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Effect of MnO_2 on Electrical Properties of ZnO-V_2O_5-Based Varistors

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Abstract: The effect of MnO_2 on the physical and electrical properties of ZnO-V_2O_5-based ceramics is investigated in this work. The microstructure and electrical properties of varistors, which are composed of ZnO-V_2O_5-MnO_2-based ceramics, were investigated in the range of 0.5-1.5 mol% MnO_2. All samples exhibit non-linear current-voltage behaviour. 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. Also maximum values of firing shrinkage were attained in specimens fired at 1200°C for 2 hours.

Key words: Electrical properties · Varistor · MnO_2 · Shrinkage

INTRODUCTION

The original varistor ceramics were developed in the early 1930s to replace early selenium rectifiers for protecting telephone system. The materials developed by the bell system consisted of partially sintered compacts of SiC particles [1, 2]. ZnO varistors are highly complex, multicomponent, polycrystalline oxide ceramics whose electrical behavior depends both on the microstructure of the device and on detailed processes occurring at the ZnO grain boundaries. Additives are usually added to improve the electric properties of varistors; increase the nonlinearity behavior or to improve the breakdown voltage of ZnO. The basic structure of ZnO varistors is formed by addition of a varistor-forming ingredient to ZnO. These are heavy elements such as Bi, Pr, Ba and Nd with large ionic radii. Now varistors are available that can protect circuits over a very wide range of voltages, from a few volts for low-voltage varistors in semiconductor circuits to tens of kilovolts for electrical power distribution networks. Varistors are electronic materials capable of protecting circuits from over voltages. They exhibit a based varistor nonlinear current-voltage relationship that can be expressed by the empirical equation:

$$I = (V/C)^{\alpha}$$

Where V is the applied voltage; I the current and C a constant corresponding to the nonlinear resistance and α is a characteristic exponent. The typical composition of a ZnO - based varistor consists of ZnO and a few mole percent of other oxide additives and dopants such as Sb_2O_3 , Bi_2O_3 , Co_3O_4, MnO and Cr_2O_3 [3]. Sintered ZnO varistors consist of ZnO grains surrounded and separated by a thin continuous intergranular phase [4]. The addition of Co_3O_4or MnO can prevent Bi_2O_3 evaporation at the sintering temperature and the addition of Cr_2O_3 can control ZnO grain growth [5]. Co_3O_4 and MnO also improve the non-ohmic property. Vanadium oxide doped ZnO system exhibits multifunctional properties, which makes it an interesting material for technological applications.

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Single phase ZnO-V_2O_5 system has been considered as a diluted magnetic semiconductor (DMS) material, as ferromagnetism in DMS is one of the interesting problems of this century in condensed matter physics [6]. Ferromagnetism in vanadium doped ZnO was predicted theoretically by Sato and Yoshida [7] and very few experimental researches on V: ZnO powders were reported [8]. ZnO-V_2O_5 system is interesting not only in terms of its room temperature ferromagnetism but also as a transparent ferromagnetic material [9]. On the other hand, multi-phase ZnO-V_2O_5 exhibits varistors behavior which is also quite interesting because in all metal oxide doped ZnO systems, varistor behavior appear due to greater metal ion but in ZnO-V_2O_5 smaller vanadium ion is responsible [10-14].

For proper understanding of different features of ZnO-V_2O_5 system like the formation of different phases, arise of ferromagnetic behavior, change in structure due to vanadium doping, optical band gap tuning, the appearance of vibrational modes induced by vanadium doping, etc., a detailed study is required to cover these aspects. Although magnetic properties of a vanadium doped ZnO system are recently of interest but structural, compositional and vibrational characterization of this material has rarely been reported. With $3d^3$ $4s^2$ electron configuration, V doping is expected to modify the defective structure and optical properties of ZnO.

This motivated us to investigate V_2O_5 (a layered crystal structure having no 3d electrons with band gap of 2 eV) doped ZnO properties in bulk form. The advantage of vanadium-doped ZnO varistors is that the ceramic can be sintered at a relatively low temperature of about 900 °C. This is important for multilayer components because such ceramics can be co-fired with a silver inner-electrode having a melting point of around 960 °C [15]. V_2O_5 is also a better sintering aid compared to Bi_2O_3 since it has been found that V_2O_5-doped ZnO materials can be densified to the same density at a lower temperature compared to Bi_2O_3-doped ZnO materials [16]. Although there were numerous studies on the effect of additives on ZnO varistors, the additives' effect on the performance of ZnO-V_2O_5 varistor systems has not been researched systematically. Other than a report on the effect of Mn_3O_4 doping in ZnO-V_2O_5 ceramics prepared by microwave sintering [17], most reports were on the combined effects of different oxide additives [16,18]. In previous work, it reported the combined effects of MnO_2, Co_3O_4 and Sb_2O_3 on the ZnO-V_2O_5 binary system [18].

It was found that MnO_2 is the most effective in increasing the nonlinear behaviour compared to Co_3O_4 and Sb_2O_3. Moreover, it was found that 0.5 mol% V_2O_5 gives the optimum electrical properties. The reaction between the ZnO and the additives at high temperatures leads to the formation of several phases at the ZnO grain boundaries [19, 20]. Thus, despite their chemical composition and phases, the processing method as well as the sintering temperature, heating and cooling rates influence the electrical properties of these ceramics fundamentally [21]. However, additives such as CoO, MnO_2 and ZnO promote high densification, which makes it possible to define the varistor behavior. A very high nonlinearity coefficient ($\alpha = 41$) was obtained in the SnO_2-CoO-Nb_2O_5 system (1.0 mol% of CoO and 0.05 mol% of Nb_2O_5) when 0.05 mol% Cr_2O_3 was added [22]. To develop nonlinear ceramics of high performance, it is very important to comprehend the influences of additives on non- linear properties. MnO2 is often added to ZnO-Bi_2O_3 system to improve the varistor properties [23, 24]. Hence, in this work, the effects of MnO2 content on water absorption, total shrinkage, the microstructure and the electrical characteristics of the ZnO-V_2O_5-MnO_2 system were examined. X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and standard electrical measurement procedures were used.

MATERIALS AND METHODS

High-purity oxide powder starting materials were used for the preparation of the ZnO varistor samples. MnO_2, in the range 0.5-1.5 mol%, was mixed with a mixture of ZnO -mol% V_2O_5 powder by ball milling with alumina balls and deionized water for 2 h. All powders were prepared using a mixed oxide method in water medium for 2h. The mixtures were then dried at 110°C for 24h and calcined in muffle kiln at 750°C for 2h.The calcined powders were sieved and then pressed into discs (1, 2 cm diameter and 0.2cm thickness). The green samples were sintered in muffle kiln with a rate of heating of 5°C/ min in temperature range between (900-1200) °C for 2 h. Both sides of the sintered samples were lapped (1mm thick) and then polished. The sinterability of the different samples was determined in terms of physical properties. To measure the electrical properties, silver pastes were coated on both sides of sintered samples. The microstructures of samples were examined via the scanning electron microscopy (SEM, Joel-JEM.T200). The phase compositions of the powder samples were analyzed by X-ray diffractometry (XRD, Philips apparatus type 170, a vanadium, λ=1.54°A and Ni-filter) and the physical properties in terms, firing shrinkage, apparent porosity, bulk density and water absorption were measured via the ASTM standard [25]. The V-I

characteristics of samples were measured at room temperature with a high-voltage source measure unit (Keithley 237). The dielectric constant, resistivity and conductivity were measured at room temperature with change of frequency (1-20) kHz using RCL meter (PM 6304 programmable automatic).

RESULTS AND DISSOCIATION

The water absorption of varistor sample doped with various amounts of ZnO-V_2O_5-MnO_2 is shown in Figure 1. A decrease in water absorption was recorded with rise in maturing temperature. Minimum water absorption was displayed in specimens fired at 1220 °C for 2 hours, minimum water absorption appears in sample M3 equal to 1.356 and at sintering temperature above 1250 °C, the water absorption of all samples increased. This increase has been attributed to the increased intergranular porosity resulting from discontinuous grain growth. Results of firing shrinkage as a function of temperature of different mixes are graphically plotted in Figure 2 showed an increase with rise in temperature. Maximum values of firing shrinkage were attained in specimens fired at 1220 °C for 2 hours.

Figure 3, shows the X-ray diffraction patterns of different mixes, namely (M1, M2, M3 and M4). XRD patterns of M1, which containing 99 wt % ZnO, 0.5 wt% V_2O_5 and 0.5 wt% MnO_2. In which ZnO can be detected by the diffraction at about 2θ = 31.84 (d = 2.80832 Å), 2θ = 56.66 (d = 1.62313 Å), hexagonal structure, the lattice constants of ZnO are a = b = 3.24880 and c = 5.2054 (PDF number is (186)-2-47.587), manganese oxide MnO_2 can lattice constants of MnO are a = b = 8.42 (PDF number is (227)-8-596.948). XRD patterns of sample M2, which containing 98.6 wt% ZnO, 0.4 wt% V2O5 and 1 wt% MnO2 in which ZnO can be detected by the diffraction at about 2θ = 31.337 (d = 2.80860 Å), 2θ = 34.51 (d = 2.59685 Å), 2θ = 36.337 (d = 2.47042 Å), 2θ = 47.638 (d = 1.90740 Å), hexagonal structure, the lattice constants of ZnO are a = b = 3.2488 and C = 5.2054 (PDF number is (186)-2-47.5807). Manganese oxide MnO_2 can be observed at about 2θ = 30.02 (d = 2.97432 Å), 2θ = 35.343 (d = 2.5375 Å), cubic structure the lattice constant are a = b = c = 8.42 (PDF number is (227)-8-596.948). The addition of MnO_2 in presence of V_2O_5 decreases the crystal size of ZnO and exerted no significant trend on the change of degree of crystallenity. There is a shift in the values of 2θ and as a result in the calculated values for the lattice spacing of ZnO with addition of MnO_2. Maximum shift of

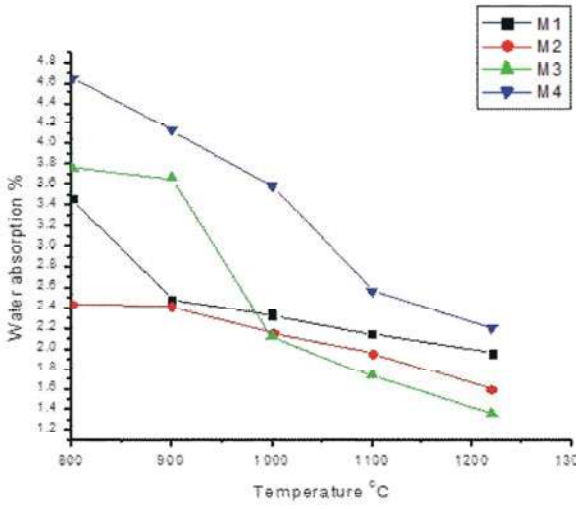

Fig. 1: Water absorption of different mixes

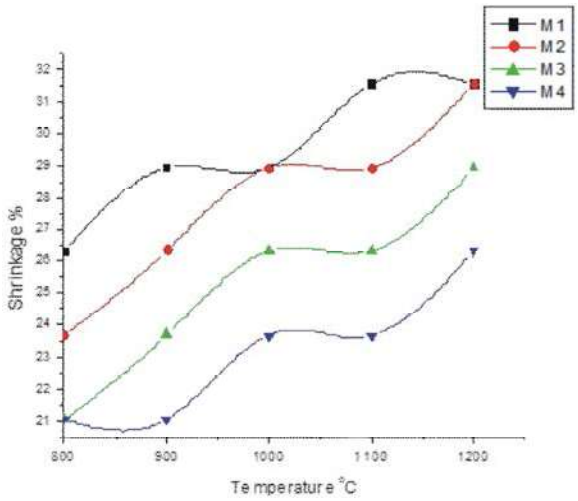

Fig. 2: Firing shrinkage % of different mixes

(0.003-0.006 Å) was recorded in mix containing 1.5 wt% MnO_2. For all samples, other than the major ZnO phase, $Zn_3(V4O)_2$ was the only secondary phase detected. No secondary phase related to MnO_2 was detected. Similar observation [26-33] was also reported and it was proposed that the V_2O_5 additive can enhance the densification and grain growth behavior of the ZnO-V_2O_5 materials due to the formation of a ZnO-V_2O_5 compound, i.e., $Zn_3(V_4O)_2$, which acts as liquid-phase sintering aid at high temperature. The type of $Zn_3(PO_4)_2$ polymorphs formed in the V_2O_5-doped ZnO varistors is dependent on the V2O5 content, as well as on the type of additive oxides introduced into the system [28, 29]. It was reported in γ-$Zn_3(V_4O)_2$ and α- $Zn_3(V_4O)_2$ phase was detected in ZnO-V_2O_5-MnO_2 and ZnO-V_2O_5-Co_3O_4, respectively, while in the ZnO-V_2O_5-MnO_2 system, when the amount of V_2O_5

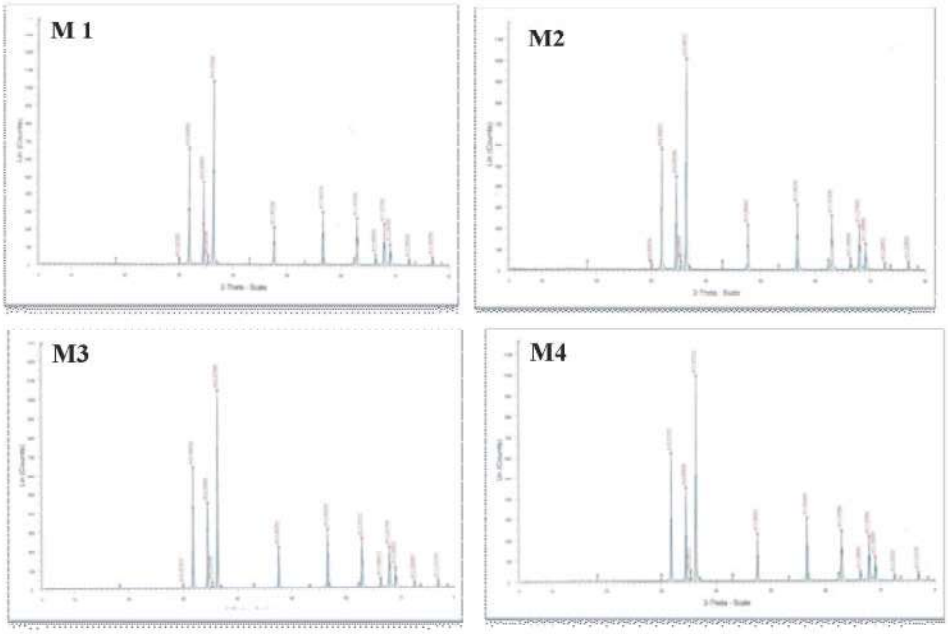

Fig. 3: XRD of different mixes ($ZnO-V_2O_5-MnO_2$)

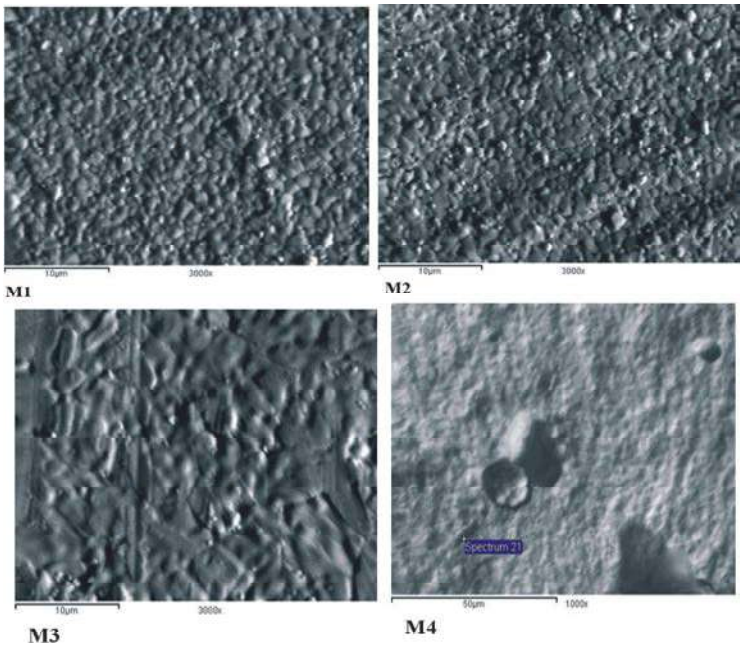

Fig. 4: SEM of different mixes ($ZnO-V_2O_5-MnO_2$).

is □ 0.5 mol% only γ- $Zn_3(V_4O)_2$ was detected in the samples. For samples containing > 0.5 mol% V2O5, both β-and γ- $Zn_3(V_4O)_2$ phase were detected.

The SEM of different mixes is present in Figure 4. The SEM of mix M2 which contains ZnO, 0.7 mol% V2O5 and 1 mol% MnO_2, M3 which containing ZnO , 1 mol% V2O5 and 1 mol% MnO_2 shows liquid phase in the triple point appears as white spots.

The SEM image of the specimens sintered at 800 °C is shown in Figure 4, M2. It is clear that since a eutectic temperature is about 600°C for V_2O_5-ZnO [34], a liquid phase sintering process might occur when the sintering temperature was higher than eutectic temperature, leading to the deification of the sintered body and ZnO grains growth. The addition of MnO_2 can restrain the growth of the ZnO grains..

CONCLUSIONS

The effect of MnO_2 on the physical and electrical properties of ZnO-V_2O_5-based ceramics is investigated. The results of EDAX microanalysis of the specimens indicate that Zn and O were detected not only in the interior of ZnO grains but also at the grain boundaries. On the contrary, V and Mn were only detected at the ZnO grain boundaries but not in the interior of ZnO grain. V and Mn simultaneously segregated at the grain boundaries and the intergranular phase should be Zinc vanadate in both ZnO-V_2O_5 and ZnO-V_2O_5-MnO_2

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