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Solid-state Activated Sintering of TiO2 and Electric Field Assisted Sintering of ZnO based Materials

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Author
Nie, Jiuyuan

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Activated Sintering of TiO$_2$ and Field Assisted Sintering of ZnO based Materials

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy

in

Chemical Engineering

by

Jiuyuan Nie

Committee in charge:

Professor Jian Luo, Chair
Professor Javier Garay
Professor Olivia Graeve
Professor Kenneth S. Vecchio
Professor Kesong Yang

2019
The Dissertation of Jiuyuan Nie is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California San Diego

2019
DEDICATION

To my mother, Ms. Yuzhi Li
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VITA

2014 Bachelor of Science Tsinghua University, China
2016 Master of Science University of California San Diego, USA
2019 Doctor of Philosophy University of California San Diego, USA

PUBLICATIONS


3. H. Leng, J. Huang, J. Nie, J. Luo, “Cold sintering and ionic conductivities of Na$_{3.256}$Mg$_{0.128}$Zr$_{1.872}$Si$_2$PO$_{12}$ solid electrolytes”, Journal of Power Sources, 2018, 391, 170.


Solid-state activated sintering of TiO$_2$-CuO system was systematically studied to reveal the effects of grain boundary structures on low temperature densification. Specifically, the eutectic temperature and composition of the TiO$_2$-CuO system were carefully measured to be 1010 ± 10 °C and 83CuO:17TiO$_2$, respectively. Subsequently, a TiO$_2$-CuO phase diagram was computed. Activated (enhanced) sintering of TiO$_2$ with the addition of CuO occurring at >300 °C below
the eutectic temperature was observed. High resolution transmission electron microscopy (HRTEM) characterization of water-quenched specimens revealed the formation of nanometer-thick, liquid-like, intergranular films (IGFs), a type of grain boundary (GB) complexion, concurrently with accelerated densification and well below the bulk eutectic temperature. Consequently, activated sintering is explained from the enhanced mass transport in this premelting-like complexion. An interfacial thermodynamic model was used to quantitatively explain and justify the stabilization of liquid-like IGFs below the eutectic temperature and the temperature-dependent IGF thicknesses. A GB \( \lambda \) diagram was computed, for the first time for a ceramic system, to represent the thermodynamic tendency for general grain boundaries to disorder.

Activated flash sintering of ZnO through a bulk phase transformation or a GB complexion transition was investigated. Specifically, in undoped and Al\(_2\)O\(_3\)-doped ZnO, the flash sintering is activated by natural thermal runways that can be quantitively predicted. In contrast, a bulk eutectic reaction and the associated formation of premelting-like IGFs in Bi\(_2\)O\(_3\)-doped ZnO can lead to a nonlinear rise in the specimen conductivity (above the Arrhenius extrapolation) to trigger flash sintering prior to the occurrence of the predicted natural thermal runaway. This work uncovers the roles of the bulk phase and interfacial (phase-like) complexion transformations in initiating flash sintering. Beyond high temperature interfacial liquids, water was used as an example of low temperature, transient, interfacial liquid to activate flash sintering at room temperature. ZnO powder pellets was water-assisted flash sintered (WAFS) to achieve \( \sim 98\% \) of the theoretical density.
in 30 s without any external furnace heating. The specimen conductivity can be increased by > 10,000 times via absorbing water vapor to enable the room-temperature flash. The initial electric field must be higher than a critical threshold to lead to densification, suggesting bifurcation in kinetic pathways.

Another method called two-step flash sintering (TSFS) was proposed as a new ceramic fabrication method to achieve fast densification with suppressed grain growth. Using ZnO as an exemplar, ~ 96.5% of theoretical density was achieved using TSFS with a grain size of ~ 370 nm, representing a > 3 times reduction of the grain size in comparison with conventional flash sintering. TSFS achieved this result in a few minutes, > 200 times faster than that needed for conventional two-step sintering to obtain comparable results.

Lastly, the effect of electric field on grain growth and grain boundary structure was studied in the presence of ionic grain boundary liquids at high temperatures. Using Bi$_2$O$_3$-doped ZnO as a model system, this study reveals the electrochemical polarization of ionic defects driven by an external electric field and current. A mixed conducting model was developed to explain the asymmetric grain growth of sandwiched single crystal, abnormal grain growth near the cathode, as well as the pore formations. The ionic blocking, electric conducting single crystal decouples the effect of electric potential and electrochemical potential on grain growth. It is assumed that electric field and current polarized ionic defects and thereafter modified local space charges. Grain boundary complexion transitions were also observed after annealing under electric field and current.
Chapter 1. Introduction

1.1. Sintering

1.1.1. Brief Overview

Sintering, a term developed by archeologists in the late 18th century, originally refers to the agglomeration and hardening of mineral particles. The definition was then significantly diversified and generalized in the modern era to refer the thermal treatment for bonding particles into a predominantly solid structure. Ancient sintered objects in human history date back to 24000 B.C. according to archeological findings. However, human history of controlling sintering process for manufacturing is only a few hundred years. And the archival literature history of pursuing the science behind sintering is less than 200 years.

There are many variations of sintering technics. Fig. 1.1 is a taxonomy of common sintering technologies from literatures [1]. Many parameters involved in modern sintering practices. For example, pressures ranging from MPa to GPa are used in sintering techniques include hot pressing, spark plasma sintering, and hot isostatic pressing in addition to heating; liquid phase can be used to improve the sintering rate, which is very common in the industry. However, it is worth noting that as the development of sintering technologies, the complete classification of sintering is difficult, especially for processes involving multiple controlled parameters.

1.1.2. Theories
Qualitative and quantitative sintering theories were developed in 1940s. Even though the development of sintering theories was far behind the commercialization of modern sintered products, they drive the success of new technologies and new products.

The sintering of single phase powder by solid-state diffusion or multi-phase powder mixtures by liquid phase are generally described in three stages. As shown in Fig. 1.2 [2], starting with a porous green body, which is usually prepared by mechanical pressing particles in a mold, a phenomenon called “neck formation” happens in the initial stage of sintering. Concave necks will form between particles. Relative density will slightly increase, but the specimen is still very porous. In the intermediate stage, there are neck evolution and grain boundary evolutions. Major densification occurs during this stage, but the pores are still open networks. In the final stage, open pores are isolated to form closed pores between grains, and part of them are removed after completion of sintering. Thermodynamically, the driving force of sintering is the reduction of total interfacial energy.

Grain growth is another important phenomenon during densification as well as in fully dense polycrystalline materials. If the relative grain sizes have a simple and invariable distribution, it is characterized as normal grain growth. However, if there are exceptionally large grains exist, forming a bimodal grain size distribution, it is referred as abnormal grain growth. During the sintering of a powder compact, the increase of density and grain size happen simultaneously [1]. Thus, when studying the grain growth during sintering, the interaction between densification
and grain growth must be considered. Other aspects that should be considered include impurities, secondary phases, atmosphere, etc.

1.1.3. Solid-State Activated Sintering

Solid-state activated sintering is a process that can dramatically improve the densification of metal or ceramic green bodies at temperatures that no stable bulk liquid phase forms by adding a small amount of solid phase sintering aids [3]. Some famous examples are Ni-doped W and Mo [4-6] and Bi$_2$O$_3$-doped ZnO [7]. The activated sintering could initiate below 60% of the corresponding bulk eutectic temperatures.

The solid-state activated sintering has been studied for over 5 decades [8-14]. Recent developments in high resolution transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) revealed the existence of stable intergranular films (IGFs) below the bulk eutectic temperatures in a wide range of ceramics and metals [15-17], suggesting enhanced mass transportation through these nanometer-thick, quasi-liquid films in solid-state activated systems.

A phenomenological interfacial thermodynamic model, Grain Boundary $\lambda$ Model, was proposed to predict the stability of nanometer thick liquid-like intergranular films [18, 19]. Chapter 2 is an example of extending the model from metallic systems to ceramic systems.

1.1.4. Electric Field Assisted Sintering
Electric Field adds another flexibility to materials sintering practices. The early application of DC current assisted sintering includes consolidation of filaments by W.L. Voelker in 1898, resistance sintering developed by Sauerwald in 1922, sintering of refractory metals by Taylor in 1933, etc. [20]. However, the idea of using electric field on sintering was not widely spread to other materials at that time. Later, formulation of this technology and idea was significantly accelerated by the development of a technology called spark plasma sintering (SPS) in 1950s, as well as its commercialization in the 1990s. In the SPS technology, a pulsed DC current is used to heat up a graphite or tungsten carbide die in vacuum or an inert gas. In the meantime, a pressure is applied on the materials [21]. SPS has the advantage of sintering at lower temperature and in a shorter time than the conventional sintering method(s). There is a significant number of publications indicating that SPS can be used to produce nanocrystalline materials [22-25]. There are also findings showings that SPS can improve materials mechanical [26, 27], optical [24, 28], or ferroelectrical properties [29].

It is worth noting that, in most of the conventional SPS process, most of the electric current passes through the graphite or tungsten carbide die rather than the specimens. In 2010, Raj and his co-workers developed the Flash Sintering technology [30], which passes current through the specimens directly. They have successfully densified 3 mol. % yttria-stabilized zirconia (3YSZ) in a few seconds at a furnace temperature of ~ 850 °C, which was a few hundred degrees below the conventional sintering temperature. Fig. 1.3 represents the flash sintering
phenomenon and its difference with traditional field assisted sintering technology (FAST), which enhances densification moderately at low external electric fields.

In a typical Flash Sintering setup, a constant, high electric field is applied on a green specimen while heating it up in a furnace. Given an electric field that is high enough, an electrical and thermal instability of the specimen occurs, leading to a fast increase of current density as well as specimen temperature. After reaching a pre-set current limit, the power supply is switched to the constant-current mode. The specimen is sintered after holding it at the current limit for a very short time. Green specimens can reach almost fully dense in a few seconds using flash sintering.

Many materials have been successfully sintered using the Flash Sintering technology since its invention. For example, 8YSZ [31], CoMnO$_4$ [32], SrTiO$_3$ [33], TiO$_2$ [34], GDC [35], MgO-doped Al$_2$O$_3$ [36], SiC-Al$_2$O$_3$-Y$_2$O$_5$ [37], etc. Independent studies carried out at University of California San Diego [38], Oxford University [39], and University of Pennsylvania [40] proposed thermal runaway models to explain the onset of flash sintering. Electrical thermal runaway has been proposed and tested to be the major cause of the onset of flash sintering in many materials. On the other hand, there are other proposed mechanisms. For example, an avalanche nucleation of Frenkel pairs driven by the high electric field will initiate the flash sintering. This proposed mechanism remains controversial and needs further study in the future [41, 42].

To understand the fast densification mechanism during flash sintering, Zhang and his co-workers investigated the densification mechanism during flash
Their study revealed the contribution of the high heating rate on the ultra-fast densification rate. Other mechanisms have also been proposed by researchers to explain the densification under electric fields. For example, Kim, Kang, and Chen proposed an electro-sintering mechanism that the surface diffusion of cations at the pores enhances the densifications [44].

The effect of electric field and current other than Joule heating during flash sintering is elaborated in Section 1.3.

1.2. Grain Boundary Complexion

Extending the Gibbs definition of bulk phases, “grain boundary complexion” is a term designated to describe the features of grain boundaries that is in thermodynamic equilibrium with its abutting phase(s) [45].

In 2007, Dillon, Hammer and their co-workers systematically characterized six grain boundary complexions (Fig. 1.4) in Al₂O₃ system based on their classification [46]: Complexion I is a Langmuir-McLean sub-monolayer adsorption with scattered dopant cations; Complexion II is “clean” grain boundary; Complexion III is a bilayer adsorption of ~0.35 nm thick; Complexion IV is a multi-layer adsorption of ~0.6 nm thick; Complexion V is an intergranular film with an equilibrium thickness of 1 – 2 nm; and Complexion VI is a wetting film.

The observation of various complexions beyond intergranular films further emphasized the complexity of grain boundaries. And, understanding the grain boundary complexions not only helps controlling the microstructural evolutions, but also explains and predicts materials mechanical, electrical, thermal, and chemical
properties [17, 18]. Thus, the new findings urge researchers to pursue a long-range scientific goal of developing grain boundary diagrams. Recently, using a lattice model and CALPHAD data, Zhou and co-workers successfully calculated and validated a grain boundary complexion diagram for Bi-doped Ni [47].

1.3. Electric Field Effects on Microstructures

In addition to the Joule heating effect, there are many evidences showing that the electric field/current also affects the microstructure evolution during field assisted sintering. For example, anomalous lattice expansion was observed in 8YSZ [48] and ceria [49] using in-situ diffractometry; reversible cubic-like phase appeared in 3YSZ under electric field and current [50]; abnormal grains were observed at the cathode side in flash sintered 3YSZ [51]; enhanced grain growth was observed at the anode side in flash sintered ZnO in air [38], but disappeared in flash sintered ZnO in reduced atmosphere [52].

Moreover, there are research on the asymmetric microstructure evolution of ceramic systems under electric field beyond the studies of sintering technologies. As one of the earliest studies on the effects of electric field on solid-state oxides processing, Mackenzie and co-workers demonstrated the improved cation mobility and their relationship with the direction of the external field in 1979 [53, 54]. Similar asymmetric grain growth in the presence of external electric field/current has also been observed by Kim and colleagues in pristine or doped Al₂O₃ systems in 2001 and 2003 [55, 56]. Recently, Hoffman and his coworkers observed the asymmetric grain growth of single crystals in SrTiO₃ [57], etc. In the fields of solid oxide fuel
cells (SOFCs), a great number of research has been conducted to understand the structural and electrical evolution of solid electrolyte during degradations, where materials typically experiences DC electric field, high temperature, and long testing/operating times [58-61].

Some mechanisms have been proposed to explain various structure changes of materials under electric fields. Some examples are shown here. (a) Jeong and co-workers proposed that electric field modified the activation energy of cations to jump across the grain boundaries, resulted the enhanced or retarded grain growth of Al$_2$O$_3$ depending on the direction of applied electric fields [62]. Similar explanations were also applied to TiO$_2$-doped and Li$_2$O-doped Al$_2$O$_3$, both of which modified the grain boundary charges compare with undoped Al$_2$O$_3$ according to the authors [63]. (b) In the presence of a liquid phase during the annealing of Nb-doped BaTiO$_3$, Jin and co-workers proposed that external electric fields modified the local bulk defect concentrations, which affected the grain boundary potentials. The liquid phase wetting was further affected by the changes in grain boundary potentials, thus resulted different grain growth behaviors at cathode and anode [64]. (c) Rheinheimer and co-workers proposed that the enhanced grain growth in SrTiO$_3$ was a result of defect redistribution across the sample through grain boundaries by comparing with grain growth data in literature [57, 65]. (d) Dong and his co-workers modelled the defect redistribution and the electrochemical reduction in YSZ under external electric field. Enhanced local cation kinetics were proposed to explain the asymmetric grain growth and pore
migrations [51, 58, 66]. The major electric field effects can vary in different materials depending on their microstructures and conducting mechanisms.

1.4. Motivation and Overview

On one hand, the research of flash sintering opens opportunities of developing new sintering technologies, especially when combined with other advanced sintering methods. On the other hand, the intriguing observations and fast development of field assisted sintering technologies urge for explorations of the electric field and current effects on bulk phases as well as the grain boundary complexions to guide the development of novel sintering technologies as a long-term scientific goal.

In Chapter 2, a solid-state activated sintering system, TiO$_2$-CuO was systematically studied to reveal the effects of grain boundary structures on low temperature densification. Specifically, the eutectic temperature and composition of the TiO$_2$-CuO system were carefully measured to be 1010 ± 10 °C and 83CuO:17TiO$_2$, respectively. Subsequently, a TiO$_2$-CuO phase diagram was computed, representing a correction and major improvement from the phase diagram available in literature. Dilatometry measurements and isothermal sintering experiments unequivocally demonstrated the activated (enhanced) sintering of TiO$_2$ with the addition of CuO, occurring at as low as >300 °C below the eutectic temperature. High resolution transmission electron microscopy (HRTEM) characterization of water-quenched specimens revealed the formation of nanometer-thick, liquid-like, intergranular films (IGFs), a type of grain boundary
(GB) complexion described in section 1.2, concurrently with accelerated densification and well below the bulk eutectic temperature. Consequently, activated sintering is explained from the enhanced mass transport in this premelting-like complexion. An interfacial thermodynamic model was used to quantitatively explain and justify the stabilization of liquid-like IGFs below the eutectic temperature and the temperature-dependent IGF thicknesses measured by HRTEM. A GB λ diagram was computed, for the first time for a ceramic system, to represent the thermodynamic tendency for general GBs in CuO-doped TiO2 to disorder.

In Chapter 3, possibilities to activate flash sintering were investigated: bulk phase transformation and/or a grain boundary (phase-like) complexion transition can cause an abrupt rise in the specimen conductivity to jump start flash sintering (prior to the occurrence of a natural thermal runaway). In undoped and Al2O3-doped ZnO, the flash sintering is activated by natural thermal runways that can be quantitively predicted from an Arrhenius extrapolation of low-temperature specimen conductivity. In contrast, a bulk eutectic reaction and the associated formation of premelting-like intergranular films in Bi2O3-doped ZnO can lead to a nonlinear rise in the specimen conductivity (above the Arrhenius extrapolation) to trigger flash sintering prior to the occurrence of the predicted natural thermal runaway. Consistent with and further supporting the proposed theory, a natural thermal runaway can still take place in Bi2O3-doped ZnO before the occurrence of the interfacial and bulk transformation if the initial electric field is increased to a sufficiently high level (800 V/cm in this case). This work uncovers the roles of the
bulk phase and interfacial (phase-like) complexion transformations in initiating flash sintering, thereby suggesting a new direction to understand and tailor the flash sintering process. The observation of ultra-fast field-induced migration of aliovalent cations during the flash sintering of Al₂O₃-doped ZnO is also reported.

In Chapter 4, water, a low temperature liquid phase in the green body, was used to trigger flash sintering of ZnO powder pellets at room temperature to achieve ~ 98% of the theoretical density in 30 s without any external furnace heating. The specimen conductivity can be increased by > 10,000 times via absorbing water vapor to enable the room-temperature flash. The initial electric field must be higher than a critical threshold to lead to densification, suggesting bifurcation in kinetic pathways. This new cost and energy saving water-assisted flash sintering (WAFS) technology can potentially be applied to consolidate other ceramic materials.

In Chapter 5, two-step flash sintering (TSFS) was proposed as a new ceramic fabrication method to achieve fast densification with suppressed grain growth. Using ZnO as an examplar, ~ 96.5% of theoretical density was achieved using TSFS with a grain size of ~ 370 nm, representing a > 3 times reduction of the grain size in comparison with conventional (one-step) flash sintering. Moreover, TSFS achieved this result in a few minutes, > 200 times faster than that needed for conventional two-step sintering to obtain comparable results, thereby representing an opportunity for significant energy and cost savings.

In Chapter 6, The effect of electric field on grain growth and grain boundary structure was studied in the presence of ionic grain boundary liquids at high
temperatures. Using Bi$_2$O$_3$-doped ZnO as a model system, this study reveals the electrochemical polarization of ionic defects driven by an external electric field and current in a series of self-comparable polycrystalline – single crystal – polycrystalline sandwich specimens. A mixed conducting model was developed to explain the asymmetric grain growth of the single crystal, abnormal grain growth near the cathode, as well as the pore formations. Additionally, the ionic blocking, electric conducting single crystal decouples the effect of electric potential and electrochemical potential on grain growth. It is assumed that electric field and current polarized ionic defects and thereafter modified local space charges. Grain boundary complexion transitions were also observed after annealing under electric field and current. Grain boundaries were metallic-like and highly ordered at electrochemically reduced locations but maintained disordered in oxidized locations. In addition, electric field induced textures of the abnormal grains were observed.
Figure 1.1 The taxonomy of sintering, showing process differentiation by various branches, starting with the application of pressure-assisted versus pressureless sintering [1].
Figure 1.2 Schematics of densification curve of a powder compact and the three stages of sintering [2].
Figure 1.3 DC electrical fields enhance the rate of sintering in yttria-stabilized zirconia (3YSZ). An instability occurs when the field is greater than a threshold value, leading to sintering in just a few seconds at unusually low furnace temperatures. This kind of sintering process is called flash sintering [21].
Figure 1.4 Schematic of the six different grain boundary complexions based on HRTEM images in Al₂O₃ systems: I, submonolayer adsorption; II, the “clean” grain boundary; III, bilayer adsorption; IV, multi-layer adsorption; V, an equilibrium thickness amorphous intergranular film; and VI, a wetting film [46].
References


[29] J.F. Li, K. Wang, B.P. Zhang, L.M. Zhang, Ferroelectric and piezoelectric properties of fine-grained Na$_{0.5}$K$_{0.5}$NbO$_3$ lead-free piezoelectric ceramics prepared by spark plasma sintering, Journal of the American Ceramic Society 89(2) (2006) 706-709.


Chapter 2. Liquid-like grain boundary complexion and sub-eutectic activated sintering in CuO-doped TiO$_2$

2.1. Introduction

Titania (TiO$_2$) has excellent electronic and optical properties that enable its applications in photovoltaic, sensing, and a variety of other types of devices (where some levels of low-temperature sintering are often involved) [1-3]. Furthermore, TiO$_2$ has excellent dielectric properties for possible applications in electronics; however, the high sintering temperatures of pure TiO$_2$, which are generally in the range of 1200-1400 °C [4], make it incompatible with the low-temperature co-fired technology [5] that requires the sintering temperature to be appreciably lower than the melting temperature of the metal conductors, such as Cu ($T_m = 1083$ °C) and Ag ($T_m = 961$ °C) [6]. Thus, researchers have made great efforts to lower the sintering temperature of TiO$_2$, e.g., via using monodisperse TiO$_2$ powder [7] or making sol-gel films [8]. A more common and practical method is to add a small amount of sintering aids to lower the sintering temperature [9]. While CuO is perhaps one of the most effective sintering aid for promoting low-temperature densification of TiO$_2$ [10, 11], its exact underlying mechanisms remain elusive, which motivated this study.

It is well known that CuO doping can reduce the sintering temperatures of TiO$_2$ to ~850-950 °C, which was generally attributed to a liquid-phase sintering effect in prior studies [10, 12, 13]. However, Lu et al reported a computed eutectic temperature of 919 °C for the TiO$_2$-CuO system [14]. Recently, de la Rubia et al
suggested that the eutectic temperature is ~1000 °C via differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis, in conjunction with hot-stage microscopy [15]. These results casted doubt on the previously hypothesized liquid-phase sintering mechanism for CuO-doped TiO$_2$, since the significant densification appeared to occur well below the eutectic temperature, though what is the exact/real eutectic temperature was still controversial prior to this study.

In this study, we conducted careful experiments to unequivocally showed that the low-temperature densification of CuO-doped TiO$_2$ is a case of sub-eutectic activated sintering, rather than the commonly believed liquid-phase sintering. First, we measured the eutectic temperature and composition of the CuO-TiO$_2$ system via calibrating the furnace and characterizing well-quenched specimens. Specifically, we showed that the eutectic reaction takes place between 1000 °C and 1020 °C in air and determined the eutectic composition to be ~ 83CuO:17TiO$_2$. Subsequently, we showed that enhanced densification can start below 700-800°C, well below the bulk eutectic temperature. Furthermore, we observed the stabilization of nanoscale liquid-like intergranular films (IGFs) well below the bulk eutectic temperature by high resolution transmission electron microscopy (HRTEM) and attributed the sub-eutectic activated sintering in CuO-TiO$_2$ to the enhanced mass transport in this nanoscale liquid-like complexion (a.k.a. 2-D interfacial phase) that is stabilized below the eutectic temperature at grain boundaries (GBs), analogous those reported previously for Bi$_2$O$_3$-doped ZnO [16] and Ni-doped W and Mo [17-19].
Furthermore, we have computed a binary phase diagram for the TiO$_2$-CuO system, which represents a major improvement from (and a correction of) the phase diagram available in literature. Subsequently, a GB $\lambda$ diagram was also computed to represent the thermodynamic tendency for general GBs in CuO-doped TiO$_2$ to disorder, for the first time for any ceramic system. We adopted an interfacial thermodynamic model to quantitively explain the stabilization of liquid-like IGFs below the bulk eutectic temperature, and to further justify the temperature-dependence of the IGF thicknesses measured by HRTEM.

2.2. Experiments

To determine the eutectic temperature and composition, rutile-phase TiO$_2$ (99.9+%, purchased from US research Nanomaterials, Inc.) was mixed with CuO powder (99.999%, purchase from Sigma-Aldrich) in a mortar. The mixed powder was uniaxially compressed to pellets at 450 MPa. The surfaces of the pellets were slightly grinded to remove any contamination from the dies. The pellets were then placed in small sapphire crucibles (> 99.9% purity, purchased from AdValue Technology), annealed isothermally at desired temperatures (with a heating ramping rate of 5 °C/min before reaching the desired isothermal annealing temperature), and water quenched. Quenched samples were then sectioned, grinded, and polished.

Specimens for sintering experiments were made by either a dry mixing or a wet chemistry method. In the dry mixing method, 4 mol. % CuO powder were mixed with rutile-phase TiO$_2$. In the wet chemistry method, an appropriate amount of
Cu(NO$_3$)$_2$$\cdot$2.5H$_2$O (99.99%, purchased from Sigma-Aldrich) was dissolved in DI water to make an aqueous Cu$^{2+}$ solution. Subsequently, rutile TiO$_2$ nanopowder was impregnated in the Cu$^{2+}$ solution. The mixtures were then dried in an oven at 85 °C for 12 hours. The dried powders were ground in a mortar for 10 minutes, followed by annealing in air at 500 °C for 1 hour (to decompose Cu(NO$_3$)$_2$ into CuO, which occurs at ~ 180°C). After annealing, the powders were ground for another 10 minutes. The final powders (made by the either method) were uniaxially pressed at ~200 MPa to make green pellets of 6.35 mm in diameter. The surfaces were slightly grinded to remove contamination from the dies. Green densities of the pellets were measured to be ~40%. Linear shrinkages of compacted pellets were measured by a dilatometer (DIL, NETZSCH Group) up to 1000 °C at a constant heating ramping rate of 5 °C/min in air.

In the second batch of sintering experiments, specimens were isothermally sintered in a muffle furnace (Thermolyne Furnace F6000, Thermo Scientific), for which the temperature profile was carefully calibrated using a second thermocouple before the experiments to ensure the accuracy of temperature controls and measurements (for accurately determining the eutectic temperature). This batch of sintered specimens were quenched in water to preserve the high-temperature GB structures for subsequent HRTEM characterization. The densities of specimens were measured using both the weight/dimension and the Archimedes method.

Microstructures and compositions were characterized by a field-emission, ultra-high-resolution scanning electron microscope (UHR SEM, FEI XL30)
operating at 10 kV, equipped with an Oxford energy-dispersive X-ray spectroscopy (EDS) analyzer. X-ray diffraction (XRD) experiments were conducted using a Rigaku Ultima IV diffractometer (Cu Kα radiation).

Transmission electron microscopy (TEM) samples were prepared using a focused ion beam (FIB, FEI Scios DualBeam). Atomic-level GB structures were characterized by HRTEM using a FEI Titan microscope operating at 300 kV.

2.3. Results

2.3.1. Determination of Eutectic Temperature and Composition

SEM images of CuO + 20 mol. % TiO₂ specimen (that was a near-eutectic composition selected for the initial experiment vs. the actual eutectic composition was subsequently measured to be ~ 83CuO:17TiO₂) after annealing at 1020 °C for 0.5 hour are shown in Fig. 2.1; here, a eutectic structure, in which the light-contrast rods were homogeneously embedded in a dark-contrast matrix, can be clearly seen. In contrast, Fig. 2.2 shows the microstructure and elemental mappings of a CuO + 20 mol. % TiO₂ (rutile) specimen after annealed at a slightly lower temperature of 1000 °C for 8 hours, where a similar eutectic structure clearly did not form. The corresponding EDS mappings revealed that the light-contrast phase is copper oxide, while the dark-contrast phase is TiO₂, with no apparent reaction and virtually no mutual (solid) solubilities. In addition to the SEM images, visual inspection of the specimens also clearly showed the specimen melt at 1020 °C but not at 1000 °C. These results (Fig. 2.1 vs. Fig. 2.2) undoubtedly suggested that the eutectic temperature of TiO₂-CuO is 1000 ± 10 °C.
The XRD patterns of the CuO + 20 mol. % TiO$_2$ specimens quenched from 1000 °C and 1020 °C, respectively, are shown in Fig. 2.3. Only the two equilibrium CuO and rutile TiO$_2$ phases were detected from specimens that were annealed at 1000 °C for 8 hours and water quenched. The CuO + 20 mol. % TiO$_2$ specimen annealed at 1020 °C melted (into a nearly-eutectic liquid so that we did not anneal it longer to prevent the spreading of the liquid and minimize its reaction with the Al$_2$O$_3$ crucible), the non-equilibrium Cu$_2$O and Cu$_3$TiO$_4$ phases, as well as the sapphire Al$_2$O$_3$ impurity phase, were found in the water-quenched specimen (where the crucible was quenched together with the eutectic liquid into the water).

Further quantitative EDS analysis from multiple measurements of the eutectic structures seen in SEM showed the average measured composition corresponded to a cation ratio of Cu: Ti = 4.95 ± 0.11, i.e., the eutectic composition is ~17 mol. % TiO$_2$ + ~83 mol. % CuO.

2.3.2. Sub-Eutectic Activated Sintering

Fig. 2.4 shows the linear shrinkage vs. temperature curves of undoped and 4 mol. % CuO-doped TiO$_2$ (rutile) measured by dilatometry at a constant heating rate of 5 °C per minute. The doped powders were prepared by either a dry mixing or a wet chemistry method described in the “Experiments” section. At 1000 °C, undoped TiO$_2$ specimen had ~15% linear shrinkage. In contrast, CuO-doped TiO$_2$ specimens had ~32% and ~28% linear shrinkage, respectively, for specimens prepared by the wet chemistry and dry mixing methods, respectively. Both doped TiO$_2$ specimens had ~99% of the theoretical density after the sintering experiments.
(including possible extra densification during the cooling in the furnace after the dilatometry experiments). These results clearly demonstrated that the addition of CuO effectively promoted the densification of rutile TiO$_2$ below the bulk eutectic temperature, where the significant enhanced densifications occurred at 200-300 °C below the bulk eutectic temperature. The specimen prepared by the wet chemistry method, where the doping was presumably more uniform, exhibited significant enhanced densifications at even lower temperatures (Fig. 2.4).

To further investigate the sintering mechanism, 4 mol. % CuO-doped TiO$_2$ specimens were isothermally annealed (sintered) at 800 °C, 850 °C, and 900 °C, respectively, for 8 hours and subsequently water-quenched. The microstructures of the fractured surfaces of the sintered specimens are shown in Fig. 2.5 and the measured grain sizes are shown in Fig. 2.6. Specifically, Figs. 2.5 (a-f) show the SEM images of sintered CuO-doped TiO$_2$ specimens that were prepared by the wet chemistry method. Low-magnification images show uniform structures and the average grain size increased substantially from 800 °C to 900 °C. Interestingly, a secondary phase (presumably CuO) appeared to wet some triple-grain junctions (with low dihedral angles that, in addition to the nanoscale IGFs at GBs, can also promote sintering and affect microstructural development, as reviewed and discussed by Castro and Gouvêa [20]) of the specimen sintered and quenched from 900 °C (Fig. 2.5(f)), but not in those at lower temperatures. Figs. 2.5 (g-i) display high-magnification SEM images of the CuO-doped TiO$_2$ prepared by the dry mixing method, sintered at 800 °C, 850 °C, and 900 °C, respectively, for 8 hours, and subsequently water quenched. Substantial neck formation and growth
were evident in all sub-eutectic sintered specimens (Figs. 2.5 (d-i)). Finally, we note that the grain growth followed similar trends for the specimens doped by the wet chemistry and dry mixing routes, both of which contained 4 mol. % CuO and were isothermally annealed at 800-900°C for 8 hours (Fig. 2.6).

2.3.3. Stabilization of Liquid-Like GB Complexion Below the Bulk Eutectic Temperature

Fig. 2.7 and Fig. 2.8 display the HRTEM images of representative GBs in 4 mol. % CuO-doped TiO₂ specimens that were equilibrated (by isothermal annealing for 8 hours) at 800 °C, 850 °C, and 900 °C, respectively, in a calibrated muffle furnace and subsequently water-quenched. In all cases, the GB planes were carefully oriented to be parallel with the incident electron beam to ensure edge-on conditions. Nanometer-thick, structurally disordered (liquid-like) IGFs were observed in all specimens quenched from 800 °C, 850 °C, and 900 °C after annealing for 8 hours, at all GBs that were examined. The measured individual and average thicknesses of the IGFs were listed in Table I. Specifically, the average measured thickness of the liquid-like IGFs formed at 800°C (and ± one standard deviation) was 0.70 ± 0.07 nm, which increased to 0.86 ± 0.06 nm for the IGFs formed at 850 °C and 0.98 ± 0.09 nm for the IGFs formed at 900°C. These nanoscale IGFs represent a liquid-like interfacial complexion that is thermodynamically stabilized at the general GBs below the bulk eutectic temperature; this stabilization will be quantitively justified by an interfacial
thermodynamic model in section 2.4.2 and its roles in activated sintering will be discussed in section 2.4.3.

2.4. Modeling and Discussion

2.4.1. The TiO$_2$-CuO Binary Phase Diagram and Bulk Thermodynamic Function

In 2001, a binary TiO$_2$-CuO phase diagram had been calculated via assuming that the liquid phase is an ideal solution, which produced an eutectic temperature of 919 °C [14], being substantially lower than the ~1000 °C eutectic temperature that was later suggested via DSC and TG analysis in 2012 [15] and largely confirmed more directly and accurately by the current study. That diagram reported in 2001 [14] represents the only TiO$_2$-CuO phase diagram available in literature and has been widely cited. The more accurate measurements of the eutectic temperature and composition obtained in this study, which were consistent with the independent DSC/TG study in 2012 [15], demand a further assessment (and correction) of that TiO$_2$-CuO phase diagram, which will also provide the thermodynamic function of the liquid phase that will be useful for the interfacial thermodynamic model presented and discussed in the following section.

To compute the binary phase diagram, we assume that CuO and TiO$_2$ are mutually immiscible in the solid states (since no detectable solid solubility was reported in literature, which was also verified by EDX analysis in the current study) and use the solid phases as the reference state. The free energy of the TiO$_2$-CuO liquid phase (referenced to the two bulk solid phases) is expressed as a Redlich-
Kister polynomial \((n = 0 \text{ and } 1 \text{ for a subregular solution})\):

\[
\Delta \bar{G}_{Liq} = X_{\text{CuO}}^\text{Liq} \Delta G_{\text{CuO}}^\text{Liq} + X_{\text{TiO}_2}^\text{Liq} \Delta G_{\text{TiO}_2}^\text{Liq} + RT (X_{\text{CuO}}^\text{Liq} \ln X_{\text{CuO}}^\text{Liq} + X_{\text{TiO}_2}^\text{Liq} \ln X_{\text{TiO}_2}^\text{Liq}) + \sum_{n=0,1} L_n (X_{\text{CuO}}^\text{Liq} - X_{\text{TiO}_2}^\text{Liq})^n X_{\text{CuO}}^\text{Liq} X_{\text{TiO}_2}^\text{Liq} \tag{1}
\]

where \(X_i^\text{Liq}\) is the bulk molar fraction of the \(i\) component \((i = \text{CuO}, \text{TiO}_2)\) and \(L_n\) is the interaction parameters. \(\Delta G_i^\text{Liq}\), the bulk molar fraction and free energy of forming the liquid phase from the solid phase of the \(i\) component, can be derived as

\[
\Delta G_i^\text{Liq} = (T_i^m - T) \Delta S_i^\text{melt} + \int_{T_i^m}^T \Delta C_P(i) \, dT - T \int_{T_i^m}^T \frac{\Delta C_P(i)}{T} \, dT \tag{2}
\]

where \(T_i^m\) is the melting temperature, \(\Delta S_i^\text{melt}\) is the molar entropy of fusion (melting), and \(\Delta C_P = C_P^\text{Liq} - C_P^\text{Sol}\) is the molar heat capacity difference between solid and liquid phases. For the TiO\(_2\)-CuO system, these thermodynamic parameters of individual components (TiO\(_2\) and CuO) were taken from Ref. [14], which were originally obtained from a CRC handbook [21]. Subsequently, we obtained the parameters \(L_0 = 8.4 \text{ kJ/mol}\) and \(L_1 = -13.0 \text{ kJ/mol}\) by solving two equations: \(\Delta G^\text{Liq} = 0\) and \(\frac{\partial \Delta G^\text{Liq}}{\partial X_{\text{CuO}}} = 0\) to match the experimentally-measured eutectic temperature \((T^\text{Eutectic} = 1010 \degree C)\) and composition \((X_{\text{CuO}}^\text{Eutectic} = 0.832)\). Here, the liquid phase is a subregular solution \((L_n = 0 \text{ for } n \geq 2 \text{ in the Redlich-Kister polynomial})\). From the derived thermodynamic function (Eq. (1)), we calculated the binary (bulk) phase diagram for the TiO\(_2\)-CuO system, which is shown in Fig. 2.9.

We should further note that CuO reduces to Cu\(_2\)O at 1029 \degree C in one-atmosphere air [22] so that the above computation only represents the cases that
CuO would remain stable at high temperatures (achievable at higher P\textsubscript{O\textsubscript{2}}). Unfortunately, there is no data available for us to calculate the exact TiO\textsubscript{2}-CuO-Cu\textsubscript{2}O pseudo-binary phase diagram in one-atmosphere air, but we sketch the possible transitions as the dotted lines in Fig. 2.9 based the Cu\textsubscript{2}O-Cu\textsubscript{2}O reduction temperature and the melting temperature of Cu\textsubscript{2}O, which are the only known points in the TiO\textsubscript{2}-CuO-Cu\textsubscript{2}O phase diagram. Nonetheless, this Cu\textsubscript{2}O-to-Cu\textsubscript{2}O reduction occurring at 1029 °C should not affect the eutectic reaction at 1010 °C and the stabilization and temperature-dependence of sub-eutectic liquid-like GB complexion (to be discussed in the next section).

2.4.2. An Interfacial Thermodynamic Model and the Computed GB λ Diagram

The thermodynamic stability of nanoscale quasi-liquid IGFs (specifically) and GB complexions (in general) have been reviewed [23, 24]. Furthermore, GB λ diagrams have been computed and proven useful for predicting trends in activated sintering in (at least) several refractory alloys [25-31]. Here, we made a first successful attempt to extend the prior successes from metallic alloys [25-31] to a ceramic system.

At the length scale of 0.5-5 nm, a phenomenological interfacial thermodynamic model can be formulated for premelting-like IGFs in multicomponent ceramics by combining a sharp-interface model of premelting in unary systems [32] and the Clarke model for equilibrium-thickness IGFs [33, 34]. Here, an IGF in the TiO\textsubscript{2}-CuO is treated as a confined liquid-like interfacial film (a.k.a. a specific 2-D interfacial phase) with modified thermodynamic properties.
The excess grand potential as a function of the film thickness \( (h) \) can be written as:

\[
\sigma^+ (h) = 2 \gamma_{cl} + \Delta G_{amorph}^{(vol)} \cdot h + \sigma_{\text{short-range}} (h) + \sigma_{\text{vdW}} (h) + \sigma_{\text{elec.}} (h) + ... 
\]  

(3)

where \( \gamma_{cl} \) is the crystal-liquid interfacial energy (that is well defined as \( h \to +\infty \)) and \( \Delta G_{amorph}^{(vol)} \) is the volumetric free energy for forming an undercooling liquid from the equilibrium solid phases. The last three terms are short-range, van der Waals (vdW) dispersion, and electrostatic interfacial interactions, which should all vanish as \( h \to +\infty \) by definition. A premelting-like GB complexion can be stabilized below the bulk eutectic temperature if the energy penalty for forming an undercooled quasi-liquid film (interfacial phase) of thickness \( h \) is overcompensated by the reduction in the total (effective) interfacial energy:

\[
-\Delta \gamma \cdot f (h) > \Delta G_{amorph}^{(vol)} h
\]  

(4)

where

\[
\Delta \gamma \equiv 2 \gamma_{cl} - \sigma^+ (0)
\]  

(5)

and \( f(h) \) is a dimensionless interfacial coefficient (that varies from \( f(0) = 0 \) to \( f(\infty) = 1 \) by definition, but not necessarily monotonically), defined as:

\[
f (h) = 1 + \frac{\left[ \sigma_{\text{short-range}} (h) + \sigma_{\text{vdW}} (h) + \sigma_{\text{elec.}} (h) + ... \right]}{\Delta \gamma}
\]  

(6)

The equilibrium thickness, \( h_{EQ} \), corresponds to the minimum of Eq. (3), which implies:
\begin{align}
\frac{d\sigma^*(h)}{dh}\bigg|_{h=h_0} &= 0 \\
\frac{d^2\sigma^*(h)}{dh^2}\bigg|_{h=h_0} &> 0
\end{align} \tag{7}

Based on the thermodynamic criterion for stabilizing a sub-eutectic, liquid-like, GB complexion (Eq. (4)), we again adopt (and, in the next step, quantify) a thermodynamic parameter, $\lambda$, to represent the thermodynamic tendency for general GBs to disorder, following earlier studies of metallic alloys [25-31], which is expressed as:

$$
\lambda \equiv \frac{-\Delta \gamma}{\Delta G_{amorph}^{(vol)}}.
$$ \tag{8}

To quantify values of $\lambda$, $\Delta G_{amorph}^{vol}$, the volumetric free energy penalty of forming an undercooling liquid below eutectic temperature, is expressed as:

$$
\Delta G_{amorph}^{vol} \approx \Delta G_{amorph}^{mol} / \left[ (1 - X_{CuO}^{IGF}) V_{m(TiO_2)} + X_{CuO}^{IGF} V_{m(CuO)} \right]
$$ \tag{9}

where $X_{CuO}^{IGF}$ is the average IGF composition and $\Delta G_{amorph}^{mol} = \Delta G_{Liq}^{(Vol)} (X_{CuO}^{IGF})$, which can be calculated using Eq. (1) and the thermodynamic function and data obtained in the prior section for the TiO$_2$-CuO liquid phase. Here, the most common and convenient way is to select the $X_{CuO}^{IGF}$ that maximizes $\lambda$, as discussed in prior studies of metallic alloys [25-31].

To quantify $\Delta \gamma$, $\sigma^*(0) = \gamma_{GB}^{(0)}$, the average general GB energy of pure TiO$_2$ (with no adsorption), was measured in a prior experiment to be 0.87 J/m$^2$ [35]. Analogous to both a “macroscopic-atoms” model [36, 37] and a lattice model [38] (with modifications), we estimate the average interfacial energy for the crystal-
liquid interface between a pure TiO\textsubscript{2} solid and a TiO\textsubscript{2}-CuO binary liquid using the following expression:

\[
\gamma_{cl} = \frac{\Delta H_{TiO_2 melt}^{melt}}{\kappa m_1^{-1} V_m^{2/3}} + \frac{\Omega_{CuO-TiO_2}^{Liq}}{\kappa m_1^{-1} V_m^{2/3}} (X_{IGF})^2
\]  

(10)

where the two terms represent the enthalpic (fusion) and chemical (interaction) contributions, respectively, to the crystal-liquid interfacial energy. Here, \(\Delta H_{TiO_2}^{melt}\) is the molar enthalpy (latent heat) of melting, \(\Omega_{CuO-TiO_2}^{Liq} = L_0\) is the regular-solution parameter for the liquid phase, \(V_m\) is the molar volume of TiO\textsubscript{2}, \(\kappa\) is a geometric factor \((\kappa \equiv A_m/V_m^{2/3}\), where \(A_m\) is the area of one mole of molecules spread as a monolayer [38]), and \(m_1\) is the fraction of bonds across the crystal-liquid interface. The value of \(\kappa m_1^{-1}\) in Eq. (10) depends on the lattice structure and orientation of the interface and we use \(\kappa m_1^{-1} = C_0 \approx 4.5 \times 10^8\) to represent the average of different orientations [39] to represent IGFs formed at the average general GBs.

Subsequently, we computed \(\lambda\) values and plotted them in the bulk TiO\textsubscript{2}-CuO phase diagram to construct a GB \(\lambda\) diagram for CuO-doped TiO\textsubscript{2}, as shown in Fig. 2.10, similar to the GB \(\lambda\) diagrams constructed in prior studies for several metallic alloys [25-31]. In the sub-eutectic two-phase region, the computed \(\lambda\) increases with increasing temperature, suggesting increasing thermodynamic tendency for average general GBs to disorder that should result in increasing densification rates, consistent with both the intuition and experiments.

A more rigorous and accurate assessment of IGF thickness \((h_{EQ})\) vs. temperature requires the quantitative information about the short-range, vDW
dispersion, electrostatic, and any other interfacial interactions in Eq. (3), which is unfortunately not available for the current case of TiO\textsubscript{2}-CuO as well as virtually all other ceramic systems. However, we may adopt a simplified model to justify the observed temperature-dependent IGF thicknesses in the intermediate temperature region (to be defined and discussed subsequently), as follows. First, prior analyses showed that the vdW dispersion interaction, which is always attractive for the IGFs, will be overwhelmed by the $\Delta G_{\text{amorph}}^{\text{vol}}$ term that represents a significantly higher attractive pressure than the vdW dispersion pressure at $\Delta T \equiv T - T_{\text{Eutectic}} \geq 100$ °C [24, 40]; thus, the vdW dispersion interaction can be neglected well below the eutectic temperature. Moreover, either the short-range or electrostatic interaction can be approximated with an exponentially-decaying form (and only one of them likely dominates in a specific ceramic system). Thus, in a simplified model, we can adopt an exponentially-decaying interfacial potential, $f(h) = 1 - \exp(-h/\xi)$, so that Eq. (3) can be rewritten and simplified to:

$$\Delta \sigma(h) \equiv \sigma^*(h) - \sigma^*(0) = \Delta \gamma \cdot f(h) + \Delta G_{\text{amorph}}^{\text{vol}} \cdot h = \Delta \gamma \cdot [1 - \exp(-h/\xi)] + \Delta G_{\text{amorph}}^{\text{vol}} \cdot h$$

(11a)

where $\xi$ is a coherent length [27]. Eq. (11a) can also be rewritten into a dimensionless form:

$$\frac{\Delta \sigma(h)}{-\Delta \gamma} = -\frac{h}{\lambda} + \exp(-h/\xi) - 1.$$  

(11b)

Minimizing Eq. (11b) with respective to $h$ produces the equilibrium IGF thickness:

$$h_{\text{EQ}} = \xi \ln(\lambda / \xi).$$

(12)

We should further make two notes. First, Eq. (12) is obtained via assuming a fixed
average film composition that maximizes $\lambda$ in Eq. (8). Alternatively, we may minimize Eq. (11a) with respective to both $h$ and $X^{IGF}_{CuO}$. Our numerical analysis showed negligible differences between the calculated “$h_{EQ.}$ vs. $T$” curves using the two approaches, so we choose the simpler approach [by using Eq. (12)]. Second, this simplified model [Eq. (11) and Eq. (12)] can only be used for the intermediate temperature region. On one hand, at higher temperatures ($T \sim T^{Eutectic}$), the divergence of $h_{EQ}$ predicted from this model should be limited by the attractive vdW dispersion interaction. On the other hand, at lower temperatures, this continuum model is no longer valid when $h_{EQ} < \sim 0.5$ nm because it does not consider the discrete nature of ion sizes and bond lengths. Nonetheless, this simplified model can be used to justify the measured temperature-dependent IGF thicknesses in the intermediate temperature region of 800-900 ºC for the current case, which is the range of interest for activated sintering.

Specifically, Fig. 2.11 plots the means and standard deviations of IGF thicknesses measured by HRTEM from specimens equilibrated at 800 °C, 850 °C, and 900 °C, along with the computed “$h_{EQ.}$ vs. $T$” curves for three different selections of the coherent length, $\xi$. The computed “$h_{EQ.}$ vs. $T$” curve with $\xi = 0.38$ nm produced the best fit to the experimental data, while the sensitivity of the different selections of $\xi$ was also tested. Although we do not have the knowledge of the exact value of the coherent length, the value that produced the best fit (~0.38 nm) is about twice of the O-Cu bond length or the size of a Cu-O$_n$ polyhedral unit, which appears to be reasonable. Thus, this rather simplified model can justify the stabilization of liquid-like GB complexions below the eutectic temperature as well
as the temperature-dependent interfacial widths (the measured “\( h_{EQ. \, vs. \, T} \)"
observed by HRTEM.

Lastly, we should also recognize the possibility that some of these IGFs exhibit discrete (instead of continuous) thickness (to form Dillon-Harmer GB complexions [23, 41]) for certain specific GBs, e.g., some special GBs with low-index grain surfaces, as shown in a prior study for a (001) // (100) GB in a (CuO + SiO$_2$) doped TiO$_2$ bicrystal specimen [41]. The origin of the discrete thicknesses and the formation of Dillon-Harmer GB complexions can be explained in the same interfacial thermodynamic framework discussed above via incorporating (adding) an oscillatory structural interaction (as a result of a fixed, finite, atomic size using a hard-sphere approximation) in Eq. (3) or the interfacial coefficient \( f(h) \) [31, 41-43].

2.4.3. Further Discussion of Activated Sintering Mechanisms and Beyond

The current study measured the eutectic temperature of the TiO$_2$-CuO system to be 1010 ± 10 °C in air, which was higher than that reported in 2001 [14], but similar to that suggested by a DSC and TG study in 2012 [15]. This warrantees our re-assessment and a correction of the TiO$_2$-CuO phase diagram reported in Ref. [14] in 2001 based our measured bulk eutectic temperature and composition to compute an improved (corrected) TiO$_2$-CuO phase diagram in Fig. 2.8; this assessment also provided the thermodynamic function for justifying the stabilization of a sub-eutectic liquid-like GB complexion, which leads to enhanced interfacial mass transport and subsequently activated sintering.
The combination of our experimental results undoubtedly demonstrated that the enhanced sintering of CuO-doped TiO$_2$ occurred in the sub-eutectic region, starting at >300 °C below the bulk eutectic temperature. Thus, this study clearly disapproved the theory that the enhanced sintering in CuO-doped TiO$_2$ at ~850-950 °C is due to liquid-phase sintering, that was widely assumed in prior studies [10, 12, 13]. Instead, this study unequivocally demonstrated, via a combination of HRTEM and thermodynamic modeling, that the addition of CuO promoted the formation of a liquid-like GB complexion in TiO$_2$ well below the bulk eutectic temperature, which provides a fast mass transport pathway to enhance sub-eutectic densification. Similar solid-state activated sintering behaviors and mechanisms have been observed/identified for several ceramic (Bi$_2$O$_3$-doped ZnO [16]) and metallic (Ni-doped W and Mo [17-19]) systems.

We should also recognize and further discuss alternative mechanisms that may enhance sintering and grain growth/coarsening below the eutectic temperatures. Specifically, a most recent study by Wu, Dholabhai, Uberuaga, and Castro showed that the reduction of Mn cations from 3+ to 2+ in Mn-doped CeO$_2$ can result in significant coarsening [44]. In the current case, CuO can also be reduced to Cu$_2$O at 1029 °C [22] (with some partial reduction starts at ~1000 °C as shown in an earlier study [15]), whereas the enhanced densification can occur at much lower temperatures (as low as 700-900°C; Figs. 4 and 5) without substantial coarsening (Fig. 2.6).

The thermodynamic stabilization of nanometer-thick quasi-liquid IGFs below eutectic temperature in CuO-doped TiO$_2$ has been well justified by
estimating relative interfacial energies via both experimental data and a statistical model as well as quantifying free-energy penalty for forming undercooled liquids using CALPHAD data. Subsequently, an interfacial thermodynamic model is used to justify the temperature-dependent interfacial width.

Following the earlier successes of constructing GB $\lambda$ diagrams to predict useful trends in high-temperature GB disordering and to subsequently forecast activated sintering behaviors (and potentially other materials properties such as creep resistance) in several W- and Mo based metallic alloys [25-31] (as well as more rigorous computed GB complexion diagrams with well-defined transition lines, such as that for Bi-doped Ni in a most recent report [45]), this study made a first successful attempt to extend the model and method to compute the first GB $\lambda$ diagram for a ceramic system (CuO-doped TiO$_2$). In future studies, similar or more rigorous "GB diagrams" should be developed for other ceramic systems, which can have broad applications. This is in part because this class of nanoscale IGFs are more ubiquitous and technologically-important for ceramics than metals in general. Furthermore, it is worth noting that nanometer-thick IGFs investigated in this study only represent one of several types of GB complexions discovered recently [23, 46-48]; such GB complexions (a.k.a. interfacial phases that are thermodynamically 2-D) exist ubiquitously in both metallic and ceramic materials, where they can often critically influence or even control a board range of transport, mechanical, and physical properties [23, 25, 27, 43, 46, 49-66] beyond sintering.
2.5. Conclusions

The eutectic temperature of the CuO-TiO$_2$ system has been determined to be 1010 ± 10 °C and the eutectic composition was measured to be ~17TiO$_2$:83CuO (or ~17 mol. % TiO$_2$ + ~83 mol. % CuO). Based on the measured eutectic temperature and composition, we computed the binary TiO$_2$-CuO phase diagram (representing a significant improvement from, and essentially a correction of, the phase diagram available in literature) and formulated the relevant thermodynamic function. A combination of dilatometry measurements and isothermal sintering experiments unequivocally demonstrated the occurrence of activated sintering in CuO-doped TiO$_2$ at as low as >300 °C below the bulk eutectic temperature. HRTEM characterization of well-quenched specimens further revealed the formation of nanometer-thick, liquid-like IGFs. The enhanced mass transport in this premelting-like complexion explained the activated (enhanced) sintering observed in this system. We further calculated a GB $\lambda$ diagram, for the first time for any ceramic system, to represent the thermodynamic tendency for general GBs in CuO-doped TiO$_2$ to disorder and used an interfacial thermodynamic model to quantitively explain and justify the stabilization of nanometer-thick, liquid-like IGFs below the bulk eutectic temperature as well as the temperature-dependent IGF thicknesses measured by HRTEM. In future studies, similar or different (more rigorous and sophisticated) types of GB diagrams should be computed for other ceramic materials, which can potentially have broad scientific and technological impacts.

The dissertation author was the primary investigator and author of this paper.
Figure 2.1 SEM images of an 80 mol. % CuO + 20 mol. % TiO$_2$ specimen isothermally annealed at 1020°C for 0.5 hour and water-quenched, showing the formation of a eutectic structure. A quantitative composition analysis of the region highlighted in (b) was performed to measure the eutectic composition (to be ~ 83CuO:17TiO$_2$).
Figure 2.2 (a-c) SEM images and (d-f) EDS elemental maps of titanium, copper, and oxygen of an 80 mol. % CuO + 20 mol. % TiO$_2$ specimen that was isothermally annealed at 1000°C for 8 hours and water-quenched, where a eutectic structure is lacking. The specimens were made by a dry mixture powders; large particles of CuO remained and the originally-smaller TiO$_2$ particles sintered, whereas no indication of any reaction was evident.
Figure 2.3 X-ray diffraction patterns of 80 mol. % CuO + 20 mol. % TiO₂ specimens isothermally annealed and quenched from (a) 1000°C and (b) 1020°C, respectively.
Figure 2.4 Linear shrinkage vs. temperature curves of pure TiO$_2$ and 4 mol. % CuO-doped TiO$_2$ prepared by two different methods (via wet chemistry and dry mixing routes). All powders were uniaxially pressed at 200 MPa and measured using a dilatometer with a constant ramping rate of 5°C per minute.
Figure 2.5 (a) SEM images of 4 mol. % CuO-doped TiO$_2$ prepared by two different methods via wet chemistry and dry mixing routes, respectively, isothermally annealed at 800°C, 850°C, and 900°C, respectively, for 8 hours, and water-quenched.
Figure 2.6 Measured grain sizes of 4 mol. % CuO-doped TiO$_2$ specimens, made by the wet chemistry (red) and dry mixing (blue) routes, isothermally annealed at 800°C, 850°C, and 900°C, respectively, for 8 hours, and water-quenched. The grain growth behaviors are similar for specimens doped by two different methods.
Figure 2.7 HRTEM images of 4 mol. % CuO-doped TiO$_2$ specimens isothermally annealed at 800°C, 850°C, and 900°C, respectively, for 8 hours and water-quenched.
Figure 2.8 HRTEM images of 4 mol. % CuO-doped TiO$_2$ specimens equilibrated and quenched at 800°C, 850°C, and 900°C, respectively, at a higher magnification.
Figure 2.9 Computed TiO$_2$–CuO phase diagram of (a) the full composition range and (b) an enlarged section of the CuO-rich region. It should be noted that CuO is reduced to Cu$_2$O at 1029°C in air [22] and CuO would remain stable at higher temperatures only at higher P$_{O_2}$. Due to the absence of the Cu$_2$O-TiO$_2$ thermodynamic data, we can only calculate the TiO$_2$–CuO phase diagram. The dotted lines represent the possible transition lines in air with the CuO–Cu$_2$O transformation, while dashed lines represent the calculated phase transformation lines for the TiO$_2$–CuO system assuming no reduction at high temperatures.
Figure 2.10 A computed GB $\lambda$ diagram, where the dash lines represent $\lambda = 2$ nm, 4 nm, and 8 nm, respectively, and the color represent the relative thermodynamic tendency for the average general GBs in CuO-doped TiO$_2$ to disorder.
Figure 2.11 The average IGF thicknesses vs. equilibration temperatures measured by HRTEM. The three solid lines represent the computed equilibrium thickness ($h_{EQ}$) as functions of temperature with three different coherence lengths ($\xi = 0.3$ nm, 0.38 nm, and 0.5 nm, respectively, where $\xi = 0.38$ nm represents the best fit with the experimental data).
Table 2.1 Measured IGF thicknesses of 4 mol. % CuO-doped TiO₂ specimens equilibrated (isothermally annealed for 8 h) at 800°C, 850°C, and 900°C for 8 hours and water-quenched. Three general GBs were measured for each of three specimens. For each of the nine GBs, the IGF thicknesses were measured at 10 different locations; the mean and standard deviations (that represent the uniformities of IGF thicknesses along the individual GBs) were reported.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>800°C</th>
<th>850°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GB #1</td>
<td>0.68 ± 0.05</td>
<td>0.89 ± 0.02</td>
<td>1.01 ± 0.03</td>
</tr>
<tr>
<td>GB #2</td>
<td>0.69 ± 0.05</td>
<td>0.82 ± 0.02</td>
<td>0.92 ± 0.03</td>
</tr>
<tr>
<td>GB #3</td>
<td>0.75 ± 0.10</td>
<td>0.86 ± 0.02</td>
<td>1.03 ± 0.03</td>
</tr>
<tr>
<td>Mean ± 1</td>
<td>0.70 ± 0.07</td>
<td>0.86 ± 0.06</td>
<td>0.98 ± 0.09</td>
</tr>
</tbody>
</table>
References


Chapter 3. Flash Sintering Activated by Bulk Phase and Grain Boundary Complexion Transformations

3.1. Introduction

Flash sintering, a novel sintering technology invented by Professor Raj and his colleagues [1, 2], has attracted significant scientific and technological interests. Because the densification can occur in seconds at much reduced furnace temperatures, the flash sintering technology has a great potential for significant time, cost, and energy savings. Flash sintering has been applied to various materials, including yttria-stabilized zirconia (YSZ), SiC, BaTiO$_3$, CeO$_2$, MgAl$_2$O$_4$, and ZnO [3-13]. Fundamental studies have been conducted to probe the cause of the flash initiation [8, 14-18], the mechanisms of rapid densification [8, 19, 20], and the effects of electric fields on phase transformation and microstructural evolution [8, 21-26]. Flash sintering is a multi-physics process that involves ultrafast temperature rise (often on the order of 100 °C/s), electric field effects, and far-from-equilibrium rapid microstructure evolution; thus, a diversifying spectrum of phenomena can occur [8, 9, 11, 24-37].

Sintering aids are often used to promote densification at reduced temperatures in conventional sintering via forming a small amount of liquid phases (in so-called “liquid-phase sintering”) [38-40] or nanoscale premelting like intergranular films (IGFs) (in so-called solid-state “activated sintering” that can occur below the bulk solidus curve) [41-50]. In a broader perspective, recent studies showed that grain boundary complexions (a.k.a. interfacial phases that are
thermodynamically two dimensional) [51] can often form and affect the sintering processing (e.g., lowering the onset of sintering via forming premelting like IGFs [41, 42, 44-46]), microstructural evolution [51-55], and the final mechanical, electrical, and thermal properties [51, 56, 57]. The possible roles of such grain boundary complexions in flash sintering have been discussed by Todd et al. [58] and Harmer et al. [52], but have been neither confirmed nor systematically investigated experimentally. This motivated us to dope ZnO with Bi₂O₃, which is known to promote the formation of premelting like IGFs (below the eutectic temperature, $T_{\text{eutectic}}$) and/or a small fraction of a wetting liquid phase (above the $T_{\text{eutectic}}$) to enhance conventional sintering [41, 59], to investigate their possible roles in the flash sintering in this current study.

Several independent studies carried out at UCSD [15], Oxford [14], and U. Penn. [16] collectively demonstrated that natural thermal runaways can trigger flash sintering. Here, we used “natural” thermal runaway to refer to the case that results from an Arrhenius increasing of the specimen conductivity with increasing temperature. Quantitative models have also been developed to show that predicted thermal runaway temperatures are consistent with the observed flash initiation temperatures in a broad range of materials examined [14-16, 19, 60-62]. Yet, these successes do not rule out the alternative possibilities that, in certain systems, the occurrence of another physical phenomenon, e.g., an avalanche of nonequilibrium defects or a bulk phase transformation or an interfacial phase-like (complexion) transformation, can result in a sudden increase in the specimen conductivity to subsequently trigger flash sintering. In such a case, a “forced”
(instead of “natural”) thermal runaway will be a secondary (instead of the primary) cause that induces the flash sintering. Here, we report, for the first time to our knowledge, such a case in Bi$_2$O$_3$-doped ZnO.

Specifically, this current study investigated and compared Bi$_2$O$_3$ vs. Al$_2$O$_3$ doping effects on the flash sintering of ZnO. In 0.5 mol. % Bi$_2$O$_3$-doped ZnO, we found that bulk/interfacial transformations could rapidly increase the specimen conductivity non-linearly (above the linear Arrhenius extrapolation) to initiate flash sintering with low and median initial applied electric fields ($E_{\text{initial}}$). At a low $E_{\text{initial}}$ of 100 V/cm, the flash sintering was triggered when the estimated specimen temperature was near the bulk eutectic temperature (~740 °C). Interestingly, increasing $E_{\text{initial}}$ to 300 V/cm further activated the flash sintering at a sub-eutectic specimen temperature through the enhanced interfacial conductivity in the nanometer-thick IGFs (i.e., a quasi-liquid complexion thermodynamically stabilized at grain boundaries below the bulk eutectic temperature). Moreover, a high $E_{\text{initial}}$ of 800 V/cm resulted in a natural thermal runaway, prior to the formation of the premelting like grain-boundary complexion. In contrast, Al$_2$O$_3$ doping increased the conductivity of ZnO to promote flash sintering via reducing the natural thermal runaway temperature. We showed that this series of diversifying and scientifically interesting observations can be fully elucidated within one consistent physics-based theoretical framework and quantitively explained related models.

In addition, Al$_2$O$_3$ has higher solid solubilities in ZnO than Bi$_2$O$_3$ [63-66] to form a substantial amount of aliovalent $\text{Al}^{\text{Zn}}_{\text{Zn}}$ defects. Here, we further discovered
fast field-induced migration of aliovalent $\text{Al}_{\text{Zn}}^+$ cations during the flash sintering, which represents an electric field effect on far-from-equilibrium, rapid microstructural evolution occurred in the flash sintering.

3.2. Experimental

3.2.1. Materials synthesis and Sintering

ZnO powder (>99.99% purity, Sigma Aldrich) and 0.5 mol. % of $\text{Bi}_2\text{O}_3$ powder (≥99.8% purity, 90-210 nm particle size; Sigma Aldrich) were mixed in an yttria-stabilized zirconia vial with a small amount of isopropyl alcohol. All powders were subsequently planetary ball milled for 10 hours, dried in an oven at 80 °C for 12 hours, and calcined at 600 °C for two hours inside an alumina crucible on a Pt foil in air. The 1.6 mol. % (1 wt. %) $\text{Al}_2\text{O}_3$-doped ZnO powder (99.95+% purity, ~15 nm particle size) was purchased from US Research Nanomaterials, Inc.

The powders were uniaxially pressed at ~300 MPa to form a pellet with a dimension of a ¼-inch diameter and ~1-mm thickness. Platinum was sputtered on both sides of the green specimens using a Denton Discovery 18 Sputter. The sides of the sputtered specimens were slightly grounded by SiC papers after sputtering.

Flash sintering experiments were conducted with an initial electric field of 100 V/cm, 300 V/cm, or 800 V/cm. The applied voltage was kept at constant while ramping the furnace at a constant heating rate of 5 °C per minute until a flash occurred, at which point the system was switched from the voltage-control to a current-control mode with a preset maximum current limit of 1 A (corresponding to the maximum current density of ~39 mA/mm²). The electric power source and
furnace were shut down 30 seconds after the occurrence of the flash. The specimens were cooled within the furnace. More details about the equipment set up and the experiments can be found in an earlier publication [19].

In addition to monitoring the specimen conductivity (prior to the start of the flash) in all flash sintering experiments, the conductivity of a ZnO + 0.5 mol. % Bi$_2$O$_3$ green specimen was measured in the same equipment setup using a high-precision digital multimeter (Tektronix DMM 4050, Beaverton, OR, USA) when the temperature was increased from room temperature to 1200 °C at 5 °C/min (identical to the ramp rate used in the flash sintering experiments) to assess the specimen conductivity in a large temperature range with a high accuracy.

3.2.2. Material characterization

The flash-sintered specimens were characterized by using an ultra-high-resolution scanning electron microscope (UHR SEM, FEI, Hillsboro, OR) equipped with energy dispersive X-ray spectroscopy (EDX, Oxford Instrument, UK). Transmission electron microscopy (TEM) specimens were prepared by using a Scios Dual Beam FIB/SEM system (FEI, Hillsboro, OR). High-resolution TEM (HRTEM) characterization of the grain boundary structures was conducted by using a JEOL 2800 microscope operated at 200 kV. In addition to flash-sintered specimens described above, a ZnO + 0.5 mol. % Bi$_2$O$_3$ specimen was equilibrated at 700 °C for 24 hours in air and then air quenched to room temperature for TEM characterization. Specifically, HRTEM was used to characterize the liquid-like IGFs
formed in both (equilibrated) isothermally-annealed and (presumably non-equilibrium) flash-sintered specimens for comparison.

3.3. Results and Discussion

3.3.1. Doping Effects on the Conductivity and Flash Sintering: Al₂O₃ vs. Bi₂O₃

The measured conductivity (in a logarithmic scale) vs. the reciprocal of the estimated absolute specimen temperature curves for undoped, Bi₂O₃-doped, and Al₂O₃-doped ZnO green specimens (i.e., un-sintered but compacted powder pellets; noting that the doped powders had been annealed/homogenized at 600 °C for two hours) are shown in Fig. 3.1. These conductivity measurements were conducted for the low-temperature regime before sintering would take place. Here, the difference between the specimen and furnace temperatures (that is small typically before the flash) was estimated by the black body radiation model [75].

On the one hand, Al₂O₃ doping increased the conductivity of ZnO (Fig. 3.1), which is well known (as Al₂O₃-doped ZnO is a transparent conductor). On the other hand, Bi₂O₃ doping decreased the conductivity of ZnO in this low-temperature region (Fig. 3.2; noting that the conductivity would increase abruptly near and above the bulk eutectic temperature, which will be discussed later and shown in Fig. 3.6(a)). Consistently, Al₂O₃ doping promoted, while Bi₂O₃ doping suppressed, the flash sintering, as shown in Fig. 3.2 and Table 1.

Fig. 3.2 shows the dissipating electric power density versus furnace temperature in these three specimens, where the initial electric field was set at 300 V/cm and current limit was set at 1 A (~39 mA/mm²). The onset flash sintering
temperature (furnace $T_F$) in undoped ZnO was 628 °C; it decreased to ($T_F =$) 570 °C for Al$_2$O$_3$-doped ZnO because of the increased conductivity, while it increased to ($T_F =$) 696 °C for Bi$_2$O$_3$-doped ZnO because of the reduced conductivity (Fig. 3.2 vs. Fig. 3.1).

The relative densities of the flash-sintered undoped, Bi$_2$O$_3$-doped, and Al$_2$O$_3$-doped ZnO specimens (with the identical processing parameters of $I_{\text{max}} = 1$ A and $E_{\text{initial}} = 300$ V/cm) were measured to be 97.2%, 89.2%, and ~69%, respectively. Since the focus here is to examine the doping effects on the flash initiation, particularly the possible influences of bulk phase transformation and grain boundary phase-like complexion transition, we kept the same flash conditions for undoped, Bi$_2$O$_3$-doped, and Al$_2$O$_3$-doped ZnO for a fair comparison (instead of optimizing the conditions individually for achieving high densities for each case). Consequently, the Al$_2$O$_3$-doped ZnO specimen has a low relative density because the specimen has a significantly higher conductivity in comparison with the other two, thereby resulting in a lower steady-state specimen temperature during flash sintering. By increasing the current limit $I_{\text{max}}$ (from 1 A) to 4 A, however, Al$_2$O$_3$-doped ZnO can also be flash-sintered to ~97% of the theoretical density.

3.3.2. Undoped and Al$_2$O$_3$-doped ZnO: Natural Thermal Runways

Following our prior procedure [15], the relationship between the temperature-dependent conductivity of the green (compacted powder) specimens was fitted into an empirical Arrhenius equation $\sigma(T) = \sigma_0 e^{-\frac{Q}{kT}}$, where $k$ is the Boltzmann constant, $Q$ is the activation energy, and $\sigma_0$ is a pre-exponential
constant, for each case. The linear regressions of $\log(\sigma)$ vs. $1/T$ (Fig. 3.1) for undoped and Al$_2$O$_3$-doped ZnO produced activation energies of 1.02 eV and 1.53 eV, respectively, where the linear correlation coefficients $R^2$ are higher than 99% in both cases. The $\log(\sigma)$ vs. $1/T$ curve is less linear for the 0.5 mol. % Bi$_2$O$_3$-doped ZnO specimen in this temperature region (Fig. 3.1), where a linear regression gave an $R^2$ of ~94% with the best fitted activation energy of 1.81 eV. The nonlinearity for the Bi$_2$O$_3$-doped ZnO increases further at higher temperatures, which will be discussed later.

The Arrhenius temperature-dependent conductivity function $\sigma(T)$, which is an extrapolation of the measurements of the un-sintered specimen at low temperatures, was subsequently used to predict the thermal runaway condition following a model that we proposed previously [14, 15]. Here, a balance between the heat generation from Ohmic (Joule) heating and heat dissipation from blackbody radiation determines the specimen temperature:

$$\sigma(T_S)E^2V_S = A_S\varepsilon\sigma_{\text{Stefan}}(T_S^4 - T_F^4),$$

(1)

where $E (= E_{\text{initial}})$ is the electric field, $V_S$ is the volume of the specimen, and $T_S$ and $T_F$ are the specimen (S) and furnace (F) temperatures, respectively, $\sigma(T_S)$ is the specimen conductivity, $A_S$ is the surface area of the specimen, $\varepsilon$ is the emissivity, and $\sigma_{\text{Stefan}}$ is the Stefan–Boltzmann constant. A coupled thermal and electric runaway predicted from the Arrhenius extrapolation of the specimen conductivities measured at low temperatures (referred to as a “natural thermal runaway" for brevity hereafter) will take place if there is more heat generated with increasing
temperature than that can be dissipated:

\[ E^2 \left| \frac{d\sigma}{dT} \right|_{T_s} \frac{V_s}{A_S} > 4\varepsilon\sigma_{Stefan} T_s^3, \tag{2} \]

Noting that we divide both sides of Eq. (1) by \( A_S \) so that all specimen related parameters are on the left side in Eq. (2).

Eq. (2) suggests a graphical construction method to find the natural thermal runaway condition, as schematically illustrated in Fig. 3.3. Here, the intersection point of differential heat generation and dissipation rates (both normalized to per unit the specimen surface area, \( A_S \)), which are the left and right sides of Eq. (2), determines the specimen temperature \( (T_S) \) that produces a natural thermal runaway. Subsequently, the corresponding furnace temperature \( (T_F) \) can be calculated based on the black body radiation model.

Via this model and the associated graphical construction method (Fig. 3.3), the furnace temperatures at the natural thermal runaways for undoped and \( \text{Al}_2\text{O}_3 \)-doped \( \text{ZnO} \) specimens \((E_{\text{initial}} = 300 \text{ V/cm})\) were determined to 628 °C and 564 °C, respectively, using \( \sigma(T) \) functions extrapolated from the measured conductivities data shown in Fig. 3.1. Experimentally, we observed onset flash temperatures to be 628 °C for undoped \( \text{ZnO} \) and 570 °C for \( \text{Al}_2\text{O}_3 \)-doped \( \text{ZnO} \), respectively. The differences are small (0 °C and 6 °C, respectively). Thus, we conclude the flash sintering in undoped and \( \text{Al}_2\text{O}_3 \)-doped \( \text{ZnO} \) specimens was triggered by natural thermal runaways.

For the \( \text{Bi}_2\text{O}_3 \)-doped \( \text{ZnO} \) specimen at the same \( E_{\text{initial}} = 300 \text{ V/cm} \), this model would predict a natural runaway temperature \((T_F = 740 \text{ °C})\) from a simple
Arrhenius extrapolation of the specimen conductivities measured at low temperatures. However, this predicted natural runaway temperature of \( T_F = 740 \, ^\circ C \) is 44 \( ^\circ C \) higher than the observed onset flash temperature (696 \( ^\circ C \)). This discrepancy is caused by the formation of premelting like IGFs in Bi\(_2\)O\(_3\)-doped ZnO, as we will discuss subsequently in §3.5.

3.3.3. Field-Driven Fast Migration of Aliovalent Cations

Fig. 3.4 shows the microstructure of the flash-sintered Al\(_2\)O\(_3\)-doped ZnO specimen. Notably, aluminum (Al) enriched “white” particles accumulated in the negative electrode (cathode) side (Fig. 3.4(e)).

Specifically, the enlarged cross-sectional SEM images in Fig. 3.4(e) vs. Fig. 3.4(c) reveal “white” particles near the negative electrode (cathode), which are absent in the positive electrode (anode). EDX analyses (Fig. 3.4(f) vs. Fig. 3.4(g)) further showed that these “white” particles are Al enriched. The compositions of these white particles were measured to be \(~54\%\) O, \(~24\%\) Al, and \(~22\%\) of Zn. The actual Al content can be even higher considering the possible beam spreading as the particles are sub-micrometer sizes. In comparison, the composition for the normal “dark” particles was measured by EDX to be \(~49\%\) O, \(~3\%\) Al, and \(~48\%\) Zn, which is close to our nominal powder composition (1.6 mol. \% Al\(_2\)O\(_3\) doped ZnO). Presumably, the white particles are a Zn-Al-O compound, most likely the spinel-structured ZnAl\(_2\)O\(_4\) [64], that precipitated during the flash sintering and/or when the specimen was cooled down.

The specimen temperature during the steady-state stage of the flash
sintering was estimated to be 930 °C. It is known that Al₂O₃ has ~0.3 mol. % solubility in ZnO to form charged Al⁰⁺ defects in the temperature range of 850 to 1200 °C [64]. Thus, we hypothesize that the applied electric field/current moved charged Al⁰⁺ defects from the positive to the negative electrode side during the flash sintering, which subsequently precipitated as Al-enriched compound particles near the negative electrode side. This represents a new discovery of ultrafast, field-driven, asymmetrical microstructural evolution during the flash sintering. It is remarkable that this whole process occurred within ~30 seconds.

An asymmetrical microstructure was also observed for the flash-sintered 0.5 mol. % Bi₂O₃-doped ZnO sample. Fig. 3.5 shows the cross-sectional SEM images of flash-sintered Bi₂O₃-doped ZnO (E_initial = 300 V/cm). The average grain size at the negative electrode (cathode) was measured to be 448 ± 28 nm, which approximately doubles that measured for positive electrode (anode) side (212 ± 16 nm).

On the one hand, Bi₂O₃ has a much lower solubility in ZnO (< 0.05 mol. %), which differs from Al₂O₃. Thus, the field-driven migration of substitutional aliovalent cations, such as that observed for Al₂O₃-doped ZnO, was not observable here in Bi₂O₃-doped ZnO due to the limited solid solubility. On the other hand, it is known that the ZnO-Bi₂O₃ solid-liquid two-phase material (above the eutectic temperature) can be used as oxygen ion transport membranes [76], where the intergranular Bi₂O₃-enriched liquid phase serves as oxygen ionic conductor. Thus, during the flash sintering of Bi₂O₃-doped ZnO, the high current density and electric field can
induce strong polarization of oxygen defects, which may lead to the asymmetrical microstructure observed (Fig. 3.4). Further investigation should be conducted to probe the detailed underlying mechanism of the observed enhanced grain growth at the cathode side in Bi$_2$O$_3$-doped ZnO.

Electric field induced asymmetric microstructure has also been observed in polycrystalline or bi-crystal SrTiO$_3$ [67-70], BaTiO$_3$,[71, 72], and YSZ [73, 74]. Electromigration of point defects has been proposed or experimentally characterized in these materials. In this work, bulk point defect (Al$^{2+}$) was unequivocally characterized to reveal the fast migration during flash sintering, which is similar to the Electromigration of oxygen ion and oxygen vacancies in SrTiO$_3$ and YSZ. However, the possibility of grain boundary oxygen defects polarization and their effects on microstructure evolution need further investigation.

**3.3.4. Bi$_2$O$_3$-doped ZnO under Low $E_{\text{initial}}$: Bulk Eutectic Induced Flash**

In addition to the natural thermal runaways that can be predicted from the Arrhenius extrapolation of the measured conductivities of the green specimen, here we report a second possibility that the occurrence of a bulk eutectic reaction could trigger flash sintering in 0.5 mol. % Bi$_2$O$_3$-doped ZnO via causing a sudden increase in the specimen conductivity (in the eutectic liquid), as a temperature lower than the predicted natural thermal runaway.

Specifically, when a low $E_{\text{initial}}$ of 100 V/cm is applied, the specimen temperature for a natural thermal runaway predicted from an Arrhenius extrapolation from the measured conductivities of the green specimen would be
1005 °C (Fig. 3.6(b)). However, flash sintering initiated at the estimated specimen temperature $T_S = 742$ °C (Fig. 3.7), which is about the bulk eutectic temperature (~740 °C). Presumably, the formation of the Bi$_2$O$_3$-enriched, ionic, eutectic liquid caused a sudden increase in the specimen conductivity, thereby triggering the flash sintering via a “forced” thermal runaway.

To confirm the above hypothesis, the electrical conductivity of a 0.5 mol. % Bi$_2$O$_3$-doped ZnO specimen was measured when the specimen was heated from room temperature to 1200 °C, and subsequently cooled down. The measured log $(\sigma)$ vs. $1/T$ curves are shown in Fig. 3.6(a). During the heating, a conductivity transition (i.e., an abrupt increase in measured conductivity) was observed between 690 °C and 840 °C, which is presumably due to the bulk eutectic reaction (that forms a conducting Bi$_2$O$_3$-based mixed conducting liquid [77]) and associated formation of Bi$_2$O$_3$-enriched, liquid-like, nanoscale IGFs at ZnO grain boundaries (Fig. 3.8) [41, 65]. During the cooling, the log $(\sigma)$ vs $1/T$ curve mostly remained linear (as the Bi$_2$O$_3$-enriched IGFs retained to room temperature). The corresponding predicted $T_S$ (for three different $E_{\text{initial}}$’s) from the natural thermal runaway model (Fig. 3.6(b)) were labeled in Fig. 3.6(a). These predictions were from the Arrhenius extrapolation (the dash line in Fig. 3.6(a)) of the conductivities of the green specimen (prior to the occurrence of a conductivity transition). Thus, the natural thermal runaways predicted from the Arrhenius extrapolation did not account for the effect of this conductivity transition.

We should further note that conductivity transition shown in Fig. 3.6(a) was measured during furnace heating (at 5 °C/min) and the actual conductivity
transition profile should also depend on the heating rate, which was much faster in the flash sintering and should also depend on $E_{\text{initial}}$.

When a low $E_{\text{initial}}$ of 100 V/cm was applied, the specimen experienced a significant increase of conductivity (~10 times higher above the Arrhenius extrapolation) before the onset of flash at $T_s = 742 \, ^\circ C$, which triggered a “forced” thermal runaway that is $>250 \, ^\circ C$ lower than predicted $T_s$ for a natural thermal runaway (from an Arrhenius extrapolation). Thus, the experimental observation (and the discrepancy between the onset flash and the natural thermal runaway predicted from an Arrhenius extrapolation) can be fully understood. In this case, the bulk eutectic reaction at $\sim 740 \, ^\circ C$ triggered a “forced” thermal runaway, and a flash event thereafter, via forming a conducting, Bi$_2$O$_3$-enriched, ionic liquid.

3.3.5. Bi$_2$O$_3$-doped ZnO under Intermediate $E_{\text{initial}}$: Interfacial Transition Induced Flash

Moreover, we observed that further increasing $E_{\text{initial}}$ initiated flash sintering at a sub-eutectic specimen temperature. When $E_{\text{initial}}$ was 300 V/cm, the estimated $T_s$ for onset flash in the experiment was 696 °C (Fig. 3.7(a)); noting the stability is lost at $>696 \, ^\circ C$ as shown in Fig. 3.7(a), coincident with a sudden rise in the specimen conductivity as shown in Fig. 3.6(a). This observed onset flash specimen temperature is $>40 \, ^\circ C$ lower than the bulk eutectic temperature, but the specimen conductivity started to increase sharply beyond the linear Arrhenius extrapolation line at this temperature as shown in Fig. 3.6(a); here, we should note 696 °C is the nominal specimen temperature for the onset flash, which is defined as the middle
point in Fig. 3.7(a); the actual onset flash occurred in a short time period where the specimen temperature further increased beyond the middle point of $T_S = 696 \, ^\circ\mathrm{C}$, after which the specimen temperature increased abruptly as shown in Fig. 3.6(a), before losing the stability to trigger the flash sintering. This was presumably resulted from the enhanced interfacial conductivity in the nanometer-thick, Bi$_2$O$_3$-based, liquid-like IGFs that are known to form a below the bulk eutectic temperature [41] (i.e., a premelting like complexion thermodynamically stabilized at ZnO grain boundaries).

It is interesting to note that this moderate increase in the interfacial conductivity of the specimen was insufficient to trigger a flash at the low $E_{\text{initial}}$ of 100 V/cm, but it became significant when $E_{\text{initial}}$ was increased to 300 V/cm. Presumably, a higher $E_{\text{initial}}$ requires a less significant non-linear increase in the specimen conductivity to trigger flash sintering via a “forced” thermal runaway. This is consistent with that the predicted $T_S$ for a natural thermal runaway was 801 °C at 300 V/cm, much lower than the 1005 °C at 100 V/cm (Fig. 3.6(b)). Experimentally, we observed that the flash sintering initiated at 742 °C (approximately the bulk eutectic temperature) at the low $E_{\text{initial}}$ of 100 V/cm, but at a sub-eutectic temperature (696 °C) at the median $E_{\text{initial}}$ of 300 V/cm (Fig. 3.7).

To confirm the above hypothesis directly, we conducted further experiments to directly characterize the grain boundary structures responsible for the increased interfacial conductivity below bulk eutectic temperature in two types of specimens, which are discussed below.

First, a 0.5 mol. % Bi$_2$O$_3$-doped ZnO specimen was isothermally annealed
at 700 °C (40 °C below the bulk eutectic temperature) and air-quenched to preserve the grain boundary structures. Fig. 3.8(b) shows TEM and HRTEM images of Bi-enriched, liquid-like IGFs that are stabilized at ZnO grain boundaries, even below the bulk eutectic temperature. The IGFs formed in the specimen equilibrated at 700 °C were measured to be ~2 nm thick in this study. Prior studies already showed that the formation of such sub-eutectic, premelting like IGFs can enhance sintering [41, 45]. In this study, the formation of these Bi$_2$O$_3$-enriched, liquid-like, nanoscale IGFs presumably increased the interfacial conductivity below the bulk $T_{\text{eutectic}}$ to trigger the flash sintering under the intermediate $E_{\text{initial}}$ of 300 V/cm.

Second, we further confirmed the ultra-fast formation of liquid-like IGFs during flash sintering directly. Specifically, we quenched a 0.5 mol. % Bi$_2$O$_3$-doped ZnO specimen after being flash sintered for 20 seconds. Fig. 3.9 shows two low-magnification and three high-magnification TEM images of the grain boundaries in this flash-sintered specimen. The liquid-like IGFs observed in the flash-sintered specimen are relatively thinner than those observed in the specimen equilibrated at 700 °C. Presumably, these liquid-like IGFs did not form at a thermodynamic equilibrium due to the ultrafast flash sintering process. Nonetheless, this result directly confirmed that such liquid-like IGFs could form very quickly (in <20 seconds) during the flash sintering, which is indeed interesting.

**3.3.6. Bi$_2$O$_3$-doped ZnO under High $E_{\text{initial}}$: A Natural Thermal Runaway**

If the above explanations and hypotheses (discussed in §3.4 and §3.5) are
correct, we should be able to further increase $E_{\text{initial}}$ to allow the occurrence of a natural thermal runaway prior to the bulk eutectic reaction and interfacial premelting like transition. Indeed, we were able to confirm this prediction by our experiment. When we further increased $E_{\text{initial}}$ to 800 V/cm, our model predicted a natural thermal runaway at a specimen temperature $T_S = 677 \degree C$ (>70 °C below the bulk eutectic temperature), as shown in Fig. 3.6(b). Indeed, we observed that the onset flash took place at an estimated specimen $T_S$ of 670 °C in our experiment (Fig. 3.7).

This agreement finally confirmed that the experimental observations of all five cases (un-doped and $\text{Al}_2\text{O}_3$-doped ZnO at $E_{\text{initial}} = 300$ V/cm, as well as $\text{Bi}_2\text{O}_3$-doped ZnO at $E_{\text{initial}} = 100, 300, \text{and } 800$ V/cm, respectively) can be fully explained within one consistent theoretical framework.

3.4. Conclusions

We investigated $\text{Al}_2\text{O}_3$ vs. $\text{Bi}_2\text{O}_3$ doping effects on the flash sintering of ZnO. On the one hand, $\text{Al}_2\text{O}_3$ doping increased the specimen conductivity to promote flash sintering. The onset flash occurred as natural thermal runaway in both undoped and $\text{Al}_2\text{O}_3$-doped ZnO at $E_{\text{initial}}$ of 300 V/cm. We also made a new observation of ultrafast field-induced migration of aliovalent cations during the flash sintering of $\text{Al}_2\text{O}_3$-doped ZnO.

On the other hand, $\text{Bi}_2\text{O}_3$ doping decreased the specimen conductivity to delay the occurrence of flash sintering to higher temperatures, while it also led to a eutectic reaction and associated premelting-like grain boundary transition that
can abruptly increase the specimen conductivity with increasing temperature. Consequently, the onset flash was initiated by a bulk eutectic reaction at a low $E_{\text{initial}}$ of 100 V/cm and by premelting like grain boundary transition at an intermediate $E_{\text{initial}}$ of 300 V/cm, respectively, in 0.5 mol. % Bi$_2$O$_3$-doped ZnO. When we further increased $E_{\text{initial}}$ to 800 V/cm, a natural thermal runaway still took place before the occurrence of interfacial and bulk transformation, as predicted by the Arrhenius extrapolation.

Notably, we demonstrated that all five cases discussed above can be fully explained within one consistent theoretical framework.

Most significantly, this study has uncovered, for the first time to our knowledge, the possibility that a bulk phase transformation and/or interfacial (phase-like) complexion transformation can trigger flash sintering (via “forced,” instead of natural, thermal runaway). This new discovery thus suggests a new direction to tailor the flash sintering process.

**Chapter 3**, in part, is a reprint of the material “Flash Sintering Activated by Bulk Phase and Grain Boundary Complexion Transformations” in preparation, Y. Zhang, J. Nie, and Jian Luo. Part of the AZO experiments was carried out by Dr. Yuanyao Zhang. The dissertation author was the primary investigator and author of this paper.
Table 3.1 Summary of the key results for the flash sintering of undoped, Al$_2$O$_3$-doped, and Bi$_2$O$_3$-doped ZnO. The thermal runaway conditions were predicted from the Arrhenius extrapolation of the conductivities measured at low temperatures from the (un-sintered) green specimens. The predicted natural thermal runaway conditions are consistent with the experimentally-observed onset flash temperatures for undoped and Al$_2$O$_3$-doped ZnO. For Bi$_2$O$_3$-doped ZnO, the occurrence of a bulk phase (eutectic) transformation and an associated interfacial phase-like (premelting type complexion) transformation can cause a nonlinear rise in the specimen conductivity, thereby triggering a "forced" runaway (prior to the occurrence of a natural thermal runaway) at the initial electric field of 100 or 300 V/cm. At a higher initial field of 800 V/cm, a natural thermal runaway still took place before the occurrence of interfacial and bulk transformation. All observations of five cases can be fully explained within one consistent theoretical framework.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Initial Electric Field $E_{\text{initial}}$ (V/cm)</th>
<th>Activation Energy for Low-T Conductivity (eV)</th>
<th>$R^2$</th>
<th>Predicted Thermal Runaway Specimen $T_S \rightarrow$ Estimated Furnace $T_F$</th>
<th>Observed Onset Flash Furnace $T_F \rightarrow$ Estimated Specimen $T_S$</th>
<th>The Cause for the Onset Flash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-doped ZnO</td>
<td>300</td>
<td>1.02</td>
<td>&gt; 0.99</td>
<td>777 $\rightarrow$ 628</td>
<td>628 $\rightarrow$ 747</td>
<td>Natural Thermal Runaway</td>
</tr>
<tr>
<td>1.6 mol. % Al$_2$O$_3$-doped ZnO</td>
<td>300</td>
<td>1.53</td>
<td>&gt; 0.99</td>
<td>610 $\rightarrow$ 564</td>
<td>570 $\rightarrow$ 607</td>
<td>Natural Thermal Runaway</td>
</tr>
<tr>
<td>0.5 mol. % Bi$_2$O$_3$-doped ZnO</td>
<td>300</td>
<td>1.89</td>
<td>0.94</td>
<td>801 $\rightarrow$ 740</td>
<td>689 $\rightarrow$ 696</td>
<td>GB Transition $\rightarrow$ Runaway</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.81</td>
<td>0.9</td>
<td>1005 $\rightarrow$ 960</td>
<td>734 $\rightarrow$ 742</td>
<td>~ Bulk Eutectic $\rightarrow$ Runaway</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>1.79</td>
<td>0.99</td>
<td>677 $\rightarrow$ 607</td>
<td>613 $\rightarrow$ 670</td>
<td>Natural Thermal Runaway</td>
</tr>
</tbody>
</table>
Figure 3.1 Logarithmic measured electric conductivity vs. the reciprocal of the absolute specimen temperature curves for undoped, 0.5 mol. % Bi$_2$O$_3$-doped, and 1.6 mol. % Al$_2$O$_3$-doped ZnO green specimens.
Figure 3.2 Measured dissipating electric power density (in a logarithmic scale) vs. furnace temperature curves for the flash sintering of undoped ZnO, 0.5 mol. % Bi$_2$O$_3$ doped ZnO, and 1.6 mol. % Al$_2$O$_3$-doped ZnO (AZO), where the initial electric field was set to be 300 V/cm and the maximum current limit was set to 1 A ($J_{\text{max}} \approx 39$ mA/mm$^2$).
Figure 3.3 Calculated differential heat generation and dissipation rates (normalized to per unit surface area) vs. specimen temperature curves for undoped, 0.5 mol. % Bi₂O₃-doped, and 1.6 mol. % Al₂O₃-doped ZnO specimens. The initial electric field was set to be 300 V/cm in each case. The thermal runaway condition can be determined by the intersection of differential heat generation and dissipation rates. The predicted thermal runaway temperatures are consistent with the observed onset flash temperatures for undoped and Al₂O₃-doped ZnO, but not for the Bi₂O₃-doped ZnO. A further investigation offers a clear explanation for the apparent discrepancy in the latter case; the natural thermal runaway predicted from the Arrhenius extrapolation of specimen conductivities measured at low temperatures would occur at a specimen temperature of 801 °C for the Bi₂O₃-doped ZnO; however, a flash actually occurred at a lower specimen temperature near the ZnO-Bi₂O₃ eutectic temperature of 740 °C, where there was an abrupt increase in the specimen conductivity (beyond the Arrhenius extrapolation) as shown in Fig. 3.6(a).
Figure 3.4 (a) Cross-sectional SEM image of Al₂O₃-doped ZnO, along with enlarged SEM images at the (b, c) anode and (d, e) cathode sides. (f, g) EDX quantitative elemental analyses of the “dark particles” and the “white particles”. The compositional analysis clearly showed these “white particles” are Al-enriched. Most “white particles” enriched in Al were observed at the cathode side.
Figure 3.5 Cross-sectional SEM images at (a) anode and (b) cathode sides of a flash-sintered Bi$_2$O$_3$-doped ZnO specimen, where the initial electric field ($E_{\text{initial}}$) was set to be 300 V/cm and the maximum current limit was set to 1 A ($J_{\text{max}} \approx 39$ mA/mm$^2$).
Figure 3.6 (a) Measured dissipating electric power density vs. (a) furnace temperature and (b) estimated specimen temperature curves for the flash sintering of 0.5 mol. % Bi$_2$O$_3$-doped ZnO specimens, where the initial electric field ($E_{\text{initial}}$) was set to be 100, 300, and 800 V/cm, respectively. For each case, two estimated specimen temperatures ($T_s$) are labelled: the start of the nonlinearity in the power density vs. furnace temperature curve and turning (middle) point as determined by an angle bisector of two tangent lines. The estimated $T_s$ at the latter (turning points) are considered as the observed specimen temperatures at the onset flash, which are also labeled in panel (b) as well as Fig. 3.7 (a).
Figure 3.7 (a) Measured electric conductivity (in logarithmic scale) vs. the reciprocal absolute specimen temperature curves for a green specimen of ZnO + 0.5 mol. % Bi₂O₃ heated from room temperature to 1200 °C (the orange line) at a ramp rate of 5 °C/min, and subsequently cooled down (the pink line). The predicted specimen temperatures (Tₜ) at natural thermal runaways from the Arrhenius extrapolation from the measured low-temperature conductivities for Eᵢₜᵣₐᵢₙ = 100, 300, and 800 V/cm, respectively, are indicated by the solid discs; the estimated specimen temperatures at the onset flash ("observed flash Tₛ") are also marked as open circles with arrows. (b) Calculated differential heat generation and dissipation rates (all normalized to per unit surface area) vs. specimen temperature curves for the flash sintering of ZnO + 0.5 mol. % Bi₂O₃ specimens with the initial electrical fields of 100, 300, and 800 V/cm, respectively. The thermal runaway conditions predicted from the Arrhenius extrapolations of specimen conductivities measured at low temperatures are determined by the intersections of differential heat generation and dissipation rates. Such predicted thermal runaway temperatures are higher than the experimental observed onset flash temperatures for Eᵢₜᵣᵢₜᵢₙ = 100 V/cm and 300 V/cm because of the nonlinear rise in specimen conductivity near the eutectic temperature. When we further increased Eᵢₜᵣᵢₜᵢₙ to 800 V/cm, the predicted thermal runaway occurred at Tₛ ~670 °C, before the nonlinear increase of the specimen conductivity, which agrees with the observed onset flash temperature.
Figure 3. 8 (a - e) HRTEM images of a ZnO + 0.5 mol. % Bi$_2$O$_3$ specimen after flash sintered for 20 seconds where the initial electric field ($E_{\text{initial}}$) was set to be 300 V/cm and the maximum current limit was set to 1 A ($J_{\text{max}} \approx 39 \text{ mA/mm}^2$). (c – e) High magnification grain boundary images, in which (c) and (d) correspond to the locations labelled in (a) and (b) respectively. (f) HRTEM image of a ZnO + 0.5 mol. % Bi$_2$O$_3$ specimen annealed at 700 °C and quenched in air as a reference, showing the formation of liquid-like Bi$_2$O$_3$-enriched intergranular film (IGF) stabilized at the ZnO grain boundary below the bulk eutectic temperature ($T_{\text{eutectic}} = 740 \text{ °C}$) where the bulk liquid is not yet stable, which explains the moderate increase of conductivity below the bulk eutectic temperature. IGFs also formed during flash sintering even in 20 seconds showing its fast kinetic.
References


[77] V.V. Belousov, Oxygen-permeable membrane materials based on solid or liquid Bi₂O₃, Mrs Communications 3(4) (2013) 225-233.
Chapter 4. Water-assisted flash sintering: Flashing ZnO at room temperature to achieve ~ 98% density in seconds

4.1. Introduction

On one hand, Raj and co-workers reported an innovative “flash sintering” technology in 2010 to use applied electric fields/currents to trigger fast densification at low furnace temperatures [1], which has been successfully applied to a broad range of ceramics [1-15] (as being recently reviewed by Yu et al. [16]). Low furnace temperatures and fast densification rates make flash sintering an energy-saving and cost-effective method to consolidate ceramics. A further pursuit of even lower onset flash temperatures was made by increasing the initial applied electric field ($E_{\text{initial}}$); specifically, the onset flash temperature of 8 mol. % $Y_2O_3$ stabilized $ZrO_2$ was lowered to 390 °C with a high $E_{\text{initial}}$ of 2250 V/cm [17], but only moderate densification (i.e., ~8.5% linear shrinkage) was achieved [17]. Another prior work demonstrated that a reduced atmosphere (Ar + 5% $H_2$) can significantly lower the flash temperature of ZnO to <120 °C (via increasing the specimen conductivity to trigger a thermal runaway at a lower temperature, as supported by a quantitative model [4, 5, 18]) with an applied $E_{\text{initial}}$ of 500 V/cm [18]. Yet, a further reduction of the flash temperature could not be achieved (e.g., even with a higher $E_{\text{initial}}$ of 1000 V/cm [18]), presumably because the reduced atmosphere cannot interact with the specimen effectively at <100 °C. Thus, a scientifically-interesting and technologically-attractive goal of triggering the flash sintering at room
temperature without any external furnace heating had remained unattainable, which motivated the current study.

On the other hand, ceramic researchers have observed enhanced or suppressed sintering rates of MgO [19], CaO [20], anatase TiO$_2$ [21], SnO$_2$ [22], ZnO [23], and doped Al$_2$O$_3$ [24] in the presence of water vapor. Recently, Randall and co-workers developed an innovative “cold sintering process (CSP)” to densify ceramics under 250 °C with the assistance of water or aqueous solutions under the pressure of several hundreds of MPa [25, 26], which has been successfully applied to BaTiO$_3$ [27], ZrO$_2$ [28, 29], ZnO [30], NaNO$_2$ and KH$_2$PO$_4$ [31], and V$_2$O$_5$ based ceramic-polymer composites [32]. Perhaps more relevantly, Guillon and co-workers recently discovered enhanced densification by adding water in nanocrystalline ZnO specimens sintered by the spark plasmas sintering/field-assisted sintering technology (SPS/FAST) [33, 34].

The above inspiring studies on electric field/current and water assisted sintering collectively motivated us to propose, and subsequently validate with experiments on the ZnO model system, a new water-assisted flash sintering (WAFS) method. In this study, we demonstrated that WAFS can reduce the onset flash of the ZnO powder specimen to room temperature and subsequently achieve ~98% of the theoretical density in 30 s.

4.2. Experiments

4.2.1. Materials Synthesis and Sintering
A >99.99% purity ZnO powder, purchased from Sigma Aldrich, was mixed with 0.5 wt. % binder (2 wt. % PVA in DI water), uniaxially pressed at ~300 MPa to form green pellets of \( D \) (diameter) = 6.4 mm and \( H \) (height) = 1.0 mm, and subsequently baked at 500 °C for 1 h to burn out the binder. The average grain sizes in the green pellets were measured to be ~120 nm, and the relative densities were measured to be 54.8 ± 0.4%. The Pt electrodes were sputtered on both sides of surfaces and specimens were loaded into a horizontal quartz tube to connect with a Pt/Cu wire system (that has a negligible total resistance as compared with that of the ZnO specimen under all experimental conditions) for applying electric fields/currents. Flash sintering experiments were conducted in wet Ar + 5 mol. % \( \text{H}_2 \), by flowing the gas through a conical flask containing DI water at room temperature (as schematically shown in the graphical abstract). The system was purged with the flowing wet gas for 1 h before conducting flash sintering experiments. The specimen resistance was recorded during this period using a multimeter (DMM 4050, Tektronix Inc.). Subsequently, the flash sintering experiments were conducted at room temperature using a DC power supply (Sorensen XHR 150-7, Ametek Programmable Power Inc.) with initial electric fields \( E_{\text{initial}} = 200, 150, \) and 100 V/cm, respectively. The power supply was automatically switched to a current-control mode after the flash once the current reach a preset maximum current of \( I_{\text{max}} = 2.4 \text{ A} \) (corresponding to a nominal current density of \( J \approx 75 \text{ mA/mm}^2 \), calculated without considering the densification of the specimen) for all flash sintering experiments. The electric power supply was shut off 30 s after the onset of flash sintering.
4.2.2. Materials Characterizations

Specimen densities were measured by the Archimedes method (for dense specimens) and/or via measuring the dimension and weight. The microstructures were characterized using a field emission scanning electron microscope (FE SEM, Philips XL30). Grain sizes were measured from polished specimens using a standard intercept method.

4.3. Results

Fig. 4.1 (a) shows the specimen conductivity vs. time curve of a ZnO green pellet after flowing with wet Ar + 5% H₂. The specimen conductivity increased steeply by more than four orders of magnitude from $3 \times 10^{-7}$ S/cm to $7 \times 10^{-3}$ S/cm in the first ~20 min after purging with the wet gas, presumably due to water absorption, and reached a steady state, approaching ~0.01 S/cm. To further understand the effects of absorbed water, we conducted an additional experiment to measure the conductivities of ZnO powder pellets in both dry and wet flowing Ar + 5% H₂ in a tube furnace with a constant heating rate of 20 °C/min (after first flowing for 1 h at room temperature to achieve the steady state). It is interesting to note from Fig. 4.1(b) that the conductivity of the specimen in wet flowing gas is almost constant and higher than that of the dry specimen until ~350 °C, at which temperature the conductivity of the dry specimen increases to the same level. This suggests that the water effects can persist at least to ~350 °C in the powder specimen at the heating rate of 20 °C/min and probably to even higher temperatures with two to
three orders of magnitude higher heating rates in flash sintering [5], which may help sustain the WAFS after the onset of a flash.

Fig. 4.2 shows the electric fields, currents, power densities, specimen conductivities, and estimated specimen temperatures ($T_S$) from a blackbody radiation model [4] during 30 s of the WAFS of three ZnO specimens with the initial electric field of $E_{\text{initial}} = 100, 150, \text{ and } 200 \text{ V/cm}$, respectively. At the low $E_{\text{initial}}$ of 100 V/cm, a flash started gradually after an incubation period of ~5 s; at the intermediate $E_{\text{initial}}$ of 150 V/cm, a flash started intermediately. In both cases, the power densities (Fig. 4.2(c)) and estimated specimen temperatures (Fig. 4.2(e)) first increased but subsequently dropped to steady states, which were due to the increasing specimen conductivities (Fig. 4.2(d)) that generated less power in the constant-current mode. Consequently, the specimens reached the steady-state temperatures of 800-900 °C after ~10 s in these two cases, which did not lead to substantial densification/sintering. In contrast, with a high $E_{\text{initial}} = 200 \text{ V/cm}$, the power density immediately reached, and subsequently sustained at, a higher level of ~ 0.6 W/mm$^3$ to sustain the specimen temperature at >1100 °C (Fig. 4.2(e)) to enable fast densification. Consistently, the specimen with $E_{\text{initial}} = 200 \text{ V/cm}$ achieved ~98.3 ± 0.7 % relative density after WAFS for 30 s with a measured average grain size of 1.83 ± 0.30 µm (Fig. 4.3(a)). The Intragranular pores embedded in the large grains are also evidence of the ultrafast grain growth. In contrast, the specimen with $E_{\text{initial}} = 100 \text{ V/cm}$ essentially did not densify/sinter appreciably (Fig. 4.3(b)) because of the lower steady-state specimen temperature of ~850 °C (Fig. 4.2(e)).
The observation that densification only occurred when the $E_{\text{initial}}$ was above a critical threshold (Fig. 4.2 and Fig. 4.3) suggested the existence of bifurcation [35] in kinetic pathways after the flash events. In other words, the final steady states set (constrained) by the preset experimental condition of $I_{\text{max}} = 2.4$ A can be satisfied by two specimen states: a low-temperature (~850 °C) un-sintered (powder) specimen with a higher conductivity (~0.3 S/cm, which is presumably due to high surface conductivity) vs. a high-temperature (~1100 °C) sintered specimen with lower bulk conductivity (~0.1 S/cm). When $E_{\text{initial}}$ was sufficiently high (e.g., 200 V/cm), the high initial power generation and the associated high temperature increasing rate led to the densification pathway and latter state of a dense, bulk specimen; otherwise, the specimen would remain un-sintered (as a powder specimen with high surface conduction) at the lower $E_{\text{initial}}$ of 100 or 150 V/cm.

In addition to triggering the flash at room temperature by substantially increasing the specimen conductivity, water could also help the mass transport as demonstrated by the water assisted SPS/FAST of ZnO that was substantial at ~250-400 °C [33, 34]. The water effects on transport could be effective in the initial stage of WAFS (before drying); Fig. 4.1(b) suggests that the water effects can persist to at least ~350 °C at the heating rate of 20 °C/min and they can persist to higher temperatures during flash sintering where the heating rate is on the order of 100 °C/s [5]; furthermore, such effects can be more pronounced with a high $E_{\text{initial}}$ that leads to extremely high initial heating and densification rates. Nonetheless, it is still difficult to determine how significant the water in fact enhanced the mass transport of ZnO, if any, in the current case of WAFS.
4.4. Conclusions

In summary, a new WAFS method was proposed for the first time. Using ZnO as a model system, this study successfully demonstrated that WAFS can start at room temperature to achieve ~98% relative density in 30 s in wet Ar + 5% H₂. This method can potentially be extended to consolidate other ceramic systems to achieve fast densification at extremely low furnace temperatures or, ideally, room temperature. Furthermore, this study suggests significant technological opportunities for energy and cost savings via exploiting and investigating new ceramic processing science through the interplay of water, electric fields/currents, and ultrafast heating rates.

Chapter 4, in part, is a reprint of the publication "Water-assisted flash sintering: Flashing ZnO at room temperature to achieve ~98% density in seconds", J. Nie, Y. Zhang, J.M. Chan, R. Huang, and J. Luo, as it appears in Scripta Materialia, 2018, 142, 79. The dissertation author was the primary investigator and author of this paper.
Figure 4.1 (a) Specimen conductivity vs. time curve of a ZnO green pellet in flowing wet Ar + 5% H₂. (b) Specimen conductivity vs. temperature curves measured from two ZnO specimens in dry and wet Ar + 5% H₂, respectively, in a furnace that was heated at a constant ramping rate of 20 °C/min.
Figure 4.2 The (a) nominal electric field, (b) current, (c) power density, (d) specimen conductivity, and (e) estimated specimen temperature ($T_s$) of ZnO vs. time curves during water-assisted flash sintering (WAFS) of three ZnO specimens with $E_{\text{initial}} = 100$, 150, and 200 V/cm.
Figure 4.3 SEM micrographs of (a) a polished cross section of a flash-sintered ZnO specimen with $E_{\text{initial}} = 200$ V/cm and (b) a fractured surface of a specimen with $E_{\text{initial}} = 100$ V/cm.
References


Chapter 5. Two-step flash sintering of ZnO: Fast densification with suppressed grain growth

5.1. Introduction

In 2000, Chen and Wang developed an innovative two-step sintering method to inhibit the final-stage grain growth that would normally occur when the relative density is above ~90% [1]. In two-step sintering, a green specimen was first heated to a higher temperature, $T_1$, to reach a critical relative density, followed by holding at a lower temperature, $T_2$ ($T_2 < T_1$), in the second step for a prolonged time to achieve a high relative density while suppressing the final-stage rapid grain growth. This method has been successfully applied to various ceramic materials, including undoped/doped Y$_2$O$_3$ [1, 2], BaTiO$_3$ [3, 4], ZnO [5], Al$_2$O$_3$ [6], and SiC [7]. Yet, there are several technical challenges for the application of two-step sintering. For example, a prolonged holding time in the second step, e.g., up to 20 hours in the case of conventional two-step sintering of ZnO [5], is typically required. Moreover, the short holding duration in the first step and (sometimes) desired fast cooling from the first to second step [2, 3, 8] may lead to large relative deviations of the exact specimen temperatures from the targeted profiles. Inspired by a novel flash sintering method developed by Raj and co-workers in 2010 [9], here we proposed and subsequently demonstrated a new two-step flash sintering (TSFS) method to achieve comparable results as those demonstrated in conventional two-step sintering of ZnO [5] in as short as ~5 minutes; this represents a >200 times reduction in the sintering time [5], thereby implying not only convenient electronic
controls (with ultrafast heating and cooling rates) but also a great potential for energy and cost savings with a drastically improved efficiency.

Flash sintering enabled fast densification at low furnace temperatures, which have been successfully applied to Y$_2$O$_3$-stablized ZrO$_2$ [9, 10], Y$_2$O$_3$ [11], ZnO [12-14], TiO$_2$ [15, 16], SrTiO$_3$ [17, 18], and other oxide [19-21] as well as non-oxide [22-25] ceramics. In most systems, the flash starts as a thermal runaway, where quantitative models [12, 13, 15, 26-28] have been developed and tested. At least for ZnO, fast densification is related to ultrahigh heating rates (~200 °C/s) since a recent study demonstrated that rapid thermal annealing with comparable heating profiles can achieve similar densification and grain growth rates [13]. However, rapid final-stage grain growth also occurred in flash sintering in a similar fashion as those observed in conventional sintering, albeit a much shorter time scale [13]. In this study, we further proposed a new TSFS method to substantially reduce the final-stage grain growth as compared with the conventional (one-step) flash sintering and subsequently demonstrated its feasibility using a model system (ZnO).

5.2. Experiments

5.2.1. Materials synthesis and Sintering

A ZnO powder (99.95% purity, purchased from US Research Nanomaterials, Inc.) was mixed with 0.5 wt. % binder (PVA in DI water). The mixtures were uniaxially pressed at ~300 MPa to form green pellets of the dimension: $D$ (diameter) = 6.4 mm and $H$ (height) = 2.8 mm. Green pellets were
baked at 500 °C for 1 hour to burn out the binder. After burning the binder, the average grain size in the green pellets was measured to be 36 ± 2 nm and the bulk densities were measured to be 57.3 ± 0.8%. The specimen surfaces were sputtered with platinum as electrodes using a Denton Discovery 18 Sputtering System. The sides of the sputtered specimens were ground using SiC papers. For flash sintering experiments, specimens were loaded into a modified dilatometer (DIL 402 PC, Netzsch, Boston, MA, USA) equipped with Pt electrodes and circuit (for applying electric fields/currents) and flowed with argon at a constant rate of 33 mL/min. The system was purged with argon for one hour before heating up to 500 °C at a constant rate of 5 °C/min. Subsequently, the flash sintering experiments were conducted isothermally at 500 °C, where a programmable DC power supply (DLM300-10, Ametek Inc., San Diego, CA, USA) was used to apply electric fields/currents.

All flash sintering experiments were conducted at an isothermal furnace temperature of 500 °C in this study (instead of a constant ramping rate as in most other flash sintering experiments, so that it can be better compared with TSFS experiments), where a flash typically started ~20-30 s after applying the constant (initial) electric field of 150 V/cm. The electric field was kept a constant (150 V/cm in this case), until the specimen current reached a preset limit and the power supply was switched from a voltage-control to a current-control mode. For conventional (one-step) flash sintering, the current limit ($I_{\text{max}}$) was kept at 3 A (corresponding to a nominal current density of $J_{\text{max}} \approx 95 \text{ mA/mm}^2$, calculated from the initial specimen dimension; noting that the actual $J_{\text{max}}$ increases with time due the densification of
specimen) for a duration of 2 s, 6 s, 15 s, and 30 s, respectively, after the onset of flash. For TSFS, the current limit was set to $I_1 = 3$ A (nominal $J_1 \approx 95$ mA/mm$^2$) for a fixed duration of 6 s ($3$ A × 6 s) in the first step and subsequently reduced to $I_2 = 2$ A (nominal $J_2 \approx 63$ mA/mm$^2$) and kept for a duration of 150 s or 300 s. After flash sintering, both the electric power and the furnace were shut down and the specimens were cooled down in the furnace; the flowing argon was shut off after the specimen cooled to room temperature.

5.2.2. Material characterization

After the completion of flash sintering experiments, the specimen densities were calculated via measuring dimensions and weights; the Archimedes method was also used, if the relativity densities were greater than 90%. Microstructures of flash sintered specimens were characterized using a field-emission ultra-high resolution environmental scanning electron microscope (UHR-SEM, FEI XL30) operating at 10 kV. Grain sizes were measured from SEM micrographs of fractured surfaces using a standard intercept method.

5.3. Results and Discussion

The grain size vs. relative density curves for both conventional (one-step) flash sintering and TSFS are shown in Fig. 5.1. Representative microstructures of the fractured surfaces of six sintered specimens are shown in Fig. 5.2. Here, the grain sizes and densities were measured from specimens that were cooled down to room temperature, where the effects of the densification and grain growth during the cooling were also included.
In conventional one-step flash sintering experiments, the relative density increased from \( \sim 57\% \) in the green specimen to \( \sim 72\% \) in the 3 A \( \times \) 2 s sintered specimen, while the grain size increased from \( 36 \pm 2 \text{ nm} \) in the green specimen to \( 214 \pm 18 \text{ nm} \) in the sintered specimen. Increasing the flash sintering duration from 2 s to 6 s, the relative density increased substantially to \( \sim 90\% \), while the grain size increased only moderately to \( 267 \pm 30 \text{ nm} \), in the 3 A \( \times \) 6 s sintered specimen. Further increasing the flash sintering duration, the relative density increased to \( \sim 95\% \) with a substantial grain growth to \( 1.18 \pm 0.14 \text{ \( \mu \)m} \) in the 3 A \( \times \) 15 s sintered specimen; the relative density and grain size, respectively, reached \( \sim 97.6\% \) and \( 1.75 \pm 0.16 \mu\text{m} \), respectively, in the 3 A \( \times \) 30 s sintered specimen. Here, the observed rapid final-stage grain growth (when the relative density was above \( \sim 90\% \)) is consistent with results measured from both conventional flash sintering, as well as rapid thermal annealing, of ZnO conducted in air [13] and it agrees with what is expected from the classical sintering theory.

The linear shrinkage was also measured \textit{in situ} by dilatometry for flash sintering of ZnO at 500 °C in argon \( (E_{\text{initial}} = 150 \text{ V/cm and } I_{\max}) \), where electric power was shut off at 30 s after the onset flash (Fig. 5.3). The specimen densified to \( \sim 93\% \) in 30 s after the onset of flash as measured by \textit{in-situ} dilatometry. The final density was measured using the Archimedes method to be 97.6\% (close to that calculated from the measured linear shrinkage at 60 s). This measured linear shrinkage \textit{vs.} time curve was used as a guide to select the duration for the first step of the TSFS experiments to be 6 s, at which time the specimen reached \( \sim 81\% \) of the theoretical density, since a prior study of conventional two-step sintering of
ZnO suggested that the first step should reach to >78% of theoretical density [5]. Noting the measured relative density of the 3 A × 6 s sintered specimen was ~90%, which included the contribution of densification during the cooling.

In the TSFS (i.e. two-step flash sintering) experiments conducted with $E_{\text{initial}} = 150$ V/cm, a fixed first step of 3 A × 6 s (i.e., $I_1 = 3$ A for a fixed duration of 6 s), and a second step of a fixed current $I_2 = 2$ A, the grain size only increased to 330 ± 28 nm with a further increase in the relative density to 94.7% (in comparison with the ~267 nm grain size and ~90% density of the 3 A × 6 s sintered specimen; see Fig. 5.1 and Fig. 5.2). A longer second step of 300 s resulted in a grain size of 370 ± 17 nm and a relative density of 96.5% in the 3 A × 6 s + 2 A × 300 s sintered specimen. As shown in Fig. 5.1, the grain growth was suppressed in the TSFS experiments, where the grain sizes were less than 1/3 of those expected in the conventional (one-step) flash sintering with identical densities from interpolation. The grain size vs. density curve obtained from the TSFS was similar to that of the optimal case of conventional two-step sintering of ZnO reported in a prior study [5]; yet TSFS achieved this result (~370 nm grain size at ~96.5% relative density) in ~5 minutes, whereas it took ~15-20 hours in conventional two-step sintering to achieve comparable results of densification and grain growth (i.e., ~500 nm at ~95% or ~650 nm at ~98% relative density, with a smaller starting particle/grain size of ~11 nm) [5]. In other words, the new TSFS method is >200 times faster in obtaining comparable (or slightly better) results than the conventional two-step sintering [5], representing a substantial opportunity for energy and cost savings via drastically improving the efficiency.
We also conducted a 2 A × 600 s one-step flash sintering experiment for an additional comparison, which produced a 95.8% dense specimen with the measured average grain size of 2.01 ± 0.18 µm. This result suggested that longer holding at 2 A could not achieve the simultaneous small grain size and high density obtained by the TSFS.

The measured time-dependent current, current density, electric field, and linear shrinkage of a representative specimen undergoing TSFS (in the first ~35 s after the flash) are shown in Figs. 5.4 (a) – (d). The calculated power density and estimated specimen temperature ($T_s$) from the blackbody radiation model [12] are shown in Figs. 5.4 (e) and (f). The actual current followed the controlled profile (3 A × 6 s + 2 A × 300 s) well with only minor fluctuations, while the relatively large fluctuations in the voltage (electric field) vs. time curve reflected the specimen response under the current-control mode. While the current was controlled to be a constant in each step (Fig. 5.4(a)), the current density increased continuously (more noticeably in the first step) due to the specimen shrinkage during densification (Fig. 5.4(b)). It was evident from the measured linear shrinkage vs. time curve (Fig. 5.4(d)) that densification was fast in the first step (0 to 6 s) and slowed down in the second step. The power density increased gradually in the incubation period under the voltage-controlled mode prior to the onset of the flash, but it largely followed a two-step function in the TSFS under the current-controlled mode (Fig. 5.4(e)). The estimated specimen temperature ($T_s$) was between 1600 and 1700 °C in the first step and between 1300 and 1450 °C in the second step; thus, the temperature difference ($\Delta T_s$) between the two steps was estimated to be
~200-300 °C (Fig. 5.4(f)). The final relative density of the $3 \text{ A} \times 6 \text{ s} + 2 \text{ A} \times 300 \text{ s}$ sintered specimen (after cooling to room temperature) was measured to be $96.5 \pm 0.3\%$ using the Archimedes method and the grain size was measured to be $370 \pm 17 \text{ nm}$.

5.4. Conclusions

In summary, a new TSFS method has been proposed to achieve fast densification (in comparison with the conventional two-step sintering) with suppressed grain growth (in comparison with the conventional flash sintering), where a specimen was kept at a higher current of $I_1$ for a short duration $t_1$ after the onset of flash, and electronically switched to a lower current of $I_2 (< I_1)$ for a longer duration $t_2 (> t_1)$. Using ZnO as a model system, this study successfully achieved ~96.5\% of the theoretical density with a grain size of ~370 nm (representing a >3 times reduction in final-stage grain growth in comparison with the conventional one-step flash sintering) in ~5 minutes using this new TSFS method, which is >200 times faster than that can be obtained in the conventional two-step sintering. This cost-effective and energy-saving TSFS method can potentially be applied on other materials to achieve fast densification with suppressed grain growth. This study further suggests a new direction to control the densification and microstructural evolution via controlling and manipulating the $I(t)$ profile in flash sintering to any preset profile to achieve better or more customized results.
Chapter 5, in part, is a reprint of the manuscript “Two-Step Flash Sintering of ZnO: Fast Densification with Suppressed Grain Growth”, J. Nie, Y. Zhang, J.M. Chan, S. Jiang, R. Huang, J. Luo, as it appears in Scripta Materialia, 2017, 141, 6. The dissertation author was the primary investigator and author of this paper.
Figure 5.1 Grain size vs. relative density of ZnO specimens fabricated by conventional (one-step) and two-step flash sintering.
Figure 5.2 SEM micrographs of the fractured surfaces of the conventional (one-step) flash sintered ZnO specimens quenched (a) 2 s, (b) 6 s, (c) 15 s, and (d) 30 s, respectively, after the onset of flash, where the current limits were 3 A, as well as the two-step flash sintered ZnO specimens quenched after (e) 3 A × 6 s + 2 A × 150 s and (f) 3 A × 6 s + 2 A × 300 s.
Figure 5.3 Measured linear shrinkage vs. time curve for (one-step) flash sintering of ZnO conducted in argon with a constant furnace temperature of $T_F = 500 \, ^\circ C$, where the applied electric field was set to 150 V/cm initially and the maximum current limit was set to 3 A. Electric power was shut off 30 seconds after the onset of flash (while the densification continues for $\sim 30$ s during the cooling of the specimen).
Figure 5.4 *In-situ* measurements of the first ~35 s in TSFS, including time-dependent (a) current, (b) current density, (c) electric field, and (d) linear shrinkage, as well as the (e) computed power density and (f) estimated specimen temperature ($T_s$).
References


[20] A. Gaur, V.M. Sglavo, Densification of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ ceramic by flash sintering at temperature less than 100 °C, Journal of Materials Science 49(18) (2014) 6321-6332.


Chapter 6. Electric Field Effect on Grain Growth and Grain Boundary Complexion Transformations

6.1. Introduction

Using electric field and/or current for materials processing has a long history [1]. Since the 1950s, the development and commercialization of a technique later known as Spark Plasma Sintering dramatically accelerated the research on materials processing using electric field [2]. As one of the earliest studies on the effects of electric field on solid-state oxides processing, Mackenzie and co-workers demonstrated improved cation mobility and their relationship with the direction of the external field [3, 4].

Recently, flash sintering, a novel material sintering method using external electric fields, invented by Prof. Raj and his colleagues [5, 6], has attracted significant interests due to its advantages of short densification times and ultra-low furnace temperatures. Flash sintering, together with related techniques like flash SPS [7], has been successfully applied to many materials including YSZ [5], CeO$_2$ [8], MgAl$_2$O$_4$ [9], SiC [10], ZnO [11], TiO$_2$ [12, 13], as well as composites [14, 15] since its invention. Several fundamental studies have successfully modelled and predicted the onset of flash sintering [11, 16, 17] using electric thermal runaway. The fast densifications of green specimens are also explained by the ultra-high heating rate under electric fields [18, 19]. However, many interesting phenomena suggest the possible electric field/current effects on materials’ structures beyond Joel heating, although some experiments are not under flash sintering conditions.
For example, anomalous lattice expansion was observed in 8YSZ [20]; reversible cubic-like phase appeared in 3YSZ under electric field and current [21]; abnormal grains were observed at the cathode side in 8YSZ [22] and flash sintered 3YSZ [23]; enhanced grain growth was observed at the anode side in flash sintered ZnO in air [11], but disappeared in flash sintered ZnO in reduced atmosphere [24]. Similar asymmetrical grain growth in the presence of external electric field/current has also been observed in Al₂O₃ [25, 26], SrTiO₃ [27], etc.

These intriguing observations and fast development of Flash Sintering [28] and Field Assisted Sintering Technologies (FASTs) [29] urge for explorations of the electric field and current effects. Some possible mechanisms have been proposed. For example, electric field interacted with space charge layers which reduces the grain boundary energies and subsequently enhances grain growth [25, 30]; or defects redistribution and electrochemical reduction enhances local cation kinetics, further enhances grain growth [23, 27, 31, 32]. Moreover, understanding electric field effects on microstructures is also crucial for improving the stability of electrolytes of like solid-state electrolytes in fuel cells [33], where high current densities and long cycles are desired for industrial applications [34].

In the current study, a classical varistor material, Bi₂O₃-doped ZnO, is used as a model to study the electric field/current effect on microstructure evolutions in the presence of ionic liquid phase. Considering that the densification of green bodies and the grain growth shares similar driving force, pre-sintered specimens are used in this work to decouple them. Specifically, Bi₂O₃-doped ZnO specimens with a special polycrystalline-single crystal-polycrystalline (PC-SC-PC) sandwich
structure were developed. We found highly diversified microstructure evolutions in the sandwich specimens annealed under electric field and current. The grain growth of single crystal towards the opposite direction of the electric field ($/\!\!\!/$-$E$) was significantly enhanced, while grain growth towards the electric field direction ($/\!\!\!/$+$E$) had little difference with specimen annealed without electric field. Bi-enriched highly ordered grain boundary structure was observed at the PC-SC interface where single crystal growth $/\!\!\!/$-$E$, while on the other side, liquid-like intergranular films (IGFs) formed at the grain boundaries. Moreover, near the cathode of the specimen, abnormal grains with strong textures and more than 10 times larger than normal grains were observed. Based on the supportive characterization of photoluminescence at the specimen cross sections, we showed that these phenomena be fully explained by electrochemical polarization of defects through ionic conducting grain boundaries. The advantage of a sandwich specimen is that the asymmetric grain growth was self-comparable, thus ruled out the geometric effect on electric conditions. Also, the ionic insulating but electric conducting single crystal deconvoluted the electric potential and defects electrochemical potential effects on grain growth. The above results indicate that, at least in this work, electrochemical potential dominates the microstructure evolution.

6.2. Experiments

6.2.1. Preparation of dense sandwich specimens

0.5 mol. % Bi$_2$O$_3$-doped ZnO powder was prepared by mixing ZnO (99.98% purity, ~18 nm, US Nanomaterials) with bismuth acetate ($\geq$99.99% purity, Sigma
Aldrich). Mixed powders were ball-milled for 10 hours with a small amount of isopropyl alcohol. Powders were subsequently dried in oven at 80 °C for 12 hours and annealing at 500 °C for 1 hour.

ZnO (11\(\overline{2}0\)) single crystals with both sides polished were purchased from MTI Corporation. Dense Bi\(_2\)O\(_3\)-doped ZnO polycrystalline-single crystal-polycrystalline (PC-SC-PC) sandwich pellets were prepared by SPS at 780 °C for 5 minutes under 50 MPa pressure, then de-carbonized at 700 °C for 9 hours. After sintering, sandwich specimens reached > 99% relative densities. All sandwich pellets were ground to 5.0 \(\times\) 5.0 \(\times\) \(\sim\)1.6 mm\(^3\) cuboids with 0.5 mm thick single crystal ZnO between two non-connecting polycrystalline regions.

**6.2.2. Annealing with electric field/current**

Dense sandwich specimens were sputtered with platinum to form two 5.0 \(\times\) 5.0 mm\(^2\) electrodes using a Denton Discover 18 Sputter System. An external DC electric field were applied on the specimen while annealing at 840 °C for 4 hours with a controlled DC current density \(J = 6.4 \text{ mA/mm}^2\). The nominal electric field direction was perpendicular to imbedded ZnO (11\(\overline{2}0\)) single crystals. More details of the equipment were shown in a previous publication [18].

**6.2.3. Annealing without electric field/current**

To rule out the Joel heating effect of electric field, the reference sandwich specimen was annealed at 30 °C higher (870 °C) for 4 hours on the same equipment without any external electric field. The annealing temperature of the reference specimen is above the upper limit of the experiment specimen.
method used for temperature estimation with respect to power density is described in a previous publication [11]. After isothermal annealing, specimens were air-quenched to room temperature.

Additionally, three dense polycrystalline specimens were prepared by SPS and de-carbonized at the same condition described above, then annealed at 880 °C for 4 hours without electric field in air, argon, or argon + 5% H₂.

6.2.4. Characterization

Bulk densities of sandwich specimens were measured using the Archimedes method. Electric potentials and currents of specimens and circuits were recorded using a high-precision digital multimeter (Tektronix DMM 4050, Beaverton, OR, USA) during the experiments. Quenched specimens were characterized by using an ultra-high-resolution Scanning Electron Microscope (Apreo SEM, FEI, Hillsboro, OR) at the cross sections after grinding and polishing. Grain growth of the single crystal was measured at 14 locations along each polycrystalline-single interface. At each location, grain growth was averaged from 16 measurements with 5 µm intervals. Spatial-resolved photoluminescence spectroscopy in the wavelength range from 400 nm to 700 nm on cross section surface of sandwich specimens was carried out on a confocal microscope (Leica SP5, Leica Microsystems) equipped with Multiphoton (MP) system. Microscope spatial resolution and penetration depth was ~ 0.4 µm and ~ 50 nm, respectively. Transmission electron microscopy samples were prepared by using a Dual Beam Focused Ion Beam (FIB) / SEM system (Scios, FEI, Hillsboro, OR). Aberration-
corrected scanning transmission electron microscopy characterization of the grain boundary structures was conducted by using a JEOL JEM-300CF STEM microscope operated at 300 kV. Electron backscattered diffraction (EBSD) mapping was acquired by using an c-wave detector from Oxford Instruments (Concord, MA, USA).

6.3. Results and Discussion

6.3.1. Electric Field Effects on Grain Growth of Bi$_2$O$_3$-doped ZnO

Prior to characterize the effect of electric field and current, grain growth of single crystals after SPS and decarbonization was characterized as a baseline before annealing experiments as shown in Fig. 6.1. Aligned holes are used to label the original single crystal surfaces. The grain growths on both sides of SC are very small and have little difference, which indicates a symmetric microstructure of the sandwich specimen before further annealing experiments.

As described in the experimental section, a sandwich specimen was annealed at 870 °C for 4 hours without an external electric field. The microstructure is symmetric as shown in Fig. 6.2. The single crystal growths of the reference specimen were 3.63 ± 0.91 µm and 3.60 ± 0.79 µm on both sides respectively.

However, by annealing the sample under DC electric field with constant a current density $J = 6.4$ mA/mm$^2$, asymmetric microstructure was clearly observed as shown in Fig. 6.3. The nominal direction of the external electric field (white arrows), location of high-magnification micrographs (dashed orange squares in Fig. 6.3(a)), as well as the direction of grain growth (blue arrows) were labelled.
Significant grain growth anti-parallel to the electric field direction (\(/-E\)) was observed. Well on the other hand, grain growth parallel to electric field (\(/+E\)) was comparable to the reference specimen. Quantitative grain growth versus the normalized location on the single crystal surfaces were summarized in Fig. 6.4 (b). Peak of the average grain growth of SC \(/-E\) was > 200% larger than the average of grain growth of SC\/+E.

In addition to grain growth, pores were observed near the single crystal at the side with small grain growth (SC\/+E). Since all the sandwich specimens were pre-densified to more than 99% relative density, and no extra porosity was observed in the reference specimen, the pores are expected to be generated during the annealing under electric field.

6.3.2. Electrochemical Polarization of Defects and Ionic Blocking Single Crystal

Defect concentrations has been demonstrated to affect microstructure evolutions in many materials[23, 27]. In this study, polarization of defects by external electric field was clearly characterized by spatial-resolved photoluminescence (PL) spectroscopy, explains the asymmetric microstructure formation of the sandwich Bi$_2$O$_3$-doped ZnO specimens under external electric field. Figure 4 shows both low and high magnification PL spectra in the wavelength ranging from 400 nm to 700 nm. Each PL spectrum in Fig. 6.5 (a, b) is an average of the intensity in the 30 µm × 1.5 µm boxes as shown in the mappings, Fig. 6.5 (c, d), respectively. Locations close to the single crystal surface growing \(/-E\) has
much higher intensities than locations near the anode. Detailed peak separations of two representative spectra were plotted in Figure 5. The broad asymmetric peak from 400 nm to 700 nm in both locations is a superposition of two peaks. In Fig. 6.6 (a) the two separated peaks centered at 523 nm and 610 nm, which are close to the corresponding PL wavelengths of $V_0^*$ and $O_i^-$ defects in ZnO. In Fig. 6.6 (b), the two separated peaks are centered at 505 nm and 577 nm. The PL signal in single crystal region is below the detection limit in the wavelength range of interest, leaving a dark area in the spatial mapping as can be seen in Fig. 6.5 (c, d). Moreover, as shown in the high magnification PL spectra (Fig. 6.5(b)), the grown region (Location ID = 6) of the single crystal (//E) has lower intensity than the adjacent polycrystalline region (Location ID = 7). Polycrystalline region near the interface //E has lower intensity than the interface //E.

The significant difference of PL spectra at different locations reveals how external electric field affects the defect concentrations in the sample. This interesting polarization behavior of ionic defects in Bi$_2$O$_3$-doped ZnO is believed due to the combined effects of ionic conducting grain boundary liquid and electric conducting bulk. At the annealing temperature of 840 °C, Bi-rich grain boundaries are good ionic conductors in liquid phase as has been demonstrated by works on Bi$_2$O$_3$-based oxygen membranes [35]. On the other hand, bulk ZnO is electric conducting dominated. So, in the sandwich specimens of this work, the Bi-doped single crystal ZnO between two Bi$_2$O$_3$-doped ZnO polycrystalline parts is an ionic blocking layer, forming continuous electric potential but “discontinuous” (in microscale) chemical potential of ionic defects along the external electric field
direction. Noting that the chemical potential of defects across the PC-SC interfaces are physically continuous. However, the transition layer cannot be observed due to the slow ion diffusions of ZnO single crystals [36] given the 0.4 µm spatial resolution of the microscope. Though commercial ZnO single crystals’ defect concentrations are very low, the grown part of the single crystal is defected according to the PL spectra at location 6, Fig. 6.5 (b). This is similar to the crystal growth behavior of ZnO from molten salts [37]. However, it is worth noting that, at current stage, it is not possible to differentiate the luminescence from the bulk and the grain boundary in the polycrystalline regions.

6.3.3. Proposed Mechanism and Schematic Potential Profiles

The above observations of ionic conducting grain boundaries and ionic blocking single crystals lead to the proposed mixed conducting mechanism as shown in Fig. 6.7. The mixed conducting mechanism explained the microstructure evolution by electrochemical polarization of defects across the sandwich specimen under external electric field and current. Using $O_2^-/O^-$ and $V_0^{**}$ as examples, positive ionic charge carriers at the polycrystalline grain boundaries, $V_0^{**}$, are oversaturated at SC front growing $//E$ as well as the location near the cathode, forming reduced environment locally in the sandwich specimen. On the other hand, negative ionic charge carriers, $O_2^-/O^-$, oversaturated at the SC front growing $//+E$ and the anode, forming local oxidized environment, which possible oxygen precipitation resulting porous structures. This proposed mechanism explains the gradient of PL intensity and pore formations as shown in Fig. 6.5 and Fig. 6.3 (a).
Additional experiments without electric field demonstrated that inert or reducing atmospheres will enhance the grain growth. Bi$_2$O$_3$-doped ZnO was quenched from 880 °C after annealing for 4 hours in air, argon, or argon + 5% H$_2$. As shown in Fig. 6.8, average grain size of specimen annealed in air is 2.02 ± 0.17 µm. But specimen annealed in argon and argon + 5% H$_2$ have larger grain sizes of 3.47 ± 0.51 µm and 5.18 ± 0.60 µm, respectively. This result agrees with the grain growth behavior in the sandwich specimen and the proposed mixed conducting mechanism. Presumably, in the presence of ionic liquid at grain boundaries, electric field/current changes local defects concentration, further decreases the space charges at grain boundaries, and subsequently enhanced grain growth. Electric reduction also significantly enhanced grain growth near the Cathode where abnormal grain growth in polycrystalline was observed, which is further discussed in section 6.3.4.

The formation of defect gradients in the polycrystalline regions also reveals that the rate-limiting steps are defect reactions. Different from experiment setups and modelling of SOFCs where the environment oxygen partial pressures are significantly different on cathode and anode sides, this work is carried out under uniform environmental oxygen partial pressure. Using the region near specimen cathode as an example, under diffusion-control condition (in another word, the defect reaction with the environmental is fast with respect to the electric field driven diffusion), there will be minimal oversaturation of $V_{O^-}^{2-}$, which is apparently not the case in this work. Under reaction-control condition, a thin layer with oxygen partial drop will form near the surface of the cathode, and a large chemical potential
gradient of \( V_O^{**} \) will form in the bulk of polycrystalline. This agrees with the observation in the current case. Additionally, the grain growth of Bi\(_2\)O\(_3\)-doped ZnO is also reaction controlled [38]. Overall, grain boundary \( V_O^{**} \) defect reactions with either environment or the bulk are slow with respect to its diffusion, which are also reasons for the observation of electrothermal polarization of defects in this work.

The profiles of oxygen partial pressure (\( \mu_{O_2} \)), electric potential (\( \phi \)), chemical potential of ionic oxygens (\( \mu_{O^{2-}} \)), and electrochemical potential of ionic oxygens (\( \eta_{O^{2-}} \)) vs. position can be complex due to the uncertainties of boundary conditions at the polycrystalline-single crystal interfaces. By assuming the single crystal ZnO is a perfect ionic insulator and has slow oxygen diffusion, the chemical potential of oxygen is sketched following the SOFC electrochemical studies [39]. A nonlinearity is believed to exist due to the local ionic transport number (\( t_O \)) difference, which is a result of change in electronic conductivity vs. oxygen partial pressure in mixed conducting materials. Similarly, the electric potential and chemical potential of \( O^{2-} \) are also plotted. Electric potential is continuous considering the electric conducting nature of the single crystal layer. However, it is not differentiable at the interfaces due to the change of media. Similarly, the chemical potential of ionic oxygen is plotted by assuming a local equilibrium defect reaction \( O^{2-} = \frac{1}{2} O_2 + 2e^- \). The electrochemical potential of \( O^{2-} \), \( \eta_{O^{2-}} = \mu_{O^{2-}} - 2e\phi \), is also nonlinear because at region with low ionic oxygen transport number, the gradient of \( \mu_{O^{2-}} \) contributes to the electrochemical gradient in addition to the constant term at constant total current density and total conductivity[40]:
\[ \frac{\partial \eta_{O_2^-}}{\partial x} = \frac{2e}{\sigma_{tot.}} + (1 - t_o) \frac{\partial \mu_{O_2^-}}{\partial x} \]

In which \( \Delta \mu_e = 0 \), is assumed to be 0 given the same electrodes. Again, both chemical potentials and electrochemical potentials at PC-SC interfaces are physically continuous, which are simplified in the sketches.

### 6.3.4. Electric Field Effects on Grain Boundary Complexion and Cathode Textures

Metallic-like Bi IGFs have been observed at locations that are electrochemically reduced. Fig. 6.9 is a summary of the HAADF and BF images of PC-SC grain boundary growing //+E, //-E, and without E (the reference). Reference grain boundaries without E have amorphous films ~ 1 nm thick as shown in Fig. 6.9 (e, f), which is reasonable for specimens quenched from liquid phase temperature. At the single crystal grain boundary //+E, where an oxidized environment is expected, similar amorphous structure is observed (Fig. 6.9 (a, b)). However, at the single crystal grain boundary //-E, where a strong electrochemical reduction is expected, highly ordered bilayer or trilayer was observed. The high brightness at the grain boundary in the HAADF image indicates that the grain boundary is enriched with ordered Bi atoms.

The possibility of reducing the grain boundary to metallic Bi is justified by estimating the local oxygen partial pressure at the polycrystalline-single crystal grain boundary. In the estimation, the sandwich specimen is treated as serial resistors under constant current density. Estimated electric potential difference across one polycrystalline region is ~ 0.7 V. Oxygen partial pressure required to
reduce Bi$_2$O$_3$ at the annealing temperature of this work, 840 °C, is only $10^{-10} \sim 10^{-11}$ atm according to Ellingham Diagrams [41]. The electrochemical reduction at the PC-SC interface provides an equivalent oxygen partial pressure ~ 10 orders of magnitude lower. Thus, it is not surprising to observe the metallic-like grain boundary complexion.

As discussed in section 6.3.2, polarization of ionic defects exists in both polycrystalline regions. Area close to specimen cathode are also highly electrochemically reduced. Fig. 6.10 (b) shows the abnormal grains close to the cathode. More interestingly, strong textures of the abnormal grains are observed under EBSD. Fig. 6.10 (c) shows the inverse pole figure with Y axis as reference, which is the same as the nominal direction of external electric field. (11-20) is clearly identified as a strong preferred orientation under electric field and current. Other orientations like (01-10) maybe preferred as well. Similar to SC-PC grain boundary growing //E, the grain boundaries of the abnormal grains are also highly ordered. These results, again, support the mixed conducting mechanism proposed in section 6.3.3. By comparing the profiles of electric potential and electrochemical potential near the cathode and the PC-SC interfaces growing //E, it is reasonable to believe that, at least in this study, the external electric field guided the microstructure evolution through electrochemical potential, rather than electric potential directly.
6.4. Conclusions

In this study, polycrystalline - single crystal - polycrystalline (PC-SC-PC) sandwich Bi$_2$O$_3$-doped ZnO specimens were designed to study the effect of external electric field/current on the microstructure evolution. Asymmetric grain growth of SC was observed after annealing at liquid phase temperature with external electric field. Photoluminescence of quenched specimen shows polarization of defects in PC regions and ionic blocking SC region. Enhanced grain growths were observed at electrochemically reduced locations. This grain growth behavior was also confirmed in reduced atmosphere without external electric field. Subsequently, a mixed conducting mechanism was proposed that explains the microstructure evolution including enhanced SC grain growth, pore formation, and abnormal grain growth. Grain boundary reduction and complexion transitions happened at locations that are electrochemically reduced. Specifically, ordered metallic-like grain boundaries with 2 – 3 atomic layers of enriched Bi were observed. In the current study, external electric field is believed to affect microstructure evolution electrochemically.

Chapter 6, in part, is a reprint of manuscript “Electric Field Effect on Grain Growth and Grain Boundary Complexion” J. Nie, and J. Luo, in preparation. The dissertation author was the primary investigator and author of this paper.
Figure 6.1 (a) Cross-sectional SEM micrograph of Bi$_2$O$_3$ doped ZnO polycrystalline-single crystal-polycrystalline sandwich specimen annealed at 700 °C for 9 hours after densified using SPS. (b, c) High magnification SEM micrographs of the single crystal-polycrystalline interfaces on two sides of the single crystal. Aligned holes are circled in (b) and (c) and used to label the original single crystal surfaces.
Figure 6.2 (a) Cross-sectional SEM micrograph of Bi$_2$O$_3$ doped ZnO polycrystalline-single crystal-polycrystalline sandwich specimen quenched from 880 °C after annealing for 4 hours without any external electric field/current. (b, c) High magnification SEM micrographs of the single crystal-polycrystalline interfaces on two sides of the single crystal. Black dashed lines indicate the original single crystal boundaries. The single crystal growth on two sides are similar. Average single crystal growths on both sides are quantitively measured as shown in Fig. 6.4 (b).
Figure 6.3 (a) Cross-sectional SEM micrograph of Bi$_2$O$_3$ doped ZnO polycrystalline-single crystal-polycrystalline sandwich specimen quenched from 840 °C after annealing for 4 hours with constant current density $J = 6.4$ mA/mm$^2$. Direction of the external electric field was from right to left as labelled on the micrograph (b) High magnification SEM micrograph and (c) EBSD Euler mapping of the single crystal growth parallel to the negative electric field direction (//-$E$). (d) High magnification SEM micrograph of the single crystal growth parallel to the electric field direction (//+$E$). Black or yellow dashed lines indicate the original single crystal boundaries. The single crystal growth //-$E$ is significant larger than the growth //+$E$. Average single crystal growths on both sides are quantitively measured as shown in Fig. 6.4 (b).
Figure 6.4 (a) Electric potential vs. annealing time of $\text{Bi}_2\text{O}_3$-doped ZnO sandwich specimen and single crystal with current density $J = 6.4$ mA/mm$^2$ at 840 °C. (b) Average single crystal growth (both sides) of $\text{Bi}_2\text{O}_3$-doped ZnO sandwich specimen annealed at 880 °C without electric field/current (SC w/o E) and sandwich specimen annealed at 840 °C with constant current density $J = 6.4$ mA/mm$^2$ (SC/-E and SC/+E).
Figure 6.5 (a, b) Average photoluminescence (PL) intensity vs. wavelength of Bi$_2$O$_3$-doped ZnO sandwich specimen annealed with current density $J = 6.4$ mA/mm$^2$ at 840 °C. PL spectroscopy was recorded by averaging the intensities in boxes of 30 µm x 1.5 µm at different locations as shown in (c, d), respectively. (c, d) Mapping of PL at 526 nm of Bi$_2$O$_3$-doped ZnO sandwich specimen annealed with current density $J = 6.4$ mA/mm$^2$ at 840 °C. In the polycrystalline region on the anode side, locations near the single crystal-polycrystalline interface have higher PL intensity. Grown part of single crystal has lower PL intensity than the adjacent polycrystalline region, higher PL intensity than the polycrystalline region on the negative cathode side.
Figure 6.6 Average photoluminescence (PL) intensity vs. wavelength in the polycrystalline region on the anode side of Bi$_2$O$_3$-doped ZnO sandwich specimen annealed with current density $J = 6.4$ mA/mm$^2$ at 840 °C at different locations: (a) near the single crystal-polycrystalline interface and (b) near the anode. PL spectroscopy were recorded by averaging the intensities in boxes of 30 µm x 1.5 µm as shown in Fig. 6.5 (c). The broad PL peak in (a) was separated into peaks centered at 523 nm and 610 nm. The broad PL peak in (b) was separated into peaks centered at 505 nm and 577 nm.
Figure 6.7 (a) The schematic of defects polarization in a polycrystalline – single crystal – polycrystalline (PC-SC-PC) sandwich specimen under external electric field, where grain boundaries in two PC regions are mixed conducting, and SC is electric conducting. $O^{2-}/O^-$ and $V_{O}^{--}$ pairs are used as examples. (b – e) The schematic profiles of oxygen partial pressure ($\mu_{O_2}$), electric potential ($\phi$), chemical potential of ionic oxygens ($\mu_{O^{2-}}$), and electrochemical potential of ionic oxygens ($\eta_{O^{2-}}$) vs. position.
Figure 6.8 Cross-sectional SEM micrographs of Bi$_2$O$_3$ doped ZnO polycrystalline specimens quenched from 880 °C after annealing for 4 hours in (a) air, (b) argon, and (c) argon + 5% H$_2$. The measured average grain sizes of specimens annealed in air and argon are $2.02 \pm 0.17$ μm, $3.47 \pm 0.51$ μm, and $5.18 \pm 0.60$ μm, respectively.
Figure 6.9 Aberration-corrected HAADF and BF STEM images of polycrystalline-single crystal grain boundaries (a, b) \(+\ E\) and (c, d) \(-\ E\) in Bi$_2$O$_3$ doped ZnO sandwich specimen quenched from 840 °C after annealing for 4 hours with constant current density $J = 6.4$ mA/mm$^2$. (e, f) Aberration-corrected HAADF and BF STEM images of the polycrystalline-single crystal grain boundary in Bi$_2$O$_3$ doped ZnO sandwich specimen quenched from 840 °C annealing for 4 hours without electric field or current.
Figure 6.10 (a, b) Cross-sectional SEM and (c) Y-IPF EBSD micrographs of the abnormal grains near the cathode of Bi$_2$O$_3$ doped ZnO polycrystalline-single crystal-polycrystalline sandwich specimen quenched from 840 °C after annealing for 4 hours with constant current density $J = 6.4$ mA/mm$^2$. (d, e) Aberration-corrected HAADF and BF STEM images of grain boundary between an abnormal grain and other poly crystalline.
References


Chapter 7. Dissertation Summary and Research Prospects

In this dissertation, a quantitative thermodynamic model of subeutectic intergranular films and high-resolution transmission electron microscopy experiments were combined to explain the mystery of enhanced sintering in CuO-doped TiO$_2$. The first grain boundary $\lambda$ diagram was calculated to represent the thermodynamic tendency for general grain boundaries in CuO-doped TiO$_2$ to disorder. In future studies, similar or different (more rigorous and sophisticated) types of GB diagrams should be computed for other ceramic materials, which can potentially have broad scientific and technological impacts.

Motivated by the advancement of electric field assisted sintering technologies, we investigated Al$_2$O$_3$ vs. Bi$_2$O$_3$ doping effects on the flash sintering of ZnO. As an example of bulk aliovalent dopant, Al increased the specimen conductivity to promote flash sintering. The onset flash occurred as natural thermal runaway. Ultrafast field-induced migration of aliovalent cations during the flash sintering of Al$_2$O$_3$-doped ZnO were observed. On the other hand, as an example of interfacial doping at the grain boundaries, Bi$_2$O$_3$ decreased the specimen conductivity to delay the occurrence of flash sintering to higher temperatures, while it also led to a eutectic reaction and associated premelting-like grain boundary complexion transition that can abruptly increase the specimen conductivity with increasing temperature. Consequently, the onset flash was initiated by a bulk eutectic reaction at a low initial electric field ($E_{\text{initial}}$) and by premelting like grain boundary transition at an intermediate $E_{\text{initial}}$, respectively. When we further
increased $E_{\text{initial}}$, a natural thermal runaway still took place before the occurrence of interfacial and bulk transformation, as predicted by the Arrhenius extrapolation. This is the first study showing that an interfacial complexion transformation can trigger flash sintering, which suggests a new flexibility to tune the flash sintering process.

In a broader perspective, an example of low temperature, transient, interfacial liquid assisting the densification of ceramics under electric field, water-assisted flash sintering (WAFS) was developed using ZnO as a model system. At room temperature, ZnO was densified to ~98% relative density in 30 s in wet Ar + 5% H$_2$. This method can potentially be extended to consolidate other ceramic systems to achieve fast densification at extremely low furnace temperatures. Furthermore, this study suggests significant technological opportunities for energy and cost savings via exploiting and investigating new ceramic processing science through the interplay of low temperature liquid and electric fields/currents.

Advanced control of electric parameters during electric field assisted sintering also contribute significantly to the advancement of flash sintering. A two-step flash sintering method (TSFS) was developed and clearly demonstrated to improve the microstructure. This study further suggests a new direction that combines the science of conventional sintering with controllable $I(t)$ profile in flash sintering to achieve customized microstructures.

Non-thermal effect of electric field and current on solid oxide microstructures is a long-lasting scientific topic, which gains significance in recent years due to the development of field assist sintering, fuel cells, and solid-state
batteries. In this dissertation, electric field effects on grain growth of in polycrystalline was investigated in the presence of high temperature liquid phase. polarization of ionic defects in PC regions is believed to be the reason of enhanced grain growths at electrochemically reduced locations. Subsequently, a mixed conducting model was developed to qualitatively explain the asymmetry. Other microstructure structure developments including pore formation and abnormal grain growth fitted in the same model. More significantly, electrochemical reduction at the grain boundaries triggered complexion transitions. This finding opens numerous opportunities for grain boundary tailoring that cannot be easily achieved using furnace heating, dopant, or annealing atmosphere. Future studies include modelling of diffusivities of grain boundary complexions induced by electrochemical reduction and reducing the ionic resistance of grain boundaries in solid-state electrolytes.