The Influence of AL_2O_3 Dopants on the Electrical Properties of ZnO-Bi_2O_3 Based Varistor at Different Sintering Temperature

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Abstract
ZnO Varistor samples with different amount of additive (0.7%Bi_2O_3, 1%Sb_2O_3,0.5%Cr_2O_3, 0.5%MnO_2, 0.8%CoO) as well as 0.1% mol of AL_2O_3 were prepared by a conventional route and sintered in air for 2h at a different sintering temperature (1000,1100, 1200)^{o}C at a heating rate of (5^{o}C . min^{-1}). The microstructure and Electrical properties of sintered samples were investigated by using X-ray diffraction (XRD), Energy Dispersive Spectroscopy (EDX), Scanning Electron Microscopy (SEM) as well as Electrical measurements. The best electrical characteristic were obtained in the sample sintered in air at (1000^{o}C) for 2h ,which exhibited the nonlinear coefficient of (46) ,breakdown voltage of (2090V) , and leakage current of (0.04mA).

Introduction

The metal oxide ZnO - based varistors (variable resistor as a function of voltage) are electronic ceramic device with non-linear (I-V) characteristic which are widely used for transients surge suppression , voltage stabilization, and provide economical and reliable protection in the electronic circuits and electric power system against overvoltage (lightning surge, transient voltage, electrostatic discharge, switching surge) at range from several volts to several hundreds of kilovolts [1,2,3].
Pure ZnO is n-type semiconductor with ohmic behavior and various dopants (metal oxides) such as Bi_2O_3, Sb_2O_3, MnO_2, Cr_2O_3, CoO, Al_2O_3 and etc. are added in certain molar percent to provide or improve the non-ohmic properties of the varistor [4,5]. This dopants effect the varistor properties by i) segregate at the ZnO grain boundaries and becoming itself a layer of intergranular phase such as(Bi_2O_3) ,or by ii) influence the grain growth and microstructure of varistor during sintering, or by iii) reducing the sintering condition (temperature , time ,rate) such as small amount of Al_2O_3 which increasing The conductivity of ZnO grains [6,7].
The manufacturing processes of this product are the same of the traditional processes of ceramic (mixing ,forming , and liquid-phase sintering technique) of ZnO powder [8]. After sintering process the ZnO varistor will consist of a matrix of conductive zinc oxide grains separated by grain boundaries with high resistivity (insulating intergranular layers) forming double schottky barriers (back-to-back) diodes at the electrically active boundaries of grains [9,10].
The varistor has unique electrical properties which represent by non-ohmic characteristic and can be define by:

$$I = kV^{\alpha} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

k = ceramic constant .
I = current pass through the varistor .
V = voltage across the varistor .
α = coefficient of non –linearity ($\alpha > 1$) [5] .

Varistor voltage (break down voltage V_b) is one of the most important properties of any varistor, it can be define as a voltage pass across the varistor when we applied current of 1mA. At this value of voltage the varistor starts to change from insulating to the conducting state . A current pass through the varistor during the normal working protected circuit is called Leakage current (I_L) [11], the value of this current can be measured at the point when the voltage is equal to(0.8V_b).

The ability of varistor sense and the degree of non-linear of varistor is represented by nonlinear coefficient (α) which determines and limits instantaneously the high voltage surge [12] .

In order to protect a circuit or device from voltage surges, the varistor connected in parallel with them, and it chosen to have breakdown voltage slightly greater than the maximum voltage of the protected device [13]. In normal use the varistor subjects to a voltage below their breakdown voltage, at this state the resistivity of the varistor is very high so it works as open circuit (insulator) and only a small current passes through it called leakage current .When the voltage exceeds the breakdown voltage during transient surge, the varistor appears the nonlinear behavior and the current through it increases rapidly as the voltage is raised slowly,so it becomes highly conducting and that means it actually shunts the current not breaks it [14].

2- Experimental

A certain molar percentage of the starting materials (as shown in table 1) are mixed with deionized water in a glass bottle for (24 hr) by using a magnetic stirrer (Gallenhamp-England)and the mixture were drying in an oven at (70^{o}C) for 24 h and then canceled for 2h at 500^{o}C at a heating rate of (5^{o}C . min^{-1}), the canceled mixture was milled by using a gate mortar to achieve a mixture powder with suitable particle size without agglomeration and pressed with pressure of (250Mpa) into a pellets (discs) with (16mm) diameter and (2mm) thickness by using a steel mold and hydraulic uniaxial press. The sample then was sintered in air from room temperature to a different sintering temperature (1000,1100,1200)^{o}C for 2hr with a heating rate of (5^{o}C.mm^{-1}) ,and classified as shown in table (1). The samples are polished by using various grades of SiC abrasive papers to insure and obtain a certain dimension (2mm thickness and 16mm diameter).

For the characterization of DC (I-V) aluminum electrodes with (400 nm) thickness and (12 mm) diameter where deposited on two sides of each pellets by using a vacuum thermal evaporation system.

Sample formula	Composition(mol%)	Sintering temp.
A	96.5%ZnO, 0.7%Bi_2O_3, 1%Sb_2O_3, 0.5%Cr_2O_3, 0.5%MnO_2, 0.8%CoO	1000^{o}C
B	96.4%ZnO, 0.7%Bi_2O_3, 1%Sb_2O_3, 0.5%Cr_2O_3, 0.5%MnO_2, 0.8%CoO, 0.1%AL_2O_3	1000^{o}C
C	96.4%ZnO, 0.7%Bi_2O_3, 1%Sb_2O_3, 0.5%Cr_2O_3, 0.5%MnO_2, 0.8%CoO, 0.1%AL_2O_3	1100^{o}C
D	96.4%ZnO, 0.7%Bi_2O_3, 1%Sb_2O_3, 0.5%Cr_2O_3, 0.5%MnO_2, 0.8%CoO, 0.1%AL_2O_3	1200^{o}C

Table (1) samples formulation.

The composition and crystalline phases of the samples were identified by Energy dispersive X-ray spectroscopy (EDS) and X-ray diffractometry (shimadzu XRD-6000) with Cu Kα1 (λ=1.54060 Å) and operation condition (V =40.0 kV, I=30 mA). The effect of Al_2O_3 doping at different sintering temperature on the grain size is investigated by scanning electron microscopy (SEM) (Inspect S 50).

The current – voltage measurement was made by using DC power supply (HIRANUNA EP – 1500), to determine the below parameters:

1- Breakdown voltage (V_b) of each varistor samples was determined at the point when (1mA) of current passed throw the varistor .

2- Leakage current was taken at the point when the voltage is equal to (0.8) from the breakdown voltage (V_b) .

3- The nonlinear coefficient was determined for all the samples by using equation (2) below And by plotting the diagrams between the electrical field (E) and current density (J).

$$\alpha = \frac{\log \frac{J_2}{J_1}}{\log \frac{E_2}{E_1}} \qquad \ldots\ldots \qquad (2)$$

When $J_1 = 1mA$,$J_2 = 10mA$ Or $J_1 = 0.1mA$,$J_2 = 1mA$

E_1 , E_2 are the voltages at J_1 and J_2 respectively.

Results and discussion

Figure (1) shows the X-ray pattern of A , B , C and D samples from which we can note that the peaks are slightly shifted from right to left with adding AL_2O_3 and with increasing of sintering temperature , also the intensity of the peaks increases with the increasing of sintering temperature due to the grains growth and the effect AL_2O_3 doping .

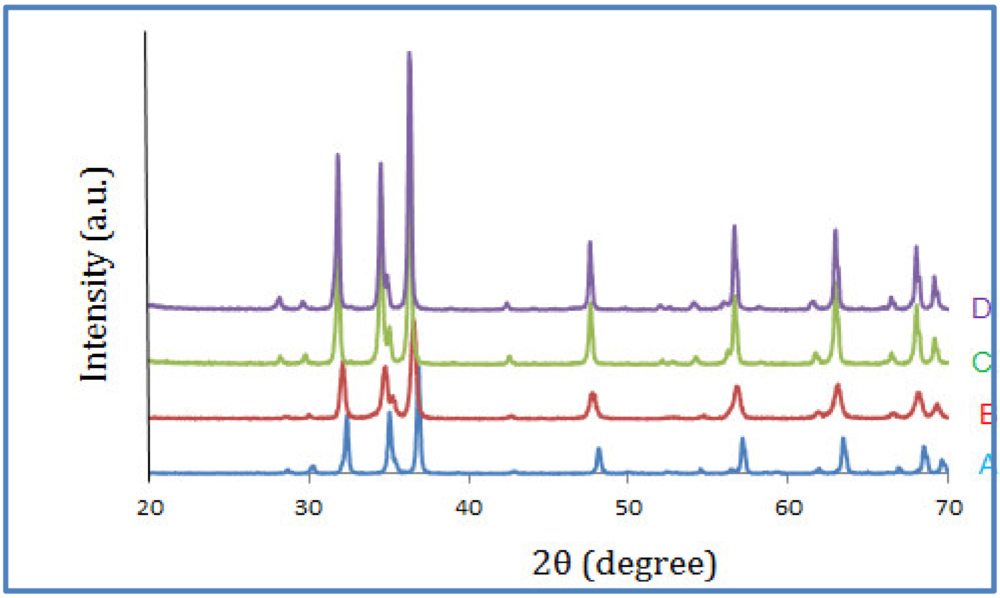

Figure (1) shows the X-ray pattern of A , B , C and D samples.

The energy dispersive spectroscopy (EDS) pattern (figure 2)taken from sample B indicate the presence of the compositions set.

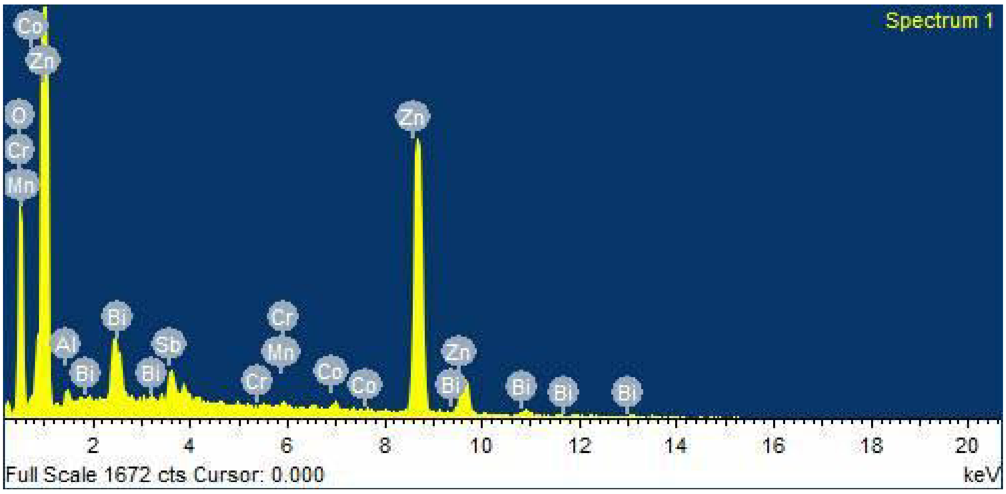

Figure (2) EDX analyses of B sample sintered in air for 2h at 1000°

The measured values of breakdown voltage, leakage current and nonlinear coefficient of all samples are listed in table (2).

Sample formula	Leakage Current (IL) (mA)	Breakdown Voltage(Vb) (V)	Nonlinear coefficient (α)
A	0.02	1883	40.5
B	0.04	2090	46
C	0.08	1280	37.6
D	0.29	255	6.09

Table (2) Electrical properties of the sample

We can note that the breakdown voltage of sample A was 1883V and increases to 2090V for sample B this due to the presence of Al_2O_3 which forming a spinal phase ($Zn_7AL_2O_4$) which inhibit the grain growth by pinning the grain boundaries causing increasing the number of grain boundaries and that leads to increases the value of breakdown voltage of varistor samples.

Figure (3) show that the values of breakdown voltage were re decreased with the increasing of sintering temperature even it reached 255V at sample D (sintered at 1200ºC for 2h) ,this can attributed to the increasing of crystalline growth at high sintering temperature which causing reduction the number of grain boundaries and that reduce the (V_b) , and this agrees with our SEM images which shows in figure (4).

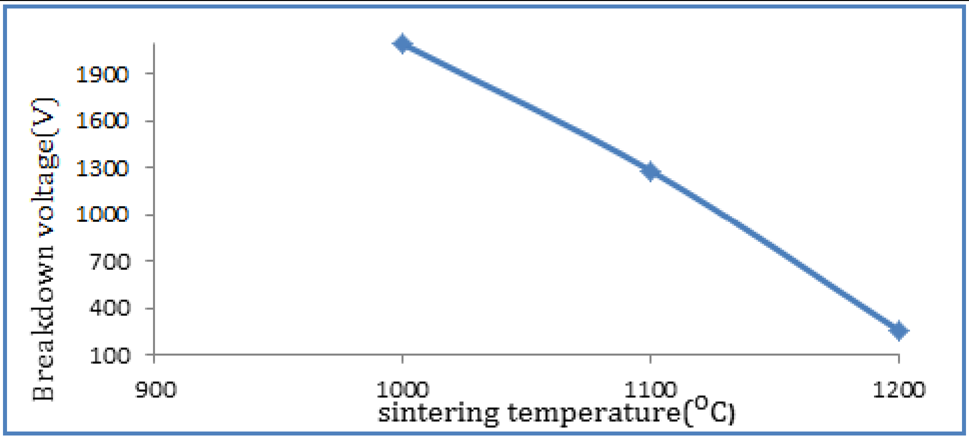

Figure (3) the decreasing of breakdown voltage with the increasing of sintering temperature.

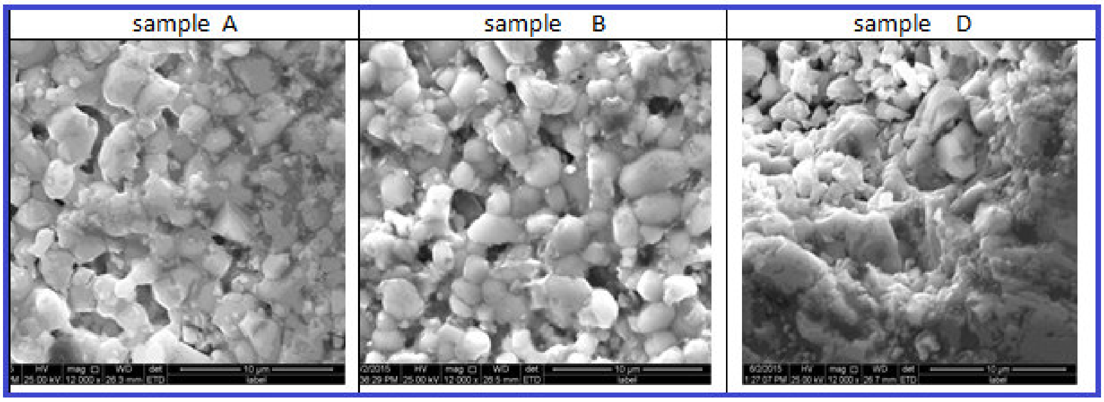

Figure (4) SEM images for samples A, B, and D

Also it can note that the leakage current was increasing with adding Al_2O_3 ,it was (0,02 mA) for sample A and increased to (0.04mA)for sample B which both were sintered at (1000ºC for 2h) , and its value will continue to rise with the increasing of sintering temperature until it reaches (0.29mA) for sample D which sintered for 2h at 1200ºC.

The increasing of leakage current may be due to accommodation of trivalent AL^{+3} ions of Al_2O_3 the host lattice sites or replace a divalent Zn^{+2} and that made the electrons move to the conduction band. The increasing of electrons causing an increasing the electrical conductivity of the grains and decreasing the resistance of ZnO grains which leads to increase the leakage current (I_L). The reaction can be written as: [5]

$$AL_2O_3 \xleftrightarrow{ZnO} 2AL_{Zn} + 2O_0^X + 2e' + \frac{1}{2}O_2 \uparrow \quad \dots\dots (3)$$

The diffusion process of AL^{+3} ions in ZnO lattice increases with the temperature, thus indicate the increases of I_L at high sintering temperature which shown in figure (5).

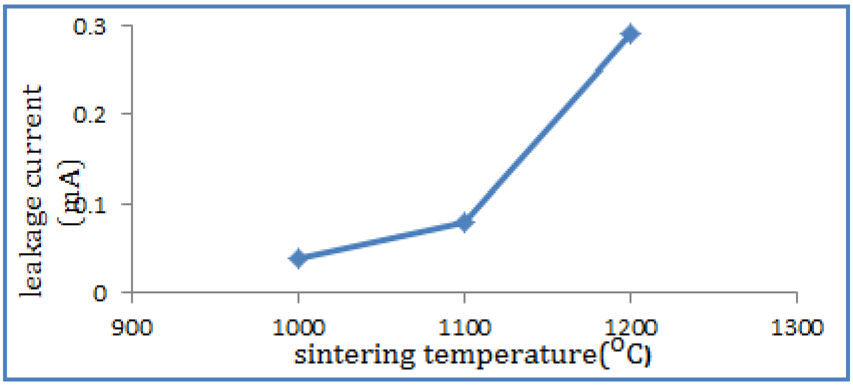

Figure (5) the values of I_L at a function of sintering temperature.

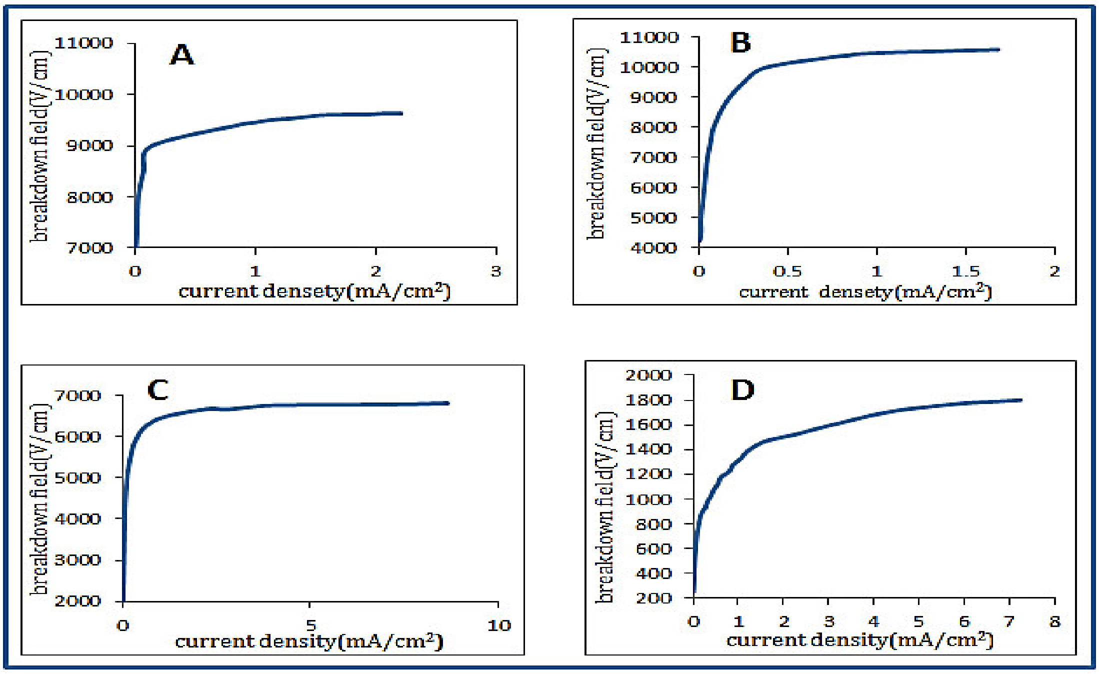

Figure (6) (E-J) diagram for each sample .

By plot the (E-J) diagram for each sample which show in figure (6) and determined the values of α which are listed in table (2) ,we can note that the maximum value of α was (46) for sample B which was sintered in air for 2h at 1000°C ,the improving of nonlinearity between sample A and sample B can be attributed to the effect of aluminum oxide on the nonlinear coefficient, because the Al ions increases the donor density in ZnO lattice(as expected for the trivalent metal) and that leads to decrease the resistance of ZnO grains and increasing the sensitivity of them against over voltage and improving the nonlinearity coefficient.

The value of α then decreased to reach its minimum value (6.09) at sample D which was sintered in air for 2h at 1200°C .

The sharping decrease of α values with the increasing of sintering temperature is shown in figure (7) which can attributed to the bad volatilization of bismuth which play an important role in originating the double schottky barrier, also high sintering temperatures Promote grain growth which lowering the height of the grain boundaries barrier and thus decreasing the nonlinearity of the samples .

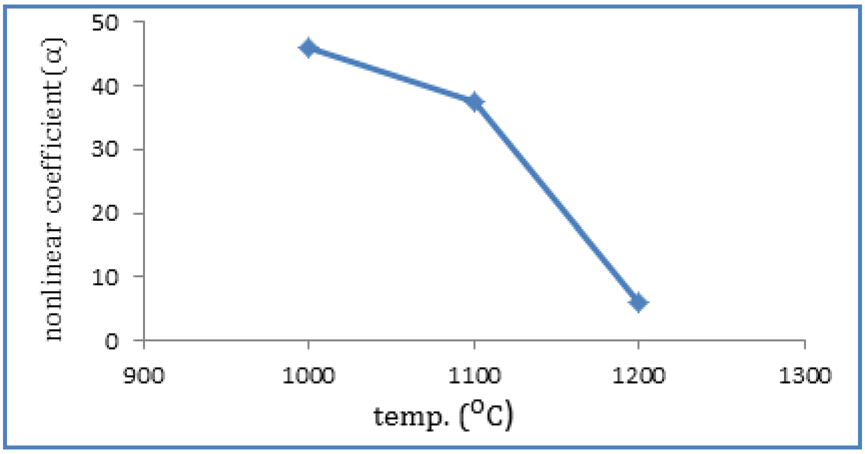

Figure (7) the values of (α) as a function of sintering temperature.

Conclusions

The experimental results of this research indicate that the ideal comprehensive electrical properties with (2090V) of breakdown voltage and (46) of nonlinear coefficient and without significantly rising of the leakage current ,can be obtained by the addition of 0.1 mol % of Al_2O_3 to the ZnO- Bi_2O_3 based varistor prepared by conventional ceramic route and sintering in air for 2h at 1000°C.

Reference

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