Mechanical, microstructure and electrical properties of ternary ZnO–V₂O₅–Mn₃O₄ varistor with sintering temperature

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MS received 9 April 2014; revised 10 July 2014

Abstract. The mechanical, microstructure and electrical properties of the ZnO–V₂O₅–Mn₃O₄ (ZVM)-based varistors were investigated at different sintering temperatures of 825–950°C. The microstructure of the samples consists mainly of ZnO grains with Zn₃(VO₄)₂, ZnV₂O₄ and VO₂ as minor secondary phases. These minor phases disappeared for samples sintered at 950°C. Energy-dispersive X-ray spectroscopic (EDS) analysis confirmed the above microstructure results. The sintered density is decreased linearly from 5.45 to 5.30 g cm⁻³ with an increase in the sintering temperature. The E_B - and α -values of ZnO-based varistor can be controlled in a straightforward manner through the control of grain size. The breakdown field exhibited the highest value (2110 V cm⁻¹) at 825°C in the sintering temperature and the lowest value (1427 V cm⁻¹) at 950°C in the sintering temperature. The non-linear coefficient exhibited the highest value, reaching 19.81 at 875°C and the lowest value, reaching 6.71 at 850°C. As the average grain size increases both the longitudinal wave velocity and the longitudinal elastic modulus decrease while the ultrasonic attenuation increases and *vice versa*.

Keywords. Ceramics; electrical properties; microstructure; varistors; ZnO–V₂O₅-doped Mn₃O₄ varistor; sintering.

1. Introduction

The basic structure of the ZnO-based varistors consists of a conductive matrix of ZnO grains separated by high insulating boundaries, which provide back-to-back p–n junctions of semiconductor non-linear characteristics, acting as a multi-junction series–parallel combination between the terminals of the device.¹ Because of this, they possess an excellent transient overvoltage handling capacity, which allowed them to be used extensively in the field of circuit overvoltage protection in different applications of either few volts electronic circuits or millions of volts in electric power systems.^{2,3} Sintered ZnO ceramics doped with a few additives exhibit entirely different electrical properties from un-doped ones. Commercial systems, e.g., ZnO–Bi₂O₃ and ZnO–Pr₆O₁₁ cannot be co-fired with a Ag inner-electrode (m.p. 961°C) in multilayered chip components because of their relatively high sintering temperature above 1000°C.^{4–8} Recent studies have shown that V₂O₅, the light-metal oxide, is a promising varistor former, which encouraged many research works,^{9–18} where different ceramic binary systems, ZnO–V₂O₅, were investigated.^{9–14,16–18} Also, effects of adding some different metal oxides and rare earths into the above binary system, on the electrical, dielectric and optical properties have been investigated by several authors, e.g., MnO₂ and Mn₃O₄,¹⁹ Mn₃O₄ and Nb₂O₅,²⁰ Mn₃O₄ and Er₂O₃,²¹ MnO₂–Er₂O₃ and

Nb₂O₅,^{22,23} MnO₂–Nb₂O₅ and Bi₂O₃,²⁴ MnO₂.^{25–27} More recently, a work is carried out by us,²⁸ to investigate the effect of Mn₃O₄ doping into ZnO–V₂O₅ varistors on the microhardness, microstructure and electrical properties.

Although, a lot of work has been carried out on ZnO–V₂O₅–Mn₃O₄ ceramics with the study, has been dealt with the electrical, dielectric and optical properties is in its early stages in many aspects since 1994.^{13,14,18,19,25,29–31} To develop useful ZnO–V₂O₅-based ceramics, it is very important to fully comprehend the influence of diverse additives and sintering processes. The sintering process for specific ceramic composition enables ZnO–V₂O₅-based varistor ceramics to exhibit good varistors properties.³² However, the published work in literature to investigate the effect of mechanical properties is very rare. This paper is aimed to investigate the effects of the sintering temperature in the range from 825 to 950°C on the microstructure, electrical and mechanical properties; ultrasonic attenuation, wave velocity and longitudinal modulus of the ternary system, 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic system.

2. Experimental

Reagent-grade raw materials of ZnO, V₂O₅ and Mn₃O₄ were used for preparing ZnO-based ceramics, by the solid-state reaction technique, according to the composition: 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄. Weighed raw

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materials were mixed by ball-milling in the presence of acetone for 31 h. The mixture was dried at 120°C for 12 h. The dried mixture was milled using an agate mortar after the addition of 0.8 wt% polyvinyl alcohol binder for 3 h. The powder was uniaxial pressed into discs of 12 mm in diameter and 1.5 mm in thickness at a pressure of 9500 psi. Then some of the discs were sintered at different temperatures, 800, 825, 850, 875, 900 and 950°C for same time, 3 h. After sintering, the furnace was turned off, allowing the sintered discs to be cooled down naturally within the furnace. The sintered samples were lapped and polished to 1.0 mm thickness. Silver paste was coated on both faces of the samples as the ohmic contact electrodes for the mechanical and the J – E electrical measurements.

The current density–electric field (J – E) characteristics were measured at room temperature by using an electric circuit composed from an 500 V dc, Gelman power supply (Model: 38207 Ann Arbor, MI, U.S.A. 48106), digital multi-meter (GW Digital Multimeter Model: GDM-8034) and autoranging microvolt (Model: 197A DMM-Keithley) to measure the current passing through and voltage across the sample, respectively. The breakdown field (E_B) was measured at a current density of 1.0 mA cm^{−2} and the leakage current density (J_L) was measured at 0.75 E_B . In addition, the non-ohmic coefficient (α) determined from the current–voltage curves were plotted on a log–log scale, from which the slope of the curve gives the value (α).⁴ The donor concentration N_d , barrier height ϕ_B , density of interface states N_s and the barrier width ω were determined by using a grain boundary defect model,^{33–35} according to which, the electric conduction in the ohmic region was associated with the thermion emission of Schottky type, i.e., emission current density

$$J = AT^2 \exp[(\beta E^{1/2} - \phi_B)/kT],$$

where $A = 4\rho emk^2/h^3$ is Richardson's constant, ρ the varistor density, e the electron charge, m the electron mass, k the Boltzmann constant, h Planck's constant, ϕ_B the potential barrier height formed at the interface, E the electric field, T absolute temperature and β a constant related to the potential barrier width by the relationship

$$\beta = [(1/(r^*\omega)) (2e^3/(4\epsilon_0\epsilon_r))]^{1/2},$$

where r^* is the number of grains per unit length (it could be obtained from SEM micrographs), ω the barrier width, e the electron charge, ϵ_0 the vacuum dielectric constant (8.85×10^{-14} F cm^{−1}), ϵ_r the relative dielectric constant (8.5 for ZnO). Then N_d can be deduced from the equation:³⁶ $\omega^2 = (2\phi_B\epsilon_0\epsilon_r)/(e^2N_d)$ and the density of states $N_s = N_d\omega$ ³⁶ can also be determined.

Density ρ of the sintered specimens was measured at room temperature 25°C by the Archimedes method with toluene as immersing liquid. Also, both surfaces of each sample for which microstructure has been finished were lapped and ground with SiC paper and polished with 0.3 μ m Al₂O₃ powder to a mirror-like surface. The polished samples were chemically etched using 1HCl : 1000H₂O for 40 s and then

coated with a thin layer of gold. The surface microstructure was examined by a scanning electron microscope (SEM, JEOL, JSM5410 and Japan). The average grain size (D) was determined by the linear intercept method by using the expression, $D = 1.56L/MN$,³⁷ where L is the random line length on the micrograph, M the magnification of the micrograph and N the number of the grain boundaries intercepted by lines. The crystalline phases were identified by powder X-ray diffraction (XRD, BRUKER, D8 Advance and Germany) CuK α radiation.

For investigating the effect of sintered temperature on the mechanical properties of the tested ceramic, the ultrasonic pulse-echo-system which explained elsewhere³⁸ has been used to determine the ultrasonic attenuation, longitudinal ultrasonic wave velocity and the longitudinal elastic modulus.

3. Results and discussion

3.1 Microstructure

3.1a X-ray diffraction (XRD): The effect of sintering temperature on (XRD) traces of the tested 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic varistor, sintered at various temperatures, 825, 850, 875, 900 and 950°C for 3 h soaking time is shown in figure 1. Observed diffractographs for all records illustrated in figure 1, confirm the presence of the wurtzite hexagonal structure of the main ZnO primary phase.^{18–27,39} All diffraction peaks corresponding to this phase were indexed corresponding to their reflections of polycrystalline orientations, (100), (002) and (101),^{38,40,41} as indicated with (101) index as the high intensity major peak. In addition to the former major phase, there are some secondary phases such as Zn₃(VO₄)₂, ZnV₂O₄ and VO₂ and no phases related to Mn are detected in figure 1. The diffraction peaks which correspond to ZnV₂O₄ and VO₂ phases shown in figure 1 are decreased with an increase in the sintering temperature and almost disappear in the ceramics sintered at 900 and 950°C, respectively, since these phases are liquid phases after 690°C.^{18,19,39} The appearance of the Zn₃(VO₄)₂ phase at 900°C is consistent with earlier reports of V₂O₅-doped ZnO ceramics.^{11,16–19} It was found that the type of Zn₃(VO₄)₂ polymorphs (α , β or γ) formed is dependent on the V₂O₅ content, as well as on the type of additives oxides introduced into the system.^{16,17} However, the γ -Zn₃(VO₄)₂ was only detected here, in agreement with Hng and Knowles^{16,17} when the amount of V₂O₅ is ≤ 0.5 mol%, where it was also suggested that the existence of this minor phase has an effect on the electrical properties.

3.1b Scanning electron microscopy (SEM): Figure 2a–e shows the typical SEM micrographs of the ceramic system: 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄, sintered at various temperatures, 825, 850, 875, 900 and 950°C for 3 h time as indicated, respectively. Inspection of this

Figure 1. XRD traces (Cu K α) for the tested 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic sintered at different temperatures: (a) 825°C, (b) 850°C, (c) 875°C, (d) 900°C and (e) 950°C for 3 h time.

figure reveals the existence of major ZnO phase of non-uniform large shape grains, other different minor phases with small grains dispersed in the former major one, such as ZnV₂O₄, Zn₃(VO₄)₂ and VO₂ and some pores (very small black regions). The above microstructural observations in figure 2a–e are consistent with those reported for liquid-phase sintering mechanism of ZnO varistor containing V₂O₅, which gives rise to exaggerated ZnO grain growth,^{10–19,25} where ZnO has an eutectic reaction with Zn₃(VO₄)₂ at about 890°C.⁴² The average values of grain size D of the samples are calculated according to Wurst and Nelson⁴³ and listed in table 1. Referring to table 1, it is noted that D is increased from 20.55 to 27.20 μm with the increase in the sintering temperature, from 825 to 875°C and then it is decreased to 24.23 μm at 950°C. However, the obtained behaviour of change of D with the sintering temperature agrees well with the works of Hng and Chan¹⁸ and Nahm,^{19,39} where ZnO grains could probably grow rapidly in the presence of rich liquid phases related to V₂O₅ (the melting point, 690°C), e.g., Zn₃(VO₄)₂. This growth of ZnO grains takes place until 875°C, hence, the grain size decreased beyond this sintering temperature (see table 1). However, the effect of grain size on the electrical and mechanical properties will be discussed in next sections (3.2 and 3.3).

In order to confirm the phase distribution in the tested ceramics, an energy-dispersive X-ray spectroscopic (EDS) analysis is done for the ceramic specimen, sintered at 850°C, since it contains all the phases. EDS results are presented figure 3.

The EDS figure, indicates that the distribution of phases at some different chosen points arrows, 1, 2, 3 and 4 on the micrograph is consistent with those obtained from XRD records, figure 1 of this work, where

- (i) EDS at points 1 and 3 show the secondary phases, Zn₃(VO₄)₂ and ZnV₂O₄ as lying near the grain boundary.

- (ii) EDS at point 2 shows a ZnO grain of the major phase with Mn dissolved in it.
- (iii) EDS at point 4 shows the secondary phase VO₂.

In general, no peak for V species is found at the grain interior within EDS detection limit though the ion radius of V is smaller than that of Zn. This means the V species are not dissolved into the ZnO grain.⁴⁴ The EDS analysis in figure 3 shows that V species are segregated at grain boundaries.

3.2 Mechanical properties

3.2a Sintered density: Figure 4 shows the variation of sintered density ρ with the sintering temperature in the tested: 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic as sintered at various temperatures, 825, 850, 875, 900 and 950°C at the same, 3 h time. This figure reveals that ρ of sintered samples is nearly decreased linearly from 5.45 to 5.30 g cm^{–3} with the increase in sintering temperature from 825 to 950°C. The observed decrease of the density with the increase in sintering temperature is in agreement with the reported results^{21–24} where it was assumed that the decrease of sintered density is ascribed to the volatility of the V-species for V₂O₅ of low melting point, 690°C when they are sintered at 900°C.

3.2b Ultrasonic attenuation and velocity: The ultrasonic attenuation A (the decay rate of the ultrasonic wave as it propagates through material) and the longitudinal velocity V_L , were investigated in the tested ceramic system. However, variations of A and V_L , with the sintering temperature of the tested ceramic system are shown in figure 5. Inspection of this figure and table 1 indicates that as the sintering temperature increases from 825 to 875°C, A increases from 2373 to 2781.5 dB m^{–1} and V_L decreases from 648.42 to 577.5 m s^{–1}, respectively. On increasing the sintering

Figure 2. (a–e) Typical SEM micrographs of the 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic sintered at different temperatures: (a) 825°C, (b) 850°C, (c) 875°C, (d) 900°C and (e) 950°C as indicated.

temperature, from 875 to 900°C, the attenuation decreased to 1770 dB m⁻¹ and the velocity has increased to 1577.56 m s⁻¹, finally, these parameters, followed their opposite behaviours of change with further increase in the sintering temperature

to 950°C, where V_L decreased to 1185.8 m s⁻¹ and A increased to 1863.5 dB m⁻¹, respectively. Anyhow, the longitudinal elastic modulus behaves similarly as V_L overall the investigated range of sintering temperatures (see table 1).

Table 1. Average calculated values of the grain size D , the bulk density ρ , ultrasonic attenuation A , longitudinal velocity V_L and longitudinal elastic modulus.

Sintering temp. (°C)	D (μm)	ρ (kg m ⁻³ * 10 ³)	A (dB m ⁻¹)	V_L (m s ⁻¹)	L (GPa)
825	20.55	5.45	2376	648.42	2.29
850	21.61	5.42	2731	586.3	1.86
875	27.20	5.39	2781.5	577.5	1.80
900	23.84	5.35	1770	1577.56	13.31
950	24.23	5.30	1863.5	1185.8	7.45

Figure 3. EDS analysis at some marked points on the SEM micrograph of the ceramic system: 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄, sintered at 850°C for 3 h holding time.

The observed dependence of the ultrasonic attenuation, the longitudinal velocity and the modulus of tested ceramics, on sintering temperature, which observed in figure 5 could be related to the microstructure, i.e., the grain size. It has been reported^{37,45} that heterogeneities, such as pores, microcracks, and grains, decrease the velocity of both longitudinal and shear ultrasonic waves. Also, particle size can affect ultrasonic velocity of wave propagation in the manner that increasing the average particle size decreases both the velocity and the modulus, and increases the ultrasonic attenuation.^{37,45} Hence, with reference to, table 1 and figure 5, it can be seen that as the grain size of the tested ceramic has increased on increasing the sintering temperature from 825 to 875°C, the velocity and the elastic modulus are decreased, while the attenuation of ultrasonic waves is increased. When the grain size decreased on increasing the sintering temperature from 875 to 900°C, the velocity and the elastic modulus are increased and the attenuation of ultrasonic waves

is decreased. However, the former conversing behaviours of changes for the mentioned investigated parameters is observed as the grain size tended to increase again up to 900°C in agreement with the previous work.^{37,45}

3.3 Electrical measurements investigations

3.3a The (*J*–*E*) characteristics: The effect of sintering temperature on the electrical properties of the tested 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic as sintered at various temperatures, 825, 850, 875, 900 and 950°C at 3 h soaking time were characterized by their current density–electric field (*J*–*E*) characteristics. Figure 6 shows the typical *J*–*E* curves obtained from the electrical measurements. Inspection of this figure reveals that all the *J*–*E* plots are basically characterized by non-ohmicity, where each of which is divided into an ohmic region before the breakdown and a non-ohmic one after it with some overlap between them.

Figure 4. Variation of sintered density of 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic with the sintering temperature with error bars are indicated.

Figure 5. Variations of the ultrasonic attenuation and longitudinal velocity with the sintering temperature as indicated.

The J – E curves are entirely different in accordance with sintering temperature. However, it can be seen that, the sharper the knee of the curves between the two regions, the better the non-linearity properties. Considering the onset point of non-linearity on each plot in figure 6 as that one which corresponds to electric field E_B at which the current density = 1 mA cm^{–2}, the average values of the electrical parameters, are determined and summarized in table 2.

3.3b The breakdown field and grain size: The dependences of the breakdown field, E_B and average grain size, D of the ceramic tested, on the sintering temperature are shown in figure 7. A converse behaviours of changes for both above parameters are obtained. However, from this figure and table 1 it is observed that, as the sintering temperature has increased, from 825 to 850°C, the E_B decreased rapidly from 2110 to 1570 V cm^{–1}, then it is slowly decreased to 1427 V cm^{–1} at 950°C. While, the average grain size has increased from 20.55 μm at 825°C to 27.20 μm at 875°C and thence it decreased, up to 24.23 μm, at 950°C.

The behaviour of E_B in accordance with sintering temperature, can be analysed according to the following relation:^{2,26,27} $V_B = N_{gb} \cdot V_{gb} = (t/D)V_{gb}$, where N_{gb} is the number of grain boundaries across the sample thickness t , V_{gb} is the breakdown voltage per grain boundary and D is the average grain size. This relation indicates that the values of D and V_{gb} are directly affecting the value of E_B . Therefore, the decrease of E_B with an increase in the sintering temperature is attributed to the decrease in the number of grain boundaries due to the increase of the average grain size D and the decrease of breakdown voltage per grain boundaries V_{gb} , from 4.34 to 3.18 V gb^{–1}, as the sintering temperature has increased from 825 to 950°C (see table 2). These results show the great dependence of the microstructure on the sintering temperature, as the secondary liquid-phase sintering mechanism for ZnO varistors containing V₂O₅, can give rise to, exaggerated ZnO grain growth.^{9–17} Besides, ZnO has an eutectic reaction with Zn₃(VO₄)₂ at ≈890°C⁴² and for sintering at temperatures ≥900°C, it has been suggested that the liquid phase Zn₃(VO₄)₂ enhances densification by solution and re-precipitation of ZnO.¹⁰

3.3c Leakage current density and donor concentration:

The variations of both the leakage current density J_L and donor concentration N_d with the sintering temperature in the tested ceramic are illustrated in figure 8. From this figure it is noted that N_d decreases from 5.15×10^{17} to 2.85×10^{17} cm^{–3} with an increase in the sintering temperatures from 825 to 875°C. However, further increase in the sintering temperature to 950°C resulted in an increase in N_d and it has a value of 9.21×10^{17} cm^{–3}. The above behaviours of N_d in figure 8, could be attributed according to the following: (i) the role of Mn species which can act as donors due to the reduction effect of the ZnO–V₂O₅ system by the Mn₃O₄ oxide ($\text{Mn}_3\text{O}_4 + \text{O}_2 \rightarrow 3\text{MnO}_2$) which affects the oxygen pressure^{31,46} and (ii) the dissociation of ZnO into positive Zn ions in interstitial sites and electrons as the sintering temperature increases.^{24,46}

Thus, the decrease of donor concentration with the increase in the sintering temperature from 825 to 875°C as observed in figure 8 is associated with an increase of partial pressure of oxygen (P_{O_2}) in the varistor according to $N_d \propto P_{\text{O}_2}^{-1/4}$ or $P_{\text{O}_2}^{-1/6}$.^{31,46} While, after 875°C, the increase of N_d -value is related to the dissociation of ZnO into positive zinc ions Zn* and electrons in interstitial defect sites according to the chemical decompositions: $\text{ZnO} \rightarrow \text{Zn}(\text{neutral}) + (1/2)\text{O}_2$ and $\text{Zn}(\text{neutral}) \rightarrow \text{Zn}^* + e^-$.^{24,46} However, the J_L showed a fluctuating change (its value increased, decreased and slightly increased in the range, 0.261–0.328 mA cm^{–2}), as the sintering temperature has increased from 825 to 950°C.

3.3d The non-linear coefficient (α) and barrier height (ϕ_B):

The dependences of both the non-linear coefficient α and the barrier height ϕ_B on sintering temperature in: 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ ceramic are shown in figure 9. A similar behaviour of change for both of α and

ϕ_B with sintering temperature is obtained. The non-linear coefficient of tested varistor is remarkably decreased from 14.91 to 6.71 with the increase in the sintering temperature from 825°C up to 850°C, increased to the value, 19.81 at 875°C and finally it decreased again to 10.33 with the further increase in the sintering temperature up to 950°C. Likely, the barrier height has shown, a decrease from 0.923 to 0.894 eV, an increase from 0.894 to 0.928 eV and finally a decrease from 0.928 to 0.914 eV, with the increase in the sintering temperature, from 825 to 850°C, from 850 to 875°C and from 875 to 950°C, respectively. According to the theory of the non-linear varistors,⁴⁷ it has been reported that the role factors affect the non-linear coefficient was the height of the Schottky barrier in the grain boundary given by the formula $\phi_B = e^2 N_s^2 / 2 N_d \epsilon$, where e is the charge of an electron, N_s , the density of the acceptors in the grain boundary in the grain, ϵ the dielectric constant of the varistors. Therefore, the behaviour of α in accordance with sintering temperature can be closely related to the variation of the Schottky barrier height ϕ_B as shown in figure 9. The behaviour of ϕ_B , in accordance with sintering temperatures accords to the behaviours of both N_s at the grain boundaries and the barrier width ω coincides with the behaviour of α (see table 2) so that the higher barrier height gives rise to the higher non-linear coefficient, which shows generally that as the barriers width on

both sides of the grain is increased a low concentration of both N_d and N_s is occurred and *vice versa*.

Now, from the above electrical results which, illustrated in figures 6–8 and summarized in table 2 it is noted that, on increasing the sintering temperature, the leakage current density J_L is closely related to the non-linear coefficient α , and the Schottky barrier height ϕ_B , at the grain boundaries of the tested 99 mol% ZnO–0.5 mol% V₂O₅–0.5 mol% Mn₃O₄ varistor. The variation of leakage current density

Figure 7. Dependences of both the breakdown field E_B and average grain size D of the ceramic tested on the sintering temperature.

Figure 6. J – E characteristics of the samples, sintered at different sintering temperatures (°C), as indicated.

Figure 8. Variations of both leakage current density J_L and donor concentration N_d with the sintering temperature in the tested ceramic.

Table 2. Electrical parameters: breakdown field E_B , voltage per boundary V_{gb} , non-linear coefficient α , current density J_L , barrier height ϕ_B , donor concentration N_d , surface state density N_s and barrier width ω .

Sintering temp (°C)	E_B (V cm ⁻¹)	V_{gb} (V gb ⁻¹)	α	J_L (mA cm ⁻²)	ϕ_B (eV)	N_d (cm ⁻³ * 10 ¹⁷)	N_s (cm ⁻² * 10 ¹²)	ω (nm)
825	2110	4.34	14.91	0.304	0.923	5.15	2.11	41.01
850	1710	3.70	6.71	0.328	0.894	3.73	1.77	47.42
875	1610	4.38	19.81	0.261	0.928	2.85	1.58	55.28
900	1536	3.66	13.97	0.290	0.923	3.30	1.69	51.23
950	1427	3.46	10.33	0.308	0.914	9.21	2.81	30.53

Figure 9. Dependences of both the non-linear coefficient α and the barrier height ϕ_B , on sintering temperature.

J_L is opposite to both variations of the non-linear coefficient α , which is consistent with the grain boundary defect model^{26,27,47} where it is apparent that the leakage current density increases with the decrease in the barrier height and also the non-linear coefficient due to the increase in the sintering temperature. Also, it was found that the type of $Zn_3(VO_4)_2$ polymorphs (α , β or γ) formed is dependent on the V_2O_5 content, as well as on the type of additives oxides introduced into the system,^{2,16,17} where the γ - $Zn_3(VO_4)_2$ was only detected, when the amount of V_2O_5 is ≤ 0.5 mol%, where the existence of this minor phase affects the electrical properties by its lower conductivity at 900°C sintering temperature. However, this secondary phase disappeared for the ceramic sintered at 950°C which indicates the rapid decrease in the barrier height and the non-linear coefficient as seen in figure 1 in agreement with previous results.^{2,16,17}

4. Conclusion

Effects of sintering temperature in the range from 825 to 950°C on the microstructure, sintered density, mechanical and electrical properties of the varistor ceramic 99 mol% ZnO–0.5 mol% V_2O_5 –0.5 mol% Mn_3O_4 , prepared by solid-state reaction, were investigated. The sintered density has approximately decreased linearly with the increase in the sintering temperature from 825 to 950°C. XRD and SEM investigations showed the presence of the major ZnO wurtzite phase of hexagonal structure and some secondary phases, such as, $Zn_3(VO_4)_2$, ZnV_2O_4 and VO_2 which confirmed by EDS analysis and disappeared after 900°C.

For the results of mechanical properties, the ultrasonic attenuation, longitudinal wave velocity and the longitudinal elastic modulus, it is noted that, on increasing the sintering temperature, all of these parameters showed great dependences on the ceramic microstructure (the average grain), i.e., as the grain size increases both the velocity and the modulus decrease while the attenuation increases and *vice versa*.

About the electrical investigations, leakage current density J_L is closely related to the non-linear coefficient α , and the Schottky barrier height ϕ_B , at the grain boundaries of the tested 99 mol% ZnO–0.5 mol% V_2O_5 –0.5 mol% Mn_3O_4 varistor which showed their dependences on the donor concentration, the surface density of states and the barrier width at either sides of grain boundaries. However, the dependences of the above electrical properties has been interpreted according to the following: (i) the role of Mn species which can act as donors due to the reduction effect of the ZnO– V_2O_5 system by the Mn_3O_4 oxide, which affects the oxygen pressure and (ii) the dissociation of ZnO into positive Zn ions in interstices defect sites and electrons as the sintering temperature increases from 825 to 950°C.

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