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HIGH PERFORMANCE PIEZOELECTRIC MATERIALS AND DEVICES FOR MULTILAYER LOW TEMPERATURE CO-FIRED CERAMIC BASED MICROFLUIDIC SYSTEMS

Wenli Zhang

University of Kentucky, alex_zhang2006@hotmail.com

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ABSTRACT OF DISSERTATION

Wenli Zhang

The Graduate School
University of Kentucky
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ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Engineering at the University of Kentucky

By
Wenli Zhang

Lexington, Kentucky

Co-Director: Dr. Richard E. Eitel, Professor of Department of Chemical and Materials Engineering
and Dr. Fuqian Yang, Professor of Department of Chemical and Materials Engineering

Lexington, Kentucky

2011

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The incorporation of active piezoelectric elements and fluidic components into micro-electromechanical systems (MEMS) is of great interest for the development of sensors, actuators, and integrated systems used in microfluidics. Low temperature co-fired ceramics (LTCC), widely used as electronic packaging materials, offer the possibility of manufacturing highly integrated microfluidic systems with complex 3-D features and various co-firable functional materials in a multilayer module. It would be desirable to integrate high performance lead zirconate titanate (PZT) based ceramics into LTCC-based MEMS using modern thick film and 3-D packaging technologies. The challenges for fabricating functional LTCC/PZT devices are: 1) formulating piezoelectric compositions which have similar sintering conditions to LTCC materials; 2) reducing elemental inter-diffusion between the LTCC package and PZT materials in co-firing process; and 3) developing active piezoelectric layers with desirable electric properties.

The goal of present work was to develop low temperature fired PZT-based materials and compatible processing methods which enable integration of piezoelectric elements with LTCC materials and production of high performance integrated multilayer devices for microfluidics. First, the low temperature sintering behavior of piezoelectric ceramics in the solid solution of Pb(Zr0.53, Ti0.47)O3-Sr(K0.25, Nb0.75)O3 (PZT-SKN) with sintering aids has been investigated. 1 wt% LiBiO2 + 1 wt% CuO fluxed PZT-SKN ceramics sintered at 900°C for 1 h exhibited desirable piezoelectric and dielectric properties with a reduction of sintering temperature by 350°C. Next, the fluxed PZT-SKN tapes were successfully laminated and co-fired with LTCC materials to build the hybrid multilayer structures. HL2000/PZT-SKN multilayer ceramics co-fired at 900°C for 0.5 h exhibited the optimal properties with high field $d_{33}$ piezoelectric coefficient of 356 pm/V. A potential application of the developed LTCC/PZT-SKN multilayer ceramics as a microbalance was demonstrated. The final research focus was the fabrication of an HL2000/PZT-SKN multilayer piezoelectric micropump and the characterization of pumping performance. The measured maximum flow rate and backpressure were 450 μl/min and 1.4 kPa respectively. Use of different microchannel geometries has been
studied to improve the pumping performance. It is believed that the high performance multilayer piezoelectric devices implemented in this work will enable the development of highly integrated LTCC-based microfluidic systems for many future applications.

KEYWORDS: Low temperature co-fired ceramics (LTCC), Piezoelectric ceramics, Multilayer structure, Microfluidics, Micropump

Wenli Zhang
Student’s signature

Date
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By

Wenli Zhang

Richard E. Eitel
Co-Director of Dissertation

Fuqian Yang
Co-Director of Dissertation

Stephen E. Rankin
Director of Graduate Studies

Date
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2011

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To my wife, Jing Yang,

for her understanding, support, and endless love
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Chapter 1. Introduction

1.1 Motivation

Microfluidics is an interdisciplinary field of research for designing and manufacturing devices with capability of fluid handling and analysis of sample volumes on the order of microliter to picoliter. Additionally, it deals with investigating the novel characteristics of fluids in such devices which are associated with the scaling down of the size [1-3]. Miniaturization of fluidic processes to the micro-scale provides significant potential benefits including: minimized consumption of reagents and power, reduced manufacturing and operation cost, rapid analysis time, high throughput, and compact instrument size [4,5]. Integrated microfluidic systems incorporating necessary functional components onto a small chip (known as “lab-on-a-chip”) are expected to be applied in many application fields, such as chemical analysis and reaction [6], biological sample processing [7-9], drug delivery [10,11], and environmental monitoring [12]. Although individual microfluidic devices with specific functions have been developed using silicon (Si), glass, and polymer materials with associated fabrication approaches [13], the integration of discrete components or modules into one multifunctional system is still at the early stage of development [14].

Low temperature co-fired ceramic (LTCC) materials and processing, used commercially for more than twenty years, were originally developed as an electronic packaging technology providing high density electrical interconnects and hermetic
packaging for integrated circuits [15]. Recently, the use of LTCC materials for integrated microfluidic device and system fabrication has been developed to take advantage of LTCC technology over other materials and associated processing methods [16]. The ability to construct multilayer modules with complex 3-D features and integrate various co-firable functional materials (e.g. insulators, dielectrics, resistors, ferrites, and conductors) is the most important merit of LTCC to be applied as a miniaturization technology for microfluidic device and system production, where LTCC plays multiple roles as a substrate, fluidic network, electrical interconnection, and package [17,18]. Since LTCC was initially designed for electronic packaging, LTCC modules are more durable than polymeric substrates and there is no need to use additional encapsulants as commonly required in Si-based micro-electromechanical system (MEMS) devices [19]. Furthermore, the manufacturing process in which all layers can be processed in parallel allows for inspection of each layer individually and rapid implementation of design modifications on individual layers prior to final stack up and the single co-firing heating treatment. This process is also highly scalable providing significant cost advantages for pilot level (100’s to 1000’s parts) production runs and rapid transition to full scale manufacturing. Growing numbers of LTCC-based microfluidic components have been developed by virtue of the versatile LTCC fabrication methodology [20]. The realization of highly integrated lab-on-a-chip systems with on-chip sample processing capabilities will decrease the reliance on external equipment [4]. The implementation of a high performance micropump incorporating piezoelectric actuators into the LTCC-based MEMS structure for providing on-chip fluidic control and delivery is one of the most interesting fields of current research.
Despite tremendous research and development on lead-free materials for piezoelectric applications, the solid solution of lead zirconate titanate (PZT) and its modified systems remain the most widely used piezoelectric materials because of their outstanding properties [21,22]. Si-based MEMS structures incorporating PZT thin films as piezoelectric elements have been extensively investigated taking advantage of the well-established Si micromachining techniques [23-25]. Using LTCC substrate materials for fabrication of thick-film PZT devices is a new attempt to extend the application fields for both LTCC technology and PZT-based MEMS devices. To date there have been only a few reports published on development of physical sensors using the combination of LTCC substrates and piezoelectric active PZT layers [26,27]. Integrating LTCC/PZT ceramics in a compatible multilayer assembly method with one co-firing process is still challenging work. The technological obstacles for fabrication of functional LTCC/PZT microdevices are formulating piezoelectric compositions which can be fired at temperature compatible with LTCC packaging materials, reducing the inter-diffusion between the LTCC package and the active piezoelectric layers, and developing a compatible co-firing profile to build LTCC/PZT multilayer structures with minimal defects [28-30]. Additionally, the resulting co-fired piezoelectric layers need to maintain desirable properties for use in specific applications.

A modified PZT ceramic with strontium (Sr), potassium (K), and niobium (Nb) addition with a stoichiometry of Sr(K$_{0.25}$, Nb$_{0.75}$)O$_3$ (SKN) demonstrates excellent piezoelectric properties with high field $d_{33}$ piezoelectric coefficient of over 600 pm/V and Curie temperature $T_c$ greater than 350°C [31]. This material is considered to be a promising material for high strain multilayer piezoelectric actuator applications.
Integration of PZT-SKN ceramics into LTCC substrate materials in a single assembly and co-firing process would provide the possibility of manufacturing highly integrated LTCC/PZT-SKN multilayer devices (e.g. microbalance and micropump) for microfluidics and other applications. However, the densification of PZT-SKN ceramics requires high sintering temperature (~1250°C) and long sintering time (>2 h) using conventional solid-state sintering process which is not compatible with typical LTCC processing (firing at 850°C-950°C for <1 h). Therefore, it is highly desirable to develop a low fired PZT-SKN ceramic with favorable properties and a multilayer fabrication method compatible with LTCC materials and processing.

The current work presents the development of a low temperature sinterable high performance piezoelectric PZT-SKN ceramic and compatible processing methods which enable integration of piezoelectric elements with LTCC materials and subsequently the production of high performance integrated multilayer ceramic devices. It is believed that the materials and processing techniques implemented in this work would offer numerous unique advantages and improved capabilities in the design and fabrication of integrated multifunctional microfluidic devices and systems.

1.2 Organization of the thesis

This thesis is organized into six chapters. The topic of each chapter follows.

Chapter 1 introduces the motivation of the present research work and the organization of the thesis.
Chapter 2 provides a literature review on LTCC materials and technology as well as PZT-based piezoelectric ceramics. Prior attempts to integrate LTCC with PZT thick films are also discussed. Next, the theoretical background of the various sintering processes for materials and multilayer structures in this study is discussed. Finally, a brief review on micropumps for microfluidic systems is presented to show a potential application of co-fired LTCC/PZT multilayer ceramics.

Chapters 3 through 5 present the research efforts on development of high performance piezoelectric materials and devices for multilayer LTCC-based microfluidic systems. In chapter 3 the low temperature sintering of fluxed PZT-SKN ceramics is introduced. The processing methods, microstructures, dielectric, and piezoelectric properties of flux-sintered ceramics are discussed. Chapter 4 follows with an investigation on the co-firing of LTCC/PZT-SKN multilayer ceramics and the resultant electric properties. Master sintering curve (MSC) approach is also introduced and applied to analyze the sintering behaviors of LTCC tapes, fluxed PZT-SKN materials, and LTCC/PZT-SKN multilayer ceramics. The resulting microstructures and elemental inter-diffusion of co-fired multilayers are also presented. Finally, a microbalance fabricated using the developed LTCC/PZT-SKN multilayer structure is presented. Chapter 5 describes the design, fabrication, and characterization of a LTCC/PZT-SKN multilayer piezoelectric micropump. In the included results the further optimization of pumping performance is reported.

Chapter 6 summarizes the research work presented in this thesis and provides suggestions for future studies on the development of highly integrated microfluidic systems using LTCC/PZT-SKN multilayer ceramics.
Chapter 2. Background

Materials, technologies, and theoretical background related to the present research work are introduced in the current chapter. First, low temperature co-fired ceramic (LTCC) materials and technologies are reviewed. LTCC has been applied in the fabrication of multilayer structured sensors, actuators, and microsystems with low cost and high productivity. Second, an overview of piezoelectric materials is presented. The solid solution of lead zirconate titanate Pb(Zr\textsubscript{x}, Ti\textsubscript{1-x})O\textsubscript{3} (PZT) and its modified systems are the most widely used piezoelectric ceramics because of their excellent properties. Recently, there is an increasing interest in the development of highly integrated micro-electromechanical systems (MEMS) incorporating active piezoelectric elements with LTCC materials. For integrating PZT piezoelectric ceramics with LTCC materials, the study on sintering behaviors for those materials is necessary for the development of a compatible co-firing process. Finally, current micropump technology is discussed.

2. 1 Low temperature co-fired ceramics (LTCC)

Low temperature co-fired ceramic (LTCC) technology is a multilayer ceramic fabrication technique that has many engineering and manufacturing advantages over both hybrid thick-film circuitry and high temperature co-fired ceramic (HTCC) technology [15]. LTCC materials, originally developed as a multilayer substrate for packaging integrated circuits, are widely used for the production of sensors, actuators, and integrated microsystems which have a wide range of applications in the automotive, aeronautic, and telecommunication areas [16-18]. Applications of LTCC-based devices in
the microfluidics field have recently emerged. Integration of microfluidics and electronics into one monolithic LTCC system for micro total analysis system (μ-TAS) or lab-on-a-chip (LOC) applications is a most interesting and challenging field of current research [32,33].

2.1.1 Introduction to thick-film technology

Thick-film technology has been developed in the electronics industry as a method for producing high-density multilayer interconnect substrates at low cost and with fast turnaround time. Thick-film circuits are widely used for both low-volume high-performance applications (e.g. military, space, and medical products) and high-volume low-cost applications (e.g. telecommunication, automobile, and solar cell products) [15]. Conductor, resistor, and dielectric pastes are screen-printed, dried, and fired or cured onto ceramic, metal, or polymer substrates in a thick-film process. The thickness of deposited films is normally in the range from several microns to around one hundred microns. Ceramic thick-film processing can be separated into three major sub-groups: hybrid thick-film circuitry, high temperature co-fired ceramic (HTCC), and low temperature co-fired ceramic (LTCC) [34].

Hybrid thick-film processing is a bottom-up manufacturing technique capable of producing multilayer high-density thick-film circuits. Successive layers with various functions are printed, dried, and fired to build up a multilayer structure on a rigid ceramic or metal substrate. Multiple firing steps are required when the layer count increases, which lowers the fabrication yield of multilayer substrates because of the increasing non-planarity of the surfaces. Therefore, the development of co-fired ceramic tape processes
has attracted remarkable attention [15]. HTCC has been used to fabricate hybrid ceramic multi-chip modules (MCM) – a package-level substrate combining multiple integrated circuits in one unit. In HTCC the multilayer ceramic substrate and refractory metal conductors (e.g. tungsten and molybdenum) can be co-fired in a single heating treatment which is significantly different from the multiple cycles of printing-firing used in hybrid thick-film processing. Individual unfired tapes are first machined and screen-printed separately, then stacked and laminated at certain sequence, and finally co-fired with conductor pastes in a typical HTCC process. Although HTCC process is applicable for high-volume production of multilayer interconnect substrates and packages at low cost, the high temperature (~1500°C) sintering prevents the use of highly electrically conductive pastes (e.g. copper, silver, and gold) required in many applications [35]. The effort to increase the interconnect density, data transmission speed, and communication frequency for computers and microwave electronics accelerated in the middle 1980s. It is now necessary to use conductor materials with low electrical resistance for high-density packaging in applications requiring low loss and high frequency. In addition, the coefficient of thermal expansion (CTE) of the interconnect substrate is needed to be close to that of the silicon components for reliable connection. Furthermore, to achieve high speed signal transmission, it is desirable to have MCM substrates or packages with a low dielectric constant [35-37]. LTCC technology was invented to fulfill all these requirements and commercialized to produce high-performance, high-speed, and high-density MCM for realization of functional, reliable, and low-cost electronic devices. A summary of advantages of LTCC technology over other thick-film processes is listed in Table 2.1.
Table 2.1 Characteristics of hybrid thick-film processing, HTCC, and LTCC.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>LTCC</th>
<th>HTCC</th>
<th>Hybrid thick-film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single printing per layer and one firing process</td>
<td>√</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Firing at low temperature (&lt;900°C)</td>
<td>√</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Using high conductive metals (e.g. copper, silver, and gold)</td>
<td>√</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>Integration of passive components, such as resistors</td>
<td></td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Adjustable CTE to match silicon and other substrate materials</td>
<td>√</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ability to form cavities and shaped substrates</td>
<td></td>
<td>√</td>
<td></td>
</tr>
<tr>
<td>Ability to integrate interconnect substrates in a hermetic package</td>
<td>√</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness control of dielectric</td>
<td>√</td>
<td></td>
<td>√</td>
</tr>
<tr>
<td>High layer count</td>
<td></td>
<td>√</td>
<td></td>
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<tr>
<td>Monolithic structure, no need for the base to support layers</td>
<td>√</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Easy inspection and rapid modification</td>
<td></td>
<td>√</td>
<td></td>
</tr>
</tbody>
</table>

2.1.2 LTCC materials and technology

As its name suggests LTCC is a ceramic substrate which can be co-fired with highly conductive metal conductors (e.g. gold, silver, and silver alloys) and other passive components at “low” temperature, typically in the range of 850°C-950°C. LTCC materials are commercially produced in tape format by tape-casting a slurry on polymeric carrier substrates (e.g. Teflon®, Mylar®, or cellophane) at varying thickness (50-350 µm). The manufacturing of LTCC tapes can be easily conducted using standard ceramic processing techniques, such as powder preparation, colloidal processing, and tape casting technique [34].
Most LTCC tapes are glass-ceramic composite materials mainly composed of ceramic fillers, glass frits, and an organic binder vehicle. The selection of ceramic fillers is related to the application of interest. Alumina (Al$_2$O$_3$) is the most widely used dielectric ceramic filler but other ceramic systems are also available for offering various properties, for example, high thermal conductive berylillia (BeO) [38], ferroelectric barium strontium titanate (Ba$_{0.7}$Sr$_{0.3}$TiO$_3$) [39], and dielectric magnesium calcium titanate (MgCaTiO$_3$) [40]. It has also been demonstrated that the CTE of LTCC materials can be adjusted by choosing proper ceramic formulations to match the other interested materials for hybrid integration, such as Al$_2$O$_3$, gallium arsenide (GaAs), and silicon (Si) [18]. Glass frits are introduced into the ceramic as low-softening-point glass or fully devitrifying glass to lower the sintering temperature for the glass-ceramic composite [41]. The glass additives should have minimum effect on the desirable properties of the base ceramic without forming new phases after firing; unless the ceramic-glass reaction is required to obtain certain characteristics for the fired ceramic [42]. The final component of the composite is the organic vehicle. This organic medium, in which the ceramic particles and glass frits are dispersed, normally consists of polymeric binders, plasticizers, dispersants, and other optional constituents which are all dissolved in an organic or aqueous-based solvent. Defect-free LTCC “green” tapes with proper strength and flexibility are prepared for further processing. A flow diagram of the LTCC manufacturing process is illustrated in Figure 2.1.
LTCC “green” tapes are first blanked to a specific size and registration holes are made simultaneously. Traditionally, electrical circuitry and interconnects are produced by punching and filling electrical via holes, followed by screen-printing of conductor, resistor, and dielectric pastes on each layer of “green” tape. Cavities are made by drilling, punching, or laser ablation on the printed tapes if necessary. The individual layers are then aligned, stacked, and laminated using an either isostatic or uniaxial press under
specified pressure and temperature. The laminated stack is finally co-fired to burnout organics and sinter the ceramic substrate and electronic components into a dense monolithic ceramic package. The shrinkage of tape (typically 10-15%) during co-firing must be accurately controlled and compensated for in the design process. Additional active and passive components can be printed, wire-bonded, or soldered on the fired surfaces according to the desired application. This processing route has been extensively applied for the production of integrated radio frequency (RF) and microwave modules.

LTCC materials and processing, as an alternative for Si materials and associated micromachining techniques, have also been considered and utilized to design and construct sensors, actuators, and micro-electromechanical systems (MEMS) in the last decade [7]. Si-based MEMS processing techniques (e.g. deep etching, bulk/surface micromachining, and anodic bonding) are well engineered and extensive work has been done to optimize this route of making MEMS devices. However, using Si technology for MEMS fabrication remains a complex, expensive, and time-consuming process. LTCC material, showing proper electrical and mechanical properties, good chemical and thermal stability, and high reliability, could expand the availability and flexibility in design and fabrication of MEMS devices. Application of LTCC processing has additional advantages compared to microfabrication techniques using Si materials [16-18]: (1) simple and inexpensive LTCC tape patterning methods (punching, machining, laser ablation) are available when feature sizes in the range from several microns to several hundred microns are required (increasing feature size in Si (e.g. >50 microns) can greatly increase production time and require significant surface area, increasing die size and cost); (2) the parallel layer-by-layer manufacturing process utilized for LTCC means that
design changes and inspections can be performed on individual layers and rapidly incorporated into the final device, leading to improved yield, short development time and lower cost production; (3) since LTCC is a true packaging technology, there is no need for an additional protective envelope as when utilizing Si-based MEMS devices.

Microfluidic systems have been fabricated in a number of materials including Si, glass, metal, and polymers. The chemical inertness, temperature and pressure stability, solvent compatibility, and ease of fabrication suggest that LTCC materials and fabrication processes are appropriate for the microfluidics. Recently, use of LTCC materials for microfluidic systems has been emphasized to capitalize on the significant advantages offered by LTCC technology. LTCC utilizes a layered assembly process and is compatible with wide range of metallic and ceramic materials, making LTCC a logical choice for the fabrication of multilayer modules with complex 3-D features and various co-firable functional materials (e.g. dielectrics and conductors). LTCC may play multiple roles as a substrate, fluidic network, electrical interconnection, and package in an integrated LTCC-based microfluidic system [17].

Several modifications and improvements in standard LTCC processing are needed in order to fulfill the requirement of MEMS and microfluidics implementation. Computer numerically controlled (CNC) milling machines are used to pattern holes, cavities, and microchannels (feature size of the order of 100 µm) onto LTCC tapes. Alternatively, laser ablation can be utilized when the small feature sizes and tolerances are needed. Sacrificial volume or fugitive materials and adhesive or organic bonding agents have been developed to prevent the sagging and other undesirable deformations after lamination [44,45]. Constrained sintering of LTCC tapes is demonstrated as an effective method to
minimize the shrinkage in x-y direction. Hybrid bonding techniques are investigated to integrate LTCC tapes with other materials in a co-fired or post-fired scheme [17].

2.1.3 LTCC applications

LTCC, originally developed as a multilayer interconnect substrate and packaging material, has been widely applied in the production of microelectronic modules and devices immediately after its commercialization by DuPont in the middle 1980s [15]. The multilayer approach and low firing temperature of LTCC technology enables the integration of dielectric ceramic tapes with electrodes made of high conductivity metals and other planar passive components (e.g. resistors, inductors, and capacitors) embedded or screen-printed on the surfaces, making a high-density, high-performance, and small-size MCM [19]. In addition, functional discrete electronic elements can be soldered or wire-bonded on the fired surfaces based on the application demands. Figure 2.2 shows an example of LTCC module integrated with various components.
RF and microwave devices for telecommunication applications are extensively developed using hybrid LTCC modules [47-49]. Although numbers of LTCC material systems including ceramic tapes and suitable functional pastes have been commercialized for this purpose, developing novel LTCC systems is still an attractive field for many researchers and manufacturers in order to meet specific electrical and thermomechanical requirements for the desired function. Several LTCC materials have been developed with desirable properties for the fabrication of RF multilayer resonators and band-pass filters [40,47]. Another example of a novel LTCC material system demonstrates ideal dielectric properties with high quality factor $Q$ and low CTE for the fabrication of devices requiring
high signal propagation speeds at microwave frequencies [49]. The resultant devices in hybrid LTCC modules are more compact in comparison with those fabricated using traditional printed circuit board (PCB) manufacturing technique. In addition, using LTCC technology for the production of RF and microwave devices is cost-effective, adaptable to changes of design, and allows rapid replacement and/or post-trimming of surface components. A comparison between PCB and LTCC technology for the construction of a microelectronic module is shown in Figure 2.3.

![Figure 2.3 Comparison of the same circuit implemented on PCB (20 mm × 20 mm, 0.8 g) and LTCC (7 mm × 7 mm, 0.2 g). (taken from M. Pudas et al. [50])](image)

Taking advantage of the versatility of LTCC materials and technology, numbers of microdevices [51-55], sensors [30,56-64], and actuators [65,66] have been developed since the first LTCC-based sensor was reported in 1996 [67]. Many microdevices and sensors are designed for use in a harsh circumstances involving high-temperature, high-voltage, and high-pressure or vacuum. LTCC material systems have excellent
thermomechanical and chemical stability and are a suitable choice for such applications. For example, LTCC material systems were used to fabricate a micro-plasma generator [26]. The LTCC was robust enough to stand up to the high voltage and high temperature conditions caused by the plasma generation. A micro-scale methanol reformer and a partial oxidation reactor were also built using LTCC technology for the miniature fuel cell energy conversion system [53]. LTCC-based systems proved to be more resistant to a strong acid environment, more compact, and less costly compared to the fuel processor made of stain-less steel or Si. LTCC-based sensors with various functions are also extensively considered to be applied in the automotive field: Schmid [59] designed a mass flow sensor to control the fuel injection under high pressure; Fonseca et al. [60] reported a pressure sensor capable of working in high temperature turbine engines; LTCC-based eddy proximity sensors for automobile wheel positioning were fabricated by Gongora-Rubio et al. [63] and Wilde et al. [64]. Other LTCC-based sensors were also developed and reported recently, including gas detection and flow sensors [31-33], force and pressure sensors [30,61], and hot-layer electrochemical sensors [62]. In addition, leaf spring vertical actuators and spherical stepper motors were made by virtue of LTCC multilayer processing [65,66].

The fields of microfluidic systems and microfluidic chemical sensors in LTCC technology have also been increasingly studied in recent years, showing an exciting new application area for LTCC material systems. The ease of integrating fluidic components (e.g. microchannels and microchambers) with both passive and active electrical and mechanical components in one module is a significant advantage of LTCC technology over Si, glass and polymer technologies. Applications of LTCC based microfluidic
devices and systems also earn interest due to its’ low price and short development time. Individual LTCC-based devices have been implemented for different steps in a continuous-flow analytical procedure, including microvalves and micropumps for fluidic sample supply and control [17,68], micromixers and microchambers for sample pretreatment [69], microreactors for chemical synthesis [70,71], and sensors for chemical detection and analysis [72-78]. The integration of these discrete functional fluidic components into one miniaturized microfluidic system is also possible using LTCC multilayer fabrication methodology. A conceptual platform of this multi-functional integration is illustrated in Figure 2.4. Further development of LTCC microfluidic systems is expected to be utilized for cell handling and sorting, drug delivery, gas or liquid chromatographs, and biological parameter monitoring [17].

![Figure 2.4](image)

Figure 2.4  A schematic of conceptual integrated microfluidic system using LTCC multilayer approach. (taken from M.R. Gongora-Rubio et al. [17])

Most of the LTCC-based devices described above were developed as stand-alone products in two major groups: (1) sensing and microfluidic platforms for microanalytical systems, and (2) electronics for actuators and signal processing [19]. The intrinsic
advantages of LTCC technology suggest the possibility for easy integration of both microfluidics and electronics functions to build a monolithic microanalytical system. Until now, few attempts have been reported which translated this conceptual approach into real functioning integrated Microsystems. Molianen et al. [79] reported the implementation of a preamplifier and multiplexing circuit module integrated with lead sulphide (PdS) detector arrays in one LTCC module. Fournier et al. [80] presented a LTCC-based fluidic multisensor with integrated control circuits for signal conditioning and amplification in a monolithic package. Figure 2.5 presents an example of a monolithic microanalyzer fabricated using LTCC technology. Using both the modular approach and monolithic integration concept for the incorporation of electronics and microfluidics shows the versatility of LTCC fabrication methodology [32]. Table 2.2 presents a comprehensive summary of LTCC devices and microsystems utilized in different areas.

Figure 2.5  (a) Bottom view of the microanalyzer with electronics for data collection and processing; and (b) top view of the microanalyzer with fluidic components and detection systems. (taken from C.S. Martinez-Cisneros et al. [32])
LTCC technology, including attractive features and various potential applications, has been introduced in this review section. Growing numbers of LTCC-based MEMS devices have been developed to take advantage of the versatile LTCC fabrication methodology. However, there are still a number of challenging issues to be solved to fulfill the potential of LTCC technology for integrated microsystems. One demanding task is to develop high performance piezoelectric ceramics with proper composition and processing method compatible with LTCC materials and technology. The development of LTCC-based micropumps which can be integrated into microfluidic systems for on-chip fluidic control and delivery is another most interesting field of research.
Table 2.2  Applications of LTCC technology in different areas.

<table>
<thead>
<tr>
<th>Type</th>
<th>Device</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensors</td>
<td>Gas detection sensors</td>
<td>Monitoring of carbon monoxide and methane</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Detection of hydrogen and ethanol</td>
<td>[57]</td>
</tr>
<tr>
<td>Flow sensors</td>
<td>Thermistor-based sensor for gas flow measurement</td>
<td></td>
<td>[58]</td>
</tr>
<tr>
<td></td>
<td>Onboard detection of high pressure fuel injection</td>
<td></td>
<td>[59]</td>
</tr>
<tr>
<td>Pressure and force sensors</td>
<td>Operation in high temperature turbine engine and compressor</td>
<td></td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>Capacitive pressure sensor suitable for stress analysis in solid media</td>
<td></td>
<td>[61]</td>
</tr>
<tr>
<td></td>
<td>Piezoresistive force sensor responding to the forces below 100mN</td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>Chemical sensors</td>
<td>Hot layer electrochemical sensor for studies of protein denaturalization</td>
<td></td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>Amperometric detection of heavy metals (e.g. mercury and copper)</td>
<td></td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>Pesticide monitoring by enzymatic inhibition and amperometric detection</td>
<td></td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>Potentiometric detection of nitrate and ammonium ions</td>
<td></td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Detection of chloride ion in drinking waters using ion selective electrode</td>
<td></td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>Separation and detection of phenolic compounds</td>
<td></td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>Optical detection using transmittance and fluorescence measurements</td>
<td></td>
<td>[77,78]</td>
</tr>
<tr>
<td>Eddy current proximity sensors</td>
<td>Precise positioning metallic objects in automotive industry</td>
<td></td>
<td>[63,64]</td>
</tr>
<tr>
<td>Actuators</td>
<td>Micropumps</td>
<td>Magnetohydrodynamic pump for handling and control of fluidic samples</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>Microvalves</td>
<td>Electromagnetic valve for fluid control</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>Leaf spring vertical actuators</td>
<td>Generating displacement in micrometer scale by electrostatic actuation</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td>Spherical motors</td>
<td>Omni-directional wheel for vision cameras and robots</td>
<td>[66]</td>
</tr>
<tr>
<td>Type</td>
<td>Device</td>
<td>Application</td>
<td>Ref.</td>
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<tr>
<td>-------------------</td>
<td>------------------------------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>Other devices</td>
<td>Microwave and RF devices</td>
<td>Chip-type low pass filter</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RF MEMS package with low-loss characteristics in a wide band range</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Integration of passive components for radar and antenna technologies</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>Micro-generators</td>
<td>In-plane rotary electromagnetic micro-generator for MEMS</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Polymerase chain reaction (PCR) and DNA detection</td>
<td>DNA identification, genomic cloning, diagnostics</td>
<td>[70,71]</td>
</tr>
<tr>
<td></td>
<td>Micro-plasma generators</td>
<td>Surface treatment, semiconductor etching, waste water treatment</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>Micro-methanol reformers</td>
<td>Supplying hydrogen for the operation of fuel cells</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>Ion mobility spectrometers</td>
<td>Identification of ground water pollutants, drugs, and explosives</td>
<td>[54,55]</td>
</tr>
<tr>
<td></td>
<td>Micromixers</td>
<td>Modular devices for chemical reaction in high temperature and pressure</td>
<td>[69]</td>
</tr>
<tr>
<td>Integrated</td>
<td>Chloride ion detection system</td>
<td>Integration of a potentiometric detection system and the electronics for data acquisition and processing</td>
<td>[32]</td>
</tr>
<tr>
<td>Microsystems</td>
<td>Lead sulphide detection system</td>
<td>Incorporating high performance preamplifier and multiplexing circuits into lead sulphide (PdS) detector array packages</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
<td>Industrial compressed air diagnostic system</td>
<td>Fluidic pressure-flow-temperature multi-sensors with integrated signal conditioning electronics</td>
<td>[80]</td>
</tr>
</tbody>
</table>
2. 2 **Lead zirconate titanate Pb(Zr, Ti)O₃ (PZT) ceramics**

Piezoelectric materials are widely used in modern industry for their capability to convert between electrical signals and mechanical energy [81]. Piezoelectric materials and solid solutions with the general ABO₃-type perovskite structure, particularly the lead zirconate titanate Pb(Zr, Ti)O₃ (PZT) based ceramics, have been extensively investigated due to their superior properties for a variety of applications. PZT ceramics show a strong piezoelectric effect for compositions near the rhombohedral-tetragonal morphotropic phase boundary (MPB). Properties of PZT can also be modified by the addition of various isovalent, subvalent (donor type), and supervalent (accepter type) impurities depending on application requirements [82-84]. There is also continued interest and progress in the integration of high performance piezoelectric PZT ceramics into Si-based MEMS devices for developing novel sensors and actuators [85].

2. 2. 1 **Piezoelectric and ferroelectric ceramics**

The piezoelectric effect, first discovered in 1880 by Pierre and Jacques Curie, exists in natural crystals (*e.g.* quartz and tourmaline), poled ceramics, and some polymers. The conversion between electrical energy and mechanical energy based on the piezoelectric effect has led to the development of novel devices for sensor and actuator applications. Depending on the application, technological piezoelectric materials may be fabricated in the form of bulk polycrystalline ceramics, single crystals, thick films, or thin films. Figure 2.6 demonstrates the piezoelectric effect in a simplified atomic structure of quartz. An unstrained quartz crystal has a network of electric dipoles which does not possess a net dipole moment. When a stress is applied, the center of positive charge does
not coincide with the center of negative charge, resulting in a net dipole moment. The dipole moments appear in every unit cell in the crystal causing a finite net polarization.

![Diagram showing unstrained and strained state of a crystal with positive and negative charges labeled Silicon Atom and Oxygen Atom.](image)

Figure 2.6 Simplified illustration of piezoelectric effect in quartz. (modified after Kistler–Knowledge Base [86])

Crystalline materials can be classified into 32 crystal classes or point groups. 20 of the 21 classes which lack a center of symmetry can show piezoelectricity. Out of such 20 classes, 10 have a unique polar axis (an electric dipole moment) in the unstrained condition. Crystals from such classes are called polar crystals exhibit a net spontaneous polarization. Polar crystals can develop an electric charge when uniformly heated. The change of polarization caused by the uniform heating is called pyroelectricity. Ferroelectricity, by analogy to ferromagnetism, is defined as the “reversible or reorientable spontaneous electric polarization by application of an electric field over some range of temperature” [87]. Ferroelectricity is an experimental phenomenon that
distinguishes one group of pyroelectric crystals from others. Ferroelectric behavior was first discovered in Rochelle salt by Joseph Valasek in 1920 [88]. Ceramic compounds of perovskite structure including Pb(Zr, Ti)O₃, BaTiO₃, and KTaO₃; ilmenite structure, LiTaO₃ and LiCdO₃; and tungsten-bronze structure, such as (Sr, Ba)Nb₂O₆ and LiNb₂O₆ are often ferroelectric [89]. Ferroelectric ceramics, with the development of ceramic processing and thin film technology, have been utilized for a variety of novel applications, such as ferroelectric thin films for high-density non-volatile memories and ferroelectric electrooptic ceramics for data storage and displays [90].

Piezoelectricity

A stress $T$ [N/m²] causes a proportional strain $S$ [m/m] related by an elastic modulus $Y$ [N/m²] ($T = YS$) for most solids. Piezoelectricity is the additional creation of a dielectric displacement $D$ [C/m²] by the applied stress $T$ (direct effect). The corresponding converse effect of piezoelectricity occurs such that an applied electric field $E$ [V/m] produces a proportional strain $S$. These piezoelectric effects can be expressed as follows:

$$D = d \cdot T \text{ (direct effect)}$$

$$S = d \cdot E \text{ (converse effect)}$$

where $d$ is the piezoelectric coefficient [C/N] or [m/V] which is numerically identical for both direct and converse effect. The general form of linear piezoelectric equations relating the electric and elastic variables can be written as follows:
where $s^X$, $c^X$ and $\varepsilon^X$ are elastic compliance [m$^2$/N], elastic stiffness [N/m$^2$], and dielectric permittivity [F/m] at constant $X$, respectively. The parameters of $d$, $g$, $h$, and $e$ are piezoelectric constants which can be defined by:

\[
\begin{align*}
\mathbf{d} &= \left( \frac{\partial \mathbf{S}}{\partial \mathbf{E}} \right)_T = \left( \frac{\partial \mathbf{D}}{\partial \mathbf{T}} \right)_E \\
\mathbf{g} &= \left( -\frac{\partial \mathbf{E}}{\partial \mathbf{T}} \right)_D = \left( \frac{\partial \mathbf{S}}{\partial \mathbf{D}} \right)_T \\
\mathbf{h} &= \left( -\frac{\partial \mathbf{T}}{\partial \mathbf{D}} \right)_S = \left( -\frac{\partial \mathbf{E}}{\partial \mathbf{S}} \right)_D \\
\mathbf{e} &= \left( -\frac{\partial \mathbf{T}}{\partial \mathbf{S}} \right)_D = \left( \frac{\partial \mathbf{D}}{\partial \mathbf{E}} \right)_S
\end{align*}
\]

The piezoelectric constant $d$, which relates dielectric displacement $D$ to stress $T$ in the direct effect and strain $S$ to electric field $E$ in the converse effect, is the most important parameter used to characterize piezoelectric properties. Since $D$, $E$ are vectors and $T$, $S$ are second rank tensors, $d$ can be transformed as a third rank tensor for both direct and converse effects [91]:

\[
\begin{align*}
D_j &= d_{jkl} T_{kl} \quad \text{(direct effect)} \\
S_{ij} &= d_{ijk} E_k \quad \text{(converse effect)}
\end{align*}
\]

The piezoelectric effect can be presented by a $6 \times 3$ or $3 \times 6$ matrix because only 18 of the total 27 tensor components are independent because of the symmetry of second rank tensors $T$ and $S$ ($T_{ij} = T_{ji}$, $S_{ij} = S_{ji}$). The matrix of piezoelectric coefficient for direct effect can be written out as:
where $d$ uses only 2 subscripts $D_i = d_{ij} T_j$ ($i = 1-3, j = 1-6$). The relationship of different tensor forms can be determined by comparing coefficients expressed in both tensor and matrix forms for $D_i$. The converse coefficient matrix can be obtained by transposing the direct effect matrix. Written out it is:

\[
\begin{pmatrix}
S_1 \\
S_2 \\
S_3 \\
S_4 \\
S_5 \\
S_6
\end{pmatrix} =
\begin{pmatrix}
d_{11} & d_{12} & d_{13} \\
d_{21} & d_{22} & d_{23} \\
d_{31} & d_{32} & d_{33} \\
d_{41} & d_{42} & d_{43} \\
d_{51} & d_{52} & d_{53} \\
d_{61} & d_{62} & d_{63}
\end{pmatrix}
\begin{pmatrix}
E_1 \\
E_2 \\
E_3
\end{pmatrix}
\]

**Ferroelectricity**

A ferroelectric is a spontaneously polarized material possessing a noncentrosymmetric point group symmetry in with an experimentally reversible or reorientable polarization. Most ferroelectric crystals undergo a structural transformation which is accompanied by the disappearance of the spontaneous polarization at the phase transition from the noncentrosymmetric polar lattice to a centrosymmetric nonpolar lattice as the temperature increases above the Curie temperature $T_c$. A ferroelectric in the high-temperature nonpolar phase above $T_c$ is called paraelectric and obeys a Curie-Weiss law [81]:

\[
K - 1 = \frac{C}{T - T_c}
\]
where $K$ is the relative dielectric constant, $C$ is Curie constant which is usually in the range of $10^3$-$10^5$ Kelvin degrees. The crystallographic and corresponding dielectric changes observed in barium titanate (BaTiO$_3$) illustrate the structural changes resulting in the paraelectric-ferroelectric state transition in a crystal, as shown in Figure 2.7. At high temperature, BaTiO$_3$ has the ideal cubic perovskite crystal structure and there is no permanent electrical dipole. When the temperature decreases to below $T_c$, Ti ions move to an off-center position resulting in a structural change from cubic to tetragonal symmetry and a corresponding permanent dipole. Neighboring dipoles are ordered, giving a domain structure with a net spontaneous polarization within the domain.

A domain is a microscopic region in a crystal where the dipoles are oriented in the same direction. Neighboring domains along different polarization directions which are basically high temperature symmetry axes (e.g. $<001>$, $<110>$, or $<111>$) are separated by domain walls. Angles between the dipoles of neighboring domains are those between such symmetry axes. For example, there exist $90^\circ$ and $180^\circ$ domain walls in a crystal with tetragonal symmetrical structure. The movement of domain walls has a profound influence on the mechanical and electrical properties of ferroelectric materials [90]. Domain structures observed in a crystal can be considered as an evidence of ferroelectricity [81].
Figure 2.7 (a) Lattice parameters of BaTiO$_3$ as a function of temperature (taken from H.F. Kay et al. [92]); and (b) dielectric constants of BaTiO$_3$ as a function of temperature. (taken from W.J. Merz [93])

As another experimental characteristic of ferroelectricity, a hysteresis loop illustrating polarization-electric field $P$-$E$ response is shown in Figure 2.8. The hysteresis arises from the electric field needed to reverse the dipoles during each excursion of the electric field.
Initially, polarization is reversible and nearly linear with the electric field. As higher fields are applied, the polarization increases more rapidly due to the switching of ferroelectric domains along the applied field. Ultimately, the highest polarization achieved is the saturation polarization $P_s$, which can be extrapolated from the slope of hysteresis loop at the highest field to $E = 0$. The $P_s$ corresponds to the spontaneous polarization with all the dipoles aligned in parallel. When the external electric field is released, the polarization does not become zero, and there is a remnant polarization $P_r$, as most of the domain alignment remains. The domain alignment can again be reoriented by reversing the polarity of the field. The field required to induce switching is known as coercive field $E_c$. The domains again align with the field as applied field increases to the
opposite polarity, resulting in the opposite polarization. The inner area of hysteresis loop in the $P-E$ relationship indicates the energy stored or lost in moving domain boundaries [81]. Polycrystalline ferroelectric materials are agglomerates of single crystals (grains) with random orientations which results in zero net spontaneous polarization. The poling process of applying a high electric field to a polycrystalline ferroelectric is necessary to realize piezoelectric behavior by orienting the ferroelectric domain structure with the applied electric field resulting in a net remnant polarization in the bulk ceramic component.

2. 2. 2 Pb(Zr, Ti)O$_3$ solid solutions

Lead zirconate titanate Pb(Zr, Ti)O$_3$ (PZT) is a piezoelectric ceramic made by a solid solution of two ABO$_3$-perovskite type oxides, namely lead zirconate (PbZrO$_3$) and lead titanate (PbTiO$_3$). The ferroelectric material PZT was first developed in both Japan and US in the mid 1950s and has become the most widely used piezoelectric ceramic to date [94-96]. The structures and properties of PZT-based solid solutions and their manufacturing processes are thoroughly studied since discovered.

*Perovskite structure*

The majority of technologically important piezoelectric ceramics crystallize in the perovskite structure, named after the CaTiO$_3$ perovskite mineral. The perovskite-like crystal is a ternary compound with the formula ABO$_3$, which can be described by a simple cubic unit cell with large cations (A) on the corners, smaller cations (B) in the body center, and the oxygen atoms at the face centers. A network of corner–linked oxygen octahedral is also used to represent this structure with the smaller cations filling
the octahedral holes and larger cations inside the dodecahedral holes. An example of the ideal perovskite cubic structure is shown in Figure 2.9.

In the ideal cubic structure, the coordination numbers for A and B cations are 12 and 6 respectively. Most perovskite materials are slightly distorted from the ideal cubic symmetry. Common distortions such as cation displacement within the octahedra and the tilting of the octahedra are caused by the substitution of A and B atoms with different characteristics, which can be used to adjust physical properties for the perovskite materials. Radius size and Jahn-teller effects have been used to explain the distortion in the ABO$_3$ perovskites. According to Golschmidt, the ideal cubic perovskite structure is characterized by a tolerance factor $t$ [97]:

$$t = \frac{r_A + r_O}{\sqrt{2} (r_B + r_O)}$$
where \( t = 1 \) and \( r_A, r_B \) and \( r_O \) indicate the ionic radius of large cations, small cations, and anions respectively. Stable perovskite structures are expected to have \( t \) in the range from 0.88 to 1.09 where the ionic radii of the A-cations are corrected for the coordination number 12 \([98]\).

\textit{Pb(Zr, Ti)O}_3 \textit{phase diagram}

The composition-temperature phase diagram of the \( \text{Pb(Zr}_x\text{Ti}_{1-x})\text{O}_3 \) solid solution is shown in Figure 2.10.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{phase_diagram.png}
\caption{Composition-temperature phase diagram of PbZrO$_3$-PbTiO$_3$ solid solution. (taken from B. Jaffe et al. \cite{81})}
\end{figure}

At high temperatures, \( \text{Pb(Zr}_x\text{Ti}_{1-x})\text{O}_3 \) (PZT) system is in the cubic perovskite phase for all values of zirconium (Zr) incorporation \( x \). Lead titanate (PbTiO$_3$) is
ferroelectric at room temperature and ambient pressure. On heating PbTiO$_3$ goes through a first-order transition from the ferroelectric tetragonal symmetry to a paraelectric cubic phase at a $T_c$ of 490$^\circ$C. Lead zirconate (PbZrO$_3$) is antiferroelectric with orthorhombic symmetry, which is transformed from paraelectric cubic phase at $T_c$ of 230$^\circ$C. A small field of stability of a tetragonal antiferroelectric phase near the $T_c$ appears as more Ti$^{4+}$ substitute for Zr$^{4+}$ at the PbZrO$_3$ end. The rhombohedral ferroelectric region is divided into two phases, as indicated by the measurement of dielectric and elastic properties, thermal expansion and neutron diffraction [99,100]. Substitution of Zr$^{4+}$ for Ti$^{4+}$ in PbTiO$_3$ reduces the tetragonal distortion and causes the appearance of another ferroelectric phase in rhombohedral form. The phase boundary between tetragonal and rhombohedral phases, observed at composition with $x = 0.48$, is often referred as a morphotropic phase boundary (MPB). The MPB is nearly independent of temperature up to around 370$^\circ$C. The MPB, at which the two ferroelectric phases are presented in equal quantity, is the most prominent feature of the PZT materials. The dielectric constant, remnant polarization, piezoelectric coefficients, and coupling factor are maximized at compositions near the MPB, as shown in Figure 2.11.
Figure 2.11 Compositional dependence of the (a) dielectric constant and remnant polarization (taken from Yamamoto et al. [101]); and (b) piezoelectric coefficients and coupling factor of PZT around MPB. (taken from B. Jaffe et al. [96])

Numerous experimental results and theoretical analyses show that the proximity to the MPB favors strong piezoelectric behavior in a ceramic partially due to the increased ability to orient the spontaneous dipoles during the poling process. There are 6 and 8 equivalent polar axes in the tetragonal and rhombohedral phases, respectively. The polarization of the PZT solid solution at the MPB composition may easily switch between ferroelectric tetragonal and rhombohedral phase, effectively resulting in 14 available equivalent polar directions [102,103]. Recent studies have also suggested the existence of a monoclinic phase near the MPB which may explain the exceptional dielectric and piezoelectric properties of PZT in that region [104-106].
Modifications of PZT ceramics

As described above, undoped PZT ceramics with compositions in proximity to MPB possess maximum dielectric and piezoelectric properties. Tailored properties for specific applications can be achieved through compositional modifications that can be summarized as donor doping, acceptor doping, and isovalent substitutions. Donor type additives of higher charges, like Nb$^{5+}$ in the B sites replacing Zr$^{4+}$ or La$^{3+}$ in the A sites substituting for Pb$^{2+}$, are compensated by cation vacancies in the crystal structure which enhance domain wall mobility [107-109]. Such ceramics are called “soft” PZT, showing high dielectric constant and loss, high remnant polarization with low coercive field, and a relatively square hysteresis loop. The “hard” PZT ceramics are doped by acceptor type additives. Ions with lower charges, such as K$^{+}$ for A sites or Fe$^{3+}$ for B sites, are compensated by oxygen vacancies which pin the domains [83,84]. These compounds demonstrate the opposite characteristics compared to the “soft” PZT materials, such as low dielectric constant and loss and high coercive field [110]. Isovalent substitutions with ions of the same valence and similar size, such as Ba$^{2+}$ or Sr$^{2+}$ for A sites or Sn$^{4+}$ for B sites, tend to inhibit domain reorientation process and reduce the $T_c$ [81]. For compensating valence substitutions, stoichiometry is maintained if one substitutes combinations instead of individual ions in such manner as described below:

$$\sum X_A V_A + \sum X_B V_B = 6$$

where $X$ is concentration and $V$ is the valance of ions entering the A or B positions. If such a combination is proved to be ferroelectric and able to be poled, the properties should be similar to isovalent modifications of PZT. In practice, the stoichiometry of
undoped PZT at MPB composition is not equivalent to the batch values because of the high volatility of PbO. The resulting lead-oxygen vacancy associates may become oriented along the local polarization vector and subsequently act as pinning sites to domain wall motion. This results in the stabilization of domain wall structure, leading to “hard” acceptor character in nominally “undoped” PZT ceramics. Intentional acceptor doping gives rise to a further “hardening” of undoped PZT ceramics by generating of additional oxygen vacancies. Donor dopants added to PZT materials compensate effects of acceptor cations that naturally existed [81]. Several examples of modified PZT ceramics with their electric properties are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Type</th>
<th>Piezo-ceramics</th>
<th>Dielectric constant $\varepsilon$</th>
<th>Piezoelectric coefficient $d_{33}$ (pm/V)</th>
<th>Coupling factor $k_p$</th>
<th>Curie Temperature $T_c$ (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Donor-doped</td>
<td>PZT-5H</td>
<td>3400</td>
<td>585</td>
<td>0.59</td>
<td>180</td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td>PZT-5A</td>
<td>1700</td>
<td>374</td>
<td>0.60</td>
<td>365</td>
<td>[111]</td>
</tr>
<tr>
<td>Acceptor-doped</td>
<td>APC 841</td>
<td>1350</td>
<td>275</td>
<td>0.60</td>
<td>320</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td>PZT-4</td>
<td>1300</td>
<td>289</td>
<td>0.58</td>
<td>328</td>
<td>[111]</td>
</tr>
<tr>
<td>Undoped</td>
<td>PZT</td>
<td>730</td>
<td>220</td>
<td>0.52</td>
<td>386</td>
<td>[113]</td>
</tr>
</tbody>
</table>

2.2.3 PZT ceramics for piezoelectric devices

There has been increasing interest in incorporating high performance piezoelectric components into MEMS for both sensing and actuating applications. PZT ceramics integrated on the micromachined Si structures have been widely investigated taking advantage of the well-established Si micromachining techniques. Large numbers of
piezoelectric MEMS devices have been developed using PZT ceramics in thin-film [114,115], thick-film [116,117], or bulk wafer forms [118] based on the various application requirements where the thickness of the PZT film is a critical parameter. Different technical approaches are applied for the integration of piezoelectric layers with the Si MEMS body. A comparison among the fabrication and integration of thin-film, thick-film, and bulk-wafer PZT ceramics on Si substrates is listed in Table 2.4.

Table 2.4  Comparison among the planar integration technologies for PZT-based piezoelectric MEMS. (modified after Z. Wang et al. [116])

<table>
<thead>
<tr>
<th></th>
<th>Thin Film</th>
<th>Thick Film</th>
<th>Bulk Wafer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Integration technologies</td>
<td>Sputtering, chemical vapor deposition (CVD), spin-coating, etc.</td>
<td>Screen-printing, aerosol deposition, sol-gel method, etc.</td>
<td>Fusion bonding, and other adhesive bonding techniques</td>
</tr>
<tr>
<td>Patterning process</td>
<td>Easy</td>
<td>Difficult</td>
<td>Very difficult</td>
</tr>
<tr>
<td>Etching process</td>
<td>Wet, dry, and lift-off</td>
<td>Wet and ion-milling</td>
<td>Wet, laser ablation, dicing, and sand blasting</td>
</tr>
<tr>
<td>Process temperature</td>
<td>500°-700°C</td>
<td>650°-900°C</td>
<td>20°-550°C</td>
</tr>
<tr>
<td>Piezoelectric properties</td>
<td>Good</td>
<td>Inferior to bulk wafer</td>
<td>Excellent</td>
</tr>
<tr>
<td>Main applications</td>
<td>Sensors</td>
<td>Actuators and transducers</td>
<td>Actuators and transducers</td>
</tr>
</tbody>
</table>

The preparation and characterization of high performance PZT thick films made on the Si substrates were first presented by Chen et al. [119,120], showing a broad variety of potential applications. Moreover, the deposition of PZT thick films directly onto the Si substrates allows for the integration of devices and control circuits onto a single chip using the compatible manufacturing technology. Implementation of PZT films with a
thickness of 50-150 µm into meso-scale piezoelectric MEMS devices using thick-film technology has attracted considerable attention during the past few years [23]. Preparation of films in that thickness range is difficult using either thin-film technology (e.g. sputtering and chemical vapor deposition) or bulk machining techniques (e.g. dicing bulk PZT and chemical polishing). Therefore, developing suitable fabrication techniques is important for making piezoelectric PZT layers with reasonable piezoelectric properties and the further implementation in MEMS devices. A summary of properties of PZT-based thick film made on Si substrates using various approaches is listed in Table 2.5. The comparison of dielectric properties for thick-film PZT ceramics and their bulk counterparts is also included for different material systems.

It can be observed that most thick-film PZT ceramics exhibit lower values of dielectric constant compared to the bulk PZT. This is consistently related to differences in the microstructure, whereby the PZT thick films normally exhibit a high degree of porosity than the bulk PZT ceramics. However, recent development in material composition and device structure allows the patterned PZT thick films to deliver equivalent functions to bulk materials, for example, using PZT multilayer actuators for piezoelectric MEMS devices requiring large generative force [23]. Functional devices, such as microresonators for mass sensing applications and micropumps for microfluidic systems, have been implemented by virtue of the corresponding modified fabrication techniques. Reviewing the design and working principles of these devices would facilitate a quick transition to realize the same functions using LTCC/PZT structures.
<table>
<thead>
<tr>
<th>Thick film processing route and temperature</th>
<th>Material composition</th>
<th>Thickness (µm)</th>
<th>$\varepsilon_r$ (&amp; dielectric loss $\tan\delta$) at 1kHz</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Screen-printing, 1100°C</td>
<td>La doped PZT (60/40)</td>
<td>100</td>
<td>190 (0.014)</td>
<td>[121]</td>
</tr>
<tr>
<td>Screen-printing, 1000°C</td>
<td>Pb(Ti$<em>{0.04}$Zr$</em>{0.68}$Fe$<em>{0.14}$Nb$</em>{0.14}$)O$_3$</td>
<td>100</td>
<td>204 (0.019)</td>
<td>[122]</td>
</tr>
<tr>
<td>Screen-printing, 1050°C</td>
<td>Doped PZT (50/50) + 3 or 4 wt% sintering aids</td>
<td>80</td>
<td>840 (0.009)</td>
<td>[123]</td>
</tr>
<tr>
<td>Screen-printing, 900°C</td>
<td>PZT (BM500) + 3 wt% sintering aids</td>
<td>20-40</td>
<td>970</td>
<td>1750</td>
</tr>
<tr>
<td>Screen-printing, 1135°C</td>
<td>Doped PZT (52/48)</td>
<td>66</td>
<td>710 (0.024)</td>
<td>–</td>
</tr>
<tr>
<td>Screen-printing, 900°C</td>
<td>0.1Pb(Zn$<em>{1/2}$W$</em>{1/2}$)O$_3$+0.9PZT (50/50)</td>
<td>25</td>
<td>703 (0.030)</td>
<td>1221 (0.032)</td>
</tr>
<tr>
<td>Aerosol deposition + annealing, 900°C</td>
<td>0.2Pb(Zn$<em>{1/3}$Nb$</em>{2/3}$)O$_3$+0.8PZT (50/50) + 2 wt% excess PbO</td>
<td>50</td>
<td>1400 (0.50)</td>
<td>–</td>
</tr>
<tr>
<td>Sol-gel process, 950°C</td>
<td>PZT (53/47) coated with Pb$_5$Ge$<em>3$O$</em>{11}$</td>
<td>10-50</td>
<td>771 (0.052)</td>
<td>1200</td>
</tr>
<tr>
<td>Sol-gel process + wet etching, 720°C</td>
<td>Nb, Sb doped PZT (52/48)</td>
<td>40</td>
<td>690 (0.013)</td>
<td>–</td>
</tr>
<tr>
<td>Sol-gel process, 710°C</td>
<td>PZT (PZ26)</td>
<td>10</td>
<td>600</td>
<td>1200</td>
</tr>
<tr>
<td>Diol sol-gel process, 700°C</td>
<td>PZT (53/47)</td>
<td>10</td>
<td>1000 (0.040)</td>
<td>1200</td>
</tr>
<tr>
<td>Sol-gel process, 700°C</td>
<td>PZT (53/47)</td>
<td>10</td>
<td>1400 (0.036)</td>
<td>–</td>
</tr>
<tr>
<td>Sputtering, 600°C</td>
<td>PZT (52/48)</td>
<td>4.6</td>
<td>1300</td>
<td>–</td>
</tr>
</tbody>
</table>
Micromachined silicon beam resonators with thick-film PZT drive and detection layer have been demonstrated by Beeby et al. [134]. The device consists of a silicon membrane and the screen-printed film PZT of 40 μm thickness, which is sandwiched between an evaporated Pt bottom electrode and an Au printed top electrode. The presented PZT thick-film resonator has proved the feasibility to use this structure for mass sensing. Another microbalance based on the PZT thick-film structure has been fabricated and presented by Ferrari et al. [135], demonstrates a mass sensitivity of 500 Hz/μg with a thickness of PZT layer in 140-150 μm. A planar capacitor structure printed onto an Al₂O₃ substrate can be operated as a thickness mode resonant structure, as shown in Figure 2.12. This structure is sensitive to mass loads applied on the free surface. This developed thick-film structure, which can be used as a chemical sensor, is coated by a chemically sensitive material that adsorbs certain molecules. Fabricating an oscillator control circuit around the sensor will provide an integrated device.

Figure 2.12  The structure of a PZT thick-film resonant sensor for microbalance application. (taken from M. Ferrari et al. [135])
Koch et al. [136] reported a micropump designed and fabricated combining screen printed thick-film PZT layers with a Si micromachined structure. Passive cantilever check-valves were incorporated into the Si structure by fusion bonding. The device is depicted in Fig. 2.13. The pump rate of up to 400 μl/min with a maximum backpressure of up to 35 kPa at 100 V driving voltage across the PZT layer is expected using finite element analysis results.

Figure 2.13 Schematic illustration of micropump made of screen printed PZT layer on micromachined Si structure. (taken from M. Koch et al. [136])
2.3 Integration of LTCC with PZT ceramics

Thick-film technologies provide the possibility of directly integrating the functional films onto the certain substrates. Most thick-film applications incorporate the substrate into the whole device structure. Hence the substrate material becomes a critical component in any sensor or actuator design [137]. Al₂O₃, glass, and Si are common substrate materials for the design and fabrication of thick-film PZT devices. However, LTCC materials provide more advantages than Al₂O₃ and Si substrates especially for the fabrication of 3-D ceramic microfluidic devices and hybrid integration of microsystems. Using LTCC material as the substrate or package for thick-film PZT devices is a new attempt to extend the application field for both LTCC technology and PZT-based MEMS devices.

2.3.1 Ceramic micro-electromechanical systems (C-MEMS)

Ceramics are widely used in the fabrication of MEMS devices and systems because of their versatile structural, chemical, and functional properties, such as: (1) chemical inertness for applications in biological fields; (2) corrosion resistance at high temperatures for chemical engineering and sensor applications in severe environments; (3) suitable mechanical and electrical properties provided for making functional components. Design and fabrication of fully ceramic MEMS (C-MEMS) is an emerging research field in MEMS technology, which has attracted increasing interest in a variety of application areas [138]. Development of such C-MEMS devices and systems requires using ceramics for construction of both MEMS body structure and functional components. Incorporating piezoelectric PZT thick films into a ceramic substrate for the
fabrication of high-performance and reliable C-MEMS is one of the most challenging tasks. Those devices are important in diverse fields such as industrial process control, environmental monitoring, communications, and medical instrumentation [139].

C-MEMS made with compatible thick-film technology on a ceramic substrate are widely used in harsh environments. In comparison with Si-based MEMS they are more robust and resistant to high operating temperature, showing better long-term stability. Al2O3 is one of widely used inert ceramic substrates for MEMS fabrication, which provides good adhesion for the printed functional thick films, compatible CTE with most thick-film pastes, high robustness, and limited capability for 3-D component integration [137]. The combination of Al2O3 substrates with integrated piezoelectric ceramic components has been studied for making novel C-MEMS devices in a miniaturized ceramic package [140-142]. Development of such devices can offer advanced sensor, actuator, and transducer solutions for new fields of application.

However, LTCC provides advantages over Al2O3 in certain applications. For example, the lower Young's modulus for LTCC compared to the Al2O3 makes it more effective for the application of thick-film pressure sensors. However, pure Al2O3 substrate require sintering above 1500°C which is not applicable for co-firing with PZT ceramics while the LTCC materials provide the possibility of co-firing with other functional elements (conductors, dielectrics, and piezoelectrics) to build multilayer structures in a more versatile approach. Several characteristics of typical MEMS substrate materials, LTCC, Al2O3, and Si are listed in Table 2.6. LTCC materials and processing are particularly suitable for the implementation of 3-D microfluidic C-MEMS devices and systems using the multilayer ceramic technology [143]. Developing C-MEMS based
on piezoelectric PZT thick films integrated on a 3-D LTCC structure has recently arisen as a challenging research topic. Technological obstacles are needed to be overcome to make such hybrid systems. A thorough understanding of electrical and piezoelectric properties of PZT thick films integrated onto the LTCC substrate is necessary for the successful usage of developed C-MEMS in sensing and actuating applications.

Table 2.6 Characteristics of common used MEMS substrate materials.

<table>
<thead>
<tr>
<th>Property</th>
<th>Fired LTCC (DuPont 943)</th>
<th>Al₂O₃ ceramics (~99.5%)</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>3.2</td>
<td>3.7 – 3.97</td>
<td>2.3</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>150</td>
<td>394</td>
<td>186.5</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>7.4 (at 40GHz)</td>
<td>~10 (at 1MHz)</td>
<td>~12 (at 1GHz)</td>
</tr>
<tr>
<td>Loss tangent (%)</td>
<td>0.2 (at 40GHz)</td>
<td>~0.2 (at 1MHz)</td>
<td>~0.5 (at 1GHz)</td>
</tr>
<tr>
<td>Resistivity (Ω cm)</td>
<td>&gt; 10¹²</td>
<td>&gt; 10¹⁴</td>
<td>10³ – 10⁵</td>
</tr>
<tr>
<td>Breakdown voltage (V cm⁻¹)</td>
<td>&gt; 4 × 10⁵</td>
<td>1.5 × 10⁵</td>
<td>3 × 10⁵</td>
</tr>
<tr>
<td>Thermal conductivity (W m⁻¹ K⁻¹)</td>
<td>4.4</td>
<td>35</td>
<td>148</td>
</tr>
<tr>
<td>TCE (10⁻⁶K)</td>
<td>6.0</td>
<td>8.4</td>
<td>2.6</td>
</tr>
</tbody>
</table>

* LTCC data source: DuPont 943 green tape data sheet; Al₂O₃ data source: Ferro Ceramic Grinding Inc., 99.5% Al₂O₃ property table; Si data source: EL-CAT Inc., online information, properties of silicon.

### 2.3.2 Compatibility between LTCC and PZT

Piezoelectric PZT thick films made on LTCC provide more possibilities for their applications in integrated microsensors and actuators [16]. However, the majority of reported LTCC-based piezoelectric devices are made by post-firing or adhesive bonding PZT components on the fired LTCC structures. For maximum utility LTCC/PZT...
multilayer structures for C-MEMS fabrication should be obtained in a single co-firing process using the advanced thick-film technology and ceramic processing techniques. Three important issues for co-firing LTCC and thick-film PZT materials are needed to be considered in advance. Firstly, the conventional sintering temperature (1100°-1300°C) of PZT needs to be lowered to be comparable with LTCC firing temperature (850°-900°C). Many types of sintering aids have already been used to reduce the PZT sintering temperature to a range of 700°-950°C [144-146]. Secondly, elemental inter-diffusion between LTCC and PZT layers during sintering is a significant problem for obtaining PZT thick films with desired properties. Thirdly, the mismatch of sintering behaviors (heating process) and CTE (cooling process) between LTCC and PZT components generates shear stress at the interface, which can cause deformations after sintering, such as delamination and camber. Structural failures may occur in the laminated multilayers after co-firing, showing collapse and macroscopic cracking. Typical deformations and failures in co-fired LTCC-based multilayer structures are shown in Figure 2.14.
There were previously several attempts to investigate co-firing LTCC/PZT multilayer ceramics. However, a serious interfacial diffusion problem and deteriorated properties were revealed. A study on the compatibility between LTCC substrate and screen printed PZT-based thick film was reported by Hrovat et al. [147]. PZT (53/47) powders with an excess 6 mol% of PbO and 2 mol% of Pb$_5$Ge$_3$O$_{11}$ (PGO) as a sintering aid were prepared by solid state route. The calcined powders were mixed with an organic vehicle to make thick-film paste for screen printing. The DuPont 951 LTCC materials were used as the substrate and compared with Al$_2$O$_3$. Gold electrode layers were printed on both types of substrates and co-fired with PZT thick films. The relative dielectric
constant of PZT layer on LTCC was only one tenth of that on Al₂O₃ and much lower than the value of bulk ceramics sintered at the same temperature. The deterioration of dielectric properties was considered to be induced by the inter-diffusion of PbO and SiO₂ upon co-firing. Golonka et al. [148] investigated the inter-diffusion of LTCC and PZT with various co-firing conditions and electrode materials. It was found that the shorter firing time and Pd/Ag electrode materials resulted in better dielectric and piezoelectric properties for the PZT layers. Belavic et al. [28,149] used a barrier layer to reduce the interfacial diffusion between LTCC and PZT during the co-firing process. The results showed a limited improvement on the electric properties, as illustrated in Figure 2.15. The additional barriers did not hinder the diffusion of Si from LTCC to PZT layer but it prevented the loss of PbO from the active PZT layer. The preliminary study using both LTCC and traditional thick-film technologies for developing C-MEMS was also reported in the same articles.

![Figure 2.15](image)

Figure 2.15  (a) Dielectric constant and (b) piezoelectric coefficient $d_{33}$ of PZT layer fired on Al₂O₃, LTCC, and LTCC substrate with diffusion barrier layer (LTCC+B). (taken from D. Belavic et al. [149])
A further study, reported by Ursic et al. [150], on the piezoelectric properties of thick-film PZT made on the LTCC substrate has not exhibited any significant improvement. Other studies on the co-firing compatibility between LTCC and other functional materials have been conducted recently, for example, co-firing magnetic ceramic layers with commercial LTCC tapes [151] and integrating different conductive layers into the LTCC modules [152,153]. To date only a few physical sensors were constructed by the combination of LTCC substrates and piezoelectric active layers [26,27]. Co-firing LTCC/PZT multilayer ceramics to fabricate actuators for C-MEMS devices and integrated microsystems is still a challenging work.

2.3.3 Current development in LTCC and PZT materials

Prior experiments do not exhibit favorable results on the compatibility between LTCC and printed thick-film PZT ceramics, particularly the inferior electric properties of PZT in co-fired LTCC/PZT structures. Current development in LTCC and PZT material systems provides new opportunities for co-firing LTCC/PZT multilayer ceramics by integrating self-constrained LTCC tapes with high performance modified PZT materials. The PZT layer in the co-fired LTCC/PZT structure is expected to show reasonable dielectric and piezoelectric properties with minimum deformation for the whole multilayer ceramics.

Self-constrained LTCC tapes

One of the limitations in LTCC technology involves the x-y shrinkage of LTCC structures during firing the process and the dimensional tolerance of that shrinkage. This affects component design, materials utilization, and surface-circuit feature location in the
LTCC fabrication process. Moreover, the shrinkage behaviors of LTCC materials are not
designed to match the densification conditions for most PZT-based ceramics, which
cause additional issues in LTCC/PZT co-firing process. A newly self-constrained
HeraLock™ HL2000 tape developed by Heraeus [154,155] provides a sintering
shrinkage in $x$, $y$ directions of less than 0.2% and a shrinkage tolerance of ±0.02%
without using sacrificial layers and external pressure during firing.

The HL2000 tapes are multilayer laminates prepared by special casting process. A
symmetric laminate with two different types of layers is laminated in the green state, as
shown in Figure 2.16, illustrating the different layers sintered at different temperature
intervals. The inner layer starts to densify in the first sintering stage while the outer layers
function as rigid substrates preventing the lateral shrinkage. In the second sintering stage,
the outer tapes shrink while the fully densified inner layer prevents the shrinkage of the
outer layers in $x$-$y$ direction. The specific composition of each LTCC layer sintered at
different temperature intervals is carefully controlled. The effective suppression of lateral
shrinkage requires that the inner layer should completely stop densification before the
outer layers start [154].

A demonstration of near-zero $x$-$y$ shrinkage of HL2000 tapes is illustrated in
Figure 2.17. A green laminate with metallization was cut in half along the diagonal. No
visible mismatch between the two parts was observed after sintering only one half.
HL2000 enables large-area metallization, integration of channels, cavities and passive
electronic components without waviness and camber.
Figure 2.16  Sintering process for the self-constrained laminate consisting of two different layers with various sintering intervals. (taken from T. Rabe et al. [154])

Figure 2.17  An illustration of self-constrained HL2000 tapes showing near-zero x-y shrinkage after firing. (taken from T. Rabe et al. [154])
Using HL2000 tapes as substrates for temperature and pressure sensors was evaluated by screen-printing and firing thick-film thermistors and piezoelectric PZT ceramics on the fired HL2000 tapes [156]. The uniform self-constrained HL2000 tape provides excellent compatibility with materials that have significantly different densification profiles, which reduces the need to tailor densification behaviors and greatly saves development time.

*High performance doped-PZT ceramics*

Recently, Donnelly et al. [31] reported a high-performance piezoelectric ceramic made by \((1-x)\text{PZT-}x\text{SKN}\) \((x = 0.2)\) that Zr/Ti ratio is fixed to undoped MPB composition \((\text{Zr}_{0.53}/\text{Ti}_{0.47})\) and the composition of Sr, K and Nb is in the formula of \(\text{Sr}(\text{K}^{1/4}, \text{Nb}^{3/4})\text{O}_3\) (SKN) with specific ratio of 4:1:3. Showing high \(d_{33}\) value and high \(T_c\), this PZT-based ceramic can be used for piezoelectric multilayer actuators which satisfy the requirements of fuel injectors for automotive application. Despite the chemical formula it is expected that both \(\text{Sr}^{2+}\) and \(\text{K}^+\) will substitute for \(\text{Pb}^{2+}\) at the A sites in the perovskite structure, as isovalent and acceptor additives respectively. \(\text{Nb}^{5+}\), as a donor dopant, occupies the B sites. However, the precise doping effect, site occupation, and defect chemistry associated with the SKN combination are complicated and remain unclear. The result is a high Curie temperature material with moderate strain-field hysteresis and an exceptionally large high field piezoelectric strain coefficient. The high field \(d_{33}\) value, which is taken as the ratio of strain to field at 20 kV/cm, is a function of SKN content. The maximum \(d_{33}\) value 779 pm/V was found at the 0.98PZT-0.02SKN composition, as shown in Figure 2.18. The variation of piezoelectric properties with the SKN addition can
be explained by the competing effects from donor doping and grain size-related phenomena or the dopant-induced shift in the MPB composition of PZT solid solutions.

Figure 2.18  The high field $d_{33}$ piezoelectric coefficient as a function of SKN addition and (inset) unipolar strain loop used for the $d_{33}^{\text{high}}$ calculation. (taken from N.J. Donnelly et al. [31])

A further attempt to lower the sintering temperature of $(1-x)$PZT-$x$SKN by the addition of fluxes was reported [157]. The most successful flux was found to be the Li$_2$CO$_3$ with 0.9 mol% addition which promotes the densification at 900°C and the sintering was carried out for 3-6 h. The partial Li substitution in the low fired ceramics may lead to the reduced resistivity and permittivity compared to the conventionally sintered samples. The Li$_2$CO$_3$ fluxed $(1-x)$PZT-$x$SKN showed a shift in the optimum
composition. The flux-sintered 0.97PZT-0.03SKN exhibited a maximum high field $d_{33}$ of 640 pm/V and $T_c$ of ~350°C. The functional properties of (1-x)PZT-xSKN ceramics conventionally sintered at 1250°C and flux-sintered at 900°C with 0.9 mol% Li$_2$CO$_3$ addition are compared in Table 2.7. A multilayer structure of fluxed PZT-SKN layers with printed silver electrodes was also successfully co-fired using the low temperature firing profile.

Table 2.7 Properties of PZT-xSKN ceramics sintered at 1250°C and flux-sintered at 900°C with 0.9 mol% Li$_2$CO$_3$ flux addition. (taken from N.J. Donnelly et al. [31,157])

<table>
<thead>
<tr>
<th>SKN (mol%)</th>
<th>Grain size (µm)</th>
<th>$T_c$ (°C)</th>
<th>$\varepsilon_r$ (1kHz)</th>
<th>$d_{33}^{\text{high}}$</th>
<th>$k_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>High fired 11.4±2.9 375 1300 668 0.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low fired 2.4±1.0 380 1214 522 0.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>High fired 6.2±2.0 356 1400 779 0.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low fired 3.4±1.0 364 1260 590 0.62</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>High fired 2.8±1.0 341 1430 713 0.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low fired 2.7±0.8 347 1339 640 0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>High fired 1.5±0.5 323 1500 651 0.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low fired 1.7±0.5 331 1398 630 0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05</td>
<td>High fired 1.5±0.5 305 1500 547 0.47</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low fired 1.5±0.5 314 1479 605 0.57</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.4 Sintering of ceramics

Sintering is the most critical processing technique used to produce a ceramic with desired microstructures and properties by applying thermal energy into a powder compact. Depending on the complex nature of different starting materials, several basic types of sintering processes have been used to analyze the densification behavior and the evolution of microstructure. In this thesis work, high-density polycrystalline PZT-SKN ceramics are prepared by solid-state sintering route. The enhanced densification rate of PZT-SKN ceramics sintered at low temperature will be achieved using low-melting-point additives, which is referred to as liquid-phase sintering. The densification of glass-ceramic composite materials like LTCC is attributed to the viscous sintering, which is controlled by the viscosity of the glass during the heat treatment [158]. The constrained sintering process can be used to explain the sintering behavior of hybrid LTCC/PZT-SKN multilayer laminates. The resulting properties of sintered piezoelectric ceramics in the multilayer structures are directly related to the performance of the fabricated devices.

2.4.1 Driving force for sintering

The sources that cause the reduction of the total free energy of the system are considered as the driving forces for sintering. There are three possible driving forces [159]: (1) surface free energy, (2) externally applied pressure, and (3) chemical reaction.

Surface free energy provides the main driving force if no external pressure and chemical reaction are involved during sintering. The surface area of a powder system consisting of one mole spherical particles with a radius $a$ is given by $3V_m/a$, where the $V_m$
is the molar volume. The change of surface free energy $\Delta G_s$ associated with the system of particles is described by:

$$\Delta G_s = 3\gamma_{sv}V_m \left( \frac{1}{a} - \frac{1}{a'} \right)$$

where $\gamma_{sv}$ is the specific surface energy. The $\Delta G_s$ is related to the difference in the reciprocal of the radius of curvature of the particles before and after sintering.

An externally applied pressure is considered as the major source of driving forces in the absence of a chemical reaction. The contribution of surface curvature change is significant smaller than that of external pressure in the reduction of the free energy of the system. The work exerted on the one-mole particle system by the external pressure can be determined by [159]:

$$W = p_a V_m$$

where $p_a$ is the applied pressure and $W$ represents the driving force for the resulting densification of the powder system.

The change in free energy $\Delta G^o$ determined by a chemical reaction is given by [159]:

$$\Delta G^o = -RT\ln K_{eq}$$

where $R$ is the gas constant, $T$ is the absolute temperature, and $K_{eq}$ is the equilibrium constant for the reaction. The driving force induced by chemical reaction is considerably greater than that caused by external pressure. However, the chemical reaction is rarely
used to facilitate densification in the preparation of advanced ceramics because the complexity of reaction makes the microstructure control extremely difficult during sintering [159]. Figure 2.19 illustrates the three main driving forces for sintering.

![Figure 2.19](image)

Figure 2.19 Illustration of three main driving forces for sintering: surface free energy, external pressure, and chemical reaction. (taken from M.N. Rahaman [159])

2.4.2 Solid-state sintering

*Driving force*

In the absence of applied external pressure and chemical reaction, the driving force for solid-state sintering is the reduction of surface free energy achieved by the atomic diffusion which results in two competing processes: densification and coarsening.
Densification is caused by the elimination of pore volume interfaces and the simultaneous formation of new but lower-energy grain boundaries. Coarsening is a result of the rearrangement of the pore surfaces without the decrease in the pore volume accompanied by grain growth. The dominant process will determine the final microstructure of the consolidated mass of particles after sintering, the production of a high-density body will be favored by densification while the production of a highly porous body by coarsening. The difference between densification and coarsening is schematically shown in Figure 2.20.

![Figure 2.20 The difference between densification and coarsening processes. (taken from W.D. Kingery et al. [160])](image)

The shape of pores defined by the grain boundaries in polycrystalline materials is important for the densification process. In equilibrium state the tension in grain boundary and the tension in the solid-vapor interface are balanced at the junction where the grain boundary intersects the pore. The balance of forces is given by:
\[ \gamma_{gb} = 2\gamma_{sv}\cos\frac{\psi}{2} \]

where \( \psi \) is defined as dihedral angle, \( \gamma_{sv} \) and \( \gamma_{gb} \) are the interface tension and grain boundary tension, respectively. The dihedral angle \( \psi \) has to be less than 180\(^\circ\) for densification to occur. When the \( \psi \) is low, the pores will stabilize in the structure and the further removal of pores is limited.

**Mechanisms of sintering**

During the sintering process, matter transports from regions of higher chemical potential (source of matter) to regions of lower chemical potential (sink of matter). The diffusion path of mass transport in polycrystalline materials defines the mechanisms of sintering, as shown in Table 2.8 and Figure 2.21.

<table>
<thead>
<tr>
<th>Mechanism number</th>
<th>Transport path</th>
<th>Source of matter</th>
<th>Sink of matter</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surface diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td>Coarsening</td>
</tr>
<tr>
<td>2</td>
<td>Lattice diffusion</td>
<td>Surface</td>
<td>Neck</td>
<td>Coarsening</td>
</tr>
<tr>
<td>3</td>
<td>Vapor transport</td>
<td>Surface</td>
<td>Neck</td>
<td>Coarsening</td>
</tr>
<tr>
<td>4</td>
<td>Boundary diffusion</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td>Densification</td>
</tr>
<tr>
<td>5</td>
<td>Lattice diffusion</td>
<td>Grain Boundary</td>
<td>Neck</td>
<td>Densification</td>
</tr>
<tr>
<td>6</td>
<td>Plastic flow</td>
<td>Dislocations</td>
<td>Neck</td>
<td>Densification</td>
</tr>
</tbody>
</table>
Figure 2.21 Six distinctive paths for matter transport during the sintering of a consolidated mass of crystalline particles. (taken from W.D. Kingery et al. [160])

All of the introduced sintering mechanisms lead to neck growth between particles, resulting in an increase in the compact strength. Certain mechanisms that do not cause the particle centers to move closer together, will not lead to densification but coarsening. The nondensifying mechanisms occur when matters transport from the particle surfaces to the neck region, including surface diffusion, lattice diffusion from the surface, and vapor transport (mechanisms 1, 2, and 3). Although not leading to densification, these mechanisms cause a decrease in the neck curvature; it hence reduces the driving force for sintering which in turn slows the densification rate. The neck growth and densification occur by grain boundary diffusion and lattice diffusion from the grain boundary to the pore (mechanism 4 and 5) in polycrystalline ceramics. Another densifying mechanism is
plastic flow by dislocation motion (mechanism 6), a common path of mass transport for sintering metal powders. The sintering rates can be measured by the rates at which the width of the neck increases and compared for the corresponding mechanisms. In addition, the rate of shrinkage of the powder compact can be used to measure the rate of densification [159].

**Stages of sintering**

Many analytical models have been proposed to describe sintering process using an idealized geometry for the powder system [161-167]. In order to simplify the analysis of micro-structural evolution and the formation of mass transport equations, the sintering process is typically divided into three sequential stages based on the connectivity of microstructure: (1) initial stage, (2) intermediate stage, and (3) final stage. The Figure 2.22 shows the idealized geometrical structures that represent each stage defined by Coble [161].

The rapid inter-particle neck growth is involved in the initial stage, which is represented as the transition between Figure 2.22(a) and Figure 2.22(b). The density increases to about 65% of the theoretical density when the densifying mechanisms dominate in this stage. The intermediate stage is characterized by continuous cylindrical pore channels coincident with three-grain junctions as illustrated in Figure 2.22(c). The density increases from 65% to about 90% by pore shrinkage which is controlled by lattice and grain boundary diffusion in the intermediate stage. In the final stage the pore channels are eventually pinched off into separate pores located at the grain corners as shown in Figure 2.22(d).
Figure 2.22 Illustration of idealized models for the three sintering stages. (a) initial stage of sintering model represented by spheres in tangential contact; (b) near the end of the initial stage: spheres have begun to coalesce; (c) intermediate stage: grains adopted shape of tetrakaidecahedron, enclosing pore channels at grain edges; and (d) final stage: pores are tetrahedral inclusion at corners where four tetrakaidecahedra meet. (taken from M.W. Barsoum [168])

The simple two-sphere model, consisting of two equal-sized spheres in contact, is used to analyze the initial sintering stage. The neck growth between particles is determined by both densifying and nondensifying mechanisms. Assuming that all the
transport paths are independent and additive, the rate of neck growth during the initial stage can be expressed as [169]:

\[
\frac{dx}{dt} = \frac{C_1 \gamma D_l R}{x^3} + \frac{C_2 \gamma D_{gb} R^2}{x^5} + \frac{C_3 \gamma D_s R^2}{x^5} + \frac{C_4 \gamma p_o R}{x}
\]

where \(x\) is the radius of neck, \(R\) is the sphere radius, \(\gamma\) is the specific surface energy, \(C_i (i = 1-4)\) is a constant relating to the specific diffusion path and the geometry of the model, \(p_o\) is the vapor pressure, and the \(D_l, D_{gb}, D_s\) are the diffusion coefficients for lattice, grain boundary, and surface diffusion respectively. The general form of equations for neck growth \((x/R)\) and shrinkage \((\Delta L/L_o)\) in the initial stage are given by [159]:

\[
\left(\frac{x}{R}\right)^m = \frac{H}{R^n} t
\]

\[
\left(\frac{\Delta L}{L_o}\right)^{m/2} = -\frac{H}{2^m R^n} t
\]

where \(m\) and \(n\) are numerical exponents that determined by the specific mechanism of sintering and \(H\) is a function that depends on the geometrical and material parameters of the powder system. Table 2.9 summarizes the values of \(m\) and \(n\) as well as the expressions of \(H\) for each sintering mechanism [170].

Most of the densification of a powder system occurs during the intermediate stage. Coble [161] first proposed a geometrical model to explain this complex process. Nondensifying mechanisms cannot be applied in this model because the chemical potential is the same everywhere on the pore surface based on the assumption that all particles are equal-sized tetrakaidecahedra and all pores are cylindrical with the same
size. Only lattice diffusion and grain boundary diffusion are considered to dominate the densification process. The porosity function, \( f(\varphi) \), can be derived as [171]:

\[
    f(\varphi) = K \left( \frac{\gamma_{sv} \Omega D}{R_{go}^m kT} \right) (t_f - t)
\]

where \( \varphi \) is the porosity, \( K \) and \( m \) are constants that determined by the sintering mechanism, \( \gamma_{sv} \) is the specific surface energy, \( \Omega \) is the atomic volume, \( D \) is the diffusion coefficient, \( R_{go} \) is the initial grain size, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( t_f \) is the extrapolated time for the vanishing of the cylindrical pores. The values of \( f(\varphi) \), \( K \), and \( m \) for lattice diffusion and grain boundary diffusion mechanisms are listed in Table 2.10 according to the different suggested models.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>( m )</th>
<th>( n )</th>
<th>( H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface diffusion</td>
<td>7</td>
<td>4</td>
<td>( \frac{56D_s \delta_s \gamma_{sv} \Omega}{kT} )</td>
</tr>
<tr>
<td>Lattice diffusion from the surface</td>
<td>4</td>
<td>3</td>
<td>( \frac{20D_l \gamma_{sv} \Omega}{kT} )</td>
</tr>
<tr>
<td>Vapor transport</td>
<td>3</td>
<td>2</td>
<td>( \frac{3p_o \gamma_{sv} \Omega}{(2\pi mkT)^{1/2} kT} )</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>6</td>
<td>4</td>
<td>( \frac{96D_{gb} \delta_{gb} \gamma_{sv} \Omega}{kT} )</td>
</tr>
<tr>
<td>Lattice diffusion from the grain boundary</td>
<td>5</td>
<td>3</td>
<td>( \frac{80\pi D_l \gamma_{sv} \Omega}{kT} )</td>
</tr>
<tr>
<td>Plastic flow</td>
<td>2</td>
<td>1</td>
<td>( \frac{3\gamma_{sv} \Omega}{2\eta} )</td>
</tr>
</tbody>
</table>

* \( D_l \), \( D_{gb} \), and \( D_s \) are the lattice, grain boundary, and surface diffusion coefficients respectively; \( \delta_s \) and \( \delta_{gb} \) are the thickness for surface and grain boundary diffusion; \( \gamma_{sv} \) is the specific surface energy; \( \Omega \) is the atomic volume; \( m \) is mass of an atom; \( k \) is the Boltzmann constant; \( T \) is the absolute temperature; and \( \eta \) is the viscosity.
Table 2.10 Parameters in the sintering models represented by equation for intermediate stage of sintering. (taken from T.A. Ring [172])

<table>
<thead>
<tr>
<th>Model</th>
<th>$f(\phi)$</th>
<th>$K$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coble [142]</td>
<td>$\phi$</td>
<td>720</td>
<td>3</td>
</tr>
<tr>
<td>Johnson [146]</td>
<td>$-\ln (1 - \phi)$</td>
<td>378</td>
<td>3</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coble [142]</td>
<td>$2/3 \phi^{3/2}$</td>
<td>80 $\delta_{gb}$</td>
<td>4</td>
</tr>
<tr>
<td>Johnson [146]</td>
<td>$\int_{\phi}^{0} \frac{\sqrt{x}}{1-x} dx$</td>
<td>1000 $\delta_{gb}$</td>
<td>4</td>
</tr>
</tbody>
</table>

* $\delta_{gb}$ is the thickness for grain boundary diffusion.

The final density and the resulting properties of the sintered ceramics are largely decided by the final stage of sintering. The shrinkage of isolated pores takes place in the final stage of sintering. In an idealized powder system, the spherical pores of the same size are located at the intersections of particles. As in the intermediate stage, only densifying mechanisms (lattice and grain boundary diffusion) account for the shrinkage of the pores because the pore geometry is uniform. Coble [161] presented a model to describe the lattice diffusion in final stage of sintering:

$$
P_s = \frac{6\pi}{\sqrt{2}} \left( \frac{D_l \gamma_{sv} \Omega}{l_p^3 k T} \right) (t_f - t)
$$

where $P_s$ is the porosity at a time $t$, $D_l$ is the lattice diffusion coefficient, $\gamma_{sv}$ is the specific surface energy, $\Omega$ is the atomic volume, $l_p$ is the edge length of the tetrakaidecahedron, $k$ is the Boltzmann constant, $T$ is the absolute constant, and $t_f$ is the time when the pores disappear. This approximate equation is valid when the porosity is less than 2%.
2.4.3 Liquid-phase sintering

The method of using one or more additives that form a liquid phase between grains at sintering temperature is referred to as liquid-phase sintering. Compared to solid-state sintering, the formation of the liquid phase leads to the enhanced densification rates, accelerated grain growth, or specific grain boundary properties [159]. The amount of liquid phase formed is normally small but needs to be sufficient for providing a path for enhanced mass transport. The comparison of diffusion paths is shown in Figure 2.23 for solid-state sintering and liquid-phase sintering using idealized two-sphere model.

![Diagram of solid-state and liquid-phase sintering](image)

Figure 2.23 Schematic illustration of an idealized two-sphere model comparing the microstructural aspects of (a) solid-state sintering with (b) liquid-phase sintering. (taken from M.N. Rahaman [159])

*Driving force*

In an idealized model of liquid-phase sintering, the solid particles and pores are separated by the surrounding liquid phase. The reduction of the liquid-vapor interface energy is the source of driving force for the densification in this system if no external
pressure and chemical reaction are involved. Considering a spherical pore of \( r \) in the liquid phase, the pressure difference \( \Delta p \) across the curved surface is given by:

\[
\Delta p = -\frac{2\gamma_{lv}}{r}
\]

where \( \gamma_{lv} \) is the specific surface energy of the liquid-vapor interface. The pressure deficit in the liquid generates a large compressive capillary stress on the particles, which provides the driving force for sintering.

Good wetting and appreciable solid solubility in liquid are fundamental requirements for liquid-phase sintering. The contact angle \( \theta \), defined by the angle between the solid surface and the tangent of to the liquid surface at the contact point, is used to characterize the degree of wetting. An equilibrium equation is derived for a solid-liquid-vapor system:

\[
\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta
\]

where the \( \gamma_{sv}, \gamma_{sl}, \) and \( \gamma_{lv} \) are specific energies for solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively. Good wetting (low \( \theta \)), which can be obtained with high values of \( \gamma_{sv} \) and low values of \( \gamma_{sl} \) and/or \( \gamma_{lv} \), is a necessary condition for liquid-phase sintering. However, the solubility of solid in the liquid leads to the detailed wetting geometry in a powder system, which is another important factor for the occurrence of liquid-phase sintering.

In the same way that a dihedral angle \( \psi \) is defined in a solid-vapor system used in solid-state sintering, the dihedral angle \( \psi \) in a solid-liquid system is derived as:
\[
\cos \frac{\psi}{2} = \frac{\gamma_{gb}}{2\gamma_{sl}}
\]

where \(\gamma_{gb}\) and \(\gamma_{sl}\) are specific energy for grain boundary and the solid-liquid interface respectively. When the ratio \(\gamma_{gb}/\gamma_{sl}\) is small, solid-state sintering mechanisms dominate the sintering process because the liquid phase penetration of the grain boundary is limited. The liquid penetration of the grain boundary is complete when the ratio \(\gamma_{gb}/\gamma_{sl} \geq 2\). The microstructures of ceramics determined by liquid-phase sintering for different ratios of \(\gamma_{gb}/\gamma_{sl}\) are described in Table 2.11.

<table>
<thead>
<tr>
<th>(\gamma_{gb}/\gamma_{sl})</th>
<th>(\psi)</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\geq 2)</td>
<td>0°</td>
<td>All grains separated by liquid phase</td>
</tr>
<tr>
<td>(\sqrt{3} - 2)</td>
<td>0-60°</td>
<td>Continuous liquid phase penetrating all three-grain junction; partial penetration</td>
</tr>
<tr>
<td>(1 - \sqrt{3})</td>
<td>60-120°</td>
<td>Isolated liquid phase partially penetrating the three-grain junctions</td>
</tr>
<tr>
<td>(\leq 3)</td>
<td>(\geq 120°)</td>
<td>Isolated liquid phase at four-grain junctions</td>
</tr>
</tbody>
</table>

**Table 2.11  Microstructure of two-phase ceramics produced by liquid-phase sintering for different ratios of \(\gamma_{gb}/\gamma_{sl}\) and the corresponding \(\psi\). (modified after M.N. Rahaman [159])**

**Stages of liquid-phase sintering**

During sintering in the presence of a liquid phase, three dominant stages of densification occur [173-175]. Firstly, rearrangement of solid particles under the influence of capillary stress gradient which gives rise to the increased density; Secondly, solution-precipitation process in which solid particles are dissolved at the solid-liquid interface, allowing the centers of particles to approach; Finally, a sintering stage
controlled by the densification of the solid particulate network. The sequential stages of liquid-phase sintering are demonstrated in Figure 2.24. There is significant overlapping in connecting densification stages in an actual powder compact during sintering. Moreover, the densification process at each stage is dependent on the volume fraction of liquid. At approximately 35 vol% liquid, complete densification can be achieved with high uniformity by the rearrangement process alone [173]. For situations in which the liquid content is low, solution-precipitation and final stage sintering dominate the densification process in the powder systems.

Figure 2.24  Schematic evolution of a powder compact during liquid-phase sintering. (taken from M.N. Rahaman [159])

Kingery [173,174] proposed a simple kinetic relationship to describe the shrinkage ($\Delta L/L_0$) in rearrangement process:
\[ \frac{\Delta L}{L_o} = C_1 t^{1+y} \quad (0 < y < 1) \]

where \( C_1 \) is the constant at fixed composition and temperature for a given powder system and \( t \) is the sintering time. The exponent \( (1 + y) \) is larger than unity because the increasing of driving force by the reduction in pore size is balanced by the increasing of resistance to rearrangement by viscous flow at the same time. Two mechanisms control the matter transport in the solution-precipitation process: (1) diffusion from the liquid and (2) interface reaction leading to either dissolution into the liquid or precipitation onto the particle surfaces. For a two-sphere particle model, the shrinkage in the solution-precipitation process which is diffusion rate controlled is given by [173]:

\[ \frac{\Delta L}{L_o} = \frac{1}{3} r^{-\frac{4}{3}} t^{\frac{1}{3}} \]

or, for phase boundary reaction rate controlled:

\[ \frac{\Delta L}{L_o} = \frac{1}{2} r^{-1} t^{\frac{1}{2}} \]

where \( C_2 \), and \( C_3 \) are the constants for any given composition and temperature, \( r \) is the radius of the particle, and \( t \) is the sintering time. The shrinkage controlled by the diffusion mechanism is proportional to the one-third power of time and inversely proportional to the four-thirds power of the initial particle size. In the case of interface reaction mechanism the shrinkage is proportional to the square root of time and the reciprocal of initial particle size.
2.4.4 Viscous sintering

Densification of amorphous materials occurs by viscous flow which reduces the free energy of the system. Frenkel [176] first analyzed the viscous sintering based on that statement. A simple model consisting two-sphere particles was constructed to study the shrinkage of the material during sintering, according to:

$$\frac{\Delta L}{L_o} = \frac{3\gamma t}{8\eta a}$$

where $L_o$ is the initial distance between the centers of the spheres and the $\Delta L$ is the change (decrease) of that distance, $\gamma$ is the surface tension, $t$ is the sintering time, $\eta$ is the viscosity, and $a$ is the initial radius of the two identical spheres. It was found that the shrinkage rate (ration of $\Delta L/L_o$ to $t$) is linear if the viscosity does not change through sintering. Other models have been used to describe the densification process during viscous sintering. Mackenzie and Shuttleworth [177] presented a spherical shell model, which is suitable for representing the final stage of sintering when the pores become isolated. Scherer [178] proposed a cylinder model which is appropriate for explaining sintering of materials with low initial densities. A good agreement was observed between these models in spite of the different microstructural geometries used [179]. The grain size, viscosity, and surface tension of the material system corresponding to the time required for full densification can be controlled by composition and temperature.

Non-reactive liquid phase sintering (NLPS) model

Ewsuk et al. [180,181] presented a sintering model to explain the densification behavior of ceramic-filled glass composites. According to the proposed non-reactive
liquid phase sintering (NLPS) model, the densification occurs by a combination of three sintering stages: (a) glass redistribution, (2) grain rearrangement, and (3) viscous flow, as shown in Figure 2.25.

![Figure 2.25](image)

Figure 2.25  Schematic evolution of sintering stages in non-reactive liquid phase sintering (NLPS) model. (taken from K.G. Ewsuk et al. [181])

Glass melts and infiltrates the ceramic-rich regions in the initial stage where the densification occurs by glass redistribution and local grain rearrangement. The glass-filled cylindrical pore channels are formed through capillary force, which is considered as the driving force ($DF$) for this process:

$$DF_{\text{redistribution}} = \frac{\gamma_{lv} \cos \theta}{r}$$
where $\gamma_{lv}$ is the glass surface tension, $\theta$ is the wetting angle, and $r$ is the radius of the cylindrical pore channel. The intermediate stage of sintering is mainly characterized by the global grain rearrangement process that accounts for the densification of the powder system from ~65% to ~90% of the theoretical density. The driving force for this process is given by:

$$DF_{gr} = 2\pi\gamma_{lv}R \sin(\varphi + \theta) - 2\pi\gamma_{lv} \frac{R^2}{r} \sin\varphi$$

where $R$ is the particle diameter and $\varphi$ is a geometrical factor related to the solid-vapor-liquid intersect. The degree of wetting and glass viscosity are the most important parameters involved in this densification process. The final stage of densification occurs once all solid-vapor interfaces disappear. The ~10% residual porosity is closed by the viscous flow, not affected by the wetting condition. The driving force for the final stage viscous flow is defined by Laplace equation as follow:

$$DF_{final} = \frac{2\gamma_{lv}}{r}$$

The time required to eliminate a pore of a radius $r$ during final sintering stage is directly related to the viscosity of the glass-ceramic composite:

$$t = \frac{2r\eta}{\gamma_{lv}}$$

Ewsuk et al [180,181] showed that the elimination of the closed pores in the glass-ceramic composite with a high filler concentration requires a glass of low viscosity while only low filler concentration can be accepted for using a glass with high viscosity. It is
also found that the densification improved with decreasing filler content and increasing filler particle size.

The densification process for LTCC, a ceramic-filled glass composite material, is examined using NLPS model [158]. This implies the glass is expected to wet the ceramic fillers in the initial and intermediate stages of sintering and a low-viscosity glass is needed to eliminate the pores in the final sintering stage. However, it was demonstrated that the glass does not wet the filler in the entire temperature range but the densification occurs by viscous flow which is controlled by the viscosity of the glass.

Figure 2.26  Schematic of the densification of ceramic-filled glass composites by NPLS through viscous flow. (taken from S. Kemethmuller et al. [158])

Figure 2.26 illustrates schematically the densification mechanism for the examined LTCC material. For ceramic-filled glass composites with glass contents above 60 vol%, like most commercial LTCC systems, it is important to control the viscosity of
the glass for sufficient densification during firing. This knowledge is important for the future evaluation and selection of glasses for developing new LTCC systems.

2.4.5 Constrained sintering

Constrained sintering is a common phenomenon in practical sintering process in which the shrinkage behavior of a material is affected by external and/or internal constraints. The constraints may be the attached substrate or laminated heterogeneous layer that has a different sintering behavior (external) or the inclusion of non-sintering particles or fibers (internal). The influence of constraints on the densification process of a material can be either positive or negative, leading to a classification of constraint components as (1) retarding constraint which results in hindrance in densification and (2) enhancing constraint which leads to the enhancement of densification [182].

The mechanical properties of the involved materials, like Young’s modulus, Poisson’s ratio, and viscosity, are important for the determination of stresses developed in the constrained sintering process. A variety of models have been proposed to calculate such stresses [183-185]. Bordia and Scherer [183] suggested a linear viscous model describing the stress-strain relationship for a porous material under constrained sintering. Based on the proposed viscous model, the constitutive equations for the strain response of an ideal isotropic and porous material are given as (in Cartesian coordinates):

\[
\varepsilon_x = \frac{\sigma_x}{\eta} - \frac{\sigma_y}{\eta} - \frac{\sigma_z}{\eta} + \varepsilon_{f_x}
\]

\[
\varepsilon_y = \frac{\sigma_y}{\eta} - \frac{\sigma_z}{\eta} - \frac{\sigma_x}{\eta} + \varepsilon_{f_y}
\]
\[ \dot{\varepsilon}_z = \frac{\sigma_z}{\eta} - \frac{\sigma_x}{\eta} - \frac{\sigma_y}{\eta} + \varepsilon_{fz} \]

where \( \dot{\varepsilon} \) and \( \dot{\varepsilon}_f \) are the strain rates with and without stresses, \( \sigma \) is the stress, \( \nu \) is the viscous Poisson’s ratio, and \( \eta \) is the uniaxial viscosity. For the case of the material under uniaxial compress (\( \dot{\varepsilon}_x = \dot{\varepsilon}_y \)) and the isotropic transverse shrinkage (\( \sigma_z \neq \sigma_x = \sigma_y = 0 \)), the strain rates are written out as:

\[ \dot{\varepsilon}_z = \frac{\sigma_z}{\eta} + \varepsilon_{fz} \]

\[ \varepsilon_{x/y} = -\frac{\sigma_z}{\eta} + \varepsilon_{fz/y} \]

The compressive stress required for the zero transverse shrinkage rate is given by:

\[ \sigma_z = \frac{\eta}{\nu} \varepsilon_{fx} \]

Multilayer laminates, commonly used as interconnect substrates and packages, consist of different conductor, resistor, and dielectric layers produced by thick-film technology. The most important manufacturing step is the co-sintering (or co-firing) of the hybrid multilayered structure. Constrained sintering has significant effects on the densification behaviors of all constituents in the multilayer structure and the resulting microstructures and properties. It can lead to microstructural defects (e.g. cracking and delamination) and anisotropic shrinkage (e.g. warping). The cause of the defects is normally attributed to the transient stresses (e.g. in-plane tensile stresses) due to the mismatch in sintering rates of the constituent layers. Cheng and Raj [186] observed cracks and void in axial symmetrical multilayers of co-fired ceramic/metal and
glass/metal systems. Jean et al. [187] analyzed stress development and curvature formation in a co-fired LTCC-silver system based on the theoretical models. The most effective solution to the problems of reduced sintering and structural defects is to minimize the difference in sintering behaviors for all component materials. However, it’s extremely difficult to fully match the sintering rate of two completely dissimilar materials.

LTCC material has been widely used in microelectronics, requiring precise control of sintering shrinkage and dimensional tolerance. The concept of zero-shrinkage processing has gained increasing interest in LTCC technology in order to minimize or eliminate the defects and deformation caused by co-firing [188]. The constrained sintering approach enables control of dimensional shrinkage during sintering process. There are three common techniques used in LTCC industry to constrain the densifying materials: (1) pressure-assisted sintering which adds an external pressure exerted on the multilayer in z direction, (2) self-constrained sintering which applies unique non-shrinking layers, and (3) pressure-less constrained sintering which uses a release tape or forms a layer that constrains the green ceramic body due to interfacial stress. These techniques involve additional cost and materials and add further steps to the manufacturing process [189].
2.5 Micropumps for lab-on-chip microfluidic systems

Recent development in microfluidic MEMS and the increased interest of biochemical companies for integrated microanalytical systems have led to the emergence of lab-on-a-chip (LOC) or micro total analysis system (μ-TAS). However, effective on-chip transport and control of small quantities of fluidic samples remains an important challenge for implementing the conceptual integrated microfluidic systems. Numbers of micropumps developed to date are Si- or polymer-based peristaltic pumps actuated piezoelectrically. However, manufacturing such pumps is complicated and expensive. In addition, it is difficult to integrate these developed micropumps with other fluidic components. Therefore, further incorporation of micropumps into the microfluidic system requires the development of other suitable substrate materials and microfabrication techniques.

2.5.1 Micropumps for microfluidics

Microfluidics is the science and technology of designing and manufacturing devices that manipulate small volumes of fluids on the order of nanoliter to attoliter. Scaling down fluidic processes to the micro-scale offers numerous benefits including reduced reagent and power consumption, rapid response for analysis, high selectivity and sensitivity in separations and detections, low cost, and small size for the devices [190-192]. The miniaturized devices enable the construction of a single integrated chip containing multiple components providing different functionalities. Such Integrated microfluidic devices or systems have attracted considerable interest for a wide range of applications from biological and chemical analysis to molecular and medical diagnostics.
Still at its beginning, the development of microfluidic devices towards commercialization has been done mostly in America and Europe during the last few years. The prospective market for the microfluidic MEMS devices and systems will exceed $3 billion in 2014, as shown in Figure 2.27.

![Figure 2.27 Expectation of market growth for microfluidic devices and systems from 2006 to 2014. (taken from EMMA Report 2009 [195])](image)

Laminar flow is expected in the developed microfluidic devices because the Reynolds number $R$ is significantly smaller than the laminar-turbulent transition number ($R_t \sim 2300$) in a wide variety of circumstances. For example, in a circular channel with diameter of 100 µm, a flow with water at a typical speed $10^{-2}$ m/sec has a Reynolds number of unity. Even increasing the flow velocity by a factor of 100 will not change the flow pattern in this simple fluidic geometry. Consequently, typical velocity profiles in
such geometries are parabolic in pressure-driven flows and nearly uniform for electro-
osmotic flows (EOF) [196]. The laminar nature of fluid flow in micro-scale fluidic
conduits enables accurate control of diffusive mixing and precise metering of multiple
streams of fluids and exploitation of the interfaces between them [197]. An extensively
reported high-density microfluidic chip with a complex network of microchannels is
illustrated in Figure 2.28, demonstrating the striking capability of fluid manipulation in
the microfluidics.

Figure 2.28 Optical image of a microfluidic device containing 2056 micro-channels. Different colored dyes used to visualize the structure of the fluidic network. (taken from T. Thorsen et al. [198])
Individual microfluidic devices have been developed using Si, glass, and other materials with associated methods of fabrication to meet the requirement of specialized applications. However, the integration of different functional components or modules into one complete system is still at an early stage of development. Micropumps are essential components for providing efficient fluid control and delivery in a LOC microfluidic system. The area of micropumping has become an active and interesting research area in microfluidics in both academia and industry. After the first micropump reported in the early 1990s [199] a large numbers of micropumps have been developed using different types of materials and the associated fabrication processing based on various actuation mechanisms [200-205]. However, the on-chip pumping remains a key challenge for the fluidic transportation in microsystems for clinical and environmental analysis which require prompt processing of samples. Therefore, the development of a chip- or package-level micropump with the capability of being easily integrated into suitable microfluidic systems is highly desirable.

Micropumps are generally divided into two categories: (1) reciprocating displacement pumps, which generate pressure by one or more moving surfaces of reciprocating membranes that compress and expand periodically on the working fluid; (2) continuous dynamic pumps, which continuously transform energy directly to the working fluid to increase its momentum or pressure [200,201]. The major structural features and characteristic performances of reported typical reciprocating displacement micropumps and continuous dynamic micropumps are summarized in Table 2.12 and Table 2.13 respectively.
Table 2.12   Characteristic features and performances of reciprocating displacement micropumps.

<table>
<thead>
<tr>
<th>Actuation mechanism</th>
<th>Valve</th>
<th>Construction materials</th>
<th>Size (cm³)</th>
<th>Driving voltage (V)</th>
<th>Driving frequency (Hz)</th>
<th>Max. flow rate (ml/min)</th>
<th>Max. Back-pressure (kPa)</th>
<th>Year &amp; Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piezoelectric</td>
<td>valveless</td>
<td>PMMA-glass + PZT</td>
<td>~0.8</td>
<td>120</td>
<td>400</td>
<td>0.22</td>
<td>9.2</td>
<td>2009 [206]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>valveless</td>
<td>Si-glass + PZT</td>
<td>~5</td>
<td>140</td>
<td>140</td>
<td>0.12</td>
<td>3.2</td>
<td>2007 [207]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>valveless</td>
<td>Si-glass + PZT</td>
<td>~1</td>
<td>385</td>
<td>130</td>
<td>0.32</td>
<td>0.29</td>
<td>2007 [208]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>valveless</td>
<td>PDMS-PMMA + Piezo-actuators</td>
<td>n/a</td>
<td>160</td>
<td>60</td>
<td>0.9</td>
<td>1.8</td>
<td>2007 [209]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>valveless</td>
<td>Si-glass + PZT</td>
<td>n/a</td>
<td>120</td>
<td>10</td>
<td>0.012</td>
<td>~ 4</td>
<td>2004 [210]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>nozzle-diffuser</td>
<td>Si + PZT</td>
<td>~0.12</td>
<td>190</td>
<td>2400</td>
<td>1.5</td>
<td>1.0</td>
<td>2002 [211]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>check-valve</td>
<td>Si + PZT</td>
<td>n/a</td>
<td>160</td>
<td>220</td>
<td>1.2</td>
<td>n/a</td>
<td>1998 [212]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>check-valve</td>
<td>Si + Thick-film PZT</td>
<td>n/a</td>
<td>600</td>
<td>200</td>
<td>0.12</td>
<td>1.8</td>
<td>1998 [213]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>nozzle-diffuser</td>
<td>Si-glass + Piezo-actuators</td>
<td>~0.26</td>
<td>200</td>
<td>3500</td>
<td>1.1</td>
<td>74</td>
<td>1997 [214]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>valveless</td>
<td>Si-Perspex + Piezo-bimorph</td>
<td>n/a</td>
<td>200</td>
<td>190</td>
<td>1.5</td>
<td>17</td>
<td>1996 [215]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>nozzle-diffuser</td>
<td>Brass + Piezo-actuators</td>
<td>~1.6</td>
<td>130</td>
<td>540</td>
<td>16</td>
<td>16.6</td>
<td>1995 [216]</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>valveless</td>
<td>Si-glass + PZT</td>
<td>~1.5</td>
<td>100</td>
<td>15</td>
<td>0.1</td>
<td>5.9</td>
<td>1990 [199]</td>
</tr>
<tr>
<td>Actuation mechanism</td>
<td>Valve</td>
<td>Construction materials</td>
<td>Size (cm³)</td>
<td>Driving voltage (V)</td>
<td>Driving frequency (Hz)</td>
<td>Max. flow rate (ml/min)</td>
<td>Max. Back-pressure (kPa)</td>
<td>Year &amp; Ref.</td>
</tr>
<tr>
<td>---------------------</td>
<td>----------------</td>
<td>-------------------------------</td>
<td>------------</td>
<td>---------------------</td>
<td>------------------------</td>
<td>--------------------------</td>
<td>----------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>valveless</td>
<td>Parylene + Cr/Au</td>
<td>n/a</td>
<td>110</td>
<td>20</td>
<td>$1.7 \times 10^{-6}$</td>
<td>1.6</td>
<td>2004 [217]</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>check-valve</td>
<td>Si</td>
<td>~0.01</td>
<td>200</td>
<td>300</td>
<td>0.16</td>
<td>29</td>
<td>1995 [218]</td>
</tr>
<tr>
<td>Thermo-pneumatic</td>
<td>valveless</td>
<td>PDMS-glass + Ti/Au</td>
<td>~0.5</td>
<td>9</td>
<td>1.2</td>
<td>0.02</td>
<td>0.49</td>
<td>2011 [219]</td>
</tr>
<tr>
<td>Thermo-pneumatic</td>
<td>valveless</td>
<td>PDMS-glass + Cr/Au</td>
<td>n/a</td>
<td>14</td>
<td>0.033</td>
<td>$0.82 \times 10^{-3}$</td>
<td>n/a</td>
<td>2006 [220]</td>
</tr>
<tr>
<td>Thermo-pneumatic</td>
<td>Nozzle-diffuser</td>
<td>Si-glass</td>
<td>~0.78</td>
<td>n/a</td>
<td>2</td>
<td>0.53</td>
<td>12</td>
<td>2001 [221]</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>check-valve</td>
<td>Polysulphone</td>
<td>n/a</td>
<td>15</td>
<td>5</td>
<td>0.044</td>
<td>3.8</td>
<td>1994 [222]</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>valveless</td>
<td>PDMS-glass + magnet</td>
<td>n/a</td>
<td>$I = 0.6$ A</td>
<td>200</td>
<td>7.2</td>
<td>n/a</td>
<td>2008 [223]</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>check-valve</td>
<td>Plastic + magnet</td>
<td>~1</td>
<td>5</td>
<td>50</td>
<td>2.1</td>
<td>10</td>
<td>1999 [224]</td>
</tr>
<tr>
<td>Pneumatic</td>
<td>check-valve</td>
<td>PDMS-glass</td>
<td>n/a</td>
<td>n/a</td>
<td>&lt; 1</td>
<td>$2.8 \times 10^{-3}$</td>
<td>30</td>
<td>2003 [225]</td>
</tr>
<tr>
<td>Pneumatic</td>
<td>valveless</td>
<td>PDMS-glass-Si</td>
<td>n/a</td>
<td>n/a</td>
<td>1</td>
<td>$6.0 \times 10^{-3}$</td>
<td>0.17</td>
<td>2003 [226]</td>
</tr>
<tr>
<td>Electrowetting</td>
<td>check-valve</td>
<td>Si-glass-SU8</td>
<td>n/a</td>
<td>2.3</td>
<td>25</td>
<td>0.07</td>
<td>0.7</td>
<td>2002 [227]</td>
</tr>
</tbody>
</table>
Table 2.13  Characteristic features and performances of continuous dynamic micropumps.

<table>
<thead>
<tr>
<th>Actuation mechanism</th>
<th>Construction materials</th>
<th>Size (cm$^3$)</th>
<th>Working Fluid</th>
<th>Driving voltage (V)</th>
<th>Max. flow rate (ml/min)</th>
<th>Max. Back-pressure (kPa)</th>
<th>Year &amp; Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electro-hydrodynamic</td>
<td>Ceramic</td>
<td>~0.64</td>
<td>3M HFE-7100</td>
<td>250</td>
<td>n/a</td>
<td>0.78</td>
<td>2002 [228]</td>
</tr>
<tr>
<td>Electro-hydrodynamic</td>
<td>Si-glass</td>
<td>~0.09</td>
<td>Ethyl alcohol</td>
<td>100</td>
<td>0.04</td>
<td>0.25</td>
<td>1998 [229]</td>
</tr>
<tr>
<td>Electroosmotic</td>
<td>Glass + packed-bed channels</td>
<td>n/a</td>
<td>Aqueous buffer</td>
<td>500</td>
<td>$0.22 \times 10^{-3}$</td>
<td>$10^3$</td>
<td>2010 [230]</td>
</tr>
<tr>
<td>Electroosmotic</td>
<td>Fused-silica based matrix</td>
<td>n/a</td>
<td>DI water</td>
<td>6000</td>
<td>$2.9 \times 10^{-3}$</td>
<td>300</td>
<td>2006 [231]</td>
</tr>
<tr>
<td>Electroosmotic</td>
<td>Soda-lime glass</td>
<td>~9</td>
<td>Water</td>
<td>1000</td>
<td>0.015</td>
<td>33</td>
<td>2002 [232]</td>
</tr>
<tr>
<td>Electroosmotic</td>
<td>Glass + packed-bed channels</td>
<td>~0.085</td>
<td>Water</td>
<td>2000</td>
<td>$3.6 \times 10^{-3}$</td>
<td>2000</td>
<td>2001 [233]</td>
</tr>
<tr>
<td>Electroosmotic</td>
<td>Glass</td>
<td>n/a</td>
<td>0.35mM NH$_4$OH</td>
<td>500</td>
<td>3.0</td>
<td>150</td>
<td>2000 [234]</td>
</tr>
<tr>
<td>Electroosmotic</td>
<td>Glass + packed-bed channels</td>
<td>~0.12</td>
<td>Aqueous-sodium solution</td>
<td>1500</td>
<td>$0.04 \times 10^{-3}$</td>
<td>4000</td>
<td>1998 [235]</td>
</tr>
<tr>
<td>Electrochemical</td>
<td>PDMS-glass + Pt/Teflon</td>
<td>n/a</td>
<td>Whole blood</td>
<td>2.5</td>
<td>$0.09 \times 10^{-3}$</td>
<td>11</td>
<td>2009 [236]</td>
</tr>
<tr>
<td>Magneto-hydrodynamic</td>
<td>PDMS + Au</td>
<td>~0.04</td>
<td>PBS solution</td>
<td>3.6</td>
<td>$12.9 \times 10^{-3}$</td>
<td>n/a</td>
<td>2011 [237]</td>
</tr>
<tr>
<td>Magneto-hydrodynamic</td>
<td>Si + magnet</td>
<td>n/a</td>
<td>Sea water</td>
<td>n/a</td>
<td>0.063</td>
<td>0.17</td>
<td>2000 [238]</td>
</tr>
<tr>
<td>Magneto-hydrodynamic</td>
<td>Si-glass + magnet</td>
<td>n/a</td>
<td>1M NaCl solution</td>
<td>n/a</td>
<td>0.018</td>
<td>0</td>
<td>2000 [239]</td>
</tr>
</tbody>
</table>
Nowadays, continuous dynamic pumps are the most desirable pumps to be fabricated directly on the microfluidic systems in a LOC format due to their small size, simple structure, and absence of moving mechanical parts. However, this type of micropumps has some intrinsic disadvantages, such as the need of high driving voltage in electroosmotic micropumps [230], specific requirements for the properties of fluid samples in electrohydrodynamic micropumps [240], and the interference of applied electric field on the pumping liquid in electrochemical micropumps [236]. Additionally, the typical flow rate for continuous dynamic pumps is in the range of pl/min to nl/min. In applications requiring rapid chemical analysis and synthesis, the high performance reciprocating pumps in small package size has attracted particular attention for pumping biological fluids on the order of several µl/min to several ml/min [202].

2.5.2 Peristaltic micropump

Peristaltic micropumps, as one of the earliest micropumps developed, have been studied for twenty years and still gain significant attention [241-245]. A variety of peristaltic micropumps using novel structures and advanced fabrication methods have been made to satisfy the pumping requirement in different applications. The pumping principle of most developed peristaltic micropumps is demonstrated schematically in Figure 2.29. Adapting directly from the macroscopic concept, a net flow across the micropump is generated by the peristaltic motion of multiple microchambers aligned in series. Most of the realized peristaltic micropumps have three microchambers with actuating membranes. Check valves are not required in peristaltic micropumps for flow rectification. Additionally, there is no need to construct specific fluid rectifiers (e.g.
nozzle/diffuser) used to manipulate fluids in other valveless micropumps, which greatly save the manufacturing cost and time.

Figure 2.29 Working principle of a peristaltic micropump with three chambers. (a) signal scheme and (b) pumping stages. (taken from N.T. Nguyen et al. [246])

In contrast to check-valve micropumps, peristaltic pumps eliminate the risk of failure due to the fatigue of check valves and reduce the risk of channel clogging and damage of biological particles in the pumping fluids. Both the reliability and the expectant life-time have greatly improved because of the removal of the unnecessary
mechanical parts. Moreover, the bidirectional flow in peristaltic pumps can be easily achieved by changing the actuation sequence of driving units. Compared with continuous dynamic micropumps, peristaltic pumps provide a wide range of flow rate without complex electrode arrangement or requirements for the conductivity of pumping fluid. Peristaltic micropumps have the potential to be used in a wide variety of microfluidic applications, such as bioengineering, pharmaceutical, and food industries. However, the leakage is a serious drawback for peristaltic micropumps. Even a small pressure difference between the outlet and the inlet will cause a back flow when the pump is not actuated. This valveless design also leads to a lower maximum backpressure compared to the check-valve pumps. A common optimization strategy for peristaltic micropumps is to increase the stroke volume $\Delta V$ (the volume change of pump chamber caused by membrane displacement) and the compression ratio $\varepsilon$ (the ratio of stroke volume to chamber volume without actuation). Several novel designs were investigated to prohibit the back flow inside the peristaltic micropumps. Cao et al. [247] reported the design of a piezoelectric peristaltic micropump with normally-closed microchannels when no power is applied. Only the analytical and experimental results on the membrane deflection were introduced and no pumping performance was presented. Trenkle et al. [241] demonstrated a functional peristaltic micropump with the same normally-closed mechanism most recently. The pump actuated in a peristaltic manner shows a maximum flow rate of 0.12 ml/min with an extraordinary maximum backpressure expected to be 180 kPa. However, the overall size of this pump is large (~20 cm$^3$), which limits its applications in which the small size of the pump is a critical requirement. More
importantly, the size of this micropump and the associated fabrication processing are definitely not compatible with on-chip integration.

2.5.3 Piezoelectric actuation

A wide range of materials (e.g. Si, glass, and PDMS) have been used for the design and fabrication of peristaltic micropumps based on various driving mechanisms including piezoelectric [199,206-210,248], thermopneumatic [220,249], electrostatic [217,250], and other actuation principles [251-253]. Figure 2.30 depicts several design examples of peristaltic micropumps based on various actuation mechanisms.

Figure 2.30  Design examples of peristaltic micropumps. (a) piezoelectric. Three piezoelectric discs glued on the pump chambers etched in silicon; (b) electrostatic. Polysilicon electrodes embedded in a silicon nitride pump body; and (c) thermopneumatic. Three heaters located inside the pressure chambers to achieve deflection. (taken from N.T. Nguyen et al. [254])
Compared with other actuation principles developed for the peristaltic micropump, piezoelectric actuation offers reliable pumping with high actuation strength and good energy efficiency. The flow rate of piezoelectrically actuated peristaltic micropumps is typically in the range from several µl/min to several hundred µl/min by virtue of the comparatively large stroke volume and a fast mechanical response which allows the pumps to be operated at high frequency. Moreover, micropumps with piezoelectric actuation have the potential to be integrated into LOC microfluidic devices at the package level [255].

Piezoelectric components are commonly deposited or mounted on pump membranes for generating necessary pressure difference inside the microchambers for the pumping [256-258]. PZT ceramics are the most widely applied piezoelectric materials for design and fabrication of micropumps due to their effective and reliable electro-mechanical response. Thin-film PZT can be deposited on different substrate materials for developing microsensors and other microdevices but it is rarely used in micropump applications since the total displacement generated by the thin-film drive is normally not large enough for the pumping purpose. Most of current developed piezoelectric micropumps, incorporating bulk PZT ceramics as the actuators, are fabricated using MEMS processing techniques often requiring additional hybrid bonding methods. The piezoelectric actuator is mounted on a Si or glass MEMS body using adhesive bonding which is critical for the reliability and yield of this type of actuator and not compatible with integrated fabrication [204]. Additionally, the fabrication of silicon/glass based reciprocating membrane micropumps is usually complex which makes it expensive and time consuming. Thick-film PZT, as the alternative to thin-film and bulk materials, has
been screen printed on Si substrates for micropump fabrication [138]. However, there are two major issues associated with this fabrication process, inter-diffusion and/or reaction between Si substrates and PZT thick films as well as the defects induced by significant stresses generated in sintering. Other thick-film preparation methods (e.g. dip/spray coating and polymerization), PZT ceramics with various sintering aids, and substrate materials (e.g. glass and polymer) have been investigated to solve the processing difficulties for the micropump manufacturing [116]. Therefore, a practical optimization of piezoelectric micropumps needs not only the high performance piezoelectric actuators but also the compatible fabrication technique.

2.5.4 Integration of micropumps in microfluidic systems

Many discrete microfluidic devices are under development ranging from single components such as micropumps, microvalves, and flow sensors, to complex microfluidic systems for chemical analysis and biomedical engineering, consisting of all necessary functional elements integrated on a single substrate or as sandwiched modules. Schabmueller et al. [259] reported the design and fabrication of a microfluidic “circuitboard” consisting micropumps, flow sensors, and micromixers mounted on a single Si-glass substrate. Wet etching and anodic bonding techniques were used to fabricate the integrated system. However, the performance of this developed microfluidic system was not introduced. Another example of integrated microfluidic system developed by Lee et al. [260] incorporates an electroosmotic pump, a micromixer, a chemical reaction chamber, and an on-chip temperature control system. The various modules were integrated on glass substrates and poly(dimethylsiloxane) (PDMS) materials. The experimental results showed a more effective polymerase chemical reaction (PCR) using
this microfluidic system compared to the results of using other conventional approaches. The schematic illustrations of these two integrated microfluidic systems are shown in Figure 2.31.

![Microfluidic System Diagrams](image)

**Figure 2.31** Schematic representations of (a) Si-glass based microfluidic system (taken from C.G.J. Schabmueller et al. [259]); and (b) glass-PDMS based microfluidic chip. (taken from C. Lee et al. [260])

Effective and precise supply and control of liquid are among most important unit operations for microfluidic systems, which need the integration of micropumps at package- or chip-level. Intensive research efforts are focused on this topic and a wide variety of novel micropumps have been developed in order to provide on-chip fluid
supply and control. A power-free valveless micropump based on the capillary and/or evaporation effects was developed for providing a steady flow in μl/min range for the flow injection analysis system [261]. A cellular micropump without check valves powered by a cultured cardiomyocyte sheet was demonstrated to produce a flow in nl/min range [262]. Yokokawa et al. developed an on-chip syringe pump for picoliter-scale liquid manipulation using electrostatically controlled actuators [263].

LTCC technology can combine materials that have different characteristics; it is therefore possible to integrate and build different types of components into one ceramic-based system [264,265]. A wide range of LTCC microfluidic devices incorporated with functional passive and active elements have been successfully fabricated and reported, such as (1) incorporation of hydrogel nanocomposites as valves into LTCC microfluidic devices [266]; (2) integration of optic fibers in a LTCC chemical analysis microsystem [78]; and (3) a magnetohydrodynamic micropump fabricated with LTCC tapes [68]. Recently, there is an increasing interest in the development of highly integrated LTCC-based MEMS incorporating active piezoelectric elements in microfluidic applications, for example, a piezoelectric unimorph valve assembled on a multilayer LTCC fluidic chip [267] and a piezoelectric cantilever controlled throttle integrated into a LTCC substrate to provide the flow manipulation [268]. However, piezoelectric actuators are usually attached on the fired LTCC body during post-firing and assembly process. The realization of co-fired piezoelectric elements with required electronics and fluidic components into one LTCC module can offer additional capabilities in the fabrication of microfluidic devices.
The unique approach of the current research is co-firing LTCC substrates with PZT-based actuators according to a low temperature sinterable high performance piezoelectric composition [269]. Piezoelectric and dielectric properties are characterized on the 1 wt% LiBiO₂ and 1 wt% CuO added 0.98PZT-0.02SKN ceramics sintered at 900°C for 1 h. Subsequently, an investigation on sintering behavior and properties of co-fired LTCC/PZT-SKN multilayer ceramics is performed to develop an optimized co-firing profile which can be used to construct hybrid multilayer microdevices [270]. The focus of following study is primarily on the fabrication and characterization of a LTCC/PZT-SKN multilayer piezoelectric peristaltic micropump. LTCC thick-film technology is applied to build multilayer micropumps, which allows a rapid and inexpensive fabrication. Further optimization of pumping performance has been studied based on the experimental and simulation results by using different microchannel geometries. The developed micropump demonstrates the possibility to be integrated into LTCC-based lab-on-a-chip microfluidic systems at the package-level, providing efficient on-chip fluid control and transport for the practical applications in chemical analysis and synthesis, biological sensing, and environmental monitoring.

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Chapter 3. Low temperature sintering and properties of Pb(Zr_{0.53}, Ti_{0.47})O_3-Sr(K_{0.25}, Nb_{0.75})O_3 (PZT-SKN) ceramics with LiBiO_2 and CuO addition

3.1 Introduction

The Pb(Zr_{0.53}, Ti_{0.47})O_3-Sr(K_{0.25}, Nb_{0.75})O_3 (PZT-SKN) system, first reported by Helke et al. [271], is considered to be a promising material for multilayer piezoelectric actuator applications. Reducing the conventional sintering temperature (~1250°C) of PZT-SKN ceramics would not only offer the advantage of a reduction in energy consumption and decrease in lead volatility but also provide the possibility of co-firing with low-melting-point electrodes and low temperature co-fired ceramic (LTCC) materials to form novel multilayered devices. As introduced in chapter 2, liquid-phase sintering is a common technique for lowering the sintering temperature by incorporating suitable additives into the original solid solution systems [272-275].

The present chapter provides a detailed description of the experimental procedures and results for preparation and characterization of low fire PZT-SKN ceramics. In order to tailor the sintering profile of PZT-SKN ceramics compatible with LTCC materials, liquid-phase sintering additives LiBiO_2 and CuO, both extensively reported as effective fluxes to lower sintering temperature for PZT-based ceramics [276-285], were used for the purpose of accelerating densification by the liquid phase generated at low temperature. Specifically, the low temperature sintering of 6 wt%
LiBiO$_2$ and 1 wt% LiBiO$_2$ + 1 wt% CuO added 0.98PZT-0.02SKN piezoelectric ceramics was studied. The microstructure, dielectric, and piezoelectric properties of flux-sintered ceramics were examined and compared with materials conventionally sintered at 1250°C to understand the structure-property relations in this flux-ceramic system.

3. 2 Experimental methods and materials preparation

The 0.98PZT-0.02SKN powder was prepared by the conventional solid-state route according to the formula Pb$_{1-3x/2}$Sr$_x$K$_{x/4}$[(Zr$_{0.53}$, Ti$_{0.47}$)$_{1-3x/4}$Nb$_{3x/4}$]O$_3$ [31]. The processing flowchart is illustrated in Figure 3.1. High-purity metal oxides and carbonates PbCO$_3$ (Halstab, Hammond, ID), ZrO$_2$ (Alfa Aesar, Ward Hill, MA), TiO$_2$ (Ishihara, Tokyo, Japan), SrCO$_3$ (Sigma Aldrich, St. Louis, MO), K$_2$CO$_3$ (Sigma Aldrich, St. Louis, MO), and Nb$_2$O$_5$ (H.C. Starck, Berlin, Germany) were stoichiometrically mixed in an aqueous solution with organic dispersant (Darvan 821®, R.T. Vanderbilt Company Inc., Norwalk, CT). Suspensions were then ball milled with 5 mm spherical highly wear-resistant Y-stabilized zirconia (YTOH, Grove City, PA) on a vibratory mill (ML16-5, Sweco, Florence, KY) for 24 h. After drying, the powder was sieved and calcined at 850°C for 4 h. A second calcination step with intermediate milling cycle was performed to achieve better homogeneity and purity of the final powders.

The fluxes were prepared as either single phase compounds or mixtures. These powders were added to the calcined PZT-SKN and vibratory milled for a further 12 h, then dried and sieved. The resulting powders were mixed with 2-3 wt% organic binder (Acrylic copolymer, R.E. Mistler Inc., Yardley, PA) in acetone, and uniaxially pressed into circular pellets with ~13 mm diameter under 200 MPa using a rigid steel die.
Following the binder burnout at 450°C for 2 h, green pellets were sintered in air atmosphere at different temperatures between 750°C and 1000°C for 1-2 h without source powder. For comparison, the unfluxed PZT-SKN samples were conventionally sintered at 1250°C for 2 h with lead source powder.

Figure 3.1 Flowchart for solid-state synthesis of fluxed PZT-SKN.

The microstructure and phase purity of sintered ceramics was determined by scanning electron microscope (SEM: S-3200, Hitachi, Tokyo, Japan) and X-ray
diffraction (XRD: Model-D500, Siemens, Munich, Germany. The bulk density of sintered samples was measured using the Archimedes method.

Sintered pellets were polished parallel to a thickness of approximately 0.5 mm and electroded on both surfaces with a conductive Ag electrode paste (DuPont 6160, Research Triangle Park, NC) fired at 850°C for 10 min, for measuring electrical characteristics. Samples were poled in silicon oil at 100°C under a DC field of 30 kV/cm for 15 min. Dielectric properties were obtained by the measurement of the capacitance and loss at several frequencies as a function of temperature performed in the range of 20°-500°C using a precision LCR meter (Agilent E4980A, Agilent, Santa Clara, CA) in combination with a temperature-controlled tube furnace (Model-F21130, Barnstead, Waltham, MA) and automated data recording by using LabVIEW™ software. The planar coupling coefficient $k_p$ was calculated from electromechanical resonance, by measuring resonance and antiresonance frequencies using an impedance analyzer (Model-HP4194A, Agilent, Santa Clara, CA) on the basis of the IEEE standard [286]. Low field $d_{33}$ piezoelectric coefficients were measured using a Berlincourt-style $d_{33}$ meter (YE2730A, APC International Ltd., Mackeyville, PA). Polarization and strain hysteresis loops were measured using a custom Sawyer-Tower circuit with a linear variable differential transducer coupled to a high-voltage amplifier (Model-610B, TReK, Medina, NY). The high field $d_{33}$ piezoelectric coefficients were calculated as the ratio of strain to electric field at 30 kV/cm on the unipolar loop.
3.3 Results and discussion

3.3.1 Effectiveness of fluxes

LTCC materials are typically sintered at temperatures in the range of 850°-900°C for less than 1 h. For the purpose of co-firing PZT-SKN ceramics with LTCC, the fluxes need to have a melting point lower than the desired sintering temperature 900°C and the ability to facilitate the densification of fluxed ceramics in a short soaking time. The densities obtained for PZT-SKN ceramics with different flux additions sintered at 900°C for 1 h are indicated in Table 3.1. Only 6 wt% LiBiO$_2$ and 1 wt% LiBiO$_2$ + 1 wt% CuO fluxed ceramics were shown to sinter to high density (> 95% theoretical density) under the given sintering condition.

<table>
<thead>
<tr>
<th>Flux</th>
<th>Melting point (°C)</th>
<th>Addition (wt%)</th>
<th>Density achieved at 900°C (relative to theoretical density)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBiO$_2$</td>
<td>~ 700</td>
<td>0.5</td>
<td>66.2%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>74.8%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>89.0%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>95.1%</td>
</tr>
<tr>
<td>LiBiO$_2$ + CuO</td>
<td>~ 600*</td>
<td>1 + 1</td>
<td>97.6%</td>
</tr>
</tbody>
</table>

* Melting occurs at ~600°C when LiBiO$_2$ and CuO both exist [287].

Based on the given results in Table 3.1, 6 wt% LiBiO$_2$ and 1 wt% LiBiO$_2$ + 1 wt% CuO were chosen as the low-melting-point fluxes to investigate the low temperature
sintering and properties of 0.98PZT-0.02SKN ceramics. Detailed information about the
determination of the amount and the type of fluxes used in this study is introduced in
Appendix.

3.3.2 Phase and microstructure

Phase development of unfluxed 0.98PZT-0.02SKN powders after calcinations and
sintering was determined using X-ray diffraction scans. Figure 3.2 shows the XRD
patterns for the raw mixture, PZT-SKN powders after first and second calcinations, and
powder from crushed pellets after sintering at 1250°C for 2 h. An intermediate secondary
phase was observed in the diffraction pattern of powders after the first calcination. Single
phase high-purity perovskite structure was confirmed after the second calcination step
with further reaction between the initial chemicals. The splitting of peaks for (100),
(200), (201), and (211) planes was clearly observed in the XRD pattern of sintered
ceramics. It was found that the conventionally sintered PZT-SKN ceramics with highly
pure perovskite structure.

XRD patterns of 6 wt% LiBiO₂ and 1 wt% LiBiO₂ + 1 wt% CuO added 0.98PZT-
0.02SKN ceramics sintered at 900°C and the unfluxed specimens sintered at 1250°C are
shown in Figure 3.3. A small diffraction peak near 28° (2θ), indicating a small quantity of
secondary phase, existed in ceramics with 6 wt% LiBiO₂ added. The intensity of the
secondary phase peak was lower in samples containing the 1 wt% LiBiO₂ + 1 wt% CuO
flux. Unfluxed specimens fired at 1250°C exhibited phase-pure perovskite structure with
no evidence of secondary phase formation. The appearance of secondary phase in the
flux-sintered ceramics could be explained by the formation of a Bi₂Pb₂O₇ pyrochlore phase during the low temperature sintering [288].

Figure 3.2  X-ray diffraction patterns for unfluxed 0.98PZT-0.02SKN ceramics (a) raw material mixture, (b) after 1st calcination, (c) after 2nd calcination, and (d) sintered at 1250°C for 2 h.
Figure 3.3  X-ray diffraction patterns for 0.98PZT-0.02SKN ceramics sintered at 900°C with (a) 6 wt% LiBiO₂, (b) 1 wt% LiBiO₂ + 1 wt% CuO addition, and (c) the unfluxed specimen sintered at 1250°C.

Fracture surface SEM microstructure of PZT-SKN ceramics sintered with (a) 6 wt% LiBiO₂ addition at 900°C for 1 h, (b) and (c) 1 wt% LiBiO₂ + 1 wt% CuO addition at 900°C for 1 or 2 h, and (d) the unfluxed specimens sintered at 1250°C for 2 h are shown in Figure 3.4. The grain size of samples with 6 wt% LiBiO₂ addition sintered at 900°C for 1 h was estimated to be around 1.2 µm, increasing to 1.8 µm with 1 wt% LiBiO₂ + 1 wt% CuO addition sintered for the same time. The grain size was unchanged for 1 wt% LiBiO₂ + 1 wt% CuO added samples sintered at 900°C when sintering time increased from 1 to 2 h. As a comparison the grain size of the unfluxed PZT-SKN ceramics sintered at 1250°C was found to be around 5.6 µm.
Figure 3.4 Scanning electron microscopic micrographs of 0.98PZT-0.02SKN ceramics sintered at 900°C for 1 h with (a) 6 wt% LiBiO₂ and (b) 1 wt% LiBiO₂ + 1 wt% CuO addition, (c) 1 wt% LiBiO₂ + 1 wt% CuO-fluxed specimen sintered at 900°C for 2 h, and (d) unfluxed specimen sintered at 1250°C for 2 h.
Figure 3.4  (continued) Scanning electron microscopic micrographs of 0.98PZT-0.02SKN ceramics sintered at 900°C for 1 h with (a) 6 wt% LiBiO₂ and (b) 1 wt% LiBiO₂ + 1 wt% CuO addition, (c) 1 wt% LiBiO₂ + 1 wt% CuO-fluxed specimen sintered at 900°C for 2 h, and (d) unfluxed specimen sintered at 1250°C for 2 h.
The bulk density of the 0.98PZT-0.02SKN ceramics sintered at different temperatures with various fluxes is given in Figure 3.5. The density was found to be low (<7.0 g/cm³) for both the fluxed composition sintered at 750°C. Density gradually increased to a maximum value of 7.75 g/cm³ (~97.6% of theoretical density) for 1 wt% LiBiO₂ + 1 wt% CuO added ceramics sintered at 900°C, and 7.65 g/cm³ (~96.3% of theoretical density) for 6 wt% LiBiO₂ added ceramics sintered at 950°C. However, the density of sintered materials tended to decrease slightly after maximum value indicating over firing.

It was found that 0.98PZT-0.02SKN ceramics without fluxes could not be fully densified at sintering temperatures below 1250°C. The inset in Figure 3.5 shows the variation of measured density for unfluxed specimens with the maximum density of 7.80 g/cm³ (~98.2% of theoretical density) when sintered at 1250°C for 2 h with lead source powder. These results confirm that the high-density 0.98PZT-0.02SKN ceramics can be obtained with either 6 wt% LiBiO₂ or 1 wt% LiBiO₂ + 1 wt% CuO addition, yielding improved the sinterability and lowering the sintering temperature by more than 300°C.
The addition of LiBiO$_2$ and CuO is believed to lower the sintering temperature of PZT-SKN ceramics due to the formation of a liquid phase. The additive LiBiO$_2$ promotes the sinterability of PZT-SKN ceramics by melting at about 700°C [279]. The additive CuO can react with PbO to form the liquid phase of Cu$_2$O-PbO at 680°C [289]. The temperature of liquid formation can be further lowered to around 600°C by adding both CuO and LiBiO$_2$ into PZT-SKN ceramics. SEM images also show evidence of liquid phase formation at grain boundaries and triple junctions, as demonstrated in Figure 3.6. However, neither SEM/EDS nor electron probe for microanalysis (EPMA) was able to quantify the localization/distribution of flux in the grain boundary regions.
3.3.3 Dielectric and piezoelectric properties

The variation in the dielectric constant $\varepsilon_r$ and loss tangent $\tan\delta$ of the 0.98PZT-0.02SKN ceramics conventionally sintered at 1250°C and flux sintered at 900°C as a function of temperature are presented in Figures 3.7(a) and (b), respectively. A lower maximum permittivity and broader permittivity and loss peaks were observed for the fluxed ceramics, compared with the conventionally sintered materials. Additionally, the 1 wt% LiBiO$_2$ + 1 wt% CuO added ceramics exhibited a larger and sharper dielectric peak than the 6 wt% LiBiO$_2$ fluxed ceramics. The Curie temperature $T_c$ for ceramics with 1 wt% LiBiO$_2$ + 1 wt% CuO addition was observed at around 351°C, only a few degrees lower than that for the unfluxed specimens (~357°C), while the $T_c$ shifted to the low
temperature side (~302°C) for the ceramics with 6 wt% LiBiO₂ addition. The \( T_c \) is particularly sensitive to small compositional fluctuations in ferroelectric materials, with reduced \( T_c \) previously observed in PZT with CuO addition [290]. The small shift of the \( T_c \) for the specimens sintered with 1 wt% LiBiO₂ + 1 wt% CuO addition suggests minimal reaction between the additives and the PZT-SKN matrix. For 6 wt% LiBiO₂ added ceramics, the substantial decrease in \( T_c \) suggests significant diffusion and incorporation of lithium and bismuth into the PZT-SKN matrix.

Figures 3.8(a) and (b) compares the polarization-electric field (\( P-E \)) hysteresis loops and unipolar strain-field loops of 0.98PZT-0.02SKN ceramics conventionally sintered at 1250°C to those of flux sintered ceramics at 900°C. The \( P-E \) hysteresis loops indicate that the remnant polarization \( P_r \) decreased from 0.34 C/m² in unfluxed samples to 0.29 and 0.27 C/m² for 6 wt% LiBiO₂ and 1 wt% LiBiO₂ + 1 wt% CuO added ceramics, respectively. Also, the coercive field \( E_c \) decreased slightly from 15.6 to 14.5 kV/cm for both flux-sintered ceramics. Unipolar strain loops taken on poled samples confirm a high strain for unfluxed PZT-SKN ceramics sintered at 1250°C yielding a high field \( d_{33} \) piezoelectric coefficient of 680 pm/V. In fluxed samples sintered at 900°C, the lower unipolar strain loops indicate a reduction of high field \( d_{33} \) piezoelectric coefficient (415 pm/V for 1 wt% LiBiO₂ + 1 wt% CuO addition and 324 pm/V for 6 wt% LiBiO₂ addition) compared to the conventionally sintered samples.
Figure 3.7 Temperature dependence of (a) dielectric constant and (b) tangent loss of 0.98PZT-0.02SKN ceramics conventionally sintered at 1250°C and flux-sintered at 900°C.
Figure 3.8 (a) $P - E$ hysteresis loops and (b) unipolar loops of 0.98PZT-0.02SKN ceramics conventionally sintered at 1250°C and flux-sintered at 900°C.
The high field $d_{33}$ piezoelectric coefficient and planar coupling factor $k_p$ of 0.98PZT-0.02SKN ceramics with flux additions as a function of sintering temperature are shown in Figure 3.9.

![Figure 3.9](image)

Figure 3.9  High field $d_{33}$ piezoelectric coefficient and planar-coupling factor $k_p$ of 0.98PZT-0.02SKN ceramics with flux additions as a function of sintering temperature.

The values of the planar coupling factor $k_p$ for both fluxed ceramics increase with increasing sintering temperature. The $k_p$ value for ceramics with 1 wt% LiBiO$_2$ + 1 wt% CuO addition is slightly higher than for 6 wt% LiBiO$_2$ added ceramics at temperature above 900°C. The high field $d_{33}$ piezoelectric coefficient reaches the highest value of 415 and 360 pm/V when the sintering temperature increases to 900°C for 1 wt% LiBiO$_2$ + 1
wt% CuO and 950°C for 6 wt% LiBiO₂ added ceramics, respectively. The $d_{33}$ value for 1 wt% LiBiO₂ + 1 wt% CuO added ceramics is consistently higher than that for 6 wt% LiBiO₂ added ceramics for all the examined sintering temperatures. The significant reduction in the $d_{33}$ piezoelectric coefficient in the fluxed PZT-SKN samples compared to high-sintered conventional PZT-SKN is largely attributed to suppressed extrinsic contributions, associated with the significantly reduced grain size in the low temperature sintered ceramics [113]. The strong interaction between the grain boundaries and the domain walls decreases the domain wall mobility which results in the reduction of dielectric and piezoelectric properties, such as dielectric constant $\varepsilon_r$ and piezoelectric coefficients $d_{33}$. The detailed functional properties of flux-sintered ceramics fired at different temperatures and conventionally sintered specimen are listed in Table 3.2. The 1 wt% LiBiO₂ + 1 wt% CuO added ceramics sintered at 900°C for 1 h exhibit favorable overall properties with high field $d_{33}$ piezoelectric coefficient of 415 pm/V, Curie temperature $T_c$ of around 351°C, dielectric constant $\varepsilon_r$ of 1235, and planar coupling factor $k_p$ of 0.54, which show the possibility to co-fire with LTCC materials.
Table 3.2  Main properties of 0.98PZT-0.02SKN ceramics with and without flux additions sintered at different temperatures.

<table>
<thead>
<tr>
<th>Flux</th>
<th>Sintering temperature (°C)</th>
<th>Density (g/cm³)</th>
<th>$\varepsilon_r$</th>
<th>tanδ</th>
<th>$P_r$ (C/m²)</th>
<th>$E_c$ (kV/cm)</th>
<th>$k_p$</th>
<th>$d_{33}^{high}$ (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6wt% LiBiO₂</td>
<td>850</td>
<td>7.42</td>
<td>1130</td>
<td>0.035</td>
<td>0.20</td>
<td>14.5</td>
<td>0.42</td>
<td>306</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>7.53</td>
<td>1116</td>
<td>0.033</td>
<td>0.29</td>
<td>14.5</td>
<td>0.49</td>
<td>324</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>7.66</td>
<td>1222</td>
<td>0.030</td>
<td>0.31</td>
<td>14.5</td>
<td>0.50</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>7.62</td>
<td>1155</td>
<td>0.040</td>
<td>0.32</td>
<td>15.2</td>
<td>0.53</td>
<td>334</td>
</tr>
<tr>
<td>1 wt% LiBiO₂ + 1 wt% CuO</td>
<td>850</td>
<td>7.20</td>
<td>1104</td>
<td>0.030</td>
<td>0.23</td>
<td>14.5</td>
<td>0.36</td>
<td>337</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>7.75</td>
<td>1235</td>
<td>0.018</td>
<td>0.27</td>
<td>14.5</td>
<td>0.54</td>
<td>415</td>
</tr>
<tr>
<td></td>
<td>950</td>
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</tr>
<tr>
<td></td>
<td>1000</td>
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<td>1239</td>
<td>0.020</td>
<td>0.30</td>
<td>13.2</td>
<td>0.58</td>
<td>402</td>
</tr>
<tr>
<td>unfluxed</td>
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<td>7.80</td>
<td>1395</td>
<td>0.015</td>
<td>0.34</td>
<td>15.6</td>
<td>0.58</td>
<td>680</td>
</tr>
</tbody>
</table>

3.3.4 Compatibility for integration with LTCC

The sintering temperature profile for LTCC materials must be taken into consideration in order to incorporate LTCC processing with the developed PZT-SKN based piezoelectric ceramics. LTCC tapes are glass-ceramic composite materials allowing sintering at the low temperature, typically in the range of 850°-900°C for less than 1 h. The densification is achieved by the viscous flow of the low-melting-point glass phase. However, significant deformations can occur under the elevated sintering temperatures and prolonged sintering time [36]. The processing conditions and properties of other reported low temperature sintered PZT-based ceramics are summarized in Table 3.3 and compared with those of 1 wt% LiBiO₂ + 1 wt% CuO added 0.98PZT-0.02SKN ceramics developed in the current work. When sintered at temperature of no more than 900°C, only the present fluxed PZT-SKN ceramics can be densified at a relatively short
soaking time, even though the piezoelectric coefficient $d_{33}$ is not as high as those of other PZT-based ceramics sintered for more than 4 h. As shown in Table 3.2, there are several other PZT-based systems which can be sintered at temperature in the range of 900°-950°C for less than 1 h, however, either the low $d_{33}$ values (~200 pm/V) [146,282] or the high sintering temperature (950°C) [144] limits their utilization in the fabrication of multilayer piezoelectric actuators with LTCC materials. Moreover, the $T_c$ of developed low fired PZT-SKN is above 350°C, higher than most of the reported fluxed PZT-based ceramics. This high $T_c$ is required for applications covering a broad temperature range. Based on the properties mentioned above and comparison with other low fire piezoelectric ceramics, 0.98PZT-0.02SKN ceramics with 1 wt% LiBiO$_2$ + 1 wt% CuO addition represent an attractive high performance piezoelectric material for applications requiring low temperature and short hold processing conditions.
Table 3.3  Comparison of functional properties of 1 wt% LiBiO$_2$ + 1 wt% CuO fluxed 0.98PZT-0.02SKN and other low fire PZT-based ceramics.

<table>
<thead>
<tr>
<th>PZT ceramics</th>
<th>Additives</th>
<th>Sintering Temp. ($^\circ$C)</th>
<th>Sintering Time (h)</th>
<th>$d_{33}$ (pm/V)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-PMN</td>
<td>LiBiO$_2$</td>
<td>800</td>
<td>12</td>
<td>504</td>
<td>225</td>
<td>[280]</td>
</tr>
<tr>
<td>PZT-SKN</td>
<td>LiBiO$_2$ + CuO</td>
<td>900</td>
<td>1</td>
<td>415</td>
<td>351</td>
<td>----</td>
</tr>
<tr>
<td>PZT-PNN-PMN</td>
<td>Fe$_2$O$_3$</td>
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<td>2</td>
<td>377</td>
<td>330</td>
<td>[291]</td>
</tr>
<tr>
<td>PZT-PNN-PMW</td>
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<td>2</td>
<td>517</td>
<td>317</td>
<td>[292]</td>
</tr>
<tr>
<td>PZT-PMS-PZN</td>
<td>CuO</td>
<td>900</td>
<td>4</td>
<td>306</td>
<td>290</td>
<td>[281]</td>
</tr>
<tr>
<td>PZT-SKN</td>
<td>Li$_2$CO$_3$</td>
<td>900</td>
<td>6</td>
<td>640</td>
<td>347</td>
<td>[157]</td>
</tr>
<tr>
<td>PZT-PZN-PMN</td>
<td>Ba(W$<em>{0.5}$Cu$</em>{0.5}$)O$_3$</td>
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<td>4</td>
<td>351</td>
<td>320</td>
<td>[293]</td>
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<tr>
<td>PZ-T-PNN</td>
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<td>4</td>
<td>600</td>
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<tr>
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<td>950</td>
<td>1</td>
<td>419</td>
<td>332</td>
<td>[144]</td>
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<td>2</td>
<td>340</td>
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<td>[276]</td>
</tr>
<tr>
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<td>ZnO + CuO</td>
<td>950</td>
<td>2</td>
<td>351</td>
<td>280</td>
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<td>PZT-PMN-PFW</td>
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<td>[297]</td>
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<td>4</td>
<td>309</td>
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<td>[275]</td>
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<td>1150</td>
<td>4</td>
<td>345</td>
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<td>[274]</td>
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</table>
3.4 Conclusions

Piezoelectric ceramics based Pb(Zr$_{0.53}$, Ti$_{0.47}$)O$_3$-Sr(K$_{0.25}$, Nb$_{0.75}$)O$_3$ (PZT-SKN) with LiBiO$_2$ and CuO addition have been synthesized by the conventional solid-state route. The addition of 6 wt% LiBiO$_2$ or 1 wt% LiBiO$_2$ + 1 wt% CuO reduces the sintering temperature by 300°-350°C through the formation of a liquid phase. It was found that the formation of the secondary phase and the smaller grain size for flux-sintered ceramics as indicated in XRD patterns and SEM micrographs, respectively, are considered to deteriorate the piezoelectric properties when compared with materials conventionally sintered at 1250°C. However, the ceramics sintered at 900°C for 1 hour with 1 wt% LiBiO$_2$ + 1 wt% CuO content exhibit desirable piezoelectric and dielectric properties with high field $d_{33}$ piezoelectric coefficient of 415 pm/V, Curie temperature $T_c$ of around 351°C, dielectric constant $\varepsilon_r$ of 1235, and planar coupling factor $k_p$ of 0.54. The reduced sintering temperature and short soaking time, together with the favorable dielectric and piezoelectric properties of the fluxed 0.98PZT-0.02SKN ceramics, demonstrate the potential opportunity of co-firing with LTCC materials and compatible low-melting-point electrodes (e.g. Ag) to fabricate multilayer piezoelectric devices.

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Chapter 4. Sintering behavior, properties, and applications of co-fired LTCC/PZT-SKN multilayer ceramics

4.1 Introduction

The incorporation of co-firable piezoelectric ceramics into commercial low temperature co-fired ceramic (LTCC) materials would offer the possibility of manufacturing highly integrated microdevices or microsystems using thick-film technology. Materials and processing conditions have been developed allowing co-firing of fluxed Pb(Zr_{0.53}, Ti_{0.47})O_3-Sr(K_{0.25}, Nb_{0.75})O_3 (PZT-SKN) materials with LTCC tapes [269,270]. As presented in chapter 3, PZT-SKN ceramics with 1 wt% LiBiO_2 + 1 wt% CuO addition are shown to sinter to high density at 900°C for 1 h with large high field $d_{33}$ piezoelectric coefficient of 415 pm/V and other favorable electric properties [269]. This reduction in sintering temperature and time enables the possibility of integration with LTCC and low fire electrode materials for the application in multilayer device fabrication. The investigation of co-firing processes and the resultant properties of piezoelectric layers in the co-fired LTCC/PZT-SKN multilayer ceramics are introduced in the current chapter.

The master sintering curve (MSC) approach has been used to study the densification behavior of fluxed PZT-SKN and LTCC tapes. Different sintering mechanisms for fluxed PZT-SKN ceramics and LTCC materials were confirmed by
analyzing the apparent activation energy $Q_a$. Using knowledge gained from MSC results, an optimized sintering profile was developed. The fluxed PZT-SKN thick films were prepared by the tape-casting method using a slurry consisting of ceramic powders and an organic binder vehicle. LTCC/PZT-SKN multilayer ceramics were first laminated and then co-fired using the derived optimal sintering profile. The microstructures, dielectric and piezoelectric properties of fluxed PZT-SKN layers co-fired with LTCC materials were investigated and compared with those of free sintered PZT-SKN samples in same composition to understand the influence of changing densification behaviors on the properties. HL2000/PZT-SKN multilayer stacks co-fired at 900°C for 0.5 h exhibited large $d_{33}$ piezoelectric coefficient (high field $d_{33}>340$ pm/V). The elemental inter-diffusion conditions were examined at the heterogeneous interface and the center of piezoelectric layer in co-fired LTCC/PZT-SKN multilayer ceramics using EDS analysis. Finally, a piezoelectric microbalance was fabricated using co-fired LTCC/PZT-SKN multilayer ceramics, demonstrating the possibility of integrating useful thick-film piezoelectric structures into LTCC-based microsystems.

### 4.2 Master sintering curve (MSC) model

As described in chapter 2, sintering is a complex process involving microstructure evolution related to different mass transport mechanisms. The sintering behavior of any specific powder compact depends on characteristics of the green body, including composition, particle size and shape, particle size distribution, degree of agglomeration, and other factors such as heating rate and sintering temperature, time, and atmosphere. The master sintering curve (MSC) approach proposed by Su and Johnson [299] has been
widely used to predict and optimize the densification behavior for a given powder compact. The capability of sintering control based on MSC analysis could lead to the process optimization for multi-materials integration, co-firing, microstructure, density and quality control [300]. In the case of fabrication of LTCC/PZT-SKN multilayer ceramics MSC study can be used for the optimization of co-firing process for heterogeneous laminates with different sintering behaviors. Development of compatible co-firing profile is required for multilayer ceramic production and will impact both the microstructure and properties of the sintered body.

MSC theory assumes that the microstructural evolution of a powder compact depends only on density and that a single sintering mechanism controls the sintering process [299-302]. The activation energy $Q$ for densification of a given material is a characteristic quantity that distinguishes different diffusion mechanisms during sintering process. In practice more than one sintering mechanism can be effective simultaneously over a certain temperature interval; if the proportional contribution of each sintering mechanism does not change with the variation of sintering temperature, then the MSC concept can still be applied [303]. The resultant temperature-independent activation energy, a weighted average of the various values corresponding to the multiple sintering mechanisms, is normally called the apparent activation energy $Q_a$. The MSC and $Q_a$ for a given material can be obtained empirically from densification data collected over a wide range of constant heating rate or isothermal heating experiments. The densification rates at any sintering stage derived from MSC are related to the linear shrinkage rates.
Theoretically, the construction of MSC model is derived from the combined-stage sintering model which predicts the densification behavior (for isotropic shrinkage) as [299]:

\[- \frac{dL}{L dt} = \frac{d\rho}{3 \rho dt} = \frac{\gamma \Omega [\Gamma(\rho)]D_o}{kT[G(\rho)]^n} \exp\left(- \frac{Q_a}{RT}\right)\]

where \(L\) is the compact size or length, \(\rho\) is the relative density, \(\gamma\) is the solid–vapor surface energy, \(\Omega\) is the atomic volume, \(\Gamma\) is the scaling factor containing density-dependent geometric terms, \(D_o\) is the diffusivity pre-exponent, \(k\) is Boltzmann’s constant, \(T\) is the absolute temperature, \(G\) is the grain size with \(n = 3\) for lattice diffusion and \(n = 4\) for grain boundary diffusion, \(Q_a\) is the apparent activation energy, and \(R\) is the ideal gas constant. It is assumed that the microstructural functions \(\Gamma\) and \(G\) depend only on density.

The above equation can be rearranged and integrated to build the relationship between the work of sintering \(\Theta\) and the density \(\rho\) at any time point \(t\) during the sintering cycle, as shown in the following equation [299]:

\[\phi(\rho) = \Theta(t, T(t))\]

The left part of this equation is related to the evolving microstructure which is a function of density while the right part is determined by the time-temperature profile and \(Q_a\). This relationship is defined as the MSC and both \(\phi(\rho)\) and \(\Theta(t, T(t))\) are defined in the following equations [299]:

\[\phi(\rho) = \frac{k}{\gamma \Omega D_o \int_{\rho_o}^{\rho} \frac{[G(\rho)]}{3 \rho [\Gamma(\rho)]} d\rho}\]
\[ \Theta(t, T(t)) = \int_0^t \frac{1}{T(t)} \exp\left(-\frac{Q_a}{RT(t)}\right) dt \]

The densification of material is thus linked to the integral thermal work through an arbitrary time-temperature profile and a given \( Q_a \). The optimal \( Q_a \) is determined on a trial-and-error basis when all the data converge to a single fitting curve. Further, the MSC can be formulated using the measured density data and the determined optimal \( Q_a \). The obtained MSC can only be applied to compacts made from the same material and by the same green-body formation processing [299].

Recently, the MSC concept has been expanded to describe other common phenomena occurred during sintering. Firstly, if the \( Q_a \) is considered not a constant as the sintering temperature varies, the sintering process can be divided into several consecutive stages, each one with its own constant \( Q_a \) [304]. Secondly, the MSC has also been used to simulate the grain growth behavior [305]. Finally, the MSC concept is further developed by analyzing the grain size effect on densification during both solid-state and liquid-phase sintering [306].

### 4.3 Tape casting technique

For incorporating piezoelectric elements into MEMS, screen printing [307,308] and sol-gel processing [309,310] have been widely investigated in order to deposit PZT-based thick films on silicon, alumina, LTCC, and other rigid substrates, particularly for the thickness of films ranging from several microns to tens of microns. However, both processes have technical problems to obtain the dense and crack-free films with uniform microstructure in building multilayer structures. For using screen printing or sol-gel
processing multiple repeating steps of coating and drying or pre-firing are required to fabricate films with certain thickness which is limited due to the accumulation of internal stress, resulting in cracking and other defects during deposition process.

Tape casting is a low-cost, well-established efficient technique to produce dense, uniform, and self-supporting ceramics sheets with a wide range of thickness (from several microns up to several hundred microns), which offers great possibilities for fabricating functional multilayer ceramics [311-313]. Cast tapes with high strength and sufficient flexibility before firing can be easily micromachined to form the laminated structures using thick-film technologies [314,315]. Cast PZT-based piezoelectric tapes with proper compositions and sintering behaviors could also be patterned, laminated, and co-fired with LTCC materials to build hybrid multilayer ceramics which have the potential to be used in sensor and actuator applications. The composition, lamination process, and firing profile of cast PZT-based tapes have significant influence on the sintering behaviors of laminated LTCC/PZT multilayer structures.

Figure 4.1 Schematic diagram of tape casting process. (taken from M.R. Gongora-Rubio [17])
Figure 4.1 illustrates the tape casting process. The prepared ceramic slurry is continuously dispensed onto a moving tape carrier under a doctor blade. The carrier is normally an organic film coated with additional elements (e.g. silicone coated Mylar) for easy separation of dried tapes from substrates. Cast slurries are dried in two steps: firstly, drying occurs by evaporation of solvent transported to the slurry surface by capillary force, and then further drying is controlled by solvent diffusion through the solidified part of the cast slurry. After drying the formed flexible green tapes with sufficient strength can be stored on take-up reels or stripped from the substrate and cut into the desired geometries for subsequent processing [159].

Considering the pressure flow under a doctor blade and the planar laminar flow generated by the moving tape carrier, the thickness of the dry tape $h_d$ is given by [316]:

$$h_d = ADh_o(1 + \frac{h_o^2\Delta p}{6\eta\nu L})$$

where $A$ is a correction factor, $D$ is the density ratio of the slurry and the dry tape, $h_o$ is the height between the doctor blade and the carrier, $\Delta p$ is the pressure difference (determined by the height of slurry in the reservoir), $\eta$ is the viscosity of the slurry, $\nu$ is the velocity of the doctor blade relative to the casting surface, and $L$ is the thickness of the doctor blade. The equation indicates a polynomial relationship between $h_d$ and $h_o$. The $h_d$ also changes linearly as the $\Delta p$ or $\nu$ various in the tape casting process. For small values of $h_o<200 \mu m$, the $h_d$ would simply be proportional to the $h_o$ if the values of $\eta$, $\nu$, and $\Delta p$ are carefully controlled in a certain range, resulting a uniform thickness for the cast tape [159]. The flat-bottom doctor blade with certain $L$ (typically 1~2 cm) is more
suitable than the knife-edged blade (small $L$) for tape casting based on the analysis of above equation.

### 4.4 Experimental procedures

The piezoelectric ceramic thick films used in the present work were prepared from low temperature sinterable ceramic powder according to the formula of $0.98\text{Pb}(\text{Zr}_{0.53}, \text{Ti}_{0.47})\text{O}_3-0.02\text{Sr}(\text{K}_{0.25}, \text{Nb}_{0.75})\text{O}_3$ (PZT-SKN) + 1 wt% LiBiO$_2$ + 1 wt% CuO. The fluxed PZT-SKN ceramic powders were fabricated using conventional solid-state ceramic processing methods as described in the experimental section of chapter 3.

#### 4.4.1 Tape casting

PZT-SKN tapes were prepared using an optimized organic-solvent based binder system. The preparation of the castable slurry is the most important step in the tape casting process. An ideal organic vehicle for tape casting requires certain properties, such as appropriate viscosity and rheological behavior, desirable wettability on the substrates and solid particles, suitable drying rate, and good dried film flexibility and strength to withstand rough handling [317]. For achieving high-density tapes, a high solid loading with a desirable mixture of solvent and additives is needed. The mixture of xylene and ethyl alcohol as solvent is selected for the current study, which has shown great adaptability and solubility for various organic additives to make a castable slurry [312]. The stability of powder suspension is largely determined by the dispersant. In order to lower the viscosity of the slurry for high particle concentration, the dispersant content needs to be optimized first for tape casting. Suspensions with 75 wt% solid loading of PZT-SKN powder were mixed with dispersant (Menhaden fish oil) at different
dispersant/powder weight ratio varying from 0.25% to 2.5%. Figure 4.2 shows the viscosity data measured at shear rate of 45 s\(^{-1}\) (similar to the shear rate under tape casting) for different suspensions. It was found that the viscosity decreased to 10.5 mPa \(\cdot\) s when the concentration of dispersant increases to about 0.8 wt% and the viscosity changed slightly when further adds the dispersant content to 3.5 wt%. The concentration of dispersant in about 0.8 wt% (dispersant/powder loading) is considered effective for colloidal property control.

![Viscosity of 75 wt% solid loading suspensions with different dispersant contents.](image)

The steps in the tape casting process are summarized in Figure 4.3. The ceramic powders with solvent and dispersant were first mixed using 5 mm spherical highly wear resistant zirconia media (TOSOH, Grove City, PA) by rotary ball milling (US Stoneware,
Mahwah, NJ) for 12 h. Then a binder (polyvinyl butyral) and plasticizers (polyalkylene glycol and butyl benzyl phthalate) in weight ratio of 1.2 dissolved in the solvent were added for another 12 h mixing to obtain a uniform castable slurry. This sequence of introducing the additives into the mixing process diminishes the competition for adsorption on the particles between the dispersant and binder/plasticizer and reduces the mechanical damage of the binder molecules [317], providing the required strength and flexibility of green tape. Before casting, a de-airing process is necessary in order to prevent the formation of bubbles in the cast tape. The exact slurry formulation utilized for tape casting is provided in Table 4.1.

![Diagram](image)

**Figure 4.3** Schematic flow diagram for the tape casting process.

A bench-top caster (TTC-1200, R.E. Mistler Inc., Yardley, PA) with a single doctor blade was used to cast the tape on silicone coated Mylar substrates (R.E. Mistler
Inc., Yardley, PA) at the speed of ~10 cm/min. The fluxed PZT-SKN tapes were dried at room temperature for 6 h. The thickness of as cast tapes was typically in the range from 80 to 120 µm.

Table 4.1  Compositions of PZT-SKN tape casting slurries. (wt%)

<table>
<thead>
<tr>
<th>Function</th>
<th>Composition</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic powder</td>
<td>Fluxed PZT-SKN</td>
<td>76.5</td>
</tr>
<tr>
<td></td>
<td>Xylene</td>
<td>10.0</td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethyl alcohol</td>
<td>9.6</td>
</tr>
<tr>
<td>Dispersant</td>
<td>Menhaden Fish Oil</td>
<td>0.6</td>
</tr>
<tr>
<td>Binder</td>
<td>Polyvinyl Butyral (PVB)</td>
<td>1.8</td>
</tr>
<tr>
<td>Plasticizer</td>
<td>Polyalkylene Glycol (PAG)</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Butyl Benzyl Phthalate (BBP)</td>
<td>0.9</td>
</tr>
</tbody>
</table>

* Organic additives were supplied by Richard E. Mistler Inc., Yardley, PA.

4.4.2 Construction of MSC

The MSC was constructed from the measured density $\rho$ data as a function of work of sintering $\Theta$ for a given sintering profile. Using constant heating rate experiments is the most efficient method to combine the data for $\rho$ and $\Theta$. The experimental sintering data were collected in the following steps for building the MSC: three layers of the LTCC and fluxed PZT-SKN tapes were stacked and laminated to obtain suitable thickness for easy handling and density measurements. The laminates were heated from room temperature to 450°C at a ramp rate of 1°C/min and then kept at peak temperature for 2 h to completely remove the organic binders. The samples then were fired at 4 different heating rates (1°C/min, 5°C/min, 8°C/min, and 12°C/min) to either 700°-950°C or 650°-
1050°C for the LTCC and fluxed PZT-SKN tapes, respectively. The green density of the pressed laminates was measured geometrically and the bulk densities of the sintered bodies were measured using Archimedes (immersion) method. With these sets of data the work of sintering $\Theta$ was initially calculated for each corresponding time-temperature data using an assumed value of the apparent activation energy $Q_a$. Then, the average residual square (sum of the residual squares divided by the total number of data points) is plotted as a function of assumed values of $Q_a$ and the minimum of the average residual square corresponds to the optimum $Q_a$ which is subsequently selected for the construction of MSC, as shown in Figure 4.4. Finally, data points from all heating rates were plotted simultaneously as density $\rho$ versus log($\Theta$) and fitted with a sigmoidal curve using optimum $Q_a$ value. The sintering behaviors of the LTCC and fluxed PZT-SKN tapes could then be predicted for an arbitrary schedule using the developed MSC models.

Figure 4.4  Example of determination of optimal apparent activation energy $Q_a$ for fluxed PZT-SKN materials by minimizing the average residual square.
4.4.3 Fabrication of LTCC/PZT-SKN multilayer ceramics

Multilayer stacks of the PZT-SKN tape as well as several commercial LTCC systems Heralock® HL2000, Heratape® CT2000, and CT800 (Heraeus Inc.-Thick Film Division, West Conshohocken, PA) were fabricated by dicing and lamination. Square PZT-SKN and LTCC tapes of several sizes (length $a = 10, 15, \text{and} 20$ mm) with and without round cavities in the center were patterned using a CO$_2$-laser milling system (VLS 3.50, Universal Laser Systems Inc., Scottsdale, AZ). Multilayer samples were fabricated by stacking patterned LTCC green tapes on the top and bottom of PZT-SKN layers with different thickness and then laminating aligned stacks under 10 MPa at 75°C for 10 min using a uniaxial press (3851, Carver, Wabash, IN). Different multilayer structures were studied to investigate the sintering behaviors and the properties of co-fired LTCC/PZT-SKN ceramics.

4.4.4 Characterization of microstructures and properties

The microstructures of co-fired PZT-SKN/LTCC multilayer ceramics were observed using an optical microscope (SZX12, Olympus, Tokyo, Japan) and scanning electron microscope (SEM: S-3200, Hitachi, Tokyo, Japan). SEM with an energy-dispersive X-ray detector (EDS: Evex detector, Evex Inc., Princeton, NJ) enabled elemental compositional determination near the interface between PZT-SKN and LTCC layers. An ARL-SEMQ electron microprobe analyzer was also used to quantify the extent of elemental inter-diffusion near the heterogeneous interface in co-fired multilayer ceramics. A conductive gold electrode paste (TC8101, Heraeus Inc.-Thick Film Division, West Conshohocken, PA) was printed on the green body of square shaped PZT-SKN
tapes and the exposed PZT-SKN surfaces in laminated multilayer structures for measuring the electrical characteristics. Next, the fluxed PZT-SKN tapes and LTCC/PZT-SKN multilayer ceramics were co-fired with gold electrodes using different sintering profiles. Sintered samples were poled by applying a DC electric field of 30 kV/cm at the temperature of 100°C for 15 min in a silicon oil bath. Characterization of dielectric and piezoelectric properties on sintered samples was conducted using the same procedures introduced in the experimental method section in chapter 3.

4. 4. 5 Microbalance fabrication and testing

Finally, a 1 cm × 1 cm piezoelectric microbalance was fabricated in a compact LTCC/PZT-SKN multilayer ceramic module using optimized processing techniques. The dependence of resonant frequency on mass loading for the developed multilayer PZT-SKN/LTCC ceramics was investigated using an impedance analyzer (4194A, Hewlett-Packard, Palo Alto, CA) with automated data acquisition program. The testing structure was securely mounted in a fixture and electrically connected to the impedance analyzer. A micropipette was used to generate uniform droplets of perfluoropolyether fluids (Galden HT-200, Solvay Solexis Inc., Thorofare, NJ) of known density and low volatility onto the top electrode surface. The experimental setup for monitoring the shift of resonant frequency is shown in Figure 4.5.
4.5 Results and discussion

4.5.1 Master sintering curve analysis

The MSC approach was used to understand the sintering mechanisms and optimize the fabrication of co-fired LTCC/PZT-SKN multilayer ceramics. The densification data obtained for fluxed PZT-SKN, HL2000, and CT2000 tapes heated at 1°C, 5°C, 8°C, and 12°C/min are shown in Figure 4.6(a), (b), and (c), respectively. A single value of theoretical density for each material (7.90 g/cm³ for fluxed PZT-SKN, 3.05 g/cm³ for HL2000, and 3.12 g/cm³ for CT2000) is defined to calculate the relative densities for samples sintered at all heating rates. In general, slower heating rates generated higher relative densities for samples sintered at equivalent temperature below the peak sintering temperature. The MSC describing the relationship between density $\rho$
and \( \log(\Theta) \) were determined using the density data and a MSC generating program (Master_Curve_V.1) using a sigmoid curve with five adjustable parameters proposed by Teng et al. [301]:

\[
\rho = \rho_o + \frac{a}{1 + \exp\left(-\frac{\log(\Theta) - \log(\Theta_o)}{b}\right)}^c
\]

where \( a, b, c \) are fitting constants, \( \rho_o \) is green density, and the \( \log(\Theta_o) \) is calculated at the initial time \( t \) of sintering cycle. The three sets of fitting parameters were calculated to obtain the MSC for fluxed PZT-SKN and LTCC tapes, listed in Table 4.2.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( \rho_o ) (%TD)</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( \log(\Theta_o) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-SKN</td>
<td>48.88</td>
<td>50.182</td>
<td>0.091</td>
<td>0.057</td>
<td>-11.690</td>
</tr>
<tr>
<td>HL2000</td>
<td>73.08</td>
<td>25.954</td>
<td>0.320</td>
<td>0.898</td>
<td>-20.391</td>
</tr>
<tr>
<td>CT2000</td>
<td>65.41</td>
<td>33.833</td>
<td>0.165</td>
<td>0.178</td>
<td>-25.324</td>
</tr>
</tbody>
</table>

All MSC results demonstrate acceptable fit with the experimental data points, as shown in Figure 4.7(a)-(c). The insets of Figure 4.7(a)-(c) illustrate the determination of the best fit apparent activation energies \( Q_a \), 268, 415, and 540 kJ/mol for fluxed PZT-SKN, HL2000, and CT2000 tapes, respectively. The obtained \( Q_a \) of 540 kJ/mol for CT2000 tapes is similar to the value of 530 kJ/mol reported by other researchers using density data calculated from precise dilatometry tests [318]. It is demonstrated that the density measurement method used in this study has high accuracy for the determination of \( Q_a \) and the generation of MSC. The resulting \( Q_a \) for fluxed PZT-SKN tapes is smaller
than those for LTCC materials. This finding corresponds to differing sintering mechanisms in LTCC and PZT-SKN ceramics. The LTCC materials are crystallizable glass-ceramics in which sintering is controlled by the viscous flow. The densification of the low temperature sintered PZT-SKN ceramics is related to the atomic diffusion through the liquid phase formed by the CuO and LiBiO₂ fluxes additions, as described in chapter 3. Comparison of the MSC suggests that dissimilar densification behaviors of the different compositional layers will have significant effects on the deformation and stress development in the co-firing process.

The densification behaviors of fluxed PZT-SKN, HL2000, and CT2000 tapes under isothermal heating at different temperatures and holding time are predicted and illustrated in Figures 4.8(a), (b), and (c), respectively. It was found that the density increases from 67% to 77% of theoretical density for fluxed PZT-SKN tapes as the sintering time increases from 0.5 h to 2 h at 700°C while the HL2000 starts to densify at the same temperature. There is no obvious densification observed for CT2000 tapes until the sintering temperature increases to 750°C. For fluxed PZT-SKN tapes, the density increases gradually from 700°C to 900°C. The relatively fast densification process of the LTCC tapes is completed within a smaller temperature window compared to that of fluxed PZT-SKN tapes. It is extremely difficult to discover a firing profile provide exactly the same sintering behaviors for heterogeneous materials with different sintering mechanisms. However, the determination of a most compatible firing profile using MSC results for every compositional layers has been shown to enable reduction of the sintering stresses during co-firing of hybrid multilayer ceramics, providing a better yield for the multilayer integration [186].
Figure 4.6 Densifications of (a) fluxed PZT-SKN, (b) HL2000, and (c) CT2000 tapes at different heating rates.
Figure 4.7 Master sintering curves of (a) fluxed PZT-SKN, (b) HL2000, and (c) CT2000 tapes based on the density data.
Figure 4.8  Prediction of sintering behaviors for (a) fluxed PZT-SKN, (b) HL2000, and (c) CT2000 tapes using derived MSC.
By comparison of sintering behaviors for various heating profiles based on the MSC predictions, similar densification behaviors of fluxed PZT-SKN and HL2000 tapes were founded in the temperature range of 780°C-820°C using an optimized firing profile, as shown in Figure 4.9. The resulting optimized co-firing profile is divided into four steps in a continuous heating process: first, the multilayer structure was heated from room temperature to 450°C at a slow ramp rate of 1°C/min; next, the temperature was held at 450°C for 1 h to allow for complete organic binder burnout; and finally, the second ramping process at the rate of ~ 3°C/min to the peak temperature (870°C-900°C) was conducted followed by soaking for 0.5-1 h.

Figure 4.9  Optimized densification behaviors of fluxed PZT-SKN and LTCC tapes obtained from MSC fitting equations, using the inset firing profile.
4. 5. 2 Microstructure and chemical composition analysis

The test structure used to fabricate hybrid LTCC/PZT-SKN multilayer samples is shown in Figure 4.10(a). The middle piezoelectric PZT-SKN layer with two additional patterned buffer layers was laminated between two stacks of LTCC green tapes having round cavities. LTCC/PZT-SKN laminates with different dimensions were prepared in the following tape length/cavity diameter (mm) combinations: 10/6.5, 15/10, and 20/15. All multilayer stacks were sintered at 870°C for 1 h using the optimized co-firing profile. The resulting HL2000/PZT-SKN co-fired ceramics did not exhibit any visible camber, delamination, or cracking following sintering. However, significant camber and minor delamination were observed after co-firing CT2000/PZT-SKN multilayer ceramics when the round cavities fabricated were larger than 10 mm.

![Figure 4.10 Co-firing structure of LTCC/PZT-SKN multilayer ceramics. (a) schematic illustration and (b) optical microscopic images of the cross-section.](image-url)
Figure 4.11 Co-fired CT2000/PZT-SKN and HL2000/PZT-SKN multilayer ceramics.

Optical microscopy images shown in Figure 4.10(b) illustrate the cross-section of co-fired HL2000/PZT-SKN multilayer ceramics. A slight concave morphology is observed at the edge of the piezoelectric layer indicating non-uniform shrinkage in the $x$-$y$ direction caused by co-firing with self-constrained HL2000 tapes which only shrink in the $z$ direction [154]. In free sintered laminates of CT2000/PZT-SKN or CT800/PZT-SKN the stresses generated due to the mismatch of shrinkage rate along $x$-$y$ direction at heating process cause significant camber and delamination, as shown in Figure 4.11. The
shear and in-plane tensile stresses developed during co-firing are relaxed from the heterogeneous interface to the middle of the PZT-SKN layer in HL2000/PZT-SKN laminates [319]. Therefore, the self-constrained HL2000 tapes minimize shrinkage variations in $x$-$y$ direction and eliminate camber development for HL2000/PZT-SKN multilayer structures.

SEM micrographs on polished cross-sections of HL2000/PZT-SKN multilayer ceramics sintered at 870°C for 1 h are shown in Figure 4.12. Figure 4.12(a) illustrates a typical interface in the co-fired HL2000/PZT-SKN structures. Porosity is observed in HL2000 layer near the interface which decreases moving towards the HL2000 surface. This observation suggests significant stress development during sintering near the HL2000/PZT-SKN heterogeneous interface. The exposed PZT-SKN area in the center of co-fired HL2000/PZT-SKN structures is shown in Figure 4.12(b). A dense and uniform piezoelectric PZT-SKN layer is obtained after co-firing with HL2000 tapes. The images of elemental mapping made on those areas are illustrated in Figure 4.13, demonstrating the elemental inter-diffusion qualitatively in the co-fired HL2000/PZT-SKN multilayer ceramics. The diffusion of Pb into LTCC layer in a limited distance (~20 µm) near the LTCC/PZT-SKN interface is clearly shown in Figure 4.13(a). The diffusion of Al, Ca, and Si from LTCC to PZT-SKN layer are also observed. The elemental mapping result shown in Figure 4.13(b) demonstrates that the diffusion of Al, Ca, and Si near the center of piezoelectric layer is less than that around heterogeneous interface.
Figure 4.12  SEM micrographs of hybrid multilayer ceramics sintered at 870°C for 1 h. (a) HL2000/PZT-SKN interface and (b) center of PZT-SKN layer.
Figure 4.13  EDS mapping results of hybrid multilayer ceramics sintered at 870°C for 1 h. (a) HL2000/PZT-SKN interface and (b) center of PZT-SKN layer.
Table 4.3  EDS elemental analysis on the cross-section of LTCC/PZT-SKN multilayer ceramics. (wt%)  

<table>
<thead>
<tr>
<th>Composition</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO</td>
<td>--</td>
<td>26.22</td>
<td>58.68</td>
<td>61.71</td>
<td>64.85</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>--</td>
<td>--</td>
<td>20.14</td>
<td>18.72</td>
<td>19.80</td>
</tr>
<tr>
<td>TiO₂</td>
<td>4.72</td>
<td>2.03</td>
<td>9.55</td>
<td>10.93</td>
<td>11.70</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>45.60</td>
<td>37.47</td>
<td>2.76</td>
<td>1.66</td>
<td>--</td>
</tr>
<tr>
<td>SiO₂</td>
<td>39.30</td>
<td>29.55</td>
<td>3.48</td>
<td>2.75</td>
<td>--</td>
</tr>
<tr>
<td>CaO</td>
<td>10.36</td>
<td>4.40</td>
<td>1.21</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Other Oxides</td>
<td>&lt; 1%</td>
<td>&lt; 1%</td>
<td>&lt; 5%</td>
<td>&lt; 5%</td>
<td>&lt; 5%</td>
</tr>
</tbody>
</table>

The elemental compositions of different regions across the PZT-SKN/HL2000 interface are compared in Table 4.3. The elemental analysis at A was consistent with the pure LTCC composition mainly composed of Al₂O₃ and SiO₂ without showing any elemental diffusion from co-fired PZT-SKN layers. The pure PZT-SKN composition was detected at E in the piezoelectric layer near the center of multilayer structure. Interdiffusion from across the interface between HL2000 and PZT-SKN layers was confirmed by analyzing the elemental compositions at B and C. The elemental analysis result at B indicates the diffusion of Pb during the co-firing process and the diffusion of Al, Si, and Ca was also determined from data collected in the PZT-SKN layer close to the interface at C. A small amount of Al₂O₃ and SiO₂ was observed at D in the piezoelectric layer near the edge of multilayer structure. However, the diffusion was minimal processing along the radial direction. The diffusion of Pb from PZT-SKN to HL2000 layer was visible by the Z-contrast image obtained using the backscattered electron detector, as shown in Figure 4.14. A lighter-colored layer was observed at the HL2000 side next to the
interface, which demonstrated the occurrence of Pb diffusion because the backscattered electrons induced from heavy element (e.g. Pb) are stronger than those from light elements (e.g. Al, Si, and Ca).

Figure 4.14  Backscattered electron image showing the Z-contrast of the interface in the hybrid HL2000/PZT-SKN multilayer ceramics sintered at 870°C for 1 h.

4. 5. 3 Dielectric and piezoelectric properties

The experimental results presented in chapter 3 indicated that the 1 wt% LiBiO₂ + 1 wt% CuO fluxed PZT-SKN ceramics sintered at 900°C for 1 h exhibit the optimum dielectric and piezoelectric properties; while the recommended firing condition for
HL2000 tapes is at 870°C and holding for 0.5 h to maintain the flat and complete structure after firing. In order to obtain the desirable piezoelectric properties and better multilayer structural integrity, a further investigation on sintering conditions for HL2000/PZT-SKN multilayer ceramics is desired to conciliate the discrepancies of peak sintering temperature and soaking time between LTCC and PZT-SKN materials using the co-firing profile suggested by the MSC analysis result. The typical dielectric and piezoelectric properties of PZT-SKN/HL2000 laminates sintered under different conditions are summarized in Table 4.4.

<table>
<thead>
<tr>
<th>Sintering conditions</th>
<th>$\varepsilon_r$</th>
<th>tan$\delta$</th>
<th>$d_{33}^{\text{low}}$ (pm/V)</th>
<th>$d_{33}^{\text{high}}$ (pm/V)</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_r$ (C/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>870°C, 0.5 h</td>
<td>1030</td>
<td>0.015</td>
<td>216</td>
<td>298</td>
<td>11.7</td>
<td>0.12</td>
</tr>
<tr>
<td>890°C, 0.5 h</td>
<td>1100</td>
<td>0.020</td>
<td>237</td>
<td>316</td>
<td>12.3</td>
<td>0.15</td>
</tr>
<tr>
<td>900°C, 0.5 h</td>
<td>1200</td>
<td>0.017</td>
<td>255</td>
<td>356</td>
<td>12.5</td>
<td>0.18</td>
</tr>
<tr>
<td>870°C, 1 h</td>
<td>1205</td>
<td>0.022</td>
<td>240</td>
<td>345</td>
<td>12.0</td>
<td>0.15</td>
</tr>
<tr>
<td>890°C, 1 h</td>
<td>1145</td>
<td>0.020</td>
<td>235</td>
<td>325</td>
<td>12.1</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The dielectric constant $\varepsilon_r$ and piezoelectric coefficient $d_{33}$ increase as the sintering temperature increases from 870°C to 900°C when sintering time is controlled in 0.5 h at peak temperature. The contrary result was observed when test multilayer ceramics were sintered at peak temperature for 1 h. The remnant polarization $P_r$ and coercive field $E_c$ increase as the sintering temperature increases for both soaking periods. However, delamination and cracking were observed in some of the PZT-SKN/HL2000 laminates sintered at 900°C for 1 h. These defects may be attributed to the elevated sintering
temperature with a longer soaking time which causes the additional stress in the multilayer structures. The fluxed PZT-SKN tapes laminated with HL2000 were sintered under pressure which also affects the densification of PZT-SKN layers. The HL2000/PZT-SKN multilayer ceramics sintered at 900°C for 0.5 h exhibit favorable properties with high field $d_{33}$ piezoelectric coefficient of 356 pm/V and dielectric constant $\varepsilon_r$ of 1200.

Table 4.5  Dielectric and piezoelectric properties of fluxed PZT-SKN thick films co-fired with different LTCC materials.

<table>
<thead>
<tr>
<th>LTCC materials</th>
<th>$\varepsilon_r$</th>
<th>$\tan\delta$</th>
<th>$d_{33}^{\text{low}}$ (pm/V)</th>
<th>$d_{33}^{\text{high}}$ (pm/V)</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_r$ (C/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL2000</td>
<td>1205</td>
<td>0.022</td>
<td>240</td>
<td>345</td>
<td>12.0</td>
<td>0.15</td>
</tr>
<tr>
<td>CT2000</td>
<td>1150</td>
<td>0.022</td>
<td>228</td>
<td>326</td>
<td>11.7</td>
<td>0.15</td>
</tr>
<tr>
<td>CT800</td>
<td>1132</td>
<td>0.020</td>
<td>235</td>
<td>335</td>
<td>11.8</td>
<td>0.14</td>
</tr>
<tr>
<td>PZT-SKN*</td>
<td>1270</td>
<td>0.018</td>
<td>313</td>
<td>450</td>
<td>12.5</td>
<td>0.28</td>
</tr>
</tbody>
</table>

* Fluxed PZT-SKN tapes were sintered at 900°C for 1 h.

The PZT-SKN layers co-fired with other LTCC materials may exhibit different properties compared with those co-fired with HL2000 tapes because the different sintering behaviors of LTCC layers have distinctive influence on the densification and the resulting properties of piezoelectric layers. The measured dielectric and piezoelectric properties of fluxed PZT-SKN thick films co-fired with different LTCC tapes at 870°C for 1 h are summarized in Table 4.5. The test structures were 10 mm on each side with a 6.5 mm diameter cavity defining the active region. The PZT-SKN/HL2000 samples co-fired with gold electrodes exhibited the dielectric constant $\varepsilon_r$ of 1205 and low field $d_{33}$ piezoelectric coefficient of 240 pm/V which demonstrated the highest values among all
the multilayer structures examined. Compared with the stand-alone fluxed PZT-SKN tapes (low field $d_{33}$ of 313 pm/V) fired using optimal sintering conditions (900°C for 1 h), the $d_{33}$ piezoelectric coefficient of PZT-SKN layer co-fired with LTCC tapes is only moderately reduced. Based on similar dielectric properties and Curie temperature $T_c$ between co-fired and stand alone materials this observed reduction can be largely attributed to the mechanical clamping effect by the inactive LTCC substrates. Further, compared with the other reported dielectric and piezoelectric properties of PZT-based thick films fired on LTCC substrates [147,149-151], the properties of currently developed PZT-SKN thick films co-fired with LTCC structures are significantly improved, indicating the possibility to be used for the device fabrication.

4.5.4 A demonstration of applications: microbalance

In order to demonstrate the utility of the developed co-fired LTCC/PZT-SKN system a resonant radial mode piezoelectric microbalance has been fabricated and characterized. Figure 4.15 depicts the cross-section of the co-fired multilayer microbalance structure. The resonant frequency shift with different mass loadings is used to characterize the performance of this resonant mass sensor. As shown in Figure 4.16, the resonant frequencies decrease linearly due to the additional mass loadings as the droplets are deposited on the top electrode surface.

The mass sensitivity can be defined as the ratio of the resonant frequency shift $\delta \omega_o$ to the accreted mass $\delta M$, where $\delta M$ is proportional to the effective mass $M_{\text{eff}}$ of the resonator [320]:

$$\delta M \approx -2 \frac{M_{\text{eff}}}{\omega_o} \delta \omega_o$$
The measured mass sensitivity of 15 kHz/mg was calculated as the inverse of the slope of the linear fit to the experimental data. A common approach to improve the mass sensitivity for the resonator is to reduce $M_{\text{eff}}$ by making the device less massive [321].

![Diagram of LTCC, PZT-SKN, and Gold electrode layers]

Figure 4.15  Schematic illustration of cross-section of co-fired multilayer ceramics for microbalance.

A preliminary simulation was conducted in order to study the effects of the geometry of piezoelectric PZT-SKN layers on the mass sensitivity using finite element modeling (FEM). The simulation results plotted in Figure 4.17 indicate that the thinner piezoelectric layer with a smaller diameter for the fixed diameter/thickness aspect ratio offers the higher sensitivity of mass detection, which is in agreement with the theoretical analysis. Also, operating this multilayer ceramic device at the higher order resonant modes would provide better mass sensitivities. The proposed method for improving mass sensitivity will require further miniaturization of this multilayer structure through additional fabrication process optimization. However, these results demonstrate the capability to integrate PZT-SKN ceramics into LTCC-based MEMS structures using commercially available materials and fabrication methods.
Figure 4.16  Resonant frequency shift as a function of the mass loading with linear fitting.

Figure 4.17  FEM simulation result of geometrical effect of piezoelectric layers on the mass sensitivity.
4. 6 Conclusions

In summary, a co-fired LTCC/PZT-SKN multilayer ceramic system for the fabrication of thick-film MEMS structures has been successfully developed and demonstrated. Master sintering curves (MSC) were constructed to understand the sintering mechanisms and investigate the sintering behaviors for the low fire PZT and LTCC materials. Dissimilar apparent activation energies obtained from the MSC models indicated different sintering mechanisms dominate the sintering behaviors in the various materials. Viscous flow controlled sintering is the dominant mechanism for LTCC materials while liquid phase sintering controls the fluxed PZT-SKN ceramics. The accurate prediction of densification behaviors using MSC analysis can significantly improve the development of hybrid LTCC/PZT-SKN multilayer ceramics and enable the co-firing process optimization. Using the optimized co-firing profile predicted by MSC, it was found that fluxed PZT-SKN ceramics co-fired with HL2000 tapes demonstrate the best sinterability without showing any defects, such as deformation, delamination, or cracking. The optimum electromechanical properties with high field $d_{33}$ piezoelectric coefficient of 356 pm/V and dielectric constant $\varepsilon_r$ of 1200 were obtained when the HL2000/PZT-SKN laminates were sintered at 900°C for 0.5 h. EDS and electron microprobe analysis revealed the inter-diffusion of Pb from PZT-SKN layers into LTCC layer in a limited length and the appearance of Al, Ca, and Si in the PZT-SKN layer near the LTCC/PZT-SKN interface. Further, elemental inter-diffusion was not detected at the center of piezoelectric layer in co-fired LTCC/PZT-SKN multilayer ceramics and no subsequent reduction in $d_{33}$ piezoelectric coefficient was observed. Finally, a piezoelectric microbalance with a mass sensitivity of 15 kHz/mg was fabricated,
demonstrating the feasibility of the current materials and processing methods for multilayer ceramic based micro-electromechanical device fabrication.
Chapter 5. Development and optimization of multilayered LTCC/PZT-SKN piezoelectric micropumps for LTCC-based microfluidic systems

5. 1 Introduction

Micropumps providing efficient fluid control and delivery are essential components in lab-on-chip (LOC) microfluidic systems. Compact integrated pumping solutions remain a key challenge in microsystems developed for clinical and environmental analysis which require prompt processing of samples [322]. The development of a chip- or package-level micropump with the capability of being easily integrated into a microfluidic LOC platform would be highly desirable. Low temperature co-fired ceramic (LTCC) materials offer a promising alternative to silicon, glass, and polymeric substrates for the fabrication of highly integrated microfluidic devices and microsystems in a multilayer ceramic module [32]. A number of LTCC microfluidic devices incorporating diverse functional elements have been successfully fabricated and reported [68,78,266-267]. As discussed in chapters 3 and 4, the realization of co-firable piezoelectric ceramics and the compatible processing methods for incorporating LTCC with low firing temperature PZT-SKN materials allows direct integration of high density electromechanical elements including actuators, fluidic networks, and electronic interconnects [269,270].
The current chapter describes the design, fabrication, and characterization of a LTCC/PZT-SKN multilayer piezoelectric peristaltic micropump implemented using the previously developed methods. Standard LTCC thick film processing methods were applied to design and fabricate the multilayer micropumps, allowing rapid development times and highly scalable production capabilities. Peristaltic pumping was achieved using 3 pairs of piezoelectric bimorph diaphragm actuators. Phase-shifted electrical signals generate a peristaltic pumping motion and enable completely reversible fluid flow. Finite element modeling (FEM) was conducting to simulate and optimize the deflection of piezoelectric bimorph actuators. Further optimization of pumping performance has been studied using modified microchannel geometries. As LTCC materials and technology have already been utilized to fabricate other microdevices (e.g. microvalves, flow sensors, and chemical detectors), the current demonstration of an LTCC-process compatible micropump promises the ability to commercialize highly multifunctional integrated LTCC-based microfluidic systems.

5.2 Design and fabrication of micropumps

5.2.1 LTCC and PZT-SKN tapes

Heralock® HL2000 green tapes, which provide a sintering shrinkage in the $x$-$y$ direction of less than 0.2%, were used as LTCC layers in the multilayer ceramic micropumps. Low-temperature sinterable piezoelectric ceramics with the composition of $0.98\text{Pb(Zr}_{0.53, \text{ Ti}_{0.47})\text{O}_3-0.02\text{Sr(K}_{0.25, \text{ Nb}_{0.75})\text{O}_3 + 1 \text{ wt}\% LiBiO}_2 + 1 \text{ wt}\% \text{ CuO}$ were prepared using a solid state route, as introduced in chapter 3. PZT-SKN tapes were fabricated by tape casting from a slip consisting of fluxed PZT-SKN powders and a PVB-
based binder vehicle, as described in chapter 4. Cast tapes of 120-130 µm thickness were used as piezoelectric layers. The raw materials used for PZT-SKN tape preparation, commercially available LTCC tapes, and conductor inks used in the fabrication of LTCC/PZT-SKN multilayer micropumps are summarized in Table 5.1.

Table 5.1   Materials used in the fabrication of PZT-SKN/LTCC multilayer micropump.

<table>
<thead>
<tr>
<th>Functional materials</th>
<th>Composition/Brand</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-SKN powder</td>
<td>PbCO₃</td>
<td>Halstab</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>Ishihara</td>
</tr>
<tr>
<td></td>
<td>SrCO₃, K₂CO₃, Li₂CO₃</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td></td>
<td>Nb₂O₅</td>
<td>H.C. Stark</td>
</tr>
<tr>
<td></td>
<td>CuO, ZrO₂</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Organic binder vehicle</td>
<td>Xylene, Ethyl alcohol</td>
<td>Fisher Chemical</td>
</tr>
<tr>
<td></td>
<td>Polyvinyl butyral (PVB), Menhaden fish oil, Polyalkylene glycol (PEG), Butyl benzyl phalate (BBP)</td>
<td>Richard E. Mistler</td>
</tr>
<tr>
<td>LTCC tape</td>
<td>HeraLock™ Tape HL2000</td>
<td>Heraeus</td>
</tr>
<tr>
<td>Conductor paste</td>
<td>TC8101 co-firing gold ink</td>
<td>Heraeus</td>
</tr>
</tbody>
</table>

5. 2. 2 Piezoelectric bimorph actuator

A bimorph piezoelectric actuator geometry was selected for use in the peristaltic micropump. The bimorph design, made possible by the multilayer LTCC/PZT-SKN co-firing process developed, utilizes two active piezoelectric layers driven in opposition to each other. This results in amplified actuator deflection and increase pump displacement relative to typical unimorph actuated pump designs. Figure 5.1(a) shows the configuration of the piezoelectric bimorph utilized in the current work. In this design, one
piezoelectric layer’s positive electrode is connected with the other layer’s negative electrode (where the negative and positive orientations refer to the directions in which the piezoelectric layers were poled). When an alternating voltage is applied, one piezoelectric layer will contract while the other will expand, resulting in a vibrating motion normally many times greater than the length or thickness change of a single layer [323,324].

Figure 5.1  Bimorph actuator for the multilayer peristaltic micropump. (a) typical configuration, (b) multilayer structure, and (c) FEM model.
For the initial prototype designs, the bimorph elements were made of two PZT-SKN tapes laminated together with the HL2000 tapes as structural support elements, as shown in Figure 5.1(b). The total device size was 15 mm × 15 mm square by 1.2 mm thick (~0.3 cm$^3$). The round cavity (10 mm diameter) in the HL2000 layers defines the actuator size. Corresponding 10 mm gold electrodes were printed on the center of PZT-SKN tapes. Additional conductor lines were printed to extend the electrical connections to the edge of the multilayer device. The laminated HL2000/PZT-SKN multilayers were co-fired using the previously optimized sintering profile. A finite element modeling (FEM) simulation constructed using COMSOL Multiphysics® 3.5 package was used to predict and optimize actuator performance. Figure 5.1(c) illustrates the schematic design and adjustable parameters utilized in the FEM model, where $R$ is the diaphragm radius and $\theta$ is the thickness of single-layer of the PZT-SKN tape. Clamped boundary conditions were applied at the circumference of the bimorph layers, corresponding to complete clamping of the active layers by the inactive LTCC substrate.

5.2.3 Multilayer design and fabrication of piezoelectric micropump

The multilayer structure of designed piezoelectric micropump consists of five distinct layers, as illustrated in Figure 5.2. The top and bottom support layers and the intermediate layer defining the fluidic network (including inlet/outlet ports, microchannels, interconnects, flow rectification elements, and pump chambers) were patterned from HL2000 tapes. Each of the two active piezoelectric bimorph layers consist of two layers of low firing temperature PZT-SKN tapes, screen printed gold electrodes, defining the active pumping regions, and additional required electrical interconnects. The resulting pumping actuators are sandwiched between the structural LTCC layers, as
illustrated. The assembled pump has three pumping chambers connected in series, with each chamber driven by two of the bimorph actuators located on the top and one on the bottom. This design doubles the stroke volume without increasing supply voltage requirement nor adding significant complexity to the design, fabrication, and assembly process. This ability to readily create stacked integrated structures exhibits one of the unique capabilities of the LTCC multilayer processing methodology.

Figure 5.2 Multilayer design of the piezoelectric peristaltic micropump.

The individual pump layers were patterned using a combination of laser ablation and screen printing. The top, intermediate, and bottom structural layers were made from three-layer HL2000 green tape stacks. A CO₂-laser system (VLS 3.50, Universal Laser
Systems Inc., Scottsdale, AZ) was used to ablate the design features in the green tapes. Three round pump chambers (diameter: 10 mm) connected by microchannels (width: 0.6 mm) were cut on the intermediate layer while the three corresponding cavities within the same geometry as the pump chamber were patterned on both top and bottom layers. The small inlet/outlet holes were made on the top layer. The piezoelectric bimorph layers were prepared by pre-laminating two PZT-SKN tapes with round electrodes (diameter: 10 mm) and electrical interconnects (width: 0.5 mm). Electrode patterns were screen printed on PZT-SKN layer using co-firable gold ink (TC8101, Heraeus Thick Film Materials Division, West Conshohocken, PA). All individual patterned layers were aligned, stacked, and laminated at ~5 MPa and room temperature. A final high temperature co-firing treatment (870°C for 1 h) was conducted to yield a monolithic sintered ceramic device. The overall size of the micropump package is about 60 mm × 15 mm × 1.2 mm (~1 cm³).

The co-fired micropump was assembled for pumping tests by the following steps. First, the piezoelectric bimorph actuators were poled in a silicon oil bath. Plastic fluidic connectors and electric leads attached to the micropump body using fast-dry epoxy (E1009, Elmer’s Product Inc., Columbus, OH) and conductive silver epoxy (CW2400, ITW Chemtronics, Kennesaw, GA), respectively. The capacitance and dielectric loss each of the three sets of bimorph actuators were measured using a precision LCR meter (E4980A, Agilent, Santa Clara, CA) to ensure the proper connection and function. Pictures of the co-fired multilayer ceramic micropump body as assembled for pumping test are shown in Figure 5.3.
Figure 5.3  Picture of the fabricated micropump. (a) micropump body and (b) assembly for pumping test.

5. 2. 4 Micropump optimization

The velocity field of pressure driven flow through a microchannel is directly related to the geometry of the channel. Diffuser/nozzle fluidic rectifiers were added into the fluid interconnects, in an attempt to enhance the pumping performance at the expense of bidirectional fluid flow. Diffuser elements replaced straight microchannels connected to pump chambers, as shown in Figure 5.4. The entrance ($W_1$) and exit ($W_2$) width of diffuser were 200 µm and 750 µm, respectively. The opening angle $\theta$ was 8° and the diffuser length $L$ was 5 mm. In a subsequent investigation four distinct micropumps were
fabricated with different microchannel aspect ratios by varying channel widths ($W$) at fixed channel height ($H$). The microchannel of initial micropump had a rectangular cross-section of $600 \, \mu\text{m} \times 300 \, \mu\text{m}$. Three other pumps with a channel width of 300, 750, and 900 $\mu\text{m}$ were fabricated to investigate the effect of changing microchannel aspect ratio ($W/H$) on the pumping performance.

![Figure 5.4 Geometry of planar diffuser element.](image)

**5.3 Experimental setup**

A schematic drawing of the experimental setup for the characterization of pumping performance is shown in Figure 5.5. The three phase shifted frequency matched drive signals were generated by a computerized DAQ board (USB-6259, National Instruments, Austin, TX) using LabVIEW™ software. The sinusoidal output signals were
routed through high speed amplifiers (4005 Type, NF Electronic Instruments, Yokohama, Japan) to achieve the required drive voltage. An initial phase shift of 120° between each successive pair of actuators was used to create a traveling pressure wave to drive fluid flow. Changing the sign of the phase shift between the individual pumps cavities allows bidirectional pumping to be achieved (phase difference of 90° and 60° were also studied). Flow rates were measured as a function of operating frequency (50-200 Hz), backpressure (0-1.5 kPa), and driving voltage (50-100 V_{pp}). Colored DI water was used as the working fluid. The volumetric flow rate was calculated from linear velocity of the water column in the outlet tubing. The backpressure was adjusted by changing the height of inlet reservoir. Pictures of the working micropump, fluidic components, and electronic control system are provided in Figure 5.6

Figure 5.5  Schematic illustration of experimental setup for pumping test.
5.4 Results and discussion

5.4.1 Modeling of piezoelectric bimorph actuator

The FEM simulation of the pump membrane deflection is shown in Figure 5.7(a). The deflection profile shows the membrane displacement increases from the perimeter to the center with a roughly Gaussian profile, to a maximum displacement $d_{\text{max}}$. The relationship between the $R/\theta$ ratio and the $d_{\text{max}}$ for the PZT-SKN bimorph at different membrane thickness is illustrated in Figure 5.7(b). FEM results suggest an optimum $R/\theta$ ratio of about 240 for the largest membrane displacement when the bimorph is actuated at the same frequency and electric field. For estimating the volumetric flow rate based on
the simulation results, it was assumed that the membrane deflection follows the deflection function of a thin circular plate [254]:

\[ d (r) = d_{\text{max}} [1 - \left( \frac{r}{R} \right)^2]^2 \]

where \( r \) is the distance from the origin of the circular membrane. The maximum change of microchamber volume can be calculated as:

\[ \Delta V = 2 \times \int_0^{2\pi} \int_0^R d_{\text{max}} [1 - \left( \frac{r}{R} \right)^2]^2 r dr d\varphi = \frac{2\pi}{3} d_{\text{max}} R^2 \]

Considering a linear relationship between flow rate and pump frequency at low operating frequency range (\(~100\) Hz) and doubling volume change to account for the two bimorph actuators for each microchamber, the estimated volumetric flow rate is:

\[ Q = 2 \Delta V f \]
Figure 5.7  FEM simulation results. (a) visualization of bimorph membrane deflection. (displacement scaled $10^3$ times for clarity) and (b) maximum displacement ($d_{\text{max}}$) as a function of membrane radius/thickness ratio ($R/\theta$) for different diaphragm radii.
Figure 5.8  Estimation of flow rate based on the FEM simulation results. (a) normalized flow rate as a function of $R/\theta$ ratio and (b) maximum flow rate as a function of membrane size $R$ at a constant $R/\theta$ ratio of 240.

The resulting relationship between the normalized flow rate and $R/\theta$ ratio for the LTCC/PZT-SKN micropump when driven at frequency of 100 Hz is illustrated in Figure 5.8(a). Similar to the membrane deflection simulation results, the micropump with membrane in the optimum $R/\theta$ ratio of 240 is expected to yield the maximum flow rate $Q_{\text{max}}$. Figure 5.8(b) plots the calculation results of the relationship between the $Q_{\text{max}}$ and the diaphragm radius $R$ at the optimum $R/\theta$ ratio. The $Q_{\text{max}}$ is lower than 1 ml/min when $R$ is smaller than 5 mm. The parabolic relationship between $Q_{\text{max}}$ and $R$ leads to a rapid increase in $Q_{\text{max}}$ with increasing $R$. In practice, however, the aspect ratio ($R/\theta$) of the bimorph actuator is expected to be limited by fabrication capabilities and durability concerns. Initially, a radius $R$ of 5 mm and layer thickness $\theta$ of 100 µm (thickness after co-firing) corresponding to an $R/\theta$ of only 50 for the PZT-SKN bimorph actuators was
used for micropump fabrication. This moderate aspect ratio leads to acceptable device yields for research scale testing and fabrication.

### 5.4.2 Micropump performance

Initial pumping trials are presented for a pump with a microchannel of constant rectangular cross-section (600 µm wide × 300 µm high). Table 5.2 reports the effect of varying the phase shift of the drive signals on flow rates at actuation frequencies of 50, 100, and 200 Hz. The three sets of bimorph actuators were driven at 100 V_{pp} with phase differences of 120°, 90°, and 60°. The experimental results show that the pump excited by signals 120° out of phase with one another produced higher flow rates for all examined actuation frequencies. One explanation for the flow rate trend is that the backflow from outlet to inlet increases as the phase difference decreases from 120° to 90°, 60° during the actuation cycle [325]. In addition, the flow resistance working on the vibrating membranes is considered to be less when the actuators are operated at phase difference of 120° rather than 90° or 60° for the peristaltic micropumps [326].

<table>
<thead>
<tr>
<th>Phase Variation</th>
<th>50Hz</th>
<th>100Hz</th>
<th>200Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°</td>
<td>230</td>
<td>440</td>
<td>760</td>
</tr>
<tr>
<td>90°</td>
<td>185</td>
<td>350</td>
<td>610</td>
</tr>
<tr>
<td>60°</td>
<td>140</td>
<td>265</td>
<td>460</td>
</tr>
</tbody>
</table>

Figure 5.9 illustrates the volumetric flow rate as a function of actuation frequency when the micropump is operated at driving voltages of 50, 75, and 100 V_{pp}. At each
actuation frequency the higher driving voltage results in the higher flow rate due to the larger displacement of bimorph membranes. Pumping rate is also effectively controlled by varying the drive frequency. The flow rate increases linearly up to a frequency of 200 Hz. Pumping became unstable and air bubbles were observed inside the tubing when the actuation frequency was increased above 200 Hz. due to cavitation. The resulting air bubbles tended to accumulate at inlet/outlet connectors forming an air gap which interfered with the normal pump operation. Mechanical failure is another critical concern for the developed all ceramic micropumps. Piezoelectric bimorph membranes actuated at high-frequency AC electric field have increased occurrences of defects in the ceramic layers, including micro-scale cracks and pores [327]. Therefore, the actuation frequency is confined at 100 Hz in the following experiment in order to avoid the cavitation phenomenon and prolong the working lifetime for the developed micropump.
Figure 5.9 Measured variation in flow rate with actuation frequency at drive voltages of 50, 75, and 100 $V_{pp}$.

The maximum blocking pressure is one of the most important pumping performance parameters in terms of limiting potential application areas for a given micropump. Experimental results show that the volumetric flow rate decreases linearly with increasing backpressure, as illustrated in Figure 5.10. The flow rate-backpressure characteristics measured at different driving voltages demonstrate that the higher driving voltage results in both higher maximum flow rate (at zero backpressure) and increased blocking pressure (i.e. extrapolated backpressure at zero flow rate). The results indicate that the developed peristaltic micropump offers a maximum flow rate of 450 µl/min and a blocking pressure of 1.4 kPa when operated at voltage of 100 $V_{pp}$ and frequency of 100
Hz. Subsequent studies exploring modified design parameters were conducted in order to enhance the pumping performance.

**Figure 5.10** Measured flow rate versus backpressure under actuation frequency of 100 Hz with various driving voltages.

5. 4. 3 Effects of microchannel geometry

*Diffuser elements*

A planar diffuser element, a channel with an expanding cross-section area in the flow direction, was integrated into the micropump to replace the constant aspect ratio $(W/H)$ rectangular-shaped microchannels. Figure 5.11 compares the measured flow
rate/backpressure characteristics of a micropump with constant width microchannels and one incorporating diffuser elements. Both pumps were driven at voltage of 100 V_{pp} and frequency of 100 Hz. The straight channels in the first micropump are formed with a uniform width of 750 µm and diffuser elements in the other micropump are tapered from a width of 200 µm at the entrance to a width of 750 µm at the exit (Figure 5.5).

Figure 5.5 Effect of microchannel geometry on flow rate–backpressure characteristics of the micropump - planar diffuser elements.

The experimental results demonstrate that the pump with straight channels yielded a higher maximum flow rate than the pump using diffuser elements. However, flow rates of the diffuser pump showed reduced dependence on the backpressure. Consequently, the extrapolated maximum back pressure of the diffuser-type micropump is about 1.75 kPa.
which is significantly higher than that of straight-channel micropump. The lower maximum flow rates and higher maximum backpressure of the micropump with diffuser elements can be explained by considering the pressure drop across the diffuser element. The pressure drop $\Delta P$ in the positive diffuser direction is determined by the fluid density, flow velocity, and the pressure loss coefficient. The net maximum volumetric flow rate $Q_{\text{max}}$ at zero backpressure can be written as [216]:

$$Q_{\text{max}} = 2 f V_o \left( \frac{\eta^2 - 1}{\eta^2 + 1} \right)$$

where $f$ is the actuation frequency, $V_o$ is the stroke volume, and the diffuser element efficiency ratio $\eta$, defined as the ratio of pressure loss coefficient in the diffuser direction $\xi_d$ to the one in the nozzle direction $\xi_n$, which is only determined by the diffuser geometry [328]. $\eta$ ranges from 1 to 5 in common diffuser structures, making the last term $(\eta^{1/2} - 1)/(\eta^{1/2} + 1)$ of the above equation less than 1. Therefore, the maximum flow rate of diffuser type micropump is expected to be less than the pump using straight channels (where $Q_{\text{max}}$ is estimated to be $2 f V_o$). However, when integrating diffuser elements into the peristaltic micropump, an additional valving effect is added to the system which makes the flow rate is less sensitive to the backpressure. The diffuser element has the ability to increase the static pressure in the nozzle direction, which is considered to be the reason for the increase of the blocking pressure [329]. The resulting effect of adding diffuser elements into the developed peristaltic micropump is the increase of the maximum backpressure at the expense of the reduction of flow rate and the characteristic of the bidirectional flow.
**Channel aspect ratio (W/H)**

The microchannel geometry has a direct impact on the pressure driven liquid flow in MEMS involving fluid transport [330]. In this study, the relationship between flow rate and backpressure of the micropumps with different microchannel aspect ratios (W/H) was characterized at a driving voltage of 100 V\textsubscript{pp}, as shown in Figure 5.11.

![Figure 5.6 Effect of microchannel geometry on flow rate–backpressure characteristics of the micropump - straight microchannel in various aspect ratios.](image)

It was observed that the maximum flow rate increases significantly as the microchannel aspect ratio increases while the blocking pressure is also slightly improved. Performance of the pump with aspect ratio of 3 exceeds other pumps showing a
maximum flow rate of 630 µl/min with a maximum backpressure of 1.55 kPa. The experimental results can be explained by the analysis of liquid flow conditions in microchannels. The flow inside the peristaltic pump is directly related to the pressure differential generated by the vibrating motion of pump chambers. Meanwhile, the surface forces working on the boundary between channel walls and fluids are important in microchannel flow due to the large surface-to-volume ratio [331]. The relationship between pressure difference $\Delta P$ and volumetric flow rate $Q$ can be expressed in the following formula [190]:

$$\frac{\Delta P}{Q} = \frac{C_{fr} L \mu}{2AD_h^2}$$

where $C_{fr}$ is the friction coefficient which only depends on the channel shape, $L$ is the length of the channel, $\mu$ is the viscosity of the fluid, $A$ is the cross-sectional area of the channel, and $D_h$ is the hydraulic diameter. In our experiment the pressure difference is considered to be constant when the bimorph actuators are actuated on the same conditions because the same stroke volume is generated in each pump chamber. Therefore, the difference of volumetric flow rate is dependent on the cross-sectional area of the channel and hydraulic diameter. The channel with higher aspect ratios shows larger cross-section area and hydraulic diameter, yielding a higher flow rate in the micropump. However, this analysis only considers the static pressure difference across the micropump. Further investigation on the dynamic differential pressure and the interaction between reciprocating membranes and the working fluid would provide a more insightful understanding for the effects of using different microchannel aspect ratios ($W/H$) on the pumping performance.
5.5 Conclusions

A package-level peristaltic piezoelectric micropump was designed and fabricated in utilizing multilayer ceramic (MLC) technology. The device was fabricated using commercially available LTCC materials and a custom designed low-fire PZT-SKN piezoelectric ceramic composition. A single co-fire LTCC process was used to prepare the micropump structure including piezoelectric bimorph actuators on the both sides of the pump chambers. FEM simulation results suggested an optimum radius to thickness \( (R/\theta) \) ratio of about 240 for the largest membrane displacement of bimorph actuator. However, the \( R \) and the \( \theta \) of the sintered bimorph membranes were \( \sim5 \) mm and 100 \( \mu \)m respectively, which were limited by the fabrication capabilities and durability concerns. Using control signals at frequency of 100 Hz with phase difference of 120° was experimentally determined for optimum pumping performance. The Initial micropump when operated at the voltage of 100 V_{pp} and frequency of 100 Hz, generated a maximum flow rate of up to 450 µl/min with a maximum backpressure of 1.4 kPa. It was shown that using diffuser elements instead of straight channels to connect pump chambers could increase the maximum backpressure at the expense of flow rate and the bidirectional flow capability. Micropumps with different microchannel aspect ratios \( (W/H) \) were also compared with respect to flow rate and backpressure. It was determined that the micropump at the aspect ratio of 3 exceeded other pumps in maximum flow rate (630 µl/min) with a limited enhancement of maximum backpressure (1.55 kPa).

One of the most attractive characteristics of the developed multilayer LTCC/PZT-SKN micropump is the capability of providing efficient flow in a compact ceramic
package compared to other valveless reciprocating pumps and continuous flow pumps fabricated using silicon, glass, or polymer. The self-pump frequency $f_{sp}$, defined as the ratio of maximum flow rate $Q_{\text{max}}$ and the package size $S_p$ [202], is used to characterize the effectiveness of the pumping. Figure 5.13 compares the LTCC/PZT-SKN micropump realized in this work with some other reported pumps in terms of $f_{sp}$ and $S_p$ (For $S_p$ not provided explicitly, an estimated value is calculated from the image with known dimensions).

Figure 5.7 Comparison of fabricated multilayer LTCC/PZT-SKN micropump with several reported micropumps based on the self-pump frequency $f_{sp}$ and the package size $S_p$. 

![Comparison of fabricated multilayer LTCC/PZT-SKN micropump with several reported micropumps based on the self-pump frequency $f_{sp}$ and the package size $S_p$.](image)
As illustrated in Figure 5.13, our proposed multilayer ceramic micropump demonstrates a higher $f_{sp}$ than the most of other valveless reciprocating pumps, with a competitive $S_p$ in that category of micropump. Although most of examined continuous flow pumps are more compact, the lower self-pumping frequency is not comparable to the developed LTCC/PZT-SKN micropump. The two pumps, showing higher $f_{sp}$ in a smaller $S_p$ than the present micropump, are both fabricated using Si materials and associated processing techniques. However, LTCC material systems provide excellent thermomechanical and chemical stability compared to the MEMS devices and systems built in Si materials, making those more suitable for applications in a corrosive circumstance involving high-temperature and high-voltage.

Another appealing part of present micropump over other pumps developed is the use of LTCC-process compatible fabrication techniques which enable the direct patterning and integration of piezoelectrically actuated membranes into LTCC microfluidic substrate materials in a single assembly and high temperature firing process. Furthermore, many functional microfluidic devices have already been fabricated using LTCC materials and technology by taking advantage of its versatility; therefore, the resulting micropump can be easily integrated into LTCC-based lab-on-chip microfluidic systems at the package-level, providing efficient on-chip fluid control and transport for the potential applications in chemical analysis and synthesis, biological sensing, and environmental monitoring.
Chapter 6. Summary and future work

6.1 Summary

The current chapter reviews the main research methodologies and results presented in this thesis. Specifically, the development of a low temperature sinterable PZT-SKN piezoelectric ceramic, detailed investigation of co-firing behavior of the developed PZT-SKN material with commercial LTCC materials, and the production of an LTCC-based piezoelectric micropump corresponding to the contents of chapters 3, 4, and 5 respectively. The discussion of the major contributions and potential impacts of this study on development of high performance LTCC-based piezoelectric devices for microfluidics is also included at the end of each section.

6.1.1 Low temperature sintering and properties of fluxed PZT-SKN ceramics

Low temperature sinterable Pb(Zr_{0.53}, Ti_{0.47})O_{3}-Sr(K_{0.25}, Nb_{0.75})O_{3} (PZT-SKN) ceramics have been synthesized and optimized with respect to microstructures, dielectric, and piezoelectric properties. 0.98PZT-0.02SKN ceramics were prepared through conventional solid-state route using high purity metal oxides and carbonates as starting materials. Various amounts and types of sintering aids were added to the PZT-SKN system in order to lower the sintering temperature (~1250°C) and accelerate densification process. It was found that the addition of 6 wt% LiBiO_{2} or 1 wt% LiBiO_{2} + 1 wt% CuO can reduce the sintering temperature by 300°-350°C through the liquid-phase sintering process.
The maximum density achieved for 1 wt% LiBiO₂ + 1 wt% CuO added ceramics was 7.75 g/cm³ (~97.6% of theoretical density) when sintered at 900°C. While the maximum density for 6 wt% LiBiO₂ added ceramics when sintered at 950°C was 7.65 g/cm³ (~96.3% of theoretical density). The dielectric and piezoelectric properties of flux-sintered 0.98PZT-0.02SKN ceramics are also influenced by the addition of fluxes compared to the conventionally sintered samples. The high temperature dielectric measurement revealed that the Curie temperature $T_c$ decreased from 357°C for unfluxed ceramics to 302°C for 6 wt% LiBiO₂ fluxed samples and to 351°C for 1 wt% LiBiO₂ + 1 wt% CuO fluxed samples. Additionally, a lower and broader permittivity peak was observed for flux-sintered 0.98PZT-0.02SKN ceramics. The $P$-$E$ hysteresis loops demonstrated that both remnant polarization $P_r$ and coercive field $E_c$ decreased for flux-sintered samples.

Reduced grain size relative to the high-temperature sintered 0.98PZT-0.02SKN ceramics has been associated with observed decrease in piezoelectric properties. However, the desirable overall properties with high field $d_{33}$ piezoelectric coefficient of 415 pm/V, Curie temperature $T_c$ of around 351°C, dielectric constant $\varepsilon_r$ of 1235, and planar coupling factor $k_p$ of 0.54 were obtained for the PZT-SKN system with addition of 1 wt% LiBiO₂ + 1 wt% CuO content sintered at 900°C for 1 h.

The first significant impact of work presented in this thesis is the development of a low fire PZT-SKN ceramic with desirable properties and compatibility with LTCC material systems. The processing conditions and piezoelectric properties of other reported low fire PZT-based ceramics have not shown the promising results for co-firing with LTCC materials. Several other PZT-based systems have been shown the capability to be
sintered to high density at temperatures of <1000°C for short time <1 h. However, utilizing these low fire ceramics in the fabrication of multilayer piezoelectric actuators with LTCC materials is limited by either the low $d_{33}$ values (~200 pm/V) or the relatively high sintering temperature (950°C). The developed 0.98PZT-0.02SKN ceramics with 1 wt% LiBiO$_2$ + 1 wt% CuO addition can be densified at 900°C for 1 h, showing a favorable dielectric and piezoelectric properties. The low sintering temperature and short soaking time for LiBiO$_2$ and CuO fluxed 0.98PZT-0.02SKN ceramics make it possible to co-fire with LTCC materials for the multilayer actuator applications. Additionally, the high Curie temperature $T_c$ (>350°C) of developed low fire PZT-SKN ceramic compared with other reported fluxed PZT-based ceramics is suitable for applications over a broad temperature range.

6.1.2 Sintering behaviors and properties of co-fired LTCC/PZT-SKN multilayer ceramics

Based on the above low-temperature sintering study, PZT-SKN ceramics fluxed with 1 wt% LiBiO$_2$ + 1 wt% CuO were selected to investigate co-firing with commercial LTCC materials. Fluxed PZT-SKN tapes were prepared using tape casting technique. A castable slurry consisting of ceramic powders and organic binder vehicle was mixed, degassed, and cast on the moving Mylar substrate using a bench-top tape caster. The composition of slurry (ceramic powder, solvent, and various organic additives) was carefully optimized to balance the viscosity of mixture as well as the strength and flexibility of cast PZT-SKN tape.
The master sintering curve (MSC) approach has been applied to understand and predict the sintering behaviors of LTCC tapes and fluxed PZT-SKN ceramics. It was assumed that the microstructural evolution of a powder compact is only a function of density and that only one sintering mechanism controls the sintering process in MSC theory. The MSC curves were constructed using measured density data obtained under constant heating rate experiment and the best determined apparent activation energy $Q_a$. The $Q_a$ of 268, 415, and 540 kJ/mol were obtained for fluxed PZT-SKN, HL2000, and CT2000 tapes, respectively. The different range of $Q_a$ values demonstrates the different sintering mechanisms for fluxed PZT-SKN ceramics (liquid-phase sintering) and LTCC materials (viscous-flow controlled sintering). However, using MSC the analysis of the sintering behaviors for LTCC and fluxed PZT-SKN ceramics an optimized sintering profile was obtained.

The fluxed PZT-SKN tapes were laminated with several commercially available LTCC tapes in a sandwich structure and co-fired using the optimized sintering profile. After co-firing the HL2000/PZT-SKN laminates exhibited a flat multilayer ceramic structure when compared to other the LTCC/PZT-SKN combinations explored. The self-constrained densification characteristic of the HL2000 tapes was considered to have a significant beneficial effect on reducing the camber development. The microstructure and elemental composition near the co-fired HL2000/PZT-SKN interfaces were analyzed using EDS. The results indicated limited inter-diffusion of Pb (from PZT-SKN to LTCC layer) and Al, Ca, Si (on the opposite direction) near the heterogeneous interface. Further, nearly pure PZT-SKN composition was observed at the center of piezoelectric layer.
Additionally, measurement of dielectric and piezoelectric properties of fluxed PZT-SKN ceramics co-fired with different LTCC materials at 870°C for 1 h indicated that the HL2000/PZT-SKN samples exhibited the best overall properties among all samples examined. The dielectric constant $\varepsilon_r$ of 1205 and low field $d_{33}$ piezoelectric coefficient of 240 pm/V showed only a moderate reduction compared with free standing flux-sintered PZT-SKN tapes. To demonstrate the device performance and potential applications of co-fired LTCC/PZT-SKN structures, a compact piezoelectric microbalance was fabricated. The mass sensitivity of the balance was experimentally determined to be 15 kHz/mg. FEM simulation results suggest that a thinner piezoelectric layer with a smaller diameter at fixed diameter/thickness ratio would provide higher mass sensitivity.

In the above section, compatible materials and processing methods for co-firing LTCC/PZT-SKN multilayer ceramics have been developed and reported for the very first time. Prior studies had focused on screen printing PZT-based thick films on the pre-sintered LTCC or alumina substrates and using additional firing steps to sinter the PZT layers. An optimized sintering profile has been constructed for co-firing LTCC materials and the developed low fire PZT-SKN ceramics by application of the master sintering curve (MSC) approach. The dielectric properties and $T_c$ were the same for both co-fired LTCC/PZT-SKN and free standing low fire PZT-SKN materials. The resultant piezoelectric properties are among the highest reported for thick-film piezoelectric multilayers integrated with or onto an inactive substrate by any fabrication method, as listed in Table 6.1. The large observed piezoelectric properties of the current co-fired LTCC/PZT-SKN laminates and relative simplicity of the co-firing scheme suggest
significant benefits and improved commercial relevance over previously reported attempts.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sintering aids</th>
<th>Sintering condition</th>
<th>ε</th>
<th>$d_{33}^{\text{low}}$ (pm/V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-SKN on LTCC</td>
<td>1wt% LiBiO$_2$ + 1wt% CuO</td>
<td>co-fired, 900°C, 1 h</td>
<td>1200</td>
<td>255</td>
<td>—</td>
</tr>
<tr>
<td>PZT (53/47) on LTCC</td>
<td>2 wt% Pb$_5$Ge$<em>3$O$</em>{11}$</td>
<td>post-fired 850°C, 1 h</td>
<td>190</td>
<td>—</td>
<td>[148]</td>
</tr>
<tr>
<td>PZT (53/47) on LTCC</td>
<td>2 wt% Pb$_5$Ge$<em>3$O$</em>{11}$</td>
<td>post-fired 875°C, 15 min</td>
<td>225</td>
<td>55</td>
<td>[149]</td>
</tr>
<tr>
<td>PZT (53/47) on alumina</td>
<td>2 wt% Pb$_5$Ge$<em>3$O$</em>{11}$</td>
<td>post-fired 850°C, 15 min</td>
<td>445</td>
<td>120</td>
<td>[150]</td>
</tr>
</tbody>
</table>

6.1.3 Development and optimization of multilayered LTCC/PZT-SKN piezoelectric micropumps

A multilayered LTCC/PZT-SKN piezoelectric micropump has been designed and fabricated using the materials and processing methods presented above. The micropump was fabricated using standard LTCC thick-film technology. LTCC structural layers defining the fluidic network components were integrated with PZT-SKN tapes providing the electromechanical actuation. A single co-firing process was applied to the LTCC/PZT-SKN micropump body and screen printed conductive patterns. The overall package size of this developed micropump is about 1 cm$^3$. The peristaltic pumping action was generated using 3 pairs of bimorph actuators located on both the top and bottom of each of 3 microchambers arranged in series. The pumping performance was optimized
using FEM tools and the expected maximum flow rate was calculated using simulation results and an analytical equation.

The characterization of pumping performance on the initially designed micropump indicated that using control signals at frequency of 100 Hz with phase difference of 120° between successive pump chambers resulted in efficient and reliable pumping. Experimental results demonstrated that the volumetric flow rate decreased linearly as backpressure increased. A maximum flow rate (at zero backpressure) up to 450 µl/min and a blocking pressure (at zero flow rate) of 1.4 kPa were observed on the micropump when operated at the voltage of 100 V_{pp} and frequency of 100 Hz. The operating frequency was confined at 100 Hz to avoid the cavitation and prolong the lifetime of micropump.

An approach for enhancing the pumping performance integrated planar diffuser elements to replace the straight microchannels connecting the pump chambers. The diffuser-type micropump exhibited a higher maximum backpressure due to the additional valving effect resulting in a flow rate which was less sensitive to backpressure. However, this increase of maximum backpressure was realized at the expense of flow rate and bidirectional flow characteristics.

In order to optimize the pumping performance micropumps with channel of different aspect ratio (W/H) were fabricated, the maximum flow rates and backpressures compared. The microchannel with higher aspect ratio led to a lower flow resistance at the constant backpressure, yielding a higher flow rate. The performance of micropump with
the largest aspect ratio showed the highest no load flow rate of 630 µl/min and the largest blocking pressure of 1.55 kPa.

In this section a compact “package-level” peristaltic piezoelectric micropump has been realized using co-firable piezoelectric ceramics and commercially accepted processing methods. The realized multilayer ceramic micropump has unique characteristics. The use of LTCC compatible fabrication methods allows the direct patterning and integration of piezoelectric drivers into LTCC-based microfluidic structures. Further, the developed micropump shows the possibility to be integrated into LTCC-based LOC microfluidic systems at the package-level, providing efficient on-chip fluid transport and control for a wide range of potential applications. The incorporation of LTCC with fluxed PZT-SKN materials provides direct integration of piezoelectric actuators, fluidic networks, and electronic interconnects into one single ceramic module using LTCC thick-film fabrication processing.

6.2 Future work

Incorporating functional elements (e.g. piezoelectrics, dielectrics, ferrites, and conductors) into LTCC-based MEMS structures for the fabrication of highly integrated microfluidic devices and systems has attracted much attention from both ceramists and chemists [16-18]. The work described in this thesis primarily investigates the integration of a developed low fire piezoelectric PZT-SKN ceramic with commercial LTCC substrate materials and the implementation of a piezoelectric micropump using the co-fired LTCC/PZT-SKN multilayer structure. In addition to the research efforts covered in the current work it is suggested that further studies can be conducted on the following
areas. First, improved understanding of the stress development during co-firing of the LTCC/PZT-SKN multilayer ceramics would help to analyze the densification behavior of the piezoelectric layer and reduce the potential processing defects. Second, there is a need to further optimize micropump performance including increasing maximum flow rate and backpressure for broadening the application areas of the demonstrated micropump structure. Finally, future attempts to integrate the developed LTCC-based piezoelectric micropump with other compatible fluidic components and electronic control circuits are expected to fully take advantage of the multifunctional capabilities and miniaturization possible using LTCC technology.

6.2.1 Investigation of stress development

As discussed in chapter 4, LTCC tapes were laminated and co-fired with low fire PZT-SKN layers to build the multilayer ceramics for microdevice development. The different sintering behaviors between LTCC and PZT-SKN layers induced both shear and in-plane tensile stresses in the ceramics. These contribute to the occurrence of delamination, camber, cracking, and other defects. However, using self-constrained LTCC tapes (HL2000) and a compatible co-firing profile for LTCC/PZT-SKN multilayer ceramics have been demonstrated. This approach resulted in a flat uniform multilayer module in a comparatively large size (compared to other tested commercial LTCC materials). However, the densification behavior of PZT-SKN ceramic is affected by the constrained HL2000 layers. The further research work to understand the sintering behavior and stress development of PZT-SKN layer under constrained sintering would help optimize the multilayer design (e.g. thickness of each component layer) and control the potential processing defects.
In other reported work [188,319,335] both linear regression analysis and the analytical modeling are used to calculate strain and stress distribution in the co-fired multilayer ceramics particularly in the densifying layer between the constraining LTCC layers. The relationship between linear shrinkage $\Delta L/L_o$ in the $x$-$y$ dimensions and temperature $T$ can be described as follows:

$$\frac{\partial (\Delta L/L_o)}{\partial T} = \sum_{i=0}^{i} a_i T^i$$

Application of this method would require numbers of measurements in order to determine the parameters $a_i$ of fitting equation for each sintering profile. Therefore, tremendous experiment work is needed, leading to a significant consumption of time and energy. An example analysis based on this method is shown in Figure 6.1(a). Both a typical morphology of the densifying layer after constrained sintering and the calculated stress distribution are presented. Similar experimental results were observed in the co-fired LTCC/PZT-SKN multilayer ceramics, as shown in Figure 6.1(b).

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Figure 6.1 (a) Morphology of polished microstructure of low-temperature co-firable glass-ceramic system under constrained sintering (taken from S.Y. Tzeng et al. [319]); and (b) observed microstructure of co-fired HL2000/PZT-SKN multilayer structure.

Using the results of master sintering curve (MSC) studies on LTCC and PZT-SKN materials introduced in chapter 4 the relationship between $\Delta L/L_o$ and $T$ can be determined for arbitrary sintering profiles based on the constructed MSC fitting equation:

$$\rho = \rho_o + \frac{a}{[1 + \exp(-\log(\Theta) - \log(\Theta_o))]}^c$$

For isotropic shrinkage the densification rate can be converted to the linear shrinkage rate by the following:

$$- \frac{dL}{L_o dt} = \frac{d\rho}{3\rho_o dt}$$

Once the sintering profile $T(t)$ is determined the $\log(\Theta)$ can be calculated and subsequently a function for $(\Delta L/L_o)$ and $T$ will be constructed. Incorporating this function
into a FEM modeling program (e.g. COMSOL® Multiphysics) would provide a more practical and effective means to analyze the strain and stress distribution in the co-fired PZT-SKN layer without the need of tedious experiment and calculation.

6.2.2 Further optimization of micropump design

Micropumps designed and used for different applications should have suitable features. For example, the high blocking pressure capabilities and pressure-independent flow rates could be important characteristics for micropumps required in drug delivery systems. In such an application high precision liquid drug dosing is required. In the case of IV delivery pumping must be achieved against the high backpressure encountered in vivo (~16 kPa) [336,337]. Tolerance to gas bubbles would also be desired when pumping a gas-liquid mixture [200]. The overall package size, pumping reliability, power consumption, manufacturing cost, and material biocompatibility are also critical issues [202]. To achieve better pumping performance (e.g. high backpressure, self-priming, and bubble-tolerance) and broaden the application area further optimization of currently developed LTCC/PZT-SKN micropump is required. Preliminary FEM simulation results suggest that modifying the electrode geometry of the bimorph actuators would increase the deflection of the pump membrane at comparable electric drive conditions and could subsequently enhance the pumping.

In the initial micropump design the conductor ink is screen printed on the entire exposed area of the bimorph actuator. Figure 6.2 illustrates the two modified electrode structures. In the first the electrode is only applied in the central region of the PZT-SKN
membrane as shown in structure (a). Alternatively, a doughnut shaped electrode could be applied as shown in structure (b).

The ratio of the electrode radius over the entire pump radius ($r/R$) has been optimized using FEM simulations. The deflection of a bimorph actuator with radius $R$ of 5 mm and thickness $\theta$ of 20 µm with various electrode geometries was studied. Figure 6.2 demonstrates the variation of maximum displacement $d_{\text{max}}$ as a function of electrode areas ($r/R$) for the two types of electrode structures. An optimum $r/R$ ratio of 0.5 is determined where the peak $d_{\text{max}}$ is obtained for both electrode geometries. The electrode in structure (a) yields larger $d_{\text{max}}$ than the electrode in structure (b) at $r/R$ ratio of 0.5. The $d_{\text{max}}$ of membrane with both types of modified electrode patterns is more than 40 times higher than that of membrane with full electrode as originally fabricated.

![Figure 6.2 Effect of electrode pattern on bimorph membrane deflection](image-url)

Figure 6.2 Effect of electrode pattern on bimorph membrane deflection
Two bimorph structures with same radius of 5 mm and different thickness of 100 µm and 150 µm are designed and used in the FEM simulation, which are similar to the fabricated bimorph geometries. The modified electrode structure (a) with \( r/R = 0.5 \) is used. The dependency of \( d_{\text{max}} \) on the driving electric field (voltage) at the actuation frequency of 100 Hz for these two bimorphs is shown in Figure 6.3. The deflection response of the bimorph membrane to the driving electric field is linear. The 100 µm thick bimorph generates a larger \( d_{\text{max}} \) than the 150 µm thick one because the \( R/\theta \) ratio for the thinner bimorph is near to the optimum value (~240) predicted by the FEM simulation results (as discussed in chapter 5).

![Figure 6.3](image)

**Figure 6.3** FEM simulation results of maximum membrane displacement of bimorph with modified electrode geometry at different electric fields.
The volumetric deflection and the resulting flow rate of the micropump are directly related to the applied voltage at low frequency range which is much less than the resonant frequency of the bimorph actuator. Applying high voltage at the constant actuation frequency can increase the flow rate. However, the voltage must be set up in a proper range because of the limitation of electric field strength for piezoelectric materials. The simulation results indicate that the larger membrane displacement is achieved by using the optimized electrode pattern, which can potentially enable the higher volumetric flow rate and backpressure with less power consumption for the micropump. Future experiment should be conducted to validate simulation results.

There are several other effective approaches for micropump optimization which would provide additional functions to enhance the pumping performance or improve the characterization method. Increasing compression ratio of the micropump by increasing the stroke volume and reducing the dead volume of the fluid chamber is one of the applicable methods. In addition, changing the direction of microfluidic connection between tubing and the micropump body from perpendicular to horizontal can also reduce the pressure loss. Moreover, flow and pressure sensors are expected to be integrated in the fluidic conduit for precisely measuring the flow rate and backpressure in the pumping characterization experiment.

6.2.3 Integration of LTCC-based microfluidic systems

There is an increasing drive toward to multiple fluidic, electronic, and mechanical components into one single miniaturized chip [19,20]. The LTCC/PZT-SKN piezoelectric micropump presented in this work is implemented using the LTCC thick-
film technology. The capability of on-chip fluid delivery and control provided by the developed micropump is highly desirable for many microfluidic applications such as chemical sensing and synthesis as well as fast manipulation of biological samples. The realization of functional LTCC-based microfluidic systems with multiple components requires further investigation and experimental studies. There are two examples of microfluidic devices fabricated using LTCC materials and associated processing methods which demonstrate the possibility and necessity of being integrated with the developed LTCC-based micropump.

A LTCC-based microfluidic reactor is designed and fabricated to provide improved control of polymerization process [338]. The designed reactor utilizes three streams of co-laminar flow to allow for the controlled introduction of reactant solutions into the reaction channel. The schematic diagram of desired reaction in microchannels is shown in Figure 6.4(a).

![Figure 6.4](image_url)

Figure 6.4  (a) Illustration of synthesis conditions via co-laminar flow in a LTCC-based microfluidic reactor; and (b) experimental setup for chemical reactions in the microchannel by laminar diffusion.
Previous experimental attempts used syringes and multiple external syringe pumps for infusing the reagents, as shown in Figure 6.4(b). Extreme care was required in order to avoid air bubble generation when loading the reagent into the syringes and connecting the syringes to the microreactor. In addition, the compatibility between the solvent and the materials used for connector/tubing/syringe/adhesive was also a critical issue. Using the LTCC/PZT-SKN micropump would help provide more efficient and accurate control of reagent pumping for the desired chemical synthesis if integrated with this LTCC-based micromixer, which exclude the need of external pumps and additional syringes not only saving the sample preparation time but also increasing the reliability of experimental results.

The other example is a cell culture platform built using an LTCC substrate [339]. Multiple cell culture wells with silver or gold electrodes are fabricated in one single LTCC-based microfluidic chip. The microchip design and electrical measurement methods are illustrated in Figure 6.5(a). The experimental setup is shown in Figure 6.5(b). On-chip transportation of cell samples achieved by valveless reciprocating micropumps is demonstrated as a practical and appropriate method for cellomics [340]. The pumping action has a minimal effect on the cell viability and proliferation. Incorporating the developed LTCC/PZT-SKN micropump into the microfluidic chip made by the same LTCC materials and fabrication techniques would provide a safe and reliable pumping of living cells with a suitable flow rate range.
As discussed in chapter 2, LTCC technology is a promising alternative to Si materials and micromachining techniques for combining microfluidic and electronic elements in one single substrate using the same fabrication methodology. The realization of a complete microanalysis system using developed individual components based on LTCC technology is the ultimate goal. A further development of highly integrated microfluidic systems requires the incorporation of an electronic control circuit into
microfluidic devices made on the same LTCC substrate. A conceptual illustration for the LTCC-based lab-on-a-chip system is shown in Figure 6.6. By completing this task, most of the sample processing steps (e.g. supply, pretreatment, and analysis) can be directly conducted in the on-chip level which results in not only the enhancement of portability but also the improvement of functionality.

![Diagram](image)

Figure 6.6  A proposed LTCC-based integrated microfluidic system
6.3 Conclusions

The aim of this research is the development of a high performance low fire piezoelectric ceramic, fabrication methods which are compatible with LTCC materials and processing techniques, and demonstration of an integrated piezoelectric micropump. It is suggested that further investigation on the stress development in the co-fired multilayer structure would help provide a better understanding on densification of PZT-SKN layer and more efforts on optimization of electrode design for micropump would be considered as an effective way to increase the micropump performance. Successful attempts on integrating the LTCC/PZT-SKN multilayer micropump with other fluidic devices and electronic components will lead to a significant progress on the development of a highly integrated LTCC-based microfluidic system.

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### Appendix

Properties of low-temperature sintered PZT-SKN ceramics with various sintering aid additions

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sintering Temperature</th>
<th>Density (g/cm³)</th>
<th>$\varepsilon_r$ (1kHz)</th>
<th>$\tan\delta$ (1kHz)</th>
<th>$d_{33}^{\text{high}}$ (pm/V)</th>
<th>$E_c$ (kV/cm)</th>
<th>$P_t$ (C/m²)</th>
<th>$T_c$ (°C)</th>
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</thead>
<tbody>
<tr>
<td>PZT-SKN + 6wt% LiBiO₂</td>
<td>850°C</td>
<td>7.42</td>
<td>1130</td>
<td>0.035</td>
<td>306</td>
<td>14.5</td>
<td>0.20</td>
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<td>324</td>
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<td>1222</td>
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<td>360</td>
<td>14.5</td>
<td>0.31</td>
<td>302</td>
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<tr>
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<td>1000°C</td>
<td>7.62</td>
<td>1155</td>
<td>0.040</td>
<td>334</td>
<td>15.2</td>
<td>0.32</td>
<td>300</td>
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<tr>
<td>PZT-SKN + 3wt% LiBiO₂</td>
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<td>820</td>
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<td>91</td>
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</table>
(continued) Properties of low-temperature sintered PZT-SKN ceramics with various sintering aid additions

<table>
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<tr>
<th>Composition</th>
<th>Sintering Temperature</th>
<th>Density (g/cm³)</th>
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<th>tan$\delta$ (1kHz)</th>
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References


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Vita

Name:  WENLI ZHANG

Date of birth:  July 11, 1981  Place of birth:  Beijing, China

Educational institutions attended and degrees already awarded:

- Master of Engineering, Materials Physics and Chemistry, Beijing University of Technology, Beijing, China, July 2006
- Bachelor of Engineering, Materials Science and Engineering, Beijing University of Technology, Beijing, China, July 2003

Professional positions held:

- Research Assistant, University of Kentucky, Jun. 2007 — present
- Teaching Assistant, University of Kentucky, Aug. 2006 — May 2007

Scholastic and professional honors:

- Winner for Student Poster Competition Award
  2010 U.S. Navy Workshop on Acoustic Transduction Materials and Device, May 2010
- Research Challenge Trust Fund I Fellowship
  University of Kentucky, June 2007 — June 2008

Professional publications:


