Middle-East Journal of Scientific Research 17 (8): 1002-1007, 2013
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2013.17.08.12295

Influence of Bi_2O_3 and TiO_2 Doping on Microstructural and Electrical Properties of ZnO-MnO_2-Co_3O_4 -Based Varistor

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Abstract: The physical properties, microstructure and electrical properties of ZnO – ceramics with different Bi_2O_3, TiO_2 contents and 0.5 mol% (MnO_2 + Co_3O_4) prepared by convential ceramic method and sintered at (900- 1200°C)/ 2hours were investigated. With increasing Bi_2O_3 content, the ZnO grain size decreases due to the Bi-rich phases inhibiting grain growth. Minimum water absorption was achieved at 1220°C for 2 hours and at sintering temperature above 1250°C the water absorption of all samples increased. The (I-V) characteristics of different mixes show clearly non-linear behavior. Also the result of capacitance and dielectric constant as a function of frequency at room temperature of different mixes show a decrease in capacitance and consequently in dielectric constant was recorded with rise in frequency (30-200) kHz.

Key words: Microstructure · Electrical properties · X–ray diffraction · Varistor

INTRODUCTION

ZnO based varistors have been widely used for voltage stabilization or transient surge suppression in electronic circuits and electric power systems [1-3]. Excellent nonohmic properties in the current–voltage response of ZnO varistors are attributed to grain boundary phenomena in relation to the phase formation in sintering and dopant-induced point defects [2, 5]. ZnO powders play a leading role in making surge protection devices (varistors), which are commonly used for protecting electric power systems from transient voltages [6]. In varistor devices, ZnO has been utilized in bulk quantities. Additives are usually added to improve the electric properties of varistors; increase the nonlinearity behavior or to improve the breakdown voltage of ZnO. Varistor manufacturing is usually based on the conventional solid-state route, where > 93 mol.% ZnO powder is homogeneously mixed with several metal oxide additives such as Bi, Sb, Co, Cr, Mn, Ni, Ba, Ti and Al [7]. Sintered ZnO varistors consist of ZnO grains surrounded and separated by a thin continuous intergranular phase [8]. The addition of CoO or MnO can prevent Bi_2O_3 evaporation at the sintering temperature. CoO and MnO also improve the non-ohmic property dramatically. The present work aims at the examination of the effect of Bi_2O_3 and TiO_2 doping on the properties of ZnO-MnO_2-Co_3O_4 (Mn/Co = 0.5) system using XRD, (I-V), RCL circuits and SEM.

MATERIALS AND METHODS

Reagent – grade raw materials were prepared for ZnO ceramics. Four mixes were suggested to study the effect of Bi_2O_3 and TiO_2 doping on the properties of ZnO –MnO_2 – Co_3O_4 (Mn / Co = 0.5) and is given in Table 1.

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Table 1: Composition of different mixes in mol%.

Oxides		ZnO mol%	MnO_2 mol%	Bi_2O_3 mol%	Co_3O_4 mol%	TiO_2 mol%
Sample	T1	98.4	0.5	0.3	0.5	0.3
	T2	98.0	0.5	0.5	0.5	0.5
	T3	97.6	0.5	0.7	0.5	0.7
	T4	97.2	0.5	0.9	0.5	0.9

The mixture was calcined in air at 750°C for 2 hours. The calcined powders were prepared into discs of 1.2 cm diameter and 0.2 cm thickness. These discs were processed by a semi-dry press method under 70 KN. The discs were sintered at 900 – 1200°C, with interval by 25°C/ min. XRD and SEM identified the phases present. The silver paste was coated on both faces of samples. The PM 6304 programmable automatic RCL meter was used for precise measurements of resistance, capacitance and inductance. From the measured values of capacitance, the dielectric constant at all frequency from 1 to 200 kHz was calculated at constant temperature. The capacitance and resistance at constant temperature were measured at different frequencies between 1-200 kHz and the respective permittivity [ϵ'] and conductivity [σ] were calculated.

RESULTS AND DISCUSSION

Minimum water absorption was displayed in specimens fired at 1220°C for 2 hours as shown in Fig. 1. The content of pores both closed and open governs the degree of densification reached at maturity. Minimum water absorption does not mean maximum densification. Also the content of closed pores affect to a greater extent the sinterability of the varistor body produced. Usually different mixes displayed a percent not exceeding 98%, minimum water absorption appears in sample (T4) equal to 1.025. This temperature was the selected as the proper maturing temperature for all mixes. Above 1220°C, deformation of all samples was started and addition of 3.828 mol% Bi_2O_3 in presence of Co_2O_3, MnO_2 and TiO_2 lead to a better densification by minimizing the presence of closed pores. Also maximum values of firing shrinkage were attained in specimens fired at 1200°C for 2 hours as shown in Fig. 2. Higher sintering temperatures (>1200°C) and longer sintering times give rise to a reduction in bulk densities. This is due to the increased amount of porosity between the large grains of ZnO, resulting from the rapid grain growth induced by the liquid phase sintering and also the loss of Bi_2O_3. Fig. 3 shows the X-ray diffraction patterns of different mixes containing ZnO, Bi_2O_3, TiO_2, Co_2O_3 and MnO_2 which are referred to as T_1, T_2, T_3 and T_4.

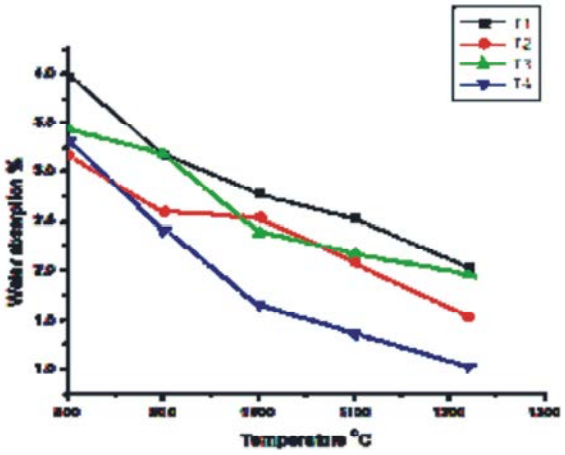

Fig. 1: Water absorption of different mixes

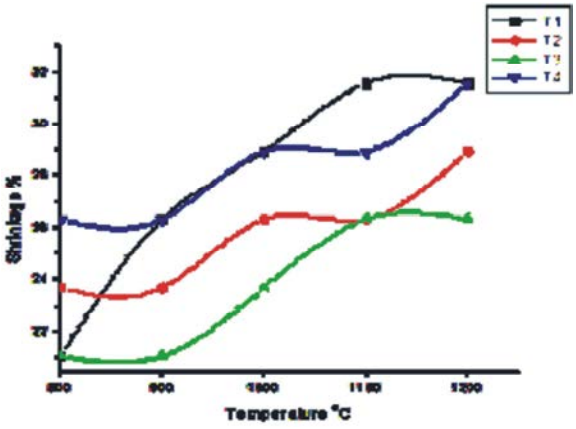

Fig. 2: Firing shrinkage % of different mixes

XRD patters of sample T_1, in which ZnO can be detected by the diffraction at about 2θ = 31.795 (d = 2.81214 Å), 2θ = 34.444 (d = 2.60174 Å), 2θ = 36.274 (d = 2.47453 Å), 2θ = 47.58 (d = 1.90959 Å), hexagonal structure, the lattice constants of ZnO are a = b = 3.2490 and c = 5.2052 (PDF number is -(186)-2-47.5847). Mausmannite- Mn2O3 can be detected at about 2θ = 28.8 (d = 3.09745 Å), 2θ = 32.549 (d = 2.74877 Å), tetragonal structure, the lattice constants are a = b = 5.76500 and c = 9.44200 (PDF number is (141)-4-313.807).

XRD patterns of sample T2, containing 97.6 wt% ZnO, 0.7 wt% TiO_2, 0.5 wt% Co_3O_4 and 0.5 wt% MnO_2 and in which ZnO can be detected by the diffraction at about

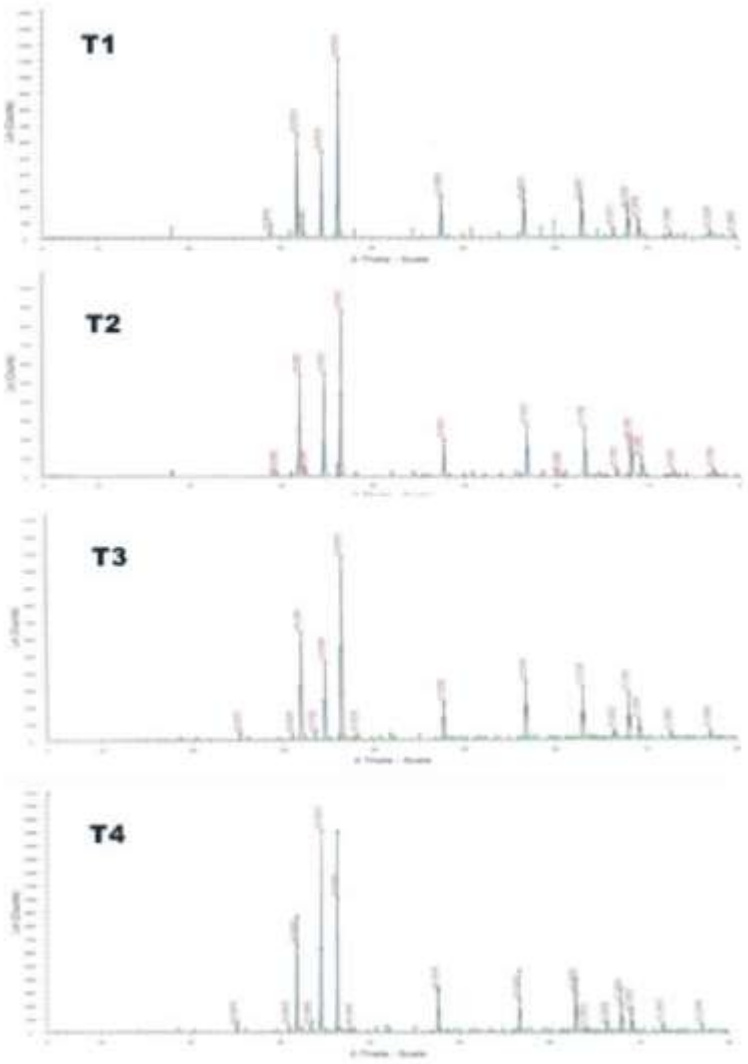

Fig. 3: XRD of different mixes

$2\theta = 31.942$ (d = 2.79957 Å), $2\theta = 34.608$ (d = 2.58972 Å), $2\theta = 36.34$ (d = 2.46427 Å), hexagonal structure, the lattice constants are a = b = 3.24170 and c = 5.18760 (PDF number is (186)-2-47.2110). Anatase-TiO_2 can be observed at about $2\theta = 29.419$(d = 3.03362 Å), $2\theta = 32.656$ (d = 2.73997 Å), tetragonal structure, the lattice constants are a = b = 3.80400 and c = 9.61400 (PDF number is (141)-4-139.119). Hausmannite Mn_3O_4 can be detected at about $2\theta = 29.419$ (d = 3.03362 Å), $2\theta = 32.656$ (d = 2.73997 Å), tetragonal structure, the lattice constants are a = b = 5.76500 and c = 9.44200 (PDF number is (141)-4-313.807).

XRD patterns of sample T3, containing 98 wt% ZnO, 0.5 wt% Bi_2O_3, 0.9 wt% TiO_2, 0.5 wt% Co_3O_4 and 0.5 wt% MnO_2, revealed that ZnO has hexagonal structure, Anatase (TiO_2) has tetragonal structure and Mn_3O_4 has lattice constants, a = b= 9.79960 and c = 3.02400 .

XRD Patterns of sample T4 containing 98.4 wt% ZnO, 0.3 wt% Bi_2O_3, 0.3 wt% TiO_2, 0.5 wt% Co_3O_4 and 0.5 wt% MnO_2 showed that the main peaks correspond to the contributing oxides, namely ZnO, TiO_2 and Mn_3O_4 , have hexagonal, tetragonal and orthorhombic structure respectively. The absence of any diffraction line Bi_2O_3, Co_3O_4, can be attributed to: (i) A complete dissolution of this dopants oxides in the lattice of ZnO and forming solid solution (ii) The presence of this dopants substituted (Bi_2O_3, Co_3O_4) in a concentration butting the deflection limit of X-Ray refractomater. (iii) The possibility of existence of TiO_2, Bi_2O_3 and Co_3O_4 in extremely small size that could not be detected by XRD. The presences of different oxides (ZnO, Bi_2O_3, TiO_2, Co_3O_4 and MnO_2) together increase the crystal size of ZnO (Clustering of ZnO particles).

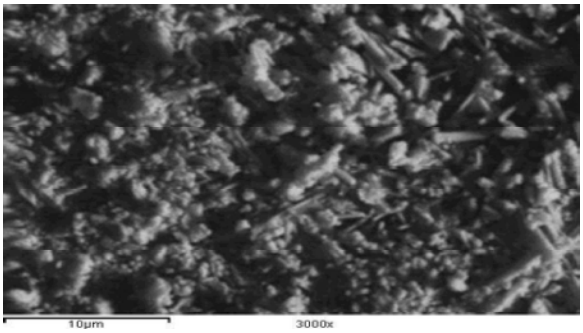

Fig. 4: SEM of mix T1,thermally etched, shows different of prismatic grains, randomly oriented X=3000

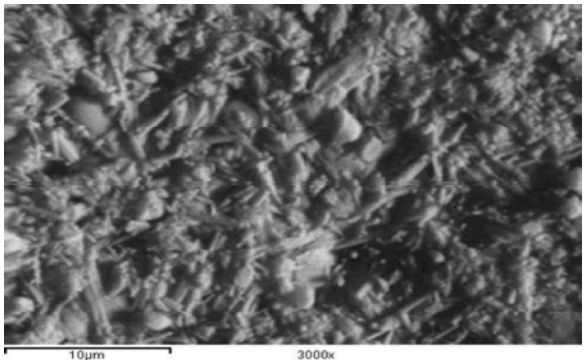

Fig. 5: SEM of mix T2 , Thermally etched, shows different prismatic grains, randomly oriented X=3000

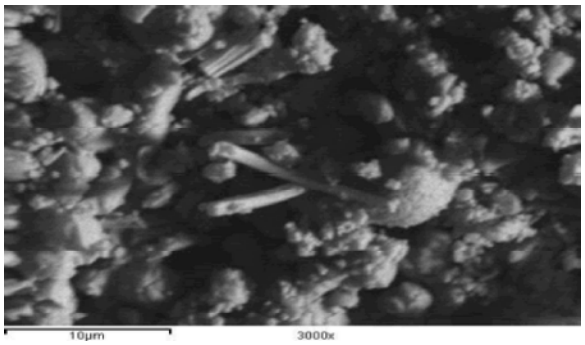

Fig. 6: SEM of sample T3, thermally etched surface, shows two phases , ZnO grain and inter-granular phase at triple point, different prismatic grains X=3000

SEM of mixes T1 shown in Fig. 4 revealed different shapes of prismatic grains of ZnO, Bi-rich phase in the triple point and an increase in the presence of liquid phase on the grain boundary. SEM of mix T_2 present in Fig. 5 showed different shapes of prismatic grains of ZnO, Bi-rich phase, also Ti, Co and Mn go into solid solution in the ZnO grains. The different prismatic grain, randomly oriented, Zn is exsoluted accumulating at grain

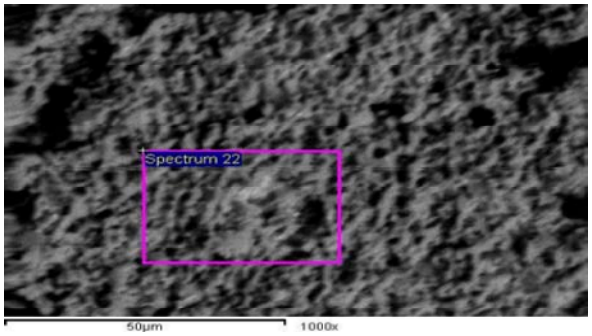

Fig. 7: Thermally etched surface, amplification of above image

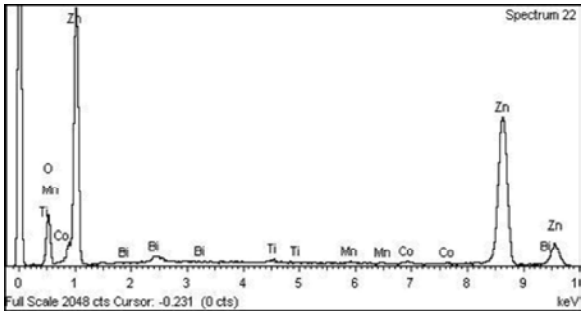

Fig. 8: EDAX of above image show the distribution of Bi_2O_3, TiO2, MnO_2 with ZnO and Co_2O_3 intergranular accumulation

boundaries. SEM of mix T3 present in Fig. 6, amplified in Fig. 7, shows two phase, ZnO grain and intergranular phase at triple point, also Bi, Ti, Co, Mn, go into solid solution in ZnO grains. There are different prismatic grains, randomly oriented, Zn is exsoluted accumulating at grain boundaries (white colour), grain growth is evident.

EDAX of mix T3 presented in Fig. 8 showed that the concentration of Bi_2O_3, TiO_2, MnO_2, with ZnO and CoO occurred in intergranular accumulation. Ceramic varistors based on Bi_2O_3-containing ZnO consists of large ZnO grains with Bi-rich phases at the grain boundaries and junctions. The characteristics of varistors relate to the developed crystalline phases. The formation mechanism of varistors occurs through three stages [6]. In the first stage, a Bi-rich liquid starts to form at 735°C, the eutectic temperature in the ZnO–Bi_2O_3 system. The liquid phase diffuses into the ZnO grains through the boundaries. In the second stage, the liquid phase acts as a densification factor. The presence of Bi_2O_3-ZnO as the phase at the equilibrium and the compositional shift of the eutectic point to higher ZnO concentration have been observed.

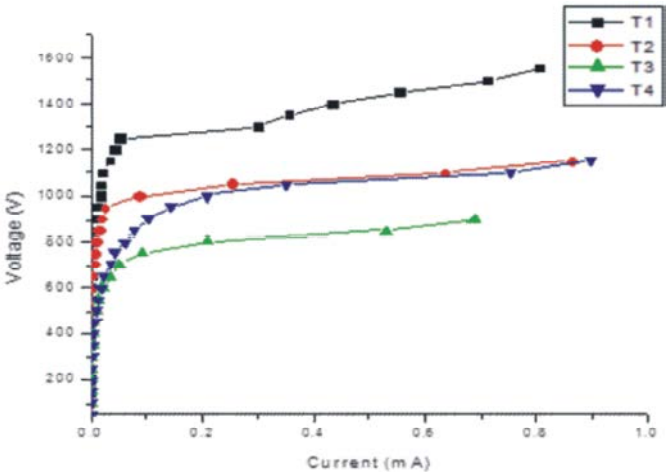

Fig. 9: I-V Characteristics of different mixes

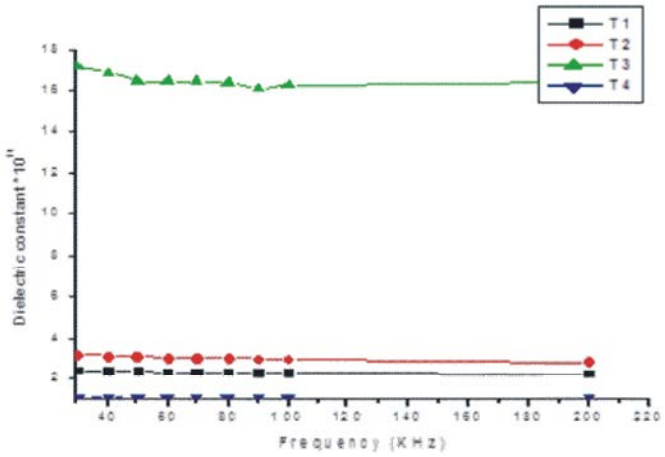

Fig. 10: AC Dielectric constant as function frequency at room of different mixes

The (I-V) characteristics were measured between (0 - 5) kV and current between (0 -10) mA. The relation between I and V for the different mixes is shown in Fig. 9. It is evident that the mixes of different groups show clearly non-linear behavior. The nonlinear (I–V) characteristic behavior is expected to be related to the development of the secondary intergranular phases along the grain boundaries and grain junctions. The secondary phases crystallized from the Bi-rich liquid phase. The Bi-rich liquid phase results from the fusion of Bi_2O_3 that diffuses into the grain boundaries of the large zinc oxide grains. The Bi_2O_3 liquid phase dissolved a considerable amount of zinc cations from the oxide grains along the boundaries, resulting in the Bi-rich liquid phase. The Bi-rich liquid phase starts to precipitate the secondary phases across the boundaries. At the same time, the liquid phase improves the sintering process. A decrease in capacitance and consequently in dielectric constant was recorded with the rise in frequency from 30 to 200 kHz as shown in Fig. 10. This decrease has been attributed to the increased intergranular porosity resulting from discontinuous grain growth and the absence of the space charge polarization at the higher frequency. The apparent dielectric constant (ε^{-}) decreased with less sharp dispersive drop with increasing frequency, which is closely associated with the polarization of dielectrics. This could be attributed to the decrease of conduction carriers as a result of the test frequency. Also, this may be explained in the light of microstructure of semi-conductive ZnO grains formed, which is surrounded by insulating glassy phase. This is similar to that of grain boundary layer capacitors as a result of the observed dielectric constant increase with the increase in dopant oxides. It is well known that the incorporation of same Zn into the intergranular layer would alter the true value of (ϵ^{-}) somewhat incorporation of varying proportions of some

the metal oxide additives into the ZnO grains. It is also possible that a heterogeneous mixture composed of two or more phase, which differs from conductivity, shows a dielectric dispersion due to the so-called interfacial polarization.

The relation between conductivity and frequency for different mixes increases with increasing frequency at room temperature. This may be attributed to the increase in the number of dipoles. The increase of frequency raised the conductivity due to the increase in the ionic response to the field. Again this is related to intergranular material at the field at any particular temperature. The addition of dopants to a ZnO-based varistor decreases the grain size of the ZnO. The diffusion of excess oxygen ions into the ZnO grain boundaries has been noted as the important acceptor-like defects that account for the double Schottky barrier of ZnO varistors [9, 10].

CONCLUSION

The physical properties, microstructure and electrical properties of ZnO – ceramics with different Bi_2O_3, TiO_2 contents and 0.5 mol% ($MnO_2 + Co_3O_4$) were investigated. Bi_2O_3 and TiO_2 also improve the non-ohmic property dramatically. Furthermore the addition of 0.5 mol% (MnO_2 + Co_3O_4) enhanced the physical properties of ZnO-cermics.

ACKNOWLEDGMENTS

This work was supported by Omar Al-Mukhtar University, Al-Bayda, Libya.

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