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Non-ohmic behaviour of the binary $ZnO–Nb_2O_5$ system

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Studies have been made of the non-ohmic behaviour of the system $ZnO-Nb_2O_5$, as a function of composition, in the range 0.1 to 0.5 wt% of Nb_2O_5 and sintering temperature varying from 900 to 1300° C. It is found that the non-linearity coefficient α varies with composition and sintering temperature. The maximum value of $\alpha(\simeq 8)$ is achieved for the samples containing 0.2 wt% Nb_2O_5, sintered at 1100° C. These results are interpreted in terms of the variation of barrier height with composition.

1. Introduction

A new class of electronic device known as 'metal oxide varistor' based on ZnO containing one or more dopant oxides like Bi_2O_3, Sb_2O_3, MnO_2, Cr_2O_3, Co_3O_4 and Al_2O_3 has been developed in the recent past [1–3], for transient surge suppression both in electrical and electronic circuits. These materials are found to exhibit pronounced non-ohmic behaviour. The voltage–current characteristics of these ceramics can be expressed by a power law

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

where α is the non-linearity coefficient, V is the voltage across the sample, I is the current flowing through it and k is a constant corresponding to the resistance. The value of the non-linearity coefficient, α, generally ranges from about 5 to 50 and often approaches 100 under special conditions [1]. Besides excellent $V–I$ characteristics, ZnO varistors are found to possess high energy handling capabilities as compared to the conventional SiC varistors [4].

The non-ohmicity is attributed to the presence of an intergranular layer of Bi_2O_3 rich pyrochlore phase surrounding the conducting ZnO grains and well faceted octahedral crystals of $Zn_7Sb_2O_{12}$ with spinel structure present usually at the grain boundaries. The electrical conduction within the ZnO grain is believed to be ohmic and the non-linearity arises due to the boundaries between the ZnO grains. Several theoretical models based on Schottky barrier, electron tunnelling, and space charge effects, have been proposed [5, 6] to explain the non-ohmic behaviour of ZnO composites.

Since ZnO is a metal-excess n-type semiconductor [7], addition of Nb_2O_5 should increase the lattice conductivity and the fact that it forms an interoxide compound with ZnO, $Zn_7Nb_2O_{12}$ or $Zn_{2.33}Nb_{0.67}O_4$ with spinel structure [8], can create a potential barrier at the ZnO grains. The two interrelated effects are expected to impart non-ohmic behaviour in ZnO doped with Nb_2O_5. The present work has therefore been undertaken to study the effect of addition of small amounts of Nb_2O_5 on the non-ohmic behaviour of ZnO and ZnO containing other additives. This paper highlights the electrical properties of the $ZnO-Nb_2O_5$ binary system.

2. Experimental procedures

2.1. Sample preparation

Dense sintered samples of ZnO containing Nb_2O_5 up to 0.5 wt %, were prepared by the conventional ceramic fabrication procedure [9]. Reagent grade (99.9% pure) ZnO and Nb_2O_5 powders were mixed in appropriate proportion in a wet ball mill using deionized water. The mixture was then dried and pressed into discs of 19 mm diameter and 3 mm in thickness. The green compacts were sintered at different temperatures ranging from 900 to 1300° C for 2 h in air and furnace cooled to room temperature. The sintered discs were then lapped with SiC abrasive of 320 mesh and the ohmic contact on both the surfaces was provided by coating with the conducting silver paint.

2.2. Characterization of samples

Density of the sintered pellets were calculated from their weight and dimensions. The bulk density of the samples varied from 85% to 97% of theoretical density, depending upon the composition and sintering temperature. Specimens for metallographic examination were prepared in the usual manner. The polished specimens were thoroughly cleaned by ultrasonic stirring and mild-etched with 10% HCl. The surface structure was examined by scanning electron microscope (SEM). The surface of the samples was metallized with a thin coating of gold to reduce the charging effects and to improve the definition and resolution of the image.

Specimens for X-ray examination were prepared as follows. Sintered samples were treated with 25% $HClO_4$ solution for 1 h at room temperature partially to leach out ZnO. The residue containing ZnO and the other minor phases was filtered, dried and used for X-ray diffraction study. This method permitted unambiguous identification of minor phases.

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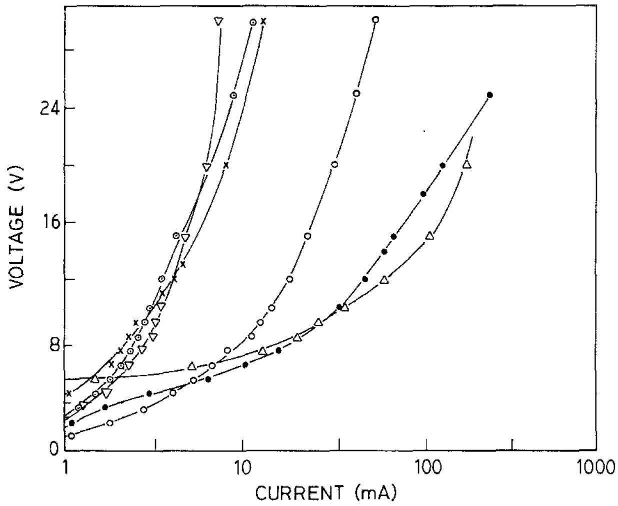


Figure 1 V–I curves of the samples sintered at 900° C. ×, pure ZnO. ZnO + percentage Nb_2O_5: ●, 0.1%; △, 0.2%; ○, 0.3%; ▽, 0.4%; ⊙, 0.5%.

2.3. Study of V–I characteristics

Variation of current as a function of the applied voltage for the samples was measured at room temperature, using a DC power supply in a current range up to 10 mA. Measurement in the high current range beyond 10 mA was carried out by applying a single pulse of 0.1 msec duration to avoid joule heating. Further, the resistivity of the pellets, sintered at 1100° C was measured as a function of temperature in a range 25 to 150° C to study the effect of composition and sintering temperature on the barrier height.

3. Results

The voltage–current characteristics of ZnO–Nb_2O_5 system as a function of composition and sintering temperature are shown in Figs 1 to 5. The non-linearity coefficient, α, was calculated using the following equation, derived from Equation 1 in a current range between 1 and 10 mA.

$$\alpha = \frac{dI/I}{dV/V} = \frac{d(\log I)}{d(\log V)} = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \quad (2)$$

where, V_1 and V_2 are the voltages at the currents I_1 and I_2 respectively.

The effect of composition and sintering temperature on non-linearity coefficient and density are summarized in Figs 6 and 7. For reasons to follow later, resistivity measurements were made on samples sintered at 1100° C to establish the influence of composition on the barrier height. Variation of the resistivity as a function of temperature is shown in Fig. 8.

Fig. 9 depicts the influence of Nb_2O_5 on the grain growth of ZnO, sintered at 1100° C.

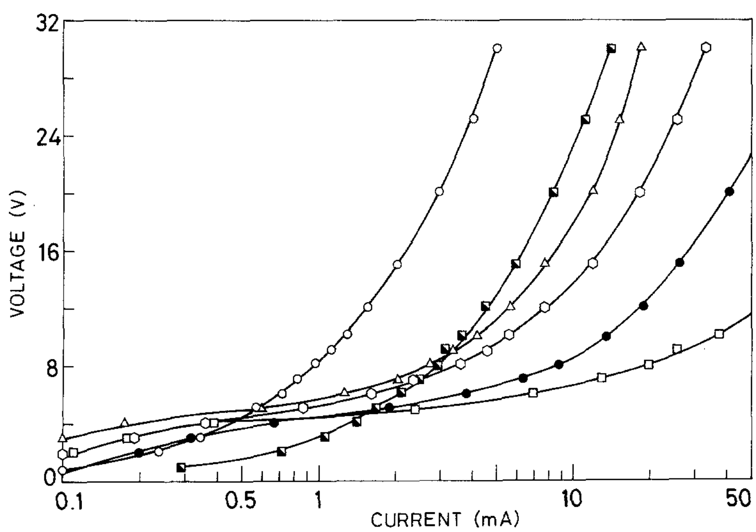


Figure 2 V–I curves of the samples sintered at 1000° C. ○, pure ZnO. ZnO + percentage Nb_2O_5: ⬡, 0.1%; □, 0.2%; ●, 0.3%; △, 0.4%; ◩, 0.5%.

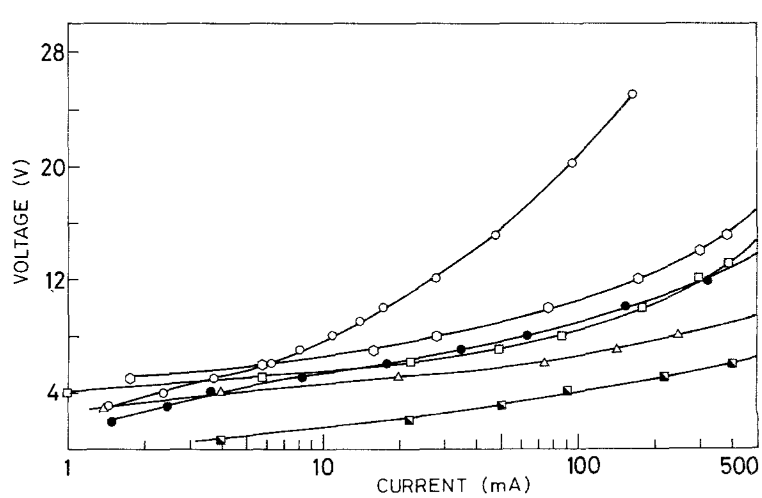


Figure 3 V–I curves of the samples sintered at 1100° C. ○, pure ZnO. ZnO + percentage Nb_2O_5: ⬡, 0.1%; □, 0.2%; ●, 0.3%; △, 0.4%; ◩, 0.5%.

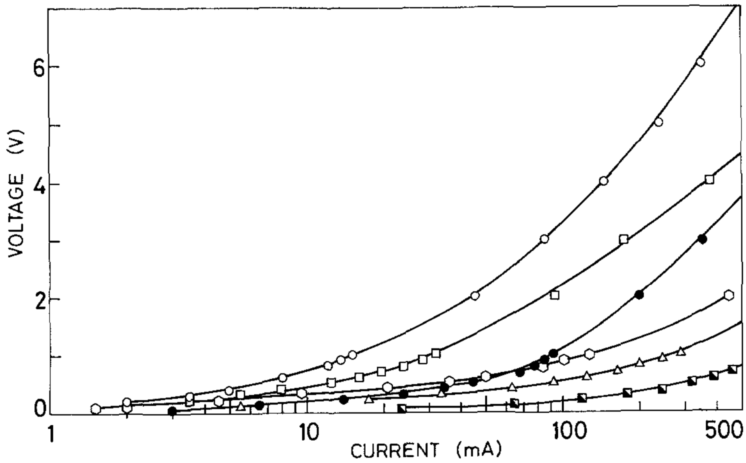


Figure 4 V–I curves of the samples sintered at 1200° C. ○, pure ZnO. ZnO + percentage Nb_2O_5: ⬡, 0.1%; □, 0.2%; ●, 0.3%; △, 0.4%; ◪, 0.5%.

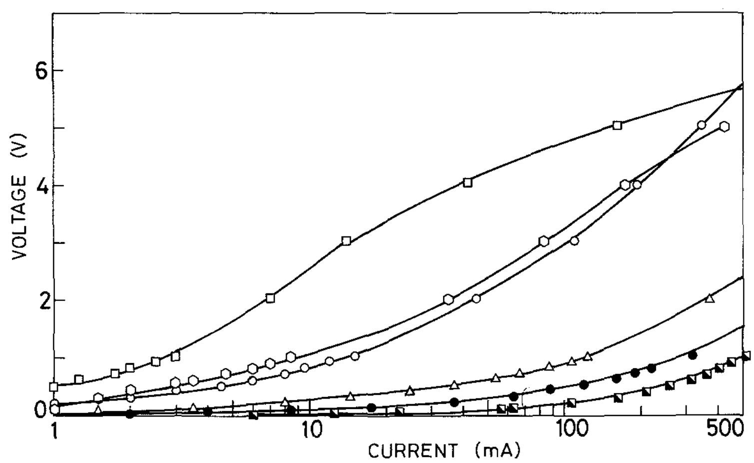


Figure 5 V–I curves of the samples sintered at 1300° C. ○, pure ZnO. ZnO + percentage Nb_2O_5: ⬡, 0.1%; □, 0.2%; ●, 0.3%; △, 0.4%; ◪, 0.5%.

4. Discussion

It is widely accepted [10] that the non-ohmic voltage–current characteristics are mainly governed by Schottky barriers at the junction of different resistive phases, formed during sintering. The V–I characteristic below the threshold voltage is expressed by the following equation

$$J = J_0 \exp\left[-(E_B - \beta' F^{1/2})/kT\right] \quad (3)$$

where J, E_B, F, k and T are the current density, Schottky barrier height, field intensity, Boltzmann's constant and temperature, respectively. J_0 and β' are constants. Change in the V–I behaviour below the threshold voltage is therefore related to Schottky barrier height. The V–I characteristic above the threshold voltage is governed by the Fowler–Nordheim tunnelling process [6] expressed by the relation

$$J \propto \exp(-\gamma/F) \quad (4)$$

where J, F are the current density and field intensity, γ is a constant. The magnitude of α calculated from Equation 2 is determined by the above processes.

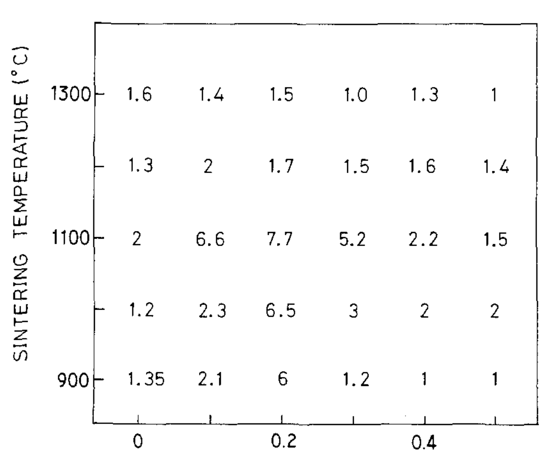


Figure 6 Variation of α as a function of Nb_2O_5 content and sintering temperature.

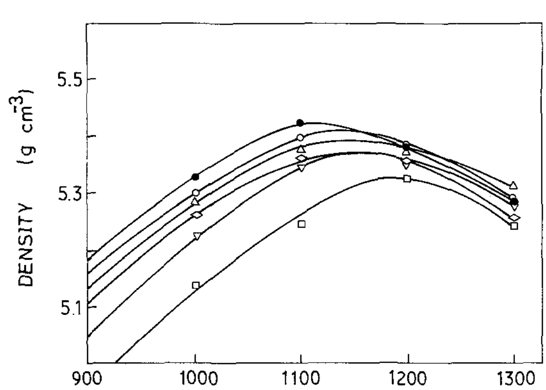


Figure 7 Plot of variation of density as a function of sintering temperature for the ZnO–Nb_2O_5 system. ○, pure ZnO. ZnO + percentage Nb_2O_5: □, 0.1%; ●, 0.2%; △, 0.3%; ◇, 0.4%; ▽, 0.5%.

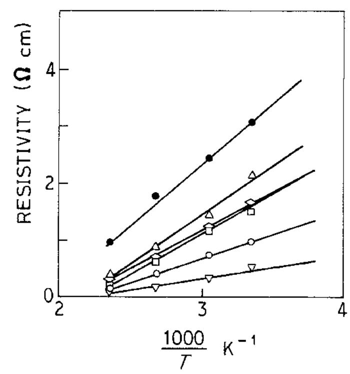


Figure 8 Dependence of resistivity with temperature for samples sintered at 1100° C. ○, pure ZnO. ZnO + percentage Nb_2O_5: □, 0.1%; ●, 0.2%; △, 0.3%; ◇, 0.4%; ▽, 0.5%.

Results summarized in Figs 6 and 7 show that the α value and the density varies with composition and sintering temperature. At a constant sintering temperature, the α value increases with Nb_2O_5 content up to 0.2 wt % and further addition of Nb_2O_5 decreases the α value. Similarly at constant composition, the α value increases with sintering temperature up to 1100° C and then decreases beyond this temperature. Within the compositional ranges of this study, several compositions have been identified to give $\alpha \geqslant 5$. It is important to note that the maximum value of α and density are achieved for samples containing 0.2 wt % Nb_2O_5, sintered at 1100° C. The scanning electron micrographs of the samples shown in Fig. 9 reveal that the average grain size increases with the addition of Nb_2O_5 up to 0.2 wt % and decreases beyond this composition at all sintering temperatures. It is also observed that the grain size increases with sintering temperature for all compositions.

The height of electrostatic barrier was calculated from the temperature dependence of the resistivity at the lowest current level, where the material shows near-ohmic characteristics. In this region, the current flow is described by the hopping conduction mechanism. The potential barrier height is calculated from the resistivity–temperature plot shown in Fig. 8 using Equation 5.

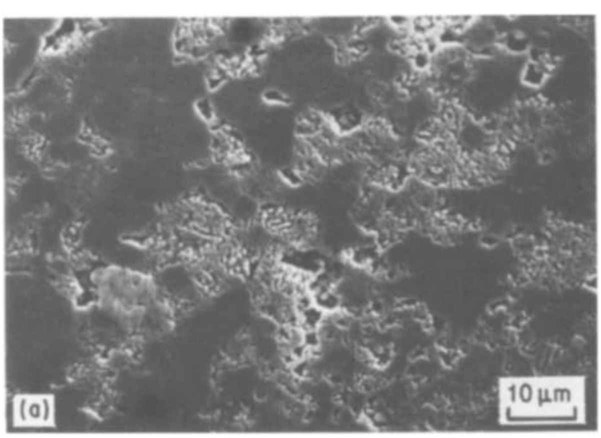
$$\varrho = \varrho_0 \exp(\phi_B/kT) \quad (5)$$

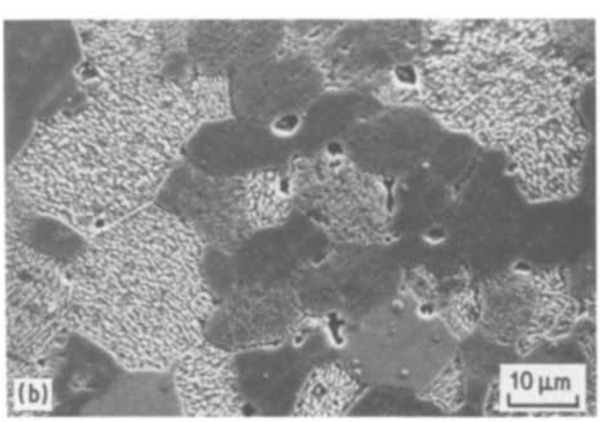
where ϱ is resistivity of the sample, ϱ_0 a constant, ϕ_B the barrier height, k the Boltzmann's constant and T the temperature in degrees Kelvin. It is assumed that the temperature dependence of the carrier density is negligibly small in the measured temperature range of 25 to 150° C. It is interesting to note that both α and ϕ_B exhibits a similar composition dependence as shown in Fig. 10, characterized by a maximum value for both the parameters around 0.2 wt % of Nb_2O_5.

Such a behaviour can be attributed to the precipitation of spinel phase, $Zn_3Nb_2O_8$. X-ray study supports this view. The spinel phase is presumed to possess different electrical resistivity compared to the matrix. In contrast to this, the formation of intergranular phase in $ZnO-Bi_2O_3$ system constitute the basis for non-ohmic behaviour. These observations indicate that either the formation of intergranular phase or precipitation of the second phase in the ZnO matrix can impart non-ohmic behaviour in ZnO based ceramics.

5. Conclusion

Results on the $V-I$ characteristics of the system, $ZnO-Nb_2O_5$, show that small addition of Nb_2O_5 improves the non-ohmic behaviour of ZnO. Maximum value of non-linearity coefficient, density and barrier height is achieved for the samples containing 0.2 wt % Nb_2O_5, sintered at 1100° C. Variation of the grain size with composition also exhibits a similar behaviour.





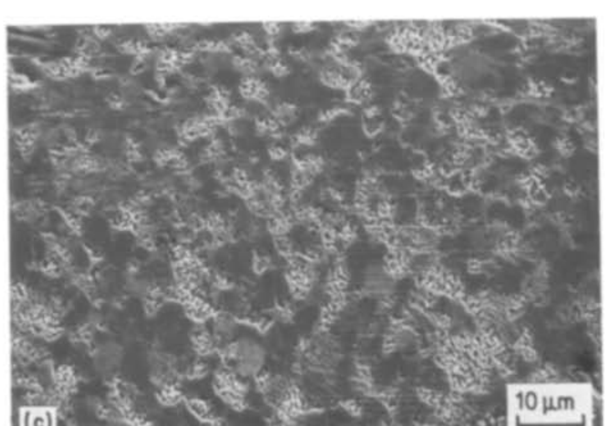


Figure 9 Scanning electron micrographs of samples sintered at 1100° C. (a) ZnO pure; (b) ZnO + 0.2% Nb_2O_5; (c) ZnO + 0.5% Nb_2O_5.

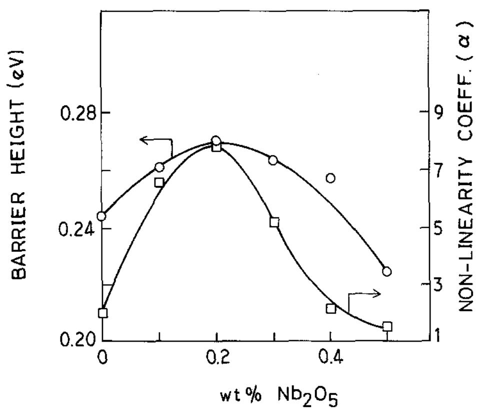


Figure 10 Variation of barrier height and α as a function of composition.

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