ACTIVATED SINTERING OF BISMUTH-DOPED
ZINC OXIDE CERAMICS

by

ELAINE PAULA ROTHMAN

B.S. CER. E., University of Illinois (1981)

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MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Signature of Author

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on Graduate Students

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Submitted to the Department of Materials Science and Engineering on May 7, 1982 in partial fulfillment of the requirements for the Degree of Master of Science in Materials Science and Engineering.

ABSTRACT

Variations in sintering behavior of four bismuth-doped zinc oxide powders from different manufacturers were examined as a function of dopant level, heating rate and peak temperature. These parameters were used to characterize microstructural evolution and shrinkage rates.

The sintering results were affected by variations in particle size, size distribution and shape, and could be related to the initial powder characteristics. Increases in the dopant level from 0.1-4.0 m/o increased the sintering rate and increases in the heating rate from 5-40°C/min substantially decreased the final shrinkage. Grain growth occurred above the eutectic temperature, 742°C. The extent of grain growth was proportional to the dopant level and the degree of densification. Below the eutectic temperature the samples formed a rigid skeletal structure, attributed to enhanced sintering.

Constant heating rate theory and some isothermal sintering studies were used to suggest a possible sintering mechanism. The presence of a Bi-rich phase at the grain boundaries was thought to enhance both surface and grain-boundary diffusion below the eutectic temperature.

Thesis Supervisor: Dr. Robert L. Coble
Title: Professor of Ceramics
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I. INTRODUCTION

Second components are added to many ceramic and metal systems to enhance the sintering kinetics and achieve higher final densities. Exact mechanisms have not been determined for many systems; however, for liquid phase or multiphase sintering to be beneficial several factors are desirable. The primary phase must be soluble in the secondary phase, and in order to form a second phase the addition must be above the solid solubility limit.

Multiphase sintering can involve liquid-phase or solid-state sintering. The formation of a liquid phase enhances the sintering rate by providing an inherently higher diffusivity path for material transport. Ideally, the solid second phase also provides a high diffusivity path.

The electrical behavior of zinc oxide (ZnO) with small additions of bismuth oxide ($\text{Bi}_2\text{O}_3$) has been investigated for ZnO varistors. These varistors are sintered at temperature above 1000°C in the presence of a liquid phase; however, additions of $\text{Bi}_2\text{O}_3$ also enhance the sintering below the eutectic temperature, 742°C. This study examines the sintering behavior of $\text{Bi}_2\text{O}_3$-doped ZnO ceramics above and below the eutectic temperature.

Constant heating rate experiments and continuously recording dilatometry were used to examine solid-state, liquid and/or multiphase sintering in the ZnO-$\text{Bi}_2\text{O}_3$ system. Initial powder differences, heating rates, dopant levels and some isothermal sintering techniques were all used to determine the effect $\text{Bi}_2\text{O}_3$ has on the sintering of ZnO.
II. LITERATURE REVIEW

1. Liquid Phase Sintering

The earliest quantitative model for sintering in the presence of a liquid phase was proposed by Kingery. Thermodynamics demands that the liquid phase partially dissolves the solid phase and Kingery assumed that the liquid completely wets the solid. In this case, the solid particles are completely coated with the liquid phase, and the driving force for sintering is the reduction of liquid-vapor surface area. The model identified three stages in liquid phase sintering: rearrangement, solution-precipitation and a coalescence process, and made several assumptions.

The rearrangement process is initiated by the formation of a liquid phase. Capillary pressure holds the particles together and rearranges them to attain maximum packing density and minimum pore surface area. Initially, the particles slide over one another due to capillary pressure, then, a transition from this viscous flow process to a plastic flow process with a yield point occurs as further rearrangement becomes difficult. Assuming a viscous flow model for the rearrangement stage the densification rate can be expressed as:

\[
\frac{\Delta L}{L_0} = \frac{1}{3} \frac{\Delta V}{V_0} \propto t^{1+y}
\]

If the exponent \(1+y\) is greater than unity, this equation corresponds to a decrease in pore size and an increase in driving force. Kingery suggests that for spherical particles with the appropriate packing densities 35 volume percent liquid is required for complete densification by rearrangement. Rearrangement ends when the process essentially reaches the yield point corresponding to a plastic flow
type mechanism, and continued rearrangement becomes impossible.

The second stage of liquid phase sintering is the solutionprecipitation process. The model system is now comprised of uniformly packed single-sized particles surrounded by liquid films, and the compressive stress is concentrated at the contact points. Because of this stress concentration, there is greater solubility of the solid at the contact points, and this results in further densification by the transfer of material away from these points. When the material transfer rate is assumed to be diffusion controlled and the increased solubility is due to the pressure at the contact point. The equation for densification is derived as:

\[
\frac{\Delta L}{L_0} = \frac{1}{3} \frac{\Delta V}{V_0} = \left( \frac{6k_2 \delta D C_0 \gamma_{LV} V_0}{k_1 RT} \right) r^{-4/3} t^{1/3}
\]

\( k_1 \) and \( k_2 \) = constants
\( D \) = diffusion coefficient
\( \delta \) = thickness of the liquid layer
\( C_0 \) = solubility of the solid in the liquid
\( \gamma_{LV} \) = surface free energy of liquid vapor interface
\( V_0 \) = molar volume
\( r \) = solid particle radius

When the shrinkage is diffusion controlled the rate is proportional to \((\text{time})^{1/3}\). However, using a similar derivation Kingery shows that for a phase boundary reaction controlled sintering mechanism the rate is proportional to the square root of time.

\[
\frac{\Delta L}{L_0} = \frac{1}{3} \frac{\Delta V}{V_0} = \left[ \frac{2k_3 k_2 \gamma_{LV} C_0 V_0}{k_1 RT} \right]^{1/2} r^{-1} t^{1/2}
\]

The third stage of liquid phase sintering is the coalescence process. This process occurs when the liquid phase no longer penetrates
all the grain boundaries. The process is similar to solid-state sintering which will be discussed in greater detail in the next section.

Several refinements have been made on Kingery's model. Hayden and Brophy\(^2\) account for a transition between the first and second stage of liquid phase sintering. Experimental evidence suggests that the initial or rearrangement stage is more complex than previously described.\(^3,4,5\)

Gessinger, Fischmeister and Lukas\(^6,7\) suggest a geometrical model for the second stage of liquid phase sintering without a completely wetting liquid. Figure 1 illustrates two partially interlocking spheres. The boundary between the spheres could be either liquid in the case of a completely wetting liquid (\(2\gamma_{LS} < \gamma_{SS}\)) or a grain boundary for a partially wetting liquid. The geometrical model assumes that the surface energies (\(\gamma_{LS}, \gamma_{SS}\)) of the spheres are isotropic, and electrostatic and gravity forces are negligible. It also assumes that the curvature of the liquid-vapor interface is constant, an assumption which Heady and Cahn\(^8\) have shown does not greatly influence the derivation of the force equation. The force equation is analogous to the capillary pressure arising from the curvature of the liquid film as the driving force for sintering in Kingery's model. With these assumptions the force equation becomes,

\[
F = 2\pi r \gamma_{LV} - \pi (r^2 - x^2) \gamma_{LV} \left(\frac{1}{F^2} + \frac{1}{x^2}\right) + 2\pi x \gamma_{SL} \sin \frac{\theta}{2}
\]

and is used to derive an appropriate rate law. The parameters are defined in Figure 1. Equation 4 can be divided into three components: the first is the force caused by the surface tension of the liquid, the second is due to hydrostatic pressure of the liquid at the neck,
and the third is caused by $\gamma_{SL}$ or the surface tension at the neck.

The shrinkage rate will be greatly effected by the wetting angle, $\theta$, of the liquid. The radius of curvature and relative neck radius will vary with $\theta$ which in turn effects the exponent in the rate equation.

Assuming that diffusion through the boundary layer is the rate limiting factor, Gessinger et al. have proposed a rate equation and have derived a rate law from it:

$$
\frac{d(h/a)}{dt} = \frac{4\Omega \delta D_b}{k \tau_{ax}} \left[ \gamma_{SL} \frac{x+\rho_1 \sin(\psi/2)}{x^2 \rho_1} + \gamma_{LV}(r \frac{\rho_2^+r}{3 \rho_2} + \frac{\rho_2^-r}{x \rho_2^2r}) \right]
$$

(5)

$$
\left( \frac{r}{a} \right)^n = k_2 \cdot t
$$

(6) the rate law

$r$ = atomic volume of the solid phase

$\delta$ = grain boundary width

$D_b$ = grain boundary diffusivity

$\gamma_{SL}, \gamma_{LV}$ = surface energies

$n$ = shrinkage exponent

$k_2$ = constant

$t$ = time

The other parameters are defined in Figure 1.

Both Gessinger et al. and Kingery predict a shrinkage exponent of $n = 3$ as will a grain boundary diffusion model. The rate at which sintering proceeds is strongly dependent on the volume of liquid and the density achieved by rearrangement.

The important parameters in the derivation are the boundary diffusivities which can vary by orders of magnitude with additives, and the liquid-solid surface energy. For a completely wetting liquid $2\gamma_{SL} < \gamma_{SS}$, however, when this is not the case a grain boundary is
FIGURE 1

PARTIALLY INTERLOCKING SPHERES

THE GFL MODEL
likely to form. For this model to be valid equation (7) must be satisfied: the wetting angle,

\[ \cos \theta \leq \frac{\gamma_{SV}}{\gamma_{LV}} \]

\( \theta \), varies with the surface energies.

Many systems exhibit liquid phase sintering. Kingery's second stage or solution-precipitation stage of liquid phase sintering has been documented in Cu-Ag, Cu-Bi, Fe-Cu, Ni-Bi, W-Ni, Al\(_2\)O\(_3\)-glass and ZnO-Bi\(_2\)O\(_3\). A controversy exists in the literature pertaining to the degree to which the solid phase must be soluble in the liquid. There is however some indication that rearrangement will cease when a solid skeleton is formed if the liquid does not dissolve the solid. This behavior has been reported in Al\(_2\)O\(_3\)-alkali borate glass, W-Cu and Ni-Mo. Once a solid skeleton is formed within a compact, coalescence or solid-state sintering mechanisms control further densification.

2. **Solid-State Sintering**

Many models have been suggested for solid-state sintering of a single component system. These include descriptions of both the transport and phenomenological mechanisms involved. Many reviews of the literature exist, and only a few aspects of single-phase sintering pertain to multiphase sintering. A survey of some of the transport mechanisms that can be adapted to multiphase sintering will be presented.

Figure 2 illustrates the six paths for matter transport in the initial stage of sintering. Three of these paths cause neck growth
FIGURE 2

THE SIX PATHS OF MATERIAL TRANSPORT

IN SOLID STATE SINTERING TO THE NECK

1. surface diffusion
2. lattice diffusion from the surface
3. evaporation-condensation
4. boundary diffusion from the grain boundary
5. lattice diffusion from the grain boundary
6. lattice diffusion due to dislocations
and shrinkage. Densification can be caused by viscous flow; this is common in noncrystalline systems, grain boundary and lattice diffusion in polycrystalline systems from the particle bulk. Transport mechanisms from the particle surface, evaporation-condensation, surface diffusion and lattice diffusion cause neck growth without shrinkage.\(^{16}\)

The driving force for densification in sintering is the free energy change due to the reduction in surface area. The surface area is reduced by the elimination of solid-vapor interfaces. The solid-solid interfaces which are formed by this process are lower in energy than the solid-vapor interfaces they replace. The energy change for this reaction is approximately 1 Joule/mole\(^{17}\), substantially smaller than that for a chemical reaction, \(\approx 1200\) J/mole.\(^{17}\) The assumption of isotropic surface energies is often made; however, in most polycrystalline ceramics the surface energies are not isotropic. Anisotropic surface energies would effect much of the modeling of multiphase sintering.

Sintering is usually divided into three stages; initial, intermediate and final. Initial stage sintering encompasses the first few percent shrinkage, and is envisioned as two interpenetrating spheres. In this stage there is material transport from either the surface or bulk to the interparticle or neck region, but no grain growth occurs. Intermediate stage sintering has been modeled using a tetrakaidecahedron or dodecahedron.\(^{19}\) This model assumes pores are located along the polyhedron edges, with transport occurring from the polyhedron faces to these pores. If the pores are continuous and are intersected by grain boundaries the intermediate stage models are valid. The final state of sintering involves the shrinkage of isolated pores with
material transport from the bulk or grain boundaries.

Most sintering models are based on steady state diffusion controlled mechanisms. Geometries have been assumed that model real compacts as monosized spheres with a diffusion width equal to the grain boundary width for boundary diffusion or neck height for volume diffusion. These assumptions have been used to determine sintering mechanisms.

Real powders rarely form ideal compacts. Therefore, other factors must be accounted for to accurately determine a sintering mechanism. Non-uniform particle size distribution, particle shape and morphology must be considered. More than one sintering mechanism could be operating simultaneously and additions of a second phase will effect the sintering behavior.

The addition of a second component can have a variety of effects on the sintering kinetics. If the second component forms a homogeneous solid solution, it can have a significant impact on the lattice boundary and surface diffusivities. Variations in the surface energy will be manifest in changes in the wetting properties and the dihedral angle. A Kirkendall type effect might also be encountered if the diffusion of one component in the lattice is higher than that of the other. This could lead to an expansion of the sample and an inhomogeneous pore distribution. Therefore, the single phase models must be refined to explain the phenomena in multiphase sintering.

3. Multiphase Sintering

Although the model of Gessinger et al. has been derived for either a solid or liquid second phase, very few other models have been derived
for the sintering of a solid second phase addition. Brophy, Shepard and Wulff\textsuperscript{19} have derived a model based on two spheres of a primary phase completely coated with a second phase. The underlying assumptions are a readily sinterable second phase, and formation of pores in the second phase which provide a driving force for densification similar to Kingery's model. It also assumes that there is rapid material transport due to the secondary phase.

Brophy \textit{et al.} proposed five rate controlling steps for the process. The initial step is dissolution of the primary phase by the second phase at the interface followed by diffusion of the primary phase radially into the second phase. The third and fourth steps are competing mechanisms: either material is transported rapidly through the bulk of the second phase, or through the interface between the primary and secondary phase. The final process consists of radial diffusion of the primary phase back through the secondary phase. The second and final steps in the process are considered negligible due to their small diffusion distances.

The assumptions made in this model limit its application to many systems. The particles are often not completely coated with a second phase and the second phase is not evenly distributed through a sample.

The model of Gessinger \textit{et al.} described earlier also pertains to solid-state multiphase sintering. Due to the model's assumption of a partially wetting second phase it can describe the phenomena associated with multiphase sintering more realistically.

4. \textbf{Constant Heating Rate Theory}

The rearrangement stage of liquid phase sintering can occur very
rapidly; therefore, it is often necessary to employ non-isothermal sintering techniques.\textsuperscript{20,21} The error associated with isothermal heating can be substantially reduced by using constant linear heating rates. This provides a relatively easy way to determine the temperature at which shrinkage begins, changes in the sintering mechanism and the degree of densification below the eutectic temperature when combined with a continuously recording dilatometer.

Many models have been suggested for isothermal stage sintering and a few of these are summarized in Table 1. The isothermal sintering rate equation is usually expressed as:

\begin{equation}
\frac{\Delta l}{l_0} = kt
\end{equation}

\(\frac{\Delta l}{l_0}\) = percent shrinkage
\(n\) = constant, varies with mechanism
\(k\) = constant, varies with mechanism
\(t\) = time

By differentiating equation (8) with respect to time and integrating, an Arrhenius type equation results.

\begin{equation}
\left(\frac{\Delta l}{l_0}\right)^n = k't \exp - \frac{Q}{RT}
\end{equation}

\(Q\) = activation energy
\(R\) = ideal gas constant
\(T\) = temperature
\(k'\) = constant

Values for \(n\) are dependent on the sintering mechanism and can be determined by the slope of a \(\ln \Delta l/l_0\) and \(\ln t\) plot. A similar technique can be used for CHR techniques.
TABLE 1

**Initial Stage Sintering Models (Sphere-on-Sphere Geometry)**

### A. Shrinkage Producing Mechanisms

<table>
<thead>
<tr>
<th>Transport mechanism</th>
<th>$K$</th>
<th>$n$</th>
<th>$m$</th>
<th>$p$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume diffusion</td>
<td>2 $D_L$</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>32 $D_L$</td>
</tr>
<tr>
<td></td>
<td>4.04 $D_L$</td>
<td>2.07</td>
<td>3</td>
<td>4.28</td>
<td>64.64 $D_L$</td>
</tr>
<tr>
<td></td>
<td>3.48 $D_L$</td>
<td>2.07</td>
<td>3</td>
<td>4.28</td>
<td>55.68 $D_L$</td>
</tr>
<tr>
<td></td>
<td>10 $D_L$</td>
<td>2.5</td>
<td>3</td>
<td>5</td>
<td>320 $D_L$</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>3$\delta D_b$</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>96$\delta D_b$</td>
</tr>
<tr>
<td></td>
<td>1.47$\delta D_b$</td>
<td>3.12</td>
<td>4</td>
<td>6.24</td>
<td>94.085$\delta D_b$</td>
</tr>
<tr>
<td></td>
<td>1.09$\delta D_b$</td>
<td>3.12</td>
<td>4</td>
<td>6.24</td>
<td>69.766$\delta D_b$</td>
</tr>
</tbody>
</table>

### B. Non-Shrinkage Producing Mechanisms

<table>
<thead>
<tr>
<th>F</th>
<th>P</th>
<th>m</th>
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<tbody>
<tr>
<td>Surface Diffusion</td>
<td>$56D_{s_o}$</td>
<td>7</td>
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<tr>
<td>Evaporation Condensation</td>
<td>$AP_o$</td>
<td>3</td>
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The fundamental assumption behind constant heating rate theory can not be proven mathematically; it has, however, been demonstrated experimentally. 22

\[
\frac{d\left(\frac{\Delta \ell}{\ell_o}\right)}{dt} \text{\textit{[isothermal}}} = \frac{d\left(\frac{\Delta \ell}{\ell_o}\right)}{dt} \text{\textit{[non-isothermal]]}}
\]

By assuming that for any combination of shrinkage and temperature the isothermal shrinkage and non-isothermal shrinkage rates are equal, and that if only one rate controlling mechanism predominates a rate equation can be derived from the general isothermal initial stage sintering model.

\[
\frac{d\left(\frac{\Delta \ell}{\ell_o}\right)}{dt} = k_o \exp -\frac{Q}{RT} \left(\frac{\Delta \ell}{\ell_o}\right)^{n-1}
\]

\[
\frac{\Delta \ell}{\ell_o} \text{ = percent shrinkage}
\]

\[
k_o, n \text{ = constants related to the mechanism}
\]

\[
Q \text{ = activation energy}
\]

\[
R \text{ = gas constant}
\]

\[
T \text{ = temperature}
\]

\[
t \text{ = time}
\]

For constant heating rates \( T = ct \), and the heating rate \( c = dT/dt \). Making this substitution in equation (11) and integrating, equation (12) results.

\[
\left(\frac{\Delta \ell}{\ell_o}\right)^n = \left(\frac{k}{C}\right) \exp -\frac{Q}{RT}
\]

In order to arrive at equation (12) an approximation must be made. Skaar4 has summarized values for the initial stage models and derived constants for the intermediate stages of sintering. These are included in Table 2. Values for \( n \) and \( Q \) can be determined from experimental CHR data, and could be indicative of the sintering mechanism if the
<table>
<thead>
<tr>
<th>Model</th>
<th>n</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial Stage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscous Flow</td>
<td>1</td>
<td>$\frac{e^{RT^2}}{2aKQ}$</td>
</tr>
<tr>
<td>Volume Diffusion</td>
<td>2</td>
<td>$\frac{5.34\gamma\Omega D_{ave}}{k\gamma^3Q}$</td>
</tr>
<tr>
<td>Grain Boundary Diffusion</td>
<td>3</td>
<td>$\frac{2.1\gamma\Omega \delta D_{ave}}{k\gamma^4Q}$</td>
</tr>
<tr>
<td><strong>Intermediate Stage</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume Diffusion</td>
<td>1</td>
<td>$\frac{72\pi \rho_0 D \gamma\Omega RT_{ave}}{\eta G^3 kQ}$</td>
</tr>
<tr>
<td>Grain Boundary Diffusion</td>
<td>.88</td>
<td>$\frac{2.09\pi^{3/2} \rho_0^{3/2} D \gamma\Omega}{kG^4 \eta^{3/2}}$</td>
</tr>
</tbody>
</table>
operating at a time were valid.

Determination of the sintering mechanism is done graphically using a range of heating rates. Plots of \( \ln c \) vs \( 1/T \) at constant shrinkage yield slopes of \(-Q/R\), and plots of \( \ln \Delta l/l_o \) vs \( 1/T \) at constant \( c \) give slopes of \(-Q/nR\). A ratio of these slopes gives a value for \( n \) as well as an activation energy. Values of \( n \) for various sintering mechanisms, viscous flow, volume diffusion and grain-boundary diffusion have been determined by assuming a constant geometry throughout the process. If only one mechanism is rate controlling, the plots generate straight lines with curved regions representing transitions to another mechanism. When a competing mechanism, surface diffusion, is in operation, a change in \( n \) value would be expected.

The CHR technique is useful for the determination of activation energies and sintering mechanisms. Errors can occur from two mechanisms operating together, and significant surface contributions to sintering have not been incorporated into the theory. A range of heating rates must also be employed to determine a mechanism. CHR studies do provide a simple method for differentiating between various sintering regions, and give an accurate idea of the mechanism if all the assumptions are valid.

5. \textbf{ZnO-Sintering}

Many researches have examined the sintering and grain-growth behavior of ZnO. This discussion will concentrate on the low-temperature studies, \(<1000^\circ\text{C}\). Studies of the initial stage and intermediate stage of ZnO have been attributed to several mechanism.

The sintering of ZnO is dominated by surface diffusion.
Gray observed zinc interstitials and there is general agreement that nonstoichiometry of ZnO plays a role in its sintering behavior. The primary defect reaction for incorporation of oxygen in ZnO is:

\[
(13)^{16} \quad \text{ZnO} \rightarrow \text{Zn}_1 + e^1 + 1/2 \text{O}_2
\]

the incorporation of zinc interstitials, and their diffusion through the ZnO lattice. The ZnO crystal structure is hexagonal wurtzite and would have channels for zinc interstitial diffusion.

The fabrication of the ZnO powders is also an important factor in the sintering behavior. Two basic processes exist for the manufacture of ZnO powders. The first involves the decomposition of zinc carbonate and zinc oxalate. This method produces high surface area powders with irregular particle morphologies. Gray attributed the high activity of powders produced by this method to an excess of interstitial zinc in the lattice. However, Dollimore and Spooner suggest an excess of oxygen at the surface. Due to the irregular particle morphology, a range of activation energies for sintering can arise. Sintering equations have not yet been adapted to a range of irregular particle shapes and sizes. The second process or French process is an oxidation of Zn vapor. Highly uniform spherical particles can be produced by this method. Higher activation energies have been reported for these powders.

a. **Diffusion in ZnO and Bi$_2$O$_3$**

Diffusivities of Zn and O in ZnO and Bi in Bi$_2$O$_3$ have been reported by a number of researchers. The range of diffusivities with temperature
is presented graphically in Figure 3. The variations in diffusion data can be explained in part by experimental techniques. The non-stoichiometry, and thermal history of a particular sample can also greatly effect the diffusion data. No values have been reported for Bi-diffusion in ZnO.

6. **ZnO-Bi₂O₃**

Due to its importance in varistor applications the ZnO-Bi₂O₃ system has been carefully examined. Phase equilibrium, defect chemistry and microstructural evolution have been studied and will be discussed below. Some questions still remain; the solubility of Bi₂O₃ in ZnO, the defect incorporation of Bi₂O₃ in ZnO, the thickness and nature of the Bi-rich boundary phase, and the wetting angle of the Bi-rich liquid on the ZnO particles.

a. **Phase Equilibria**

Several phase diagrams for the ZnO-Bi₂O₃ system have been published. The most complete is shown in Figure 4. Kosov et al. found two eutectics at temperatures of 747 and 742°C which correspond to compositions of 6.5 and 27 mole percent ZnO, respectively. He also found two compounds: 9Bi₂O₃·ZnO which melts incongruently at 747°C and 6Bi₂O₃·ZnO which melts congruently at 755°C. The former compound passes through an intermediate structure while undergoing a polymorphic transformation at 737°C. The intermediate structure is a cubic sillenite structure.

Conversely, Safronov et al. indicate an α-β Bi₂O₃ transition at 735°C of a 24Bi₂O₃·ZnO compound. This 24Bi₂O₃·ZnO compound possesses a sillenite-like crystal structure. Kosov et al. also found a sillenite-like structure for their 9Bi₂O₃·ZnO. This, however, is part of a two
phase region with sillenite-like crystals. Safronov proposed phase diagram is included in Figure 4. Kosov\textsuperscript{30}, however, claims that this diagram is inaccurate, because there was no accurate chemical analysis performed on the compounds.

Maruyama\textsuperscript{31} has proposed a diagram for the ZnO-rich side of the phase diagram, and is included in Figure 5. He estimates the solubility of Bi\textsubscript{2}O\textsubscript{3} in ZnO to be 0.17±0.01 mole percent at the eutectic temperature, 742°C.

b. Defect Incorporation

Several suggestions have been made for the incorporation of Bi\textsubscript{2}O\textsubscript{3} in ZnO. Moriyoshi\textsuperscript{32} has stated that Bi\textsubscript{2}O\textsubscript{3} could either be incorporated as Bi-interstitials, or it could substitute for Zn on the zinc lattice. Using Kröger's\textsuperscript{33} notation the possibilities for Bi\textsubscript{2}O\textsubscript{3} incorporation are:

\[(A) \quad \text{Bi}_2\text{O}_3 \rightarrow \text{Zn}^0_{2\text{Bi}_2\text{O}_3} + 2\text{Zn}^0 + 3\text{O}^0_0\]

\[(B) \quad \text{Zn}^0 \rightarrow 2\text{Bi}_2\text{Zn}^0 + 2\text{O}_0^0 + 2\text{O}^0_0\]

\[(C) \quad \text{Zn}^0 \rightarrow 2\text{Bi}_1^\cdot + 3\text{Zn}^0 + 3\text{O}^0_0\]

Due to general structural constraints, hexagonal wurtzite structure, and the energetics associated with O-interstitial, the most likely reaction would be (A). The majority of Bi\textsuperscript{3+} substitutes for Zn\textsuperscript{2+} and the remainder forms Bi-interstitials.

c. Microstructural Evolution

Many of the properties of ZnO varistors have been attributed to the thickness and nature of the intergranular Bi-rich region. The
thickness of the intergranular region has been documented as varying from as small as 50 Å to 1.0 μm. A variety of Bi-phases have also been reported, an amorphous Bi-rich phase, $\beta$-Bi$_2$O$_3$, $\alpha$-Bi$_2$O$_3$ and ZnO·24Bi$_2$O$_3$ the bcc or sillenite phase. The development of these phases depend upon the thermal history and Bi$_2$O$_3$ content. Although it is generally agreed that the intergranular phase is not amorphous, the exact nature of the specific phase appears to be sample and/or thermal history specific.

Earlier work indicated that the intergranular phase was completely wetting. This corresponded to an amorphous phase. More recent work has established a 50° wetting angle for the Bi-rich phase. Morris and Cahn used TEM to illustrate that the wetting angle of the $\beta$-rich phase was 60° although spreading appeared to occur on some boundaries. They attributed this difference to anisotropy in the thermal expansion of ZnO, which upon cooling may leave a film coating the boundary or cause the film to break up into a lath-type structure. Clarke found that the boundaries where liquid had spread were always the basal plane in one of the grains and suggested that a narrow cusp in the Wulff plot of the ZnO surface energy could be responsible for the wetting behavior. There is also evidence that Bi segregates at the grain boundary. A substitutional solid solution is formed at the boundary with Bi$^{3+}$ replacing Zn$^{2+}$ creating an extra positive charge or space charge region at the boundary surface.

d. ZnO–Bi$_2$O$_3$ Sintering

The fabrication of varistors occurs by liquid phase sintering at 1200–1400°C. Morris stated that the presence of Bi$_2$O$_3$ actually inhibited the sintering of ZnO initially, and the presence of a liquid
FIGURE 3

COMPARISON OF DIFFUSION COEFFICIENTS

LOG D (cm²/sec)

Bi in Bi₂O₃

Zn in ZnO

O in ZnO

1/T x 10⁴ K
FIGURE 4

SUGGESTED PHASE DIAGRAMS

THE Bi$_2$O$_3$-ZnO SYSTEM
Figure 5

SOLID SOLUBILITY OF Bi$_2$O$_3$ IN ZnO

Temperature °C vs Mole % Bi$_2$O$_3$

- ZnO (ss) + L
- ZnO (ss)
- 6Bi$_2$O$_3$ + ZnO
phase does not enhance the sintering below 1000°C. There is more recent evidence, however, that small additions of Bi$_2$O$_3$ to ZnO can enhance the sintering of ZnO at temperatures substantially below the eutectic.

Maruyama$^{31}$ conducted constant heating rate studies on the ZnO-Bi$_2$O$_3$. He divided his results into four distinct sintering regimes: pure ZnO, 0-0.1 m/o Bi$_2$O$_3$; 0.2-2.0 m/o Bi$_2$O$_3$; and >4.0 m/o Bi$_2$O$_3$. For pure ZnO the sintering behavior was controlled by grain-boundary diffusion and was further influenced by surface diffusion. The addition of 0.1 m/o Bi$_2$O$_3$ was found to inhibit sintering at slow heating rates (<5°C/min); however, at higher heating rates the Bi$_2$O$_3$ addition enhanced the sintering. Maruyama's explanation for this phenomena is the time factor for diffusion of Bi$^{3+}$ into the ZnO lattice, at slow heating rates the small addition of Bi$_2$O$_3$ diffuses into the ZnO completely forming a uniform solid solution, while a faster heating rate does not allow this process to occur.

The third region, 0.2-2.0 m/o Bi$_2$O$_3$, is characterized by a sinterability proportional to Bi$_2$O$_3$ content. The sintering was interpreted to be by grain-boundary diffusion. The microstructures for samples in this region consisted of ZnO grains surrounded by a second phase. Diffusion of Zn$^{2+}$ or O$^{2-}$ occurred through the bulk of the second phase. Maruyama suggests that this intergranular phase provides a high diffusivity path for the diffusing species. At >4 m/o Bi$_2$O$_3$ he found that the sintering was inhibited by grain growth and formation of the sillenite-type crystals discussed earlier in the intergranular region.

The current work is an effort to study the ZnO-Bi$_2$O$_3$ system in even greater depth. An analysis of the effect of variations in ZnO starting
powders, variations in heating rate and effect of dopant level are considered. Determination of a possible sintering mechanism is also done by constant heating rate techniques. Microstructural evolution is also examined in an attempt to understand the sintering behavior in this system.
III. PROCEDURE

1. Initial Powder Characterization

Reagent grade zinc oxide powders from four manufactures, Mallinkrodt, Baker, MCB and Fisher, were studied. The suppliers' chemical analysis from the four powders is included in Table 3. The bismuth oxide used in the study was Baker analyzed reagent grade and its chemical analysis is also included in Table 3. Surface area and average particle size measurements were preformed on each of the four ZnO powders by B.E.T. and these results are included in Table 4. First the ZnO powders were dispersed in isopropanol and ultrasonically agitated with a sonifacator ultrasonic tip, then the solution was desired to remove air bubbles. Then the sedigraph was used to determine particle size distribution.

The powders were also examined with a Phillips 300 transmission electron microscope (T.E.M.), to determine if there were any inherent, differences in particle shape, size and agglomeration tendencies. To do so, the ZnO powders were ultrasonically dispersed in methanol and then an eyedropper was used to place a small amount on 3 μm carbon-coated copper grids.

2. Powder Treatment and Analysis

After the initial characterization the ZnO powders were doped with Bi₂O₃, Bi₂O₃ additions of 0, 0.1, 0.5, 1.0, 2.0 and 4.0 mole percent were dissolved in 2 mls of nitric acid. Eight grams of ZnO powder were dispersed in deionized water, then the two mixtures were combined. The mixture was stirred, dried, and ground with a porcelain mortar and pestle. The dry powder was calcined in a fused silica crucible at
<table>
<thead>
<tr>
<th>Substance</th>
<th>Arsenic</th>
<th>Chloride</th>
<th>Iron</th>
<th>Lead</th>
<th>Manganese</th>
<th>Nitrate</th>
<th>Sulfate</th>
<th>Sulfur</th>
<th>Sub not In</th>
<th>Particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.0002</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mallinckrodt</td>
<td>0.0003</td>
<td>0.0003</td>
<td>0.003</td>
<td>0.01</td>
<td>0.0005</td>
<td>0.0001</td>
<td>0.0007</td>
<td>0.1</td>
<td>0.0003</td>
<td>Baker</td>
</tr>
<tr>
<td>Plsher</td>
<td>0.2 ppm</td>
<td>0.2 ppm</td>
<td>1 ppm</td>
<td>5 ppm</td>
<td>0.0008</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0010</td>
<td>MCB</td>
</tr>
<tr>
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<td>0.0001</td>
<td>0.01</td>
<td>0.01</td>
<td>5 ppm</td>
<td>0.0001</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0005</td>
<td>0.0001</td>
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</tr>
<tr>
<td>217 ppm</td>
<td>0.0001</td>
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<tr>
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<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>Baker</td>
</tr>
<tr>
<td>Baker 3</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>Baker</td>
</tr>
</tbody>
</table>

Concentrations are in percent unless otherwise noted.
**TABLE 4**

**B.E.T. Results**

<table>
<thead>
<tr>
<th>Variation with Manufacturer</th>
<th>Surface Area m²/gm</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As Received Powder</td>
<td>Doped 2 m/o Bi₂O₃</td>
</tr>
<tr>
<td>Mallinkrodt</td>
<td>7.2</td>
<td>4.1</td>
</tr>
<tr>
<td>MC3</td>
<td>2.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Fisher</td>
<td>2.8</td>
<td>3.0</td>
</tr>
<tr>
<td>Baker</td>
<td>3.7</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variation with Dopant Level</th>
<th>Treated Powders</th>
<th>Surface Area m²/gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mallinkrodt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>2.3</td>
</tr>
<tr>
<td>ZnO + 0.1 m/o Bi₂O₃</td>
<td></td>
<td>3.6</td>
</tr>
<tr>
<td>+ 2.0 m/o Bi₂O₃</td>
<td></td>
<td>4.1</td>
</tr>
<tr>
<td>+ 4.0 m/o Bi₂O₃</td>
<td></td>
<td>4.6</td>
</tr>
</tbody>
</table>
analyzed with the B.E.T., sedigraph and TEM.

After the characterization the powders were pressed in a 3/16" diameter stainless-steel die at 40,000 psi. The green density of the powders ranged from 55-60% of theoretical density. A summary of the analysis is included at the end of this section.

3. Sintering Studies

The sintering experiments utilized constant heating rates and dilatometry. The heating rates were generated by a Leeds and Northrop Electromex and a Eurotherm 211 programmer/controller with a Eurotherm power pac. The samples were placed in a fused silica dilatometer as illustrated in Figure 6, and set in a platinum wound furnace. Fused silica was used for the dilatometer due to its low thermal expansion. The change in sample height was measured with an (LVDT) linear variable differential transducer, and its voltage signal was recorded on a Leeds and Northrop standard chart recorder. A type S platinum-platinum 10° rhodium thermocouple was placed next to the sample to obtain a precise temperature reading for the sample; this was recorded on a linear recorder. The dilatometer was also counter-balanced to avoid putting additional pressure on the samples. Atmosphere was not controlled in the furnace.

A summary of the sintering experiments is included at the end of this section.

4. Microstructural Evolution

The results of the sintering experiments were examined for micro-
FIGURE 6

SCHEMATIC OF THE CONTINUOUS RECORDING
DILATOMETER AND FURNACE ARRANGEMENT

LVDT

CONSTANT HEATING RATE
CONTROLLER/POWER SUPPLY

COUNTERWEIGHT

FURNACE
KANTHAL WINDINGS

ALUMINA TUBE

FUSED SILICA TUBE

FUSED SILICA ROD

SAMPLE

FUSED SILICA PLATES
structural evolution. The sintered pellets were fractured, and then the fractured surfaces were mounted on scanning electron microscope (SEM) stubs with silver paint. The coatings for the SEM were either evaporated gold or carbon-palladium for better resolution. An AMR SEM was used for the analysis.

5. **Summary of Procedure**

**Analysis:**

The four ZnO powders used were characterized using:

- B.E.T. for surface areas
- T.E.M. to determine shape, agglomeration.

After treating and doping, the powders were characterized again using:

- B.E.T.
- T.E.M.
- SEDIGRAPH to determine particle size distribution.

**Experiments:**

The Mallinkrodt ZnO was doped with 0, 0.1, 0.5, 1.0, 2.0 and 4.0 m/o Bi₂O₃.

Samples at each dopant level were heated at 5, 10, 20 and 40°C/min to 850°C to determine the effect of Bi₂O₃ additions on sintering rate and the effect of the heating rate. The microstructures were examined by SEM.

All four powders, MCB, Baker, Fisher and Mallinkrodt were heated at 20°C/min to 850°C at the six dopant levels to examine powder effects on sintering. Microstructures were examined by SEM.

Mallinkrodt ZnO and ZnO + 1.0 m/o Bi₂O₃ were heated rapidly
\~350°C/min to 705, 720 and 760°C to try and determine a sintering mechanism using solid-state isothermal techniques. Again the result was examined by SEM.

The MCB ZnO powder generated the most homogeneous microstructures, and was therefore used in all further experiments.

MCB ZnO was also doped and heated at 20°C/min to just below the eutectic 730°C to compare the microstructure of samples heated to temperatures above and below the eutectic; this was done with an SEM.

Further experiments were done where MCB ZnO with 0, 0.5 and 1 m/o Bi₂O₃ were heated to 1730°C and held for 1 hr to examine the effect on the microstructure.

Finally, a comparison of freshly processed powders and "old" powders was done to determine if there were aging effects.
IV. RESULTS

1. Characterization

All the micrographs and graphs are located at the end of this section.

a. Sedigraph Results

These indicated a wide binodal particle or agglomerate size distribution for the treated MCB, Fisher and Baker powders. All three appeared to have peaks at 8 μm and 0.8 μm. The Mallinkrodt powder had a single mode distribution ranging from 50-0.1 μm; however, as the dopant level was increased in the Mallinkrodt powder, it developed a bimodal distribution. The distribution ranged from 50-0.1 μm with peaks at 6 μm and 0.6 μm for a Mallinkrodt sample doped with 4 m/o Bi₂O₃. These results are illustrated in Figure 7.

b. TEM

Micrographs of the as received powders indicated strong agglomerates/aggregates. Although the particle sizes varied for the four powders, there was a characteristic morphology. Most of the particles were rectangular in shape with strong bonding at interparticle necks. Individual particle sizes ranged from 0.5 μm in the MCB powder to less than 0.1 μm in the Mallinkrodt powder, Figure 8.

The morphology of the treated and doped powders changed significantly. All the powders seemed to have more sharply defined crystallites and both larger agglomerates and smaller fines. The samples that were not doped with Bi₂O₃ were more spherical in nature than the doped powders. Again the powders appear to have rough edges; they are not smooth spheres. (Figure 9)
2. **Sintering Behavior**

a. **Constant Heating Rate Studies**

   **General Trends:**
   
   (1) The densification rate increased with increasing Bi$_2$O$_3$ content.
   
   (2) The densification achieved at temperature decreased with increased heating rate.
   
   (3) The sintering behavior was powder specific.

   **Dopant Level**

   For all four powders addition of small amounts of Bi$_2$O$_3$ (0.1 m/o), below the suggested solubility level 0.17±0.01 m/o Bi$_2$O$_3$ in ZnO at the eutectic, enhanced the sintering rate slightly.

   From 0.5-4.0 m/o Bi$_2$O$_3$ additions increased the sintering rate and final density of the compacts.

b. **Activation Energy Determination**

   The constant heating rate data was plotted as ln $\Delta_t/\Delta$ vs 1/T for a constant heating rate and ln c vs 1/T for a constant shrinkage in the method described in the introduction. The slope varied above and below the eutectic for Mallinkrodt ZnO from Figures 10 and 11.

c. **Heating Rate Effects**

   Slower heating rates resulted in denser structures and densification began at lower temperatures, Figure 12. There was a decrease in the sintering rate above the eutectic temperature for all powders at all heating rates.

d. **Powder Specificity**

   At a CHR of 20°C/min the four powders sintered differently below the eutectic. Figure 13 illustrates that although the slopes of the
ln Δl/l₀ vs 1/T plots varied below the eutectic, once a liquid phase had formed the slopes were almost identical.

e. Rapid Heating

Mallinkrodt ZnO and Mallinkrodt ZnO + 1.0 m/o Bi₂O₃ were heated almost instantaneously to 705°C and 760°C, and held at temperature for 10 minutes. The results indicated that the addition of 1.0 m/o Bi₂O₃ significantly enhanced the shrinkage. Plots of ln Δl/l₀ vs ln t were used to determine an n value for shrinkage; Figures 14-16.

3. Microstructural Evolution

a. Variations with Dopant Level

All the ZnO powders were doped with varying amounts of Bi₂O₃ and heated at 20°C/min to 730°C and 850°C. Figure 17 illustrates the changes in microstructure for Mallinkrodt ZnO with a variety of dopant levels at 850°C.

ZnO + 0.1 m/o Bi₂O₃ microstructures are compared in Figure 18 for both temperatures. The 120° temperature difference did not affect the microstructure greatly at this composition. The high temperature samples appear slightly coarser.

For samples with higher Bi₂O₃ contents, Figures 19-21 show the difference in microstructure for samples heated above and below the eutectic temperature. At temperatures above the eutectic, additions of 0.5, 1.0, 2.0 and 4.0 m/o Bi₂O₃ cause second phase formation. The amount of second phase formed increased with increased Bi₂O₃ content. The Bi-rich phase appeared at three and four grain junctions with a 60° wetting angle. However, some grains appeared to be coated by a continuous film of the second phase. Just below the eutectic temperature,
730°C, a second phase is not visible in the SEM micrographs at all dopant levels. At 850°C the amount of grain growth in the samples seemed to be proportional to the amount of liquid phase present. Table 6 includes a summary of the average grain size at 730°C and 850°C taken from line counts on SEM micrographs for the various dopant levels.

b. **Heating Rate Effects on Microstructure**

For the Mallinkrodt ZnO the SEM micrographs indicated that for high rates of heating there was less densification, less coalescence of individual grains, and a generally more open structure for Bi$_2$O$_3$ contents from 0-0.5 m/o. Higher Bi$_2$O$_3$ contents (2 and 4 m/o) gave similar microstructures regardless of the heating rate. Due to the amount of liquid present at these compositions, the grains tended to be surrounded by the liquid phase. The final densities were only slightly higher for slow heating rates, Figure 22.

c. **Powder Effects on the Microstructure**

SEM micrographs were used to related the anomalous sintering behavior of the different ZnO powders. The MCB powder yielded the most homogeneous microstructures. The Baker and Fisher powders were similar in that both exhibited some large pores and pore channeling. The Mallinkrodt ZnO results were the most varied; the microstructure was generally inhomogeneous. Regions in a sample could vary from densely packed areas to large pores with little grain coalescence, Figure 23.

Microstructures of samples treated to isothermal sintering techniques, and CHR to temperature with an isothermal hold are represented in Figures 24 and 25. Here the addition of Bi$_2$O$_3$ created a denser microstructure.
4. **Aging Effects**

Samples that were sintered more than a few months after powder preparation showed the same general trends; however, the shrinkage was not as pronounced.
### TABLE 5

**Determination of Activation Energy and n Valued for ZnO + 0.5 m/o Bi₂O₃**

<table>
<thead>
<tr>
<th>Constant Heating Rate</th>
<th>Below Eutectic</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C/min</td>
<td>-Q/nR</td>
</tr>
<tr>
<td>5</td>
<td>-31,000</td>
</tr>
<tr>
<td>10</td>
<td>-30,000</td>
</tr>
<tr>
<td>20</td>
<td>-40,000</td>
</tr>
<tr>
<td>40</td>
<td>-110,000</td>
</tr>
</tbody>
</table>
TABLE 6

Grain Growth in MCB ZnO Doped with Bi$_2$O$_3$
From 730°C to 850°C CHR 20°C/min

<table>
<thead>
<tr>
<th>Dopant Level Bi$_2$O$_3$ m/o</th>
<th>Grain size μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>730°C</td>
</tr>
<tr>
<td>0.1</td>
<td>0.79</td>
</tr>
<tr>
<td>0.5</td>
<td>0.83</td>
</tr>
<tr>
<td>1.0</td>
<td>0.73</td>
</tr>
<tr>
<td>2.0</td>
<td>0.83</td>
</tr>
<tr>
<td>4.0</td>
<td>1.26</td>
</tr>
</tbody>
</table>
FIGURE 7

SEDIGRAPHS DISTRIBUTIONS

MALLINKRODT ZnO-4.0 m/o Bi₂O₃

BAKER, FISHER, AND MCB
ZnO-0.1 m/o Bi₂O₃

MALLINKRODT ZnO-0.1 m/o Bi₂O₃

EQUIVALENT SPHERICAL DIAMETER, µM

CUMULATIVE MASS PERCENT
FIGURE 8
TEM: AS RECEIVED POWDERS

MALLINKRODT 7.2 m²/gm

BAKER 3.7 m²/gm

MCB 2.7 m²/gm

FISHER 2.8 m²/gm
FIGURE 9

TEM: TREATED POWDERS

UNDOPED

MALLINKRODT 2.3 m²/gm

BAKER

4.1 m²/gm DOPED 1.0 m/o Bi₂O₃
FIGURE 10
VARIATION IN SHRINKAGE WITH HEATING RATE
MALLINKRODT ZnO-Bi₂O₃

LN AXIAL SHRINKAGE

5 °C/MIN

10 °C/MIN

20 °C/MIN

40 °C/MIN

1/TEMPERATURE x 10⁴ (K⁻¹)
FIGURE 11

CONSTANT HEATING RATE DATA
AT CONSTANT SHRINKAGE
ZnO-0.5 m/o Bi₂O₃

\[
\ln \text{HEATING RATE (°C/min)}
\]

\[
\frac{L}{L} = 2\%
\]

\[
\frac{L}{L} = 5\%
\]

1/TEMPERATURE \times 10^4 (°K⁻¹)
FIGURE 12
SHIFT IN SHRINKAGE WITH CONSTANT HEATING RATE
MALLINKRODT ZnO-Bi₂O₃

TEMPERATURE (°C)

LOG AXIAL SHRINKAGE

1/TEMPERATURE x 10⁴ (°K⁻¹)

Teutetic = 742°C

0.5 m/o 5°C/Min
2.0 m/o 5°C/Min
2.0 m/o 40°C/Min
0.5 m/o 40°C/Min
Figure 13
Shrinkage variations by powder
ZnO-0.5 w/o Bi₂O₃
CHR to 850°C 20°C/min

\( \ln \Delta L/L \) axial shrinkage

\( 1/Temperature \ (K^{-1}) \)

MCB
FISHER
BAKER
MALLINKRODT

Teutectic
Figure 14

Analysis of sintering mechanism for solid state isothermal sintering

Mallinkrodt ZnO rapid heating to 705°C

Slope = 0.85

At Tmax hold
FIGURE 15

ANALYSIS OF SHRINKAGE
MECHANISM FOR SOLID
STATE ISOTHERMAL SINTERING

MALLINKRODT ZnO-1.0 m/o Bi₂O₃ \( T = 705 \text{ C} \)

\[ \text{LN AXIAL SHRINKAGE} \]

\[ \text{LN TIME (MINUTES)} \]

slope = 0.44

at \( T_{\text{max}} \)

2 minutes

\( T_{\text{max}} \)
FIGURE 16

ISOThERMAL INSTANT HEATING
TO 750°C HOLD 10 MINUTES
ZnO-1.0 m/o Bi₂O₃

Ln AXIAL SHRINKAGE

Ln TIME (Seconds)

n = 0.39
FIGURE 17
MALLINKRODT ZnO-B_2O_3
DOPANT EFFECT ON THE MICROSTRUCTURE
HEATING RATE 20°C/MIN

0.5 m/o B_2O_3

0.1 m/o B_2O_3

1.0 m/o B_2O_3

2.0 m/o B_2O_3

4.0 m/o B_2O_3
FIGURE 17
MALLINKRODT ZnO-Bi₂O₃
DOPANT EFFECT ON THE MICROSTRUCTURE
HEATING RATE 20°C/MIN

0.1 m/o Bi₂O₃

0.5 m/o Bi₂O₃

1.0 m/o Bi₂O₃

2.0 m/o Bi₂O₃

4.0 m/o Bi₂O₃
FIGURE 18

MCB ZnO-0.1M/o B_{2}O_{3}

EFFECT OF DIFFERENT PEAK TEMPERATURES
HEATING RATE 20°C/MIN

730°C

850°C
FIGURE 18

MCB ZnO-0.1 m/o B\textsubscript{2}O\textsubscript{3}

EFFECT OF DIFFERENT PEAK TEMPERATURES
HEATING RATE 20°C/MIN

730°C

850°C
FIGURE 19

MCB ZnO-0.5 m/o Bi₂O₃
EFFECT OF DIFFERENT PEAK TEMPERATURES
HEATING RATE 20°C/MIN
730°C

850°C
FIGURE 19

MCB ZnO-0.5 m/o Bi₂O₃

EFFECT OF DIFFERENT PEAK TEMPERATURES

HEATING RATE 20 °C/Min
730 °C

850 °C
FIGURE 20

MCB ZnO-1.0 m/o Bi$_2$O$_3$

EFFECT OF DIFFERENT PEAK TEMPERATURES

HEATING RATE 20°C/MIN

730°C

850°C
FIGURE 20

MCB ZnO-1.0 m/o B12O3
EFFECT OF DIFFERENT PEAK TEMPERATURES
HEATING RATE 20°C/MIN

730°C

850°C
FIGURE 21

MCB ZnO-4.0 m/o Bi₂O₃
EFFECT OF DIFFERENT PEAK TEMPERATURES
HEATING RATE 20°C/MIN

730°C

850°C
FIGURE 21

MCB ZnO-4.0 m/o Bi₂O₃
EFFECT OF DIFFERENT PEAK TEMPERATURES
HEATING RATE 20°C/MIN

730°C

850°C
FIGURE 22

MALLINKRODT ZnO-Bi₂O₃
TWO DIFFERENT HEATING RATES
TWO DOPANT LEVELS

0.5 m/o Bi₂O₃

5°C/MIN

2.0 m/o Bi₂O₃

40°C/MIN
FIGURE 22
MALLINKRODT ZnO-Bi$_2$O$_3$
TWO DIFFERENT HEATING RATES
TWO DOPANT LEVELS
FIGURE 23

THE FOUR ZnO POWDERS
0.5 m/o Bi$_2$O$_3$, 20°C/MIN TO 850°C
FIGURE 23

THE FOUR ZnO POWDERS
0.5 m/o Bi₂O₃, 20°C/MIN TO 850°C
FIGURE 24

ISOHERMAL HEATING

a. ZnO heated to 705°C

b. ZnO-1.0 m/o Bi₂O₃ heated to 705°C

c. ZnO-1.0 m/o Bi₂O₃ heated to 750°C
FIGURE 24
ISOThERMAL HEATING

a. ZnO heated to 705°C

b. ZnO-1.0 m/o \( \text{Bi}_2\text{O}_3 \) heated to 705°C

c. ZnO-1.0 m/o \( \text{Bi}_2\text{O}_3 \) heated to 750°C
FIGURE 25
ISOTHERMAL HEATING
1 HOUR HOLD AT 730°C

a. ZnO

b. ZnO-0.5 m/o B₃O₃

c. ZnO-1.0 m/o B₃O₃
V. DISCUSSION

The results presented in the previous section require some discussion; in terms of variations due to powder supplier, and then related to the sintering behavior of each powder. The effect of the dopant level on the sintering characteristics, and the effect of varying heating rates on the microstructure and sintering behavior will be used to determine activation energies and a sintering mechanism for the process. Shrinkage and microstructural evolution above and below the eutectic temperature will be examined as well as the effect on the microstructure and apparent sintering mechanism of some isothermal sintering runs.

1. Powder Effects

The analyses of the "as received" ZnO powders showed a wide range of variation in surface area, particle shape and size distribution, and the amount of impurities also varied from powder to powder. The Mallinkrodt ZnO had the highest surface area 7.2 m²/gm; its small particle size is illustrated by the TEM micrographs. The MCB ZnO had a much larger particle size, and appeared more spherical. The large variation in particle size and morphology could indicate different processing techniques, the French process (Zn vaporization) produces a generally more spherical particle morphology. Although the chemical analyses were not the same, the Fisher and MCB powders had approximately the same surface area 2.7 m²/gm and the TEM micrographs seemed similar. These two powders could be produced by the same manufacturer, but distributed by different companies.

Treatment of the powders with nitric acid, calcination and doping
with Bi$_2$O$_3$ changed their initial characteristics substantially. The nitric acid treatment together with calcination reduced the surface area of the powders (Table 4) and created a more spherical, highly aggregated particle network. The nitric acid is also thought to leave an activated ZnO coating on the particles from decomposition of Zn(NO$_3$)$_2$ which could be responsible in part for the particle coalescence. Additions of Bi$_2$O$_3$ reduced the particle size and increased the surface area, Table 4. Bi is thought to act as a grinding aid$^{62}$, and the effects could be clearly seen in the TEM micrographs. The doped powders had rough edges characteristic of fractured surfaces and very fine crystallites.

The sedigraph results for the treated and doped powders provided more insight into the effect of doping. With very small additions of Bi$_2$O$_3$ (0.1 m/o) the MCB, Baker and Fisher powders showed a bimodal particle size distribution. However, the sedigraph results for Mallinkrodt ZnO indicate a very wide single mode particle size distribution. By increasing the Bi$_2$O$_3$ content in Mallinkrodt ZnO to 2 m/o the distribution shifted to a smaller average particle size with a bimodal size distribution.

The effects of all these variations in particle size, shape and distribution have a large effect on the sintering behavior, especially in the initial stage. Although more indepth discussion of the sintering behavior will be included later, an analysis of the effects of the various powders on the kinetics and microstructure is necessary here. Figure 13 and 23 illustrate the difference in sintering rate and microstructure for the four powders doped with 0.5 m/o Bi$_2$O$_3$ and heated at a constant rate to 850°C. The slopes of the ln $\Delta l/L_o$ vs 1/T vary
substantially for the various powders below the eutectic temperature. However, once the liquid phase has formed, all the powders sinter at the same rate. Therefore, although the sintering behavior may vary in the initial stage due to differences in powder, the same sintering mechanism is dominant for all the powders when a liquid phase is present, and they achieve the same degree of densification.

The microstructures corresponding to the graph illustrate the variation between powders. Both the Mallinkrodt and Fisher sintered powders appear highly porous, a great deal of neck growth and a small amount of grain coalescence are characteristic. The Baker ZnO had the highest final density, and the MCB the most homogeneous microstructure. All the microstructures were examined after the initial stage of sintering, but the differences between powders were still apparent.

2. **Dopant Effects**

All the ZnO powders were doped with 0, 0.1, 0.5, 1.0, 2.0 and 4.0 m/o Bi$_2$O$_3$. Additions of Bi$_2$O$_3$ generally increased the sintering rate, shifted the onset of shrinkage to lower temperatures and yielded higher final densities for the samples. The results of samples heated at 20°C/min to 850°C will be discussed in terms of shrinkage rate and final microstructure.

The effect of the dopant level on ZnO sintering can be divided into three regions: pure ZnO and ZnO + 0.1 m/o Bi$_2$O$_3$, 0.5 m/o Bi$_2$O$_3$ and 1.0–4.0 m/o Bi$_2$O$_3$. At this heating rate 0.1 m/o Bi$_2$O$_3$ added to pure ZnO enhanced the sintering rate slightly. There was no change in the slope of the ln $\Delta l/l_o$ vs 1/T plots at the eutectic temperature.
A 0.1 m/o $\text{Bi}_2\text{O}_3$ addition is within the solid solubility range and most likely forms a solid solution with the ZnO grains. SEM micrographs of these samples indicate that there was no liquid phase present at the peak temperature; however, the presence of Bi in the ZnO or its segregation to the grain boundaries could enhance the sintering rate.

In the samples containing 0.5 m/o $\text{Bi}_2\text{O}_3$ the liquid phase does not appear as a distinct second phase; however, the shrinkage behavior is indicative of liquid phase formation. SEM micrographs showed a great deal of neck formation and grain coalescence. Below the eutectic temperature, the presence of a Bi-rich phase coating the ZnO grains enhanced the sintering much the same way a liquid is thought to enhance material transport properties. Once a liquid is formed in this system the sintering rate decreases, this could be due to several factors. If a rigid skeleton has formed, the presence of a liquid is not likely to cause the rearrangement stage in liquid phase sintering, and once past the initial stage of sintering the samples exhibit more grain growth leading to a decrease in shrinkage rate. SEM micrographs indicate a large degree of particle coalescence above the eutectic temperature. The liquid appears to concentrate at the neck region, decreasing the neck curvature and thus the driving force for sintering. Above the eutectic the rate of grain growth increases, possibly causing a change in the sintering mechanism. As the $\text{Bi}_2\text{O}_3$ content increases from 1.0-4.0 m/o the amount of liquid present in the sample increases dramatically, indicating a definite second phase. Again, there is a decrease in the sintering rate as the sample approaches the eutectic temperature evident from the dilatometer output. The wetting properties of the liquid phase are evident in the SEM micrographs, Figure 21. The liquid
appears to form a 60° wetting angle with the grains at some of the grain boundaries; however, at other boundaries it appears to be completely wetting. This phenomena has been observed previously and is explainable in terms of surface energy anisotropy, thermal expansion anisotropy or variations in interfacial energies.

The argument for surface energy anisotropy was proposed by Clarke. He found that the Bi-rich liquid spread only parallel to the Basal plane (001) direction. By assuming there is a cusp in the Wulff plot of the ZnO surface energy at this plane, he gives a plausible explanation for the wetting behavior. Morris and Cahn, however, found that the boundaries where spreading occurred were curved with no sharp variations in curvature. Therefore, they do not expect strong anisotropy in the surface energy. Morris and Cahn maintain that in order to achieve a minimum total surface energy, the free energy of the inter-phase boundary must be greater than half the grain-boundary energy to achieve the observed structure. The Bi-rich liquid penetrates the three and four grain junctions; the concentration of Bi-rich liquid falls off rapidly from the junction forming a triangular open network. In this case the addition of Bi$_2$O$_3$ simply thickens the phase as has been observed. Their explanation for the apparent spreading behavior on the occasional boundary is due to anisotropic thermal expansion stresses upon cooling. When the stresses are enough to cause fracture above the eutectic, the liquid phase would then cover the interface between grains, creating what appears to be a completely wetting liquid. A final observation from the SEM microstructures is the amount of grain growth relative to dopant level. As the Bi$_2$O$_3$ content increases the ZnO grain size also increases (Table 6). This could be due to the
greater densities achieved by the compacts with more liquid present or simply due to the presence of the liquid. At higher densities the compacts could be entering the final stages of sintering, a slower process involved in the shrinking of pores and grain growth. If the grain growth is due to the presence of the liquid, the liquid must change the transport properties providing a high diffusivity path and easier coalescence.

3. **Determination of a Possible Sintering Mechanism from CHR Theory**

The previous results have been described qualitatively in order to illustrate the effect of Bi$_2$O$_3$ on the sintering of ZnO. An attempt to determine a sintering mechanism quantitatively was also undertaken. Mallinkrodt ZnO with 0.5 m/o and 1.0 m/o Bi$_2$O$_3$ was heated at constant rates of 5, 10, 20 and 40°C/min. The results were plotted as ln Δ$l$/l$_0$ vs. 1/T at a CHR and ln CHR vs. 1/T at a constant shrinkage (Figures 10 and 11). Combining these results with constant heating rate theory yielded a quantitative description of the process.

The results for sintering below the eutectic temperature for both the 0.5 and 1.0 m/o Bi$_2$O$_3$ samples yielded an n value of approximately 1.0-2.0. As was presented in the literature review, n=1 for a CHR technique indicates a viscous flow mechanism for sintering, and n=2 indicates grain boundary diffusion at the initial stage of sintering. For the intermediate stage, Skaar determined that n=1 indicated grain boundary diffusion controlled sintering. Since these models have been derived on the assumption that only one mechanism is occurring at a time, and are derived from single-phase solid-state sintering models, they may not be entirely applicable. The activation energies for the
process are 29.7/R kcal/mole for 0.5 m/o Bi$_2$O$_3$ and 36.0/R kcal/mole for 1.0 m/o Bi$_2$O$_3$. These values are lower than those for [Zn]$^+$ diffusion reported in the literature indicating that the Bi-film even in the solid-state must provide a rapid path for material transport.

An analysis of the defect equilibria in ZnO doped with Bi$_2$O$_3$ indicates that a greater number of zinc vacancies will be formed. Since the Bi$_2$O$_3$ contributes 3 O$_6$ to the ZnO lattice, the addition should inhibit oxygen diffusion which is thought to occur by a vacancy mechanism. Zinc diffusion in ZnO has been shown by most studies to be orders of magnitude higher than that of oxygen (Figure 3). Therefore, the addition of Bi$_2$O$_3$ should enhance the zinc diffusion in the lattice. In polycrystalline samples, Roberts and Wheeler found that diffusion was predominantly along the grain boundaries and related the activation energies for volume and grain-boundary diffusion as:

\[
\Delta H_{gb} = \frac{1}{2} \Delta H_v + (24 \pm 8) \text{ kcal/mole}
\]

By decreasing the activation energy for volume diffusion, or increasing the diffusivity, this should also increase the grain-boundary diffusivity.

Micrographs of MCB ZnO-doped samples below the eutectic temperature indicate that no grain growth occurs before liquid formation, suggesting that it should be possible to use an initial stage sintering model. However, a viscous flow mechanism is not appropriate for this system. There is also a shift to higher slopes, lower n, with increasing heating rate. At higher heating rates there is less time for diffusion processes to occur, leaving a boundary phase richer in Bi. If Bi enhances the surface transport properties of Zn, this could account for the higher apparent activation energy at higher heating rates. A combination of
grain-boundary diffusion coupled with enhanced surface diffusion due to the presence of excess Bi at the surface of the ZnO grains could explain the low $n$ values.

Above the eutectic temperature there is a substantial slowing down of the process demonstrated by a gradual change in slope. The slope change is indicative of the microstructural evolution, formation of the liquid phase and possibly a change in the sintering mechanism. SEM micrographs indicate that just below the eutectic temperature the samples had already formed a rigid structure. The dilatometer output indicated that more than a few percent shrinkage had already occurred, suggesting intermediate stage sintering. The change in slope was gradual reflecting more of a change due to the structure than due to the formation of the liquid phase. The change in slope due to structure is also reflected in the shift of the shrinkage curves with heating rate (Figure 10). At faster heating rates a higher temperature is required to achieve the same shrinkage, therefore, the slope change occurs at higher temperatures.

In the temperature regime about the eutectic it is difficult to analyze the results using constant heating rate theory. The theory is not adequate for interpretation of a multiphase system with a liquid phase present. Geissinger et al. suggest a model for liquid phase sintering with a partially wetting liquid. The quantity of the liquid does not effect the shrinkage rate, but the wetting angle effects the radius of curvature at the neck and thus the driving force. Although no method for interpretation of the mechanism with CHR data is suggested, an idea of the interactions becomes more evident. Above the eutectic temperature from previously reported data on ZnO the sintering mechanism
could be grain-boundary diffusion especially for lower Bi$_2$O$_3$ contents where less grain growth is apparent. Volume diffusion could become controlling for the larger grain sizes. From these data it is difficult to deduce an exact mechanism; more than one process is probably occurring simultaneously.

4. Other Sintering Studies

An attempt was made to determine at what temperature grain growth began in the samples, and to determine a possible sintering mechanism by isothermal techniques. The effect of an isothermal hold below the eutectic temperature to examine the effect on the microstructure will also be discussed.

By heating samples at a constant rate to temperatures above and below the eutectic temperature, it became apparent that little grain growth occurred below the eutectic temperature. The dopant level had the greatest effect on the microstructures above the eutectic. Figures 17-20 illustrate the difference in grain growth from 730°C to 850°C and the effect of increase Bi$_2$O$_3$ content. Table 6 shows that the amount of grain growth was dependent on Bi$_2$O$_3$ content. Final grain sizes varied from 0.82 μm - 3.7 μm for 0.1 m/o - 4.0 m/o Bi$_2$O$_3$. The addition of the Bi$_2$O$_3$ appears to have a large effect on the transport properties in ZnO. The SEM micrographs did show substantial neck growth below the eutectic suggesting a strong skeletal structure. This would explain the absence of the rearrangement stage of liquid phase sintering, and possibly contribute to the grain growth. The more liquid present the higher the final density of the sample, and therefore the greater degree of grain growth might be expected.
In order to clarify the modeling problem due to CHR theory in a multiphase/liquid phase system, some isothermal rapid heating experiments were preformed. Samples of pure treated ZnO and ZnO + 1 m/o Bi$_2$O$_3$ were heated to 705°C and 750°C and held for 10 minutes. Plots of ln $\Delta l$/$l_0$ vs. ln $t$ were interpreted as suggested by Johnson$^{43}$ to determine a sintering mechanism. Johnson states that in a system with pure grain-boundary diffusion the slope of the plot will give $n = 0.33$ and $n = 0.52$ for pure volume diffusion. Assuming that the surface and grain-boundary contributions will behave in the manner illustrated in Figure 26, a surface diffusion contribution will shift the line downward and increase its slope. For the pure ZnO sintered in this manner $n = 0.85$ at 705°C indicating a substantial contribution from surface diffusion. The ZnO + 1 m/o Bi$_2$O$_3$ yielded a value $n = 0.44$ at 705°C and 0.39 at 760°C indicated a somewhat smaller contribution by surface diffusion and/or some combination of grain boundary and volume diffusion. The problem with this analysis again is its derivation for a single-phase system.

In the samples that were heated at a constant rate at 20°C/min to 730°C and held at temperature for 1 hr, adding Bi$_2$O$_3$ to pure ZnO increased the amount of coalescence between grains and decreased the amount of grain growth. The dilatometer output indicated that once the samples were at temperature the amount of shrinkage occurring over the next hour was substantially less than heating it to 100°C above the eutectic temperatures. The microstructures that evolved were also substantially different; there is no indication that a second phase is present. The pure ZnO samples shrank only a few percent, and had well-defined grains, but the doped specimens sintered more rapidly due
FIGURE 26

THE RELATIONSHIP BETWEEN SURFACE AND BOUNDARY DIFFUSIVITIES
to the second phase.

5. Aging Effects

Although no definitive testing was done to determine the effect of age on the powders, several general trends were observed. In powders that were over a year old, but had been processed by the same technique, little enhancement of sintering was observed below the eutectic temperature. The agglomeration tendencies of the powders were very dependent on age and humidity. Aged powders had to be reground in order to form samples at the same pressing pressures. Older powders showed a greater tendency toward endcapping and delaminating, as did dryer powders. The degree of "activated" sintering was also reduced. This could be due in part to the nitric acid treatment, which alone was found to enhance the sintering of ZnO slightly. The adsorption or desorption of water could effect the activated complex formed from the decomposition of Zn(NO₃)₂ on the surface of the ZnO grains. Since slight difference in powders have already been shown to effect the sintering kinetics, it is not surprising that age also plays a role. In order to attain a degree of reproducibility in the sintering characteristics, it is important to maintain a consistent processing method.
VI. CONCLUSIONS

The results presented in the discussion section showed four general trends.

1. The sintering results were size, size distribution, shape and powder specific.

2. In all cases the addition of Bi$_2$O$_3$ enhanced the sintering of ZnO.

3. At lower dopant levels higher constant heating rates caused lower final densities.

4. Isothermal sintering techniques correlated well with the suggested sintering mechanism; grain-boundary diffusion.

The four ZnO powders showed a range of sintering behavior in the initial stages; however, above the eutectic temperature their behavior was uniform. The variations in powder shape, size and particle size distribution caused large variations in the constant heating rate data before liquid formation. Once the liquid was present the powders sintered at the same rate.

The addition of Bi$_2$O$_3$ to ZnO enhanced the sintering below the eutectic temperature. Above the solubility limit (~0.17±.01 m/o at the eutectic) the degree of enhancement increased with increasing Bi$_2$O$_3$ content. This was probably due to the presence of a second phase which provided a high diffusivity path. At low Bi$_2$O$_3$ contents (0.1 m/o) the sintering could be enhanced by the formation of more zinc vacancies as the Bi$_2$O$_3$ went into solid solution with the ZnO.

At low dopant levels the high heating rates (20 and 40°C/min) sintered to a lesser degree than at lower heating rates (5 and 10°C/min). This heating rate effect is due to the time factor involved in the
sintering processes. Compacts heated at slower rates have a greater
time period for diffusion processes to occur. At higher dopant levels
2 and 4 m/o Bi$_2$O$_3$ the heating rate had a lesser effect due to the
amount of liquid formed at the eutectic temperature. Although the
liquid did not enhance the sintering it did fill voids and cause
greater amounts of grain growth above the eutectic temperature.

From the CHR data an effort was made to specify a sintering
mechanism. However, due to the limitations of the models no definitive
mechanism could be determined. Microstructural evolution and isothermal
techniques suggest that below the eutectic temperature a combination
of grain boundary and surface diffusion controls the sintering. Above
the eutectic temperature a change in mechanism occurs due to the liquid
formation that could be interpreted as either grain boundary or volume
diffusion depending on dopant level and grain size.
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BIOGRAPHICAL NOTE

Elaine Rothman was born in Rochester N.Y. December 22, 1959. She grew up in Champaign, Illinois. Spent 3 years overseas before attending the University of Illinois at Champaign-Urbana as an undergraduate in ceramic engineering. During that time she was a co-op student for Ford Motor Co. in both Detroit and Nashville. After spending 5 months in New Zealand Elaine returned to finish her degree in ceramics and spend a summer at the Naval Research Laboratory in Washington D.C.

Arriving at M.I.T. in January 1981, she began her thesis work with Prof. R. L. Coble on activated sintering of ZnO.