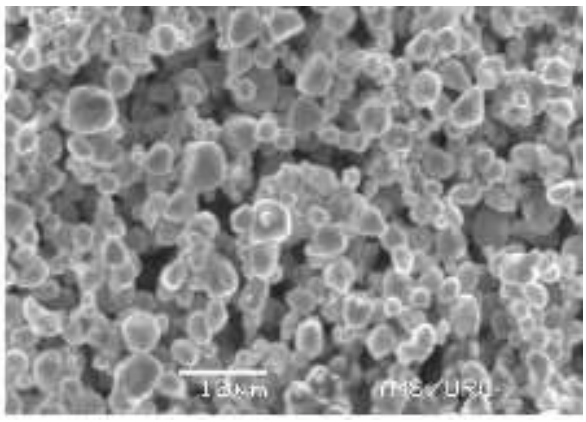

Figure 6(c) The SEM Images of ZnO based Varistor with five additive oxide (composition x = 0.03)

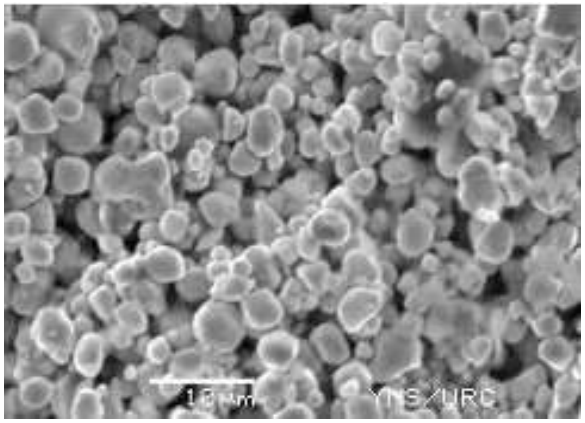

Figure 6(d) The SEM Images of ZnO based Varistor with five additive oxide (composition x = 0.04)

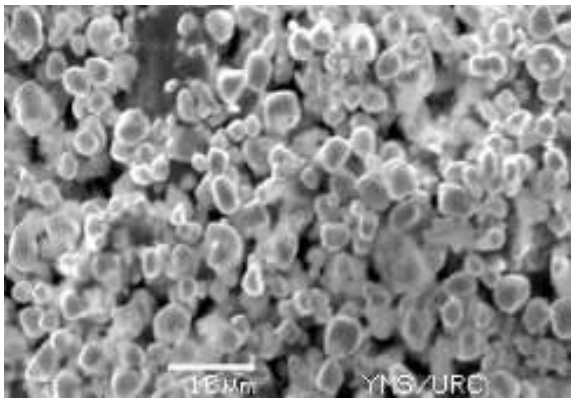

Figure 6(e) The SEM Images of ZnO based Varistor with five additive oxide (composition x = 0.05)

Varistor behaviour of prepared samples are studied from the current - voltage characteristic of the samples (ln V vs. ln I plots), as displayed in figure (7).

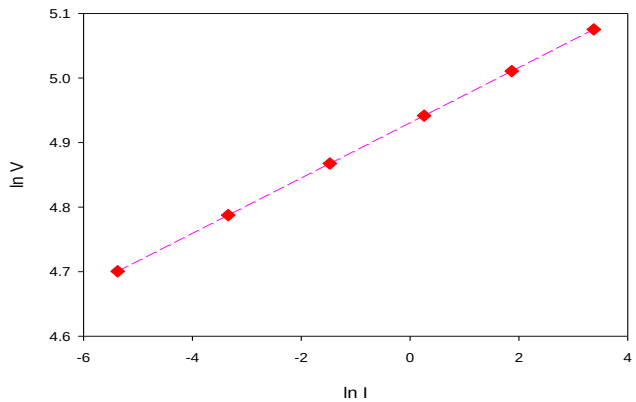

Figure 7(a) Non- linear behavior of ZnO based Varistor with five additive oxide (composition x = 0.01).

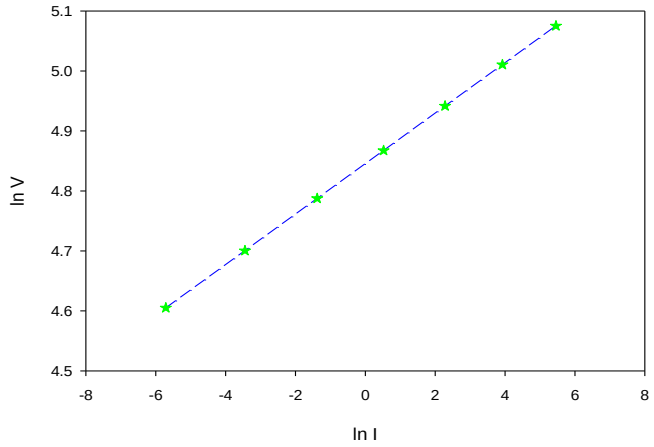

Figure 7(b) Non- linear behavior of ZnO based Varistor with five additive oxide (composition x = 0.02).

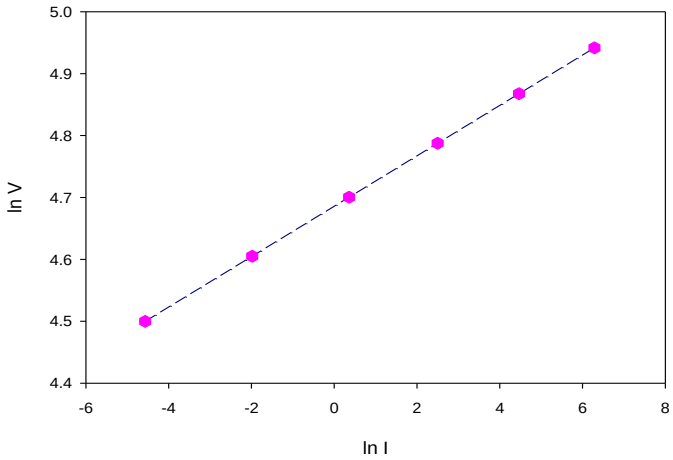

Figure 7(c) Non- linear behavior of ZnO based Varistor with five additive oxide (composition x = 0.03).

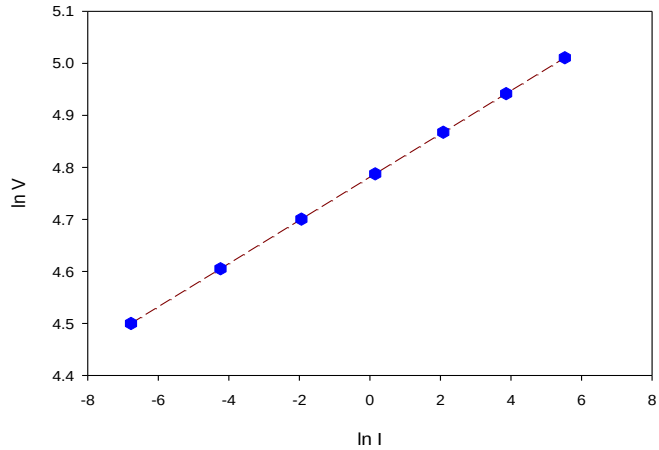

Figure 7(d) Non- linear behavior of ZnO based Varistor with five additive oxide (composition x = 0.04)

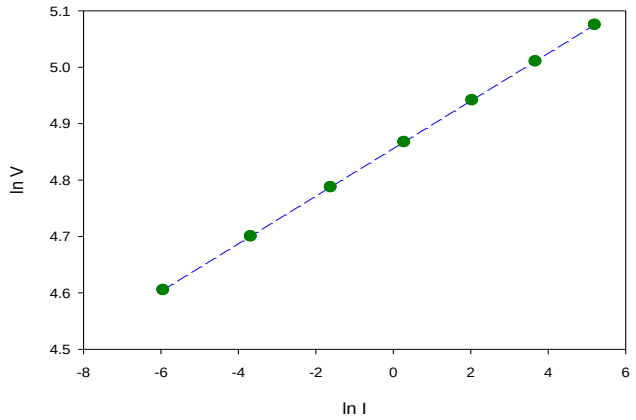

Figure 7(e) Non- linear behavior of ZnO based Varistor with five additive oxide (composition x = 0.05).

From the ln V vs. ln I plots, non - linear coefficients (α values) are examined by using the equation (5):

$$\propto = \frac{\log\left(I_2/I_1\right)}{\log\left(V_2/V_1\right)} \qquad (5)$$

where I_2 = 1 mA and I_1 = 10 mA and, V_2 and V_1 are the voltages corresponding to currents I_2 and I_1. Threshold voltages (V_{1mA}), which is measured at current 1 mA and the leakage currents are studied at 0.8 $V_{1\,mA}$. Variator properties are collected and listed in table (4).

Table 4 Varistor properties of prepared samples.

Composition x (%)	Non-linear Coefficient (α)	Threshold Voltage V_{TH}(V)	Leakage Current I_L (mA)
1	24.46	83.5	4.31
2	24.79	78.7	3.97
3	24.97	76.3	3.86
4	25.18	73.6	3.70
5	25.46	70.2	3.47

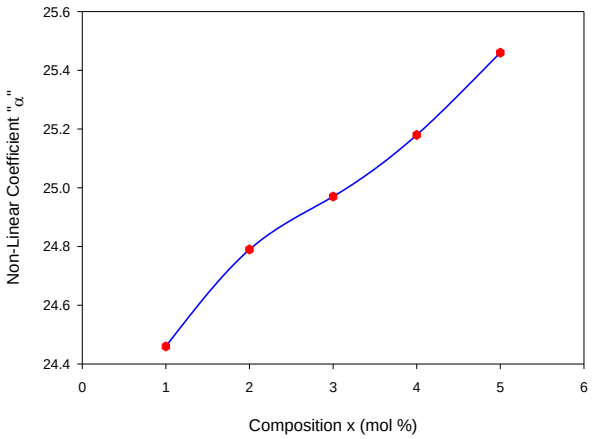

Figure 8 Influence of composition " x "(mol %) on the non - linearity factor " α " of prepared varistors.

Figure (8) represents the influence of composition " x " on the non - linearity factor " α " of prepared varistors. Figure (8) represents the influence of composition " x " on the non - linearity factor " α " of prepared varistors. It is noticed that, non - linearity factor " α " increases as composition " x " in prepared varistors. It is well known that, Bi ions are non - linearity inducer and Co, Mn, Sb, and Cr ions are non - linearity enhancers in ZnO based varistor. Further, the transition metal oxides are involved in formation of interface states and deep traps, both of which are contribute to non - ohmic behavior [Poonsuk Poosimma 2014].

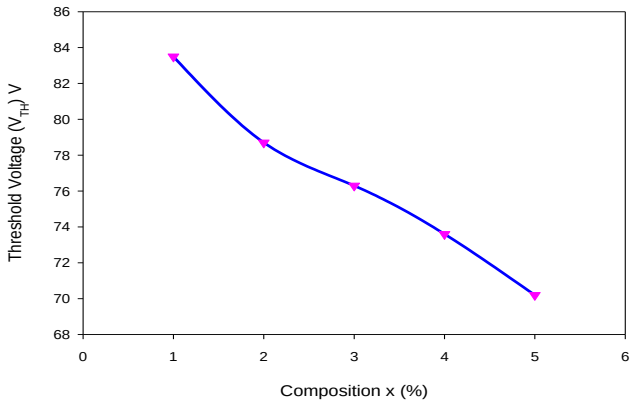

Figure 9 Variation of composition " x " (mol %) with threshold voltage (V_{TH}) of prepared varistors.

Figure (9) illustrates the variation of composition " x " with threshold voltage (V_{TH}) of prepared varistors. It is obvious that threshold voltage (V_{TH}) decreases as composition "x" increases in prepared varistors. Threshold voltage depends on the all types of stresses, such as thermal, mechanical, electrical and chemical stresses. In addition, threshold voltage is affected by the numbers of grain boundaries across the series between the two electrodes, which is inversely proportional to the grain size. In this study, increase of grain size leads to lower the threshold voltage in prepared varistors, as shown in figure (9).

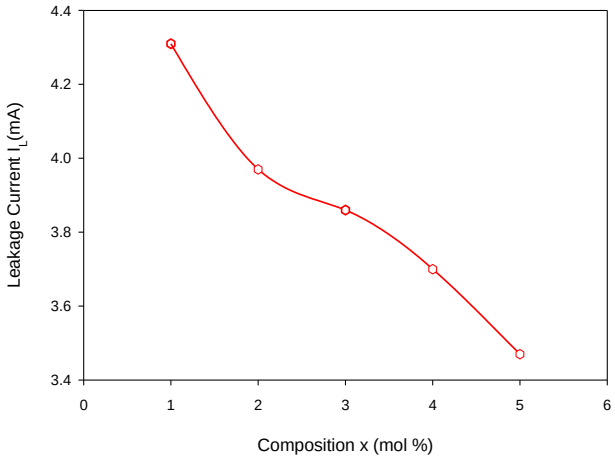

Figure 10 Effect of composition " x "(mol %) on leakage current " I_L " of prepared varistors.

Figure (10) shows the effect of composition " x " on leakage current " I_L " of prepared varistors. It is obvious that leakage current " I_L " decreases when the composition " x " is raised in prepared varistors. During the clamping of transient voltages, the non - linearity factor "α " is

required to suppression of leakage current, which is measured at nominal voltage (below 1 mA at medium and high voltage). The higher the non - linearity factor, the lower the leakage current, as listed in table (4) and the better the varistor's performance.

Conclusion

ZnO based varistors with 5 additive oxides Bi_2O_3, MnO_2, Co_3O_4, Cr_2O_3 and Sb_2O_3 are successfully prepared in this research work. The additive oxides are well known as non - linearity factor inducers and non - linearity enhancers in ZnO based varistors. Weighting, mixing, primary ball milling, drying, secondary ball milling, sieving, sintering, pressing into circular shape disc, electroding, and varistor re - heating processes are performed.

X - rays diffraction studies are carried out to examine the structural features of prepared variators. It is believed that appearance of compressive stresses during the solid state sintering processes. Further, additional Bi, Mn, Co, Cr and Sb ions doping create the dislocations, defects, and vacancies in host ZnO structures. These facts are the main reasons for the changes of unit cell dimensions of ZnO structures. But, there are no significant change of hexagonal, wurtzite ZnO structure after additive oxides doping.

Microstructural properties of prepared varistors are characterized with the help of SEM technique. It is noticed that all SEM images are not remark different. Agglomerations of grain are formed on all images.

Further, irregular micro grains are uniformly distributed in all SEM images. Average grain sizes are in micron scale, crack free and no pin hole arrangement in all images. It is also observed that average grain size slightly increases as composition " x " increases in prepared varistors.

Important parameters of prepared varistors, such as non - linearity factor " α ", threshold voltage " V_{th} " and leakage current " I_L " are examined by using the high voltage DC power supply. Non - linearity factor is estimated from the slope of ln V vs. ln I variations. It is obtained that non - linearity factor increases when the composition " x" is raised. Additive oxides, used in this study are known to be non - linearity factor inducers and enhancers. In addition, the transition metal oxides are involved in formation of interface states and deep traps, both of which are contributed to high non - ohmic behaviour.

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