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Grain Growth in MnO-added ZnO–6 wt% Bi_2O_3 Ceramic System

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Abstract: The grain growth kinetics in the 0–5 wt% MnO-added ZnO–6 wt% Bi_2O_3 system was studied using the simplified phenomenological grain growth kinetics equation $G^n = K_o.t.\exp(-Q/RT)$ together with the physical properties of the sintered samples. The grain growth exponent value (n) and the apparent activation energy for the ZnO–6 wt% Bi_2O_3 system was found to be 5 and 200 kJ mol^{-1}, respectively. These values support the published data for the grain growth mechanism of the ion diffusion model in liquid phase sintering. The addition of MnO lowered the grain growth exponent value to 4 and the apparent activation energy for the grain growth process was increased systematically from 200 kJ mol^{-1} to 250 kJ mol^{-1} for the additions of MnO from 0 to 5 wt%. This was attributed to the reduction of the equilibrium solubility of ZnO in liquid Bi_2O_3 phase present between the ZnO grains during sintering. © 1997 Published by Elsevier Science Limited

1 INTRODUCTION

The grain growth phenomena in ZnO based varistor ceramics are important since the electrical properties of the material are dependent on the microstructure.[1] It is well established that the varistor breakdown voltage is affected by the grain size. It is also known that the addition of Bi_2O_3 and Sb_2O_3 to the composition of a varistor is an essential requirement in order to obtain the desired nonlinear current–voltage characteristics. In addition to these additives, other metal oxides such as MnO, Cr_2O_3, CoO, Al_2O_3, SnO_2, etc., are also needed to obtain the required electrical properties. Therefore, it is important to study in a systematic way the effect of these additives to the microstructural development and to the grain growth kinetics of the material.

Among these additives, Bi_2O_3 carries a special importance since it enhances the grain growth and effects the stability of the nonlinear current–voltage characteristics of the material. Among the numerous works published on the subject, Senda and Bradt presented the most detailed study covering the grain growth kinetics in ZnO ceramics containing up to 4 wt% Bi_2O_3.[2] In their work, Senda and Bradt used the simplified grain growth kinetics equation;

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

where G is the average grain size at time t, n is the kinetic grain growth exponent value, K_o is a constant, Q is the apparent activation energy, R is the gas constant and T is the absolute temperature. Using this equation, Senda and Bradt have calculated the grain growth exponent value (n) as 3 and apparent activation energy (Q) as 224 ± 16 kJ mol^{-1} in the sintering of the pure ZnO system. However, in a recent study Dey and Bradt studied the grain growth kinetics of ZnO having Bi_2O_3 addition from 3 wt% to 12 wt%.[3] They found that the rate of grain growth of ZnO was affected by the increased amounts of Bi_2O_3 addition and the apparent activation energy for the grain growth of the system was raised from 160 kJ mol^{-1} to

270 kJ mol^{-1}, respectively. They attributed this to the change of the grain growth mechanism from the phase-boundary reaction in the liquid phase sintering process for low Bi_2O_3 contents ($<$5–6 wt%) to that of an ion diffusion controlled mechanism in a liquid phase.

Therefore, the aim of this work is to study the grain growth kinetics of ZnO containing 6 wt% Bi_2O_3 which was found to be the critical level in the change of the grain growth kinetics. A further aim of the work is also to study the effect of MnO addition as a third component to the microstructure of this system.

2 EXPERIMENTAL

High-purity ZnO ($>$99.8%, Metal Bileşikleri A.Ş. Gebze, Kocaeli, Turkey) and Bi_2O_3, MnO (Merck-pure grade) were used in the preparation of six basic compositions; ZnO–6 wt% Bi_2O_3 and those containing 1, 2, 3, 4, 5 wt% MnO. The transmission electron microscope study of the ZnO powder showed that the powder consisted of needle-like ZnO crystals *ca.* 0.5 μm and ca. 0.5–2 μm in length. The calculated amounts of oxides for the indicated compositions were ball-milled at 70 rpm in ashless rubber-lined ceramic jars for 6 h using zirconia balls and distilled water as the milling media. The mixtures were dried to *ca.* 10–15% moisture level and then granulated. Specimens of 10 mm diameter, *ca.* 8 mm thick were prepared by semi-dry pressing of the granules of $-150\,\mu$m, $+75\,\mu$m in size at a pressure of 100 MPa. The specimens were sintered in air at 1100, 1200 and 1300°C for 1, 2, 3, 5, 10 h using a heating rate of 10°C min^{-1}. After sintering, the specimens were naturally cooled in the furnace.

The bulk densities of the samples were determined from their weights and dimensions. Characterisation of the phases in the sintered specimens were done by X-ray diffraction using CuKα radiation. The microstructural observations were carried out by an optic microscope using the optically polished samples and etched in a 20% acetic acid-distilled water solution.

The quantitative grain-size measurements were done on the micrographs of the samples using the following equation,

$$\overline{G} = 1.56x\overline{L} \tag{2}$$

where, $\overline{G}$ is the average grain size, $\overline{L}$ is the average grain boundary intercept-length of four random lines on two different micrographs of each sample.[4]

3 RESULT AND DISCUSSION

3.1 Properties of the sintered samples

The X-ray powder diffraction study in all compositions sintered at different temperatures showed the presence of only ZnO and β-Bi_2O_3 (ASTM card Nos: 36–1451, 27–50, respectively). This shows that MnO forms solid solution with ZnO as indicated by the phase diagram of ZnO–MnO binary system. The presence of Bi_2O_3 in β-form is in agreement with the results of Wong and Morris.[5]

The reported work on the densification process of pure ZnO and that of the ZnO–Bi_2O_3 system showed decrement in the bulk density data with increasing sintering temperature and time.[2,6] This was attributed to the entrapment of gas giving rise to closed pores in ZnO grains and also to the Bi_2O_3 losses due to volatilisation. Therefore, the volatility of Bi_2O_3 was also investigated in this work for the 0 and 5 wt% MnO-added ZnO–6 wt% Bi_2O_3 system. The weight loss data for these samples is shown in Fig. 1. The weight loss data was determined by weighing the green-pressed pellets before and after heating to the indicated temperatures by employing the same heating rate used in sintering and 1 h of soaking time. Both the 0 and 5 wt% MnO contained samples showed *ca.* 1.5–2.0% weight losses up to 1200°C resulting mainly from the moisture content of the green pellets. However, above 1200°C appreciable weight loss was found due to volatilisation of Bi_2O_3 which showed a slight increment with the MnO content. The total weight loss of *ca.* 4.5–5.0% determined at 1300°C

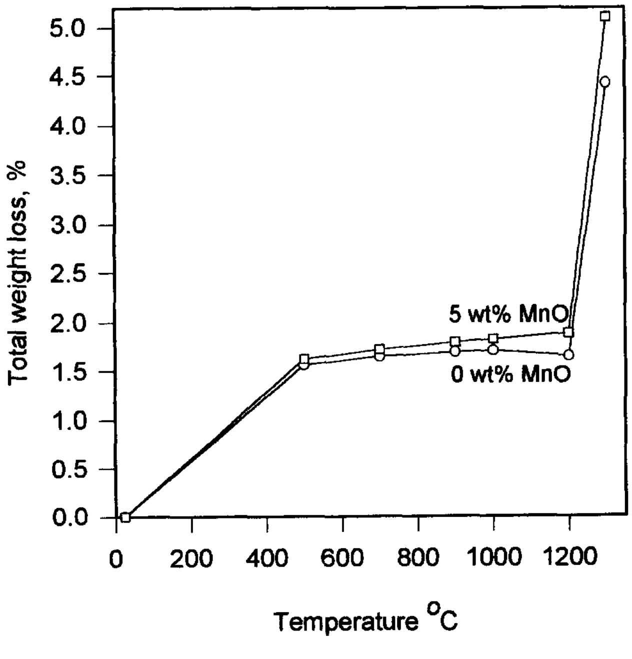

Fig. 1. Total weight loss in percent after sintering 1 h at the indicated temperatures.

agrees with the data reported by Wong who also observed pronounced losses in Bi_2O_3 content in the ZnO–Bi_2O_3 system above 1200°C.[7] A test carried out in a prolonged sintering showed that Bi_2O_3 losses up to 25% can occur even at 1200°C for a 10 h sintering.

The bulk density data given in Fig. 2 shows the effect of sintering temperatures, extreme sintering times employed (1 and 10 h) and the MnO content on the densification of the ZnO–6 wt% Bi_2O_3 system. As reported by other researchers, the highest densification is attained at a low sintering temperature due to liquid phase sintering, in this case 1100°C for the samples having no MnO additive. Higher sintering temperatures and longer sintering times give rise to a reduction in bulk density due to increased amount of porosity between and within the large grains of ZnO resulting from the rapid grain growths induced by the liquid phase sintering and also by the Bi_2O_3 losses especially in sinterings over 1200°C, [Fig. 3(a) and (b)]. The addition of MnO also results in a slight reduction in the bulk densities of the samples sintered at 1100°C. Since Bi_2O_3 losses are minimal at this temperature, this reduction mainly arises from the differences in the densities of ZnO (5.68 $g\,cm^{-3}$) and that of MnO (5.36 $g\,cm^{-3}$). However, in sinterings at 1200°C and especially at 1300°C, the optimum densification is attained in the 1 w% MnO-added samples, mainly due to the reduction of the amount of the intergranular porosity. But, the noticable reduction in the bulk densities with increased MnO content at these temperatures is mainly accounted for by the Bi_2O_3 losses due to volatilisation.

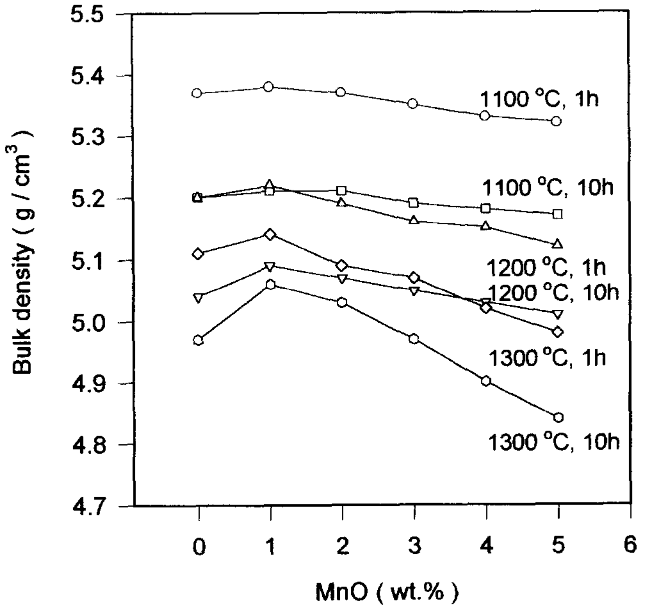

Fig. 2. Variation of bulk density with MnO content for the 1 and 10 h sintered samples.

3.2 Grain growth kinetics in the MnO-added ZnO–6 wt% Bi_2O_3 system

The grain growth kinetics can be determined using the simplified phenomenological kinetics [eqn (1)]. The kinetic grain growth exponent value (n) in the equation can be found at isothermal conditions when the kinetic equation is expressed in the form of

$$n \log G = \log t + \{\log K_o - 0.434(Q/RT)\} \qquad (2)$$

The n value can be calculated from the slope of the log(grain size) vs log(time) line plot which is equal to $(1/n)$. Such plots were made for the isothermal conditions employed at the sintering temperatures and the n values were calculated from the slopes of the line plots constructed by the linear regression method. An example for such a plot is given in Fig. 4 for the sinterings at 1100°C and the average n values calculated from these plots is given in Table 1.

The average grain growth exponent value of 5 determined for the ZnO–6 wt% Bi_2O_3 system is equal to the values obtained by Senda and Bradt and Dey and Bradt. However, with the addition of 1 wt% MnO the n value was reduced to 4 and the further addition of MnO did not affect the grain exponent value.

When eqn (1) is expressed in the form

$$\log(G^n/t) = \log K_o - (0.434.Q/R)(1/T) \qquad (4)$$

the apparent activation energy Q for the grain growth process can be calculated from the gradient of the Arrhenius plot of log (G^n/t) vs $(1/T)$. Such plots constructed for the studied system are shown in Fig. 5(a)–(f) and the calculated apparent activation energies along with the logarithm of the pre-exponential constant K_o are also listed in Table 1.

The numerous studies carried out on the grain growth kinetics of ZnO have revealed that the rate-controlling mechanism is the solid-state diffusion of Zn^{+2} cations. The apparent activation energy for this process is about 225 $kJ\,mol^{-1}$. Whereas, the studies on the ZnO–Bi_2O_3 system showed that the grain growth of ZnO proceeds in liquid phase of Bi_2O_3 by a mechanism of solution-precipitation at phase boundaries.[2,3,7–10] Among these studies, the notable work of Senda and Bradt showed that a low level of Bi_2O_3 addition (~0.5 wt%) to ZnO reduced the apparent activation energy to 150 $kJ\,mol^{-1}$ and further additions up to 4 wt% did not have a pronounced effect on the apparent activation energy.

However, in a later work Dey and Bradt showed that the addition of Bi_2O_3 beyond this level

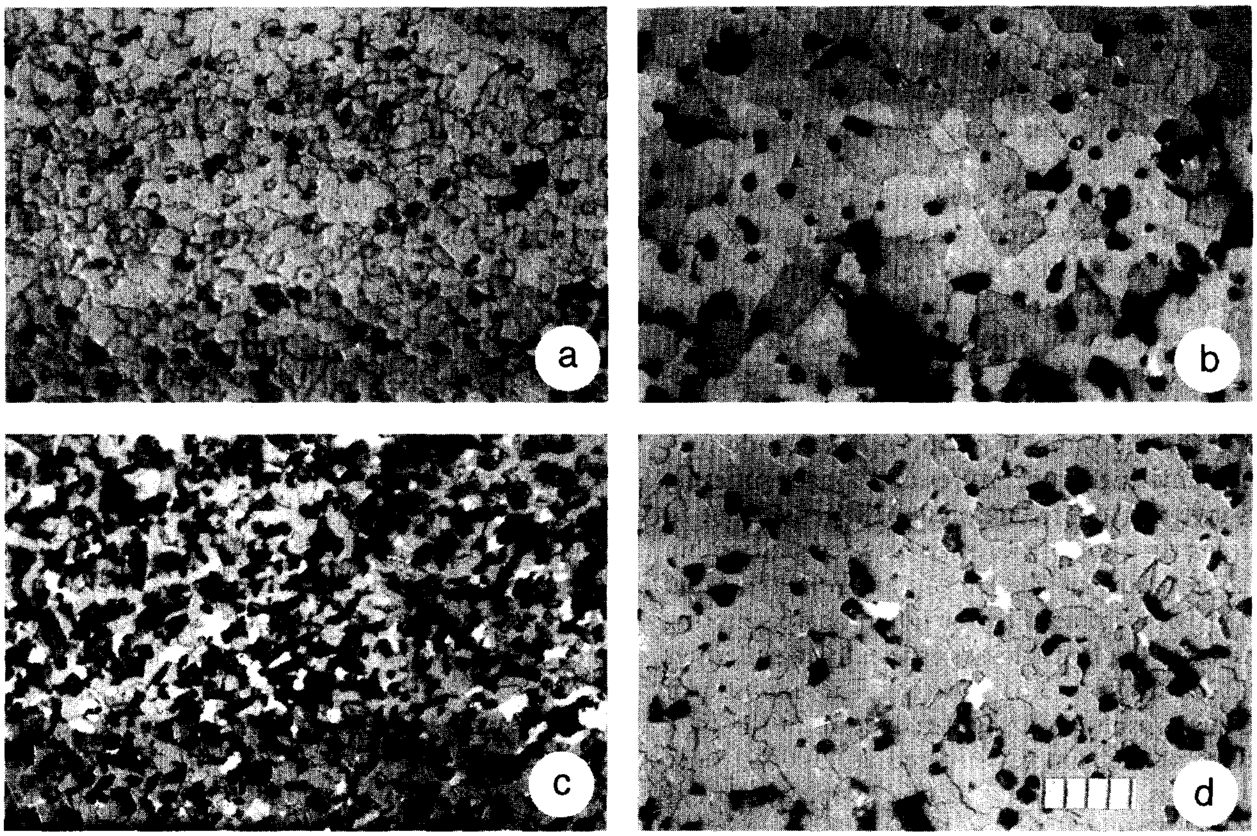

Fig. 3. Microstructures of the ZnO–6 wt% Bi_2O_3 system (a,b) and 5 wt% MnO added system (c,d) sintered at 1100 and 1300°C 1 h, respectively (1 division = 10μm).

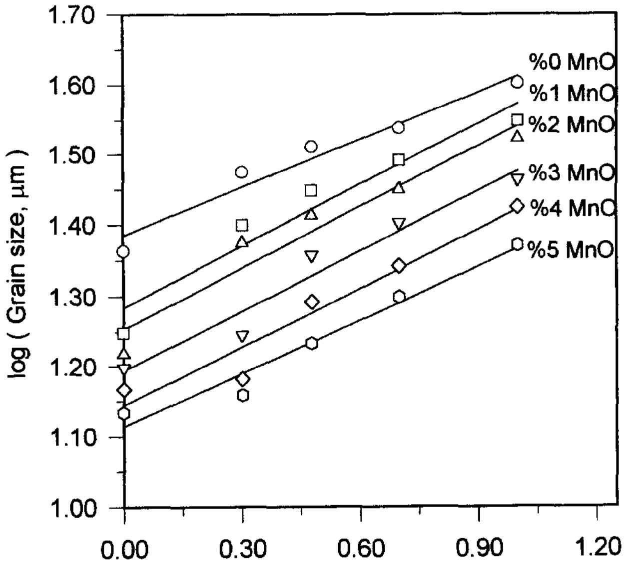

Fig. 4. Log(grain size) vs log(time) plots for sinterings at 1100°C.

Table 1. Calculated grain growth exponent (*n*), apparent activation energy (*Q*) and pre-exponential constant (K_o) values

MnO (wt%)	*n* values	*Q* (kJ mol^{-1})	logK_o
0	5	200	12.95
1	4	210	12.63
2	4	215	12.74
3	4	225	13.39
4	4	235	13.49
5	4	250	13.98

increased the apparent activation energy gradually and 274 kJ mol^{-1} was found for the 12 wt% Bi_2O_3 addition. They also showed that this increase in the activation energy was due to the change of the grain growth mechanism from the phase-boundary reaction in liquid-phase sintering to that of a ion diffusion mechanism in a thicker layer of liquid phase. They also proposed that this change became effective at Bi_2O_3 additions of *ca.* 5–6 wt%.

In this study, the apparent activation energy of the ZnO–6 wt% Bi_2O_3 system was calculated as 200 kJ mol^{-1}. This figure agrees with the figure of 232 ± 24 kJ mol^{-1} quoted for the same composition by Dey and Bradt. However, the additions of MnO to this system resulted in a gradual increase in the apparent activation energies. The Q value obtained from the Arrhenius plots in Fig. 5 are 210 kJ mol^{-1} for 1 wt% MnO, 215 kJ mol^{-1} for 2 wt% MnO, 225 kJ mol^{-1} for 3 wt% MnO, 235 kJ mol^{-1} for 4 wt% MnO and 250 kJ mol^{-1} for 5 wt% MnO. As a result, this increase in apparent activation energy is accompanied by a decrease in ZnO grain size

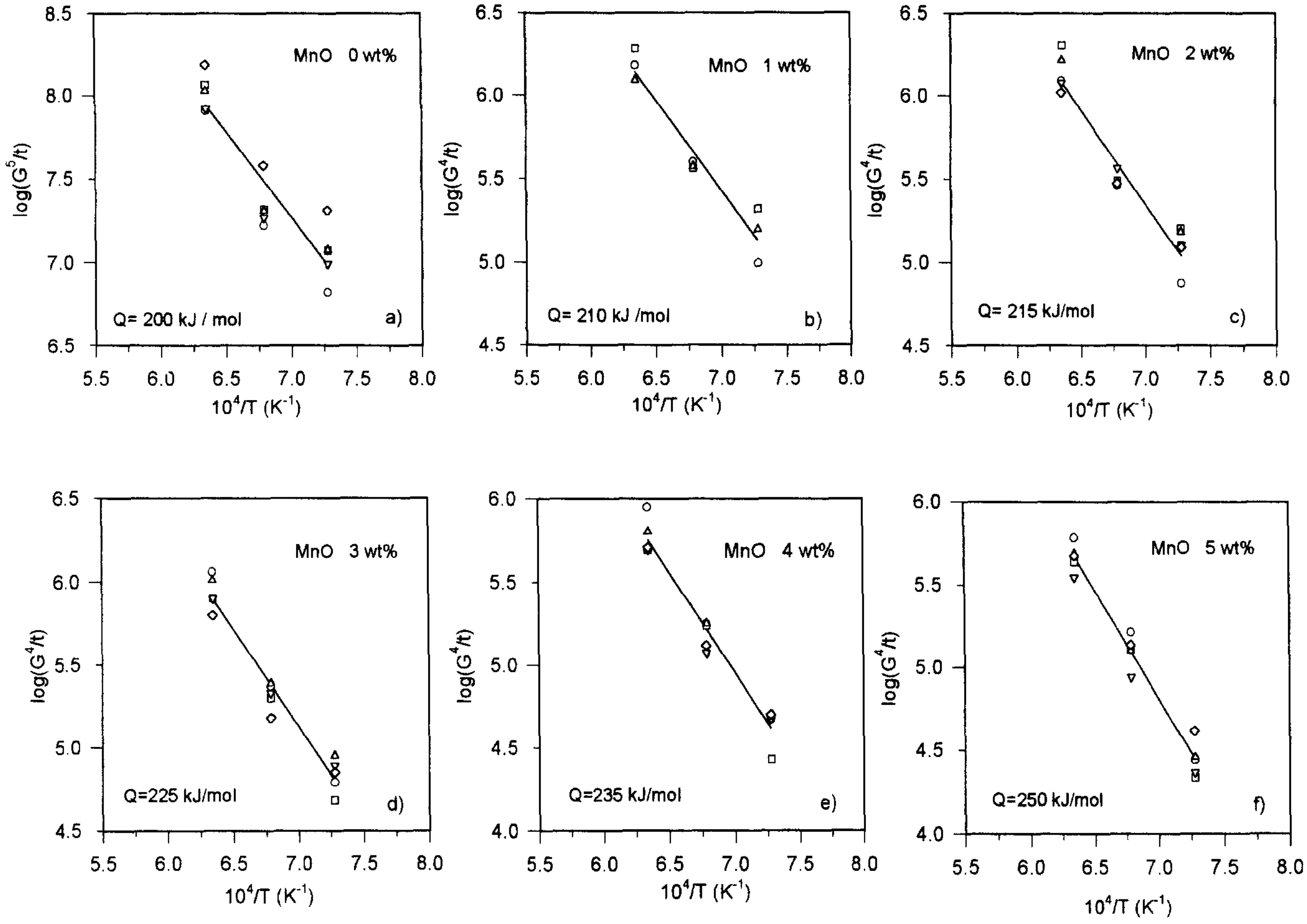

Fig. 5. Arrhenius plots for the grain growth in ZnO–6 wt% Bi_2O_3 system containing 0–5 wt% MnO (a)–(f).

resulting in smaller and pore free grains at 5% wt MnO addition as shown in Fig. 3(c) and (d). The details of grain growth mechanism of diffusion controlled process in liquid-phase sintering will not be covered here since it was discussed in detail by Dey and Bradt. In such a mechanism, the grain growth is effected mainly by the thickness of the liquid phase between the grains and also by the equilibrium solubility of ZnO grains in the liquid Bi_2O_3 phase. Since the Bi_2O_3 content in the studied system was kept at 6 wt%, also in view of the effectiveness on Bi_2O_3 losses above 1200°C for sinterings of long periods, it is reasonable to assume that the thickness of the liquid phase is constant for all compositions sintered in similar conditions. Hence, the increment in apparent activation energy can be attributed to the reduction of the equilibrium solubility of ZnO in liquid Bi_2O_3 in the presence of MnO.

4 CONCLUSIONS

The effect of MnO additions 0–5 wt% to the sintering characteristics and to the grain growth mechanism of the ZnO–6 wt% Bi_2O_3 system was studied. The highest densification was found at 1100°C. At higher sintering temperatures and longer sintering times, the bulk densities were reduced mainly due to the volatilisation of Bi_2O_3. The grain growth exponent value of 5 and the apparent activation energy of 200 kJ mol^{-1} found for the system with no MnO addition showed a good correlation with the published data for the grain growth mechanism of the diffusion-controlled process in liquid-phase sintering. The addition of MnO to the system reduced the grain growth exponent value to 4 and the apparent activation energy increased systematically to 250 kJ mol^{-1} for the 5 wt% MnO content. This resulted in a small and pore-free grained microstructure. The increment in the apparent activation energy was attributed to the reduction in the equilibrium solubility of ZnO in liquid Bi_2O_3 in the presence of MnO.

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REFERENCES

1. LEVINSON, L. M. & PHILLIPP, H. R., Zinc oxide varistors — a review. *Am. Ceram. Soc. Bull.*, **65**(1) (1986) 639–646.
2. SENDA, T. & BRADT, R. C., Grain growth in sintering ZnO and ZnO–Bi_2O_3 ceramics. *J. Am. Ceram. Soc.*, **73**(1) (1990) 106–114.
3. DEY, D. & BRADT, R. C., Grain growth in sintering ZnO and ZnO–Bi_2O_3 ceramics. *J. Am. Ceram. Soc.*, **75**(9) (1992) 2529–2534.
4. *Metals Handbooks*, Vol. 8, 8th edn. American Society for Metals, Warrendale, PA, 1973, p. 46.
5. CERVA, H. & RUSSWURM, W., Microstructure and crystal structure of bismuth oxide phases in zinc oxide varistor ceramics. *J. Am. Ceram. Soc.*, **71**(7) (1988) 522–529.
6. KIM, J., KIMURA, T. & YAMAGUCHI, T., Effect of bismuth oxide content on the sintering of zinc oxide. *J. Am. Ceram. Soc.*, **72**(8) (1989) 1541–1544.
7. WONG, J., Sintering and varistor characteristics of ZnO–Bi_2O_3 ceramics. *J. Appl. Phys.*, **51**(8) (1980) 4453–4459.
8. GUPTA, T. K. & COBLE, R. L., Sintering of ZnO: I. Densification and grain growth. *J. Am. Ceram. Soc.*, **51**(9) (1968) 521–525.
9. DUTTA, S. K. & COBLE, R. L., Grain growth in fully dense ZnO. *J. Am. Ceram. Soc.*, **53**(1) (1970) 61–62.
10. ASOKAN, T. A., IYENGER, G. N. K. & NAGABHUSHANA, G. R., Studies on the microstructure and density of sintered ZnO-based nonlinear resistors. *J. Mater. Sci.*, **22**(6) (1987) 2229–2236.