Ceramics International 30 (2004) 105–110

CERAMICS INTERNATIONAL

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Grain growth kinetic in xCoO–6 wt.% Bi_2O_3–(94−x) ZnO ($x = 0, 2, 4$) ceramic system

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Received 30 October 2002; received in revised form 12 December 2002; accepted 15 March 2003

Abstract

The grain growth kinetics in the 0, 2, 4 wt.% CoO added ZnO–6 wt.% Bi_2O_3 system was studied using the simplified phenomenological grain growth kinetics equation $G^n = K.t.\exp(-Q/RT)$ 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 5.2 and ∼200 kJ/mol respectively. The addition of the CoO to the ZnO–6 wt.% Bi_2O_3 system had no effect in the grain growth. At 0% CoO addition the apparent activation energy was calculated as 204 kJ/mol and with 4 wt.% CoO addition it was calculated as 203 kJ/mol.

Keywords: A. Grain growth; A. Sintering; D. Zinc oxide; E. Varistors; Kinetics

1. Introduction

The semiconduting property of zinc oxide is utilized in gas sensor and in varistors [1]. 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. It is now well established that the voltage breakdown per unit thickness in a varistor is directly related to 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.

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 work published on the subject, Senda and Bradt [2], presented the most detailed study covering the grain growth kinetics in ZnO ceramics containing up to 4 wt.% Bi_2O_3. In their work, Senda and Bradt [2] used the simplified grain growth kinetics equation

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

where, G is the average grain size at time t, n is the kinetic grain growth exponent value, K 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 [2] have calculated the grain growth exponent value (n) as 3 and apparent activation energy (Q) as 224±16 kJ/mol in the sintering of the pure ZnO system. However, in a subsequent study Dey and Bradt [3], studied the grain growth kinetics of ZnO having Bi_2O_3 addition from 3 to 12 wt.%. They found that the rate of grain growth of ZnO was affected by the increased amounts of Bi_2O_3 addition and the apparent

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doi:10.1016/S0272-8842(03)00071-3

activation energy for the grain growth of the system was raised from 160 to 270 kJ/mol 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 ($\leqslant$5–6 wt.%) to that of a ion diffusion controlled mechanism in a liquid phase.

The addition of MnO to the ZnO–6 wt.% Bi_2O_3 and to the ZnO–6 wt.% Sb_2O_3 systems was studied by our group [4,5] and this present work is the continuation of the previous works in the grain growth kinetics of ZnO varistors. The aim of the present work is to study the grain growth kinetics of ZnO containing 6 wt.% Bi_2O_3 which was found to be critical level in the change of the grain growth kinetics. A further aim of the work is also to study the effect of CoO additions as a third component to the microstructure and to the sintering behaviour of this system.

2. Experimental procedure

High purity ZnO (99.7%, Metal Bilesikleri A.S., Gebze, Turkey), Bi_2O_3 and CoO (as Co_3O_4) powders from Merck (pure grade) were used in the preparation of three basic compositions; ZnO–6 wt.% Bi_2O_3 and those containing 2 and 4 wt.% CoO. As reported in our previous papers [4,5] ZnO powders revealed a needle like fine crystals c. 0.5 μm width and c. 0.5–2 μm length. The calculated amounts of oxides for the indicated compositions were ball milled in an ashless rubber lined ceramic jars for 6 h using zirconia balls and distilled water as the milling media. The mixtures were dried to c. 10–15% moisture level and then granulated. Specimens of 10 mm diameter and c. 8 mm thick were prepared by semi-dry pressing of the granules of −150 μm +75 μm in size at a pressure of 100 MPa. The specimens were sintered in air at 1000, 1100, 1200 and 1300 °C for 1, 3, 5 and 10 h using a heating rate of 5 °C/min, and were naturally cooled in a PID controlled furnace (Nabertherm).

The bulk densities of the samples were determined from their weights and dimensions. Characterization of the phases in the sintered specimens were carried out by X-ray diffraction using CuK_α radiation. For the microstructural observations both scanning electron microscopy (SEM) of the fracture surfaces and optical microscopy of polished and etched (in a 20% acetic acid-distilled water solution) surfaces were used. Grain size measurements were carried out on the micrographs of the etched samples using the following equation,

$$G = 1.56 \times L \tag{2}$$

where, G is the average grain size, L is the average grain boundary intercept length of four random lines on two different micrographs of each sample [6].

3. Results and discussion

3.1. Properties of the sintered samples

The X-ray powder diffraction study in all compositions at different sintering temperatures and at various times showed the presence of only ZnO and β-Bi_2O_3 (ASTM card Nos: 36-1451 and 27-50 respectively). This shows that CoO forms solid solution with ZnO. The presence of Bi_2O_3 in β-form is in agreement with the results of Cerva and Russwurm [7] and Ozkan et al. [4]. At 1300 °C, there was no peaks indicating of β-Bi_2O_3 due to the volatilization of this phase.

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. It was observed that all samples showed the decrease in weight of the samples with increasing sintering temperatures and also with increasing sintering time. Weight losses of samples with different CoO contents against sintering temperatures are shown in Fig. 1. The addition of CoO to the system had no effect on the weight losses and the total weight losses were around 5%. There was a sharper increase in weight losses above 1200 °C and this was attributed to the change of volatilization behaviour at high temperatures of Bi_2O_3 as reported by Wong [8].

Bulk densities of all the samples showed decreament with increasing sintering temperatures and times [2,9]. As shown in Fig. 2a and b, that with increasing temperature and time the bulk densities of the samples with 2 wt.% CoO addition, were decreased from 5.41 g/cm^3 at 1000 °C to 5.07 g/cm^3 at 1300 °C at sintering time of 1 h. Similar behaviours were observed at sintering times of 3, 5 and 10 h with lowering density values. The

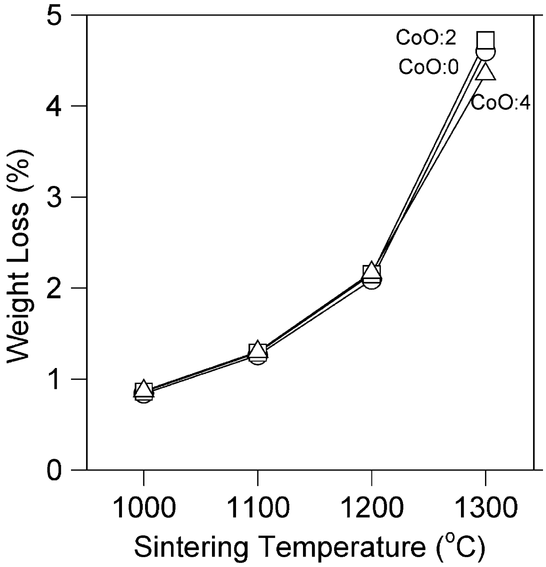

Fig. 1. Weight losses of the samples with sintering temperatures and times.

highest densification was at a low sintering temperatures and time due to the liquid phase sintering, in this case 1000 °C for the samples having 2 wt.% CoO additive. Higher sintering temperatures and longer sintering times give rise to a reduction in bulk densities 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 sintering above 1200 °C. The microstructures of the samples with no addition of CoO and with 4% CoO additions were shown in Fig. 3a–d. These optical micrographs were taken from the polished and etched surfaces of the samples which were sintered for 1 h at 1100 and 1300 °C. The grain sizes of the samples which were sintered at 1100 °C, were similar as ~18 μm for ZnO–6 wt.% Bi_2O_3 and 4 wt.% CoO added systems. The mean values of the grain sizes were ~39 μm, for the samples sintered at 1300 °C for 1 h. As shown in the microstructure that the addition of CoO to ZnO–6 wt.% Bi_2O_3 system had no effects on the grain sizes.

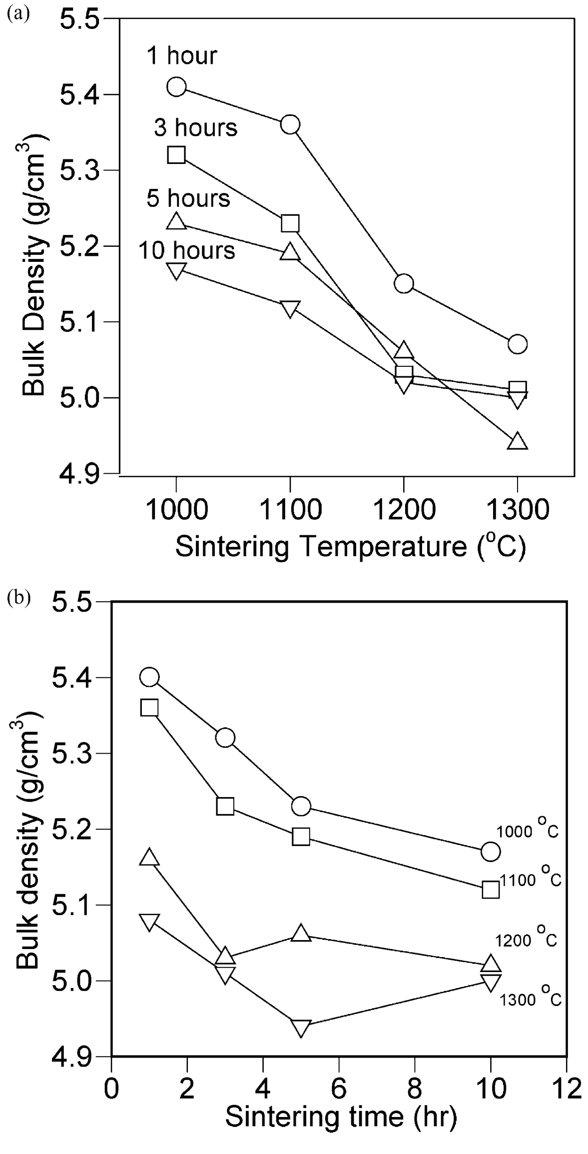

Fig. 2. Changes in bulk densities with, (a) sintering temperatures and (b) sintering times.

3.2. Grain growth kinetics

The grain growth kinetics can be determined using the simplified phenomenological kinetic Eq. (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

$$n\log G = \log t + (\log K - 0.434(Q/RT)) \tag{3}$$

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

The average grain growth exponent value of 5.3, determined for the ZnO–6 wt.% Bi_2O_3 system is very close to the values obtained by Senda and Bradt [2] and Dey and Bradt [3]. The addition of 2 and 4 wt.% CoO gave the values of n as 5.6 and 5.2, respectively. These values are also very close to that of ZnO–6 wt.% Bi_2O_3 system. These results indicated that the addition of CoO to ZnO–6 wt.% Bi_2O_3 system had no effects on the grain growth.

When Eq. (1) is expressed in the form;

$$\log(Gn/t) = \log K_0 - (0.434Q/R)(1/T) \tag{4}$$

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 were constructed for the system studied are shown in Fig. 5a–c and the calculated apparent activation energies along with the logarithm of the preexponential constant K_0 are also listed in Table 1.

Table 1
Calculated grain growth exponent (n), apparent activation energy (Q) and preexponential constant (K_0) values

CoO (wt.%)	n	log K_0	Q (kJ/mol)
0	5.3	15.098	204±20
2	5.6	15.695	187±15
4	5.2	15.952	203±31

In all calculations, "$n=5$" was used.

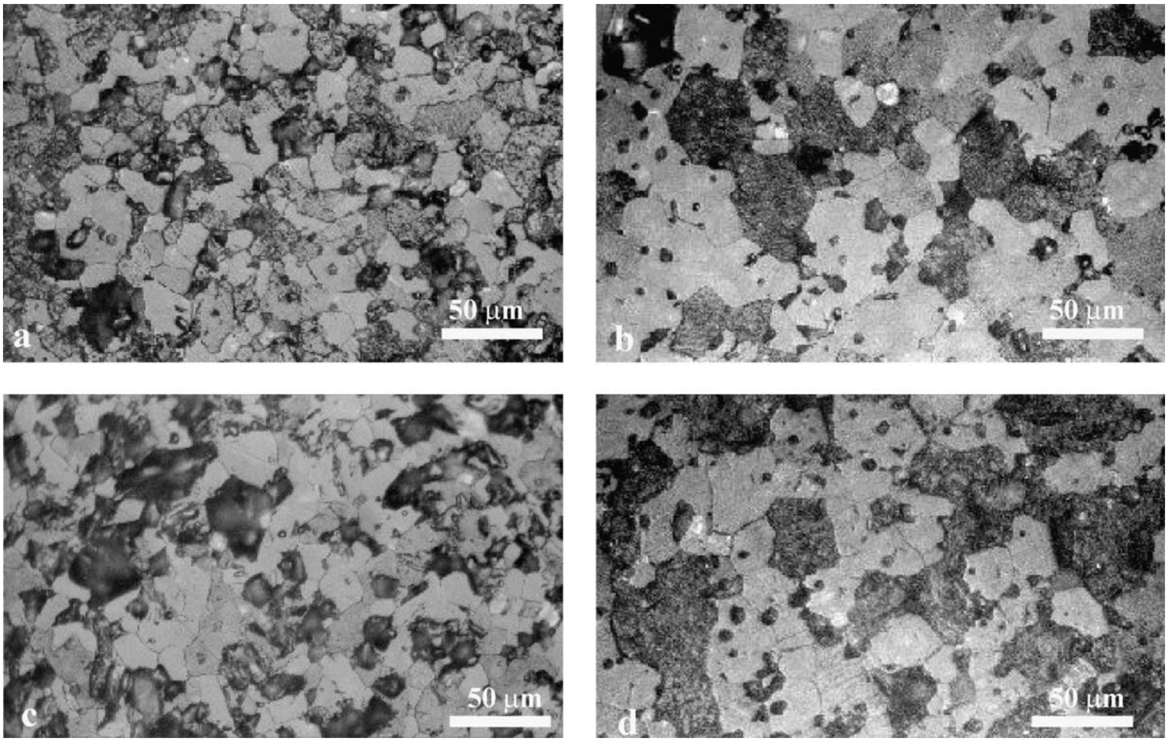

Fig. 3. Optical micrographs of polished and etched surfaces of (bar = 50 μm); (a) ZnO–6 wt.% Bi_2O_3 at 1100 °C, (b) ZnO–6 wt.% Bi_2O_3 at 1300 °C, (c) ZnO–6 wt.% Bi_2O_3–4 wt.% CoO at 1100 °C, (d) ZnO–6 wt.% Bi_2O_3–4 wt.% CoO at 1300 °C.

The numerous studies 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. 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 [2,3,8]. Among these studies, the notable work of Senda and Bradt [2] showed that a low level of Bi_2O_3 addition (~0.5 wt.%) to ZnO reduced the apparent activation energy to 150 kJ/mol and further additions up to 4 wt.% did not have a pronounced effect on the apparent activation energy.

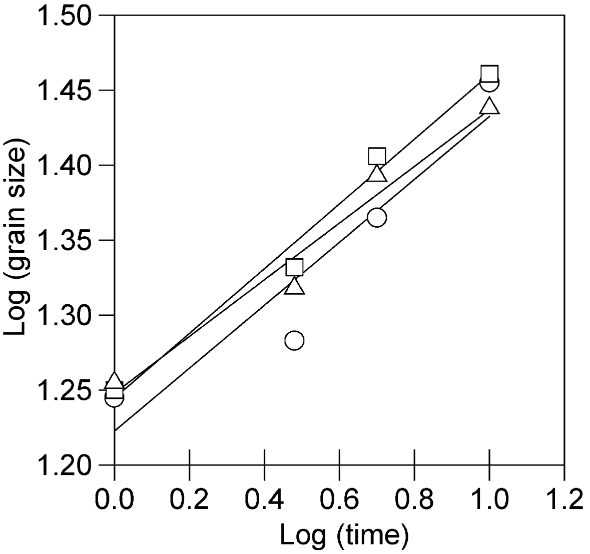

Fig. 4. Log (grain size, μm) vs log (time, h) plots of samples at 1100 °C.

However, in a later work by Dey and Bradt [3] showed that the addition of Bi_2O_3 beyond this level increased the apparent activation energy gradually and 274 kJ/mol 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 grain growth mechanism from the phase-boundary reaction in a 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 c. 5–6 wt.%.

In this study, the apparent activation energy of the ZnO–6 wt.% Bi_2O_3 system was calculated as 204 kJ/mol. This figure agrees with the figures of 232 kJ/mol quoted for the same composition by Dey and Bradt [3] and 200 kJ/mol quoted by Ozkan et al [4].

The apparent activation energies of the ZnO–6 wt.% Bi_2O_3 ceramic system with the addition of 2 and 4 wt.% CoO, were calculated as 187±15 and 203±31 kJ/mol, respectively. These values are close to the apparent activation energy value of ZnO–6 wt.% Bi_2O_3 system,

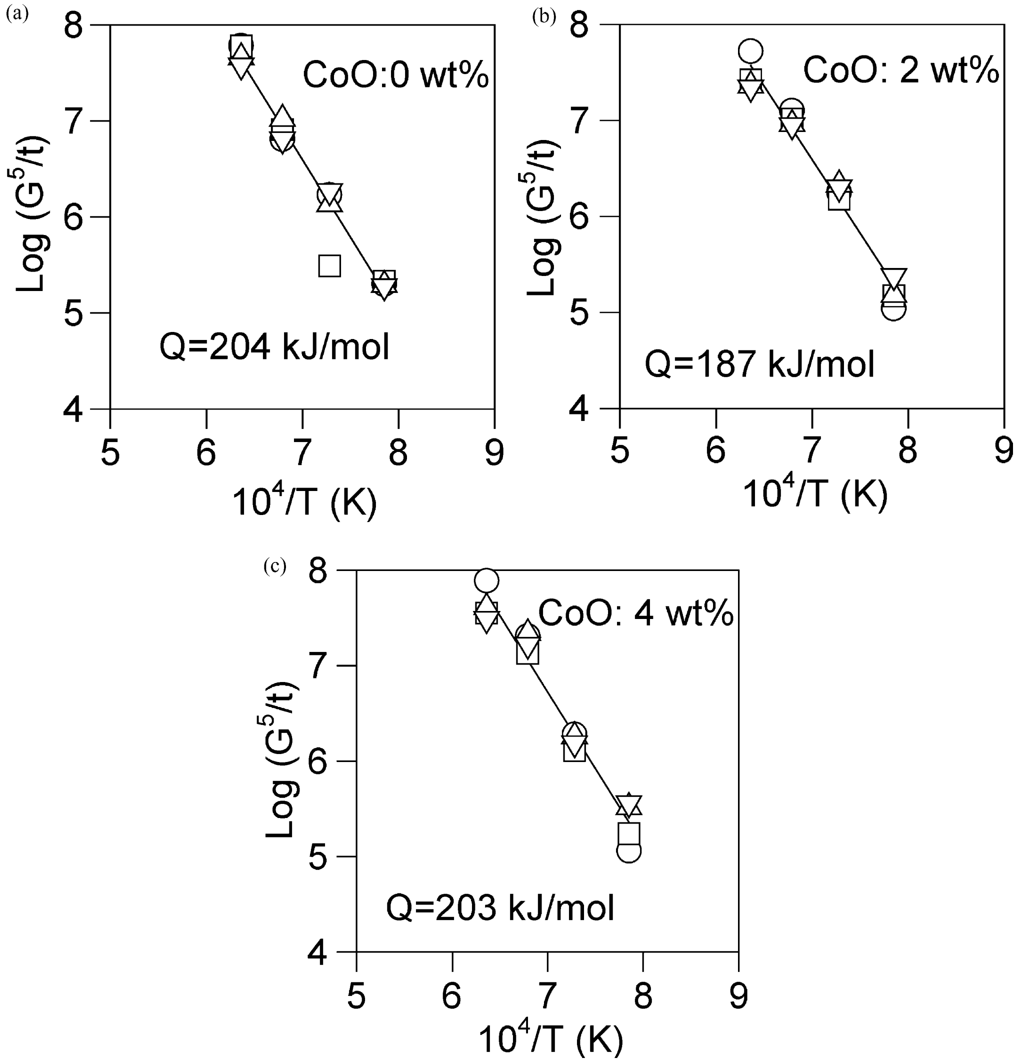

Fig. 5. Log (G^n/t) vs ($1/T$) plots of ZnO–6 wt.% Bi_2O_3 system with (a) 0 wt.% CoO, (b) 2 wt.% CoO, (c) 4 wt.% CoO additions.

which was calculated as 204±20 kJ/mol as reported earlier in this paper. All these results indicate that the addition of CoO to the ZnO–6 wt.% Bi_2O_3 ceramic sytem had no effect on the grain growth kinetics.

4. Conclusions

The effect of CoO additions of 0–4 wt.% to the sintering behaviour 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 volatilization of Bi_2O_3. The grain growth exponent value of 5 and the apparent activation energy of 204 kJ/mol found for the system with no addition of CoO, showed good correlation with the published data for the grain growth mechanism of the diffusion-controlled process in liquid phase sintering. The addition of CoO to ZnO–6 wt.% Bi_2O_3 ceramic system in this study, had no effect on the apparent activation energies and as a result no effect on grain growth kinetics.

Acknowledgements

This paper is part of the MSc thesis of O. Gelecek-Sulan and the authors express their gratitute to TÜBİTAK, Marmara Research Centre and to the Research Fund of ITU (Istanbul Technical University) for supporting this work. The authors are also grateful to Prof. Dr. R.C. Bradt of the University of Alabama, USA for giving valuable guidance at the beginning of these serious of works in the area of grain growth kinetics in ZnO-based varistors.

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