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EXPLORATION OF THE COLD SINTERING PROCESS FOR FUNCTIONAL METAL OXIDE ELECTROCERAMICS

A Dissertation in

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by

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Abstract

Lowering the sintering temperature of electroceramics proves beneficial in numerous applications, such as co-firing with metal electrodes, suppressing volatilization of some cationic ions, or synthesizing complex composite structures, etc. The cold sintering process (CSP), a recent discovery, is one of the sintering techniques for low-temperature densifications. It uses uniaxial pressure and an appropriate solvent, promoting the pressure-solution creep between ceramic particles; densification is then completed efficiently at low temperatures in a short time. In this study, the CSP was used to densify three different types of electroceramics, yttrium-stabilized Bi₂O₃ for oxygen ion conductors, BaTiO₃ for capacitors, and (K_{0.5},Na_{0.5})NbO₃ for lead-free piezoelectrics.

Yttrium-doped bismuth oxide (BYO) is known for its high ionic conductivity of oxygen. Lowering the sintering temperature of this material might be useful to synthesize the bi-layer structure of SOFC electrolyte, which provides much higher energy efficiency. It is demonstrated that the CSP enabled densification of BYO ceramics at 300 °C. The relative density reached was ~ 90 % of the theoretical density (T.D.). The as-sintered BYO ceramic had a total conductivity > 1 mS/cm at 500 °C. The conductivity slightly increased after the annealing process. The scanning and transmission electron microscopy analysis revealed that a metastable secondary phase formed adjacent to BYO grains in the as-CSP specimens. Once annealed, the secondary phase was recrystallized and there was an associated total conductivity improvement.

The CSP work was then extended to BaTiO₃. Dense nanocrystalline BaTiO₃ ceramics are prepared at 300 °C, under a uniaxial pressure of 520 MPa for 12 h using a molten hydroxide flux (NaOH-KOH). The average grain sizes are 75-150 nm depending on the flux amount. The dielectric permittivity is 700 – 1800 at room temperature at 10⁶ Hz, with a dielectric loss, tan $\delta \sim 0.04$. The differences in permittivity and phase transition behavior are explained in terms of the intrinsic ferroelectric size effect of the $BaTiO_3$. The nanocrystalline $BaTiO_3$ ceramics still show a macroscopic ferroelectric switching *via* a hysteresis loop. The obtained dielectric & ferroelectric properties are comparable to reported values for nanocrystalline $BaTiO_3$, but at this time, these are achieved with the lowest processing temperatures ever used.

A similar approach was taken for the densification of the KNN piezoelectric ceramics. The final densities were all over 92% with the use of a NaOH-KOH transient sintering aid at approximately 200 °C, at 400 MPa within the total 2 hours of sintering time. The grain size was ~200 nm; grains were limited in coarsening at isothermal holds at these temperatures. The insulation resistance and low field dielectric permittivity were similar to conventional sintered KNN ceramics. High electric field strengths can be applied ~ 100 kV/cm, without high losses or electric breakdown, suggesting a reasonable dielectric strength. Despite these observations, these high fields did not yield high piezoelectric performance. All previous poling strategies were considered to aid the poling of the domains, but the piezoelectric properties remained low ($d_{33} < 30$ pC/N). A Rayleigh analysis showed difficulties in moving the domains, as reflected in the lower non-linear Rayleigh coefficients. A thermal annealing process improves the non-linear coeffecients along with the piezoelectric coefficients and the establishment of higher remanent polarization. These results suggest that the presence of defects in the core-region of the grain limits the domain alignment process and thereby the piezoelectric properties obtained under the present CSP. This is supported by TEM observation showing a high concentration of defects in the core of grains.

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Chapter 1

Introduction

1.1 Background and Motivation

Sintering is a processing technique that adheres a compact powder to a rigid body. This process has been utilized in ceramic manufacturing for more than 25,000 years.¹ Sintering for ceramics has become more important since their functional properties were practically explored in the mid-1900s.^{2–6} Nowadays, sintered functional ceramics are used for many applications, such as building materials, passive components in electronics, and optically transparent ceramics.



Figure 1-1: (a) Venus of Dolní Věstonice, found at the Paleolithic site Dolní Věstonice in the Moravian basin (created in 39,000-25,000 B.C.E.)⁷ (b) Ceramic potteries found at Xianrendong cave, Southern China (created 18,000 B.C.E)^{8,9} (c) Incipient Jomon pottery (10,000 B.C.E.)

Sintering of ceramics is typically performed at 1000-1500 °C (or higher for refractory materials). Such high-temperature processing leads to several technical issues. For example, current industrial standards in LTCC and/or MLCC production require the integration of conductive metals into ceramics and co-fired with ceramic components.¹⁰ The sintering process must be performed below the melting point of metal electrodes, as the diffusion of metal ions into the ceramics

degrades the desired properties of the device. Metals that have melting points above the typical sintering temperature are relatively expensive (e.g. Pt, Pd), so lowering the sintering temperature is often desirable. Typically, this is accomplished with sintering aids such as glass additives.¹¹

It has been reported that that the volatilization of materials containing volatile elements (Li, Na, K, Bi, Pb) often results in poor densification or/and deviation from the stoichiometric composition.¹² Since many of industrially important materials such as solid-state batteries and lead-free piezoelectric materials contain volatile alkali elements, lowering the sintering temperature of these materials is of interest.

Lowering sintering temperatures is done by controlling sintering parameters (e.g. initial particle size, heating rate) or using sintering aids, (e.g. adding liquid phase, applying external pressure, etc.). **Chapter 2** discusses the historical development of low-temperature sintering. In recent years, the cold-sintering process (CSP) has been utilized as a new sintering technique that can densify many types of ceramics below 300 °C with the aid of uniaxial pressure and transient liquids.^{13,14} **Figure 1-2** shows a schematic representation of CSP. In CSP, an appropriate solvent (1-20 vol. %) is mixed with an initial ceramic powder. Then, the wetted powder is pressed (20-500 MPa) and heated to the sintering temperature (25-400 °C). Under these conditions, the liquid and solid phase are uniformly distributed. Then, contact points of the two grains, where the chemical potential is higher due to the capillary force, are preferentially dissolved into the liquid phase. Finally, the dissolved ions are transported to and precipitated on the surface of the grains at the porous area. The high degree of densification produced at extremely low temperature in CPS will likely solve some of the technical issues in sintering.



Figure 1-2: Schematic evolution of a powder compact during cold sintering: Grain boundary region in dominant stages have been magnified. The figure is adapted from ref 13.

Previously, CSP studies focused on densifying alkaline molybdates^{13,15–17} or ZnO ceramics^{18,19}; a few studies on CSP for BaTiO₃ have been reported.²⁰ The reported methodology for densifying BaTiO₃ by CSP required an additional heat-treatment after CSP to attain the desired dielectric properties.²⁰ Therefore, the purpose of this dissertation is to explore the feasibility of densifying functional oxides by CSP at extreme low-temperatures. **Chapter 3, 4 and 5** demonstrate the cold-sintering of ionic conductors, dielectrics and piezoelectrics, respectively. Those functional properties are characterized, evaluated and compared to the properties processed by the conventional sintering method. Some preliminary results and remaining issues are discussed as future work in **Chapter 6**.

Chapter 2

Literature Reviews on Ceramic Sintering

This chapter discusses a brief introduction of sintering from a theoretical point of view. A comparative review of low-temperature sintering techniques is presented in **Section 2.2**. The current status of sintering techniques for each of the materials system studied in this dissertation (i.e. barium titanate, sodium, potassium niobate) will be reviewed separately in later chapters. This chapter to familiarize the reader with the opportunities cold sintering offers the electro-ceramic community.

2.1 Sintering of Ceramics

2.1.1 Thermodynamics of Sintering

The reduction of the total interfacial energy is the driving force of the sintering process. The total interfacial energy of the powder compact is defined as the product of the specific surface energy, γ , and total surface area, *A*. The reduction of the total interfacial energy during the sintering is then expressed as;²¹

$$\Delta(\gamma A) = \Delta \gamma A + \gamma \Delta A \tag{2-1}$$

The first term is ascribed to the surface energy reduction due to the replacement of solid/vapor interface to solid/solid interface caused by the densification. The second term is the reduction in the surface area of the particles associated with the particle coarsening. A schematic figure is shown in **Figure 2-1**, explaining the surface area reduction with coarsening and densification.



Figure 2-1: Basic phenomena occurring during sintering under the driving force for sintering.²¹

As is clear from Eq. (2-1), smaller initial particles have more surface area, and are thus a larger driving force in sintering. Barringer and Bowen demonstrated the effect of particle size on the sintering temperature of TiO₂. They found that well-dispersed TiO₂ nanopowders of 70-300 nm could be synthesized by the hydrolysis of titanium tetra-isopropoxide; they then densified at temperatures as low as 800 °C. Thus, nanopowders can be sintered at lower temperatures than larger particle sizes.²² Yan and Rhodes investigated the densification behavior of TiO₂ with average particle sizes of 80 and 400 nm. As can be seen in Eq. (2-4), the driving force of the densification increased five times with the use of 80 nm size particles. As a result, the sintering temperature decreased from 1200 to 800 °C (Figure 2-2).²³ The same approach has proven effective for lowering the sintering temperature of other functional oxides.^{24,25} To take advantage of the high surface area it is important that particle agglomeration and aggregation is minimized. This increases the benefit of the small initial powder, as the agglomerates create low green packing density. Thus, 100 nm to 1 μ m average particle sizes is often desirable in typical ceramic processing.



Figure 2-2: Influence of the particle size on the sintering temperature in TiO₂.²³

2.1.2 Kinetics of Sintering

As discussed in the previous section, the surface area reduction is the driving force for the densification and/or particle coarsening. These processes proceed by diffusion in the solid. The mass transport during sintering is caused by the difference in the chemical potential of the curvature (between neck and surface of the particle). It is known that multiple diffusional processes simultaneously occur in-grain, grain boundary, and at the solid/air interface, as schematically shown in **Figure 2-3**. Only diffusion that transfers the atoms from the particle volume or grain boundaries to the surface result in densification.²⁶ The activation energies are typically scaled as: $Q_s < Q_{GB} < Q_l$ where *s*, GB and *l* are surface, grain boundary and lattice, respectively.²⁷ Therefore, surface diffusion often dominates at lower temperature while grain and lattice diffusion dominate at higher temperature (**Figure 2-3**). Particle coarsening often occurs first at lower temperature upon

heating, due to the low activation energy of the surface diffusion and this process results in reduction of the driving force for densification.²⁸ Hence, it is critical to control the diffusional process to achieve the desired microstructure.



Figure 2-3: Schematic multiple diffusion path (a) and their temperature dependence (b).^{27,28}

Transport Path	Source of Matter	Sink of Matter	Densification
Surface diffusion	Surface	Neck	Ν
Lattice diffusion	Surface	Neck	Ν
Vapor transport	Surface	Neck	Ν
Boundary diffusion	Grain boundary	Neck	Y
Lattice Diffusion	Grain boundary	Neck	Y
Lattice Diffusion	Dislocations	Neck	Ν

Table 2.1: Alternate path for matter transport during the initial stage of sintering²⁹

2.2 Sintering Techniques for low-temperature densification

Many sintering techniques have been proposed and utilized for industrial & academic purposes. This chapter presents a brief review of those features and discusses the uniqueness of each technique. A chronological review of the development of low-temperature sintering technology can be found in ref. 30,31.

2.2.1 Liquid Phase Sintering

Liquid phase sintering is a widely accepted sintering technique that leads to lower sintering temperatures. An additive, such as a glass or metal oxide with a low-melting point or a metal oxide that forms eutectic with matrix ceramics is typically chosen as a sintering aid. A 0.1-10 wt% of the additive significantly enhances the densification rate and/or decrease the sintering temperature. With the existence of the liquid phase at the particle contact point, the resulting capillary force causes a compressive pressure. This is expressed as;³²

$$\Delta P \sim \frac{-2\gamma_{lv}}{\rho_l} \tag{2-2}$$

where γ_{lv} and ρ_l are the surface energy of the liquid/vapor interface and the meniscus radius of the liquid at the interface of two particles, respectively. The compressive stress increases the solubility of the solid into the liquid phase as;³²

$$c/c_0 = \exp\left(\frac{2KV_m\gamma_{l\nu}}{RT\rho_l}\right) \tag{2-3}$$

where K, V_m, R, T are the constants representing the contact area, molar volume, gas constant and temperature, respectively. Thus, the dissolution preferentially occurs at the particle contacts, and the dissolved ions are transported and then precipitated at the stress-free interface. The mass transport is much faster due to the presence of the liquid phase. Therefore, the primary requirement for the liquid phase sintering is materials having 1) an appreciable amount of liquid phase, 2) an appreciable solubility of the solids in the liquid and 3) a good wettability of the liquid on the surface of the ceramic particles.²⁹ This technology is widely used in industrial applications, such as ZnO- Bi_2O_3 , $BaTiO_3$ -TiO₂, WC-Co SiC or Si_3N_4 -glass additives.²⁷

2.2.2 Hot Press Sintering (HPS)

As the compressive pressure of capillary force exerting on the particle gives the driving force for the densification, the external pressure promotes densification.²⁷

(Total Pressure on a particle)
$$= \frac{\gamma}{\rho} + \frac{P_a(2r)^2}{\pi x^2}$$
 (2-4)

where P_a is the applied external pressure, ρ is defined as $\rho \sim x^2/4r$ (*r* and *x* are the radius of the particle and the particle contact point). The first term is the capillary force at a contact point, the same as in pressure-less sintering. The second term is associated with external pressure at a contact point. The additional driving force in the second term allows the densification to become more efficient than pressure-less sintering.³³ For example, the sintering temperature of BeO was decreased from 1800 to 1600 °C by applying 2000 psi of uniaxial pressure.²⁹ As each pellet needs to be sintered in the die, hot-presseing is not suitable for mass production. Thus, it is mainly used for special applications such as refractory ceramics (carbide, nitride), or transparent ceramics.

2.2.3 Field-Assisted Sintering Technology / Spark Plasma Sintering (FAST/SPS)

FAST/SPS can be categorized in pressure-assisted sintering. The uniaxial pressure is applied to the ceramic green body in the graphite die during FAST/SPS. The external pressure promotes diffusion processes at lattice and grain boundaries, enhancing the densification rate. The main difference from HPS is that FAST/SPS utilizes D.C. pulsed current through the sample applied via a graphite die, realizing an extremely high heating rate. Similar to the conventional fast firing technique,³⁴ it also gives higher driving force of the densification in SPS system.^{31,35}

A complete understanding of the densification mechanisms in FAST/SPS has not yet been achieved. Local joule heating,³⁶, spark discharge,³⁷ and other effects³⁸ are thought to contribute to densification in SPS. More studies are needed however, as the semi-closed experimental system and fast heating with temperature gradient make it difficult to study FAST/SPS by either theoretical (Modeling) and experimental (in-situ observation) situations.^{38,39} Currently, FAST/SPS are used in a number of different materials: refractory metals, ceramics and their composites, and nanostructured materials and transparent materials.³¹

It was recently demonstrated that SPS can densify some materials system that can't be conventionally sintered because of their lower decomposition temperatures (e.g. copper acetate diamine).⁴⁰ Authors claimed that uniaxial pressure stabilized the low-temperature phase and increased the decomposition temperature. The efficient densification of SPS led to sintering temperatures lower than the decomposition temperature. Thus, the SPS method may make it possible to explore new groups of materials whose properties were not previously reported because of the difficulty of sintering in bulk bodies.

2.2.4 Hydrothermal Sintering (HS) / Hydrothermal Hot-Pressing (HHP)

Hydrothermal sintering, or hydrothermal hot pressing, is a processing technique that consolidates particles with continuous uniaxial pressure under hydrothermal conditions. It mimics the lithification of sedimentary rock in nature.⁴¹ Solidification under hydrothermal conditions was reported in a study of cement by Roy in 1972.⁴² Later, this technique was developed and investigated by some research groups in Japan.^{41,43} In recent years, the Bordeaux group has further

developed the HP/HHP method from both the fundamental and application sides. However, the sintering mechanism in HHP is complicated. Roy *et al.* concluded that the reduction in the porosity of Portland cement was due to the pore-filling of the low-volume phase by hydration reaction.⁴² Ndayishimiye *et al.* suggested that densification in the silica system started with the polycondensation of the siloxane bonds followed by the dissolution-precipitation reaction with the solvent (water, NaOH).^{44,45} Nishioka, *et al.*, on the other hand, suggested the initial stage of the sintering of borosilicate glass was governed by the viscous flow followed by the dissolution precipitation reaction in the intermediate-final stage of sintering.⁴⁶ It seems that even though the instrumentation is the same or quite similar, the densification mechanism of the HHP is quite different depending on the materials system. More complete studies or comparative studies are required to understand the actual mechanism and global underlining phenomena.

2.2.5 reactive Hydrothermal Liquid Phase Densification (rHLPD)

rHLPD is a new sintering technique for low-temperature densification introduced by a group at Rutgers.⁴⁷ In rHLPD, a porous ceramic matrix is first fabricated by firing the green pellet at a little lower than the optimum sintering temperature. At this stage, the preform of the ceramic body has interconnected pores (open pores), but is still rigid, owing to the necking formed between particles. The fired ceramic is then infiltrated with an appropriate solution in the hydrothermal vessel. The hydrothermal reaction between the preform and solution converts it to the desired product. It has been reported that various materials such as BaTiO₃, Ca(PO₄)F₂ and CaC₂O₄ can be densified at temperatures below 400°C using rHLPD.⁴⁷ One follow-up study recently reported promising electrical properties in BaTiO₃ sintered by this method.⁴⁸ Though this method requires a relatively high firing temperature to synthesize the pre-form, it is a promising sintering method for synthesizing complex ceramics at low-temperatures.

2.2.6 Cold Sintering Process (CSP)

The cold sintering process (CSP) is a recently developed low-temperature sintering method, using uniaxial pressure (100-500 MPa) and transient liquid (1-10 vol%) at temperatures below 300 °C.^{18,49–52} As introduced in **Chapter 1.1.**, it is believed that densification at such a low-sintering temperature is driven by the pressure-solution creep. The dissolution of the ceramic particles into the transient liquid would preferentially occur at the contact point of particles on which the local pressure concentrates. The dissolved ions ares transported by the liquid along a chemical potential gradient, and precipitated on to the ceramic particle where chemical potential is low.^{53–55} **Table 2-2** summarizes the material systems reportedly densified by CSP. There are more than 100 inorganic materials reported to be densified by CSP. The low-sintering temperatures achieved in CSP allows ceramics to be co-fired with polymers or non-noble metals previously considered difficult due to their chemical stability at high-sintering temperatures.^{56,57} More recently, a new type of ceramic (matrix) - polymer (additive at GBs) composite was designed and successfully fabricated by CSP.^{58–61} It was found that the addition of polymer layers at ceramic grain boundaries significantly modified the electrical and dielectric properties.

Binary		Ternary		Quaternary	Quinary
MoO ₃	PbTe	Li ₂ CO ₃	Na ₂ WO ₄	LiFePO ₄	LiAl _{0.5} Ge _{1.5} (PO ₄) ₃
^{a)} WO ₃	Bi ₂ Te ₃	CsSO ₄	LiVO ₃	LiCoPO ₄	$Li_{0.5x}Bi_{1-0.5x}Mo_xV_{1-x}O_4$
V_2O_3	NaCl	Li ₂ MoO ₄	BiVO ₄	KH_2PO_4	^{c)} Na ₃ ZrSi ₂ PO ₁₂
V_2O_5	ZnTe	$Na_2Mo_2O_7$	AgVO ₃	$Ca_5(PO_4)_3(OH)$	$^{f)}Li_{13.9}Sr_{0.1}Zn(GeO_4)_4$
ZnO	AgI	$K_2Mo_2O_7$	Na ₂ ZrO ₃	(Li _{0.5} Bi _{0.5})MoO ₄	
Bi ₂ O ₃	CuCl	ZnMoO ₄	BaTiO ₃	^{b)} Pb(Zr,Ti)O ₃	
CsBr	ZrF_4	$Gd_2(MoO_4)_3$	NaNO ₂	e)CsH2PO4	
MgO	ZrO_2	Li_2WO_4	$Mg_2P_2O_7$		
^{a)} CuO	^{a)} MnO	$^{a)}Bi_2WO_6$	^{d)} γ-AlOOH		
^{d)} γ -Al ₂ O ₃	$^{c)}CeO_2$				

Table 2-2: Selected material systems that has been sintered by CSP

Most of the materials shown are reported in the supplementary file of ref. ⁵³. And some materials are added according to following publications; a): ref. ⁶² b): ref. ⁶³, c): ref. ⁵², d): ref. ⁴⁹, f): ref. ⁹⁹

2.2.7 Brief Summary

As reviewed in **Sections 2.2.1-2.2.6**, a number of sintering techniques have been proposed and developed. A primary driving force of the densification needed in sintering is the reduction of the surface energy of the particles. New sintering techniques utilize an additional driving force (e.g. external pressure, use of liquid phase) in order to lower the sintering temperature. **Figure 2-4** shows the schematic experimental instrumentation of SPS, HHP, rHLPD and CSP. It is noted that HHP and rHPD are performed in closed vessel, so that water can exist in the liquid form above 100 °C. In contrast, CSP occurs in an open systems, so that liquid evaporates upon heating. Therefore, the thermodynamical conditions in a CSP systems dynamically change with time, while HHP and rHPD are more static. The main difference of rHLPD from HHP is the use of a pre-formed pellets with a larger amount of liquid content. As a result, densification is driven by the crystal growth in rHLPD, while it is driven by pressure-solution creep or viscous flow in HHP. The difference in these instrumentation and densification mechanism are summarized in **Table 2-4**.



Figure 2-4: Experimental setups for FAST/SPS (a), HHP (b), rHLPD (c), and CSP (d). Figures are reproduced from ref. 30,64

2 and 2 et Characteristics of 10 () temperature sintering teening tees				
Sinteirng Technique	Pressure	Liquid	System	Densification mechanism [*]
Solid State	N	N	Open	Surface energy reduction
Liquid Phase	Ν	Y	Open	Capillary force
HPS	Y	Ν	Open	External pressure
FAST	Y	Ν	Open	External Pressure, Rapid heating, Local joule heating, Spark discharge
HS/HHP	Y	Y	Close	Solution-Creep, Viscous flow
rHLPD	Y	Y	Close	Crystal growth
CSP	Y	Y	Open	Solution-Creep, Crystal growth

 Table 2-3:
 Characteristics of low-temperature sintering techniques

* Surface energy reduction should exist as a driving force for all the techniques. The additional driving force that is specific for each technique are listed for the low-temperature sintering techniques

Chapter 3

Doped Bismuth Oxide^a

Commensurate with the goals of this dissertation, the author will consider the application and material science and material physics behind different electroceramic systems. All of these materials have their own unique characteristics. In this chapter, the author will consider an oxygen ionic conductor. Developing a high-density ceramic requires the optimized performance of ionic transport from grain to grain. In cold sintering, low temperatures limit coarsening and high defect densities in grains and grain boundaries limit the mobility of the ions. Therefore, this dissertation explores the processing conditions, microstructural analysis and electric properties of a model ionic conductor, yttrium-doped bismuth oxide.

3.1 Introduction

Solid Oxide Fuel Cells (SOFC) are efficient devices that convert chemical to electrical energy.⁶⁵ These devices are already commercialized, but it is desirable to lower their operation temperature for faster cycles, larger resilience against degradation rates and lower operating costs.^{66,67} Thus, continuous efforts have been made to realize the Intermediate temperature (IT, 650-800 °C) and Low-temperature (LT, < 650 °C) SOFCs technology.^{67–69}

Yttria-stabilized zirconia (YSZ) is the most common electrolyte for the SOFC because of its high transference number (ratio of ionic conduction to total conduction) and chemical stability at high temperature. However, the relatively low conductivity of YSZ requires the operation temperature higher than 900 °C. Alternative candidates were investigated and discussed for the

^a Portions of this chapter have been reproduced from: K. Tsuji, T.H. de Beauvoir, A. Ndayishimiye, K. Wang, C. A. Randall, "Cold Sintering of yttria-stabilized cubic bismuth oxide: conductivity and microstructural evolution of metastable grain boundaries with annealing", *J. Appl. Phys.*, **128** (2020) 215104. DOI: 10.1063/5.0014287.

SOFC electrolyte.⁷⁰ Doped-ceria is regarded as a potential electrolyte material for both its higher conductivity and relatively low material cost. One of the key challenges of the doped-ceria is its mixed electronic-ionic conductivity in reducing atmospheres, due to the partial reduction of cerium. The electronic leakage current is particularly problematic for short-circuiting the cell. Bismuth-based compounds also represent an interesting group of materials for the IT-SOFC electrolyte due to their high-conductivity.^{71–74} The cubic structure of undoped Bi₂O₃ (δ -Bi₂O₃) is a highly defective structure that has two partially occupied sites for oxygen atoms.⁷⁵ The undoped δ -Bi₂O₃ indeed possesses the highest oxygen conductivity among the oxide electrolytes ever reported above 730 °C (**Figure 3-1(a**)).^{71,76} The δ -Bi₂O₃ structure is stabilized by rare-earth doping (Y, Er, Dy) while maintaining high ionic conductivity.^{72,76,77} Unfortunately, these materials also have potential issues, such as the reduction to Bi metal and long-term chemical stability in the operating temperature.^{78,79}



Figure 3-1: (a) Temperature dependence of ionic conductivity in different oxides. Figure reproduced from ref.⁸⁰. Conductivity of the undoped Bi₂O₃ was taken from ref.⁸¹. Crystal structure of Bi₂O₃, high-temperature δ -form (b)⁸² and low-temperature α -form, (c)⁸³ drawn by VESTA.⁸⁴. Red and purple balls represent oxygen and bismuth atoms respectively. In Figure (b), all possible oxygen sites are shown. The detailed local distribution of oxygen is explained in ref.⁸².

With such limitations of material properties, the bi-layer structure of multiple electrolytes has been investigated. For example, Wachsman *et al.* fabricated SOFC devices with a bilayer of CeO₂/doped-Bi₂O₃ electrolyte (i.e. (anode, fuel)|(Ceria/doped-Bi₂O₃) |(cathode, air).^{85,86} In this structure, the doped-Bi₂O₃ on the cathode side is structurally stable, because it is blocked from the reducing atmosphere of the anode by the ceria layer. On the other hand, the transference number of doped-Bi₂O₃ is so high that it blocks the electronic current from the ceria and selectively transports only the oxygen ions. The authors demonstrated high power densities (~2 W·cm⁻² at 650 °C) in prototyped devices, thereby showing promise for future IT-SOFCs.⁸⁷

Looking at this promising concept from a processing point of view, it would be ideal to fabricate in a single firing process.⁸⁸ The potential problem in such cases is that each composite material shrinks at a different temperatures and rates during the firing process, resulting in the formation of cracks and/or warpage distorting the desired planar stacks.⁸⁹ For example, bismuth compounds are usually sintered at 900-1100 °C, while ceria is usually sintered at 1400 °C. Therefore, if they are sintered together as a bilayer, the bismuth compounds will be sintered first, and a strain will be created at the interface of two electrolytes.

The Cold Sintering Process (CSP) is a recently reported sintering method that sinters many materials, such as battery materials or many oxides, mainly at temperatures below 300 °C.^{18,49–52} It is thought that the mechano-chemical effect plays a role in reducing the sintering temperature.^{53–55} Thanks to the extremely low temperature and similar sintering window for a wide range of materials, it has already been proven that CSP is an effective approach to synthesize composite structures, as well as cofiring of ceramics/metal electrodes in multilayered devices.^{90,91} The authors also recently reported that CSP can be used to densify undoped bulk ceria ceramics at around 350°C.⁹² Considering these recent results, CSP could potentially be a useful processing approach for co-firing SOFC devices at lower temperatures.

This work aims to see the feasibility of low-temperature densification of the rare earth doped-bismuth oxide by CSP and evaluate its essential properties. The yttrium doped bismuth oxide ceramics were sintered at 300 °C using acetic acid as a transient solvent to drive densification through the CSP dissolution and precipitation mechanism. The chemical reaction in CSP caused a secondary phase, which resulted in the grain boundary resistance. The relationship between recrystallization and respective changes in grain and grain boundary resistance has been discussed extensively.

3.2 Experimental Procedures

Polycrystalline $Bi_{1.5}Y_{0.5}O_3$ (yttria-stabilized bismuth oxide, BYO) specimens were fabricated by the conventional solid-state route. The stoichiometric ratio of α -Bi₂O₃ (Sigma-Aldrich, 99.9%) and Y₂O₃ (Alfa Aesar, 99.99%) powders were mixed and ball-milled in ethanol with ZrO₂ media for 24 hours. The resultant slurry was dried in the oven at 120 °C and calcined at 800 °C for 16 h. The powder was ball-milled again for 24 h prior to the cold sintering. Then, 15 wt% of 1M acetic acid was added to the ball-milled powder and mixed with mortar and pestle. Then, powders were uniaxially pressed at 420 MPa and heated at 300 °C for 2 h. After the heater was turned off, the pressure was released when the die temperature reached 50 °C. The density was measured by the Archimedes' method.

Phase purity was investigated by X-ray diffraction (XRD, Empyrean, PANalytical). XRD was performed in the powder form by crushing the sintered pellet. The theoretical density of the powder was calculated from the diffraction peaks. The surface area of the initial powder and the cold-sintered pellet was measured by an N₂ gas molecule adsorption with Brunauer–Emmett–Teller (BET) theory (ASAP 2020 Automated Surface Area and Porosimetry System). The sample's microstructures were observed by Scanning Emission Microscopy (FEI Nova NanoSEM 630) on

fracture surfaces. Thermogravimetric analysis (TGA) was performed with a heating rate of 5 K/min (SDT Q600, TA Instruments). The specimen was cut into small pieces (~25 mg) and TGA was performed in the pellet form. The transmission electron microscope (TEM) samples were prepared by the Focused Ion Beam (FEI Helios NanoLab 660 FIB) system and the TEM analysis was done by FEI Talos F200 ×. For the electrical measurements, 80 nm thickness of platinum and gold electrodes were deposited by sputtering on both sides of BYO ceramics. Electrical impedance was measured from 300 °C to 650 °C with a temperature step of 25 °C, in a computer-controlled furnace with a Solartron ModuLab XM impedance analyzer from 10^{-1} to 10^{6} Hz. Some inductance responses at the high frequency were removed. During the impedance measurement, temperature increased approximately 10 °C/min, and a hold of 4 min was implemented before the measurement to stabilize temperature in the furnace.

3.3 Experimental Results

3.3.1 Densification

Figure 3-2 shows the effect of sintering temperature on the relative densities of BYO ceramics. The relative densities increased with sintering temperature. The relative density of the as-CSP pellet was $88\pm3\%$ of theoretical density (8.12 g/cm^3) at 300 °C of the sintering temperature, which was the maximum temperature for the experimental setup used in this study. Although it is not perfectly densified, some literature reported excellent ionic conductivity with similar values of relative densities.^{93,94} Bismuth oxide is known to dissolve in acetic acid at around 100 °C through forming bismuth acetate as an intermediate compound.⁹⁵ The densification in CSP is facilitated by the dissolution-precipitation of ceramic particles with an aqueous solution. In our system, dynamic surface reactions enabling low temperature sintering may be similar to those previously described

in the ZnO-acetic acid system.⁹⁶ In general, the sintering process is often driven by surface energy reduction.⁹⁷ BET surface area was indeed reduced from $3.8 \text{ m}^2/\text{g}$ (initial powder) to $1.4 \text{ m}^2/\text{g}$ (sintered pellet) as densification proceeded.



Figure 3-2: Effect of sintering temperature on the relative densities of BYO ceramics. CSP was conducted under 420 MPa of uniaxial pressure and 2 h of dwell time.

3.3.2 Impedance Measurement

Figure 3-3(a) shows the temperature dependence of the total conductivities, σ_T , of assintered BYO ceramics. The ionic conductivity is described by the following well-known equation;⁹⁸

$$\sigma_i = \sum_j q Z_j n_j \mu_j \tag{3-1}$$

where q, Z_j , n_j , μ_j , E_a , k and T are the elementary charge (1.602×10⁻¹⁹ C), the charge number, carrier concentration, carrier mobility, activation energy, Boltzmann constant, and temperature, respectively. In the case where one carrier is dominant, Eq. (3-1) can be simplified as;

$$\sigma_i = \sigma_0 / T \exp(-E_a / kT) \tag{3-2}$$

where σ_0 is the pre-exponential factor. For ceramic materials, the total resistance includes all electrically inhomogeneous elements.

$$1/\sigma_T = \sum_i t_i / \sigma_i A_i \tag{3-3}$$

where *i* is electrical components in the sample such as grains, grain boundaries, secondary phase and electrode interface. t_i and A_i are thickness and area of each component. Each electrical component reacts (relaxes) at a certain frequency in the applied a.c. field. Therefore, the a.c. field is often used for the conductivity measurement as it distinguishes each dielectric relaxation. The relationship among total conductivity, d.c. conductivity and frequency dependent part of a.c. conductivity is expressed as follows;⁹⁹

$$\sigma_{a.c.}(\omega) = \sigma_{d.c.} + B\omega^s \tag{3-4}$$

The d.c. resistance is the summation of the all-electrical components. Thus, in the case that grain and grain boundary resistance dominates total resistance, total conductivity can be rewritten as follows;

$$1/\sigma_T = (1/R_g + 1/R_{GB})t_T/A_T \approx 1/\sigma_{d.c.}$$
(3-5)

The frequency dependence of the conductivity is shown in **Figure 3-3(a-2)**. The lowfrequency part of the **Figure 3-3(a-2)** is extrapolated for $\sigma_{d.c.}$ and σ_T . Activation energies were calculated from **Eq. (3-2)** to be 1.21 ± 0.02 eV (for T < 550 °C) and 0.86 ± 0.05 eV (for T > 550 °C). The transition temperature (T_i) in activation energy has been explained in terms of the volumetric expansion,⁷² or order-disorder transition.¹⁰⁰ The obtained E_a is in good agreement with reported values for oxygen conduction in a doped bismuth oxide system.^{76,100,101} This indicates that the dominant conduction mechanism in the as-CSP BYO is the same as reported. However, the total conductivity of as-CSP BYO ceramics reached ~ 2×10^{-3} S/cm around 500 °C, which is still lower than that of conventionally sintered BYO ceramics ($\sigma_T \sim 10^{-2}$ S/cm, dots line in **Figure 3-3**).³⁶

It is noted that total conductivity slightly increased after the first impedance measurement cycle as shown in Figure 3-3(b) and Figure 3-4. The specimens could be "heat-treated" as the temperature range of the measurement (up to 650 °C) is higher than the sintering temperature (300 °C). Similar observations have been observed in previous CSP work.^{51,102} In such cases, relatively low conductivity was observed due to a low crystalline metastable phase, which formed via the dissolution-precipitation process during CSP. The conductivities were significantly improved by the high-temperature annealing, owing to recrystallization of the metastable phase.^{51,102} Similarly, in this work, the secondary phase may have also formed during CSP, and partially blocked the ionic conduction. The secondary phase was likely recrystallized during the high-temperature impedance measurement, providing a higher conductivity. This process will be discussed in the later section, including other possible causes of the change in the conductivity. Impedance measurements were repeated 5 times, and no significant changes were observed after the 1st cycle. It should be noted that relative density increased by only 2-3 % after the high-temperature impedance measurement. It is then reasonable to assume that the high-temperature electrical measurement did not affect the degree of the densification. The higher conductivity after the 1st cycle of the impedance measurement should be related to the other factors. Hereafter, the BYO ceramic after the 1st cycle of impedance measurement is called "annealed BYO". The conductivities of the cold-sintered and the annealed BYO are compared with the reported values in Table 3-1.


Figure 3-3: Temperature and frequency dependence of conductivities in as-CSP (a) and Annealed (b) BYO ceramics. The a.c. dependence in some of (b-2) was so small below 400 °C that the data is not fitted.



Figure 3-4: Temperature dependence of total conductivity of a typical cold sintered pellet. The solid and dashed lines represent the conductivity of conventionally sintered BYO ceramics reported by *Jiang *et al.*⁷⁹ and **Takahashi *et al.*⁷⁶

Sintering Temp. (°C)	Relative Density (%)	Conductivity at 500 °C (S/cm)	Ref.
870	>95	~10 ⁻²	103
845-930	N.A.	~10-2	79
300	88	6×10 ⁻³	This Work
$300 + 650^{*}$	91	2×10-3	This Work

Table 3-1: Summary of sintering temperature, relative density and conductivity in $Bi_{1.5}Y_{0.5}O_3$ ceramics.

* 650 °C is associated with the annealing effect during the impedance measurement

Figure 3-5(a) shows the complex impedance plot of the as-CSP and annealed BYO ceramic at 400 °C. Both as-CSP and annealed BYO ceramics show two semi-circles corresponding to grain and grain boundary (or secondary phase at grain boundary) impedance. The experimental data sets were well-fitted with two parallel *RC* circuit elements based on the so-called brick-layer microstructural model.^{104,105} A constant phase element (CPE) component is used to describe an imperfect capacitor.¹⁰⁶ R_1 and R_2 were ascribed to R_g and R_{GB} and scaled by the geometric factor to be easily compared with total conductivity in **Figure 3-3**. The calculated total conductivity from

summation of R_g and R_{GB} ($\sigma_T = t_s/(R_g + R_{GB})A_s$) corresponds to the d.c. conductivity calculated from the Jonscher's law shown in **Figure 3-3**. The temperature dependence of R_g and R_{GB} is shown in **Figure 3-5(b)**. As-CSP BYO ceramic shows the same order of R_g and R_{GB} for the measured temperature range. After annealing, R_{GB} became much smaller than R_g for most of the temperature range, while R_g also became smaller. Therefore, the enhanced total conductivity in **Figure 3-3** is owing to the decrease of both R_g and R_{GB} during annealing. Activation energies for each component are summarized in **Table 3-2**. The grain conductivity and its activation energy remained similar. The larger change in T_i and E_a for grain boundary resistance at high-temperature indicates that microstructure at grain boundary (e.g. secondary phase, stoichiometry, crystallinity) was modified during annealing. These changes, especially for the grain boundary, are discussed later.



Figure 3-5: (a) complex impedance plot at 400 °C and (b) temperature dependence of grain and grain boundary resistance of as-CSP and annealed BYO.

_		As-CSP	A	Annealed		
_	$T < T_{i}$	$T_i < T$	$T < T_i$	$T_i < T$		
E_{a} (Total)	1.21(2)	0.86(2)	1.19(2)	0.67(5)		
E_{a} (Grain)	1.38(2)	-	1.18(10)	-		
E_{a} (GB)	1.11 (3)	1.07(4)	1.16(9)	0.30(2)		

 Table 3-2: Activation energies of total, grain and grain boundary conductivities of as-CSP and annealed BYO at high- and low-temperature

* T_i is determined to be 550 °C for CSP and 450 °C for annealed ceramics, based on the best linear fitting. The difference is associated with the compositional change due to secondary phase formation.

** Grain resistances do not show a clear transition point. Thus, E_a for high temperature are not reported.

3.3.3 Structural Analysis

Figure 3-6 shows powder refined X-ray diffractograms. The initial powder clearly shows the δ -Bi₂O₃ crystal structure. No secondary phase is evidenced after CSP, but the peak widens. A secondary phase appeared in the annealed BYO, which is identified as the BYO rhombohedral crystal structure. It is often seen as a result of a phase transformation from cubic δ -Bi₂O₃ resulting from long-term annealing (>72 h) below 650 °C.^{79,107,108} The refined crystallite sizes from the diffractograms were 70, 23, and 100 nm for the calcined powder, as-CSP and annealed BYO respectively. These results indicate a partial dissolution of BYO particles during CSP, precipitated as low-crystalline secondary phase or nanocrystalline grains, leading to a decreased crystallite size (70 nm \rightarrow 23 nm). The skeletal density measured by He-pycnometry evolved from 7.92 g/cm³ (initial powder) to 7.72 g/cm³ (as-CSP). The decrease in the skeletal density may be ascribed to the mix of crystalline/amorphous phases¹⁰⁹ in as-CSP BYO ceramics, that cannot be obviously detected by XRD. The amorphous phase recrystallized during the annealing process as evidenced by the increased crystalline size to 100 nm. When BYO powder compact was fired at 650 °C for 5 h without CSP process (i.e. in the absence of the low crystalline phase), the amount of the rhombohedral phase was less significant (**Figure 3-7**). Therefore, it is reasonable to assume that rhombohedral phase in the annealed BYO resulted from the low crystalline phase that formed in CSP.



Figure 3-6: XRD patterns of calcined BYO powder, as-CSP BYO ceramics, and annealed BYO ceramics. All diffractions were measured in the powder form. Peak positions are shown on the bottom for cubic (upper) and rhombohedral (lower) phase of BYO.



Figure 3-7: XRD patterns of the BYO ceramics prepared by conventional solid state sintering at 650 °C (a), and CSP followed by the annealing at 650 °C (b). Peak positions are shown on the bottom for cubic (upper) and rhombohedral (lower) phase of BYO.

As-CSP BYO shows a well-packed microstructure with minor porosities in **Figure 3-8(a)**. It consists of large faceted grains (~500 nm) and needle-like small grains (< 100 nm) (**Figure 3-8(b**)). It is believed that the larger grains come from the initial powder and the smaller grains resulted from the precipitation during the CSP. The low magnification TEM micrograph (**Figure 3-8(c**)) also finds the microstructure consisting of large grains and small precipitates with some porosity. An obvious grain boundary is not seen in **Figure 3-8(c**). High magnification TEM micrograph in **Figure 3-8(d**) shows the presence of small precipitates at intergranular areas. These small precipitates (< 10 nm) are likely to be poorly crystalline solids as they are consistent with the broader peak in XRD (**Figure 3-6**) and the lower He-pycnometry density previously discussed. The segregation of Bi and Y was not observed in STEM-EDS mapping (**Figure 3-9**).

Figure 3-8(e-h) show the microstructure of the annealed BYO ceramics. Though there was no significant relative density change of the ceramic before and after the annealing (88% and 90 % of T.D. for as-CSP and annealed BYO respectively), some coarser grains (>1 μ m) were observed (**Figure 3-8(e)**). The platelet-like grains observed in **Figure 3-8(e,g)** are also characteristic of the BYO rhombohedral phase,¹¹⁰ detected by XRD. The most noticeable change following the annealing step is the disappearance of the small precipitates, (**Figure 3-8(f,g**)) and the formation of flat grain boundaries (**Figure 3-8(h**)). The higher number of interfaces due to the presence of nanosized precipitates, as well as the low crystallinity of grain boundaries is consistent with high R_{gb} observed in impedance measurement of as-CSP BYO. Nanosized precipitates probably merged into large grains during high-temperature annealing following an Ostwald ripening mechanism.¹⁰⁹ The grain coarsening and the formation of flat grain boundaries, resulting from the annealing step, contribute to the enhanced electrical properties.



Figure 3-8: Microstructure of as-CSP(a-d) and annealed BYO(e-h). (a,e) fracture surface with low-magnification SEM, (b,f) fracture surface with high-magnification, (c,g) typical microstructure of polished surface with TEM, (d,h) grain boundary microstructure.



Figure 3-9: Elemental mapping of the as-CSP BYO ceramics.

3.4 Discussion

The improvement in the grain and grain boundary resistance after the annealing is discussed based on the structural and microstructural analysis. The grain and grain boundary resistivity used in **Figure 3-5** ceramics are;

$$\sigma_{\rm g}^{\rm app} = L/R_{\rm g}A(=1/\rho_{\rm g}^{\rm app}) \tag{3-6a}$$

$$\sigma_{\rm GB}^{\rm app} = L/R_{\rm GB}A \left(= 1/\rho_{\rm GB}^{\rm app}\right) \tag{3-6b}$$

where *A* and *L* are electrode area and sample thickness. ρ_g^{app} and ρ_{GB}^{app} are the apparent grain and grain boundary resistivity. These are often used to describe the grain and grain boundary conductivity. It is important to recall the true grain and grain boundary resistivity defined as follows; ^{104,111,112}

$$\rho_{\rm g}^{\rm true} = \frac{R_g A}{L - (n-1)\delta_{GB}} \approx \left(\frac{R_g A}{L}\right) = \rho_{\rm g}^{\rm app} \ (L \gg \delta_{\rm GB}) \tag{3-7a}$$

$$\rho_{GB}^{\text{true}} = \frac{R_{GB}A}{\delta_{GB}} \left(\frac{d_g + \delta_{GB}}{L}\right) \approx \left(\frac{R_{GB}A}{L}\right) \left(\frac{d_g}{\delta_{GB}}\right) = \rho_{GB}^{\text{app}} \left(\frac{d_g}{\delta_{GB}}\right)$$
(3-7b)

where d_g and δ_{GB} are the average grain size and grain boundary thickness, respectively. *n* is defined as the number of the grain boundary ($\approx L/d_g$). As can be seen, ρ_g^{true} is approximately the same as ρ_g^{app} because the total volume of grains is nearly the same as the sample dimension. On the other hand, grain boundary resistance cannot be scaled by sample geometry, because the actual scale of the grain boundary is much smaller than the sample geometry. This results in a discrepancy between ρ_{GB}^{true} and ρ_{GB}^{app} by a factor of d_g/δ_{GB} as shown **Eq. (3-7b)**. The calculated ρ_{GB}^{app} was 2462 and 254 Ω ·cm for as-CSP and annealed BYO at 400 °C, respectively. As the sample geometry, (*A/L*) should not change during the annealing; it simply indicates that R_{GB} decreased nearly 1/10 during the annealing. From **Eq.(3-7b)**, it is expressed as $R_{GB} = (\rho_{GB}^{true} \delta_{GB} L)/(d_g A)$. The decrease in R_{GB} can be simply caused by the change in ρ_{GB}^{true} due to clear grain boundary formation, as observed in **Figure 3-8**. It is also possible that grain coarsening and the disappearance of the nano-precipitates would decrease the ratio of (δ_{GB}/d_g), thereby decreasing R_{GB} . The change in microstructure, total volume ratio of grain boundary, or combination of both should have contributed to the decrease of R_{GB} in **Figure 3-5(b,c**). Grain conductivity enhancement by the annealing also remained unclear. One possible explanation is that lower crystallinity of as-CSP hindered the hopping probability of the oxygen, resulting in a higher ρ_{g}^{app} . Hopping probability is included in the pre-exponential factor in Eq(3-1).⁹⁸ This qualitatively explains grain conductivity changes while maintaining similar activation energy (Figure 3-5(b)). It should be noted that organic residue was detected by thermogravimetric analysis. It is possible the residue had an influence on the observed conductivity, as a similar observation was reported in the ZnO-acetic acid system.¹⁸ Based on the fact that it mostly evaporates below the lowest temperature of impedance measurement (Figure 3-10), and there is no sudden change in the conductivity with the temperature scan (Figure 3-4), the influence of the residue on the conductivity may be minor. However, further investigation is needed to clarify the dominant factor for the suppressed conductivity in this work.



Figure 3-10: Thermogravimetric analysis (TGA, left-axis) and Differential thermal analysis (DTA, right-axis) of as-CSP BYO Ceramics.

As the electrical measurement at relatively high temperatures (<650 °C) caused microstructure changes and hence improved the total conductivity, one may wonder if the

properties of the annealed BYO could be achieved by firing BYO ceramics at 650 °C without CSP. In order to elucidate this critical question, a BYO ceramic was prepared by conventional solid-state sintering at 650 °C as a reference sample. The final relative density was \sim 70 % of T.D. and the microstructure looked porous with some degree of coarsening (Figure 3-11(a)). These results are not surprising as the typical sintering temperature of BYO ceramics is > 800 °C. The poor densification resulted in the 2-3 order of magnitude lower total conductivity than that of coldsintered specimens (Figure 3-11(b)). Figure 3-11(c,d) show impedance spectra of the reference sample sintered at 650 °C. At 300 °C, the impedance spectrum indicates very conductive grains (Figure 3-11(c) inset) and resistive grain boundaries. The grain conductivity is indeed comparable to those in CSP or reported values. R_{GB} , which is more than 100 times larger than R_g , limits the low total conductivity. The large R_{GB} is believed to originate from the absence of necking between several BYO grains. At 400 °C, the relaxation from the grain is out-of the measurement range (Figure 3-11(d) inset) and only one semi-circle from grain boundaries is seen. In comparison with the impedance spectra of as-CSP in Figure 3-5(a), the grain boundary and total resistivity are much higher in BYO ceramics sintered at 650 °C. From these results, it can be concluded that firing of BYO ceramics at 650 °C alone is not sufficient to achieve high density and high conductivity; heat treatment at 650 °C was effective in improving conductivity by recrystallizing the metastable interfacial phase formed in the CSP, but it was not high enough for densification. In other words, CSP was an important step in obtaining comparable properties at temperatures lower than those reported in the literature, although the recrystallization step was necessary. In that sense, future studies should focus on alternative transient phases for CSP that provide lower resistance grain boundaries. Recent studies showed that some sintering aids allowed to have well-crystalline single phase, thus achieving desired functional property without the annealing step.^{62,92,113} However, for all cases where CSP is in the unusual situation of enabling densification below an operational

temperature, it would be advisable to have a stabilizing anneal to remove any unknown metastable states before use.



Figure 3-11: Microstructure (a), temperature dependence of the total conductivity (b), complex impedance plot at 300 $^{\circ}$ C (c) and 400 $^{\circ}$ C (d) of BYO ceramics prepared by solid-state sintering at 650 $^{\circ}$ C without CSP.

3.5 Conclusions

Yttria-stabilized cubic bismuth oxide was densified by cold-sintering at 300 °C. The total conductivity of as-sintered ceramics reached ~ 2 mS/cm at 500 °C. The conductivity was further increased to 5 mS/cm after the first cycle of electrical measurement at 650 °C. The enhancement of total conductivity is owing to the grain coarsening with better crystallinity in grain as well as

formation of clear grain boundaries following the annealing process. This was determined through a modelling of impedance data and the use of the brick wall model. The fundamental understandings of processing-property relationship gained in this study would be potentially useful for lowering the processing temperature of SOFC.

So, this chapter points to the fact that there is a metastable grain boundary structure despite the high levels of densification that have been obtained. With this system, a modest annealing condition the crystallinity of the grain boundaries increases and then the ionic conductivity is very close to the temperature dependences and magnitudes of the conventionally sintered materials.

Chapter 4

Barium Titanate^{b,c}

In following the advancements trend of the Multilayer Ceramic Capacitor (MLCC), there has been an extensive effort made to decrease dielectric layer thickness in order to gain larger volumetric efficiency. As the dielectric layers become thinner, the electric field applied to the dielectrics inevitably becomes higher. Such a high electric field (> 10 V/ μ m) is high enough to cause some technical issues, such as resistance degradation, electrical breakdown and decrease in the dielectric permittivity, etc.

Cold Sintering Process of BaTiO₃ may provide opportunities to solve these issues. Namely, the typical sintering temperature range of CSP is compatible or close to the processing temperature of some polymers. It is hypothesized that if a polymer can be distributed along the grain boundary of BaTiO₃, polymer layers will hinder the migration of oxygen vacancies or electronic charges, improving lifetime and insulation resistance. Moreover, such an electrically inhomogeneous microstructure would alter the amplitude of the local electric field. The major voltage drop is expected to occur at the resistive polymer layer. If so, non-linear properties can be tuned.

Therefore, this chapter focuses on densifying $BaTiO_3$ and obtaining reasonable dielectric properties without high-temperature annealing. A previous work on $BaTiO_3$,¹¹⁴ as well as BYO in **Chapter 3**, indicates that the formation of secondary phase limits functional properties and requires high-temperature annealing for better crystallization. Therefore, inspired by a crystal growth technique,^{62,115} a hydroxide based high-temperature solution is used for the sintering aid of $BaTiO_3$

Portions of this chapter have been reproduced from the following publications:

^b K. Tsuji, A. Ndayishimiye, S. Lowum, R. Floyd, K. Wang, M. Wetherington, J.-P. Maria, C. A. Randall, "Single Step Densification of High Permittivity BaTiO₃ Ceramics at 300 °C," *J. Eur. Ceram. Soc.* **40** (2020) 1280-1284. DOI: 10.1016/j.jeurceramsoc.2019.12.022, A.

^c Ndayishimiye, M. Y. Sengul, D. Akbarian, Z. Fan, K. Tsuji, S.H. Bang, A.C.T. van Duin, C.A. Randall, "Dynamics of the Chemically-driven Densification in the Cold Sintering of Barium Titanate using Molten Hydroxides", *Nano Letters*, **21** (2021) 3451-3457. DOI: 10.1021/acs.nanolett.1c00069

in the CSP. The dielectric properties of the sintered ceramics are characterized and compared to the previously reported values in terms of the sintering temperature and grain size.

4.1 Introduction

BaTiO₃ is one of the most important electroceramic materials. It is the basic compound that is doped to produce high permittivity dielectric materials used in multilayer capacitor components. These components are extremely useful in the control of modern electronic circuit charge supply.¹¹⁶ Over three trillion multilayer ceramic capacitors are used each year.¹¹⁷ Of those, more than half of the components are manufactured with inner electrodes of nickel that are cofired with a formulated BaTiO₃ at sintering temperature of ~ 1250 °C and a reducing atmosphere of pO_2 ~ 10^{-12} atms with a gas mixture of N₂-H₂-H₂O.¹¹⁸ Cold Sintering Process (CSP) is a relative new concept but has been applied to a number of materials, many of which could also be densified at temperatures below 300 °C.^{13,14,16,119} In some materials, including perovskite-based ferroelectrics such as BaTiO₃,¹¹⁴ Pb(Zr,Ti)O₃,⁶³ and SrTiO₃,¹²⁰ high densities were accomplished at low temperature conditions; however, the dielectric properties, such as the permittivity and remanent polarization, were limited without secondary thermal treatment. In the case of the earlier studies on BaTiO₃,¹¹⁴ as described in **Figure 4-1**, a transient liquid with stoichiometric adjustments was used to reduce the incongruent dissolution of the BaTiO₃ particles. This was helpful for the densification but still led to glassy phases in the grain boundaries (Figure 4-1(a,b)) that had a major limitation to the dielectric properties of these ferroelectric materials (Figure 4-1(c)). However, on heat treatments ranging from 700 °C to 900 °C, these grain boundaries equilibrate, and the glassy phase was incorporated into the crystalline material (Figure 4-1(d-f)). The metastable glass in the BaTiO₃ microstructure was associated with a $BaCO_3$ phase. This phase had to decompose to allow the

complete densification of the microstructure and the glassy interface dominated the dielectric properties limiting performance without this secondary heat treatment.¹¹⁴

Since the earlier work described above, there has been a broad consideration of the all important selection of transient chemical phases, including alkali-metal hydroxide fluxes.⁶² Alkali metal hydroxide fluxes have been employed as "high-temperature solutions" to aid synthesizing new oxides and grow crystals of known compositions and structures.¹²¹ The NaOH-KOH mixture has an eutectic point of 170 °C and it has been used for synthesizing a variety of complex oxides at low temperatures.^{122–126}

The objective of this study is to utilize hydroxide additives to aid cold sintering of $BaTiO_3$ and avoid a secondary heat-treatment. The microstructure and dielectric properties are compared to previous reports on high quality $BaTiO_3$ materials fabricated at high temperatures with submicron grain sizes.



Figure 4-1: (a,d) Schematic microstructure, (b,e) TEM micrographs at the grain boundaries, (c,f) temperature dependence of dielectric properties, in the case $Ba(OH)_2$ -TiO₂ suspension is used as sintering aid for the CSP. (a-c) As-CSP, (d-f) after annealing at 900 °C. Figures are taken from ref. ¹¹⁴

4.2 Experimental Procedures

BaTiO₃ nanopowder (Toda BT-020 (Toda Kogyo Corp.)), BET surface area, $A_{BET} = 30.2 \text{ m}^2 \text{ g}^{-1}$) was used in this study. The BET surface area was determined by N₂ gas molecule adsorption (ASAP 2020, Micromeritics). Based on BET specific surface area, the particle size of initial powder, \bar{d} , was calculated to be ~33 nm ($\bar{d} = 6000/A_{BET}/\rho$. ρ : density of BaTiO₃ (= 6.03 g cm⁻³). The as-received powder (0.80 g) was mixed with 4-6 wt% of mixture of NaOH (Fisher Scientific, >98%) and KOH (Fisher Scientific, >85%) in 50:50 molar ratio. After being thoroughly ground, the powders were uniaxially pressed at 350-520 MPa and heated to 300 °C for 1-12 h. Detailed experimental setup is described elsewhere.^{127,128} The linear shrinkage was monitored with dilatometer setup.¹²⁹ The densities of the cold-sintered pellets were geometrically measured based on the mass and volume of the pellets.

Phase purity was investigated by X-ray diffraction (XRD, Empyrean, PANalytical) with a scan rate of 0.067 °/s using Cu K α . Raman spectra were measured with a Raman microscope (Horiba, Vlabinir, 532 nm). The microstructures were observed by Field Emission Scanning Emission Microscopy (Leo 1550, Carl Zeiss, Inc., Jena, Germany) for fracture surfaces. The transmission electron microscope (TEM) samples were prepared by the Focused Ion Beam (FEI Helios NanoLab 660 FIB) system and the TEM analysis was done by FEI Talos F200 ×. Average grain size was calculated from the polished surface using the line intercept method.¹³⁰ The 80 nm of Pt electrodes were deposited by sputtering (Q150R Plus, Quorum) for the electrical measurement. Dielectric properties were investigated with HP 4284A precision LCR meter. The polarization-field (*P-E*) hysteresis loop of the BT-75 nm was measured using a Sawyer-Tower circuit with a Trek Model 30/20 high voltage amplifier system (Trek, Inc., Lockport, NY).

4.3.1 Densification Behavior

Figure 4-2 shows a linear shrinkage during cold sintering of BaTiO₃ at 300 °C under 350 MPa of uniaxial pressure. Large linear shrinkage ($\sim 40\%$) occured within 3 hours, presumably due to the particle rearrangement and densification of BaTiO₃. It may also includes a minor contribution from unknown instrumental artifacts, or/and particle/flux leaks from the die, as it is not a perfectly sealed system. The quantitative discussion for the shrinkage at the first stage is avoided here. The shrinkage kept until ~8 hrs and it became stable as the densification was completed. The measured density was >94 % of theoretical density (6.03 g/cm³). Frey et. al. reported the same degree of densification of BaTiO₃ ceramics by hot-isostatic pressing at 700 °C with 8 GPa of uniaxial pressure.¹³¹ Walker et al. also attempted to lower the sintering temperature of BaTiO₃ ceramics by the use of uniaxial pressure and liquid phase of alkaline fluorides.¹³² They reported a rapid densification in the range of 650-700 °C with ~30 MPa of uniaxial pressure, which was much lower pressure than work by Frey et al.¹³¹ However, the approaches by Walker et al. and Frey et al. still required a sintering temperature of over 600 °C. Though these results can not be directly compared to this work due to the different experimental conditions (i.e. pressure, physical properties of the sitering aid), based on the significantly lower sintering temperature, it is reasonable to assume that the NaOH-KOH flux acted as a sintering aid for $BaTiO_3$ very efficiently. The primary reasons for the effectiveness of the NaOH-KOH flux in lowering the sinteirng temperature can be ascribed to a lower melting temperature of the NaOH-KOH (T_m~180 °C). Such a low-temperature range enabled the use of a stainless steel die for CSP that withstands a higher pressure (>100 MPa) than the graphite die in the hot-pressing system. The combined effect of the uniaxial pressure and the presence of the liquid at such temperature must have promoted the ion transport. A reactivity of the hydroxide with oxide may also have been the reason, as the sintering temperature of the work with alkaline fluorides by Walker *et al.* was much higher than the melting point of alkaline fluorides, indicating that the limiting factor of the densification of their study was not only the melting point of the flux, but the reactivity of the liquid. The effectiveness of the hydroxide flux has been discussed and suggested for the oxide nanoparticle synthesis and single crystal growth.^{115,133,134} The formation mechanism of BaTiO₃ in NaOH-KOH system is explained by the presence of a hydroxide-soluble Na₂TiO₃/K₂TiO₃ compound. The chemical reaction is expected as follows:¹²⁶

$$2AOH + TiO_2 \rightarrow A_2 TiO_3 + H_2 O \tag{3-1}$$

$$A_2 TiO_3 + Ba(OH)_2 \rightarrow BaTiO_3 + 2AOH$$
 (3-2)

where A is Na or K. Previous studies of CSP reported that the presence of soluble intermediate compounds facilitated the solution-precipitation process and then promoted the densification at low temperatures.⁹⁶ It is speculated that NaOH-KOH effectively densified BaTiO₃ by creating a soluble intermediate compound in the hydroxide system. These reactions are theoretically confirmed to be reasonable under CSP conditions by the Reactive force-field (ReaxFF) approach.¹³⁵



Figure 4-2: Linear shrinkage rate of BaTiO₃ ceramics under CSP condition (6 wt% of NaOH-KOH, 350 MPa, and 300 °C) is shown in black line. Temperature profile during CSP is shown in blue.



Figure 4-3: (a) Photograph of as-sintered BaTiO₃ ceramics (thickness is ~0.8 mm) (b) SEM micrograph of the fracture surface of the as-sintered BaTiO₃ ceramics.

The sintered $BaTiO_3$ pellet by CSP was nearly fully densified as indicated by the microstructure and the translucent pellet shown in Figure 4-3. Some preliminary results suggest that the translucency can be further improved by optimizing the sintering conditions (Figure 6-2). The translucency of the sintered pellet can be ascribed to the fact that the as-CSP BaTiO₃ ceramics retain small grain size (< 100 nm) with minimal porosity, and such properties are difficult to obtain by the conventional pressureless sintering. Therefore, it would be worthwhile to further explore the optical properties in the ferroelectric ceramics prepared by CSP in future studies. Frey et. al. reported translucent, light blue BaTiO₃ ceramic prepared by hot-pressing (700 $^{\circ}$ C with 8 GPa), suggesting that the pellet was partially reduced during sintering. On the other hand, the coldsintered $BaTiO_3$ in this study is a light-yellow color. Differences in sintering conditions, such as temperature or/and the presence of flux may have affected the oxygen concentration in the sintered pellet. As as a result, as-CSP pellet showed ~ $10^{12} \Omega \cdot cm$ of d.c. resistivity without any additional high-temperature heat-treatment, which is comparable to the typical resistivity of pure $BaTiO_3$. Notably, the experimental conditions used in this work aren't fully optimized; this study does not aim to optimize the sintering condition for each property, but rather to show the possibile use of CSP for BaTiO₃. It is emphasized that BaTiO₃ ceramics could be densified within 3 hours under similar conditions.¹¹³ A relatively long sintering time (6-12h) was used in this study to minimize porosity.

Another specimen was prepared with a smaller amount of NaOH-KOH flux (4 wt%) as the hydroxide was expected to be harmful to the electrical properties. It was found that 4 wt% was a nearly lower limit for densifying BaTiO₃. Below this limit, the relative density resulted in lower than 90 % of T.D. The bulk densities were 5.55 and 5.80 g·cm⁻³ using 4 and 6 wt% of NaOH-KOH, respectively. These values correspond to 92 and 96 % of the theoretical density of the pure BaTiO₃ (6.03 g cm⁻³). As the real density of the pellet should be different from the theoretical value because of the presence of the hydroxides, real densities of the specimens were determined by He

pycnometry to be 5.67 and 5.83 g·cm⁻³, for BT-150 nm and BT-75 nm. Relative densities to the measured densities by He pycnometry were therefore 98 % and 99 %. BET surface area substantially decreased from $30.2 \text{ m}^2 \cdot \text{g}^{-1}$ of the initial powder to 0.3 and 0.4 m² · g⁻¹ after CSP for BT-150 nm and BT-75 nm, respectively. Significant surface area reduction is another indication of a high degree of BaTiO₃ densification at 300 °C.

4.3.2 Microstructure Analysis

Figure 4-4(a,d) and (b,c) show microstructures of the two cold-sintered specimens, at low and high magnification of transmission electron microscopy (TEM). It is clearly seen that two specimens possess highly dense microstructures with homogeneous grain sizes. The average grain sizes were 150 nm and 75 nm for 4 and 6 wt% of hydroxide fluxes. Hereafter, these specimens are named as BT-150 nm and BT-75 nm respectively. Scanning TEM mode reveals that some internal defect inclusions exist in grains of $BaTiO_3$ in Figure 4-4(c,g). These are often observed in the sintered BaTiO₃ ceramics when low temperature hydrothermally- or solvochemically- synthesized BaTiO₃ powders are used, due to the presence of a hydroxyl group.^{136–138} FTIR and TGA showed the presence of a hydroxyl group in the initial nanopowder (Figure 4-5). The final microstructure was also very similar to the reported literature on conventionally sintered BaTiO₃ ceramics with hydrothermally-derived starting powder.¹³⁶ Based on these facts, it should be reasonable to conclude that the internal defects in Figure 4-4(c,g) are not a specific consequence of CSP. The observed dense shell region in Figure 4-4(c) is believed to grow during CSP. The core-shell like microstructure in Figure 4-4(c) indicates that a major dissolution-precipitation process occurred at the surface of the initial BaTiO₃ particles while the core-region of BaTiO₃ particles did not react with NaOH-KOH. Therefore, it is speculated that grain boundary diffusion, which is known to be critical for densification, was significantly enhanced by the liquid phase and was high enough to

complete the densification at the sintering temperature within a reasonable sintering time. This may also be the reason why the grain growth was limited in this study. Without the liquid phase, grain boundary diffusion usually remained less than the surface evaporation/condensation until the system temperature rose close to the sintering temperature (dotted line in **Figure 4-6**). Thus, in conventional solid-state sintering, particle coarsening occurs upon heating and results in grain growth.³⁴ In CSP, grain boundary diffusion was sufficiently high at the CSP condition, at which surface evaporation/condensation processes are still not active (solid line in **Figure 4-6**).

Besides these minor defects and closed pores, specimens showed equiaxed grains with equilibrated triple points, a feature of the final stage of sintering. Ferroelectric-ferroelastic non-180° domain structures were not observed in the grains. **Figure 4-4**(d) and (h) reveal the well-crystallized grain boundaries after cold sintering. The clean grain boundary formation was previously not observed until a second heat treatment was applied after cold sintering to temperatures 800-900 °C.¹¹⁴ It should be noted, though the hydroxides are not shown in **Figure 4-4**, the presence of the remaining hydroxides are observed in some places. Some hydroxides seem to leak from the die during CSP in liqud form (**Figure 4-7(b**)). Also, the majority of the hydroxide flux is believed to exist as segregated precipitates with a relatively large scale (> 1 μ m). The large hydroxide "island" was observed on a fracture surface by Scanning Electron Microscopy (**Figure 4-7(c**)). An elemental mapping with energy dispersion spectroscopy in the TEM shows that some alkaline ions remain at the triple point of grains (**Figure 4-7(d-2**)). With all the microstructural observations, incorporation of alkline ions into grains was not observed. This is consistent with the Curie temperature of cold-sintered BaTiO₃, which is discussed in the next chapter.



Figure 4-4: TEM bright field micrographs of BT-150 nm (a-d) and BT-75 nm (e-h). Overview of grain morphology with low magnification (a,e) and high magnification (b,f). Grain morphology with STEM mode (c,g) Grain boundary microstructures (d,h). All images were taken by Dr. Ke Wang.



Figure 4-5: (a) Thermogravimetric analysis of BaTiO₃ initial nanopowder. The mass losses around 300 and 800 °C are related to the release of the chemisorbed water that incorporated in the lattice as hydroxyl group, and the decomposition of the barium carbonate, respectively.¹³⁶ (b) Fourier-transform infrared spectroscopy of BaTiO₃ initial nanopowder. The peaks in IR spectra (**Figure 4-4(b**)) are attributed to BaTiO₃ at 470 cm⁻¹, CO_3^{2-} in barium carbonate at 1440 cm⁻¹, OH^- in absorbed water at ~1640 and 3500 cm⁻¹, respectively.¹³⁶



Figure 4-6: Schematic representation of temperature dependence of the diffusion process at lattice (D_l) , grain boundary (D_{GB}) and surface (D_s) . Dot and solid lines indicates the diffusional process in the solid state sintering and CSP, respectively. This figure is drawn with the modification of the figure in ref.³⁴



Figure 4-7: Schematics (a) and images (b,c) showing the place where the residual hydroxide flux remains. (c) SEM-EDS image of fracture surface of the cold-sintered BT-75 nm. (d-1) High-angle annular-dark-field scanning transmission electron microscopy (HAADF-STEM) and (d-2) the corresponding scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) mapping of a triple junction in BT75 nm. TEM micrograph was taken by Dr. Zhongming Fan.

Figure 4-8(a-1) shows X-ray diffraction of the initial BaTiO₃ powder (BT-powder) and the cold-sintered specimens, respectively. All the specimens appear to possess a perovskite phase as a major phase. A small amount of the impurity phase (BaCO₃) was seen in the initial powder. This result is consistent with the TGA and FTIR results (**Figure 4-5**). The weight loss at 800 °C is believed to be a result of the decomposition of barium carbonate.¹³⁶ The weight loss of ~0.5 wt% indicates the initial powder has 2.2 wt% (~3.1 vol%) of barium carbonate. The peak from BaCO₃ in XRD is not seen in the cold-sintered BaTiO3 ceramics (**Figure 4-8(a-1**)). The result indicates that molten hydroxide reacted with BaCO₃ and formed undetected impurity phases, such as barium hydroxide. However, it is also possible, if equivalent Ti-atoms were around, molten hydroxide might have reacted with barium carbonate and Ti-based compound and formed BaTiO3 as indicated in **Eq. (4-1,2)**. No obvious peaks from hydroxide phases are found in the X-ray diffraction pattern, likely due to their small proportion and/or their low crystallinity. **Figure 4-8(a-2)** shows a peak from 200 reflection. The single peak of 200 reflection indicates that all the specimens contain pseudo-cubic structure.

In addition, Raman spectroscopy was performed, as it has already been successfully used to reveal the local structure of BaTiO₃.^{131,137} **Figure 4-8(b)** shows Raman spectra of BT-75 nm, 150 nm and BT-powder (~20 nm) at room temperature. While cubic structure (*P*m-3m) is not Raman active, the tetragonal crystal symmetry (*P*4mm) should show the $3A_1+B_1+4E$ Raman active modes. The spectra in the sintered ceramics shows 5 peaks at 187 [A_1 (LO)], 260 [A_1 (TO)], 306 [B_1 , E(TO+LO)], 515 [A_1 , E(TO)] and 715 [A_1 , E(LO)] cm⁻¹ respectively. More than one mode is assigned because the peak position of *A* and *E* mode is close. A complete peak assignment can be found elsewhere.¹³⁹ The spectra is consistent with earlier work of orthorhombic or tetragonal BaTiO₃.¹⁴⁰⁻¹⁴² Orthorhombic and tetragonal phase identification is not discussed in this study as the Raman spectra in the nanocrystalline BaTiO₃ are alike and difficult to differentiate due to the diffused phase transition at the nanograin size.¹⁴⁰ As many authors have proposed,^{131,140,143,144} the co-existence of these phases is possible. The presence of the Raman band suggests that coldsintered specimens should have at least locally tetragonal and/or orthorhombic structure; therefore ferroelectric properties are expected.



Figure 4-8: XRD patterns (a), and Raman spectrum (b), of initial powder (BT-powder) and cold sintered BaTiO₃ ceramics. (a-2) shows expanded view of 200 reflection. Peak position for cubic (upper: PDF# 04-013-5284) and tetragonal (lower: PDF#04-015-6089) are identified with the bars

4.3.3 Electrical and Dielectric Properties

Figure 4-9(a) shows the temperature dependence of the dielectric properties. The frequency dependences of the dielectric properties are also presented in **Figure 4-10**. The room temperature permittivity is 1830 and 690 for BT-150 nm and BT-75 nm, respectively. The high permittivities and distinct Ferroelectric-Paraelectric phase transition indicate the dielectric properties are comparable to those sintered at high temperature. As seen in **Figure 4-9(a)**, smaller grain size (BT-75 nm) contains a lower dielectric permittivity in a measured temperature range. The difference in the dielectric permittivity is explained in terms of the intrinsic size effect below 100 nm. Arlt *et al.* and others explained that the maximum of the permittivity appears around grain

sizes of 0.8-1 μ m due to the 90° domain extrinsic contribution. Below this size, the permittivity constantly decreases due to the limited 90° domain wall mortion.¹⁴⁵ Fundamentally, grain size effects can be observed in $BaTiO_3$ with control of the grain sizes. The most comprehensive study on BaTiO₃ was conducted with the use of spark plasma sintering (SPS) and controlled grain sized materials from the late Nanni group.^{141,146,147} In addition, hot pressing and crystallization of BaTiO₃ has yielded good size effect data.^{131,143,148} Here the cold sintering data is compared with that of the earlier size effect reports. The permittivities in the present work follow trends in a number of studies on the grain size dependence (Figure 4-9(b)).^{143,146,148–153} The slightly different findings in this study may be due to remaining hydroxides and/or intragranular pores but the values in this study are comparable to those in SPS study. A dielectric anomaly appeared around 120 °C (Figure 4-9(a)). This is associated with the tetragonal - cubic displacive phase transition. The corresponding inverse permittivity shows a linear relationship with the temperature (Figure 4-9(c)). It is clear that the phase transitions obey the Curie-Weiss law $(1/\varepsilon_r = (T - \theta_c) / C^2$: θ_c is Curie-Weiss temperature and C' is constant). The parameters obtained are listed in **Table 4-1**. The Curie-Weiss constant, C' for BT-150 nm and BT-75 nm, are reasonable values for the reported values in BaTiO₃.^{154,155} A number of theoretical and experimental studies show that the transition temperatures of $T_{\text{O-T}}$ and T_{C} have grain (crystalline size) dependence.^{143,146,148–152,156,157} Namely, the phase transition becomes diffused character; a slight increase of $T_{\text{O-T}}$ and decrease of T_{C} are expected with decreasing the grain size. As shown in Figure 4-9(d), the T_{O-T} and T_C in this study are in good agreement with reported intrinsic size dependences.^{143,146,148–153} Likewise, the values of $\theta_{\rm C}$ in the present study are in the range of the reported values of BaTiO₃ using SPS and Hot-Press Sintering methods.^{146,148,149} Overall, the dielectric properties and phase transition behaviors of the cold-sintered $BaTiO_3$ nanocrystalline ceramics are well-explained by the size effect. It is noteworthy that these cold sintered BaTiO₃ dielectrics are densified under the lowest sintering temperatures with high

permittivity values. Previously, it was thought that only high permittivities could be obtained with higher thermal treatments.¹⁵⁸



Figure 4-9: (a) Temperature dependence of dielectric properties of cold sintered $BaTiO_3$ ceramics at 10^6 Hz. (b) Grain size effect on the relative permittivity for bulk $BaTiO_3$ ceramics. (c) Curie – Weiss plot. (d) Grain size dependence of phase transition temperature of the cold-sintered $BaTiO_3$. R, O, T and C indicate Rhombohedral, Orthorhombic, Tetragonal, and Cubic crystal structure, (e) Grain size dependence of Curie-Weiss temperatures. Data in (b), (d) and (e) is taken from ref.^{143,146,148–153}

Samples	ε' [-]	tanδ [%]	<i>C</i> ' [×10 ⁵ ℃]	<i>T</i> c [°C]	<i>Т</i> ₀-т [°С]	θ _C [℃]
BT-75 nm	690	3.5	1.4	121±1	34±3	27±1
BT-150 nm	1830	4.3	2.7	122±1	38±4	61±1

Table 4-1: Dielectric properties and physical constants obtained from Curie-Weiss analysis



Figure 4-10: Temperature and frequency dependencies of cold sintered $BaTiO_3$ ceramics. (a) BT-150 nm, (b) BT-75 nm

Figure 4-11 shows the polarization-field (*P-E*) hysteresis loop of the BT-75 nm at 10 Hz. A hysteresis loop indicates ferroelectric switching with a remanent polarization, P_r , of 15.0 µC cm⁻² and coercive, E_c , of 18.6 kV cm⁻¹. There are very few reports of "macroscopic" ferroelectric switching behavior in BaTiO₃ nanocrystalline ceramics.^{147,148,159,160} Bulk *P-E* hysteresis were often nearly linear; evidence of ferroelectric switching in the nano-grain ceramics was limited in the "local" phenomena by piezoresponse force microscopy.^{159,160} It is not clear why BT-75 nm in this study shows macroscopic ferroelectric switching behavior. This could be due to sharp grain boundary microstructures that minimize the dilution of ferroelectric properties resulting from non-ferroelectric grain boundary layers, or simply due to relatively larger grains compared to 20-50 nm in the ref.^{148,159,160} Notably, the d.c. resistance of the specimen was ~10¹² Ω ·cm, a value comparable to the BT/PTFE system, which was densified with Ba(OH)₂·8H₂O.¹⁶¹ The high insulating resistance indicates that space change should not dominate the observed *P-E* loop.



Figure 4-11: *P*-*E* hysteresis loop of BT-75 nm at 10 Hz.

4.4 Conclusions

In summary, this chapter has successfully densified BaTiO₃ ceramics at 300 °C without any secondary heat treatment with the cold sintering technique. The resulting dielectric permittivities are 700-2000 depending on processing conditions. The dielectric properties are comparable to the reported values considering the grain size effect. The dielectric properties are comparable to the highest quality reported data that required preparation by high temperature sintering techniques (> 1000 °C) reported previously (**Figure 4-12**). The sintering temperature in this work is even lower than the processing temperature for high quality BaTiO₃ thin films. The cold-sintered BaTiO₃ ceramic shows a *P-E* loop with relatively high remanent polarization. This work should open up the possibility to densify more inorganic materials at low temperatures in a single step.



Figure 4-12: Comparison of property-processing relationship by different sintering method (Solid State Sintering(SSS),^{162,163} Hot-Press Sintering(HPS),¹⁴³ Spark Plasma Sintering (SPS)^{147,159,164–166} Microwave Sintering(MWS^{162,167} Cold Sintering Process (CSP), (Two data points at $T_s = 180$ °C were from ref ²⁰ and two data points at $T_s = 150$ and 230 °C were from ref ⁶⁰. Two data points at $T_s = 350$ and 400 °C were synthesized with a modification of this study ^d). It is reported that an additional annealing treatment was performed in some of SPS and HPS work.

^d Two data points are added, that synthesized with the following condition. (i) Initial powder: Sakai01 (average particle size 100 nm), 10 vol% of NaOH-KOH, $T_s = 350$ °C $P_s = 350$ MPa, $t_s = 6$ h, (ii) Initial powder: Sakai04 (average particle size 400 nm), 15 vol% of NaOH-KOH, $T_s = 400$ °C $P_s = 520$ MPa, $t_s = 12$ h

Chapter 5

Potassium Sodium Niobate-based System^e

Following the promising results in $BaTiO_3$, the author extended the work to $(K_{0.5}Na_{0.5})NbO_3$ (KNN) ceramics. This materials system is known for lead-free piezoelectric applications. It is an interesting contrast as the piezoelectric ferroelectric requires ferroelectric domain alignment and properties will be more determined from the bulk of the grains than the interfaces as has been the case with Bi₂O₃ and BaTiO₃. Therefore, this chapter will first focus on the feasibility of the low-temperature densification of KNN ceramics by CSP.

5.1 Introduction

Piezoelectric ceramics are nowadays widely used for sensors, actuators, transducers, and many other devices. The successful development of piezoelectric ceramics is due to the discovery of high piezoelectricity around the morphotropic phase boundary in lead zirconate titanate ceramics, following developments in lead-based piezoelectric ceramics.¹⁰ Meanwhile, the search for lead-free piezoelectric ceramic materials has been actively carried out due to concerns about the environmental impact of lead and its impact on the human body. The KNN-based material system is now considered to be one of the promising systems of lead-free piezoelectrics because of its high piezoelectric and coupling constants.¹⁶⁸

^e Portions of this chapter have been reproduced from the following publication: K. Tsuji, K., Z. Fan, S.H. Bang, S. Dursun, S. Trolier-McKinstr, and C.A. Randall, (2021). "Cold Sintering of the Ceramic Potassium Sodium Niobate,(K_{0.} ₅Na_{0.5}) NbO₃, and Influences on Piezoelectric Properties", *J. Eur. Ceram. Soc.*, In press. DOI: 10.1016/j.jeurceramsoc.2021.10.002

The study of KNN itself began more than half a century ago. The ferroelectricity of the alkali niobate system was first reported by Bell Laboratory in 1949.¹⁶⁹ Pepinski *et al.* extended studies to the KNbO₃-NaNbO₃ solid solution system and reported the structural & electrical properties of the KNN system in 1954,¹⁷⁰ followed by the report of piezoelectric properties by Egerton *et al.*¹⁷¹ Later, extensive structural investigations were conducted by Glazer and his colleagues.^{172,173}

However, processing conditions have limited the densification of KNN with good functional properties .^{171,174} This is likely because KNN is sensitive to humidity and is a volatile alkaline element. Additionally, the sintering temperature window is close to that of KNN's liquids, which causes compositional shift during sintering.^{175–177} Therefore, special sintering techniques^{178,179} and sintering agents are used to lower the sintering temperature.^{180–182}

It has been reported that various ceramic oxides can be sintered below 300°C by the cold sintering process.^{14,53} This is realized by the pressure-solution creep between ceramic particles promoted by the addition of an appropriate solvent and uniaxial pressure; sintering is completed efficiently at low temperature in a short time. In the case of BaTiO₃, which is same perovskite structure as KNN, very dense microstructure and a high dielectric constant were obtained at 300°C with the addition of alkaline molten salts.¹¹³ Based on these results, the sintering of KNN using a similar approach appears to be promising. In this study, a similar approach used in the BaTiO₃ system is first applied to KNN system. KNN (K/Na =1.0) was chosen to understand densifying KNN ceramics by CSP. The properties of cold-sintered ceramics are then characterized and compared with those of the KNN ceramics sintered by conventional methods. The discussion is extended to understanding the processing-structure-property relationship, taking into account processing-derived lattice defects.

5.2 Experimental Procedures

K₂CO₃ (99.997 %, Alfa Aesar), Na₂CO₃ (99.95-100.05 %, Alfa Aesar), Nb₂O₅ (99.9 %, Alfa Aesar) were dried at 200 °C for > 2 weeks prior to use. Then, the powders were mixed with a stoichiometric composition of $(K_{0.5}, Na_{0.5})$ NbO₃ and ball-milled with 3mm of YSZ in ethanol for 24 h. After being dried at 120 °C for 12 h, the powders were calcined twice at 800 °C for 4 h followed by 24 h of ball milling after each calcination. The calcined powder was mixed with 4 - 10 vol % mixture of NaOH (Fisher Scientific, >98%) and KOH (Fisher Scientific, 99.99%) in 50:50 molar ratio of Na to K. After being thoroughly ground, the powder mixture was uniaxially pressed at 400 MPa and heated to 150-300 °C for 0 - 3 hours. Sintering time is defined as the total time at the maximum temperatures (isothermal dwell time, t_{dwell}). The Nickel foils were used to cover specimens to minimize contamination from the die. The linear displacement was monitored using a contact sensor (Keyence GT-H32) under semi-automatic hydraulic pressure.¹²⁹ The change in linear displacement was compared between KNN powder and KNN powder with 10 vol% of NaOH-KOH flux. The specimens were dried at 200 °C, and then densities of pellets were measured geometrically. A density of 4.51 g/cm³ was used to calculate relative density of the sintered KNN ceramics.¹⁸³ Phase purity was investigated by X-ray diffraction (XRD, Empyrean, PANalytical) with a scan rate of 0.067 % using Cu Ka radiation. The microstructures were observed by Field Emission Scanning Emission Microscopy (ZEISS GeminiSEM, Carl Zeiss). Prior to the microstructure observation, all specimens were polished with 50 nm diamond paste. Then, the surface was etched with a diluted HCl-HF solution for 5-10 seconds. More than 350 grains were counted; grain sizes were estimated by the linear intercept method.¹³⁰ The initial particle size was also estimated from SEM micrograph using the equivalent circle diameter.¹⁸⁴ 80 nm thick Pt was sputter-deposited (Q150R Plus, Quorum) and used for the electrical measurements. Dielectric properties were measured with a HP 4284A precision LCR meter. The polarization-field (P-E) hysteresis loop was measured using a Sawyer-Tower circuit with a Trek Model 30/20 high voltage amplifier system (Trek, Inc., Lockport, NY). The KNN pellets were poled under different conditions (electric field, E_p : 40-70 kV/cm, poling temperature, T_p : R.T. to 100 °C, poling time, t_p :10 and 30 min). After poling, the field was maintained during cooling to room temperature in order to minimize backswitching and maximize the poled state. The direct piezoelectric coefficient d_{33} was determined by a Berlincourt meter (PM 300, Piezotest Pte. Ltd.). The subgrain defects were visualized by Transmission Electron Microscopy (TEM) in a Talos F200X (FEI), with the specimen prepared using Focused Ion Beam (Scios 2, FEI).



Figure 5-1: Flow diagram of the experimental process

5.3 Result and Discussion

5.3.1 Densification

Figure 5-2(a) shows the relative densities of cold-sintered KNN ceramics with different sintering temperatures and amounts of hydroxide flux based on the pellet geometry. It was found that a higher sintering temperature and a higher amount of NaOH-KOH flux resulted in higher relative densities within the experimental window in this study. Good dielectric properties ($\varepsilon'_r \sim 500$, tan $\delta \sim 2.5\%$ at 1 kHz) and insulation resistance (>10¹¹ $\Omega \cdot cm$) were obtained with the sintering temperature as low as 230°C with 10 vol% of NaOH-KOH flux, and significant improvement was not observed for other conditions. These properties are comparable to the high-quality specimen
values reported in references.^{177,185} Therefore, further characterization focuses on specimens sintered at 230 °C under 400 MPa of uniaxial pressure for 3 h of isothermal dwell with 10 vol% of NaOH-KOH flux.

Figure 5-2(b) demonstrates the change in linear displacement and temperature profile as a function of time. Three different cases were tested, using the same sintering temperature of 230 °C and applied pressure of 400 MPa, to accurately interpret the displacement evolution. The calibration indicates no powder and transient phase was placed in the sintering die. Hence, the resulting displacement of 0.30 mm was reasonably due to the axial thermal expansion of sintering instrument. When only KNN powder was placed for the same experiment, the resulting displacement change was reduced down to 0.23 mm. Although the axial thermal expansion is still a dominant factor that affects the degree of displacement, the radial thermal expansion and powder packing possibly cause the shrinkage. However, for the case of KNN powder with 10 vol.% of NaOH+KOH flux, the resulting displacement change of 0.03 mm and the presence of an inflection point clearly suggest that other factors may largely influence the displacement such as densification and possibly some extrusion. According to the relative density measurement, the proposed flux can drive the densification of KNN powder, indicating that the pore volume is sufficiently removed under the cold sintering condition. Therefore, the removed pore volume pertains to the linear shrinkage. Regarding the extrusion, some mass can be extruded from the sintering die through the small but a finite gap between sintering die punch and sleeve. However, when input and output weights were compared, the difference was less than 5%, which is considered to be a minor factor. Note that the relative density at 0-minute isothermal dwell was 93.8%, so the displacement does not noticeably change during the isothermal dwell. The highly repeatable temperature profiles confirm that the possible presence of thermal artifact is minimum in the given analysis.



Figure 5-2: (a) Effect of sintering temperature and amount of NaOH-KOH flux on the relative densities of KNN ceramics. A uniaxial pressure (400 MPa) and sintering time (3 h) were used for all conditions. The pressure is fixed before in raising of the temperature, and so is deemed constant over the sintering runs (b) Change in linear displacement (ΔZ) and temperature profile (Temp.) in a function of time. Positive ΔZ indicates expansion and negative ΔZ means shrinkage.



Figure 5-3: Comparison of property-processing relationship by different sintering method (Solid State Sintering(SSS),^{174,178} Hot-Press Sintering(HPS),¹⁷⁸ Liquid Phase Sintering (LPS),^{180,181,186} Spark Plasma Sintering (SPS),^{179,187} Microwave Sintering(MWS),¹⁸⁸ Cold Sintering Process (CSP, this work). The experimental conditions for each data point correspond to Figure 5-2.

5.3.2 Microstructure Analysis

Figure 5-4 shows SEM micrographs of the initial powder and cold-sintered KNN ceramics with different isothermal dwell time ($t_{dwell} = 0$ and 180 min). The sintered ceramics shows dense microstructure. The cuboidal grains in Figure 5-4 (b,c) represent typical grain morphology in KNN ceramics.^{189,190} As can be seen, the porosity is minor, even with a very short sintering time ($t_{dwell} =$ 0 min, $t_{\text{total}} = 75$ min). It is obvious that densification was almost completed during the nonisothermal heating process, which is consistent with the linear shrinkage measurement in Figure 5-2. No significant microstructure change is seen following the isothermal hold at the cold sintering temperature. Average grain sizes were calculated to be 304 and 297 nm for samples sintered for 0 and 3 hours, respectively. As the initial grain size was about 240 ± 14 nm, some degree of grain growth should have simultaneously occurred with densification during the non-isothermal process. The reason for the limited grain growth in the isothermal process is not clear at this point. Previous work of CSP in BaTiO₃ showed that the hydroxide flux was pushed from the grain boundary and segregated at the triple points as densification proceeded. Because of less medium for transporting ions between grains, the diffusion of ions gradually became inefficient as densification proceeds. As a result, grain growth may be limited after densification is completed (~92 % of T.D.). Future studies should focus on the non-isothermal part, where the major densification and grain growth occurred at the same time.



Figure 5-4: SEM micrograph of KNN initial powder (a) and cold sintered ceramics (b-e). (b,c) fracture surface (d,e) polished surface of the Cold-Sintered ceramics. The sintering time is $t_{dwell} = 0 \min (b,d)$, $t_{dwell} = 180 \min (c,e)$

Figure 5-5 shows XRD patterns for the initial powder and as-CSP KNN pellet sintered at 230 °C for 3h. The diffraction patterns of both initial powder and cold-sintered pellet are identified as orthorhpmbic crystal structure, as expected.^{173,191} No secondary phase was not detected. It is then

considered that the perovskite phase is preserved during the dissolution-precipitation process in the CSP.



Figure 5-5: XRD patterns of the initial KNN powder and as-CSP KNN pellet. Black bars on the bottom represent peak position of K_{0.5}Na_{0.5}NbO₃ (PDF#: 00-061-0310).¹⁹¹

5.3.3 Dielectric and Piezoelectric Properties

The d.c. resistivity is $2.0 \times 10^{11} \Omega \cdot \text{cm}$ at R.T. These properties are comparable to the highquality specimen values reported in ref. ^{177,185}. As the insulation resistivity was high enough for poling, the direct piezoelectric coefficient (d_{33}) was measured with different poling conditions. **Figure 5-6(a)** shows the d_{33} as a function of poling field (E_p) with fixed poling time (t_p) & temperature (T_p). The initial condition ($T_p = 50$ °C, $E_p = 40$ kV/cm $t_p = 10$ min) was chosen based on previous studies (**Table 5-1**). However, d_{33} resulted in a low value (~10 pC/N), indicating that it did not provide a fully poled state. As the E_p increased, the d_{33} value also gradually increased, but it was still limited to less than 30 pC/N. The poling condition was further investigated by increasing the temperature, as shown in **Figure 5-6(b)**. While d_{33} increased slightly with poling temperatures above 50 °C, it was limited to < 30 pC/N. A significant difference in the maximum d_{33} was not seen with E_p of 40 or 60 kV/cm when T_p was sufficiently high. The obtained value of d_{33} is much lower than the typical value of KNN ceramics in the reported literature ($d_{33} = 110-160$ pC/N).¹⁷⁷ The poling conditions used in this study should be sufficient to pole undoped KNN (**Table 5-1**). Additionally, considering that the dielectric properties are comparable to reported values, it is unlikely that d_{33} was limited by the impurity phase (e.g. undetected secondary phase or hydroxide flux).

As the piezoelectric coefficient is directly related to the polarization ($d_{33} = 2Q_{33}P_s\varepsilon$), we then investigated the polarization-electric field (*P-E*) characteristics. **Figure 5-7** shows a *P-E* hysteresis loop of cold-sintered KNN. The maximum electric field of 80 kV/cm used in **Figure 5-7** is much higher than the coercive field of KNN ceramics. However, the loop appeared to be pinched and did not show polarization saturation. The value of the remanent polarization (P_r) in the unpoled KNN ceramics was < 2 µC/cm², a much lower value in as-CSP ceramics than typically found in KNN ($P_r = 20-30 \ \mu C/cm^2$).¹⁷⁷ A pinched hysteresis loop is often seen when the ferroelectric domain wall motion is inhibited by some defect dipoles.¹⁹² Note that neither increasing the electrical field up to 100 kV/cm, nor cycling the a.c. field up to 10³ times, nor a combination of those, led to an opening of the *P-E* loop.



Figure 5-6: Piezoelectric coefficient with different poling conditions

Authors	Temp. (°C)	Field (kV/cm)	Time (min)	ref
Egerton&Dillon (1959)	220-230	12-20	0*	171
Haertling (1967)	R.T.	~15	N.A.	193
Zhang, et al., (2011)	R.T.	40-50	N.A.	177
Hollenstein, et al., (2007) **	50	50	5-15	194
Saito, et al., (2006)	100	30-50	10	195

 Table 5-1:
 Typical poling conditions of undoped KNN ceramics

* Field cooling was used. ** Li-modified KNN



Figure 5-7: P-E hysteresis of the cold-sintered KNN ceramics

Rayleigh analysis provides insight into extrinsic contribution and an indirect assessment of associated defect pinning sites. The Rayleigh law describes the field dependence of the dielectric permittivity as follows;¹⁹⁶

$$\varepsilon' = \varepsilon_{\rm ini} + \alpha_{\rm e} E_0 \tag{5-1}$$

$$P(E) = (\varepsilon_{\rm ini}\alpha_{\rm e} + E_0)E \pm \frac{\alpha_{\rm e}}{2}(E_0^2 - E^2)$$
(5-2)

where ε_{ini} is the dielectric permittivity, resulting from intrinsic lattice response and reversible motion of domain walls. α_e is the irreversible Rayleigh parameter, E is the applied a.c. electric field and E_0 is its amplitude ($E=E_0\sin(\omega t)$). The second term of Eq. (5-1) represents the contribution from irreversible components to the total dielectric permittivity. Figure 5-8(a) shows the field dependence of the dielectric permittivity below the coercive field (E_c). The measured dielectric permittivity shows a clear linear relationship with the amplitude of the a.c. electric field, as expected from **Eq. (5-1**). The Rayleigh parameters, α_e and ε_{ini} , are obtained from the slope and intercept of the linear fitting in **Figure 5-8(a)** ($\alpha_e = 8.4 \times 10^{-5}$ (m/V) and $\varepsilon_{ini} = 513$). The low-field *P-E* hysteresis was calculated with **Eq. (5-2)** using the obtained Rayleigh coefficients. **Figure 5-8(b)** shows a good agreement of the calculated hysteresis with the measured value, indicating that the low-field polarization characteristics of KNN ceramics can be well described by the Rayleigh law. The Rayleigh coefficient of 8.4×10^{-5} (m/V) in cold-sintered KNN is significantly lower than the reported value in high-temperature sintered KNN ceramics (c_cf . $\alpha_e = 1.08 \times 10^{-3}$ (m/V)).¹⁹⁷ The lower α_e indicates the irreversible domain wall motion is less active. The extrinsic contribution calculated from the ratio of measured permittivity to the second term of **Eq. (5-1)** at 5 kV/cm was 7.5% and 61% for cold-sintered and conventionally sintered KNN ceramics, respectively.^{197,198}

It is also possible that the increased interface (grain boundary) inhibited domain wall motion. In the present study, the grain size is much smaller than commonly reported in KNN ceramics and thus, the interfacial effect should be high. Indeed, a similar observation, showing high ε_r with low P_r and/or low d_{33} has already been reported in fine-grain BaTiO₃ ceramics.^{199,200} The irreversible domain wall motion requires overcoming an energy barrier that originates from pinning (often due to defects) in the specimen (**Figure 5-9(a)**). The lower α_e and the higher ε_{ini} indicate that the potential wells are deeper, but broader in cold-sintered KNN ceramics than in conventionally sintered KNN ceramics (**Figure 5-9(b,c**)). As a result, the extrinsic contribution was significantly suppressed, and a low d_{33} was observed. The origin of the strong pinning site is not clear. It is possible that the increased interface (grain boundary) inhibited domain wall motion, as is known with grain size effects with PZT.²⁰¹ In the present study, the grain size is much smaller than commonly reported in KNN ceramics, and thus, the interfacial effect should be high. Indeed, a similar observation, showing high ε_r with low P_r and/or low d_{33} , has already been reported in fine-

grain BaTiO₃ ceramics.²⁰² A strong pinning effect of grain boundaries has been also reported in PZT thin films.²⁰³ An additional possibility that is also important to consider is the possibility of a high point defect concentration. Some point defects can be introduced due to imperfect crystallization during CSP in grain boundary regions or in the bulk of grains due to powder synthesis, with insuffecient homogeneity and crystallization in the calcination step, or dislocation generation in the milling of powders.

To understand the nature of the defects, a bright field diffraction contrast imaging of the grain structures of the CSP KNN ceramics was made. Figure 5-10(a) shows highly defective grains with many dislocations; it is speculated that these defects may have disrupted the irreversible motion of ferroelectric domain walls. The central grain is darker, as it is undergoing a strong diffraction condition, and this reveals both the high density of defects and also the grain boundary outline. The grain boundary is also seen to be made up of many terrace kinks, or steps reflecting the epitaxial growth, that were previously noted in the cold sintering of Na₂MoO₇.⁵³ Figure 5-10(b) shows a high-resolution image with lattice fringes in adjacent crystallites. The interface is atomically sharp with no glassy phases between the grain boundaries. Figure 5-10(b) also reveals the interlocking of the steps across the grain boundary. It is apparent that there are no grain boundary glass phases that would reduce the permittivity and degrade poling. Therefore, KNN ceramics cold sintered under the conditions utilized here have a high concentration of line defects, crystalline grain boundaries, and small grain sizes. It is inferred that although high-density ceramics with crystalline grain boundaries can be prepared by CSP, the properties are limited by grain growth and the preponderance of grain boundary rather than bulk diffusion. As a result, defects that are inherent in the starting powders are retained throughout CSP. Thus, it will be critical in the future to carefully design the calcination and milling steps so that powders with low initial defect densities are utilized for cold sintered piezoelectrics.

The importance of mixing and solid-state reactions and the evolution of high crystallinity in conventionally sintered KNN ceramics has been reported.²⁰⁴ Thong *et al.* reported improvements in the powder crystallinity with a calcination temperature ~1000 °C.²⁰⁵ They used a structuring of KNN powders with a dielectrophoretic assembly method in a polymer undergoing in situ crosslinking. To obtain high performance, Deutz *et al.* used a rigorous calcination condition (1050 °C for 3 h and 950 °C for 20 h) for KNN powder to achieve excellent piezoelectric properties in the KNN-PDMS composites.²⁰⁰ The relatively lower calcination temperature was used in this study for better densification with fine particles, but future studies need to focus on the quality of the initial powder.²⁰⁵



Figure 5-8: (a) Field dependence of dielectric permittivity, (b) *P-E* hysteresis at 5 kV/cm. Circle: Measured values, Blue line: calculated value



Figure 5-9: (a) Potential energy landscape for the domain wall motion in ferroelectric ceramics. Proposed local potential well for the conventionally sintered KNN (b) and the cold-sintered KNN (c).



Figure 5-10: (a) A representative grain with high density of linear defects; (b) a representative kinked grain boundary with good crystallinity in the cold-sintered KNN ceramics prepared at 230°C with 10 vol% of NaOH-KOH under 400 MPa of uniaxial pressure.Rayleigh analysis for the cold-sintered KNN ceramics (black circles) and after annealing at 700 °C (blue triangles).

5.4 Conclusions

The densification of KNN piezoelectric ceramic materials can be readily accomplished via cold sintering at temperatures $T_s/T_m < 0.2$ (T_s : Sintering temperature, T_m : Melting temperature of KNN). The final relative densities are over 92% with the use of NaOH-KOH at approximately 200 $^{\circ}$ C, at 400 MPa. The densification is largely complete within two hours. The grain size is ~200 nm and grain-growth is limited in coarsening at isothermal holds at these temperatures. X-ray diffraction shows the phase purity is maintained through the cold sintering steps. The low field dielectric permittivity is similar to conventionally sintered KNN ceramics. High electric field strengths can be applied $\sim 80 \text{ kV/cm}$, without high losses, suggesting that there is reasonable dielectric strength and control over nonlinear conduction mechanisms. Despite these observations, high poling fields do not provide high piezoelectric performance. A Rayleigh analysis showed difficulty moving the domain walls; this is reflected in lower nonlinear Rayleigh coefficients. TEM observation revealed a high concentration of line defects in the grains. These are believed to originate from the imperfect crystallization at the calcination step. The bulk defect states did not change under cold sintering, as the major diffusion processes that drive densification are surface and grain boundary diffusion pathways. The bulk diffusion processes that participate in conventional sintering are limited during cold sintering, so the residual defect states and concentrations in the calcined powders are not changed. Future work for piezoelectric ceramics will need to consider not only the grain boundary interfaces, but also the defect types and concentrations in the powders to be utilized in cold sintering. Clearly, in the case of cold sintering and piezoelectric properties, the dislocation concentration will be a very important consideration, given its role in domain and/or domain wall pinning.

Chapter 6

Future Work and Conclusions

6.1 CSP for Ferroelectric & Piezoelectric Perovskites

Chapter 4 and 5 demonstrated that a strong alkaline solvent is effectively densifies BaTiO₃ and (K,Na)NbO₃ ceramics. A similar approach may be effective for other perovskite systems. The author attempted to densify the (Bi,Na)TiO₃-BaTiO₃ (BNT-BT) system using NaOH. **Figure 6-1** is the microstructure of as-CSP BNT-BT, showing well-densified grains of faceted morphology. This preliminary work could be useful for piezoelectric applications with BNT-BT,²⁰⁶ or in an oxygen conductor in slightly sodium-rich BNT.²⁰⁷

Chapter 4 demonstrated the possibility of synthesizing a transparent ferroelectric oxide by CSP. The transparency of the cold-sintered $BaTiO_3$ can be further improved with different processing conditions. **Figure 6-2** shows a micrograph of as-sintered $BaTiO_3$ sintered at 350 °C for 12 hours. The pellet was transparent with light yellow color. It would be interesting to explore new applications with this unique property in polycrystalline ferroelectric ceramics.



Figure 6-1: SEM microstructure of the BNT-BT ceramics. Cold-sintering was performed at 350 °C under 350 MPa of uniaxial pressure for 3 hr with 10 vol% of NaOH.



Figure 6-2: Photograph of the Cold-Sintered BaTiO₃ with better transparency. A similar condition used in Chapter 4 was used except the initial powder of Toda050 (Toda Kogyo Corp., initial particls size ~ 50 nm) and sintering temperature at 350 °C.

6.2 Exploring New Ceramic-Polymer Composites^f

In **Chapter 4**, the author has shown that BaTiO₃ ceramics can be densified at 300 $^{\circ}$ C using a mixture of NaOH-KOH. The work has been extended to a series of studies in BaTiO₃-polymer composites using Ba(OH)₂·8H₂O.^{60,208} The purpose of synthesizing composites is to enhance their electrical properties by dispersing electrically resistant polymers (e.g. PTFE) at grain boundaries; this concept is briefly explained in **Section 1.1**. The concept looked promising as is obvious from the improved d.c. resistance of BT-5% PTFE composites compared to cold-sintered BaTiO₃ ceramics (Figure 6-3(a)). The BT-5% PTFE composite shows almost 2 order of magnitude higher resistivity than pure cold-sintered BT from R.T. to 200 °C. The difference in the resistivity between the cold-sintered and the conventionally sintered $BaTiO_3$ ceramics may result from the remaining hydroxide or nature of the bonding at GBs. Still, the resistivity of the cold-sintered BT-5% PTFE composite is even higher than conventionally sintered BT. Therefore, the addition of a small amount of polymer counteracts detrimental sources (e.g. remaining hydroxide) and maintains decent resistance of BaTiO₃ by CSP. The better resistivity in cold-sintered BT-5%PTFE was retained at higher temperatures and higher electrical field regime (Figure 6-3(b)). The d.c. conduction in BaTiO₃ is often dominated by the bulk-limited Poole-Frenkel (P-F: $I \propto$ $E \exp[(\beta E^{1/2} - q\phi_t)/kT]$) type or Electrode-limited Schottky emission (SE: $J \propto T^2 \exp[(\beta E^{1/2} - q\phi_B)/kT])$ type.^g Whether SE or P-F is typically determined from the slope $(=\beta/kT)$ in the SE plot $(\text{Ln}(I/T^2) \text{ vs } \sqrt{E})$ and P-F plot $(\text{Ln}(I/E) \text{ vs } \sqrt{E})$. Figure 6-3(c) shows SE

^f More detail discussions & experimental procedures can be found at K. Tsuji, T. Sada, A. Ndayishimiye, Z. Fan and C.A. Randall, "Reimagining High Performance Dielectrics: Modifying Ceramic Grain Boundary Interfaces with Polymers Via Cold Sintering", *J. Appl. Phys.* (2021) *Submitted* ^g T is the absolute temperature and E is the electric field between electrodes ($\therefore E_{ave}$), A^* is the effective

Richardson constant, ϕ_B is the Schottky barrier height, ϕ_t is the trap level below the conduction band, k is the Boltzmann constant, q is the electric charge, V is applied voltage, ε_0 is vacuum permittivity and ε_{∞} is dynamic permittivity ($\equiv n^2$), where n is the refractive index. $\beta = \sqrt{q^3/\eta\pi\varepsilon_0\varepsilon_r}$ and η is defined as 1 for Poole-Frenkel and 4 for Schottky emission conduction.

and P-F plot of BaTiO₃ – PTFE nanocomposite at 150 °C. Then, ε_r was calculated from the slope of each plot; the value was 0.02 and 0.27 for SE and P-F respectively. These values are not physically reasonable for the dielectric constant of PTFE, meaning that the DC conduction in the composite cannot be described either by the electrode-limited Schottky-type or the bulk $(BaTiO_3)$ limited Poole-Frenkel conduction. The unreasonably small ε_r is often seen in the GB-limited conduction, where the voltage drop occurs on a local scale so that an underestimation of the actual electrical field, namely, using E_{ave} , instead of E_{loc} , gives a larger β , thereby resulting in the extrapolated and unrealistic values of ε_r .²⁰⁹ Then, assuming the major voltage drop occurs at GBs, $E_{\rm loc}$ is estimated as $E_{\rm loc} \equiv \Delta V / \delta \approx V_{app} / \delta n$, where ΔV , V_{app} , δ and n are the voltage drop per GB, the applied voltage, the depletion layer thickness and the number of GB between electrodes, respectively. The slope of the plot of $Ln(I/T^2)$ and Ln(I/E) as a function of \sqrt{V} , should be given as $\beta/n\delta kT$. Then, assuming $\varepsilon_r \approx 2.1$ for PTFE layers at GBs, $\bar{d} \sim 90$ nm and L = 1.10 mm for the specimen,⁶⁰ the calculated δ was then far more reasonable with ~1.0 and ~10 nm for SE and PF plot, respectively. The ~ 10 nm of the blocking layer at GBs seems to be quite reasonable considering the observed thickness of PTFE at GBs by TEM and the adjacent depletion layers at BaTiO₃/PTFE interfaces. More experimental work is necessary to understand the underlying mechanism of the leakage current in the cold-sintered composite. Still, it is unambiguously clear from the discussion above that a small amount of PTFE addition significantly alters the DC conduction characteristics and PTFE layers at GBs play a dominant role in controlling the leakage current in BaTiO₃ – PTFE composites.



Figure 6-3: (a) Temperature dependence of DC resistivity, (b) Current density – Electric field characteristics at 150 °C, of the cold-sintered BaTiO₃ ceramics, BaTiO₃ – PTFE composite (5 vol %) and the conventionally air sintered BaTiO₃ ceramics. Cold-sintering was performed at 225 °C under 350 MPa of uniaxial pressure for 1 hr. The reference samples were prepared by firing the same BaTiO₃ powder at 1260 °C for 2 hrs.

Figure 6-4(a) shows *P-E* hysteresis of the cold-sintered BT-5% PTFE. It is interesting that the BT-PTFE composite shows linear response at high electrical field (70 kV/cm). In BaTiO₃ ceramics, non-linear response typically appears in the range of 10-20 kV/cm. This suppression of the non-linear dielectric properties is also accomplished by the redistribution of the field strength, now largely localized in the grain boundary regions. **Figure 6-4(b)** shows the relative permittivity as a function of electric field with an essentially constant permittivity ~900 at room temperature. The dielectric permittivity magnitude of the cold sintering nanocomposites is superior to other linear pure ceramic dielectrics at room temperature in materials such as TiO₂ ($\varepsilon_r \sim 90$), Bi(Zn_{1/3}Nb_{2/3})₂O₇ ($\varepsilon_r \sim 140$), SrTiO₃ ($\varepsilon_r \sim 350$), and Ag(Nb,Ta)O₃ ($\varepsilon_r \sim 410$).²¹⁰⁻²¹³ All, these observation suggest exciting new opportunities for developing high-*k* capacitors with better voltage-dependence as under high fields, with a relative permittivity of ~ 1000, high resistivity, and low losses.

In short summary, very promising and interesting features in the cold-sintered BT-polymer composite have been shown in this section. Preliminary studies have mostly focused on BT-PTFE system at this point. There should be many opportunities to find a suitable polymer for the desired properties. At the same time, it is necessary to find a better way to disperse the polymer in BaTiO₃

ceramics. Using a polymer solvent mixed in liquid form is of interest, if the solvent is available. If not, cryo-milling should be explored.



Figure 6-4: (a) *P*-*E* hysteresis loop of $BaTiO_3 - PTFE$ composite with 100 Hz of a.c. field at R.T. (b) a.c. field dependence of dielectric permittivity of $BaTiO_3 - PTFE$ composite.

6.3 Promoting Grain Growth

Grain size is one of the critical factors determining dielectric and piezoelectric properties.¹⁹⁹ The author has used fine (< 500 nm) nanoparticles for CSP in this study as the higher surface area of nanoparticles was believed to be helpful to minimize the amount of sintering aid. However, relatively limited piezo- and dielectric properties in **Chapter 4 and 5** could also be due to the nano-size of final grain sizes. Though the optimum grain size should be different in each materials system, the maximum piezo- and dielectric properties often reported in the range of 1 μ m of average grain sizes.²¹⁴ The final grain size reported in this work is much smaller than that range (50-500 nm). Further processing condition optimizations will be needed to balance out the sinterability and functional properties that are determined by the initial particle size, amount of the flux, and final grain size.

Promoting grain-growth in the sintering process is important for fabricating textured piezoelectric ceramics for better piezoelectric properties.²¹⁵ With the help of Dr. Dursun, the author attempted to cold-sinter $BaTiO_3$ ceramics with 5 vol% $BaTiO_3$ templates to see the possibility of the textured ceramics by CSP. SEM microstructure of the cold-sintered BT ceramics is shown in Figure 6-5(a). The microstructure looks dense, and there are epitaxial nucleations at the interface of the template (Figure 6-5(b)). However, most of the grain morphology is isotropic and randomly oriented because of limited grain growth. In the ideal texture grain growth process, the templates need to (1) let the matrix particles to epitaxially nucleate on the interface, then (2) grow via the Ostwald ripening process after densification.²¹⁶ It seems that the microstructure in Figure 6-5(b) is in the middle of the process (1) and (2). The limited diffusional process at the low sintering temperature may be the reason why large-scale grain growth did not occur. The grain-growth mechanism was activated once the specimen was annealed at 800 °C and oriented grains were observed in Figure 6-5(c). For the ultimate goal to have textured ceramics by CSP without the annealing process, one should have better control of the grain-growth mechanism. It is noted that large grain sizes have been observed in some materials systems sintered by the CSP while it is somewhat limited in BaTiO₃ and KNN systems. Such large grain growths in CSP have been observed in the highly soluble ionic molecules.^{50,217} Therefore, it is speculated that the growth rate may be related to the dissolution rate of ceramic particles into the solution or flux. In this sense, surface modification of the ceramic particles or finding a more reactive solution would be interesting approaches for promoting grain growth.



Figure 6-5: SEM microstructure of the cold-sintered BT with 5 vol% of templates. (a) Low-magnification (b) High-magnification. Arrows in (b) show good interfaces between template and matrix BaTiO₃ particles. (c) CSP+Annealing at 800 °C for 5h.

6.4 For Higher Piezoelectric Properties

In Chapter 4, the TEM micrograph of BaTiO₃ clearly showed that lattice defects in the initial particles remained at the core region of the grain, while it seemed relatively defect-free in the shell region. This core-shell-like microstructure indicates that diffusion during the CSP mainly occurred at the grain boundary or surface of grains via the dissolution-precipitation process. Thus, it is believed that the lattice diffusion in the grain is less active in CSP, so that lattice defects in the initial powder are likely to remain in the final sintered pellet. This could contribute to suppressed piezoelectric response in the cold-sintered KNN ceramics shown in Chapter 5. The Rayleigh analysis showed that there is difficulty in moving the domain walls, possibly due to the defects in the grains. TEM analysis also revealed a high concentration of defects in the cold-sintered KNN. The author has tried annealing for the cold-sintered KNN ceramics to remove the defects in the ceramics. However, there were only limited improvements of ferroelectric and piezoelectric properties by annealing the cold-sintered pellet (Figure 6-6(c), d_{33} ~78 pC/N after annealing at 700 °C). It is still lower than the reported value of d_{33} of KNN ceramics. The annealing at a higher temperature, 800 °C, resulted in the formation of unknown impurity phases (Figure 6-6(c)), presumably because of the reaction between KNN grain and the remaining hydroxide flux. With these results, high-temperature annealing may not be a suitable strategy for realizing good

piezoelectric properties in the cold-sintered KNN system with NaOH-KOH. Instead, future work should focus on optimizing the calcination and milling conditions to obtain higher piezoelectric properties with less defect concentration in the ceramics.



Figure 6-6: *P-E* hysteresis (a) and field dependence of dielectric permittivities (b) of as-CSP ceramics and after 700 °C. (c) XRD patterns of KNN initial particle, as-CSP and annealed at 500-800 °C for 2h. * represents peak positions of unknown impurity phase.

6.5 Remaining Hydroxide

It was shown in **Chapter 4 and 5** that alkaline flux is effective for densifying BaTiO₃ and $(Na,K)NbO_3$ systems. However, **Figure 4-5** shows that the flux still exists in the ceramics, which could be detrimental for the properties under high-field and/or high-temperatures. **Figure 6-7** shows the stability of the dielectric loss of the cold-sintered BaTiO₃ over 10 days. The dielectric loss was stable until 3 hours, but then started to increase with time. This is believed to be due to the hydroscopic nature of the alkaline flux that remained in the cold-sintered BaTiO₃. Future studies should focus on this issue for practical application. Kähäri *et al.* have already addressed a similar issue in the cold-sintered Li₂MoO₄ ceramics, which is also hydroscopic material. They reported that a conformal coating of silicone significantly improved the humidity resistance of dielectric properties.²¹⁸ In case the silicone or the other polymers are not desirable due to the thermal

resistance, coating of oxide layers by atomic layer deposition would be an alternative choice for future studies.²¹⁹



Figure 6-7: Time dependence of dielectric loss of BaTiO₃ ceramics cold-sintered Ba(OH)₂·8H₂O in ambient condition. Temperature and humidity are maintained 20 ± 2 °C and 25 ± 7 %.

6.6 Processing with Hydroxide

The author and Dr. Dursun have attempted to synthesize BaTiO₃ MLCC by CSP. It was found that the strong-base, and hydroscopic characteristics of hydroxides are problematic for making the ceramic tape for MLCCs. **Figure 6-8** shows the schematic processing process for MLCCs by CSP. For example, when NaOH-KOH was mixed with ceramics powders and polymer binder by ball-milling, the hydroxides interacted with the polymer binder, and changed the viscosity of the slurry. As a result, it failed to make a good quality of the ceramic tape. Although this problem can be overcome by using less reactive Ba(OH)₂·8H₂O as an alternative sintering aid, Ba(OH)₂·8H₂O reacted with moisture in the air and forms BaCO₃ during the drying and/or binder burnout process. The amount of Ba(OH)₂·8H₂O at the cold sintering stage thus dropped relative to the original formulation and then resulted in poor densification. Therefore, extra care for the humidity is needed for the future study to make MLCC by CSP with the hydroxide, or one may need to find other effective sintering aid for perovskite systems, that is less reactive with polymer and humidity. It is this challenge of binder removal and deactivation through dehydration of the sintering aid that limits the next stage in multilayer devices with the BaTiO₃-based dielectrics prototypes.



Figure 6-8: Schematic representation the copper cofired ceramic/polymer multilayer device fabricated by CSP. As shown in the figure, circles correspond: (a,b) metal ink preparation, (c) slurry preparation for tape casting, (d,e) performing of tape casting and cutting, (f) screen printing on the tape, (g) green forming and binder burn out of the multilayer sample under gas flow, (h) CSP, (i) sintered MLV device and the termination of electrodes for the material characterizations. The figure is adapted from ref.⁵⁹

6.7 Processing Efficiency

Batch processing is a limitation to mass production using CSP at this time. Therefore a transition to a continuous cold sintering approach is needed. Limitations found in batch processing are similar to those in SPS and hot-pressing. There are a number of examples of commercialization of these types of sintering, but the adoption is in niche markets, and requires many sintering presses on a factory floor. There are early signs with the CSP being an open process that a continuous process could be accomplished. Bang *et al.* demonstrated that some ceramics (ZnO, ZnO-based composites, Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃) could be densified by CSP in sizes as large as $5 \times 5 \times 0.1$ cm^{3,220} These materials were densified at < 200 °C of sintering temperature, < 50 MPa of uniaxial pressure and for 0-60 min of sintering time, respectively. The uniaxial pressure used in the study was much less than the vapor pressure of water in the isochoric condition, meaning that CSP does not require a closed system. The facts that CSP has a fairly fast densification rate and does not require the closed system, suggest that a continuous process such as the rolling process seems quite feasible in the future, at least for some material systems.

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Kosuke Tsuji was born and grew up in Ibaraki, Japan. He attended Tohoku University, Japan and received a B.Sc. degree in March 2014. During his undergraduate career, he spent one year at the Pennsylvania State University (2011-2012) as an exchange student. He then joined Professor Clive Randall's research group in 2014 to pursue an M.S. degree in Materials Science and Engineering. He earned M.S. degree for his thesis entitled: "Characterization of Localized Electronic Structures Enabling Colossal Permittivity Ceramic Capacitors". He then started working on Cold Sintering Process for his Ph.D dissertation. His current research interests include electrical characterizations and low-temperature processing for ferroelectric and piezoelectric ceramics. ORCID: 0000-0001-9346-4450