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COLD SINTERING OF LEAD ZIRCONATE TITANATE BASED COMPOSITES

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Materials Science and Engineering

by

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Abstract

Medical ultrasound and other devices that require transducer arrays are difficult to manufacture, particularly for high frequency devices (>30 MHz). To enable focusing and beam steering, it is necessary to reduce the center-to-center element spacing to half of the acoustic wavelength. Conventional methodologies prevent co-sintering ceramic-polymer composites due to the low decomposition temperatures of the polymer. Moreover, for ultrasound transducer arrays exceeding 30 MHz, methods such as dice-and-fill cannot provide the dimensional tolerances required. Other techniques in which the ceramic is formed in the green state often fail to retain the required dimensions without distortion on firing the ceramic.

This dissertation explores use of the cold sintering process to produce dense lead zirconate titanate (PZT) ceramics for application in high frequency transducer arrays. PZT-polymer 2-2 composites were fabricated by cold sintering tape cast PZT with Pb nitrate as a sintering aid and ZnO as the sacrificial layer. PZT beams of 35 μ m width with ~5.1 μ m kerfs were produced by this technique. The ZnO sacrificial layer was also found to serve as a liquid phase sintering aid that led to grain growth in adjacent PZT. This composite produced resonance frequencies of > 17 MHz.

This dissertation also explored cold sintering of PZT using alternative sintering aids. It was shown that lead acetate trihydrate lowers the optimum cold sintering temperatures to 200°C. Densification entailed a 2 step process: cold sintering of PZT with Pb acetate trihydrate and post annealing the as cold sintered PZT ceramics. Unlike in the case of lead nitrate, PZT densification with lead acetate trihydrate occurs by a liquid phase assisted sintering mechanism, leading to an as-cold sintered relative density of 84% at 200°C. After performing a post anneal step at 900°C, >97% relative densities were achieved in samples that were cold sintered with Pb acetate trihydrate. This

step not only densified PZT but also refined the grain boundaries. In the post-annealed samples, the room temperature relative permittivity at 100 Hz was ~1600, slightly higher than that reported in samples that used lead nitrate as a sintering aid; the loss tangent was about 3.8%. For measurements at 10 Hz, the remanent polarization in both cases was $\sim 28\mu$ C/cm². Both Rayleigh analysis and ageing studies showed that a higher irreversible contribution to the permittivity exists in samples that used Pb nitrate as a cold sintering aid.

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Chapter 1

Statement of Purpose

There is a growing interest in developing composite materials for various applications. The drive to develop such composites arises from the need to engineer combinations of properties that cannot be obtained using a single-phase material. Various connectivity patterns allow composite properties to be tailored¹. For example, 2-2 connectivity patterns are used in the design of medical ultrasound transducer arrays². However, array fabrication is challenging particularly in high frequency devices, for which mechanical dicing cannot be utilized. Conventional methodologies prevent co-sintering lead zirconate titanate (PZT)/polymer composites due to the low decomposition temperatures of the polymer. Moreover, for ultrasound transducer arrays exceeding 30 MHz, 3D printing, laser machining and deep reactive ion etching cannot achieve the dimensional tolerances required. As a result, the geometries available for 1-3 or 2-2 composites are typically limited by what can be achieved using a diamond saw for inexpensively manufacturing transducers as needed for high frequency ultrasound systems. Recently, low temperature processing techniques have garnered interest as they can facilitate the processing of multiphase materials with dissimilar physical and chemical characteristics. Among these techniques, the cold sintering process utilizes the lowest processing temperature which allows the fabrication of various ceramic-polymer, ceramic-metal and ceramic-ceramic composites for a variety of applications. For example, the cold sintering process has demonstrated the ability to manufacture multilayer structures of dissimilar materials. This ability makes the cold sintering process a candidate to fabricate PZT-polymer 2-2 composites for ultrasound transducer arrays.

In this work, the mechanisms of the cold sintering process of PZT with different sintering aids were studied. Cold sintered 2-2 composites with tape cast layers of PZT were also explored. Emphasis was placed on the development of sacrificial layers that allow narrow gaps between ceramic elements to be processed.

Chapter 2 summarizes the various densification process and describes, in detail, the fundamentals of the cold sintering process. A discussion of PZT densification via cold sintering and a comparison of sintering aids is found in Chapter 4.

Chapter 3 describes the fabrication of a fine-scaled PZT-polymer 2-2 composite, operating at > 17 MHz via the cold sintering process, for use in high frequency ultrasound transducers. 2-2 composite arrays were successfully fabricated. Grain growth within PZT was found, likely due to the use of ZnO sacrificial layers leading to a liquid phase sintering at 900°C³. This composite was characterized for compositional and electrical properties. The resulting k₃₃ and d₃₃ were found to be low.

Initial work on the cold sintering process for a single step densification of PZT is described in Chapter 6. Clear evidence for densification was observed, albeit in the presence of excess secondary phases. Potential use of PZT-ZnO composites for multilayer actuators having ZnO as the electrode was also discussed.

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Chapter 2

Cold Sintering Process: Literature Review

Low temperature ceramic processing techniques are needed to reduce energy consumption and carbon emissions during materials production. Moreover, ceramics have been progressively integrated with other ceramics, polymers and metals to produce composites¹⁻⁴. Fabrication of such composite systems by co-firing is difficult due to the differences in sintering temperatures, thermal properties, and chemical incompatibilities of each component in these systems^{5,6}. For these reasons, lowering the sintering temperature of ceramics is critical.

By conventional methodologies, green bodies of ceramics are sintered to >95% relative densities at temperatures ranging from 50-75% of their melting point⁷. Various processing methods including hydrothermal sintering,⁸ spark plasma sintering,^{9,10} microwave sintering,¹¹ liquid phase sintering,¹² and cold sintering¹³ have been developed to lower sintering temperatures. Among these methods, the cold sintering process significantly reduces the processing temperature for many ceramics (<300°C). This technique has been utilized in several applications such as battery materials,¹⁴ capacitors,¹⁵ varistors¹⁶, and piezoelectric actuators and sensors¹⁷, and others¹⁸. This chapter begins with a brief overview of the ceramic sintering process followed by a summary of the development of the cold sintering process. Several mechanisms for the densification of different material systems will be described in the second half of this chapter.

2.1 Sintering of Ceramics

In ceramic processing, sintering is an important step that utilizes thermal energy and/or pressure to densify powders into a dense sample with increased mechanical strength¹⁹. The sintering process of powder compacts is driven thermodynamically by the reduction of surface free energy; the final

stages of sintering, such as grain growth, are driven kinetically²⁰. Powder compacts, known as green bodies, are prepared into desired shapes or forms by various forming methods such as die pressing, isostatic compaction, casting, extrusion, plastic forming, solid free-form fabrication and so on⁷. The relative density of the green bodies obtained by such methods are only 50-70%. On sintering these green bodies, mass transport occurs between ceramic particles as a result of diffusion⁷. Figure 2-1 shows 6 types of diffusion mechanisms that occur during sintering.



Figure 2-1. The 6 diffusion mechanisms during sintering: 1. Surface diffusion. 2. Lattice diffusion from the surface. 3. Vapor transport. 4. Grain boundary diffusion. 5. Lattice diffusion from the grain boundary. 6. Plastic flow. Figure adopted from Rahaman et al. (2003)⁷.

Conventional sintering methods can be categorized as solid state or liquid phase sintering. Solid state sintering employs heat to promote diffusion. As stated above, due to their high melting temperatures, ceramic powder compacts require very high sintering temperatures (>1000°C) in order reach >95% relative density. This process can be described in three main stages: the initial stage, intermediate stage and final stage²¹. The initial stage is associated with diffusion between

two particles and the formation of interparticle necking. During the intermediate stage, diffusion expands the necks between particles, forming a tetrakaidecahedron morphology. The continuous pore phase formed at the grain edges shrinks to reduce in cross section and eventually becomes unstable and pinches off, leaving behind isolated porosity. In the final stage, pores shrink continuously until they disappear²¹. While solid state sintering provides a widely used and inexpensive batch process, it has some drawbacks: isolated pores with concave dihedral angles can coarsen at higher temperatures, it is unsuitable for materials and material systems with low compositional stability at sintering temperatures (e.g. BiFeO₃ ²², polymer-ceramic composites²³), and the continuous use of a furnace at high temperatures can reduce its lifetime.

On the other hand, liquid phase sintering (LPS) makes use of a molten sintering aid to increase the rate of diffusion²⁴⁻²⁶. The sintering aid lubricates each ceramic grain, facilitating particle rearrangement. As densification from particle rearrangement slows, the solubility of the ceramic particles in the sintering aid becomes important, triggering a dissolution-precipitation mechanism²⁴. The solid-liquid interfaces with high chemical potential act as sites for dissolution. The solid then diffuses through the liquid and precipitates on those interfacial sites with lower chemical potential. The liquid is then released from the more efficiently packed areas and may flow into isolated pores^{7,25,26}. LPS can also help reduce the sintering temperature of ceramics with incongruent solubility. For example, compounds such as Cu₂O/PbO, V₂O₅, P₂O₅, or LiBiO₂ facilitate densification of lead zirconate titanate (PZT) ceramics at <1000°C; without such liquid phases, PZT is typically sintered at 1200-1300°C ²⁶⁻²⁹.

Besides the reduction in surface free energy, sintering of ceramic powders is also driven by applied pressure and chemical reaction⁷. This is illustrated schematically in Figure 2-2. During the sintering process, an externally applied pressure can provide a major driving force for densification. This force is significantly higher than that provided by the surface curvature⁷. Examples of processes where this applied pressure is a major contributor to the driving force for densification are hot pressing, hot isostatic pressing, hydrothermal hot pressing and cold sintering⁷. In reactive sintering, chemical reaction of the starting powder and densification occurs in a single step. Systems such as ZnFe₂O₄ are densified using reactive sintering³⁰. This process eliminates the calcination step and can produce an end product containing single or multiple phases. The decrease in free energy, as a result of this process, is much larger than that obtained due to surface area changes. Currently, there is no definite evidence that shows that the energy of the chemical reaction is the driving force for densification⁷.



Figure 2-2. The 3 main driving forces for sintering: (1) reduction in surface free energy, (2) applied pressure, (3) chemical reaction. Figure adopted from Rahaman et al. (2003)⁷.

Several advancements have been made in sintering techniques to reduce the amount of energy consumed by accelerating diffusional processes with different types of rapid volumetric heating methods. Among these techniques, microwave sintering¹¹, flash sintering³¹, and spark plasma sintering^{9,10} increase the inter-particle heating to promote diffusion. Nonetheless, these processes require high temperatures to overcome slow solid-state diffusion required for densification³². High temperatures are also required to convert some materials into a liquid state to couple these processes with liquid phase sintering.

The cold sintering process (CSP) eliminates the requirement for high temperatures in order to achieve densification³³. CSP is a low temperature, energy efficient technique which can be used to densify ceramics at 25-300°C within several minutes under the application of a moderate amount of uniaxial pressure (typically 100s of MPa)³⁴. As in liquid phase sintering, the CSP occurs as a result of particle rearrangement, dissolution-precipitation mechanisms and grain growth, albeit in the presence of a transient liquid phase sintering aid³⁴. Ideally, the sintering aid provides a transient phase which partially dissolves the ceramics, promotes particle rearrangement, and allows precipitation of the supersaturated solution at the pores as the transient phase evaporates^{33,34}. The process can be schematically described as shown in Figure 2-3.



adopted from Guo et al).33

2.2 Historic Overview

In the past 5 years, the cold sintering process has received significant interest. However, the origin of this process can be dated back to the 1950s when the role of moisture in lowering the sintering temperature of certain metal oxides and sulfates was first studied³⁵. In the 1970s, further advancements were made in studying the effect of pressure coupled with heat on the densification of ceramics³⁶. Roy et al.³⁷ first studied the effect of uniaxial pressures and solvents in densifying ceramic pastes. In the following decade, Hydrothermal Hot Pressing (HHP) was developed; this process was later used to densify a variety of compounds such as SiO₂, ZrO₂, TiO₂, Ca(OH)₂, CaCO₃ etc. as well as many polymer-ceramic composites ³⁸⁻⁴⁰. As in hydrothermal sintering, HHP involved a closed system where evaporation of the liquid phase was restricted. Gutmanas et al.⁴¹ first coined the term 'cold sintering' in 1983 to refer to a plastic deformation in metals at low temperatures by utilizing extremely high uniaxial pressure: ~ GPa's. Pressure sintering of alumina powders was studied by Neto³⁵ in the 1900s. Despite obtaining 90% relative density, their work showed that due to poor interparticle adhesion, the ceramic hardness was 10 times lower than that

obtained by conventional sintering³⁵. Riman et al.⁴² developed a Reactive Hydrothermal Liquid Phase Densification process (r-HLPD) to densify BaTiO₃ at 240°C. However, due to slow reaction kinetics, this process needed to be carried out for 72 h to reach a density of 90%. More recently, Kähäri et al.^{43,44} demonstrated that the addition of water to Li₂MoO₄ can promote its densification near room temperatures under applied uniaxial pressure. This method later inspired the work of Guo et al.³³ to densify a wider range of compounds at >300°C at moderate uniaxial pressures, thus giving rise to the cold sintering process. The most commonly used sintering aid in CSP is water; however, other ionic and organic liquids are also utilized.

2.3 Mechanisms

It is important to note that unlike hydrothermal sintering or HHP, the cold sintering process takes place in an open system under non-equilibrium conditions³⁴. Pressure-solution creep is known to be the governing mechanism for densification during CSP ⁴⁵. This mechanism takes place upon a solid under uniaxially applied pressures in the presence of a fluid in an open system. Similar to the mechanism for liquid phase sintering, this mechanism is mediated by chemical potential gradients arising from highly constrained areas where dissolution occurs and less constrained particle surfaces with low chemical potential where precipitation occurs⁴⁶. This mass transport takes place at the particle contact points through a liquid film with thickness of only a few nanometers. Pressure-solution creep, comparable to Nabarro-Herring creep laws, is driven by grain boundary and intergranular diffusion^{45,46}. However, since the activation energy for diffusion is lower in liquids than bulk diffusion in solids, this pressure solution creep can occur at much lower temperatures than the Nabarro-Herring creep.

Depending on the material cold sintered, several chemical pathways exist for obtaining dense materials, as shown in Figure 2-4. These pathways have been categorized based on the physical and chemical properties of the initial powder and solvent selection. These pathways indicate that upon cold sintering, the final product either: (1) retains the chemical composition or phase of the starting powders (e.g., ZnO, magnetite), (2) has a different chemical composition or phase than the starting powders (e.g., α -quartz), or (3) results in a new compound or chemical doping (e.g. BaTiO₃ cold sintered with Ba(OH)₂•8H₂O or Sr(OH)₂•8H₂O).⁴⁶

Based on the chemical interaction between the particles and the sintering aid, the dissolution of the particle surface can be either congruent or incongruent. In congruent dissolution, the particle surface dissolves in the sintering aid, which then undergoes dissolution-precipitation to complete densification⁴⁶. Densification of ZnO in the presence of acetic acid is a widely studied CSP with congruent dissolution. Funahashi et al.⁴⁷ were the first to study cold sintering of ZnO. In their work, they found a reduced activation energy for grain growth (43 kJ/mol) nearly 5 times lower than in conventional sintering⁴⁸.



Figure 2-4. Various chemical pathways for the cold sintering process of different materials.

(Figure adopted from Ndayishimiye et al.)⁴⁶

Congruent dissolution:

Most materials with congruent dissolution follow path $A \rightarrow A$. This pathway leads to a single step densification of materials. This mechanism is enhanced by the concentration of the mobile species generated due to particle dissolution in the liquid phase. To illustrate, a comparison of water and acetic acid as sintering aids for the cold sintering of ZnO was studied⁴⁶. It was found that with the increased solubility of ZnO in acetic acid, the pressure-solution creep mechanism was enhanced^{46,47}. In another example, cold sintering of spinels was demonstrated by the use of chelating agents such as metal-acetylacetonates⁴⁹. The use of chelating agents enables high chemical activity at the surface of the particles creating chemical potential gradients that drive the pressure-solution creep, leading to densification.

Incongruent dissolution:

Ceramics such as Pb(Zr,Ti)O₃⁵⁰, YBa₂Cu₃O_{7- δ}⁵¹ and BaTiO₃⁵² tend to dissolve incongruently in most common solvents, and thus pose a challenge in the cold sintering process. In the absence of dissolution, densification processes in incongruent systems require a high temperature anneal step to enhance mass transport by diffusion and to decompose any second phases that form in the grain boundaries^{18,53,54}.

Wang et al.¹⁸ conducted early work on the cold sinter-assisted densification of PZT using moist Pb nitrate as a sintering aid. In that work, late stage densification occurred due to a viscous phase sintering mechanism via plastic deformation of Pb nitrate⁵⁵. This mechanism has been explained in detail in Chapter 4. However, upon cold sintering, Pb nitrate was found between PZT grains, severely degrading electrical performance. A post anneal at 900°C was carried out to obtain clean grain boundaries which significantly improved the electrical properties of PZT¹⁸.

Cockburn et al.⁵³ performed cold sintering of YBa₂Cu₃O₇₋₈. The applied pressure allowed for preferential crystallographic orientation of the YBa₂Cu₃O₇₋₈ crystallites; their c-axis aligned perpendicular to the direction of the uniaxial pressure. During their experiment, they found that the addition of water to the powders during grinding caused particle cracking. These cracked surfaces consisted of an amorphous layer. This provided a wider range of particle sizes and hydrated surfaces that produced efficient packing by particle rearrangement and capillarity. When water evaporated, the voids between grains were filled by smaller particles, leading to a densified ceramic⁵⁰.

Guo et al.⁵⁴ first demonstrated the use of water to cold sinter high permittivity BaTiO₃. They found that water leached Ba²⁺ ions from the surface of the BaTiO₃ particles, ultimately precipitating as an amorphous layer of BaCO₃ at the grain boundaries. The resulting hydrated Ti-rich layer passivated the surfaces of these particles. Furthermore, formation of amorphous BaCO₃ phase degraded the dielectric properties of the cold sintered BaTiO₃. In another experiment, they used aqueous suspensions of Ba(OH)₂ and TiO₂ to prevent incongruent dissolution. Nonetheless, the formation of BaCO₃ at the grain boundaries as a secondary phase was inevitable. Consequently, their process required a high temperature anneal step (900°C) to decompose the BaCO₃ phase as well as to further densify the cold sintered BaTiO₃ ^{54,56}.

Flux-assisted methods:

Among other methods of circumventing this problem of incongruent dissolution in BaTiO₃, salts containing structural water, molten hydroxide fluxes, and hydrofluxes have been explored as sintering aids. The eutectic mixture of NaOH and KOH at 170°C can be used to lower the synthesis temperature of various complex oxides^{57, 58}. For example, Tsuji et al.⁵⁹ employed this alkali flux in a one-step cold sintering process for BaTiO₃ at temperatures as low as 300°C in 12 h at 520

MPa. Studies have also been conducted where densified BaTiO₃ was obtained by cold sintering using an NaOH flux with small amounts of water in 1 h at 240°C at 240 MPa⁴⁶. Below its melting temperature ($T_m \approx 318$ °C), the NaOH flux has a very high viscosity which hinders the dissolution precipitation process. However, the chemical activity at the contact points between the particles was still high enough to consume the surface of the BaTiO₃ grains. It was explained that the addition of water maintained the chemical activity at these surfaces by decreasing the viscosity of the flux. However, when the amount of added water was increased, the obtained relative densities were much lower. As was previously explained by Guo et al.,⁵⁴ the excess water leached out the Ba²⁺ ions.

Sada et al.⁶⁰ further reduced the cold sintering temperature of BaTiO₃ to 225°C by using Ba(OH)₂ octahydrate as the flux. As stated above, non-equilibrium conditions drive the pressure-solution creep mechanism; a highly reactive particle surface can enhance the rate of densification. In their experiments, Sada et al.⁶⁰ surface-treated their powder with acetic acid to provide the outer surface of each particle with a barium deficient amorphous layer. This reactive outer layer is the region for active dissolution. Upon dissolution of this amorphous layer, the crystalline surface of the grain serves as the low chemical potential area where precipitation occurs. Figure 2-5 summarizes the dielectric constants obtained by different cold sintering approaches. Sada et al. reported the lowest process temperature with relatively high dielectric constants. Following a similar procedure, Sada et al.⁶¹ showed the ability to dope BaTiO₃ with strontium *in situ* using Sr(OH)₂ octahydrate as the cold sintering flux. Their product, upon cold sintering, was phase pure perovskite with a reasonable relative density (92%). This doping method follows the pathway A+B→C. In this process, it is important that the flux (dopant) dissociates and reacts with the oxide particles before the completion of the precipitation step of the pressure-solution creep mechanism.



Figure 2-5. Dielectric constant as a function of cold sintering temperature summarized for different cold sintering techniques used for BaTiO3. Figure adopted from Sada et al.⁵⁷

2.4 Cold Sintered Multiphase Materials and Applications

Lower processing temperatures provide opportunities to bridge the processing gap between ceramics and other materials, allowing the fabrication of multifunctional composites. Sada et al.⁶⁰ used the cold sintering process to co-sinter BaTiO₃ with polytetrafluoroethylene (PTFE) in a single step to produce a unique dense nanocomposite with high relative permittivity. Unlike the NaOH-KOH eutectic flux, the use of Ba(OH)₂ octahydrate as the cold sintering flux maintained the molecular integrity of the polymer under the processing conditions. The incorporation of a polymer at the grain boundaries decreased the dielectric loss to 1.4% and increased the resistivity of the composite by at least 4 orders of magnitude compared to the BaTiO₃ ceramic. Such grain boundary engineering can enhance multilayer ceramic capacitor (MLCC) production by providing a novel ferroelectric with high reliability.

CSP also has potential in the processing of solid-state electrolytes. Li-ion battery electrolytes such as $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) have been densified by CSP to 80% relative densities at 120°C in 20 min⁶². Upon heat treatment at 650°C, their ionic conductivity was 5.4×10^{-5} S/cm at room

temperature. An improvement in the ionic conductivities was seen in the LAGP-(PVDF-HFP) system by soaking in a liquid electrolyte⁶². Cold sintering has also been studied in other systems for high temperature electrochemical applications such as LAGP-LiTFSI⁶³, LLZO garnet⁶⁴, CeO₂ ⁶⁵, Y₂O₃ stabilized ZrO₂ ^{66,67}, Na₃Zr₂Si₂PO₁₂ ⁶⁸, BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-δ} ⁶⁹, yttrium-doped Bi₂O₃ ⁷⁰ and WO₃ ⁷⁰.

Interest in developing novel composites by cold sintering has grown during the last 5 years. Magnetic ceramic composites containing Li₂MoO₄ as a matrix and MnZn ferrite as an additive were fabricated at room temperature for the first time using cold sintering by Väätäjä et al.⁷¹ MnZn ferrite is prone to oxidation at the processing temperatures of 685°C; such oxidation could be avoided by cold sintering. Densities obtained were comparative to those achieved by conventional sintering. In another work, Baker et al.⁷² cold sintered a screen printed Li₂MoO₄ paste on nickel and polyethylene terephthalate (PET) foils. Their work showed that the cold sintering process can densify dissimilar, oxygen-sensitive materials in the absence of an inert atmosphere; this is not possible using conventional sintering. The resulting composites had properties comparable to those made using conventional sintering. Co-sintering of PZT with metals for energy harvesters has been explored. Wang et al.⁷³ observed that cold sintering green PZT tapes on Cu foil did not densify the PZT due to constrained sintering. However, when they replaced Cu foil with Cu tape and co-cold sintered it with PZT tape, they obtained a well densified composite with no cracks or delaminations. Researchers have also produced NaNbO3-PVDF nanocomposites using cold sintering for high energy density capacitors with a discharge efficiency of 64%.⁷⁴ Upon CSP, the β -phase of the PVDF was crystallized, and on further annealing at 300°C, α + γ phase was stabilized. ZnO is a widely investigated cold sintered ceramic due to its large processing window and range of applications. A broad range of metallizations (e.g., Cu, Al and Fe) for potential use in MLCC

have been demonstrated on ZnO as the model ceramic⁷⁵. Metal ink was screen-printed on ceramic tapes which were stacked to form a multilayer structure. Due to the low processing temperature (260°C), no defects or diffusion between the ZnO and the metal layers were observed upon cold sintering. Novel varistors have been produced by evenly distributing PTFE in 1-10 nm wide grain boundaries of ZnO during CSP at 285°C at 300 MPa ¹⁶. 2D-MXenes have also been incorporated along the grain boundaries of ZnO ⁷⁶. The addition of 5 wt% MXene improved the electrical conductivity of the composite by 2 orders of magnitude with a 40-50% increase in its elastic modulus. Funahashi et al.⁷⁷ co-sintered multilayer thermoelectric devices containing ZnO and Ca₃Co₄O₉ layers with PTFE insulator as a separating layer by CSP at 300°C. This work showed the potential of CSP in single step densification of multi-material systems. Cold sintering has also enabled the fabrication of multilayer systems of ZnO/polyethylimine and ZnO-polydimethylsiloxane with metal electrodes in a single step^{70,78}.

2.5 Conclusions

Among the low temperature densification processes, CSP can densify ceramics at the lowest processing temperatures (<300°C). Most congruently soluble ceramics follow a pressure-solution creep mechanism. Several pathways for CSP have been described depending on the composition of the starting ceramic powders and the sintering aids. These pathways serve as a guideline to understand how the pressure-solution creep mechanism manifests itself in the densification process. However, in the absence of an *in situ* inspection, specific details on the reactions at the solid-liquid interfaces under the processing conditions are still not fully understood. Even though the development of CSP is currently underway, the process shows promise in producing a wide range of ceramics with properties comparable to their conventionally sintered counterparts. CSP

has also encouraged inventions of newer composite systems which have shown better properties than those produced by conventional methods. Among these newer composite systems, multilayer structures have been of particular interest. As discussed above, their applications have, thus far, been limited to thermoelectric materials⁷⁷, MLCC metallization⁷⁵ and energy harvesters⁷³. Another area that makes extensive use of multilayer structure is in ultrasound transducer arrays. The usefulness of CSP in the fabrication of 2-2 PZT-polymer composites for this application will be discussed in the next chapter.

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Chapter 3

Cold sintering of PZT 2-2 composites for high frequency ultrasound transducer arrays

3.1 Introduction and Literature Review

Ultrasound transducers are utilized for medical diagnostics, underwater sonar, structural heath monitoring, and non-destructive evaluation¹⁻⁸. The need for improved image resolution has prompted interest in developing transducers with high frequencies. Very high frequency (>20MHz) ultrasound transducers have potential applications in dermatology, ophthalmology, intravascular imaging and so on^{1,2,5,9,10}. Ultrasound backscatter microscopes (UBMs) have been developed as high frequency (>20MHz) imaging tools that function utilizing a mechanically scanned, single-element transducer¹¹.

A generic single element transducer is made up of a piezoelectric ceramic with backing and matching layers, as shown in Figure 3-1¹². When the transducer is excited, sound waves are emitted from both the front and back surfaces of the device. The backing layer absorbs the sound wave emitted from the back surface and so avoids interference from the signals generated from the rear end of the transducer. The matching layer increases the usable sound intensity by decreasing the acoustic impedance mismatch between the ceramic and the human body or water ^{5,12}.



Figure 3-1. Illustration of the various parts of a single element transducer. Figure reproduced from Mina et al.¹²

Composite ultrasound transducer arrays are advantageous compared to single-phase transducers as they both allow a wider range of materials properties to be accessed, and enable beam steering and focusing, as discussed further below. The electromechanical properties of the transducer strongly depend on the arrangement of the various phases in the composite. Diphasic composite transducers are comprised of an active element (which is the piezoelectric ceramic) and a passive element, typically, a polymer. The concept of 'connectivity', first developed by Skinner et al.¹³ and Newnham et al.¹⁴, is used to describe the means by which each phase of the composite is self-connected. In a diphasic system, each phase can be continuous in 0, 1, 2 or 3 dimensions. As a result, 10 connectivities are possible as shown in Figure 3-2(a), where the first digit represents the active phase. Based on the connectivity pattern utilized, many important composite transducers were developed as listed in Figure 3-2(b)^{15,16}.



(a)



(b)

Figure 3-2. (a) 10 connectivity patterns for diphasic composite materials and (b) various composite transducer designs derived from the 10 connectivity patterns. Figure adopted from

Akdogan et al.¹⁵

Composite transducers:

Initial research on the development of piezoelectric composites focused on underwater hydrophone applications due to the requirement of a higher hydrostatic piezoelectric coefficient than PZT. The composite hydrophones were demonstrated to have sensitivities 2 to 3 orders of magnitude higher than their single-phase counterparts, which then led to the use of composite materials in most other applications utilizing transducers¹⁷.

For instance, one-dimensional transducer arrays for medical ultrasound utilize a 2-2 connectivity in the composite geometry. This geometry enables timing of the excitation signals for different elements to be utilized to allow focusing and steering of the acoustic beam¹⁸. Moreover, 2-2 composites have high coupling coefficients and thus increase the transducer bandwidth relative to the bulk piezoelectric ceramic alone^{8,19}. The dielectric constant of the composite is lower than the monolithic ceramic, leading to higher piezoelectric voltage constants^{15,17}. The piezoelectric voltage constant governs the receive sensitivity of a transducer¹⁷. The overall composite density is lower than that of the ceramic, which results in improved acoustic impedance matching between the transducer and human body or water. Lastly, the composite geometry provides some level conformability which facilitates manufacture of focused transducers. Table 3-1 lists the advantages and disadvantages of each type of material¹⁵.

Parameter	Ceramic	Polymer	Composite
Acoustic Impedance	High (-)	Low (+)	Low (+)
Coupling factor	High (+)	Low (-)	High (+)
Spurious modes	Many (-)	Few (+)	Few (+)
Dielectric constant	High (+)	Low (-)	Intermediate (+)
Flexibility	Stiff (-)	Flexible (+)	Flexible (+)
Cost	Inexpensive (+)	Expensive (-)	Intermediate (+)

Table 3-1 Comparison of materials properties used in transducers. (+) indicates favourable, and (-) indicates detrimental properties. Table adopted from Akdogan et al.¹⁵

For several decades, the active material in ultrasound transducers has been polycrystalline lead zirconate titanate (PZT) with a composition engineered near the morphotropic base boundary (MPB). The search for alternative MPB materials has directed research towards relaxor materials²⁰. Single crystal relaxor materials of the composition Pb(Zn1/3Nb2/3)O3–PbTiO3 (PZN-PT) and Pb(Mg1/3Nb2/3)O3–PbTiO3 (PMN-PT) have attracted much attention as suitable materials for transducer applications due to their exceptionally high coupling (k > 0.9) and piezoelectric (d₃₃ > 2000 pC/N) coefficients²¹. This work, however, focuses on polycrystalline PZT-based 2-2 composites for high frequency ultrasound transducer arrays.

Design considerations:

Vibration modes in piezoelectrics depend on the sample geometry and the equations of motion that govern the induced mechanical response. The IEEE standard shows the sample geometries for exciting the various modes of vibration and the associated equations²². In the case of a 1-

dimensional transducer array element, only the thickness mode should be excited for a compact impulse response²³. The thickness mode coupling becomes compromised if other modes are excited within the composite. This will lead to unwanted resonances being generated from reflected Lamb waves from the composite microstructure. These Lamb waves become strongly attenuated over a band of frequencies near the resonance known as the stopbands. The stopband edges are governed by the spatial scale, and lateral resonances (piezoelectrically coupled edge resonances). To avoid the lateral resonances, the width of the piezoelectric element and the kerf must be less than a fraction of the wavelength such that the stopband edge resonance frequency is well above the thickness mode resonance^{23,24,25}.

Both finite element modeling²⁶ and dynamic models²⁷ have been developed to evaluate the spatial scale for composite arrays. However, the ratio of spatial dimensions for a 2-2 PZT-polymer composite can be approximated by using certain guidelines based on simpler calculations. Assuming a broad bandwidth transducer, the stopband edge must be kept above twice the center frequency (f_c). The first lateral resonance occurs when the wavelength of the Lamb waves is at about half-wavelength of the shear wave of the polymer (c_s). The first lateral resonance also occurs at half wavelength resonance of a longitudinal wave across the width of the ceramic (c_l)^{24, 25}. These guidelines give rise to the following conditions for 2-2 composites:

Ceramic width $\leq \frac{c_s}{4 \times f_c}$ (Equation 3.1)

$$\text{Kerf width} \le \frac{c_l}{4 \times f_c} \tag{Equation 3.2}$$

 c_l can be determined using the equation²⁸:

$$c_l = \sqrt{\frac{C_{11}^E}{\rho}}$$
 (Equation 3.3)

where, C_{11}^E is the elastic stiffness, which is the ratio of longitudinal stress in the 1-direction to the longitudinal strain in the same direction, and ρ is the density of the piezoelectric ceramic. Using the equations 3.1-3.3, the dimensions of a 2-2 composite operating above 20 MHz can be determined.

Processing:

Fabrication of a high frequency transducer (>20 MHz) is particularly challenging considering the design requirements described above. Various processing methods have been developed to fabricate composite ultrasound transducers such as align-and-fill²⁹, dice-and-fill³⁰⁻³², injection molding³³, lost mold technique^{34,35}, tape lamination³⁶⁻⁴⁰, laser or ultrasonic machining^{41,42}, coextrusion⁴³, jet-machining⁴⁴, deep reactive ion etching (DRIE)⁴⁵, and solid freeform fabrication (SFF)⁴⁶. Among these techniques, dice-and-fill, injection molding, and lost mold techniques are used for fabricating 2-2 composites for medical imaging applications.



Figure 3-3. Illustration of presently utilized fabrication processes for ultrasound transducers: (a) dice-and-fill method, (b) injection molding process, (c) Rapid prototyping, and (d) soft mold technique. Figures adopted from Zhen *et al.*⁴⁷, Zhang *et al.*⁴⁸, Chabok *et al.*⁴⁹, and Günther *et al.*³⁴ respectively.

First introduced in 1981, dice-and-fill is a widely used and cost-effective technique³¹. This technique involves using a diamond saw to make parallel cuts to form slivers in a conventionally sintered piezoelectric ceramic and backfilling the gaps with a polymer (typically, epoxy) to form a 1-3 connectivity (Figure 3-3(a)). After curing the epoxy in the gaps, the base of the ceramic is removed by polishing or lapping to achieve a 2-2 connectivity. The ceramic grain size and the width of the blade have a strong influence on the fineness achieved in the dicing process^{15,50}. Kerf widths of about 19 μ m have been achieved by this technique in polycrystalline PZT⁴. In single

crystal PIN-PMN-PT, kerf widths of 12 μ m were obtained using a 10 μ m diamond saw blade⁵¹. With narrower kerfs, the diced ceramic is fragile and the thin ceramic slivers prone to crack propagation. Dicing at a very fine scale can also become time consuming. As a result, this technique has severe drawbacks when fabricating transducers >10 MHz frequency¹⁵.

Injection molding can, in principle, provide ease of fabrication of fine features in 1-3 and 2-2 composites. Using this technique, it is possible to fabricate sheet composites of 25 μ m thickness and rod composites of 30-40 μ m.⁵² This process is illustrated in Figure 3-3(b). Rapid production and flexibility in transducer design make this technique attractive. However, this process falls short in terms of complexity, cost and time involved in manufacturing molds. Moreover, since the ceramic is formed in a green state, it is prone to deformation on sintering.

SFF is a rapid prototyping process that produces complex structures with high dimensional precision and modest surface finish⁴⁶. This process was also extended to robocasting⁵³. Using robocasting, complex piezoelectric lattice structures were created which were then backfilled with polymers to manufacture composites (Figure 3-3(c)). The main drawback of these rapid prototyping techniques is low density of the end product which leads to poor overall performance of the transducer⁴⁹.

Lost mold or soft mold techniques, first implemented by Rittenmeyer et al.⁵⁴, utilizes a soft plastic mold containing the required structure as the negative in which ceramic slurry is filled. After drying, the mold is burned out, leaving behind a green body of the required structure (Figure 3-3 (c)). This green body is then conventionally sintered to > 98% relative density. Günther et al.³⁴ adopted this technique to fabricate a 40 MHz transducer with pillar diameters as low as 30 μ m with 10 μ m spacing. However, when their diameter was reduced to 15 μ m, the pillars were subject to deformation on firing.

Tape casting is often used in the manufacturing of multilayer ceramic capacitors (MLCCs)⁵⁵. The use of tape casting in conjunction with sacrificial layers eliminates the need for dicing to form kerfs and provides control over the thickness of the kerf. This technique was used by Kwon et al.³⁷ in forming fine scale PZT-polymer 2-2 composites. They screen printed carbon black on PZT tapes which were then vertically stacked and laminated together in a 3-side support geometry. Carbon black acted as a sacrificial layer which was removed along with other organics during the binder burn out process. The ceramic was then conventionally sintered, and epoxy was backfilled into the gaps created by the release of carbon black. This process resulted in 25 μ m beam widths and 5 μ m kerf widths. However, when fabricated in a 2-side support geometry, the structure began to fail. It is anticipated that the reason for their structural failure was the low green density of the ceramic during the release of the carbon black causing warped PZT beams. Therefore, if the density of the ceramic was high enough before the release of the sacrificial layer, it would be possible to produce structurally stable 2-2 composites with fine feature sizes.

As mentioned in Chapter 2, the cold sintering process (CSP) has shown promise in fabrication of multilayered structures and has demonstrated the ability to co-sinter ceramics with other ceramics, metals or polymers⁵⁶⁻⁵⁸. In the cold sinter-assisted densification of PZT, Wang et al. achieved 89% relative density in the cold sintering step⁵⁹. This chapter discusses the possibility of harnessing this high CSP density in the forming process to ameliorate the structural stability of the PZT beams in the final composite.

Sacrificial layers can be either thermally or chemically released. Thermally released sacrificial layers should be chosen such that the no phase change or decomposition occur at temperatures up to 300°C (which is the CSP temperature), but the decomposition temperature must be less than the post anneal temperature (900°C). These include screen printed or tape cast carbon black, graphite

foil, and so on. In addition to the work done by Kwon et al., several other reports make use of sacrificial layers^{60,61}. Another method of releasing the sacrificial layer is by chemically etching it with a solvent that does not affect PZT. ZnO is a useful sacrificial layer as it can be released easily by dissolving in acetic acid⁶². For example, Liu et al.⁶³ used ZnO as a sacrificial layer in a PZT thin film release process to fabricate flexible piezoelectric devices. In this work, ZnO sacrificial layer is used to define the kerfs between the PZT elements in fabricating the 1-dimensional transducer array. Aside from the ease in releasing, ZnO was chosen as a suitable candidate as: (1) it can be co-sintered with PZT, (2) it is thermally and chemically stable at the post anneal temperature of PZT ($900^{\circ}C$)⁶⁴ (3) its thickness can be tailored, and (3) it acts as a rigid spacing between the PZT layers that does not deform under CSP pressure, thus preventing deformation of the kerf.

3.2 Experimental Procedure

3.2.1 Design and fabrication of PZT-ZnO 3-0 composites

From the previously described design considerations, the dimensions of the final 2-2 composite to operate above 30 MHz were determined based on material constants shown in Table 3-2.

	PZT	Polymer
Туре	PZT-5A (PKI-509,	Spurr resin (Polyscience Inc.,
	PiezoKinetics Inc.,	Warrington, PA)
	Bellefonte, PA)	
C_{11}^E (GPa)	121 [Ref. 65]	5.28 [Ref. 25]
Density (kg/m ³)*	7600	1135
Velocity (m/s)	<i>c</i> _{<i>l</i>} = 3938	$c_s = 976 [\text{Ref. 25}]$
Width (µm)	≤ 34	≤ 8

Table 3-2: Material properties used to determine dimensions of the ceramic-polymer 2-2 composite using equations 3.1- 3.3.

From equations 3.1- 3.3, for the transducer to operate at a center frequency >30 MHz, the width of the PZT elements and the kerfs should be 34 μ m and 8 μ m, respectively. Obtaining these fine features in the ceramic and polymer is beyond the capability of the dice-and-fill techniques, mandating an alternative approach for fabrication.

The forming process involves tape cast sheets of PZT/Pb nitrate with a sacrificial layer that can be stacked to form a 3-0 composite. Tape cast process helps maintain the uniformity in thickness of each element of the 2-2 composite. As an alternative, initial work was carried out using a 25 μ m

³⁹

^{*} Manufacturer reported values

graphite foil as a thermally degraded sacrificial layer. The procedure for the fabrication of each of these samples is described in this section.

To begin, an attrition-milled PZT-5A nanopowder containing a bimodal distribution of particle sizes (50-300 nm)⁶⁶ was utilized. Using this powder, a PZT-Pb nitrate slurry containing 40 vol% ceramic was prepared using a procedure described elsewhere⁶⁷. The slurry composed of 4 g of PZT, 0.4 g (15 vol%) Pb nitrate, 2.76 g Vehicle A (95 wt% methyl ethyl ketone (MEK), 5 wt% polypropylene carbonate), 1.36 g Vehicle B (vehicle B consisted of 65 wt% MEK, 28 wt% polypropylene carbonate, and 7 wt% butyl benzyl phthalate), and 1 g MEK was added to adjust the viscosity of the slurry. This slurry was cast using a stationery Mylar (polypropylene) carrier film of \sim 76 µm thickness (Figure 3-4(a)). Mylar film provides flexibility in handling the tape, does not react with the tape and allows the tape to be easily peeled off. The doctor blade height was adjusted to 14 mil (\sim 355 microns). Before pouring the slurry onto the Mylar film, the region where the doctor blade attains steady speed was noted and the slurry was poured in that region. After casting, the tape was allowed to dry in air for 4 h. The tape was then cut into square sheets with side 1.27 cm (0.5 inch). These square sheets were peeled off the Mylar and stacked vertically to achieve a total height of 125 µm as illustrated in Figure 3-4(b). Each stack serves as an individual PZT element in the 2-2 composite. These stacks were then cut into circles using a cookie cutter or hole punch with 1.27 cm diameter. This process is illustrated in Figure 3-4(c).



Figure 3-4. Fabrication process sequence for 3-0 PZT- sacrificial layer composites. The figures illustrate the following 10 steps: (a) casting PZT/Pb nitrate slurry into a tape (b) cutting into squares with side 1.27 cm. (c) stacking square sheets to the required height. (d) cutting stack into circular sheets with a hole punch and (e) uniaxially laminating at 100 MPa. (f) burning out the binder from the composite stack in a box furnace. (g) hanging sample in a beaker on a hot plate for steaming. (h) cold sintering composite sample in a die. (i) post annealing sample in a box

furnace. (j) dicing post annealed sample to expose the sacrificial layers.

Graphite foils were cut into circles with diameter 0.635 cm (0.25 inch) and placed atop each PZT tape cast sheet concentrically as shown in Figure 3-4(d). PZT stack containing the sacrificial layer was then placed into a stainless-steel die (Wartburg Tool & Die, Inc., Wartburg, TN) with 1.27 cm diameter, with the layers parallel to the plungers. Lamination of this composite stack was carried out for 15 min at 70°C by applying a 100 MPa uniaxial pressure on a Carver Model M press (Figure 3-4(e)). Uniaxial lamination compresses the tapes, tacking them together, and helping reduce the thickness of each layer³⁷. The organics in the tapes were then burned out in a box furnace for 24 h

by slowly ramping up the temperature $(0.4^{\circ}C/min)$ to $280^{\circ}C$ in ambient air. This has previously been shown to enable effective binder burnout⁶⁶.

After the binder burn out process, a steaming process was carried out to reintroduce moisture in the sample. As seen in Figure 3-4(g), steaming was carried out by hanging the sample into a beaker containing water at 120°C. This process allowed lead nitrate in the tapes to absorb the water vapor that condensed onto the sample. After steaming for 1.5 h, the sample was immediately loaded into the die for cold sintering (Figure 3-4(h)).

As described by Wang et al.⁵⁹, the cold sinter-assisted densification process of PZT using Pb nitrate as a sintering aid involves 2 steps: (1) cold sintering (CSP) and (2) post annealing. Following their work, CSP of the composite was carried out at 300°C at 500 MPa for 3h. Subsequently, the sample was post annealed in a box furnace. In order to remove the graphite foil, initially, a 1°C/min ramp rate was used to reach 500°C where the temperature was held for 30 min. The temperature was increased at a 5°C/min ramp rate to 900°C with a 3 h hold time⁶⁶ (Figure 3-4(i)). Since graphite foil burns out at temperatures ~400°C, the post anneal step leaves behind a kerf. The microstructure of one such kerf is shown in Figure 3-5. Good fidelity of the patterned feature is apparent. To achieve the geometries required for a higher frequency composite, thinner graphite foils would need to be employed.



Figure 3-5. Microstructure of a kerf created by the release of the graphite foil during the post anneal step.

As an alternative, ZnO was also considered as a sacrificial layer. The process involves stacking tape cast sheets of ZnO between the PZT tapes to form a 3-0 composite (Figure 3-4). ZnO was chemically removed to form kerfs in the PZT ceramic. The width of the elements and the kerfs is dictated by the amount of shrinkage occurring in the PZT and ZnO layers respectively.

ZnO tapes were cast following a previously established procedure⁵⁷. In this case, however, the doctor blade height was adjusted to 7 mil (177.8 μ m). After drying for 4 h, the ZnO tapes, 17-18 μ m thick, were carefully peeled off the Mylar film and cut into circular sheets with diameter 0.635 cm (0.25 inch). Each ZnO sheet was then placed atop each PZT stack in a concentric manner, as shown in Figure 3-4(d)). The process is described in Figure 3-4. Samples containing 16 and 32 PZT elements were fabricated using this process.

3.2.2 Fabrication and characterization of PZT-polymer 2-2 composites

Two parallel cuts, 0.6 mm apart, were made in the densified composite sample using a wire saw (Princeton Scientific Tech, Easton, PA) to obtain a 3-0 geometry as shown in Figure 3-4(j). The cross section was fine polished in a Leica TXP polisher using lapping films of 9 μ m, 2 μ m, and

0.5 μm. PZT grain size measurement was made using a linear intercept method shown in equation 3.4:

Average grain size =
$$1.5 \times \frac{\text{total length of lines } (\mu m)}{\text{total grain boundary count}}$$
 (Equation 3.4)

To release the ZnO sacrificial layer, the sample was placed in a beaker containing 50% glacial acetic acid. To increase the ZnO etch rate, the acetic acid was heated to ~75°C on a hot plate and the system was agitated using a magnetic stir bar. The process was carried out for 48-96 h to release the ZnO completely. The resulting geometry is shown in Figure 3-6(a). The release of the ZnO was characterized using a scanning electron microscope (Apreo SEM, Thermo Fisher Scientific) operated at 15 kV with an energy dispersive spectroscopy (EDS) detector.

The sample was diced on one end as shown in Figure 3-6(a). The kerfs left behind by the release of the ZnO layer were then backfilled by immersing the sample in Spurr resin in a vacuum chamber for 30 min (Figure 3-6(b)). The polymer was then cured overnight at 70°C for 8 h. The excess epoxy was polished off the sample surfaces after which the sample was cut to obtain a 2-2 composite geometry as shown in Figure 3-6(c). The resulting microstructure was obtained using SEM.



Figure 3-6. Illustration of the process to fabricate PZT-polymer 2-2 composite. (a) shows the kerfs formed in PZT after etching the ZnO layers. The sample was diced along the red dotted lines marked on the PZT. (b) illustrates the epoxy backfilling process. (c) shows the 2-2 composite prepared after backfilling it with Spurr resin and polishing. The black arrow in (c)

shows the poling direction.

In order to make quantitative measurements of the piezoelectric properties, the final dimensions of the composite must meet the requirements stipulated by the IEEE standard to avoid spurious modes. In the thickness extensional (k_1) mode, the thickness of the overall composite should be 10 times smaller than the sample length or diameter, such that when operating in the 33 mode, the sample is clamped along the 1 and 2- directions²³. The width of the sample can be 3 times smaller than the sample length. Thus, to comply with these requirements, the sample was diced, and lapped to a length of 3 mm, thickness of 110 microns and a width of 1 mm.

In order to compare electrical properties of the composite to a single element of PZT, PZT-Pb nitrate sheet stacks were also cold sintered and post annealed using the method described in Figure 3-4.

3.2.3 Electrical characterization

The top and bottom faces of the sample in the orientation shown in Figure 3-6(c) were electroded by sputter depositing gold. The dielectric permittivity and loss tangents were measured using a Hewlett-Packard 4284A LCR meter (Agilent Technologies, Inc., Palo Alto, CA). A system with a Trek Model 30/20 high voltage amplifier system (Trek, Inc., Lockport, NY) and LabVIEW software (National Instruments Corporation, Austin, TX) were used to measure the polarizationelectric field hysteresis loops (P-E loops) at room temperature at a frequency at 10 Hz. The samples were DC poled at 70°C at 2 times the coercive field (35kV/cm) for 1 h in the direction shown by the black arrow in Figure 3-6(c).

For resonance frequency measurements, impedance analysis was carried out using Precision impedance analyzer (Agilent E4980A). The frequency measurement range was set to 100 kHz to 30 MHz. Piezoelectric coefficient (d₃₃) and coupling coefficient (k₃₃) were derived from the resonance and antiresonance frequencies. The piezoelectric coefficient d₃₃ was also measured using a direct method with a d₃₃ PiezoMeter system (PM 300, Piezotest Pte. Ltd., Singapore).

3.3 Results and Discussion

3.3.1 PZT-ZnO 3-0 composite

Figure 3-6 (a) shows a photograph of the 30 element sample after the binder burn out step. Lamination flaws are distinctly visible on the edge of the sample. However, these flaws are not seen in the sample after CSP (Figure 3-6 (b)).



Figure 3-6. PZT-ZnO 3-0 composite placed on a metal cylinder after (a) the binder burn out step containing lamination defects, and (b) after the cold sintering step.

During CSP of PZT with moist Pb nitrate as sintering aid, densification results in particle rearrangement assisted by a plastic deformation of Pb nitrate.^{67,68} It is possible that the combination of particle rearrangement under uniaxial pressure and evaporation of water as the transient liquid phase helped mitigate the lamination flaws. In the post anneal step, as described by Wang et al., PbO (formed by the decomposition of Pb nitrate at ~400°C) acts as a liquid phase at 900°C and densification proceeds via a liquid phase sintering mechanism which leads to >97% densities in PZT. It must be noted that since no transient liquid phase, such as acetic acid, was added to the ZnO tape cast sheets, densification of ZnO occurred only during the post anneal step.

Figure 3-7 shows a microstructure of a cross section of a 16 element PZT-ZnO 3-0 composite before and after etching ZnO. This process achieved a reasonable uniformity in thickness of each layer.



Figure 3-7. Cross section of a 16 element PZT-ZnO 3-0 composite after the post anneal step demonstrating uniformity in thickness along the length of the composite showing (a) the multiple layers of PZT and ZnO. Magnified microstructure of the composite showing the thickness of the

ZnO layer (b) before and (c) after etching with acetic acid.

The PZT and ZnO widths were measured for the 16, and 32 element samples, and listed in Table 3-3. A 17 μ m ZnO green tape cast sheet, upon densification reduced to 5.4 μ m in the sample with 32 elements. This corresponds to a ~68% shrinkage in each of the ZnO layers. Thus, to reach the desired thickness of ~34 microns, PZT tapers were stacked to 125 μ m thickness for each element. After densifying the composite, the thickness of these stacks reduced to 39 μ m (consistent with the previous observation of a ~68% shrinkage in the PZT layers).

It is notable that the cold sintering approach results in well-controlled geometries even of fine ceramic layers. There is no evidence for warping or distortion of the PZT elements that would complicate fabrication of a 2-2 ultrasound transducer, even at high resonant frequencies. In comparison to the previous methods involving sacrificial layers, such as the work by Kwon et al., and Zhang et al., this method provides a much higher fine-scale dimensional control on the PZT beams as well as the kerfs.^{37,38} Indeed, increasing the green density of the ceramic is instrumental in improving the fidelity of the composite geometry.

Table 3-3. PZT and ZnO width measurements for the 2-2 composites containing 16 and 32 PZT beams.

	16 elements		32 elements	
Layer	PZT	ZnO/kerf	PZT	ZnO/kerf
Width	39	5.1	35	6.2
Standard deviation	0.7	0.2	1.1	0.3



Figure 3-8. SEM microstructures of polished cross sections of the PZT layers in (a) 16 element and (b) 32 element composites. The microstructure in (a) shows a 39 μm thick PZT beam and that in (b) shows a 34.8 μm thick PZT beam. Samples were coated with iridium prior to imaging. The dark grains in the PZT beam in (a) are oxidized IrO₂.

The microstructures in Figures 3-8(a) and (b) show PZT grains in a polished cross section of the composite. For the PZT beams with thicknesses > 35 μ m, in the region up to 14 μ m below and above the ZnO layers, the average grain size of the PZT was 4.3 μ m (Figure 3-8(a)). In contrast, further from the ZnO sacrificial layers, the average grain size of the PZT was 2 μ m, leading to a bimodal distribution of the grain sizes in these PZT beams. In cases where the PZT beams were

less than 35 μ m thick, this bimodal distribution was absent, and the average grain size was 5.1 μ m (Figure 3-8(b)). ZnO is known to enhance densification of PZT by acting as a liquid phase at 900°C.⁶⁹ It is speculated that the ZnO serves as a liquid phase sintering aid that accelerates the grain growth adjacent to the PZT-ZnO interface. When the thickness of the PZT layer was reduced (<35 μ m), the ZnO/PZT ratio was increased, thereby increasing the amount of liquid phase available for sintering at 900°C which leads to more extensive grain growth. However, it is likely that during the process, Zn also partially replaces the B-site cation (Zr⁴⁺/Ti⁴⁺) in PZT due to comparable ionic radii.⁷⁰ As a result, PZT becomes acceptor doped and oxygen vacancies are created in PZT according to equation 3.5. or 3.6, depending on the amount of residual lead oxide.

$$ZnO \xrightarrow{PZT} Zn''_{Zr/Ti} + 2V_o^{\bullet\bullet} + V''_{Pb} + O_o^{\times}$$
(Equation 3.5)

$$Pb0 + Zn0 \xrightarrow{PZT} Pb_{Pb}^{\times} + Zn_{Zr/Ti}^{\prime\prime} + V_0^{\prime\prime} + 20_0^{\times}$$
(Equation 3.6)

It can be argued that if ZnO as a liquid phase at 900°C can lead to a 94% relative density in PZT⁶⁹, it would be possible to eliminate the cold sintering step entirely. To assess this, PZT-ZnO composites were fabricated using an identical forming process of laminating tape cast layers of PZT (125 μ m) and ZnO (17 μ m). The resulting part had 16 PZT elements and was conventionally sintered at 900°C in air for 3 h. As seen in Figure 3-9, the thickness reduction in ZnO ranged was ~35%, whereas it was 57% in PZT was upon sintering. This compares to a thickness reduction of 68% for both cases in the cold sintered samples. Thus, the conventionally sintered samples have lower densities than cold sintered PZT-ZnO composites. Thus, it is important to employ the cold sintering step before the heat treatment.



Figure 3-9. SEM image of a cross section of a conventionally sintered PZT-ZnO 3-0 composite.

3.3.2 Electrical measurements

The PZT-polymer 2-2 composite was electroded on the top and bottom faces shown in Figure 3-6(c) such that the PZT and polymer were connected in parallel. Using the mixing rule for parallel connectivity, the dielectric constant of the composite (ε_r^{comp}) can be calculated using equation 3.7.⁷¹ The value of relative permittivity of Zn-doped PZT (ε_r^{PZT}) was taken from Ref. 68 as an estimate. The relative permittivity of Spurr resin ($\varepsilon_r^{polymer}$), 2.1, was measured at 1 kHz at room temperature. Volume fractions of the electroded parts of PZT (V^{PZT}) and polymer ($V^{polymer}$) were evaluated, and used to estimate the relative permittivity of the composite.

$$\varepsilon_r^{comp} = (V^{PZT} \varepsilon_r^{PZT} + V^{polymer} \varepsilon_r^{polymer})$$
Equation 3.7
$$\varepsilon_r^{comp} = (1200 * 0.85 + 2.1 * 0.15)$$
$$\varepsilon_r^{comp} = 1020$$

Figure 3-10 shows the relative permittivity as a function of frequency; it was found that the relative permittivity dropped as a function of frequency from \sim 987 to \sim 816. The dielectric loss obtained at 1 kHz was as low as 0.013. It is apparent that the measured permittivity is slightly below that of

the capacitor in parallel model. The reduced permittivity could be due to: ZnO in grain boundaries in some of the PZT layer, reducing its effective permittivity, acceptor doping of the PZT which drops its effective permittivity, or imperfect alignment of the electrodes with respect to the kerfs.



Figure 3-10. Relative Permittivity of the 30 element PZT-polymer 2-2 composite as a function of log of frequency.

The samples were poled at 20 kV/cm at room temperature. The resulting d₃₃ obtained was 122 pC/N using Berlincourt measurement. It is well known that acceptor doping of PZT results in lower values of d₃₃ compared to their soft doped counterparts. Typical values of hard doped PZT, such as PZT-4 and PZT-8 (Boston Piezo Optics) are 295 pC/N and 225 pC/N respectively[#]. A lower value of the d₃₃ could result from insufficient poling or the presence of ZnO in the grain boundaries. Considering the thickness mode frequency constant for an acceptor doped PZT is 1882 Hz-m,¹² for the fundamental thickness mode resonance to occur at a frequency >30 MHz, the thickness of

[#] Manufacturer reported values (https://www.bostonpiezooptics.com/ceramic-materials-pzt).

the sample must be \sim 53 µm. In this work, however, since the sample thickness was 110 µm, the resonance frequency is expected to occur at 17.1 MHz.

Figure 3-11 shows resonance and anti-resonance frequency for the 2-2 composites. As stated earlier, for a transducer array, only the thickness mode (33-mode) should be excited. The third set of harmonics will represent the 33-mode.



Figure 3-11. Impedance spectra of PZT-polymer 2-2 composite containing 32 elements.

Typical coupling coefficient k₃₃ values for a hard doped PZT are 0.64-0.7.[#] As shown in Figure 3-10, the resonance and antiresonance frequencies obtained were 17.01 MHz and 17.94 MHz respectively. The coefficient k_t was derived from these resonance (f_r) and antiresonance (f_a) frequencies using the following equation²²:

$$k_t^2 = \frac{\pi}{2} \times \frac{f_r}{f_a} \times \cot \frac{\pi}{2} \left(\frac{f_r}{f_a} \right)$$
 Equation 3.6

[#] Manufacturer reported values (https://www.bostonpiezooptics.com/ceramic-materials-pzt).

The open circuit compliance is given by equation 3.7 which was used to derive the closed circuit compliance (equation 3.8)²²:

$$c_{33}^{D} = 4\pi f_{a}^{2} t^{2}$$
Equation 3.7

$$c_{33}^{D} = 4.9 \times 10^{10} \text{ Pa}$$

$$c_{33}^{E} = c_{33}^{D} (1 - k_{t}^{2})$$
Equation 3.8

$$c_{33}^{E} = 4.3 \times 10^{10} \text{ Pa}$$

where, *t* is the thickness of the composite.

The stiffness values were lower than those previously reported by Ritter et al. and Hackenberger et al.³⁶ that used a similar fabrication process. A higher stiffness of the resin could lead to a higher composite stiffness, but the elastic stiffness of Spurr resin is 5.28 GPa (Table 3-2), which is higher than that of the epoxy resin (Epo-tek 301) used by Hackenberger et al. \sim 3 GPa^{Υ}. The coefficient kt also had a comparatively low value, perhaps due to insufficient poling. This is also suggested by the small (12°) phase change in the impedance spectra. When poled at higher electric fields, the composite was subject to dielectric breakdown. This behavior might be tied to either an excess amount of acceptor doping generating a larger amount of oxygen vacancies in PZT, or the presence of ZnO at the grain boundaries of PZT reducing coupling between the PZT grains.

[°] Manufacturer reported values (https://www.epotek.com/docs/en/Datasheet/301.pdf)

3.4 Conclusions

The cold sintering process designed for PZT with Pb nitrate as sintering aid can be extended to facilitate the fabrication of multilayer composite structures with stable geometries. Tape casting produces flat, well-defined kerfs and beams with tailorable thicknesses. In this work, PZT-ZnO and PZT-graphite composites were successfully cold sintered, then post-annealed to produce well-controlled geometries, without significant warping of the ceramic part. Cold sintering helped mitigate the lamination flaws in the PZT-ZnO composites. The ZnO sacrificial layer produced composite geometries that can be scaled to produce a transducer which can operate at high frequencies. Utilizing this method provided a novel pathway to develop composite geometries with high fidelity and to overcome the processing challenges posed by some of the previously used techniques.

It was found that the ZnO sacrificial layer also acted as a liquid phase sintering aid during the post anneal process, which led to grain growth in PZT while acceptor doping the adjacent PZT. The permittivity and loss tangents in the PZT polymer 2-2 composites closely matched the theoretical values obtained by using a parallel mixing rule. The resonance frequency of the composite was > 17 MHz. If the thickness of the overall composite is lowered, it is possible to increase the resonance frequency > 30 MHz. The derived coupling coefficient and d_{33} value obtained were lower than expected, possibly due to a larger amount of acceptor doping in the PZT. In the future, additional characterization must be carried out in order to determine the main cause for the degradation of the electrical properties. EDS analysis can be used to characterize the distribution of Zn in the PZT beams. Measuring dielectric constant as a function of temperature can help analyze the shift and drop in the Curie temperature with respect to that of cold sintered PZT.

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Chapter 4

Comparison of Different Sintering Aids in Cold Sinter-Assisted Densification of Lead Zirconate Titanate

4.1 Introduction

Various processing methods including hydrothermal sintering,¹ spark plasma sintering,^{2, 3} microwave sintering,⁴ liquid phase sintering,⁵ and cold sintering⁶ have been developed in an effort to lower sintering temperatures for bulk ceramics. In many of these approaches, a secondary liquid phase, often called a sintering aid, is used to lower processing temperatures significantly⁷⁻⁹ via a liquid phase sintering mechanism. For example, compounds such as Cu₂O/PbO, V₂O₅, P₂O₅, or LiBiO₂ facilitate densification of lead zirconate titanate (PZT) ceramics at <1000°C; without such liquid phases, PZT is typically sintered at 1200-1300°C.¹⁰⁻¹³

Recently, the cold sintering process (CSP) has enabled densification of a number of ceramic materials at temperatures of 25°C-300°C in the presence of a transient liquid phase and applied uniaxial pressure: ~100 to 500 MPa (in an open system).¹⁴ A broad range of material chemistries and material structures including metal oxides,¹⁵ inorganic salts,¹⁶ composites,^{17, 18} and multilayer systems¹⁹ have been densified using this approach, enabling preparation of prototyped varistors,²⁰ battery materials,²¹ capacitors,²² and piezoelectric actuators and sensors,^{23, 24} etc.

Wang et al.²⁵ recently reported a model for densification of PZT by a cold sinter-assisted process using moistened lead nitrate as the sintering aid. This model assumes that plastic deformation of lead nitrate leads to viscous phase sintering, resulting in a relative density of 89% following the cold sintering step at 300°C and 500 MPa uniaxial pressure. In their experiments, water was utilized as a solvent for lead nitrate to assist in the initial particle rearrangement. However, due to limited control of the water evaporation rate, this procedure can produce varied results depending on the amount of residual water available for densification during CSP.²⁶

In this work, lead acetate (PbAc) trihydrate is explored as a sintering aid to densify PZT by CSP. This approach is 'water-free' in that only the structural water is used in the densification process. Residual PbAc also serves as a lead source during the post anneal to complete densification. This chapter describes limits of densification by cold sintering PZT with lead acetate trihydrate as a sintering aid and compares densification mechanisms and dielectric properties with previous work on cold sintering of PZT with lead nitrate.²⁵

4.2 Experimental Procedure

4.2.1 Densification of PZT

In this work, densification of PZT is described as a 2 step process:

Step 1: Cold sintering of PZT with lead acetate trihydrate (PbAc trihydrate):

CSP with PbAc trihydrate as the sintering aid at varying pressures and temperatures was studied in order to determine the densification mechanism during the process. For this purpose, PZT-5A (PKI-509, Piezo Kinetics, Inc., Bellefonte, PA) of ~3 μ m average particle size was attrition milled to ~400 nm average particle size and combined with a sol-gel derived soft PZT powder of ~100 nm particle size by a process described elsewhere.²⁴ For a single pellet, 0.5 g of this PZT powder was combined with 0.035 g (~15 vol%) of lead acetate trihydrate powder (Sigma-Aldrich Corp., St. Louis, MO, purity ≥99.99%, density 2.55 g/cm³) and hand ground in a mortar and pestle to homogenize the mixture. This composition provided: (1) low residual PbO in the grain boundaries upon post anneal, (2) no extrusion of material from the die due to excess liquid phase and (3) sufficient liquid phase to wet the PZT particles. This powder mixture was then transferred into a cylindrical die (Wartburg Tool & Die, Inc., Wartburg, TN) with a 1.27 cm inner diameter and pressed at uniaxial pressures of 100 MPa-500 MPa. Each experiment was conducted for 3 h at different temperatures (50°C, 100°C 150°C, 200°C, 250°C, 280°C, and 290°C). Pellet densities were measured using the geometric method.

In order to understand the decomposition process at different cold sintering temperatures, two batches of PbAc trihydrate powder were heated in air at ambient pressure conditions at either 200°C or 290°C. The decomposed phases were identified using X-ray diffraction (XRD, Empyrean, PANalytical Corp., Almelo, The Netherlands) with Cu K α radiation. Scans were taken from $2\theta = 5^{\circ}$ to 70° with a step size of 0.026° 2 θ and a scan rate of 0.067°/s. Using a simultaneous DSC/TGA (SDT, TA Instruments Q600, New Castle, DE), the melting point and decomposition of PbAc trihydrate was also measured by heating the powder from room temperature to 400°C at a continuous ramp rate of 20°C/min in air.

Step 2: Post annealing the cold sintered PZT parts:

Post annealing of the cold sintered samples was carried out in a box furnace using a ramp rate of 5°C per minute to 900°C with a 3 h hold time at 900°C, prior to furnace cooling.

For grain size measurement, the samples were polished using 15 μ m, 9 μ m, 6 μ m, 3 μ m and 1 μ m diamond polish successively using a rotation speed of 200 rpm. The average grain size was calculated using the linear intercept method described by eq.4.1 ²⁷:

Average grain size =
$$1.5 \times \frac{\text{total length of lines } (\mu m)}{\text{total grain boundary count}}$$
 Eq. (4.1)

4.2.2. Dielectric measurements:

The following samples were used to investigate dielectric and piezoelectric properties:

 PZT cold sintered with Pb acetate trihydrate at 200°C for 3 h at 500 MPa and post annealed at 900°C for 3 h. PZT cold sintered with Pb nitrate at 300°C for 3 h at 500 MPa and post annealed at 900°C for 3 h.

These samples were electroded by sputter depositing silver on the front and back surfaces. The dielectric permittivity and loss tangents were measured using a Hewlett-Packard 4284A LCR meter (Agilent Technologies, Inc., Palo Alto, CA). A system with a Trek Model 30/20 high voltage amplifier system (Trek, Inc., Lockport, NY) and LabVIEW software (National Instruments Corporation, Austin, TX) was used to measure the polarization-electric field hysteresis loops (P-E loops) at room temperature at 10 Hz. The same system was used for DC poling the samples at 35 kV/cm for 1 h at room temperature.

4.3 Results and Discussion

4.3.1 Densification of PZT

Step 1: Cold sintering of PZT with lead acetate trihydrate (PbAc trihydrate):

Cold sintering experiments were conducted to determine the dependence of final cold sintered density on the applied uniaxial pressure. A series of experiments was carried out using a cold sintering temperature of 200°C for 3 h. It was observed that increasing pressure yielded a monotonic increase in relative density, as shown in Figure 4-1(a). The maximum pressure applied (500 MPa) yielded a maximum relative density of ~84%. The relative densities were calculated by normalizing the as-cold sintered densities to the theoretical density of PZT (7.8 g/cc).



Figure 4-1. As-cold sintered density as a function of (a) pressure and (b) temperature during the cold sintering step. All experiments were carried out for 3 h. Error bars show the range achieved in multiple experiments; variability in the measured densities may be due to the change in the ambient relative humidity. In both figures, the lines are guides to the eye.

It is clear in Figure 2-1(b) that the as-cold-sintered PZT composite density showed a nonmonotonic trend as a function of temperature, where the as-cold-sintered density underwent a maximum as a function of cold sintering temperature, with the peak relative density occurring near a CSP temperature of 200°C. This behavior could be related to the phase changes that occur in PbAc trihydrate which cause a change in densification mechanisms at different CSP temperatures. To understand the difference in the densification mechanisms with CSP temperature, the following regions have been considered: (1) Below ~60°C: PbAc trihydrate retains its solid crystalline form at ambient pressures (supplemental Figure S4-2), (2) Between ~60°C and ~200°C: PbAc trihydrate progressively loses its water of hydration and melts, (3) By 200°C: lead acetate exists in an anhydrous form (Figures S4-1(a), S4-2 in the Appendix A), and (4) $>250^{\circ}$ C: lead acetate decomposes (supplemental Figure S4-2).²⁸

To probe these different regimes, dilatometry was carried out at cold sintering set temperatures of 50° C, 200° C, 250° C, and 290° C. To do this, the temperature ramp was started, then the pressure was applied. Typically, the pressure stabilized within approximately 2 seconds; the time at which the pressure stabilized was treated as time zero. Depending on the set temperature, the desired temperature was reached within a few minutes. The linear contraction was measured during uniaxial pressing using a set up designed by Floyd et al.²⁹ Figure 4-2 is a comparison of the percent contraction data for the PZT/PbAc trihydrate composite during cold sintering. Given the fixed radius of the die, the measured linear contraction (Δ L) (i.e. the thickness reduction of the sample) is the same as its volume contraction. Thus, a larger Δ L corresponds to higher density. The percent thickness reduction was calculated from Δ L and the initial thickness of the powder bed (L_o), as shown in equation 4.2:

%thickness reduction =
$$\frac{\Delta L}{L_0} \times 100$$
 (Eq. 4.2)

The dilatometer was set to collect data every 5 seconds starting from the point when the set pressure was reached. From Figure 4-2, it is apparent that there is initial rapid densification, probably due to particle rearrangement, with plateaus to different densities:



Figure 4-2. Percent thickness reduction of the powder bed as a function of cold sintering process time. The line color denotes the setting temperature of the die during cold sintering. The dots mark times at which particular temperatures were reached. For example, the red dot on the blue curve indicates when a die temperature of 200°C was reached.

PbAc trihydrate melts at ~60°C and progressively loses the waters of hydration, as shown by the SDT thermogram in the supplemental Figure S4-2. It is evident from Figure 4-1(b) that the as-cold sintered densities below this temperature are the lowest, as only particle packing occurs between the PZT and the PbAc trihydrate grains. This corresponds to an ~18% reduction in thickness, as seen in Figure 4-2. The resulting microstructure of the as-cold sintered part is shown in Figure 4-3(a). PbAc trihydrate crystals occupy areas between PZT grains as is expected during dry pressing. The melting of PbAc trihydrate produces higher as-cold sintered densities above ~60°C by providing a liquid phase that assists in particle rearrangement via lubrication of the PZT grains and pore filling due to capillarity. As described by Svoboda et al.,³⁰ the rate of densification due to particle rearrangement is driven by 2 factors: the capillary forces exerted on the solid grains by the liquid phase and any mechanical pressure existing at the points of contact between the solid grains.

These factors provide an unbalanced force that drives further densification to a solid obtained by random dense particle packing in the absence of a liquid phase.³⁰

Even though PbAc trihydrate begins to melt at ~60°C at ambient pressures, a steep increase in ascold sintered density is observed between cold sintering temperatures of 150°C and 200°C in Fig.1(b). As shown by Svoboda et al.,³⁰ the rate of densification due to particle arrangement varies inversely with the liquid viscosity. Given that viscosity decreases exponentially with increasing temperature, it is possible that the increases in densification is due to improved particle rearrangement in the presence of the liquid phase. Moreover, under ambient pressure conditions, lead acetate is anhydrous at 200°C (Appendix A, Figures S4-1(a), S4-2).²⁸ It is possible that as the structural water is released progressively, it further decreases the viscosity of the liquid phase, aiding densification.

The highest reduction in thickness of ~28% was obtained for samples cold sintered at 200°C. In Figure 4-2, the black dot on the red curve indicates the time when the temperature of 50°C was reached. A change in slope at about 2 min indicates the melting of lead acetate (>70°C). Another slight change in slope occurs at 6 min, at which point the die temperature reached 200°C. The densification continues even after the set temperature was reached. As seen in the densification curve for samples cold sintered at 200°C in Figure 4-2, even though a die temperature of 200°C is reached within the first 6 min (indicated by the red dot on the red curve), significant thickness reduction occurs up to cold sintering times of 11 min, after which the curve plateaus. Figure 4-3(b) shows the microstructure of the as-cold sintered PZT at 200°C. The resolidified Pb acetate occupies areas around the PZT grains.

A decrease in ceramic density is observed for cold sintering temperatures above 200°C. A continuous decomposition of lead acetate occurs at temperatures above 250°C (Figure S4-2 in the

supplemental).²⁸ Thus, during cold sintering in this temperature range, there is reduced pore filling and lubrication of PZT particles provided by the available liquid phase. This leads to a \sim 25% thickness reduction in samples that were cold sintered at 250°C as seen in Figure 4-2.

When cold sintering PZT at 290°C, the time period for which sintering aid remains molten as lead acetate (e.g. before the temperature rises to the point at which it starts to decompose, ~ 10 min) is far less than for the case when PZT is cold sintered at 200°C (180 min). As the molten lead acetate decomposes, lubrication of the PZT grains is reduced. In other words, there is an insufficient amount of time for the liquid phase to facilitate adequate particle rearrangement; this leads to low densities in these samples. The densification curve in Figure 4-2 saturates at 18 min when the die temperature reached 290°C. The thickness reduction was ~24%. At this temperature, the decomposed phases are identified as PbCO₃ and Pb₃(CO₃)₂(OH)₂ using X-Ray diffraction available in the supplemental information (Figure S4-1(c)). The microstructure in Figure 4-3(c) indicates this decomposed phase around the PZT grains.

This shows that the densification of PZT during the cold sintering step is determined by the phase of the sintering aid at the cold sintering conditions. It is presumed that the dominant densification mechanism for CSP of PZT with PbAc trihydrate at 200°C is a liquid phase-assisted particle rearrangement.



Figure 4-3. SEM images showing (a) Pb acetate trihydrate crystals accumulated between larger PZT grains after cold sintering at 50°C. (b) resolidified Pb acetate particles between PZT particles when cold sintering was performed at 200°C. (c) PZT particles with decomposed lead acetate particles when cold sintered at 290°C.

(c)

Wang et al.²⁵ studied cold sintering of PZT ceramics with lead nitrate as a sintering aid. In the initial stages of pressing, particle rearrangement led to rapid densification. As a control, if no lead nitrate was added, the densification was limited to some particle rearrangement, and therefore the compact is not considered to undergo a sintering process. However, with lead nitrate, additional

densification could be well described as viscous sintering based on the assumption that lead nitrate undergoes plastic deformation under the applied pressure and temperature during CSP. A viscous phase sintering model was developed for that system that described the late stages of densification. Murray et al.³¹ proposed that for viscous sintering, the density (ρ) varies exponentially with applied pressure (σ) according to the equation:

$$\rho = 1 - e^{\left(-\frac{3\sigma}{4\eta}\right)t+c}$$
(Eq. 4.3)

where, η , t, and c are viscosity, time, and the integration constant respectively.⁴¹ Both the Vogel-Fulcher-Tamman and an Arrhenius relationship between temperature and viscosity described the available data well.

Using PbAc trihydrate as a PZT sintering aid, it was found that the pressure dependence of the densification can be described either with the viscous phase sintering model^{25, 31} or the liquid phase sintering model as seen in Figure 4-4(a).^{32, 33} Therefore, the pressure dependence of the relative density alone cannot be used to determine the densification mechanism. However, as shown in Figure 4-4(b), the density dependence on CSP temperature does not fit a viscous phase sintering model at temperatures >200°C due to the phase changes and decomposition occurring in the sintering aid. Presumably, particle rearrangement and pore filling contribute to densification during cold sintering of PZT with PbAc trihydrate. According to Felten,^{32,33} particle rearrangement is a dominant mechanism in the initial stage of densification during uniaxial pressing. The observation that the densification at 200°C is the highest suggests that a liquid phase sintering aid increases particle packing due to increased capillarity and lubrication.



Figure 4-4. Density variation with applied uniaxial pressure and temperature. The dots are experimental data points, and the line is the best-fit to the data (a) The pressure dependence on

density (at CSP temperature of 200°C) agrees with the model. However, the temperature dependence (b) is not described by the simple viscous sintering model given that PbAc trihydrate dehydrates, melts, and ultimately decomposes over the cold sintering temperature range studied. In comparing Figure 4-4 with work done by Wang et al.²⁵, it can be seen that PZT cold sintered at 200°C, with either lead nitrate or PbAc trihydrate, can reach a relative density of ~84%. Since the viscous phase mechanism is enhanced at higher temperatures, PZT-Pb nitrate composite can reach a relative density of 89% at 300°C when cold sintered with 15 vol% lead nitrate. With Wang et al.²⁵ conducting their dilatometry studies at room temperature, no definitive comparison can be made between the two sintering aids based on dilatometry.

Step 2: Post annealing the cold sintered PZT parts:

As seen from the trends in the data shown in Figure 4-5, it can be seen that higher cold sintered densities lead to higher PZT packing densities. By increasing PZT packing density, the diffusion distance between the PZT grains is reduced during the post anneal step. Therefore, as expected, high cold sintered densities corresponded to high post anneal densities. On post annealing samples cold sintered using PbAc trihydrate as the cold sintering aid at 50°C, 200°C and 290°C, the final densities obtained were $82.1\% \pm 1.8\%$, $97\% \pm 2.8\%$ and $86\% \pm 0.97\%$, respectively as indicated in Figure 4-5.



Figure 4-5. Relative densities of all PZT samples after the post anneal step plotted as a function of CSP relative densities. Relative densities evaluated by normalizing all measured densities to the theoretical density of PZT (7.8 g/cc). The data points come for the CSP temperature and pressure studies.

Figure 6(a) shows the microstructure of the post annealed sample that was cold sintered at 200°C at 500 MPa. PbAc trihydrate is fully decomposed into lead oxide above 376°C at ambient pressures (also Figure S4-2).²⁸ Since PbO melts at 880°C, at the post anneal temperature of 900°C, PbO acts as the liquid phase promoting mass transport and PZT is fully densified by liquid phase sintering. Since the major byproduct of the decomposition of lead nitrate at 470°C is also a PZT-PbO composite,³⁴ the densification mechanism in the post anneal step should be identical in both cases. Figure 4-6(b) shows the microstructure of a post annealed sample that was cold sintered at 300°C with Pb nitrate (98.1% relative density). The powders used were the same in both cases, however, some grains in Figure 4-6(a) are slightly larger than those in Figure 4-6(b). The average grain size

calculated for samples cold sintered with PbAc trihydrate and lead nitrate was 498 nm and 409 nm, respectively.



Figure 4-6. SEM microstructures taken after post annealing at 900°C samples that were cold sintered (a) using PbAc trihydrate at 200°C and (b) using Pb nitrate at 300°C.

4.3.2. Dielectric properties

Figure 4-7(a) shows relative permittivity and loss tangent as a function of frequency for post annealed samples that used PbAc trihydrate and Pb nitrate as sintering aids. The relative permittivity and loss tangent were also measured for the as-cold sintered samples (Figure S4-3 the supplemental information). It was found that for post-annealed samples, ceramics cold sintered using PbAc trihydrate showed a higher relative permittivity and lower loss tangents than those cold sintered with Pb nitrate. However, in both cases, the remanent polarization and coercive field had similar values.

In order to assess domain wall contributions to the properties at small AC electric fields, Rayleigh analysis was carried out by measuring the relative permittivity as a function of AC field (Figure

4-7(c)) at 100 Hz. The irreversible (α) and reversible ($\epsilon_{initial}$) Rayleigh coefficients were extracted from the data in Figure 4-7(c) using:

$$\varepsilon_{33} = \alpha E_0 + \varepsilon_{initial}$$
 (Eq. 4)

where α and $\varepsilon_{initial}$ are the irreversible and reversible Rayleigh coefficients and E₀ is the peak amplitude of the applied electric field.³⁶ $\varepsilon_{initial}$ includes both lattice and reversible domain wall contributions; the α E₀ term comes from irreversible domain wall displacement. The percent of extrinsic contribution was determined using the highest field data and equation 5: ³⁶

% Extrinsic contribution =
$$\frac{\alpha E_0}{\varepsilon_{33}} \times 100$$
 (Eq. 4.5)

Extrinsic contributions arise predominantly from the motion of domain walls in PZT ceramics. From Table 1, it can be seen that samples that used Pb(NO₃)₂ as a sintering aid have a larger extrinsic contribution to the relative permittivity at 3 kV/cm. In samples that used PbAc trihydrate as a sintering aid, a larger fraction of the total relative permittivity comes from the reversible mechanism.



Figure 4-7. Comparison of dielectric properties of post annealed samples cold sintered with PbAc trihydrate at 200°C or lead nitrate at 300°C. (a) Relative permittivity and loss tangent as a function of frequency at room temperature. (b) P-E hysteresis loops at 10 Hz performed at room temperature. The green lines on the y-axis and the x-axis indicate the remanent polarization and coercive field respectively for a conventionally sintered bulk PZT ceramic. The average data from three samples is plotted in (a) and (b). (c) Relative permittivity as a function of AC field in the Rayleigh region at room temperature and 100 Hz for representative samples cold sintered with different sintering aids. (d) Room temperature measurements of relative permittivity as a function of time measured at 100 Hz after poling at room temperature at 35 kV/cm for 1 h.

Dashed lines indicate linear fitting of each curve in (c) and (d).

The ageing of these samples was studied. The domain state of the samples was perturbed by DC poling at room temperature at 35 kV/cm (~2 times the coercive field) for 1 h. In ferroelectric materials, ageing occurs as the domain state gradually approaches local equilibrium after an excitation.^{35,37,38} Thus, a faster ageing rate can be characteristic of material with either larger domain wall mobility and/or where there is a larger driving force for the domains and domain walls to be pinned.

The rate of change of relative permittivity as a result of ageing is described by the following equation ³⁸:

$$\frac{\varepsilon(t) - \varepsilon(t_0)}{\varepsilon(t_0)} = \frac{A}{100} \log \left(t/t_0 \right)$$
(Eq. 4.6)

where A is the ageing rate per decade; $\varepsilon(t_0)$ refers to the relative permittivity at unit time t_0 (100 seconds in this study) and $\varepsilon(t)$ is the relative permittivity at time t after poling. The ageing rates for the cold-sintered PZT ceramics from Figure 4-7(d) are listed in Table 1.

Ageing was also studied using the piezoelectric coefficient, d₃₃, as a function of time measured using PiezoMeter system (PM 300, Piezotest Pte. Ltd., Singapore) as shown in Figure S4-4 in the supplemental information. The data are shown in Table 1. It must be noted that these values are a result of room temperature poling at 2 times the coercive field. However, when the samples were poled at 120°C for 1h at 2.2 times the coercive field, a d₃₃ of 310 pC/N was obtained.

Table 4-1. Rayleigh coefficients and percent extrinsic contribution extracted from linear fit of the data in Figure 4-7(c). Ageing rate for the relative permittivity extracted from Figure 4-7(d). $\varepsilon_{initial}$ is expressed as a range denoting sample-to-sample variations.

	Rayleigh coefficients			Ageing Rate (A)	
	a (cm/kV)	Einitial	Extrinsic contribution (at 3 kV/cm)	εr	d33
PZT samples that used Pb Nitrate as the cold sintering aid	289 ± 4	1100- 1400	39%	2.5% per decade	3% per decade
PZT samples that used PbAc Trihydrate as the cold sintering aid	161 ± 3	1500- 1700	23%	1.3% per decade	2.1% per decade

The samples with lead nitrate as a sintering aid show larger irreversible contributions to the permittivity, as well as larger aging rates. These two observations would be consistent with a potential energy distribution that has a significant population of smaller energy barriers, relative to PZT ceramics cold sintered using PbAc trihydrate as a sintering aid. It is not clear what the

microstructural origin of such pinning sites is, as the average grain size is larger for the samples cold sintered with PbAc trihydrate. Since the number of defects should be inversely proportional to the Rayleigh coefficient α , this suggests that grain boundaries may not be the origin of the pinning for these samples.³⁹

4.4 Conclusions:

Lead acetate trihydrate was introduced as a 'water-free' sintering aid for cold sinter-assisted densification of PZT ceramics. The highest as-cold-sintered relative densities were achieved using a cold sintering temperature of 200°C. Unlike cold sintering with lead nitrate, it was shown that PZT with PbAc trihydrate does not follow a viscous phase sintering mechanism during cold sintering due to the phase changes PbAc trihydrate undergoes with increasing temperature. Upon post annealing at 900°C, PZT relative densities of >97% were obtained in the samples that were cold sintered with Pb acetate trihydrate. These samples showed high relative permittivity values (1500-1700) and low loss tangents with well-developed P-E hysteresis loops. From Rayleigh analysis and ageing studies, it was concluded that the high relative permittivity in these samples (compared to those cold sintered with lead nitrate) was due to a larger reversible contribution. Even though the liquid phase sintering process by Corker at al. using a CuO-PbO sintering aid can provide better densities at the same processing temperatures, the cold sinter-assisted process presented in this work shows that comparable dielectric and piezoelectric properties can be obtained in PZT ceramics. Further, this work can be extended to composite systems where reactive sintering aids such as CuO-PbO can invoke undesirable chemical reactions or unwanted residue at the grain boundaries.

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Chapter 5

Conclusions and Future Work

5.1 Conclusions

The low processing temperature of the cold sintering process has facilitated the fabrication of various composite geometries. This thesis studied the fabrication of PZT-ZnO 3-0 composites using a cold sinter assisted process. Tape cast layers of PZT and ZnO provide uniformity as well as the ability to tailor the thickness of each layer. Cold sintering step of the densification of PZT utilized moist Pb nitrate as a sintering aid. The thicknesses achieved in the PZT and ZnO layers were as low as 35 µm and 5.1 µm. ZnO was used as the sacrificial layer which also provided an additional liquid phase sintering aid at 900°C. This led to acceptor doping in PZT as well as extensive grain growth in the PZT near the PZT- ZnO interface due to enhanced densification. Relative permittivity values were 905 with loss tangents as low as 0.02 at 1 kHz. These permittivity values were a close match to those theoretically predicted by a parallel mixing rule. However, low d₃₃ values were obtained, suggesting a higher amount of acceptor doping occurred during the post anneal step. The composite produced a resonance frequency of >17 MHz, albeit with low values of coupling coefficients. Either insufficient poling or a higher amount of acceptor doping could be possible causes for the degraded performance. Additional characterization is required to determine the main cause for the degradation of properties. In particular, it is recommended in the future that changes in lattice parameter and Curie temperature be used to assess whether or not some of the ZnO dissolved into the PZT. Likewise, additional EDS is required.

Cold sinter-assisted densification of PZT with alternative sintering aids was also studied. Pb acetate trihydrate was identified as a 'water-free' sintering aid which helped reduced the processing temperature of the cold sintering step to 200°C leading to a relative density of 84%.

Since Pb acetate trihydrate exists in a molten state at 200°C, the densification mechanism during the cold sintering step was identified as a liquid phase assisted process. Upon post anneal, ~97% relative densities were achieved. Relative permittivities as high as ~1500 were obtained with low loss tangents. Upon poling at 2.2 times the coercive field, a d₃₃ of 310 pC/N was obtained. It was determined from Rayleigh analysis and ageing studies that high permittivity was a result of a larger reversible contribution.

It must be noted that due to its low decomposition temperature, Pb acetate trihydrate cannot be used as sintering aid in cold sintering tape cast sheets of PZT. Having said that, it is also important to recognize that with the use of the two sintering aids explored in this work (Pb nitrate and Pb acetate trihydrate), cold sintering process for PZT by itself does not provide a significant advantage over conventional methods that use sintering aids. However, the process of introducing sacrificial layers that can be co-sintered with PZT is promising in developing ceramics with various geometries.

5.2 Proposed Future Work

5.2.1 Use of alternative sacrificial layers in the fabrication of PZT-polymer 2-2 composites A new process for fabricating PZT-polymer 2-2 composites was described in Chapter 3. The process used tape cast ZnO as a sacrificial layer which helped develop geometries that can be scaled to produce very high frequency transducers (>30 MHz). The use of ZnO as sacrificial layer was used to demonstrate this ability. However, the slow etch rate as well as the poor electrical properties are an indication that the use of other sacrificial layers must be considered. For example, thermally degradable sacrificial layers such as screen-printed carbon black and acetylene black previously employed as sacrificial layers in conventionally sintered composites can be used in this

process^{1,2}. Their decomposition temperatures (400-600°C) are above the cold sintering temperature (300°C) and below the post anneal temperature (900°C). The need for an additional step to release the sacrificial layer is eliminated as they are removed during the post anneal step. In the previous reports, these sacrificial layers were removed during the binder burn out step during which the parts had lower green density leading to structural defects in the finished parts. Since the green density of the ceramic is important in producing high fidelity in the composite geometry, the proposed work is expected to improve the structure and dimensional stability of the composite. Screen printing these materials on the PZT tapes helps produce thicknesses lower than what can be achieved by tape casting. Using these sacrificial layers, the composition of PZT can also remain unaltered leading to better dielectric and piezoelectric properties.

5.2.2 Single step densification of functional lead barium zirconium titanate (PBZT) ceramics by the cold sintering process

Co-firing ceramics with other materials has always faced the hurdle of high processing temperatures of ceramics. Co-firing piezoelectric ceramics (such as PZT) with metals for developing actuators has faced several challenges such as: (1) warpage and delamination due to inhomogeneous strain changes during cofiring, (2) electromigration of metal ions and dendritic electrode growth at the ceramic-metal interface, (3) partial oxidation of the electrode while firing or during binder burn out, (4) interfacial reactions (such as PbO-CuO at low temperatures) and (5) Cu²⁺ ion causing acceptor doping of PZT, decreasing the piezoelectric coefficient³. Flux selection has been deemed critical as it lowers the firing temperature which helps overcome some of these problems. To avoid oxidation of the electrodes, some groups have suggested that the electrode

surfaces be coated using either precious metal or inorganic layer coating³, although this would increase cost of production.

This is also important for ceramic-polymer composites. As stated in the conclusions section, in fabricating 2-2 composites, sacrificial layers are useful in introducing kerfs in PZT ceramics. However, if the ceramic can be processed at a temperature low enough to co-sinter ceramics and polymers, it would then be possible to develop PZT-polymer 2-2 composites in a single step. Cold sintering process provides a direction toward this goal. Realizing this goal can provide a significant breakthrough in surpassing processing barriers. This section will discuss one such opportunity for PZT-based ceramics.

Various transient chemistries have been developed to facilitate the densification of PZT ceramics by the cold sintering process.^{4,5} The choice of transient chemistry determines whether the cold sintering process should proceed as a single step or two step densification process. Upon cold sintering, ceramics that dissolve incongruently in most water-based solvents, required a post anneal step to achieve functional properties.^{6,7} However, the requirement of this post anneal step was eliminated by the use of flux-assisted cold sintering process to produce functional ceramics.

As discussed in Chapter 2, Sada et al. have demonstrated the ability to fabricate high permittivity BaTiO₃ ceramics at 150°C with Ba(OH)₂ octahydrate as the cold sintering flux⁸. In their work, they used BaTiO₃ powder with average particle size of 100 nm. The outer core of each BaTiO₃ particle was made amorphous by leaching the Ba ion from the particle surface. This provided a high chemical activity for dissolution to occur in the outer layer of the particles, whereas precipitation occurred on the inner core of the grain due to low chemical potential. The formation of BaCO₃ at grain boundaries was persistent until a quasi-total disappearance of this phase was observed as the CSP temperature was increased.

Several researchers have studied the effects of doping PZT with barium. The electrical properties of the ceramic depend on the Ba/Pb ratio. As shown by the several phase diagrams by Ikeda et al.⁹ and Haertling et al.¹⁰, the amount of Ba that can be incorporated into PZT(52/48) having high dielectric and ferroelectric properties without entering the paraelectric or relaxor region is 20%. In this chapter, the cold sintering experiments will aim to achieve a ceramic with this composition (Pb_{0.8}Ba_{0.2}[Zr_{0.52}Ti_{0.48}]O₃).

To examine the viability of the Ba(OH)₂ octahydrate flux for the densification of PZT, preliminary CSP experiments were carried out using the attrition milled commercially available PZT powder (PKI-509, Piezo Kinetics, Inc., Bellefonte, PA) of 500 nm average particle size. 0.5 g of this powder was hand ground using a mortar and pestle with 20 vol% of Ba(OH)₂ octahydrate flux. The cold sintering process was similar to the process carried out by Sada et al. The powder mixture was loaded into a 12.7 mm inner diameter stainless steel die (Wartburg Tool & Die, Inc., Wartburg, TN) and uniaxially pressed under 350 MPa for 10 h. Initially, the temperature was held for 30 min at 80°C which is just above the melting point of the flux (78°C) allowing for uniform distribution of the flux within the PZT powder. Two experiments were conducted using these conditions wherein the CSP temperature was (1) kept at 80°C and (2) increased to 225°C. The density of the ceramic obtained in both cases was 90% and 98% relative to the theoretical density of PZT (7.8 g/cc). In both cases, densification was evident by the formation of clear triple points between grains as shown in the microstructure in Figure 5-1. This process encountered 2 main issues: incomplete densification and formation of excess secondary phases in the grain boundaries.



Figure 5-1. SEM image showing evidence of densification of PZT upon cold sintering with Ba(OH)₂•8H₂O flux for 10 h at 350 MPa at (a) 80°C and (b) 225°C. The formation of secondary phases around the grains can be clearly seen in both cases.

Powder preparation:

The formation of secondary phases during CSP can be caused by the presence of excess A-site cations. It is important to make PZT powders A-site deficient as Ba^{2+} would preferentially occupy this position due to the reactions occurring during the dissolution stage of CSP. Unlike $BaTiO_3$, it is difficult to completely dissolve lead from the outer layer of the PZT particles using weak acids such as acetic acid. For this reason, it was necessary to synthesize starting PZT powders that are lead deficient.

PZT powders with 20% lead deficiency were prepared using the sol-gel process following a procedure described elsewhere^{11,12}. The names and amount of precursors to produce a 20% A-site deficient PZT in this process have been tabulated below (Table 5-1).

Table 5-1. Amounts of precursors utilized for the sol-gel synthesis of 20% A-site deficient PZT powder

Precursor	Weight (g)
Pb acetate trihydrate	14.566
Zr propoxide	11.68
Ti isopropoxide	6.751

Since Ba ions readily react with CO₂ in ambient environment to form BaCO₃, reducing the amount of flux available for densification. It is, therefore, important to complete the densification at a rate faster than the formation of BaCO₃. The densification mechanism of cold sintering is strongly dependent on the dissolution step. The reactivity of the PZT powder was increased by using partially calcined PZT particles to retain their amorphous pyrochlore phase. The calcination step of the synthesis process was carried out for carbon removal only and not for crystallization. The partial calcination of the sol-gel derived PZT powder was carried out at 400°C for 48 h and then 450°C for 6 h by flowing oxygen at 300 cc/min flowrate in a box furnace. Hereon, the fully amorphous powder synthesized using this process will be termed 'powder 1'.

Cold sintering PZT with Ba(OH)₂ octahydrate flux:

<u>Crystallization of amorphous PZT powder:</u> To understand the effect of the flux on the sol-gel derived PZT powder (amorphous), cold sintering was carried out in the presence of a stoichiometric amount (16.1 wt%) of Ba(OH)₂ octahydrate flux at 80°C for 1 h at 350MPa uniaxial pressure. In another experiment, cold sintering was carried out under the same conditions in the absence of the flux. Both experiments lead to densification, however, as seen in the X-Ray

diffraction (XRD) pattern (Figure 5-2), the powder crystalized in the perovskite phase, albeit with the formation of BaCO₃. Without the flux, the powder consolidated upon CSP but remained in the amorphous pyrochlore phase. This shows that reaction with Ba(OH)₂•8H₂O flux helps densify as well as crystallize the PZT powder during CSP.



Figure 5-2. X-Ray diffraction pattern showing the crystallization of Ba-doped PZT.

Improved reactivity of PZT during CSP:

As explained earlier, improved reactivity of the PZT starting powder can help densify the ceramic and mitigate the formation of secondary phases such as BaCO₃ in the grain boundaries. To test this hypothesis, sol-gel derived PZT powder containing only a trace amount of pyrochlore phase (powder 2) was cold sintered with 16.1 wt% flux under the same conditions described above. On comparing the XRD data with that in Figure 5-2, upon CSP powder 2 retains a small amount of unreacted pyrochlore phase which is not observed upon cold sintering using powder 1. Therefore, it is possible to harness the high reactivity of the PZT powder in the pyrochlore phase.


Figure 5-3. X-Ray diffraction pattern of cold sintered Ba-doped PZT using powders containing different amounts of pyrochlore phase. (a) CSP of amorphous PZT powder with the flux, (b)CSP using PZT powder with trace amount of pyrochlore and (c) shows an X-Ray diffraction pattern of this PZT powder containing trace amount of pyrochlore.

The presence of secondary phases is comparable to that reported for residual fluxes and formation of BaCO₃ at the grain boundaries in the previous flux-assisted CSP studies of BaTiO₃⁸. Even though this flux shows promise in crystallization as well as *in situ* doping of amorphous PZT by CSP, it was difficult to avoid secondary phase formation. The secondary phases in the grain boundaries severely degrade the electrical properties as they pose a capacitor-in-series problem. In the future, further optimization of the cold sintering process must be carried out to produce functional Ba-doped PZT ceramics with high densities. On developing this process, densification of PZT in fabricating transducer arrays described in Chapter 3 can be reduced to a single step process.

5.3. Cold sintered PZT-ZnO multilayer actuators (MLAs)

Compared to their single element counterparts, multilayer actuators are advantageous as they operate on low driving voltages, they are compact, and can generate large forces and high electromechanical coupling. Aksay et al.¹³ patented a process wherein they replaced metal electrodes with a conductive ceramic. Antimony-doped ZnO was cofired with PZT using conventional sintering. However, their structure could only produce dome shaped geometries. Wang et al demonstrated the ability to use the cold sintering process for PZT to cofire with Cu tapes. However, due to the oxidation of Cu, formation of a Cu₂O layer at the PZT-Cu interface degraded their electrical properties.

In Chapter 3, a fabrication process of a PZT-ZnO 3-0 composite was described. ZnO is known to possess a finite amount of conductivity.¹⁴ In co- cold sintering PZT and ZnO, uniformity in the geometry of both PZT and ZnO was achieved. This process can be extended to MLAs with ZnO as the electrode. The cold sintering process provides opportunity for such multilayer structure.

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Supplementary information for Chapter 4



Figure S1. X-Ray diffraction patterns of (a) Pb acetate trihydrate decomposed to anhydrous lead acetate (polymorph-α) by heating in air at 200°C for 3 hr at ambient pressures and (b) Pb acetate trihydrate decomposed to Pb₄O(Ac)₆ and Pb₂O(Ac)₂ by heat-treatment 290°C for 3hr at ambient pressures, (top curve) reference patterns for below for the two phases, and (c) as cold sintered

PZT at 200°C and 290°C for 3h at 500MPa.



Figure S2. Simultaneous DSC-TGA thermograms obtained for Pb acetate trihydrate heated in air at a rate

of 20°C /min.



Figure S3. Relative permittivity and loss tangents as a function of frequency measured at room temperature for as-cold sintered PZT samples at 500 MPa using lead acetate trihydrate as sintering aid cold sintered at 200°C and lead nitrate as sintering aid cold sintered at 300°C.



Figure S4. Ageing studied using d₃₃ as a function of time for PZT samples using Pb nitrate and Pb acetate trihydrate as sintering aid.