Microstructural and Nonlinear Electrical Properties of ZnO Ceramics with Small Amount of MnO$_2$ Dopant
(Sifat Mikrostruktur dan Elektrik Tak-linear Seramik ZnO dengan Kuantiti Kecil Dopan MnO$_2$)

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ABSTRACT

A small amount of MnO$_2$ dopant was added to ZnO system to see the improvement of the ceramic varistor microstructural and nonlinear electrical properties. The samples were prepared using solid-state reaction method and the microstructure and nonlinear electrical properties of the ZnO-xMnO$_2$ system were investigated for x = 0.011 to 0.026 mol%, at three sintering temperatures, 1180°C, 1240°C and 1300°C for 1 and 2 h sintering time. The XRD and EDAX analyses showed that the main phase was ZnO while ZnMnO$_3$ and ZnMnO$_7$ as the secondary phases developed and distributed at the grain boundaries and triple point junction. The SEM observation revealed that prolonged sintering temperature and time improved the microstructure uniformity and strongly influences the nonlinear behavior of the samples. The maximum density and grain size have been observed at 92% of theoretical density and 10.8 µm, respectively and occur at the highest sintering temperature which is 1300°C. The value of nonlinear coefficient α is found to increase with the increase of MnO$_2$ doping level up to 0.016 mol% and drop with further doping level increment for all sintering temperatures and time.

Keywords: MnO$_2$; nonlinear coefficient; ZnO varistor

ABSTRAK

Kuantiti kecil bahan dop MnO$_2$ ditambah kepada sistem ZnO untuk melihat peningkatan sifat-sifat mikrostruktur dan keelektrikan tak-linear seramik varistor. Sampel telah disediakan melalui kaedah tindak balas keadaan pepejal dan ciri-ciri mikrostruktur dan elektrik tak-linear bagi sistem ZnO-xMnO$_2$ telah dijalankan untuk kuantiti kecil x = 0.011 sehingga 0.026 mol%, pada tiga suhu pensinteran, 1180°C, 1240°C dan 1300ºC dengan masa pensinteran 1 dan 2 jam. Analisis XRD dan EDAX menunjukkan bahawa fasa utama adalah ZnO manakala ZnMnO$_3$ dan ZnMnO$_7$ sebagai fasa kedua terbentuk dan tertabur di sempadan butiran dan titik simpang tiga. Pemerhatian melalui SEM menunjukkan bahawa pemanjangan suhu dan masa persinteran memperbaiki keseragaman mikrostruktur dan mempengaruhi kelakuan tak-linear sampel. Ketumpatan dan saiz butiran maksimum telah diperhatikan pada 92% daripada ketumpatan teori dan 10.8 µm, masing-masing, berlaku pada suhu pensinteran tertinggi iaitu 1300ºC. Nilai daripada pekali tak-linear α didapati meningkat dengan peningkatan paras dop MnO$_2$ sehingga tahap 0.016 mol% dan menurun dengan penambahan paras dop seterusnya untuk semua suhu dan masa pensinteran.

Kata kunci: MnO$_2$; pekali tak-linear; varistor ZnO

INTRODUCTION

Zinc oxide varistors are semiconductor ceramics devices, which are widely used as a protecting device against voltage transients in electronics and industrial equipment as surge arrestors (Subasri et al. 2009). Varistors exhibit high nonlinear current-voltage characteristics, where the nonlinear characteristics are attributed to the formation of Double Schottky Barriers (DSB) at the ZnO grain boundaries (Nahm 2008).

The nonlinear current-voltage (I-V) behavior of ZnO varistors is derived from the addition of small amount of other metal oxides (Hng & Knowles 2002) such as Bi$_2$O$_3$, Sb$_2$O$_3$ and Co$_3$O$_4$ since dopant are responsible for the formation of varistor behavior (Han et al. 2002). It was believed for the application of the ZnO varistors, dopant play an important role to modify the defect concentration at the ZnO grain and/ or of grain boundary where the performance of ZnO is sensitive to the presence of some additives even when their amount is very low (Lao et al. 2009).

Careful control on the microstructure is required to produce a high performance varistors (Kelleher & Hashmi 2008). The electrical performances of ZnO varistors critically depends on the microstructure characteristics where the electrical characteristics can be controlled by modifying the microstructure at the grain boundary (Shinha & Sharma 1997). ZnO varistors exhibit nonlinear I-V characteristics and other electrical properties that are directly related to their microstructure (Han et al. 2000). There are many variables involved such as chemical composition phases, sintering temperature, sintering

time, heating and cooling rates that are fundamental to control the electrical properties of ZnO ceramics (Filho et al. 2006).

Numerous studies on the effect of additives such as Bi_2O_3, Sb_2O_3 and Co_3O_4 of ZnO varistors show that the transition metal oxides can improve the nonohmic properties of ceramics by increasing the surface state density through the formation of interstitial states and deep bulk traps. There are quite a substantial number of researchers have investigated ZnO ceramics doped with reasonable large amount of MnO_2 and most of the work has been devoted to the nonlinear electrical properties that are related to the Double Schottky Barrier at the grain boundary (Han et al. 2000, 2002; Hng & Knowles 2002; Nahm, 2008; Orlandi et al. 2003; Wu et al. 2012). The typical range of MnO_2 doping used in these previous works are between 0.1 and 2.0 mol%. However the effect of 'small amount' MnO_2 dopant which referring to the use of MnO_2 below the range of 0.03 mol% in ZnO varistor ceramic has not been fully investigated especially in term of microstructure. The present investigation was undertaken with a view for looking out the effect of 'small amount' MnO_2 dopant on the microstructure and electrical properties in ZnO system.

MATERIALS AND METHODS

High purity oxide powders as starting materials were used for the preparation of the ZnO varistor samples. Small amount of MnO_2 in the range of 0.011 - 0.026 mol% was ball milled in the deionized water for 24 h. The slurry were dried and pre-sintered at 800°C for 2 h in open atmosphere. 1.75 wt% polyvinyl alcohols binder was added to avoid cracks in the samples and then granulated by sieving through the 75 μm mesh screen. The powder from each ceramics combination was pressed into pellets with 10 mm diameter and 1 mm in thickness at a pressure of 2 ton/m². The pellets were then sintered in an open atmosphere at the sintering temperatures of 1180, 1240 and 1300°C for

1 and 2 h sintering time at the heating and cooling rate of 3°C min⁻¹. The pellets from each ceramics combination was mirror like polished and then thermally etched for microstructure analysis.

For XRD analysis, the sintered samples were ground into powder and carried out by using XRD instrument (PANalytical (Philips) X'Pert Pro PW3040/60) with CuKα radiation and the data were analyzed using the X'Pert high score software. The surface microstructures were examined by scanning electron microscope (SEM, JEOL JSM6400) equipped with energy dispersive X-ray analysis (EDAX) that is used to determine the compositional analysis of the selected areas. The density of sintered sample was measured by Archimedes method and the average grain size was determined by line intercept method.

The electrical characterization of the pellets at room temperature was carried out by using a source measure unit (Keithley 236) to obtain their non-linear coefficient (α). Prior to that for electroding, they were coated with silver conductive paint and cured at 550°C for 10 min. The varistor voltage (V_{1mA}) was measured at a current of 1.0 mA and the leakage current (I_L) was measured at 0.80 V_{1mA}. The coefficient was obtained by the following empirical relation:

$$\alpha = \frac{\log\left(I_2/I_1\right)}{\log\left(V_2/V_1\right)}, \tag{1}$$

where $I_1 = 1$ mA, $I_2 = 10$ mA (Onreabroy & Sirikulrat 2006) and V_1 and V_2 are the voltages corresponding to I_1 and I_2, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of ZnO doped with 0.011 mol% of MnO_2 doping at all sintering temperatures (1180, 1240 and 1300°C) for 1 and 2 h sintering time. The main ZnO phase is presented in all specimens according to ICSD code: 00-005-0664 with the presence of $ZnMnO_3$ (ICSD
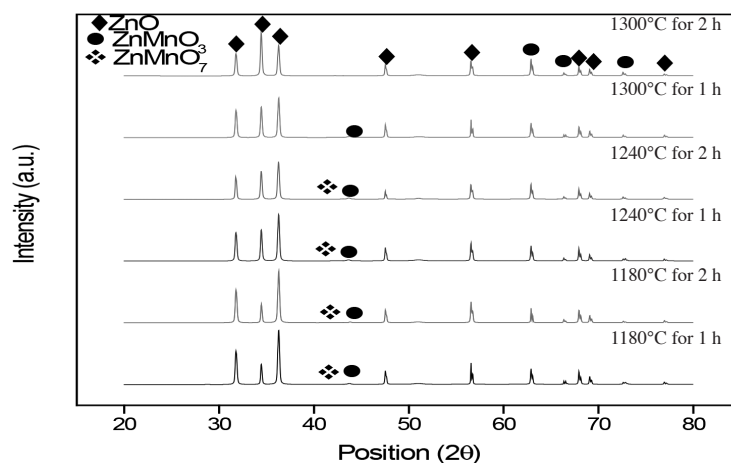

FIGURE 1. XRD pattern for ZnO doped with 0.011 mol% MnO_2 sintered at 1180°C until 1300°C for 1 and 2 h

code: 00-028-1468) and $ZnMn_3O_7$ (ICSD code: 00-030-1483) as a secondary phases, formed at the grain boundaries (Spectrum 5) and triple point junction (Spectrum 3) from EDAX observation (Figure 2). This is due to the Mn^{2+} ions (0.80 Å), which have larger ionic radii compare to Zn^{2+} (0.60 Å) segregated at the grain boundaries as secondary phases. However, this phase reduces when the sintering temperature was increased to 1300°C due to its volatility at higher sintering temperatures (Onreabroy & Sirikulrat 2006). Moreover, there is no secondary phase related to MnO_2 detected at low amount of dopant possibly due to below detection limit of XRD equipment (Filho et al. 2006).

Figure 3 shows the SEM micrographs of the ZnO-MnO_2 system for different content of MnO_2. The grain structure is nonuniformly distributed throughout the sample. However, with the increasing amount of MnO_2 content, this nonuniformity was significantly reduced. All the samples show uniform equiaxed grains and free from abnormal grain growth, where the grain growth of the ZnO is promoted by MnO_2 doping and sharp corners of the grain shape is observed. A high amount of trapped pores in the grains may be the result of the slow grain growth rate during sintering (Filho et al. 2006). The overall trend in the grain growth is increasing as the increasing of MnO_2 doping level for all sintering temperature. This indicates that the grain size increases due to the grain enhancer MnO_2, since MnO_2 is a strong grain enhancer (Han et al. 2000).

At 1240°C sintering temperature (Figure 4) slow grain growth occurred and this is due to the high amount of trapped pores in the grains (Filho et al. 2006). Also at 1180°C sintering temperature, the grain size decreases slightly at 0.016 mol%, but further increases as the increasing of doping level up to 0.026 mol% grain size. The decrement is due to the development of these two secondary
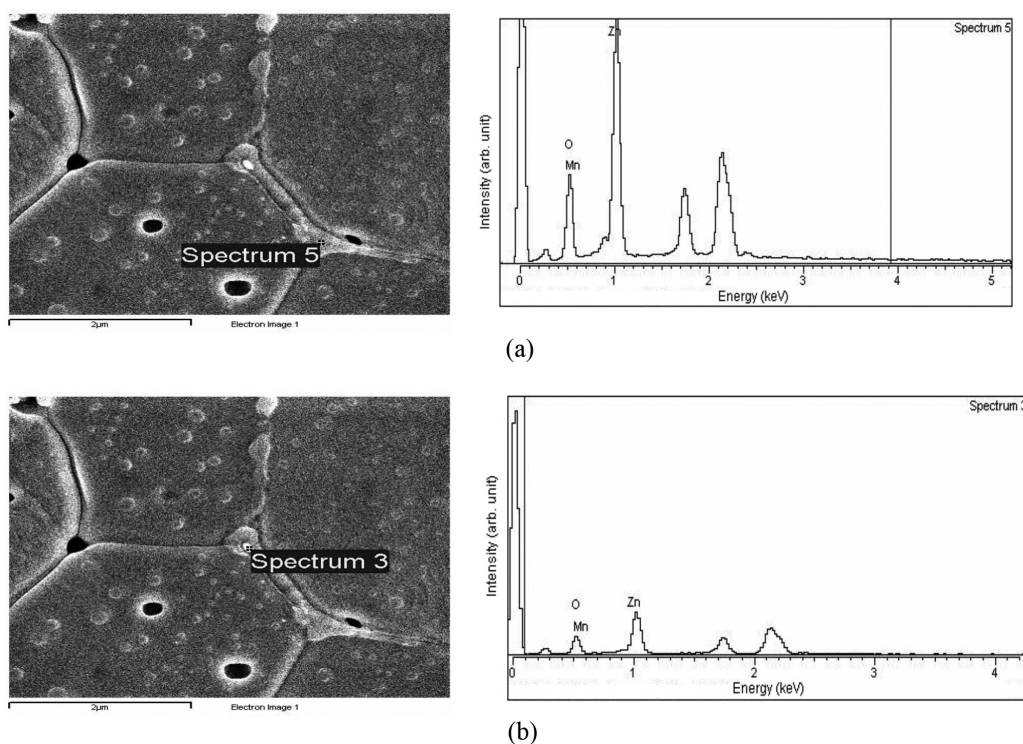

FIGURE 2. EDAX spectra obtained from (a) the grain boundary and (b) triple point junction of ZnO doped with MnO_2
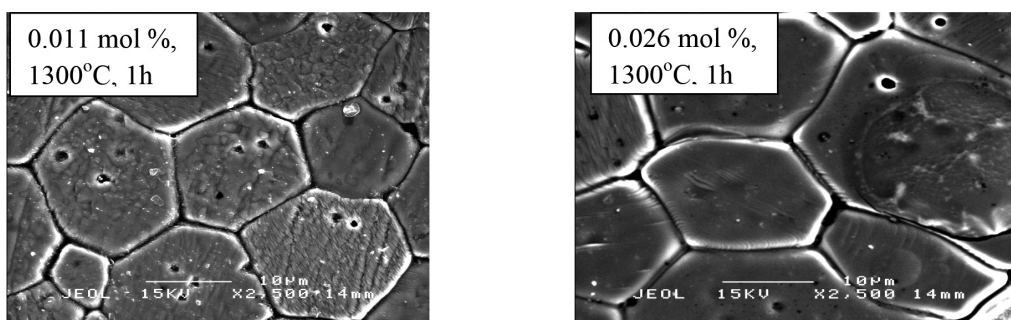

FIGURE 3. SEM micrograph of the ZnO - MnO_2 system for different content of MnO_2
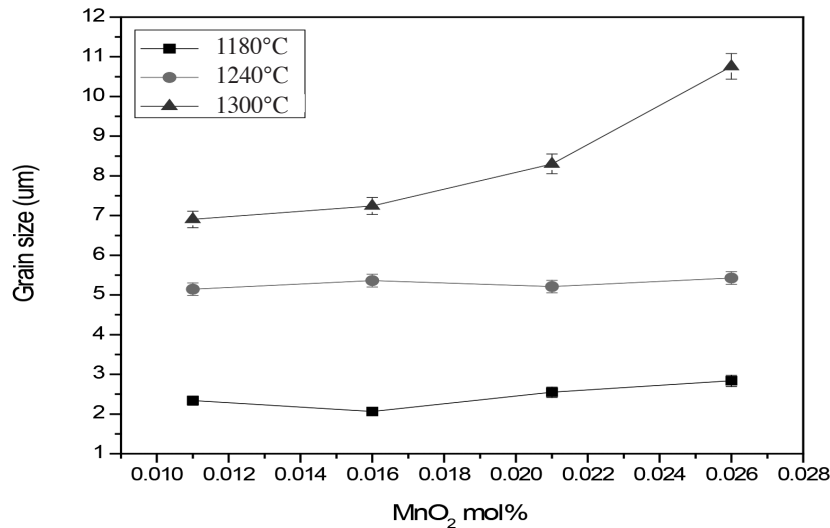
FIGURE 4. Variation of grain size with MnO_2 doping level for 1 h sintering duration time

phases which inhibits the grain growth mechanism (Wang et al. 2008). At all doping level of MnO_2, the grain size increases with the increase of sintering temperature, indicating the grain growth is enhanced at higher sintering temperature (Han et al. 2000). It is also observed that the highest value of grain size (10.8 μm) is at highest sintering temperature which is 1300°C at 0.026 mol% doping level. Sintering temperature enhanced the ability of the particle to adhere to each other through diffusion mechanism. Prolong sintering temperature also enhanced material mobilities, hence diffusion mechanism increases (Goujon & Goeuriot 2001) among the particle, thus increases the average grain size. The relative density increases with increasing sintering temperatures (Onreabroy & Sirikulrat 2006) from 1180 to 1300°C at all doping level of MnO_2 (Figure 5). This indicates that the pores decreased with the increase of sintering temperature. The prolonged sintering

temperature until 1300°C result in the elimination of pores. The maximum value of densification is at 92% at 0.026 mol% of Mn doping level. During the liquid phase sintering, the segregation of Mn continue filling the pores and vacancies at the grain boundaries, thus, the pores are decreased or densification increased.

The variations of α against MnO_2 doping levels, sintering temperature and time are depicted in Figure 6. α is enhanced when MnO_2 content increases from 0.011 up to 0.016 mol%. This suggests that segregation of Mn in grain boundary has promoted the development of essential potential barrier at interface (Bueno et al. 2001; Leite et al. 1992; Orlandi et al. 2003). Adversely, excessive MnO_2 doping encouraged spinel formation ($ZnMnO_3$ and $ZnMn_3O_7$) that could lead to poor non-linearity and higher bulk resistance (Filho et al. 2006; Hng & Knowles 2002; Sawalha et al. 2009). Reduction in the number of grain
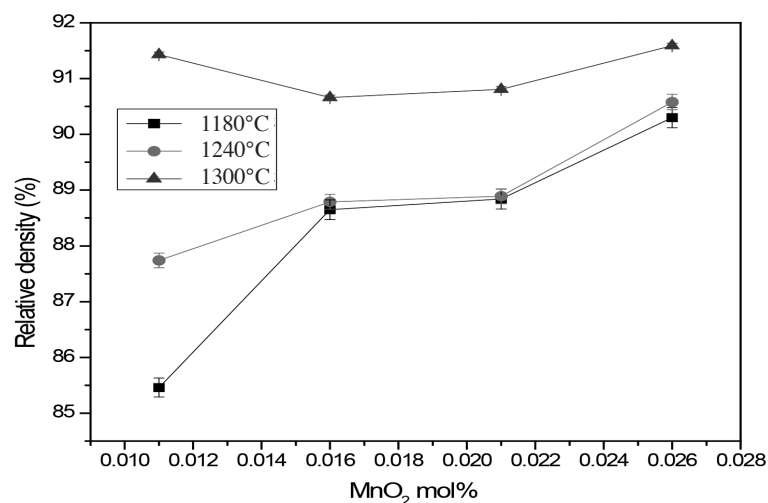

FIGURE 5. Density variation with MnO_2 doping level for 1 h sintering duration time
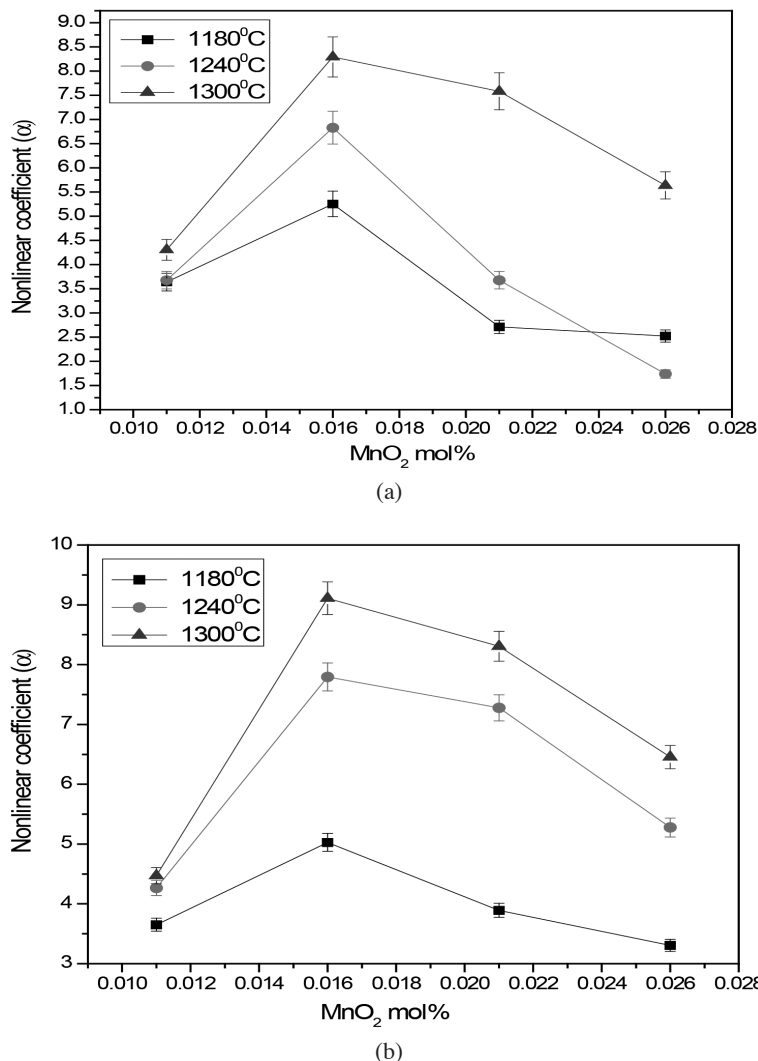
(a)

(b)

FIGURE 6. Variation of α against MnO$_2$ doping level
for (a) 1 and (b) 2 h sintering time

boundary per unit thickness due to grain enlargement should have cause a drop in α value. In agreement with Hng and Knowles (2002), the α value improves with increasing sintering temperature and time. During heating, the solubility of Mn ions was increased because of Mn^{2+} reduction to Mn^{3+} or Mn^{4+} with lower ionic radii (Riyadi et al. 2007). As a result, more Mn ions segregated in grain boundary and improved the non-linearity characteristics. The highest α (9.11) was obtained from ZnO ceramic doped with 0.016 mol% MnO$_2$ and sintered at 1300°C for 2 h.

CONCLUSION

The effect of small amount of MnO$_2$ dopant on ZnO system was investigated in the range of 0.011-0.026 mol%. This amount of MnO$_2$ dopant influences the microstructure and nonlinear properties of the ceramics. The large ionic radii of Mn^{2+} compare to Zn^{2+} are responsible for the segregation of dopant at the grain boundary, thus influences the microstructure properties of ZnO systems.

Segregation of Mn^{2+} in the grain boundary enhances the nonlinear coefficient at certain extend (0.016 mol%) and decreases with excessive doping due to formation of secondary phases.

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