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Grain growth in TiO_2-added $ZnO–Bi_2O_3–CoO–MnO$ ceramics prepared by chemical processing

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Abstract

The effect of TiO_2 on the grain growth of the $ZnO–Bi_2O_3–CoO–MnO$ ceramic system prepared by chemical coprecipitation, was studied between 1150 and 1300 °C in air. Bi_2O_3 melts during firing, and then TiO_2 dissolves into Bi_2O_3-rich liquid. TiO_2 initially reacts with Bi_2O_3 to form $Bi_4Ti_3O_{12}$. Above ≈1050 °C, $Bi_4Ti_3O_{12}$ reacts with ZnO to form Zn_2TiO_4 spinel phase. The kinetic study of grain growth carried out using the expression $G^n - G_o^n = K_o \cdot t \cdot \exp(-Q/RT)$ gave grain exponent (n) value as 6 and the apparent activation energy (Q) as 226.46 kJ/mol. 1.00 mol% TiO_2 addition increased the grain growth exponent value from 6 to 7 and apparent activation energy with 1.00 mol% TiO_2 addition was found to be 197.10 kJ/mol. The ZnO grain size gradually increases with increasing TiO_2 content. Addition of TiO_2 may increase the reactivity of the Bi_2O_3-rich liquid towards the ZnO grain, thus affecting the ZnO grain growth.

Keywords: A. Grain growth; $ZnO–Bi_2O_3–CoO–MnO$ ceramics; TiO_2 additive; Chemical processing

1. Introduction

Zinc oxide varistors are highly non-ohmic resistors widely used in electronic appliances and especially in high voltage lines as voltage surge protection devices [1,2].

The grain size of ZnO based varistor ceramics is important since electrical properties of the materials depend on the microstructure. It is well established that the varistor breakdown voltage is affected by the grain size [3]. 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 non-linear current-voltage characteristics. In addition to these additives, other metal oxide such as TiO_2, MnO/Mn_2O_3, Cr_2O_3, CoO/Co_2O_3, 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 on the microstructure development and grain growth kinetics.

In early studies, Senda and Bradt [4,5] have reported such a study in pure ZnO and in Bi_2O_3, Sb_2O_3 added ZnO systems. Also, Suziki and Bradt [6] have reported ZnO grain growth in a ZnO–6 wt.% Bi_2O_3 ceramics with systematic additions of TiO_2.

The isothermal rate of grain growth can be expressed by the well known kinetic grain growth equation:

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

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

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

Using this equation, Senda and Bradt [4] have calculated the grain growth exponent of pure ZnO as 3 and the apparent activation energy for grain growth as 224±16 kJ/mol. Also, Suziki and Bradt [6] showed that in $ZnO–Bi_2O_3–TiO_2$ ceramic system the kinetic exponent for ZnO grain growth to be 3 for temperatures below ≈1050 °C, but 6 above 1050 °C when the

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Zn_2TiO_4 spinel phase forms. The activation energy for the grain growth of the ZnO is 300 kJ/mol for temperatures below 1050 °C, but increases to 360 kJ/mol above 1050 °C, independent of the TiO_2 content.

Therefore, the aim of this work is to study the grain growth kinetics of ZnO–Bi_2O_3–CoO–MnO–TiO_2 ceramic system prepared by chemical coprecipitation. A further aim of the work is also to study the effect of TiO_2 addition to the microstructure of this system.

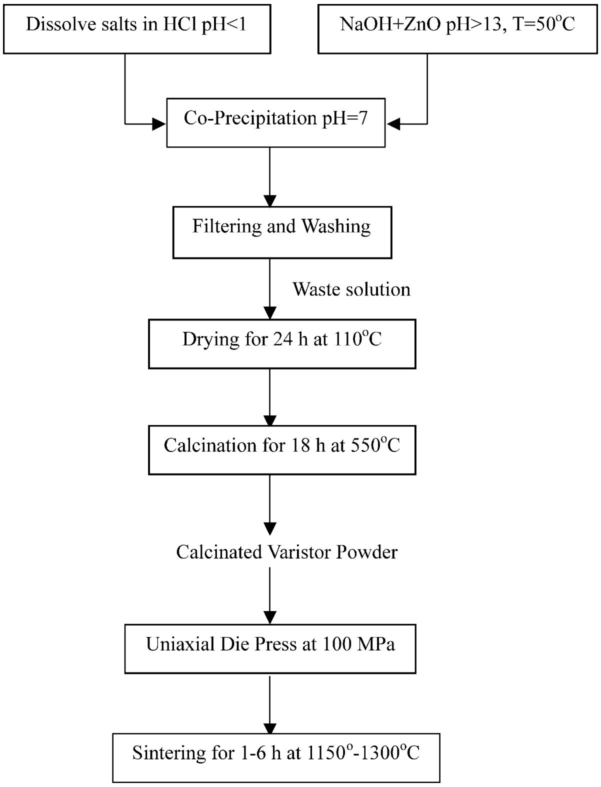

Fig. 1. Block diagram of the chemical processing route.

2. Experimental

The ZnO varistor powders were prepared by a chemical process whose flowsheet is shown in Fig. 1. High-purity ZnO, $Bi(NO_3)_3{\cdot}5H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $Ti(C_2H_5O)_4$, HCl and NaOH were used to prepare the 3 compositions with 0.25, 0.5, 1.0 mol% TiO_2. After drying, the mixture were granulated in moist conditions and then semi-dry pressed at 100 MPa. The pellets were sintered at 1150, 1200, 1250 and 1300 °C in air for 1, 2, 3, and 6 h using a heating rate of 10 °C/min and natural cooling in a furnace.

Sintered specimens were studied by X-ray diffraction using CuK_α radiation and by scanning electron microscopy (SEM) and optical microscopy of polished and thermal etched surfaces. Grain size measurements were done on the photomicrographs of the etched samples using the following equation

$$\overline{G} = 1.56{\cdot}\overline{L} \qquad (3)$$

where $\overline{G}$ is the average grain size, $\overline{L}$ is the average grain boundary intercept-legth of four random lines two micrographs [7].

3. Results and discussion

3.1. The effect of TiO_2 on microstructural evolution

Zinc oxide is amphoteric, soluble in both acids and bases. When ZnO is added to a NaOH solution, the following reaction partially occurs [8]:

$$ZnO_{(s)} + 2NaOH_{(aq)} \rightarrow Na_2ZnO_{2(aq)} + H_2O_{(l)} \qquad (4)$$

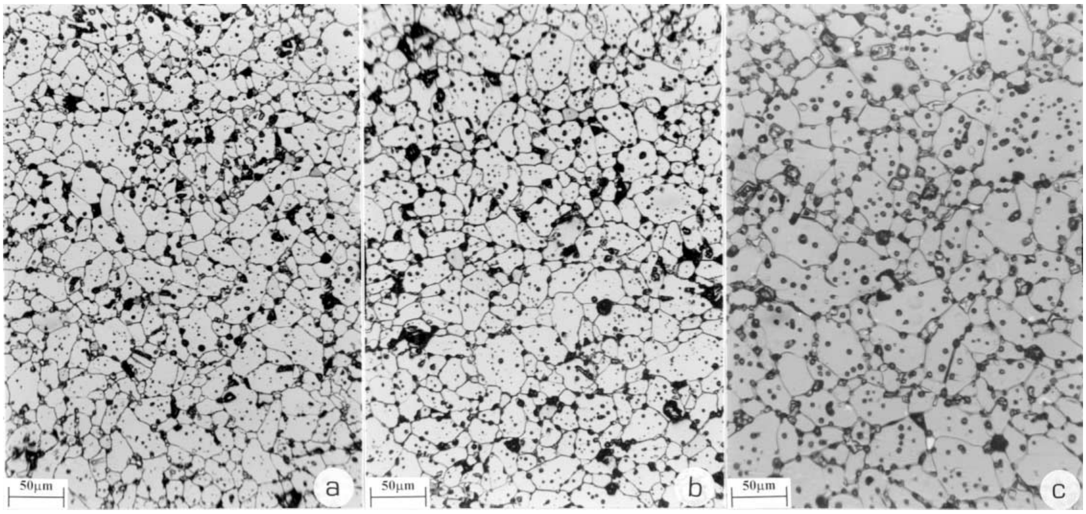

Fig. 2. SEM micrographs of (a) 0.25, (b) 0.50 and (c) 1.00 mol%TiO_2 added samples sintered at 1300 °C for 1 h respectively.

Then it becomes a Na_2ZnO_2 (solution)+ZnO+NaOH (solution) mixture. The other metal salts are dissolved in water with adding HCl to have a clear solution. The acid and the base solutions were rapidly mixed, then the metal hydroxides [$Bi(OH)_3$, $Ti(OH)_4$, $Co(OH)_2$ and $Mn(OH)_2$] and $ZnO/Zn(OH)_2$ were precipitated. As a result, the final product of the process was filtered, washed and dried for 24 h at 110 °C and calcined at 550 °C for 18 h. The homogeneous low voltage ZnO varistor powder have been successfully prepared by a single step chemical processing.

Pellets sintered at different temperatures were examined by X-ray diffraction. Presence of $Bi_4Ti_3O_{12}$ (ASTM No: 12-213) and ZnO (ASTM No: 5-0664) phases has been detected in samples fired at 1030 °C, but $Bi_4Ti_3O_{12}$ disappears after firing at 1150 °C and is accompanied by the formation of Zn_2TiO_4 spinel. Therefore, ZnO (ASTM No: 5–0664), β-Bi_2O_3 (ASTM No:27-50) and Zn_2TiO_4 (ASTM No:18–1487) are present in the samples fired at 1150 °C and over. These results are consistent with those of Suziki et al. [6], Sun and Kim [9] have also reported that during the beginning of the liquid-phase-sintering process in the $ZnO–Bi_2O_3–TiO_2$ system, the TiO_2 rapidly dissolves in the Bi_2O_3-rich liquid, and reacts to $Bi_4Ti_3O_{12}$ according to

$$2Bi_2O_3(l) + 3TiO_2(solution) \rightarrow Bi_4Ti_3O_{12}(s) \quad (5)$$

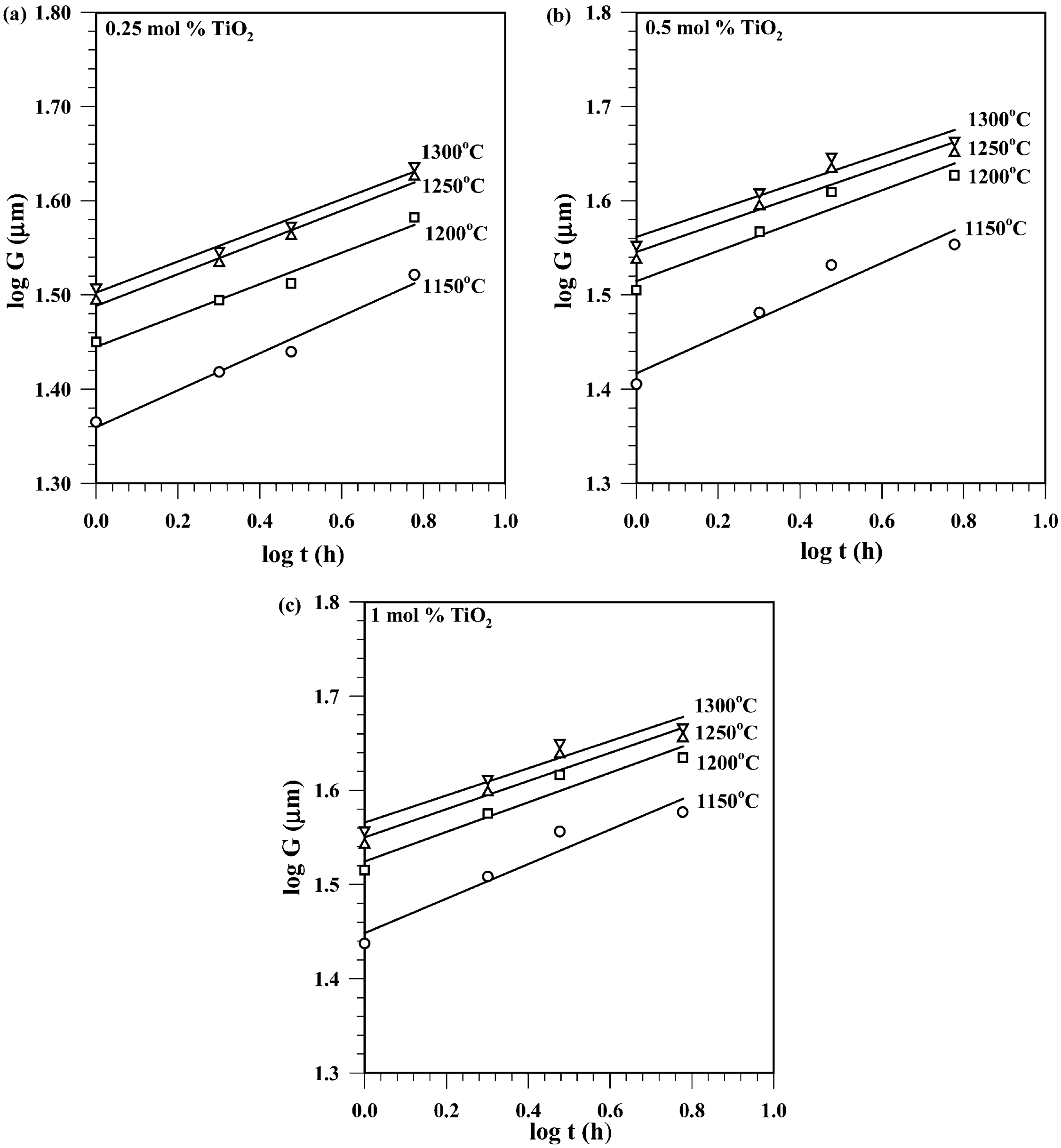

Fig. 3. Isotermal grain growth of $ZnO–Bi_2O_3–CoO–MnO$ ceramics containing (a) 0.25 (b) 0.50 and (c) 1.00 mol% TiO_2 at different sintered temperatures.

The solid $Bi_4Ti_3O_{12}$ is then reported to decompose and react with the solid ZnO grains at ~1050 °C, according to the reaction [10]

$$Bi_4Ti_3O_{12}(s) + 6ZnO(s) \rightarrow 2Bi_2O_3(l) + 3Zn_2TiO_4(s) \tag{6}$$

This latter reaction yields the Zn_2TiO_4 spinel phase. The reactivity of the Bi_2O_3-rich liquid toward the solid ZnO grains may be enhanced by formation of $Bi_4Ti_3O_{12}$.

3.2. Grain growth kinetics

Micrographs of sintered pellets are shown in Fig. 2(a)–(c). Grain size and grain growth kinetics were obtained from these figures. Then grain growth kinetics can be determined using the simplified phenomenological kinetics [Eq. (2)]. The grain growth exponent value (n) in the equation can be found at isothermal conditions where the kinetic equation is expressed in the form of

$$n\log G = \log t + \left\{\log K_o - 0.434(Q/RT)\right\} \tag{7}$$

and the reciprocal of the slope of the log (grain size) vs log(time) gives the n value. Fig. 3(a)–(c) depicts the log G vs log t plots for the different TiO_2 contents at the different sintering temperatures. Calculated n values are listed in Table 1.

Values of 3, 4, 5 and 6 for the grain growth exponent of ZnO have been reported by different researchers in

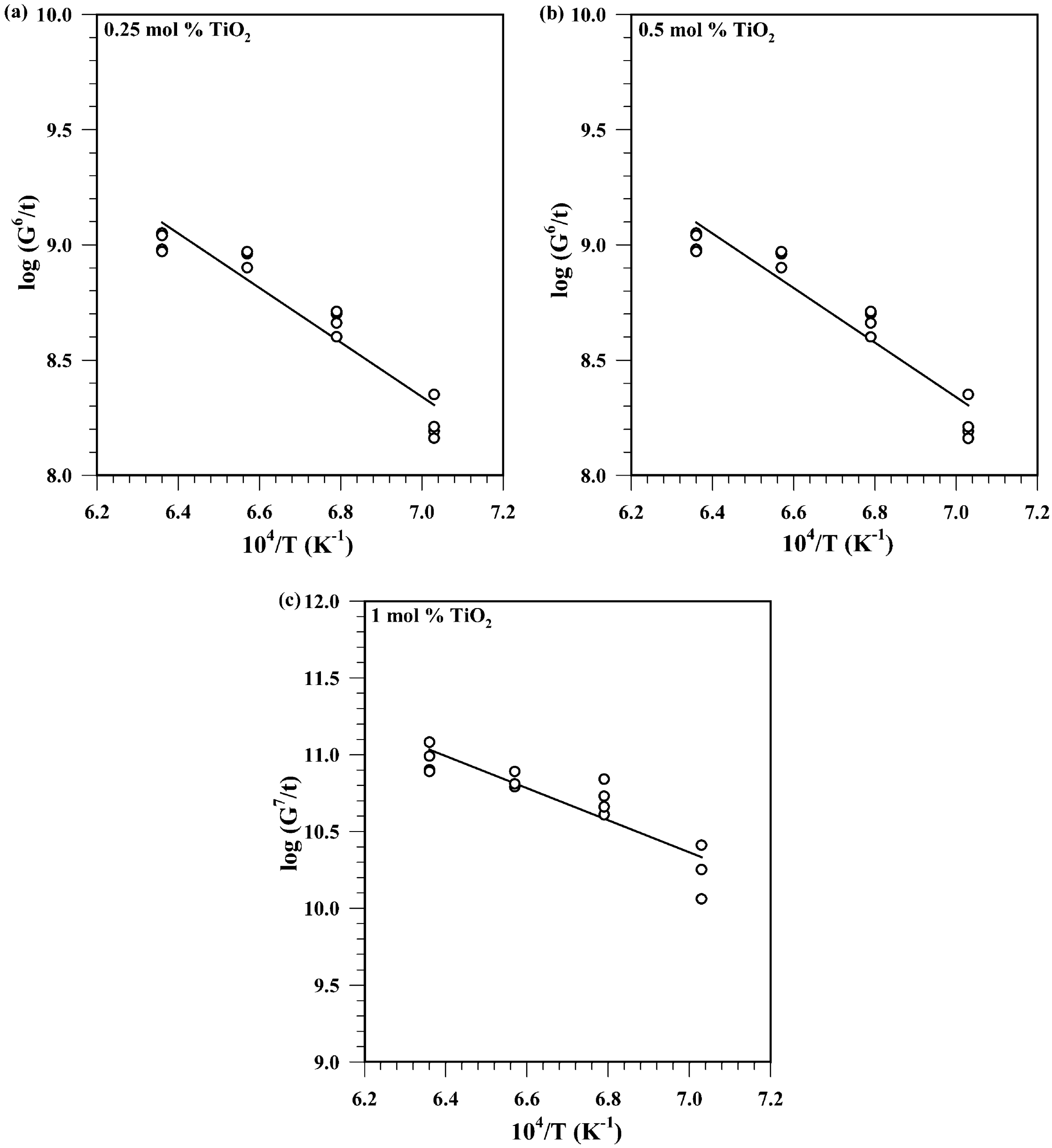

Fig. 4. Arrhenius plots for the grain growth of ZnO–Bi_2O_3–CoO–MnO ceramics containing (a) 0.25 (b) 0.50 and (c) 1.00 mol% TiO_2.

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

Mol% TiO_2 content	n Values at different temperatures				n Values used in Arrhenius plots	Log K_o	Q (kJ/mol)
	1150 °C	1200 °C	1250 °C	1300 °C			
0.25	5	6	6	6	6	16.61	226.46
0.50	5.1	6.2	6.7	6.9	6	16.49	213.44
1.00	5.6	6.5	6.7	7	7	17.58	197.10

different ceramic systems. The grain growth exponent for solid-state grain growth of pure ZnO has been confirmed to be 3 [4]. In a commercial ZnO varistor composition, an n value of 6 has been reported for ZnO grain growth exponent by Chen et al. [11]. Suziki and Bradt [6], have reported a ZnO grain growth exponent of 6 for TiO_2 (0.068–0.55 wt.%) added ZnO–6 wt.% Bi_2O_3 ceramics at high sintering temperatures. They also pointed out that the increase in the grain growth exponent indicates that the rate of ZnO grain growth is being reduced by effects such as second phase particle drag, pore drag, or perhaps by solid solution effects of metal oxide additions to the ZnO [6].

If Eq. (2) is expressed in the form of

$$\log(G^n/t) = \log K_o - 0.434(Q/RT) \tag{8}$$

the apparent activation energy Q of a grain growth process can be calculated from the Arrhenius plot of $\log(G^n/t)$ vs $10^4/T(K^{-1})$. Such plots for the studied system are given in Fig. 4(a)–(c). Table also lists the n values calculated in the construction of these plots along with calculated values of the logarithm of the rate constants and the apparent activation energies.

The results confirm the slight increase of the ZnO grain size with increasing TiO_2 contents. The activation energy for the ZnO grain growth appears not to be too much dependent on the TiO_2 content, ranging from 197.1 to 226.46 kJ/mol for the 3 compositions.

The effects TiO_2 additions on ZnO grain growth during liquid-phase sintering are distinctly different from those of the other two spinel-forming additives, Al_2O_3 and Sb_2O_3 [12,13]. With increasing Sb_2O_3 and Al_2O_3 levels, which cause increasing $Zn_7Sb_2O_{12}$ and $ZnAl_2O_4$ spinel contents, the ZnO grain size continually decreases. For the TiO_2 system, the ZnO grain size gradually increases with increasing TiO_2 content and, thus the Zn_2TiO_4 spinel content. Trontelj et al. [14], have observed and increase in the ZnO grain size with TiO_2 additions to about the 1 wt.% level, but they suggest a slight decrease with further TiO_2 addition in a commercial ZnO–Bi_2O_3–Mn_2O_3–Co_3O_4–TiO_2 material. Similar trends have been observed by Peigney et al. [12].

4. Conclusions

A sintered varistor materials of very uniform grain size and shape has been prepared by a chemical process. The grain size of the sintered ZnO increases slightly with increasing TiO_2 content. The activation energies for grain growth were determined between 197.10 and 226.46 kJ/mol.

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