



EFFECT OF NIOBIUM DOPING ON ELECTRICAL PROPERTIES OF ZnO BASED VARISTORS

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ABSTRACT

Varistors are electronic devices whose primary function is to sense and limit transient voltage surges and to do so repeatedly without being destroyed. Zinc oxide ceramic varistors, based on ZnO with small amount of additives, such as Bi₂O₃, Sb₂O₃, Co₂O₃, MnO₂ and Cr₂O₃ shows excellent non-ohmic current – voltage (I-V) characteristics. In the present investigation ZnO varistors ceramic system containing BaO, Bi₂O₃, Sb₂O₃ has been doped with niobium oxides to study its influence on sintering, phase development and the electrical behavior of these ceramics. Proportionate amount of different compounds were mixed, calcined and sintered in the temperature range 1050 to 1100°C for 3 and 6 hours. Phase structures were studied using X-ray diffraction. I-V characteristics for various samples were measured at room temperature. These samples show high value of nonlinear coefficient.

Keywords: ZnO Varistors; V-I characteristics; Non - linear coefficient and Breakdown voltage and niobium oxide

1. INTRODUCTION

The most commonly used varistors are ZnO based and their non-linear electrical properties were well studied and documented¹. As a result, they are widely used as surge absorbers and stabilizers in electric power systems and electronic circuits². Pure ZnO is a non-stoichiometric n-type semiconductor with linear I-V behavior. To make it non-linear, various additive oxides are incorporated in the ZnO. Chief among these oxides is Bi₂O₃ (an alternative is Pr₂O₃) which can be considered as a varistor former, without which it is difficult to make varistor. It has been found that the electrical properties of ZnO varistors depend strongly upon the type and content of additives especially monovalent and trivalent metal oxides. Incorporation of these oxides causes atomic defects to form at the grain and grain boundary, with donor or donor like defects dominating the depletion layer and acceptor and acceptor like defects dominating the grain boundary states. Selim et al.³ were the first to develop a defect model with bismuth doping, which takes into account the role of oxygen in developing the non-linear behavior of ZnO. The relevant defect species are $V_{Zn}^{\cdot\cdot}$, V_{Zn}^{\cdot} , V_O^{\cdot} , $V_O^{\cdot\cdot}$, Zn_i^{\cdot} , $Zn_i^{\cdot\cdot}$, D_{Zn}^{\cdot} , D_i^{\cdot} where D_{Zn}^{\cdot} and D_i^{\cdot} represent all the externally incorporated donor and acceptor atoms, respectively. Since the electrical properties of ZnO varistors have been attributed to their grain boundary barriers, the effect of additives must be related to the changes they cause in the grain boundary barriers. The non – ohmic property of ZnO varistors is largely affected by the addition of metal oxides⁵⁻⁶ in which the addition Mn and Co can enhance the non-linear coefficient of the varistors. However, the effects of valence states of additives on varistors, particularly on their electrical properties, have not been clear till now. In the present investigation we studied the electrical properties of ZnO-BaO varistors with dopant of Nb₂O₅. The ZnO based varistors samples were made by conventional ceramic fabrication techniques. The doping of the Nb₂O₅ enhances the resistance of the grain boundaries and also promotes the nonlinearity of the ZnO varistors.

2. EXPERIMENTAL PROCEDURES

In this study, a five component system consisting of ZnO with different oxides viz. Bi_2O_3 , BaO , Sb_2O_3 and Nb_2O_5 was used. The composition is shown in Table 1. Appropriate amounts of various constituents were weighed and thoroughly mixed using ball mill and acetone as a mixing media for 8 hours.

After drying, powders were calcined at 800°C for 6 hours. The calcined powders were ground by mortar and pestle, and pressed in to discs of 12 mm diameter and 2mm in thickness at a pressure of 75 KN. These pressed green bodies were sintered at 1050°C and 1100°C in air atmosphere for 3 and 6 hrs with a ramp rate of $5^\circ\text{C}/\text{min}$ and then cooled to 500°C with same ramp rate. The densities of all the samples were measured with Archimedes method. Diffraction patterns for each sample were recorded using Rigaku Diffractometer employing $\text{Cu K}\alpha$ radiation over a 2θ range of 20 – 80° with scan rate of $2^\circ 2\theta/\text{min}$. Phases were identified using powder X-ray diffraction (XRD) analysis. Finally sintered samples were coated with conductive silver paint on both surfaces to provide a good electrical contact. The I-V characteristics were measured using a dc source (APLAB regulated dc power supply, 0-200V), an electrometer (Keithely, 616 digital electrometer, 2mA) and a digital multimeter (HIL 2665) with a locally fabricated measuring cell furnace. The electric field at current density $0.5 \text{ A}/\text{cm}^2$ ($E_{0.5}$) is selected as a measure of breakdown voltage. The non-linear coefficient was obtained by the following equation:

$$\alpha = d \ln I / d \ln V$$

3. RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION STUDY

ZnO varistor materials are multiphase materials. These materials contain ZnO as major phase. Spinel, pyrochlore and some other phases are present in the varistors. The presence of these minor phases is dependent on the nature and amount of various additives and the processing parameters⁷⁻⁸. Representative X-ray diffraction patterns of ZnO varistors doped with Nb_2O_5 and sintered at 1050°C and 1100°C for 3 and 6 hours respectively are shown in Fig. 1. All the varistors samples sintered at different temperatures were found to have hexagonal ZnO as the major phase along with some secondary phase of zinc antimony oxide ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) and zinc niobium oxide (ZnNb_2O_6). From the XRD patterns it observed that there is not much change in phase constitution of varistors samples sintered at 1050 and 1100°C for the 3 and 6 hours respectively while a little change is observed in their relative intensities of XRD peaks of various phases in these samples.

It can be concluded that sintering temperature and soaking time only influences the magnitude of the peaks of major phase of ZnO and secondary phase of pyrochlore. Thus, the fractions secondary phases zinc antimony oxide ($\text{Zn}_7\text{Sb}_2\text{O}_{12}$) and zinc niobium oxide (ZnNb_2O_6) in these samples depend on sintering temperature and soaking time. Varistor samples codes, sintering temperature and sintered density of various samples are listed in table 1 and crystal structure and lattice parameters of major phase are listed in Table 2. Sintered densities values are lie in the range 4.869 – $5.682 \text{ gm}/\text{cc}$ (Table1). Sintered densities are found to increase with sintering temperature and soaking time.

3.2 I-V CHARACTERISTICS

Fig. 2 (a, b, c and d) depicts the I-V characteristics of various varistor samples ZBBSNb1050T, ZBBSNb1050S, ZBBSNb1100T and ZBBSNb1100S respectively. Doping of Nb_2O_5 significant

effect the electrical properties of ZnO - BaO based varistors system. Good nonlinear I-V characteristics were observed in these Nb₂O₅ doped ZnO -BaO based varistors ceramic samples. The electric field (E) current density characteristics of the ZnO ceramics doped with Nb₂O₅ were measured in the low and medium current density region. From the observation of Fig 2 (a, b, c and d), it can be recognized that the breakdown voltage increases considerably when Nb₂O₅ was added. The break down voltage and initial value of nonlinear coefficient for various samples are listed in table 2. In these samples the breakdown voltage is very high. It is discussed in the literature that it can increase considerably as the content of Nb₂O₅ increases. The low current pre-breakdown region has been identified to be controlled by the grain boundary resistance and capacitance. It is observed that increasing Nb₂O₅ to an appropriate level will lead to abrupt enhancement of grain boundary resistivity. It is observed that the prebreak down resistance is more for sample sintered at 1100°C while it is $0.12 \times 10^6 \Omega$ for sample sintered at 1050°C for 3 and 6 hours soaking time.

The nonlinear coefficient and prebreak down resistance is not strongly dependent on the sintering temperature on the soaking time. The break down voltage of the varistors samples was found to lay in the range 49.01 to 49.31 V/cm. From the Table 2 it is observed that the break down voltage for the varistors sample ZBBSNb1100S is highest. The effect of Nb₂O₅ on the electrical properties of ZnO based ceramics can be commented with grain boundary barrier model for ZnO based varistors. The defects generated by the presence of Nb₂O₅ as Nb⁵⁺ are fundamental in the formation of depletion layers at the grain boundaries in that they lead to the creation of potential barriers when compensated by the negative charges at the grain boundary interface. It is observed that higher Nb₂O₅ doped ZnO should have higher concentration of Nb⁵⁺ near the grain boundaries resulting in more positive charges (Nb⁵⁺) in the depletion layer. Accordingly the concentration of compensating charge increased in order to maintain electrical neutrality in the grain boundary interface. The barrier height and breakdown voltage are thus high due to the increasing concentration of oppositely charged ions that constitutes the barrier at the grain boundary. Consequently there was a corresponding improvement of non-linearity, as the concentration Nb₂O₅ increases beyond the certain level the width of potential barrier will increase to such a degree that it will impact the tunneling process through the grain barrier act intermediate current density region.

4. CONCLUSIONS

Electrical properties of the various varistor samples in the ZnO –BaO system doped with Nb₂O₅ have been studied. Density of these varistor samples increases with increasing sintering temperature and soaking time. Doping of Nb₂O₅ enhances the nonlinear I-V characteristics and also enhances the grain boundary resistance.

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Table 1. Composition, density and firing schedule of various ZnO varistors samples

Sample Code	ZnO	Bi ₂ O ₃	BaO	Sb ₂ O ₃	Nb ₂ O ₅	Firing Schedule		Sintered Density (gm/cc)
	Wt%	Wt%	Wt%	Wt%	Wt%	Temp.	T.	
ZBBSN1050T	95	2	1	1	1	1050 ⁰ C	3h	4.869
ZBBSN1050S	95	2	1	1	1	1050 ⁰ C	6h	5.240
ZBBSN1100T	95	2	1	1	1	1100 ⁰ C	3h	4.910
ZBBSN1100S	95	2	1	1	1	1100 ⁰ C	6h	5.682

Temp.-Temperature

T.-Time

h.-hours

Table 2: Varistor samples code, sintering temperature, crystal structure, lattice parameters nonlinear coefficient, break down voltage and pre-break down resistance.

Varistors Sample Code	ST (⁰ C)	Crystal Structure	Lattice Parameter (Å)	Non-linear Coefficient	Breakdown voltage (E _b in V/cm)	Pre- break down resistance (10 ⁶ Ω)
ZBBSNb1050T	1050	Hexagonal	a =3.279 c =5.225	1.98	49.29	0.12
ZBBSNb1100T	1100	Hexagonal	a =3.279 c =5.222	1.62	49.20	0.13
ZBBSNb1050S	1050	Hexagonal	a =3.278 c =5.212	1.96	49.01	0.12
ZBBSNb1100S	1100	Hexagonal	a =3.278 c =5.212	1.63	49.31	0.13

ST-Sintering Temperature

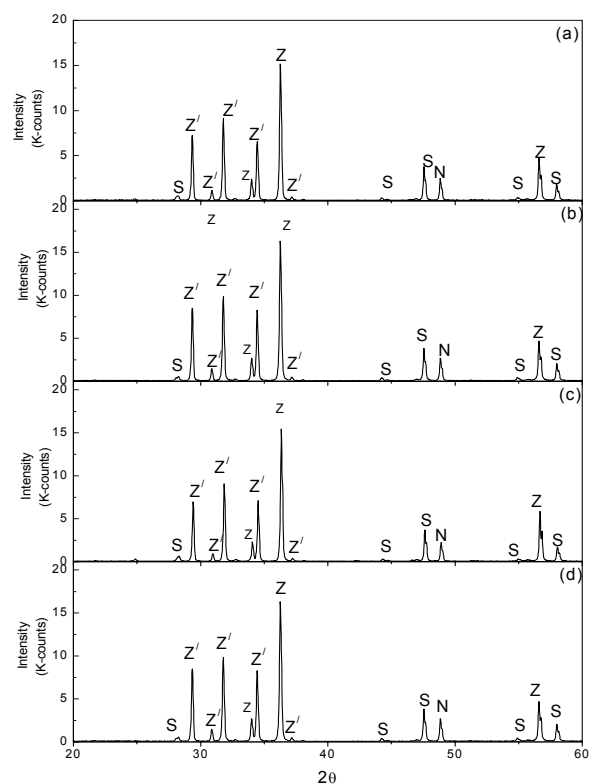


Fig 5.6 : X-ray Diffraction pattern for Nb doped ZnO varistor samples sintered at (a) 1100°C (6h) (b) 1100°C (3h) (c) 1050°C (6h) (d) 1050°C (3h)

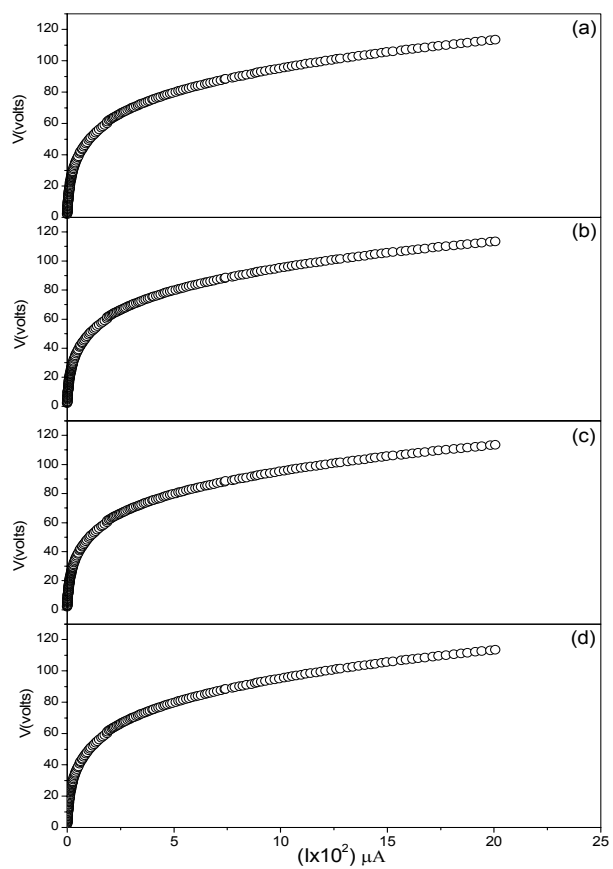


Fig. 2 V-I characteristics for ZnO varistors samples (a) ZBBSNb1050T (b) ZBBSNb1050S (c) ZBBSNb1100T and (d) ZBBSNb1100S