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Grain Growth in the MnO Added ZnO–6 wt% Sb_2O_3 Ceramic System

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Abstract: The effect of MnO additions between 0 and 5 wt% to the grain growth of the ZnO–6 wt% Sb_2O_3 system was studied between 1000 and 1300 °C in air. The kinetic grain growth study carried out using the expression $G^n - G_o^n = K_o.t.\exp(-Q/RT)$ gave the grain exponent (n) value as 6 and the apparent activation energy (Q) for the grain growth process as 630 kJ/mol. The MnO addition systematically lowered the grain growth exponent value from 6 to 4. The apparent activation energy for the grain growth process with MnO additions up to 2 wt% was found to be 560 kJ/mol, which was lowered to 470 kJ/mol in MnO additions over 2 wt%. It was also observed that the twinned ZnO grains found in the Sb_2O_3 added system disappeared with the MnO additions. This indicated that the formation of fine spinel particles on the ZnO grains is the main source of the grain growth inhibition process in Sb_2O_3 added ZnO systems. Published by Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The semiconducting property of zinc oxide is utilized in gas sensors and in varistors.[1,2] The zinc oxide based varistors are widely used in electronic appliances and especially in high voltage lines as voltage surge protection devices. The nonlinear current–voltage characteristics of these materials are controlled by the addition of several metal oxides to the composition and also by varying the sintering conditions in production, which in turn affects the microstructure of the material. Most of the numerous published works in the last decade have been directly related to the electrical properties of the material. It is now well established that the voltage breakdown per unit thickness in a varistor is directly related to the grain size. Hence, systematic study of the grain growth kinetic of the zinc oxide system having various additives becomes of prime importance.

Recently, Senda and Bradt have reported such a study in pure ZnO and in Bi_2O_3, Sb_2O_3 added ZnO systems.[3,4] In their study, they applied the well-known kinetic grain growth equation:

$$G^n - G_0^n = K_o.t.\exp(-Q/RT) \qquad (1)$$

where G is the average grain size at time t, G_0 is the initial grain size, n is the grain growth exponent value, K_0 is a constant for the equality, Q is the apparent activation energy for grain growth, R is the gas constant and T is the absolute temperature of sintering. In this expression the initial grain size G_0 can be omitted because it is significantly smaller than the grain size G at time t. Hence, the equation is simplified to

$$G^n = K_0.t.\exp(-Q/RT) \qquad (2)$$

Using this equation, Senda and Bradt[3] have calculated the grain growth exponent of pure ZnO as 3 and the apparent activation energy for grain growth as 224 ± 16 kJ/mol. They also showed that the addition of Sb_2O_3 up to 2.38 wt% to ZnO increased the n-value to 6 and the activation energy

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to the order of 600 kJ/mol. The grain growth inhibition observed in ZnO by the Sb_2O_3 addition was attributed to the grain boundary drag mechanism caused by the formation of small $Zn_7Sb_2O_{12}$ spinel particles on the ZnO grains and to the reduction of grain boundary mobility caused by the formation of twinning in the ZnO grains.[4] The addition levels of Sb_2O_3 employed in this work were lower than the levels usually employed in high voltage varistor compositions. Hence, in this study, ZnO + 6 wt%-Sb_2O_3 was adapted as a main composition which is the maximum level found in varistors and the effect of the MnO addition up to 5 wt% to the grain growth kinetics was investigated.

2 EXPERIMENTAL PROCEDURE

High-purity ZnO, Sb_2O_3 and MnO were used to prepare the six compositions of ZnO + 6 wt% Sb_2O_3 and with 1, 2, 3, 4, 5 wt%MnO added. The transmission electron microscope study of the ZnO powder revealed needle-like fine crystal *c.* 0.5 μm width and *c.* 0.5–2 μm length. The calculated amounts of oxides for the compositions were ball-milled in an ashless rubber lined jar for 6 h using zirconia balls and distilled water as milling media. After drying, the mixtures were granulated in moist conditions and then semi-dry pressed at 100 MPa to prepared specimens at 10 mm diameter and 8 mm thick. The specimens were sintered at 1000, 1100, 1200 and 1300 °C in air for 1, 2, 3, 5 and 10 h, using a heating rate of 10 °C/min and natural cooling in a PID controlled SiC-furnace.

The bulk densities of the sintered samples were determined from their weights and dimensions. The characterization of the sintered specimens was carried out by X-ray diffraction using CuKα radiation. For the microstructural observations both scanning electron microscopy (SEM) of the fracture surfaces and optical microscopy of polished and HF etched surfaces were used. Grain size measurements were done on the photomicrographs of the etched samples using the following equation.

$$\bar{G} = 1.56.\bar{L} \qquad (3)$$

where $\bar{G}$ is the average grain size, $\bar{L}$ is the average grain boundary intercept-length of four random lines on two micrographs.[5]

3 RESULTS AND DISCUSSION

3.1 The effect of MnO on densification

The X-ray powder diffraction of the MnO-added samples sintered at different temperatures and for different periods of time showed the presence of only ZnO and $Zn_{2.33}Sb_{0.67}O_4$ (ASTM Card No: 15-687) phases. This indicated that MnO formed a solid solution with ZnO as expected from the phase diagram of the ZnO–MnO binary system.[6] The broad diffraction peak for the $Zn_{2.33}Sb_{0.67}O_4$ phase at 1000 °C became sharp at 1100 °C and the peak intensities did not charge in other sintering conditions caused by the fixed amount of Sb_2O_3 used in the compositions. These results are consistent with the results of Kim *et al.*[1]

The effects of MnO on the densification of the samples is given in Fig. 1. In the figure, the sintering times of 1 and 10 h were compared in order to show the effect of the extreme sintering conditions. Similarly, the SEM micrographs of the fracture surfaces of the samples with 1, 2 and 5 wt% MnO content sintered at 1000 and 1300 °C for 1 h were compared in Fig. 2.

The green densities of all die-pressed samples were *c.*2.9 g/cm^3. The sintering at 1000 °C for 1 and 10 h raised the bulk density of the samples having no MnO to 3.20 and 3.65 g/cm^3, respectively, and the MnO additions did not show any significant effect on the densification. The sinterings at this temperature resulted in a porous and fine (< 1 μm) crystalline microstructure [Fig. 2 (a)–(f)].

The sintering at 1100 °C for 1 h raised the bulk density of the sample with no MnO additive to 3.58 g/cm^3 and the additions of MnO up to 2 wt% did not affect the densification. But addition above

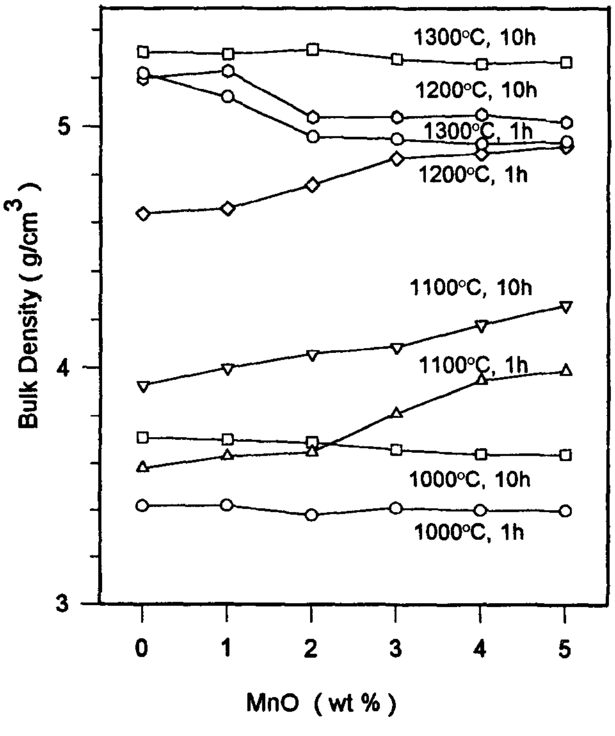

Fig. 1. Effect of MnO on the densification of ZnO–6 wt% Sb_2O_3 ceramic system.

this level showed a positive effect, giving the highest bulk density value of 3.95 g/cm^3 in the samples containing 5 wt% MnO. The prolonged sinterings at this temperature also showed similar effects which were also observed in sinterings at 1200 °C for 1h, at which the density values of 4.63 and 4.85 g/cm^3 were obtained for 0 and 5 wt% MnO added samples. The prolonged sintering at 1200 °C resulted in marked densifications in 0 and 1 wt% MnO-contained samples. However, higher MnO contents resulted in lower bulk densities. This effect was very pronounced in sinterings at 1300 °C for 1 h. As can be seen from the micrographs given in Fig. 2 (d), the 1 wt% MnO addition results in a dense structure with quite uniform grains of 2–3 μm in size. The addition of MnO above 1 wt% causes a sudden grain-growth, which in turn entraps a high amount of porosity within and among the grains [Fig. 2 (e,f)]. The prolonged sinterings at 1300 °C result in the elimination of these pores without greatly affecting the grain size and the maximum value of densification is attained at *c.* 5.3 g/cm^3.

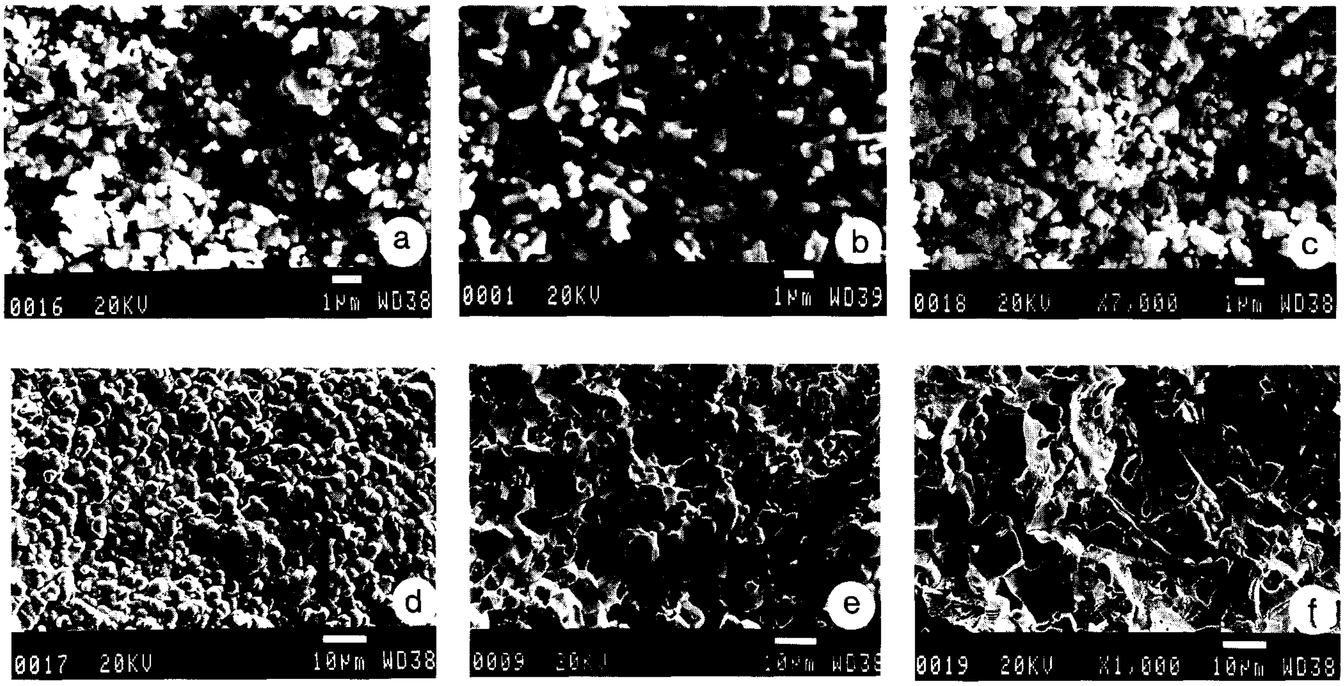

Fig. 2. SEM micrographs of the 1, 2 and 5 wt% MnO added samples sintered at 1000 °C/1 h (a, b, c) and at 1300 °C/1 h (d, e, f), respectively.

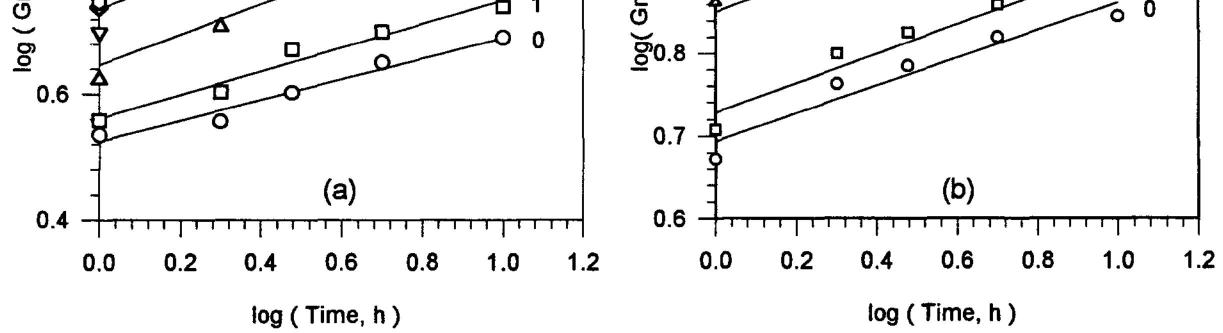

Fig. 3. Isothermal grain growth of ZnO–6 wt% Sb_2O_3 ceramics containing 0–5 wt% MnO sintered at (a) 1200 °C and (b) 1300 °C.

3.2 Grain growth kinetics

The grain growth kinetic exponent in eqn (2) can be calculated from isothermal grain size data when the equation is expressed in the form,

$$\log G = (1/n)\log t + (1/n)((\log K_o - 0.434(Q/RT)) \quad (4)$$

the reciprocal of the slope of the log(grain size) vs log(time) gives the n value. Figure 3(a,b) shows such plots for the isothermal sinterings at 1200 and 1300 °C and the calculated n values are listed in Table 1. Similar plots could not be constructed for the isothermal sinterings at 1000 and 1100 °C, since the samples had a fine crystalline size (< 1 μm) and a very porous microstructure, which gave rise to a large amount of grain pull-outs in the sample polishing process for the optical microscopy. Therefore the grain size values used as a starting point for the plots in the evaluation of the activation energies were deduced from the SEM micrographs in the samples sintered only at 1000 °C.

Table 1. Grain growth (n) and apparent activation energy (Q) values

wt% MnO content	n values at 1200 °C	n values at 1300 °C	n values used in Arrhenius plots	log K_o	Q (kJ/mol)
0	6.0	6.0	6.0	25.18	630
1	5.4	6.0	6.0	22.87	560
2	4.3	5.5	5.0	22.80	560
3	3.8	4.5	4.0	19.39	470
4	3.8	4.3	4.0	19.89	480
5	3.4	4.1	4.0	20.04	490

Senda and Bradt[3,4] have reported the n values for ZnO and that of the ZnO-added up to 2.38 wt% added system as 3 and 6, respectively. They also pointed out that a high n value in a system indicates a grain growth inhibition mechanism. The grain growth exponent for the ZnO–6 wt% Sb_2O_3 system studied in this work was also found to be 6 in sinterings at 1200 and 1300 °C. This shows that the n value is not affected by the high level of the Sb_2O_3 addition used in this work.

If eqn (2) is expressed in the form of

$$\log(G^n/t) = \log K_o - 0.434(Q/RT) \quad (5)$$

the apparent activation energy Q of a grain growth process can be calculated from the gradient of the Arrhenius plot of log (G^n/t) vs $1/T$ (K^{-1}). Such plots for the studied system are given in Fig. 4(a)–(f).

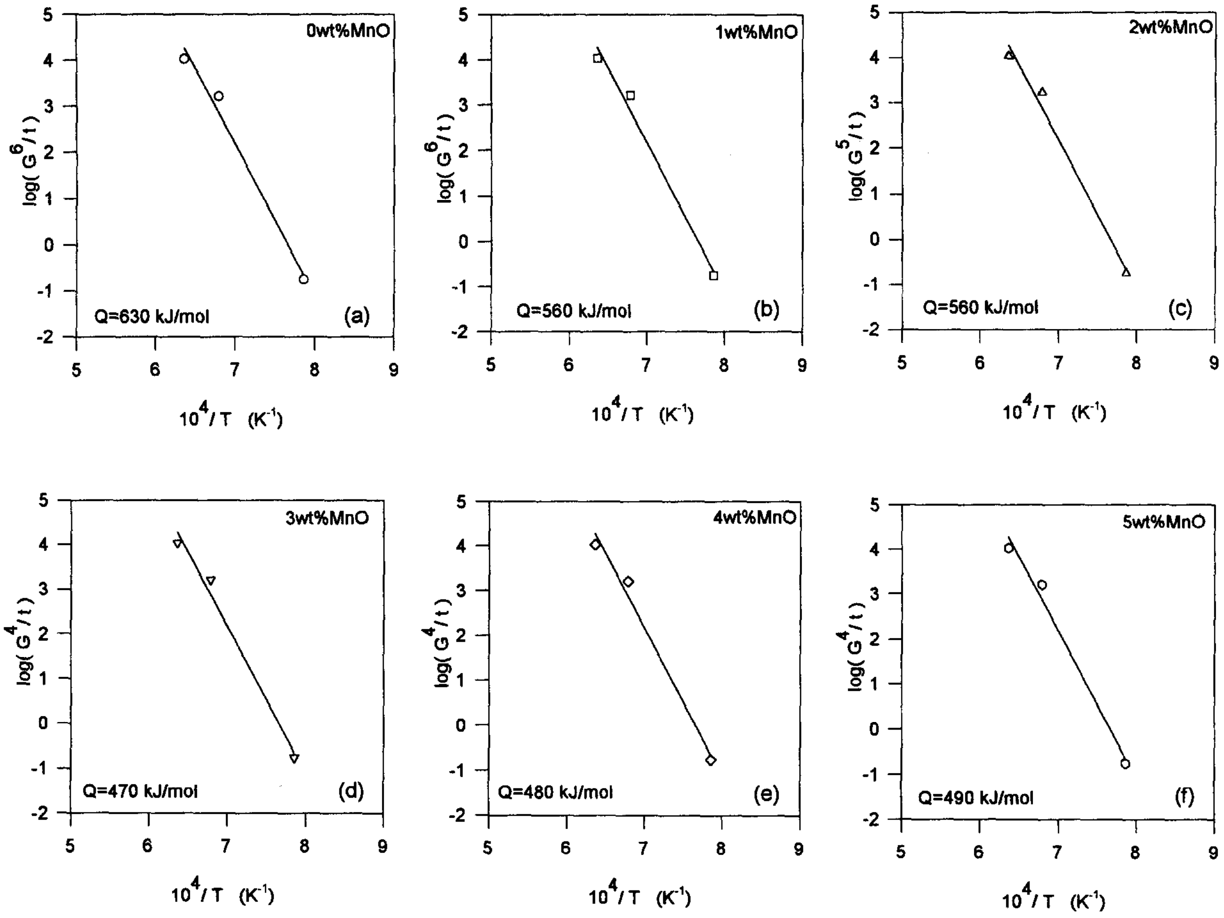

Fig. 4. Arrhenius plots for the grain growth of ZnO–6 wt% Sb_2O_3 ceramics containing 0–5 wt% MnO (a)–(f).

Table 1 also lists the n values accepted in the construction of these plots along with the calculated values of the logarithm of the rate constants and the apparent activation energies. The apparent activation energy value of 630 kJ/mol found for the grain growth process in the ZnO–6 wt% Sb_2O_3 system is very close to the value of 600 kJ/mol quoted by Senda and Bradt. The higher value obtained can be attributed to the excess amount of the spinel phase formed which inhibits the grain growth process by pinning the grain boundary movements.

The additions of the increased amounts of MnO to the ZnO–6 wt% Sb_2O_3 system results in lower n values in sinterings at 1200 °C. This and the densification data given in Fig. 1 indicates the suppressing effect of MnO in the grain growth inhibition process of Sb_2O_3. Since the grain growth kinetic rate constant (K_0) did not show a pronounced dependance on the MnO content, this effect can be explained by the easier coagulation of the fine spinel particles on ZnO grains into the large ones, which also supports the results of Kim *et al.* However, at 1300 °C the n values show a slight increment which indicates a slower grain growth process at this temperature. This also supports the discussion given in the previous section that the densification in prolonged sinterings at this temperature was related to a pore elimination process rather than the grain growth. As indicated in Table 1, the apparent activation energy value of 560 kJ/mol was found for the 1 and 2 wt% MnO added systems. A sudden lowering in the apparent activation energy to a value of 470 kJ/mol was found for the 3 wt% MnO added system. Further MnO additions had no significant effect on the activation energy value. These results also show a good correlation with the discussions presented above.

The formation of twinning in ZnO grains in the Sb_2O_3-added ZnO system reported by Senda and Bradt was also observed in this work in the samples having no MnO. The twinning became less with increased MnO additions and the samples containing 3 wt% MnO and over showed almost no twinning. This indicated that the grain inhibition of Sb_2O_3 in ZnO can only be related to the fine spinel particles forming on the ZnO grains and the twinning was the result of the forces imposed by the strong grain inhibition process.

4 CONCLUSIONS

The effect of the MnO additions to the grain growth of the ZnO–Sb_2O_3 was studied between 1000 and 1300 °C in air. The grain growth exponent value of 6 and the apparent activation energy value of 630 kJ/mol were found for the system with no MnO addition, which showed a good correlation with the published data. The addition of MnO lowered the grain growth exponent value to 4. The apparent activation energy value of 560 kJ/mol was found for the MnO addtions up to 2 wt%. Additions over this value resulted in the sudden lowering in the apparent activation energy value to 470 kJ/mol. The MnO additions also resulted in the disappearance of the twinning in ZnO grains, which indicated the grain growth inhibition of Sb_2O_3 in the ZnO system is related only to the formation of the spinel phase on the ZnO grains.

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