GRAIN GROWTH OF ZnO AND OF ZnO IN $ZnO-Bi_2O_3$ AND $ZnO-Sb_2O_3$ CERAMICS

TETSUYA SENDA and RICHARD C. BRADT

Ship Research Institute
6-38-1 Shinkawa, Mitaka
Tokyo 181, JAPAN.

Mackay School of Mines
University of Nevada-Reno
Reno, NV 89557-0136, U.S.A.

ABSTRACT

The grain growth of ZnO is reviewed for sintered "pure" ZnO ceramics and also for ZnO ceramics with systematic additions of Bi_2O_3 and Sb_2O_3, two oxides which are commonly added to commercial ZnO varistor ceramics. The grain growth of ZnO is described and analyzed according to the phenomenological grain growth equation:

$$G^n - G_0^n = K_0 \ t \ \exp(-Q/RT).$$

The grain growth of ZnO in the three systems is then compared on the basis of the grain growth exponents (n-values) and the activation energies (Q-values).

In pure ZnO, the kinetic grain growth exponent is observed to be three and the activation energy is observed to be 224 kJ/mol, indicative of zinc ion diffusion as the rate controlling mechanism for grain growth. Liquid phase sintering with grain growth in the presence of Bi_2O_3 increases the grain growth exponent to five, but decreases the activation energy to 150 kJ/mol. There is a change of the rate controlling mechanism of ZnO grain growth to that of the phase boundary reaction between ZnO and the Bi_2O_3-rich liquid. At higher levels of Bi_2O_3 additions, above ten weight percent, the activation energy for ZnO grain growth increases to 270 kJ/mol, suggesting that the rate controlling grain growth mechanism becomes one of ZnO diffusion through the Bi_2O_3-rich liquid phase.

Additions of Sb_2O_3 react with the ZnO to form the zinc-antimony spinel, $Zn_7Sb_2O_{12}$, which pins the grain boundaries and strongly inhibits ZnO grain growth. It also causes the formation of basal inversion twins in the ZnO. The presence of the spinel phase and its grain growth inhibition of ZnO increases the grain growth exponent to six and the activation energy to nearly 600 kJ/mol. The rate controlling mechanism is characteristic of a particle drag mechanism of grain growth inhibition. The twin formation is also considered and a mechanism for twin formation is proposed which explains why there is only a single twin in each ZnO grain and how the addition of Sb_2O_3 nucleates the twin boundary in the early stages of sintering.

1. INTRODUCTION

ZnO ceramics with other metal oxide additions, such as Bi_2O_3, Sb_2O_3, CoO, Nb_2O_5 and MnO_2, exhibit non-ohmic current-voltage characteristics [1-4] and are utilized as varistors for surge protection devices in electric circuits. These are known as metal oxide varistors, sometimes MOV's. Some of the electrical properties, as well as the mechanical properties, of these ceramics are directly related to the microstructure. The grain size of the ZnO is one of the most important microstructural parameters in these ceramic varistors, because the ZnO grain size determines the break down voltage of the device [5, 6]. For this reason, numerous studies have been conducted to investigate the sintering and the microstructural development of ZnO [7-12] and ZnO with oxide additions [12-23].

However, the grain growth of ZnO in commercial metal oxide varistors is very complex because of the presence of several oxide additives. It has not been fully understood. It is, therefore, desirable to investigate the individual effects of each metal oxide on the ZnO grain growth. Among the many additions, two metal oxides with low temperature melting points, Bi_2O_3 and Sb_2O_3, are invariably present in most commercial ZnO varistors. These metal oxides have been of interest to many researchers, including Wong [13], Asokan et al. [15], Kim et al. [18-20], Trontelj and Krasevec [21], Senda and Bradt [12, 22] and Dey and Bradt [23]. When Bi_2O_3 is present, it is known to form a liquid phase during sintering and to promote the grain growth of ZnO. In contrast, Sb_2O_3 additions react with ZnO to form the $Zn_7Sb_2O_{12}$ spinel which retards both the densification and the ZnO grain growth of the ceramic during firing.

Grain growth during the sintering of polycrystalline ceramics can be described by the phenomenological kinetic equation:

$$G^n - G_0^n = K_0 \, t \, \exp(-Q/RT), \qquad (1)$$

where G_0 is the initial grain size and G is the grain size after sintering for the time t at the temperature of T (K). The n-value is the kinetic growth exponent, K_0 is the preexponential constant, Q is the activation energy for grain growth and R is the gas constant. When the initial grain size, G_0, is small, the term G_0^n may be considered negligible relative to G^n and the equation can be simplified to:

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

Since the logalithmic form of Equation (2) is:

$$\log G = (1/n) \log t + (1/n)[\log K_0 - 0.434(Q/RT)], \qquad (3)$$

the grain growth exponent or n-value is readily determined from the slope of the (log G) versus (log t) plots which is (1/n). Once the kinetic growth exponent is determined, Equation (2) can be rearranged into the form:

$$\log (G^n/t) = \log K_0 - 0.434 \ (Q/RT). \qquad (4)$$

Using the kinetic growth exponent, a plot of log (G^n/t) versus (1/T), which is an Arrhenius plot, is readily constructed. The slope, (-0.434 Q/R), provides the apparent activation energy, Q, and the intercept, which is log K_0, provides the preexponential constant for the grain growth phenomenon.

Only a few researchers have attempted to study the grain growth of ZnO in terms of these kinetic equations, although many others, among which Yamaguchi and his co-workers [16-20] are prominent, have investigated the microstructural character and phase assemblage. Recently, researchers have completed a series of the studies of ZnO grain growth for pure ZnO, for ZnO-Bi_2O_3 to 4 wt% Bi_2O_3, and for ZnO-Sb_2O_3 ceramics [12, 22]. Compacts of high purity ZnO powder, which was prepared by the French process, and the same ZnO with additions of Bi_2O_3 or Sb_2O_3 were prepared at several sintering temperatures from 900°C to 1400°C for 0.5 h to 16 h in air. The additive contents were systematically chosen on the basis of similar volume percentages for the Bi_2O_3 and Sb_2O_3 additions. Sintering temperatures were chosen for equal spacings in terms of $1/T$ (K^{-1}). Grain sizes were measured on the micrographs of the polished surfaces of the sintered samples by the intercept length method [24]. Recently studies have been extended and completed which address the grain growth of ZnO-Bi_2O_3 ceramics with higher Bi_2O_3 contents, to the 12 wt% level, in a similar manner [23].

During the microstructural observation of ZnO-Sb_2O_3 ceramics and commercial ZnO varistors, as well, it is observed that each of the ZnO grains contains a single twin boundary located near to its center [4, 22, 26]. There has been considerable speculation as to the role of these twins in the determination of the electrical properties of zinc oxide varistors and equally extensive consideration of the mechanism of the formation, or the origin of these twins. Yamamoto et al. [26], Kim and Goo [27], and Senda and Bradt [28] have all addressed the twins in ZnO-Sb_2O_3 ceramics from various perspectives.

This paper summarizes and reviews the above studies of the microstructural development of pure ZnO, ZnO-Bi_2O_3, and ZnO-Sb_2O_3. Emphasis is directed toward analysis in terms of the phenomenological kinetic grain growth equation and the discussion of quantitative parameters such as the n-values and the activation energies for ZnO grain growth. First, the grain growth of pure ZnO during sintering from 900°C to 1400°C is addressed and then the effects of Bi_2O_3 additions from 0.5 to 12.0 wt% are considered and compared. Next the grain growth of ZnO with Sb_2O_3 additions is described and, finally, twinning in ZnO-Sb_2O_3 ceramics is discussed and explained.

2. GRAIN GROWTH IN PURE ZnO

Typical sintered densities of pure ZnO ceramic bodies are shown in Figure 1. The densification process is essentially completed in 1 h, even at 900°C. Densities of about 98% of theoretical (5.61 g/cm^3) can be consistently obtained, except for sintering at the higher temperatures for extended times, where the density decreases slightly. The density decreases at higher temperatures have also been consistently observed by Gupta and Coble [9] and others and are believed to be related to the entrapment of insoluble gas in the pores or perhaps the

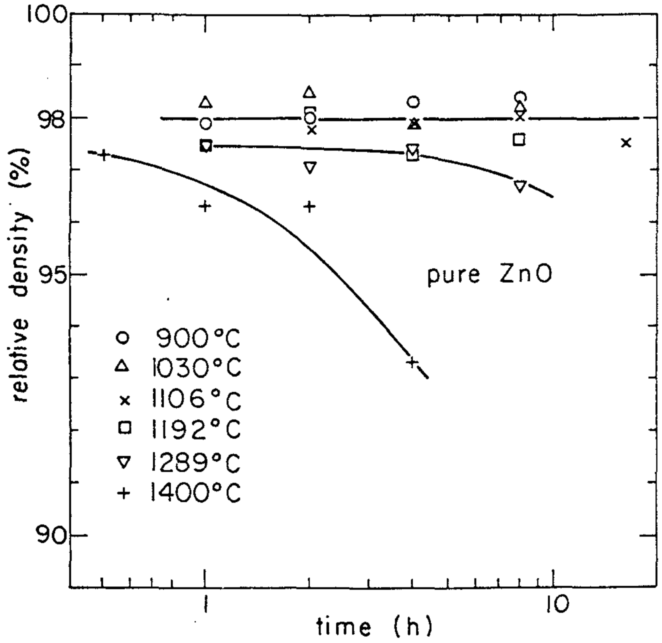

Figure 1. Densities of a pure ZnO ceramic sintered at temperatures from 900°C to 1400°C in air.

vaporization of ZnO itself.

A series of microstructures of a pure ZnO ceramic fired at 1289°C for various times is depicted in Figure 2. It is obvious that the average grain size increases with increasing sintering time. Figure 3 illustrates the isothermal grain growth results for a pure ZnO without other oxide additions. At the higher sintering temperatures the slopes are equal to 1/3, the reciprocal of which is a grain growth exponent of three. This is consistent with the exponent reported for pure ZnO by other researchers including Nicholson [7], Gupta and Coble [8], Dutta and Spriggs [10] and Readey et al. [11]. A kinetic grain growth exponent of three may in fact be the expected value as has been discussed by Atkinson [29].

Applying an n-value equal to three, an Arrhenius plot in which log (G^3/t) is plotted versus the reciprocal of the absolute temperature $(1/T)$ is presented in Figure 4. There exists a good linear relationship between log (G^3/t) and $(1/T)$ from 900°C to 1400°C. This implies that the rate controlling mechanism for the grain growth of pure ZnO is the same over this temperature range, even though the grain growth appears to exhibit a slightly higher kinetic grain growth exponent at the lowest temperature, 900°C. It is also significant that the linear relationship includes and can be satisfactorily applied to the density decrease region at higher temperatures. The apparent activation energy for the grain growth of pure ZnO as calculated from the slope of Figure 4 is 224 ± 16 kJ/mol.

Table I summarizes the kinetic grain growth exponents and the activation energies which have been reported by different researchers in previous investigations of ZnO grain growth [7, 8, 10-12, 14]. The activation energy derived from the slope of Figure 4 is in good agreement with the values reported by Gupta and Coble [8] and Dutta and Spriggs [10]. It is of interest that the results of Dutta and Spriggs were obtained for hot pressed dense ZnO compacts without any porosity. The close agreement for both the n-values and the activation energies implies that the small content of porosity does not significantly affect the grain growth of pure ZnO. From their activation energy, about 250 kJ/mol, Gupta and Coble concluded that the

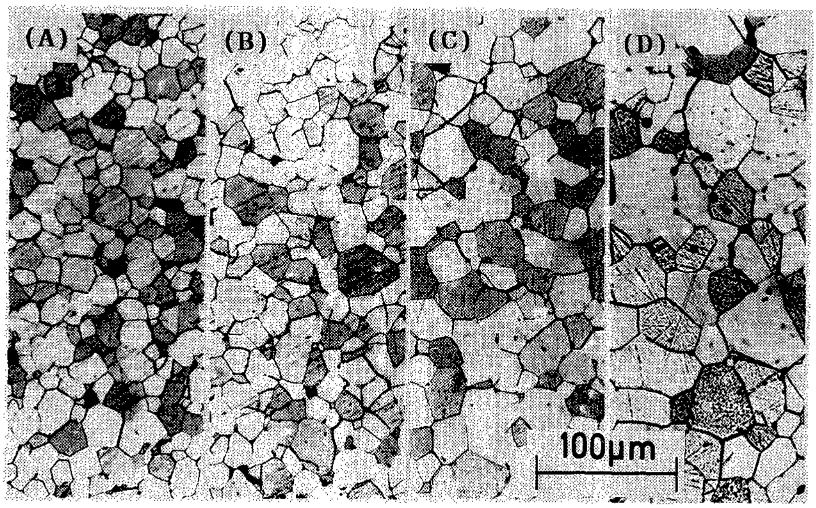

Figure 2. Microstructures of pure ZnO sintered at 1289°C for **(A)** 1 h, **(B)** 2 h, **(C)** 4 h, and **(D)** 8 h.

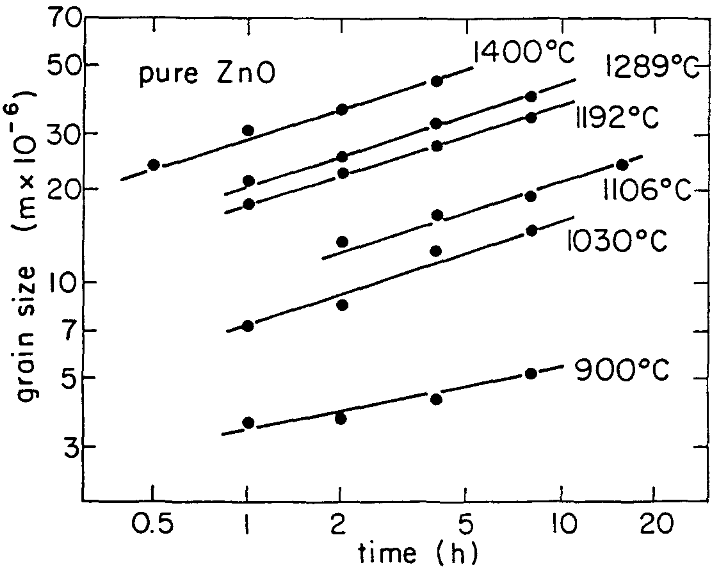

Figure 3. Grain growth of a pure ZnO ceramic. All of the lines, except for 900°C, have a slope of 1/3 indicating a kinetic grain growth exponent equal to three.

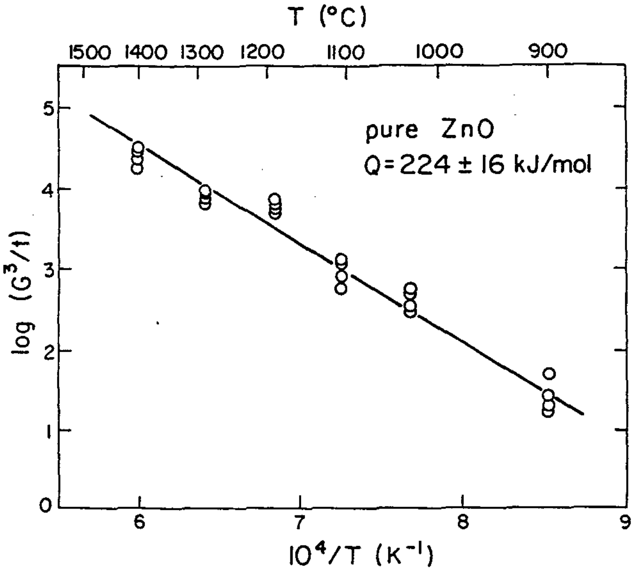

Figure 4. An Arrhenius plot for the grain growth of pure ZnO from 900°C to 1400°C for a kinetic grain growth exponent of three.

Table I. Summary of grain growth activation parameters for pure ZnO.

Reference	Grain growth exponent (n-value)	Activation energy (kJ/mol)	Preexponential constant, log K_0
Nicholson [7]	3	409	–
Gupta and Coble [8]	3	253±42	–
Dutta and Spriggs [10]	3	213	–
Gupta [14]	5	–	–
Wong [13]	6*	243*	–
Readey et al. [11]	3	326	–
Senda and Bradt [12]	3	224±16	11.49±0.35

*: Estimated by Senda and Bradt [12].

mechanism of grain growth is related to the diffusion of zinc ions in the ZnO wurtzite structure [8]. Subsequent results of activation energies varying from about 200 to 250 kJ/mol all support this conclusion. Some researchers have reported much higher apparent activation energies for the grain growth of ZnO [7, 11]. Those results appear to be derived from the initial stages of sintering where other processes such as evaporation and condensation may be dominant rather than solid state diffusion, or perhaps impurities may have been involved in the grain growth.

3. GRAIN GROWTH OF ZnO IN ZnO-Bi_2O_3 CERAMICS

The metal oxide Bi_2O_3 is a common addition to ZnO for commercial varistors. In sintered ZnO-Bi_2O_3 ceramics, Bi_2O_3 exists at the grain boundaries and multigrain junctions, but it does not diffuse throughout the ZnO grains to form a uniform solid solution [30, 31]. The Bi_2O_3-containing intergranular phase has been considered essential to the non-ohmic characteristics, with the possible mechanism of forming Schottky barriers. Since the melting point of Bi_2O_3 is only 825°C, it melts during the sintering of ZnO-Bi_2O_3 ceramics to effect liquid phase sintering of the varistor compositions. Sintering in the presence of a liquid phase has been studied by numerous researchers [32-39]. Recently, German [40] has completed a thorough review of liquid phase sintering.

Several researchers have studied the effects of the presence of a Bi_2O_3-rich liquid phase during sintering on the densification and the subsequent microstructural development of ZnO-Bi_2O_3 binary ceramics. Figure 5 summarizes the effects of Bi_2O_3 additions on the grain growth of ZnO in ZnO-Bi_2O_3 ceramics from several previous studies [12, 13, 15, 20, 23]. It is difficult to directly compare all of the results which are illustrated in Figure 5 because the powders were different and the sintering conditions in each experiment are not precisely the same. However, this plot does express the general trends of the effects of Bi_2O_3 additions. Initial additions of 0.5 wt% or 0.1 mol% of Bi_2O_3 strongly increase the sintered ZnO grain size. With further increases of the Bi_2O_3 content, the ZnO grain size appears to be less affected by the Bi_2O_3 level and rather appears to be independent of the Bi_2O_3 content to a Bi_2O_3 level of several weight percent. Further additions of Bi_2O_3 decrease the resulting ZnO grain size, which is, however, still much larger than that of pure ZnO for similar sintering conditions. All of the experiments reported in Figure 5 agree with this tendency, although the critical Bi_2O_3 levels for each of the transitions are not exactly the same, probably because of the characteristics of the different original ZnO powders. The dependence of the sintered ZnO grain size on the Bi_2O_3 content depicted in Figure 5, initially an increase, then a decrease, implies that the rate controlling mechanism of the process of ZnO grain growth changes depending on the Bi_2O_3 content of the ceramic.

Among the previously reported studies of the grain growth of ZnO in ZnO-Bi_2O_3 binary ceramics as illustrated in Figure 5, only Senda and Bradt [12] and Dey and Bradt [23] have completed activation analyses of the grain growth process. Micrographs of ZnO-Bi_2O_3 ceramics for the Bi_2O_3 levels through 4 wt% fired at 1192^oC for 4 h are shown in Figure 6 [12]. The average grain size of the ZnO when sintered with Bi_2O_3 additions is consistently larger than that of the pure ZnO. Figure 7 depicts the isothermal grain growth for the ZnO with the additions of 0.5 to 4 wt% Bi_2O_3 [12]. The grain growth exponents which are the reciprocals of the slopes of these plots exhibit more scatter than those in Figure 3. These vary from about two to more than ten, but generally appear to be larger than the value of three which was observed for the pure ZnO as shown in Figure 3.

Arrhenius plots of log (G^n/t) versus (1/T) for the same compositions as previously shown in Figure 7 are depicted in Figure 8 [12]. For the construction of the Arrhenius plots, a grain growth exponent of five has been applied to all of the ZnO-Bi_2O_3 compositions on the basis of the best fit for the plots. In fact, the plots in Figure 8 exhibit good linear relationships in spite of the scatter of the n-values. An exception is the sintering of the compositions with 0.5 to 2 wt% Bi_2O_3 at 900^oC, the lowest sintering temperature. From these plots, the apparent activation energies and the preexponential terms for grain growth have been calculated and are summarized in Table II

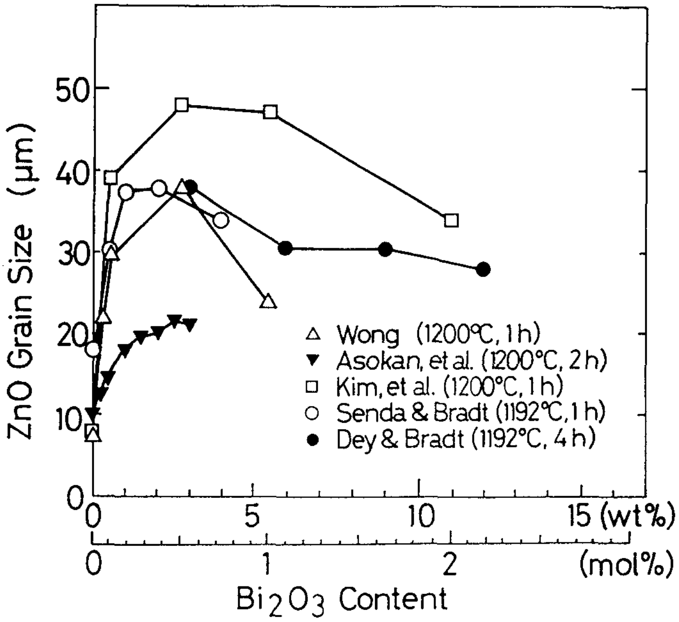

Figure 5. Effects of the Bi_2O_3 content on the ZnO grain size in sintered ZnO-Bi_2O_3 ceramics from previous studies for sintering at about 1200°C in air.

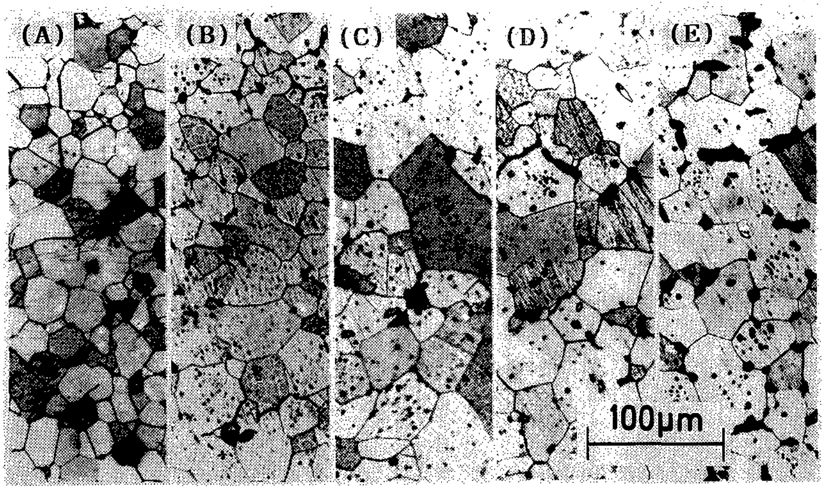

Figure 6. Microstructures of ZnO-Bi_2O_3 ceramics sintered at 1192°C for 4 h: **(A)** pure ZnO, **(B)** 0.5 wt% Bi_2O_3, **(C)** 1% Bi_2O_3, **(D)** 2% Bi_2O_3, and **(E)** 4% Bi_2O_3.

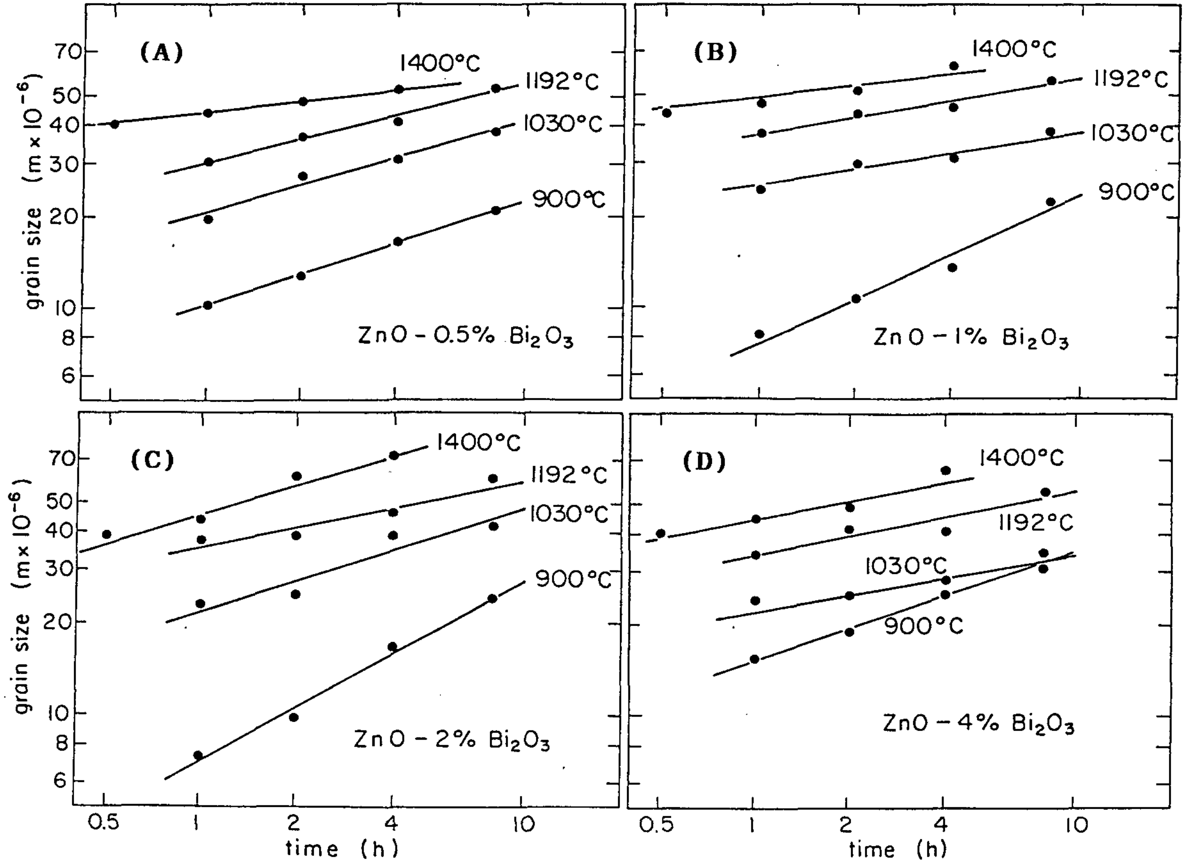

Figure 7. Grain growth of ZnO in ZnO-Bi_2O_3 ceramics with Bi_2O_3 contents from 0.5 wt% to 4 wt%: **(A)** 0.5%, **(B)** 1%, **(C)** 2%, and **(D)** 4%.

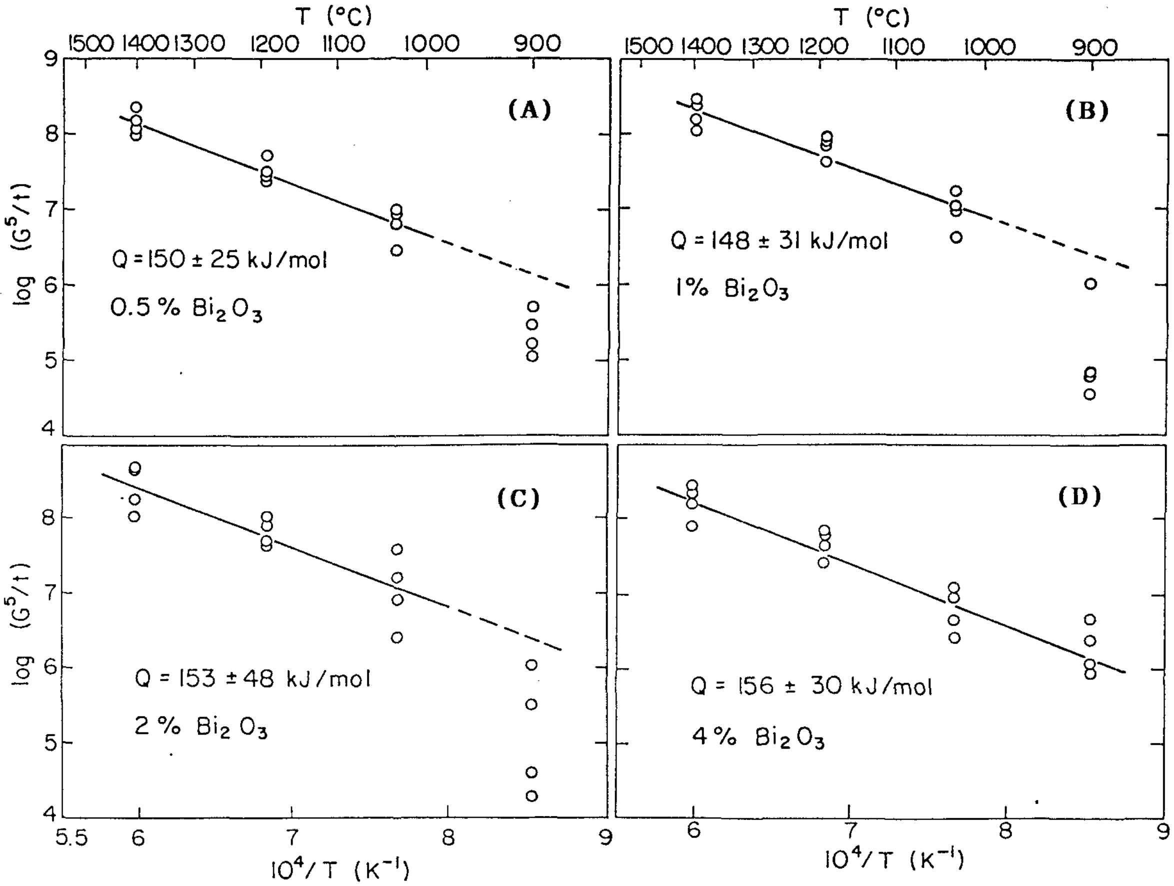

Figure 8. Arrhenius plots for the grain growth of ZnO in ZnO-Bi_2O_3 ceramics with additions of Bi_2O_3 from 0.5 wt% to 4 wt%: **(A)** 0.5%, **(B)** 1%, **(C)** 2%, and **(D)** 4%.

[12, 23]. Figure 9 [12, 23] illustrates the activation energies for the grain growth of ZnO in the pure ZnO and with the additions of Bi_2O_3 to 12 wt%, including results from various studies [8, 10, 13]. The Bi_2O_3 additions initially decrease the activation energy for the grain growth of ZnO from about 220 kJ/mol for the pure ZnO to about 150 kJ/mol for Bi_2O_3 levels through about 4 wt%. With increases of the Bi_2O_3 levels beyond 4 wt%, the activation energy for the grain growth of ZnO increases. However, the rate of the activation energy increase decreases for Bi_2O_3 contents in the vicinity of about 9 wt%. The activation energy for ZnO grain growth then appears to reach a plateau at about 270 kJ/mol, a value that is higher than that for grain growth of ZnO in pure ZnO ceramics.

Similar to the activation energy, the preexponential term is essentially constant for Bi_2O_3 levels from 0.5 to 4 wt%, but increases with further Bi_2O_3 additions and again appears to achieve a constant value beyond 9 wt%, as shown in Table II. Unfortunately, since the units of the K_0 term depend on the n-values, it is difficult to directly compare the K_0 values for ZnO-Bi_2O_3 ceramics with that for pure ZnO, which exhibits a smaller n-value of three.

Grain growth during sintering in the presence of a liquid phase has been determined to be the result of a solution-precipitation process. When the liquid phase wets the solid grains and the solid grains have substantial solubility in the liquid phase, then the smaller grains dissolve into the intergranular liquid phase and subsequently precipitate on the larger grains. This grain growth process is controlled either by the solution-precipitation reaction at the solid-liquid phase boundary, or by the diffusion of the solid component through the liquid phase from the smaller grains to the larger ones.

Initial additions of Bi_2O_3 increase the ZnO grain size and the kinetic grain growth exponent, but decrease the activation energy for ZnO grain growth. This can be explained by the change of the rate controlling mechanism for ZnO grain growth from one of the solid state diffusion of zinc ions within the ZnO wurtzite structure as suggested by Gupta and Coble [8] for pure ZnO to one of solution of ZnO in the Bi_2O_3-rich liquid phase and

Table II. Summary of ZnO grain growth activation parameters for sintered ZnO-Bi_2O_3 ceramics.

Reference	Bi_2O_3 Content (wt%)	Grain growth exponent (n-value)	Activation energy (kJ/mol)	Preexponential constant, log K_0
Wong [13]	0.57	5*	194*	–
	2.8	3*	163*	–
Senda and Bradt [12]	0.5	5	150± 25	12.83±0.31
	1	5	148± 31	12.96±0.39
	2	5	153± 48	13.19±0.61
	4	5	156± 30	13.13±0.60
Dey and Bradt [23]	3	5	178± 16	13.37
	6	5	232± 34	14.65
	9	5	269± 37	15.87
	12	5	274± 44	15.94

*: Estimated by Senda and Bradt [12].

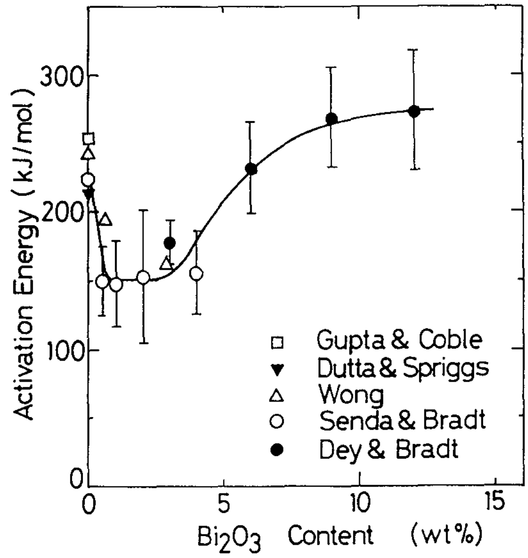

Figure 9. Effect of Bi_2O_3 content on the activation energy for ZnO grain growth in ZnO-Bi_2O_3 ceramics.

then precipitating on the larger ZnO grains. If diffusion through the liquid controls the rate of ZnO grain growth, it must be affected by the thickness of Bi_2O_3-rich liquid phase layer between grains which would depend on the Bi_2O_3 content. The independence of both the activation energy and the preexponential term, as well as the ZnO grain size and n-value, on the Bi_2O_3 content from 0.5 to about 4 wt% Bi_2O_3 suggests that the phase boundary reaction is the rate controlling process for the grain growth of ZnO at these Bi_2O_3 levels.

In contrast to the initial Bi_2O_3 additions, further increases of the Bi_2O_3 content beyond the 4 wt% level increases both the activation energy for ZnO grain growth and the preexponential term, indicative of a change in the rate controlling mechanism. The ZnO grain size decreases with an increase of the Bi_2O_3 content in this region. According to the derivation of Lay [37], if it is the diffusion through the Bi_2O_3-rich liquid phase which controls the rate of ZnO grain growth, then the rate of ZnO grain growth should be inversely related to the thickness of the liquid phase layer between the solid grains. An increase in the Bi_2O_3 content can be expected to increase the thickness of the Bi_2O_3-rich liquid layer between the grains. This increased diffusion path reduces the rate of ZnO grain growth, yielding smaller ZnO grain sizes. Thus, the higher the Bi_2O_3 contents, the longer is the diffusion distance and the smaller are the ZnO grain sizes, exactly as reported by the various researchers and illustrated in Figure 5. This reveals that the diffusion of ZnO through the Bi_2O_3-rich liquid phase is the rate controlling process at higher Bi_2O_3 contents.

From observations of the microstructures on cooled specimens using a scanning electron microscope, Kim et al. [20] have reported that the Bi_2O_3-rich phase is concentrated at multigrain junctions and does not appear to be present at the boundaries between two grains (homojunctions) for compositions with as high as 2 mol% Bi_2O_3. They concluded that the decrease of the ZnO grain size at higher Bi_2O_3 levels may be the result of a change of the grain growth process from one of mass transport through the Bi_2O_3-rich liquid phase to transport in ZnO-ZnO solid boundaries. However, from observations by high resolution transmission electron microscopy, Tomokiyo and co-workers [30, 31] have concluded that a continuous intergranular Bi-containing phase does in fact exist. It is likely that an even thicker layer of Bi_2O_3-rich liquid phase exists between the solid ZnO grains for compositions with higher Bi_2O_3 contents during sintering. Furthermore, if zinc ion diffusion through the ZnO-ZnO solid grain boundaries is the rate controlling mechanism for the ZnO grain growth, then the activation energy should be similar to that for pure ZnO. The activation energy results in Figure 9 suggest that the change in the rate controlling mechanism for ZnO grain growth at higher Bi_2O_3 contents is that from the phase boundary reaction to diffusion through the liquid phase. This is further substantiated by the grain size trends in Figure 5.

4. MICROSTRUCTURAL DEVELOPMENT IN ZnO-Sb_2O_3 CERAMICS

(1) GRAIN GROWTH OF ZnO

Similar to the effect of Bi_2O_3, the grain growth of ZnO in ZnO-Sb_2O_3 ceramics has also been investigated by several researchers [15, 16, 18, 21, 22]. They have consistently reported that the addition of Sb_2O_3 retards densification and decreases the rate of ZnO grain growth during sintering. Previous phase studies of ZnO-Sb_2O_3 ceramics have also confirmed that the Sb_2O_3 additions exist as $Zn_7Sb_2O_{12}$ spinel particles at the grain boundaries and multigrain junctions of the ceramics after firing [17]. In fact, the resulting microstructures of ZnO-Sb_2O_3 ceramics contain numerous small spinel particles at the grain boundaries and multigrain junctions, as shown in Figure 10 [22]. As a result, it has been concluded that the ZnO grain growth inhibition by the additions of Sb_2O_3 is one of grain boundary pinning by the second phase $Zn_7Sb_2O_{12}$ spinel particles, a phenomenon which was originally suggested by Zener [41].

Figure 11 [22] illustrates the fired densities for ZnO ceramics with 1.18 wt% Sb_2O_3. This composition was still in the process of densification even after 16 h at 1106°C, although the pure ZnO had achieved a final density of 98% theoretical for the same sintering conditions as previously shown in Figure 1. This

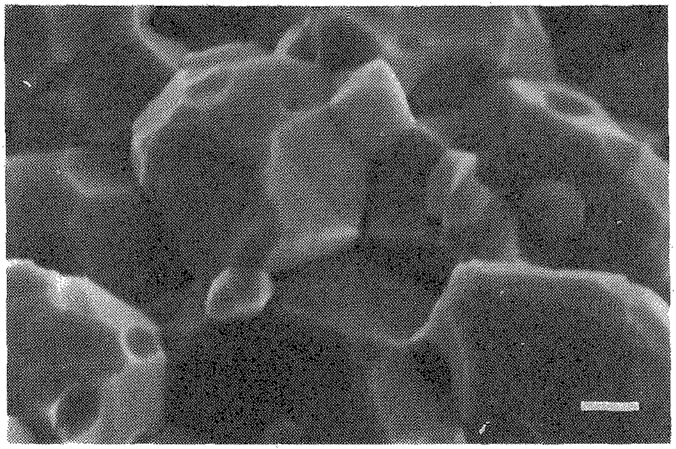

Figure 10. Scanning electron micrograph of the fracture surfac of ZnO containing 2.38 wt% Sb_2O_3 fired at 1400°C for 4 h. Not the small $Zn_7Sb_2O_{12}$ spinel particles. (bar= 3μm)

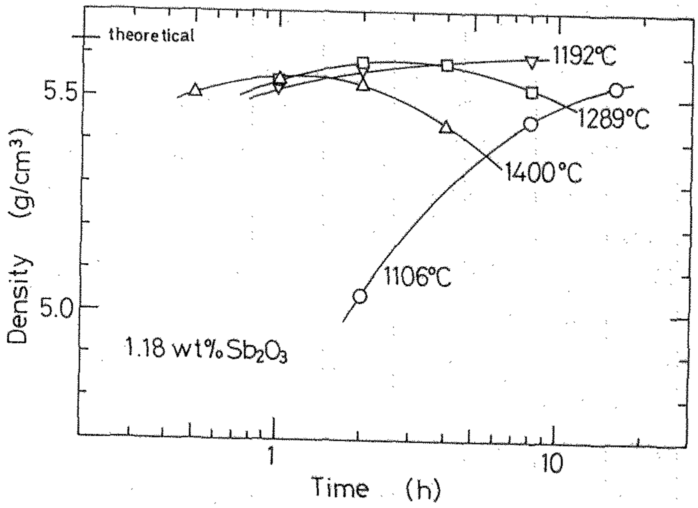

Figure 11. Densities of $ZnO-Sb_2O_3$ ceramics with 1.18 wt% Sb_2O_3 sintered between 1106°C and 1400°C.

retardation of the densification of ZnO by Sb_2O_3 additions is consistently reported in literature [17, 21, 22].

Figure 12 [22] illustrates a series of microstructures of polished and etched ZnO ceramics with additions of 0.29 to 2.38 wt% Sb_2O_3, as well as for pure ZnO, all fired at 1400°C for 1 h. It is readily observed that finer ZnO grain sizes result for the higher Sb_2O_3 levels. The addition of Sb_2O_3 decreases the grain growth of the ZnO in these ZnO-Sb_2O_3 ceramics. The presence of a single twin in each of the individual ZnO grains is also apparent for all of the ZnO-Sb_2O_3 compositions, a point which will be explained later in this paper.

Figure 13 [22] illustrates the isothermal grain growth of the ZnO for four Sb_2O_3 compositions and for pure ZnO at different firing temperatures from 1106°C to 1400°C. The average ZnO grain sizes for each of the Sb_2O_3-containing compositions are consistently smaller than those of the pure ZnO which was fired under the same set of conditions, with a single exception, that for firing at 1400°C for 0.5 h. There exists a substantial dependence of the ZnO grain size on the Sb_2O_3 content. Figure 14 [22] depicts the dependence of the ZnO average grain size on the Sb_2O_3 content at several stages during sintering: at 1192°C for 1 h; at the stage where maximum density is achieved (1289°C for 4 h); and for conditions where the density is in a decreasing stage, 1400°C for 4 h. The three conditions are compared with ZnO grain sizes in the ZnO-Bi_2O_3 system for the basis of similar volume percentages of the original oxide additions, although it is realized that these volume percentages change during firing and reaction. The sintered ZnO grain sizes decrease continuously with increasing Sb_2O_3 levels at all stages of the sintering, whereas the similar plots for Bi_2O_3 additions clearly reveal both the enhancement of the ZnO grain growth and a distinct independence of Bi_2O_3 level. It should be recalled, however, that at higher Bi_2O_3 contents a ZnO grain size decrease occurs as summarized previously and shown in Figure 5.

The grain growth exponents in Figure 13 range from about 4 to 12 for the individual lines, consistently larger than the value of three for pure ZnO. However, there does not appear to be any consistent trend in these grain growth exponents, either

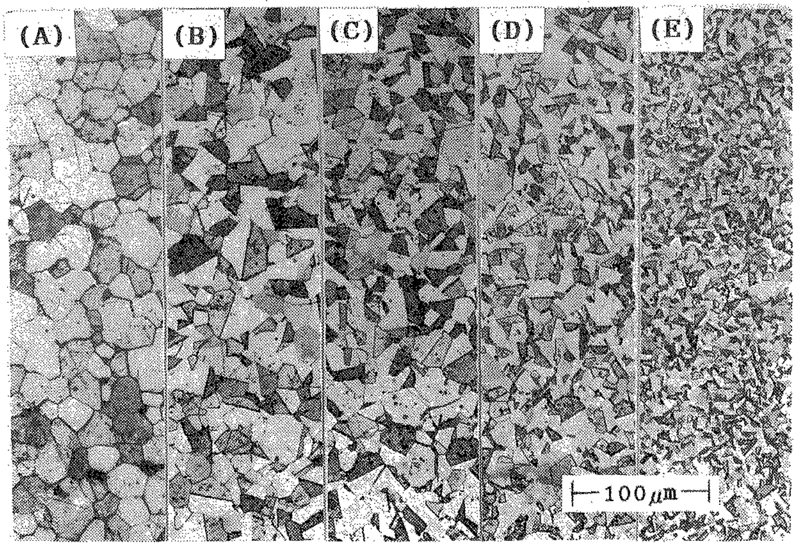

Figure 12. Microstructures of ZnO-Sb_2O_3 ceramics sintered at 1400°C for 1 h: **(A)** pure ZnO, **(B)** 0.29 wt% Sb_2O_3, **(C)** 0.58% Sb_2O_3, **(D)** 1.18% Sb_2O_3, and **(E)** 2.38% Sb_2O_3. Note the presence of twins in the Sb_2O_3-containing compositions.

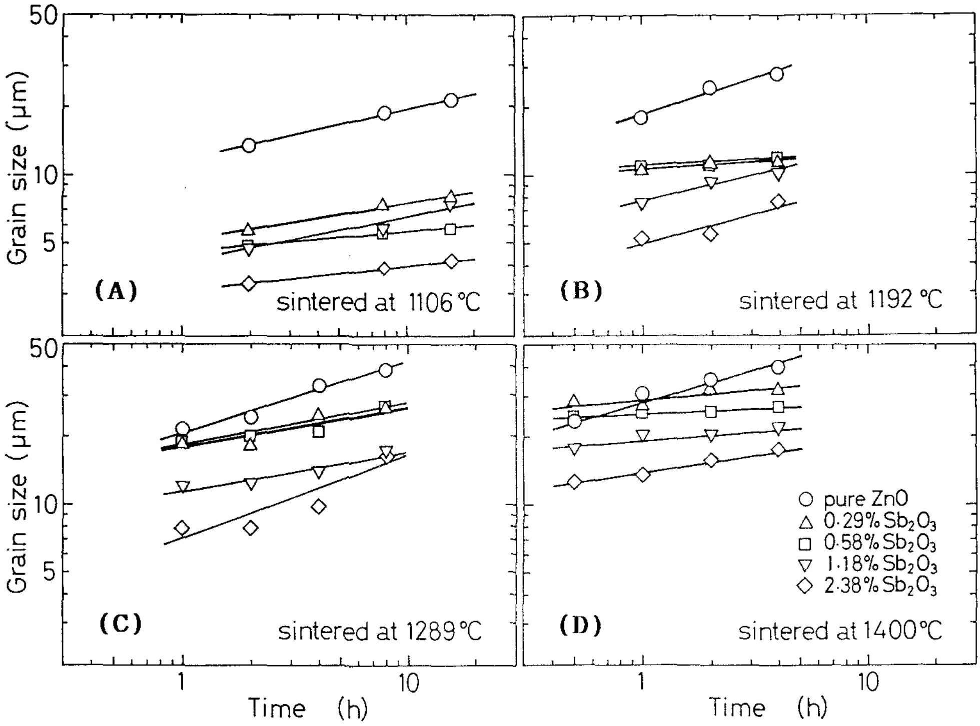

Figure 13. Grain growth of ZnO in ZnO-Sb_2O_3 ceramics sintered at: **(A)** 1106°C, **(B)** 1192°C, **(C)** 1289°C, and **(D)** 1400°C for different times.

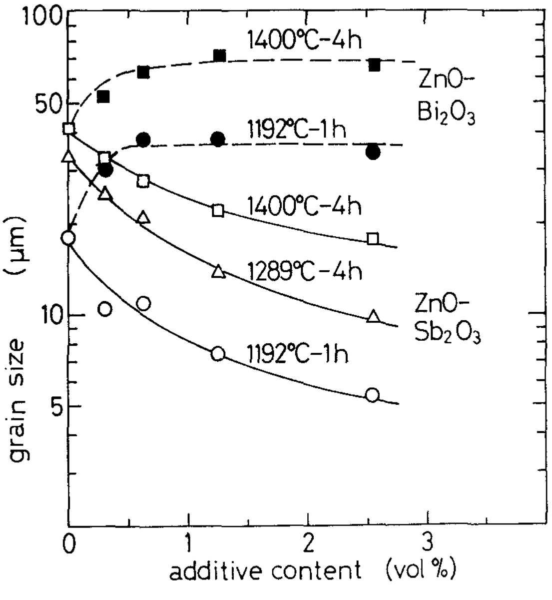

Figure 14. Effect of additive content on the ZnO grain size in ZnO-Sb_2O_3 compositions. Results for ZnO-Bi_2O_3 ceramics at similar volume percentage levels are included for comparison.

with variations in the Sb_2O_3 content, or for changes in the sintering temperatures. The n-value estimated from an average of 1/n, is 6.4, while the median n-value is found to be 6.2 from the 16 different slopes. Thus, for determining an n-value to be utilized for the Arrhenius plot construction, an integer value of six for the grain growth exponent has been applied.

The Arrhenius plots of log (G^6/t) versus 1/T are illustrated in Figure 15 [22]. In spite of the aforementioned variations in the kinetic grain growth exponents, these four Arrhenius plots present reasonably good linear relationships for each of the four Sb_2O_3 contents. The activation energies determined from the slopes of the regression lines in Figure 15 vary from 563 to 698 kJ/mol. The values are summarized in Table III [22] with the preexponential terms. The effects of Sb_2O_3 content on the activation energy for the grain growth of ZnO are presented in Figure 16 [22], also in comparison with the effects of Bi_2O_3 additions at the same volume percentages. The apparent activation energies for ZnO-Sb_2O_3 grain growth do not exhibit any obvious trend with Sb_2O_3 content. They are consistently larger than the 224 kJ/mol value which has been observed for pure ZnO grain growth and the 150 kJ/mol for ZnO-Bi_2O_3 with the same volume levels of additions. The preexponential constant, K_0, summarized in Table III, varies from 25 to 31 in terms of log K_0, not significantly dependent on the Sb_2O_3 content either. These results of the activation analyses do not suggest any change in the rate controlling mechanism for ZnO grain growth inhibition over the compositional range from 0.29 to 2.38 wt% Sb_2O_3 in ZnO-Sb_2O_3 ceramics.

Several researchers have investigated the sintering of Sb-containing ZnO powder compacts through detailed phase studies or thermal analyses [17, 42, 43]. From those studies, a possible scenario can be proposed for the early stages of the ZnO-Sb_2O_3 sintering processes during firing. Upon heating, the Sb_2O_3 first oxidizes to Sb_2O_4 at about 400°C. It next evaporates above 500°C, but condenses on the ZnO grains to form a very thin, but continuous, noncrystalline film around 600°C. Crystallization of this film to form the $Zn_7Sb_2O_{12}$ spinel occurs at about 700°C, maintaining the form of a thin coating film. It

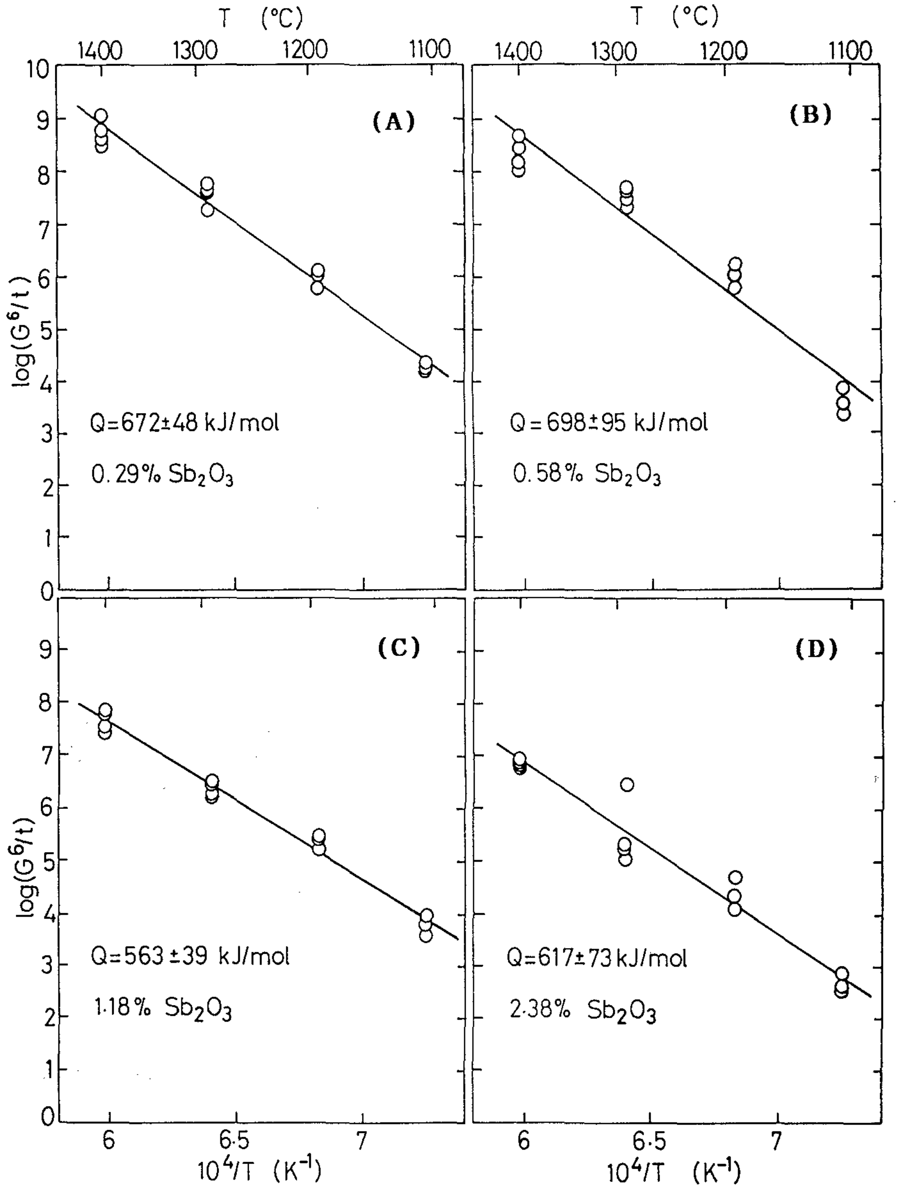

Figure 15. Arrhenius plots for the grain growth of ZnO in ZnO-Sb_2O_3 ceramics: **(A)** 0.29 wt% Sb_2O_3, **(B)** 0.58%, **(C)** 1.18%, and **(D)** 2.38%.

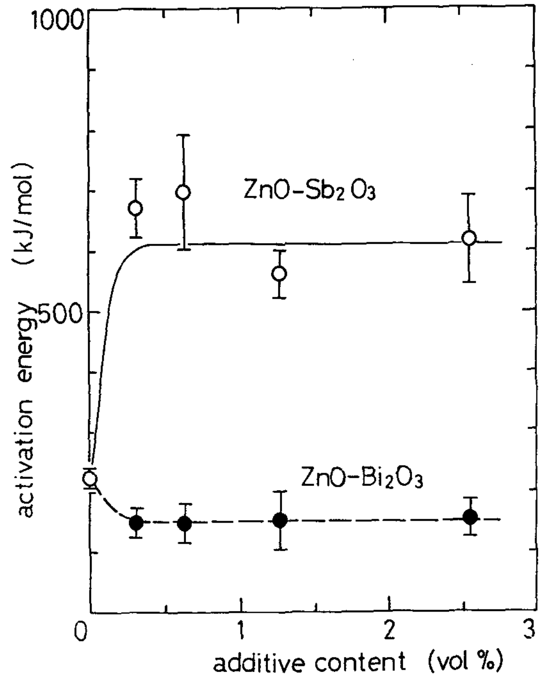

Figure 16. Effect of Sb_2O_3 content on the activation energy for ZnO grain growth in ZnO-Sb_2O_3 ceramics. Results for ZnO-Bi_2O_3 ceramics at similar volume percentage levels are included for comparison.

Table III. Summary of the ZnO grain growth activation analysis parameters for ZnO-Sb_2O_3 ceramics.

Reference	Sb_2O_3 Content (wt%)	Grain growth exponent (n-value)	Activation energy (kJ/mol)	Preexponential constant, log K_0
Senda and Bradt [22]	0.29	6	672 ± 48	29.87 ± 0.44
	0.58	6	698 ± 95	30.50 ± 0.88
	1.18	6	563 ± 39	25.24 ± 0.36
	2.38	6	617 ± 73	26.17 ± 0.67

has been reported that the (111) spinel layer stacking of the $Zn_7Sb_2O_{12}$ forms on the (0001) basal planes of ZnO after firing at 700°C [43]. The thin film form of the spinel then fragments and coalesces to form very fine particles before extensive contact between solid ZnO grains is achieved at about 900°C. Densification of ZnO-Sb_2O_3 compacts only readily proceeds above 1000°C, whereas pure ZnO starts to densify as low as 600°C.

Krasevec et al. [43] have reported that the Sb_2O_3-rich film which coats the ZnO grains not only retards the densification of the ZnO, but also hinders the initiation of subsequent ZnO grain growth processes, resulting in a smaller average ZnO grain size in the sintered ZnO-Sb_2O_3 microstructures. In this sense, the evaporation-condensation of the Sb_2O_3-containing phase has a distinct effect on the ZnO grain growth inhibition. In their studies, Trontelj and Krasevec [21] have reported n-values of three for both Sb_2O_3-doped ZnO and for pure ZnO, concluding that the $Zn_7Sb_2O_{12}$ spinel particles which form at higher temperatures do not affect the grain growth of ZnO. Unfortunately, since they did not present any further analyses, there is little additional evidence supporting their conclusion.

The activation analyses clearly demonstrate that both the n-values and the activation energies for ZnO grain growth in ZnO-Sb_2O_3 ceramics are consistently larger than those which have been observed for pure ZnO during sintering from 1106°C to 1400°C. These results are not in agreement with the conclusion of Trontelj and Krasevec [21] who propose that the ZnO grain growth mechanism both in pure ZnO and in ZnO-Sb_2O_3 ceramics are the same for sintering at higher temperatures where the Sb_2O_3 exists in the form of $Zn_7Sb_2O_{12}$ spinel particles. It is a reasonable concept in a general sense that inclusion particles must increase the energy which is required for grain boundary migration and thus inhibit grain growth [44]. It is logical to conclude that the increase of the activation energy for ZnO grain growth in ZnO-Sb_2O_3 ceramics is probably the result of the presence of $Zn_7Sb_2O_{12}$ particles that act through a mechanism of grain boundary pinning. However, controversy exists on this point.

Similar inhibition of grain growth in the presence of second phase particles has been observed for other ceramic systems, including MgO-rich inclusions in Al_2O_3 [45], ZrO_2 in Al_2O_3 [46], etc. etc. Unfortunately, those researchers have not determined either the activation energies for grain growth, or the grain growth exponents. Therefore, the large increase of the activation energy for the grain growth of ZnO in the presence of particles, which is evident in ZnO-Sb_2O_3 ceramics, cannot be directly compared with other ceramic systems. Some models, including the original one by Zener [41], which have been proposed for grain growth inhibition by second phase particles have been summarized by Olgaard and Evans [47]. However, those models generally approach the problem from an equilibrium, stabilized final grain size, while the microstructures observed in the experiments described in this paper are still in a dynamic transient state.

(2) TWINNING IN ZnO CERAMICS WITH ADDITIONS OF Sb_2O_3

Twinning is a crystallographic phenomenon of particular interest in the microstructures of the ZnO-Sb_2O_3 ceramics as previously shown in Figure 12. It is well known that the individual grains of ZnO in commercial ZnO varistors with Sb_2O_3 additions always contain these twins, whereas the microstructures of pure ZnO have no twins, as Gupta has noted [4]. The microstructures of the ZnO ceramics with the additions of Sb_2O_3 consistently have a single twin in every grain, regardless of the Sb_2O_3 content, or the sintering conditions [22, 29]. From these facts it may be concluded that the addition of antimony oxide in the form of Sb_2O_3 to ZnO leads to twin formation in the ZnO grains.

Yamamoto et al. [26] have demonstrated through extensive statistical analyses that only a single twin boundary exists and that it is always located near to the center of the ZnO grain. Kim and Goo [27] have completed a very detailed study of the twin boundary region in ZnO by transmission electron microscopy. They have identified the cation and anion stacking sequences which are associated with the ZnO basal plane inversion twin boundary and have described the head-to-head configuration which results from twinning in the polar hexagonal ZnO wurtzite structure.

Twinning as a crystallographic process has been documented to readily occur in three specific instances; (i) during phase transformations, (ii) as a deformation process, and (iii) as a growth fault in the stacking layer sequence or pattern of crystal planes. Twinning which is associated with phase transformations results in a very high density of twins, yielding very complex twin structures with interpenetrating twin patterns. Deformation twins are also frequently quite numerous and usually lens shaped, sometimes extending only across a portion of an individual grain. The appearance of the twins in ZnO is quite different from both of the above descriptions. In addition, no phase transformations nor deformation histories are known to exist for the sintered $ZnO-Sb_2O_3$ ceramics, thus, neither of the two mechanisms is very likely to be the origin of the ZnO twinning in $ZnO-Sb_2O_3$ ceramics. By elimination, it must be concluded that the ZnO twinning is a type of crystallographic growth twin.

ZnO has the wurtzite structure and belongs to the $P6_3mc$ space group which is hexagonal and polar. The wurtzite structure of ZnO has alternate close packed zinc cation and oxygen anion layers stacked along the [0001] direction. The stacking layer sequence is:

$$AaBbAaBbAaBb, \qquad (5)$$

where "ABC" and "abc" designate planes or layers of zinc ions and oxygen ions, respectively. In terms of only the oxygen anion planes, the layer stacking sequence can be simplified to:

$$abababababab, \qquad (6)$$

the normal stacking layer sequences for hexagonal structures.

Kim and Goo [27] have determined that the ZnO twins are inversion twins which are parallel to the (0001) basal planes. They have determined the cation-anion stacking layer sequence of a twinned region to be:

$$AaBbAa\underline{BbAaAcC}aAcCaA, \qquad (7)$$

which can be reduced to the stacking sequence of the oxygen anion layers only as:

$$\text{aba}\underline{\text{bac}}\text{aca}, \qquad (8)$$

where the underlines designate the twin boundary region.

Bayer has reported that the $Zn_7Sb_2O_{12}$ structure is an inverse spinel [48]. The cubic spinel structure is also one of a stacking sequence of close packed oxygen anion layers in the <111> direction which may be expressed as:

$$\text{abcabcabcabc}, \qquad (9)$$

the normal stacking sequence for close packed cubic structures. It is evident that the stacking sequence of the oxygen anion layers which are associated with the inversion twin structure, bac (or cab), is identical to the cubic spinel structure oxygen anion layer stacking sequence. It must be concluded that the basal inversion twin boundary of the hexagonal wurtzite structure of ZnO contains a sequence of cubic spinel close packed oxygen anion layer stacking which is identical to that which is present in the $Zn_7Sb_2O_{12}$ spinel.

This structural similarity suggests a possible mechanism for twin nucleation and subsequent twin growth in sintered ZnO ceramics with Sb_2O_3 additions. The likely possibility is that the formation of a cubic spinel oxygen layer stacking on the ZnO grains creates an embryo of the oxygen anion layer twin stacking fault, which is a small region of $Zn_7Sb_2O_{12}$ oxygen anion stacking. As previously noted, Krasevec et al. [43] have observed $Zn_7Sb_2O_{12}$ spinel layers to form with their (111) planes precipitating on the ZnO (0001) wurtzite structure basal planes, which confirms the proposed mechanism. This observation also suggests that the nucleation of the ZnO twinning process occurs at a very early stage during ZnO sintering, even before the rapid densification actually starts.

If the inversion twin boundaries (stacking faults) are nucleated at such an early stage of the ZnO grain growth process and if the primary ZnO grain growth form is a radial one of the grain boundary mobility away from the twin boundary region, it also explains why virtually every ZnO twin appears to be near to the center of the individual ZnO grains. In fact, since the grains of ZnO are equiaxed, it suggests that the radial grain growth mode is a reasonable one to be assumed. The wurtzite structure has a polarization which is a head-to-head configuration. This feature provides the explanation as to why each of the ZnO grains contains only a single twin. In order for there to be more than a single inversion twin within each ZnO grain, the ZnO wurtzite structure would also have to accommodate the tail-to-tail type of twin configuration. This is impossible according to the observations of Kim and Goo [27] who determined that only the head-to-head configuration is allowed.

5. SUMMARY

The grain growth of pure ZnO and of ZnO in ceramics with individual additions of either Bi_2O_3 or Sb_2O_3 is reviewed and described in terms of the phenomenological kinetic grain growth equation. For pure ZnO, a grain growth exponent of three and an activation energy of about 220 kJ/mol are consistently reported. Review of these results substantiates the conclusions of Gupta and Coble that the grain growth of pure ZnO is controlled by the solid state diffusion of zinc ions in the ZnO wurtzite structure.

Additions of Bi_2O_3 effect liquid phase sintering of ZnO and change the mechanism for the grain growth of ZnO. Initial additions of about 0.5 wt% Bi_2O_3 increase the resulting ZnO grain size. The grain growth exponent increases to five and the activation energy for grain growth decreases to about 150 kJ/mol. The ZnO grain size, the grain growth exponent, the activation energy, and the preexponential term, K_0, remain nearly constant over the range of Bi_2O_3 contents from about 0.5 to 4 wt%. Further additions of Bi_2O_3 beyond the 4% level decrease the ZnO grain size with increasing Bi_2O_3, while the activation energy for ZnO grain growth increases to about 270 kJ/mol, a value which is larger than that for pure ZnO. As the sintering of ZnO-Bi_2O_3 ceramics occurs through liquid phase sintering in the presence of a Bi_2O_3-rich liquid phase, the ZnO grain growth is the result of solution-precipitation process involving the ZnO solid grains and the Bi_2O_3-rich liquid phase. For the Bi_2O_3 additions less than about 4%, the grain growth of ZnO is controlled by the phase boundary reaction between the ZnO and the Bi_2O_3-rich liquid phase. Neither of the activation parameters for grain growth are dependent on the Bi_2O_3 level. In contrast, the grain growth of ZnO at higher levels of Bi_2O_3 depends on the Bi_2O_3 content and the rate controlling mechanism changes to one of ZnO diffusion through the Bi_2O_3-rich liquid phase.

The grain size of ZnO in sintered ZnO-Sb_2O_3 ceramics decreases with increasing Sb_2O_3 contents. The Sb_2O_3 additions increase the grain growth exponent to six and the activation energy to about the 600 kJ/mol level. These activation parameters are independent of the Sb_2O_3 content. The ZnO grain growth inhibition through the addition of Sb_2O_3 is considered to be related to the formation of $Zn_7Sb_2O_{12}$ spinel particles at the ZnO grain boundaries and multigrain junctions. The grain growth inhibition mechanism is the pinning of the ZnO grain boundaries by the spinel particles and thus reducing their mobility as originally suggested by Zener.

Additions of Sb_2O_3 to ZnO also create a single crystallographic twin boundary in each of the ZnO grains. The proposed mechanism for the nucleation of these inversion twins in the ZnO wurtzite structure is one of the reaction of antimony oxide with the zinc oxide to create an embryo of twin structure oxygen anion stacking sequence which is identical to the oxygen layer sequence within the $Zn_7Sb_2O_{12}$ spinel structure. This mechanism is supported through independent observations by transmission electron microscopy and further explains why each grain contains only a single twin boundary and also why the twin boundaries are located at or near to the center of the individual ZnO grains.

ACKNOWLEDGMENT

The authors acknowledge D. Dey, T.K. Gupta, T. Kimura, L.M. Levinson, S. Nunes, W.D. Scott, J.A. Varela, T. Watari, O.J. Whittemore, and T. Yamaguchi for making contributions to the understanding of concepts advanced in this manuscript through various discussions, reprint exchanges, etc. Without their input, this review would not have been possible.

REFERENCES

[1] M. Matsuoka, "Nonohmic Properties of Zinc Oxide Ceramics," Jpn. J. Appl. Phys., **10** [6] 736-46 (1971).

[2] L.M. Levinson and H.R. Philipp, "Zinc Oxide Varistors - A Review," Am. Ceram. Soc. Bull., **65** [4] 639-46 (1986).

[3] R. Einzinger, "Metal Oxide Varistors," Ann. Rev. Mater. Sci. 1987, 299-321 (1987).

[4] T.K. Gupta, "Application of Zinc Oxide Varistors," J. Am. Ceram. Soc., **73** [7] 1817-40 (1990).

[5] J. Wong, "Barrier Voltage Measurement in Metal Oxide Varistors," J. Appl. Phys., **47** [11] 4971-74 (1976).

[6] T.K. Gupta, "Influence of Microstructure and Chemistry on the Electrical Characteristic of ZnO Varistors"; pp.493-507 in Tailoring Multiphase and Composite Ceramics. Edited by R.E. Tressler et al. Plenum Press, New York, N.Y., U.S.A. (1986).

[7] G.C. Nicholson, "Grain Growth in Zinc Oxide," J. Am. Ceram. Soc., **48** [4] 214-15 (1965).

[8] T.K. Gupta and R.L. Coble, "Sintering of ZnO: I, Densification and Grain Growth," J. Am. Ceram. Soc., **51** [9] 521-25 (1968).

[9] T.K. Gupta and R.L. Coble, "Sintering of ZnO: II, Density Decrease and Pore Growth During the Final Stage of the Process," J. Am. Ceram. Soc., **51** [9] 525-28 (1968).

[10] S.K. Dutta and R.M. Spriggs, "Grain Growth in Fully Dense ZnO," J. Am. Ceram. Soc., **53** [1] 61-62 (1970).

[11] D.W. Readey, T. Quadir, and J.H. Lee, "Effects of Vapor Transport on Microstructure Development,"; pp.485-96 in Ceramic Microstructures '86. Edited by J.A. Pask and A.G. Evans. Plenum Publishing Co., New York, N.Y., U.S.A. (1988).

[12] T. Senda and R.C. Bradt, "Grain Growth in Sintered ZnO and ZnO-Bi_2O_3 Ceramics," J. Am. Ceram. Soc., **73** [1] 106-14 (1990).

[13] J. Wong, "Sintering and Varistor Characteristics of ZnO-Bi_2O_3 Ceramics," J. Appl. Phys., **51** [8] 4453-59 (1980).

[14] T.K. Gupta, "Inhibition of Grain Growth in ZnO," J. Am. Ceram. Soc., **54** [8] 413-14 (1971).

[15] T. Asokan, G.N.K. Iyengar, and G.R. Nagabhushana, "Studies on Microstructure and Density of Sintered ZnO-based Non-linear Resistors," J. Mater. Sci., **22** [6] 2229-36 (1987).

[16] T. Kimura, H. Kajiyama, J. Kim and T. Yamaguchi, "Effect of Inclusion Size on the Densification of $ZnO-Zn_7Sb_2O_{12}$," J. Am. Ceram. Soc., **72** [1] 140-41 (1989).

[17] J. Kim, T. Kimura and T. Yamaguchi, "Sintering of Sb_2O_3-doped ZnO," J. Mater. Sci., **24** [1] 213-19 (1989).

[18] J. Kim, T. Kimura and T. Yamaguchi, "Microstructure Development in Sb_2O_3-doped ZnO," J. Mater. Sci., **24** [7] 2581-86 (1989).

[19] J. Kim, T. Kimura and T. Yamaguchi, "Sintering of Zinc Oxide with Antimony Oxide and Bismuth Oxide," J. Am. Ceram. Soc., **72** [8] 1390-95 (1989).

[20] J. Kim, T. Kimura and T. Yamaguchi, "Effect of Bismuth Oxide Content on the Sintering of Zinc Oxide," J. Am. Ceram. Soc., **72** [8] 1541-44 (1989).

[21] M. Trontelj and V. Krasevec, "The Microstructure of Sb-doped ZnO-ceramics"; pp. 915-20 in Science of Ceramics, Vol. 14. Edited by D. Taylor, Institute of Ceramics, Shelton, U.K. (1988)

[22] T. Senda and R.C. Bradt, "Grain Growth of Zinc Oxide During the Sintering of Zinc Oxide-Antimony Oxide Ceramics," J. Am. Ceram. Soc., **74** [6] 1296-1302 (1991).

[23] D. Dey and R.C. Bradt, "Grain Growth of ZnO during $ZnO-Bi_2O_3$ Liquid Phase Sintering," to be published.

[24] M.I. Mendelson, "Average Grain Size in Polycrystalline Ceramics," J. Am. Ceram. Soc., **52** [8] 443-46 (1969).

[25] J. Wong, "Microstructure and Phase Transformation in a Highly Non-Ohmic Metal Oxide Varistor Ceramic," J. Appl. Phys., **46** [4] 1653-59 (1975).

[26] T. Yamamoto, Y. Suzuki, H. Hirata and K. Okazaki, "Twins in ZnO Varistors (2)"; pp.56-57 in Proc. 2nd Fall Symp. Ceramic Society of Japan (in Japanese). Ceramic Society of Japan, Tokyo, Japan (1989).

[27] J.C. Kim and E. Goo, "Inversion Twin Boundaries in Zinc Oxide," J. Am. Ceram. Soc., **73** [4] 877-84 (1990).

[28] T. Senda and R.C. Bradt, "Twinning in ZnO Ceramics with Sb_2O_3 Additions," Seramikkusu Ronbunshi (J. Ceram. Soc. Jpn.), **99** [9] 727-31 (1991).

[29] H.V. Atkinson, "Theories of Normal Grain Growth in Pure Single Phase Systems," Acta Metall., **36** [3] 469-91 (1988).

[30] Y. Tomokiyo and Y. Suyama, "Microstructural Observations of Electronic Ceramics with Analytical Electron Microscope"; pp.141-42 in Proc. Fall Symposium of Japan Institute of Metals (in Japanese). Japan Institute of Metals, Tokyo, Japan (1989).

[31] Y. Suyama, Y. Tomokiyo and K. Terasaka, "Grain Boundary Structure of a ZnO-Bi_2O_3-CoO Varistor"; pp. 374-75 in Proc. XIIth International Congress for Electron Microscopy. San Francisco Press, Inc., San Francisco, CA., U.S.A. (1990).

[32] F.V. Lenel, "Sintering in the Presence of a Liquid Phase," Trans. A.I.M.E., 175, 878-905 (1948).

[33] W.G. Morris, "Electrical Properties of ZnO-Bi_2O_3 Ceramics," J. Am. Ceram. Soc., **56** [7] 360-64 (1973).

[34] J. Wong and W.G. Morris, "Microstructure and Phases in Nonohmic ZnO-Bi_2O_3 Ceramics," Am. Ceram. Soc. Bull., **53** [11] 816-20 (1974).

[35] W.D. Kingery, "Densification during Sintering in the Presence of a Liquid Phase. I. Theory," J. Appl. Phys., **30** [3] 301-06 (1959).

[36] W.D. Kingery and M.D. Narasimhan, "Densification during Sintering in the Presence of a Liquid Phase. II. Experimental," J. Appl. Phys., **30** [3] 307-10 (1959).

[37] K.W. Lay, "Grain Growth in UO_2-Al_2O_3 in the Presence of a Liquid Phase," J. Am. Ceram. Soc., **51** [7] 373-76 (1968).

[38] G.W. Greenwood, "The Growth of Dispersed Precipitates in Solutions," Acta Metall., **4**, 243-48 (1956).

[39] C. Wagner, "Theory of Precipitate Change by Redissolution," Z. Elektrochem., **65** [7/8] 581-91 (1961).

[40] R.M. German, Liquid Phase Sintering. Plenum Press, New York, N.Y., U.S.A. (1985).

[41] C. Zener, quoted by C.S. Smith in "Grains, Phases, and Interfaces: An Interpretation of Microstructure," Trans. A.I.M.E., **175**, 15-51 (1948).

[42] S.R. Sainker, S. Badrinarayanan, A.P.B. Sinha and S.K. Date, "X-ray Photoelectron Spectroscopic Studies on ZnO-Sb_2O_3 Varistors," Appl. Phys. Lett., **39** [1] 65-66 (1981).

[43] V. Krasevec, M. Trontelj and L. Golic, "Transmission Electron Microscope Study of Antimony-doped Zinc Oxide Ceramics," J. Am. Ceram. Soc., **74** [4] 760-66 (1991).

[44] W.D. Kingery, H.K. Bowen and D.R. Uhlmann, Introduction to Ceramics; Second Edition. John Wiley and Sons, New York, N.Y., U.S.A. (1976).

[45] H.A. Haroun and D.W. Budworth, "Effect of Additions of MgO, ZnO and NiO on Grain Growth in Dense Alumina," Trans. Br. Ceram. Soc., **69** [2] 73-79 (1970).

[46] F.F. Lange and M.M. Hirlinger, "Hindrance of Grain Growth in

Al_2O_3 by ZrO_2 Inclusions," J. Am. Ceram. Soc., **67** [3] 164-68 (1984).

[47] D.L. Olgaard and B. Evans, "Effect of Second-Phase Particles on Grain Growth in Calcite," J. Am. Ceram. Soc., **69** [11] C-272 - C-277 (1986).

[48] G. Bayer, "Double Oxides of Antimony Pentoxide with Spinel Structure," Naturwissenschaften, **48**, 46-47 (1961).