ABSTRACT

Conventional methods for fabricating ultrasound imaging transducer arrays, especially for high frequency range (>20 MHz), are expensive, time consuming and limited to relatively simple geometries. In this paper, the development of an additive manufacturing (AM) process based on digital micromirror devices (DMDs) is presented for the fabrication of piezoelectric devices such as ultrasound transducer arrays. Both green-part fabrication and the sintering of fabricated green-parts have been studied. A novel two-channel design in the bottom-up projection system is presented to address the piezocomposite fabrication challenges including a small curing depth and viscous ceramic slurry recoating. A prototype system has been developed for the fabrication of green-parts with complex shapes and small features. Based on the fabricated green-parts, the challenges in the sintering process for achieving desired functionality are discussed. Various approaches for increasing the density of sintered components are presented. Dielectric and piezoelectric properties of the fabricated samples are measured and compared with those of bulk PZT samples. Based on the identified challenges in the DMD-based AM process, future work for achieving fully functional piezoelectric ceramic components is discussed.

KEYWORDS
Additive manufacturing, ultrasound transducer arrays, mask image projection, piezocomposite fabrication

1 INTRODUCTION

Ultrasonic imaging is an important medical imaging technique. Since ultrasound poses no known risks to patients, the technology has become one of the most widely used diagnostic tools in modern medicine [1]. As shown in Figure 1.a, an ultrasound probe is required in an ultrasonic imaging system. One of the core components of the ultrasound probe is a transducer array, which can produce mechanical energy in response to electrical signals, and conversely, produce electrical signals in response to mechanical stimulus. The ultrasound transducer array in the probe is generally made of a piezoelectric ceramic material such as lead zirconate titanate (PZT). Due to high bandwidth, fast response, high sensitivity, and other advantages, the piezoelectric device can send an ultrasound, and accordingly detect and visualize muscles, tendons, and many internal organs.

Recent developments on ultrasonic imaging have focused on improving the performance of 1-3 ceramic/polymer composites, which have been shown to offer improved sensitivity and better acoustic matching to the human body [1]. Obtaining high frequency resonance in these devices requires control and reduction of the composites spatial scale [2]. An example of a transducer array based on 1-3 composites is shown in Figure 1.d. In addition, new ideas based on aperiodic and non-rectangular array shapes have been developed in the latest ultrasound transducer design. One of such design examples is shown in Figure 1.e, where a hexagonal pattern is used [3]. Such a design is found to have less lateral mode...
coupling, hence better acoustic efficiency. However, an ultrasound transducer array with complex array shapes and small dimensions poses significant challenges on its fabrication. Current manufacturing methods such as the dice-and-fill technique have become increasingly difficult in fabricating such piezoelectric components. To address such a challenge, we investigated the fabrication of piezoelectric ceramic components using additive manufacturing processes. A mask-image-projection based additive manufacturing process was developed. Its capability in achieving the desired dimensional and functional characteristics was measured and related challenges were identified.

![Image](https://via.placeholder.com/150)

**Figure 1:** An illustration of ultrasound transducers in an ultrasound system.

### 1.1 Related Work

Current approaches on fabricating piezoelectric components are mainly based on a machining approach. The main steps of the approach are shown in Figure 2.a. Functional ceramics are first built in bulk and geometries are then added by a machining process such as dice-and-fill techniques [4, 5]. However, cutting bulk piezoelectric materials becomes more difficult as current trends on piezoelectric component design require more complex geometries to enhance their performance [6]. A precise dicing saw machine will limit the feature resolution and geometry complexity of small features in such a component. Other machining processes such as laser dicing techniques [7, 8] have also been developed. However, the ablation side effects and conic shape of the ceramic array have also been observed, which will affect the piezoelectric performance.

Another approach of fabricating piezoelectric components is based on molding and additive manufacturing (refer to Figure 2). In this approach, PZT slurry is first made by mixing PZT powders with various polymers and solutions in certain mixture ratios. Various techniques have been developed to define the desired geometry in green-parts. An example is composite micro molding and lost silicon molding techniques [9, 10], which consist of following steps: a silicon (or plastic) mold is first made using the LIGA (lithography, galvano-forming and plastic molding) process [11]; then the PZT slurry is casted into the mold; and finally the mold is removed after applying a high temperature. The lost silicon molding or injection molding processes follow similar steps [12, 13]. However, such methods are indirect processes with multiple steps and each step requires significant effort. Another example includes chemical vapor deposition (CVD) [14] and tape casting methods [15], which have been developed to directly deposit PZT atoms or very thin tapes on a semiconductor substrate. However, the resulted geometry in these methods is usually simple and would be difficult to control for more complex shapes.

During the last twenty-five years, many novel additive manufacturing (AM) processes such as Stereolithography (SLA), Selective Laser Sintering (SLS), and Fused Deposition Modeling (FDM) have been successfully developed and commercialized. The AM processes are generally flexible in fabricating a given digital model with good control on the resulting geometry. Recent advances in material, process, and machine development have enabled AM processes to evolve from prototyping usage to product manufacturing [16]. In the AM processes, various types of tools such as nozzles and lasers have been used in fabricating piezocomposites. For example, the fused deposition of ceramics [17, 18] and robocasting processes [19] can directly fabricate piezoceramics parts by extruding PZT slurry from a controlled nozzle. However, such processes have a limited resolution and building speed. Consequently they are not suitable for the fabrication of high frequency ultrasound transducer arrays. Several variations of stereolithography [20-23] have also been developed by using a highly focused laser beam to scan over the ceramic slurry. However, such processes are usually slow due to long scanning processes.

![Image](https://via.placeholder.com/150)

**Figure 2:** A comparison of piezoelectric component fabrication based on machining and AM processes.
The latest developments on digital devices such as Light Crystal Displays (LCDs) and Digital Micromirror Devices (DMDs) present powerful tools that can simultaneously and dynamically control the energy input of a projection image. Hence an AM process based on such digital devices can be much faster especially for complex shapes such as those required by ultrasound transducer arrays. Several research and commercial projection systems based on DMD have been developed [24-29]. However, most of the research focuses on the fabrication of photocurable polymers or structural ceramic such as alumina. In comparison, the ultrasound transducer arrays are built in functional ceramics, which require certain piezoelectricity properties in order to acquire ultrasonic images. Some previous work that considered PZT ceramics (e.g. [21]) only studied the green-part fabrication. The heat treatment procedure and related experimental data on the resulted piezoelectric properties are lacking. Such material property measurement of the fabricated components is crucial for understanding the capability of developed AM processes in piezocomposite fabrication.

1.2 Overview of Piezocomposites Fabrication based on Additive Manufacturing

As shown in Figure 2, the AM processes to fabricate ceramic components usually involve two main steps: (1) green-part fabrication to define part geometry; and (2) pyrolysis and sintering of green-parts to achieve fully functional components. We investigated the use of the DMD-based additive manufacturing process in fabricating piezoelectric ceramic components. A set of techniques including two-channel bottom-up projection and sol-gel infiltration have been developed for achieving feature size and piezoelectric property requirements in the ultrasound transducer array fabrication.

In the green-part fabrication process, an AM process needs to fabricate fine features such as a large number of pillars in various shapes (refer to Figure 1.d and e). Previous AM processes such as fused deposition of ceramics [17, 18] can only fabricate ceramic parts with a relative big features (e.g. >0.5mm). Other AM processes such as the SLA process [20-23] are relatively slow. The advent of the digital micromirror device overcomes both resolution and speed limitations. Accordingly an additive manufacturing process based on controlled mask image projection using a DMD has the potential to be a low-cost and high-speed manufacturing process for the green-part fabrication of high-frequency ultrasound transducer arrays. However, challenges such as limited curing depth and spreading viscous slurry into uniform thin layers need to be addressed in such a process.

The heat treatment of PZT green-parts with photocurable polymers and delicate features is challenging. Unlike structural ceramics, piezoelectric ceramics have additional requirements on material composition and density. For example, in the sintered PZT components, certain ratios of lead, zirconate, and titanate are required in the sintered PZT ceramics in order for the component to be functional. In addition, better cracking and distortion control is required in the heat treatment process for the delicate features in the green-parts. This is also different from the bulk material sintering in the machining approach as shown in Figure 2.(a). Various techniques such as sol-gel infiltration and mechanical hot pressing have been investigated in order to achieve satisfactory piezoelectric performance in the sintered components.

The remainder of the paper is organized as follows. The green-part fabrication using a DMD-based AM process is presented in Section 2. The pyrolysis and sintering process for fabricating functional PZT components is presented in Section 3. The measured material properties are also presented in the section. Finally conclusions with future work are presented in Section 4.

2 GREEN-PART FABRICATION USING A DMD-BASED ADDITIVE MANUFACTURING PROCESS

The performance of 1-3 ceramic/polymer composites array is highly related to the fabrication resolution such that the shapes and positions of the pillars are designed in the array can be well controlled. Thus, high-resolution feature is another challenge in ultrasound transducer fabrication.

The DMD-based AM process is quite similar to the SLA process except that it simultaneously and dynamically exposes the energy in whole area instead of a single small spot that is defined by a laser beam. In addition, piezocomposite slurry of photocurable resin and PZT powders is used in the process instead of liquid resin. An illustration of the process is shown in Figure 3.

The three-dimensional (3D) CAD model of an object is first sliced by a set of horizontal planes. Each slice is then converted into a two-dimensional (2D) mask image. The related mask images are then sent to a DMD and projected onto the slurry surface such that the composite slurry can be selectively cured to form the layer of the object. By repeating the process, 3D objects can be formed on a layer-by-layer basis. Since the original input is the 3D CAD model, this process can build arbitrary shape and has potential of building functional parts with complex shapes.

A DMD chip used in defining a projection image is composed of hundreds of thousands of micro mirrors. Thus this process can achieve a relatively high resolution for PZT
green-part fabrication. For example, using a DMD chip with 1024×768 micro mirrors, each pixel size is only 13.7µm for a platform size of 14mm×10.5mm. Techniques such as optimized pixel blending [30] and mask video projection [31] can be used in improving the resolution of the DMD-based AM process.

2.1 Curing Characteristics of PZT Slurry

The curing of photocurable resin follows the Beer-Lambert law of absorption, which can be formulated as follows [32].

\[ C_d = D_p \ln \left( \frac{E}{E_c} \right) \]  

(1)

\[ Q = \left( \frac{\Delta n}{n_0} \right)^2 \left( \frac{d}{\lambda} \right)^2 \]  

(2)

\[ \phi = 0.33 \text{ mm}, 100 \]  

(3)

Where \( d \) is the mean diameter of ceramic particles, \( \phi \) is the volume fraction of the PZT powder in the slurry, \( n_0 \) is the refractive index of the resin, \( \Delta n \) is the refractive difference between the PZT and the resin, and \( \lambda \) is the UV wavelength.

As can be seen from Equation (2) and (3), the cure depth is predominantly controlled by the square of the refractive index difference between the PZT particles and the resin. Experimental results also verified that the cure depth is proportional to the logarithm of exposure, inversely proportional to volume fraction of the PZT powder, and inversely proportional to the square of the refractive index difference between the ceramic powder and the medium.

Sun and Zhang [22, 34] performed a Monte Carlo simulations and related experimental studies on the ceramic micro fabrication. The result demonstrated that the fabricated line is wider in width and smaller in depth due to the scattering. A doping technique [22] was used to reduce the light scattering and consequently enhance the fabrication precision. For the PZT composite fabrication, it was also found that the strong scattering occurs at a high refractive index contrast between the particle and the resin, which also conforms well to the formulations in Equation (2) and (3).

Thus, in order to improve the performance of the PZT composite fabrication using the DMD-based AM process, several principles need to be followed. (1) It is desired to use PZT powder with lower refractive index. In our study, PZT 5H powders from Piezoelectric Technology Inc. (Indianapolis, IN) were used. (2) It is desired to reduce the volume ratio of the PZT powder in the slurry for the curing purpose. However, the reduced volume ratio of the PZT powder will also lead to a lower density in the sintered components. Hence a ratio that balances the curing requirement and piezoelectric property is required. (3) It is desired to have smaller PZT particle size in the slurry to reduce the scattering effect. The average particle size of commercially available PZT 5H powders is around 5µm. To achieve a larger cure depth, post-processing has been performed to reduce the PZT particle size in the slurry down to sub-micron level.

The PZT slurry used in our study is prepared as follows. The micron size Pb(Zr0.65Ti0.35)O3 powders (PZT 5H) are used with an average particle size of about 5 µm in spherical shape. The dielectric constant and piezoelectric coupling coefficient (kt) are 1,350 and 0.54, respectively. The PZT-5H powder (100 g) is milled with zirconia media (ZrO2 beads, φ= 0.33 mm, 100 g) in the presence of photocured resin (V-Flash F246 material, 3D Systems Inc., Rock Hill, SC) and IPA (isopropanol) solution (IPA 230 mL and dH2O 20 mL), using a Fritsch Pulverisette (Fritsch GmbH, Idar-Oberstein, Germany) milling machine at the room temperature using 200rpm for 24 hours. A mixture of PZT powder with ZrO2 beads is then washed by distilled water (dH2O). The particle size of the ground PZT powder is in the range of 220–430 nm. The average size is about 400 nm obtained by high-energy ball milling process. The particle size distribution yielded by this milling process is uniform and homogenous. The mass ratio of PZT powder, PZT solgel and photocurable resin is 0.95: 0.02: 0.03 in the PZT slurry.

In addition, another technique we used to address the penetration problem caused by high refractive index of ceramics in the PZT composite fabrication was to use an ultrafine layer thickness in the developed AM process, which is discussed below.

2.2 Bottom-up Projection for Slurry Recoating

Compared to photocurable resin, the curing depth of PZT slurry is reduced due to the light scattering on the PZT particles. Consequently, in the developed AM process, a smaller layer thickness is needed to accommodate the shorter curing depth. At the same time, the viscosity of PZT slurry is increased due to the added ceramics particles. Such a higher viscosity would pose significant challenge in the recoating of ceramic slurry into thinner layers for piezocomposite fabrication.

Typically, the DMD-based additive manufacturing systems have two projection approaches: (i) image projection from top down to a free liquid surface, and (ii) image projection from bottom up to a constrained surface. In the top-down projection approach (refer to Figure 3), the platform steps down for each layer. After the Z-movement of the platform, a sweeping system is then required to flatten the top surface in order to build the next layer. For liquid with small viscosity, a deep-dip recoating technique can also be used without using any...
the object to break or deform when the build platform moves up from the vat during the building process. Hence the photocurable resin can be guaranteed by ensuring the flatness of the bottom surface and the platform. (2) Much smaller layer thickness can be achieved since the gap size is only determined by the Z stage resolution regardless of the viscosity of ceramic slurry. (3) The cured layer is sandwiched between the previous layer and the vat. The constraining forces may reduce the part distortion in the curing process. (4) The curing of slurry is sealed from the vat. The constraining forces may reduce the part distortion in the curing process. Although such an approach was developed for photocurable resins, we tested the two-channel system design in the PZT composite fabrication. It was found the approach worked well for PZT slurry even though it has a higher viscosity. In addition, the X translation between the vat surface and the build platform that is required in the two-channel system is beneficial for spreading viscous PZT slurry into uniform thin layers. Based on such a slurry recoating approach, a higher ratio of the PZT powders can be added in the green-part fabrication. Consequently, the density of sintered PZT components increases which may lead to better piezoelectric performance.

Despite the advantages, the bottom-up projection based system has not been widely used in the SLA or DMD-based AM processes. A main reason is because the separation of the cured part from the tank surface is difficult. That is, in the bottom-up projection based process, a cured layer is sandwiched between the previous layer and the slurry vat. The solidified material may adhere strongly to the corresponding rigid or semi-rigid transparent solidification substrate, causing the object to break or deform when the build platform moves up from the vat during the building process.

One approach to conquer the attachment force is to increase the exposure to significantly over-cure the current layer such that its bonding force with the previous layer can be increased. However, over-curing can also lead to poor surface quality and inaccurate dimensions. Another approach to address the problem is to apply a certain type of coating to the resin vat so that the attachment force of a cured layer will be reduced. Suitable coatings, including Teflon and silicone films, can help the separation of the part from the vat [35, 36]. Even with the intermediate material, the separation force can still be large. Huang and Jiang [36] investigated the attachment force of photocurable resins on an elastic silicone film. Based on a developed on-line force monitoring system, test results indicate that the pulling force increases linearly with the size of the working area. Experiments indicate that, for a square of 60×60mm, the pulling force to separate the part from the film is greater than 60 N. Such a large attachment force between the cured layer and the vat is a key challenge that needs be addressed in the development of the bottom-up projection based AM process.

In our previous study for the multi-material fabrication using the DMD based AM process [37], a two-channel design was developed for the bottom-up projection system, which can significantly reduce the separation force in the building process. For the recoating and curing purpose, a bottom-up projection based system has several advantages over a top-down projection based system. (1) Recoating is achieved by constraining slurry between the previously cured layers and the slurry tank. Hence no additional sweeping is needed for flattening the slurry surface. The accurate and uniform layers can be guaranteed by ensuring the flatness of the bottom surface and the platform. (2) Much smaller layer thickness can be achieved since the gap size is only determined by the Z stage resolution regardless of the viscosity of ceramic slurry. (3) The cured layer is sandwiched between the previous layer and the vat. The constraining forces may reduce the part distortion in the curing process. (4) The curing of slurry is sealed from the oxygen-rich environment. Hence the photocurable resin can be cured faster by eliminating the oxygen inhibition effect.

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The PZT slurry recoating approach developed in our DMD-based AM process is shown in Figure 4. A transparent Polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) film is first applied on half of the bottom surface of a transparent glass vat. Hence the resin vat is divided into two channels, with and without the PDMS film. A mask image is exposed for PZT slurry recoating. Note that the coated PDMS film can form a very thin oxygen-aided inhibition layer (~2.5 μm) due to its ability of inhibiting free-radical polymerization near its surface [38]. The attaching force can thus be reduced since the cured layer is prevented from attaching to the PDMS film.

As shown in Figure 4.(a), after a layer is cured at Position (1), the vat is moved along the X axis such that the part is moved to the channel without PDMS (i.e. Position 2). Hence the large suction force between the cured layer and the PDMS film would be avoided. If the PDMS film is thick enough, the
part would be easily separated from the vat. After moving the part up by a certain distance $d$ (position 3), the vat is moved back such that the part is on top of the channel with PDMS (position 4). Finally the platform moves down by a distance $(d - \text{layer thickness})$ for the building of a new layer. Note that the platform can easily bring sufficient slurry when it moves from position (3) to (4). Accurate layer thickness is achieved when the platform moves down to position (1). Also, note that the motion in the $X$ direction is by the vat and the related frame. Hence the accuracy of the DMD-based AM system is not affected by the $X$ translation since there is no relative motion between the platform and the projection device.

Figure 5: Prototype system of the DMD-based AM process for PZT composite fabrication.

2.3 Experimental Setup and Test Results

A prototype system has been built to verify the developed DMD based AM process for PZT composite fabrication. The developed testbed is shown in Figure 5. In the prototype system an off-the-shelf projector (Acer H5360) was used as the projection device. The DMD resolution of the projector is 1024×768. The optical lenses of the projector were modified to reduce the projection image size to 14mm × 10.5mm. Various projection settings including focus, key stone rectification, brightness and contrast were adjusted to achieve a sharp projection image on the designed projection plane. Two precise linear stages from Aerotech Inc (Pittsburgh, PA) were used in the prototype system. One linear stage is used as the elevator for driving the platform in the $Z$ axis, and another one is used to drive the tanks back and force in the $X$ axis. A high performance 4-axis motion control board with 28 Bi-directional I/O pins from Dynomotion Inc. (Calabasas, CA) is used for driving the linear stages. A flat and clear glass Petri dish is used as resin tank. A PDMS film (Sylgard 184, Dow Corning) is coated on the glass dish. A mask planning software system has also been developed, which integrates the geometry slicing and the motion controlling. It also synchronizes the image projection with the $X$ and $Z$ movements.

In the experimental setup, the layer thickness was set at 25$\mu$m or 0.001 inch. Such a layer thickness is much smaller than the one that is typically used in the SLA process (i.e. 100$\mu$m or 0.004 inch). The thinner layers can effectively address the penetration problem caused by high refractive index of ceramics. The linear sliding motion in the $X$ axis can spread viscous slurry to fully fill the formed small gap. Hence flat surface of a thin layer can be achieved by constraining the slurry between the previous layer and the PDMS film.

We first tested the prototype system by using two different photcurable resins, V-Flash FTI-GN material (white) from 3D Systems Inc. (Rock Hill, SC) and Perfatory™ Acryl R5 (red) from EnvisionTec Inc. (Ferndale, MI). Both the resins belong to Acrylate and can be cured by blue light with a wavelength around 410nm. Even though the two resins have different viscosities, the developed two-channel system can successfully recoat a set of uniform ultrathin layers. Consequently the built objects can have satisfactory quality. Some of the built models are shown in Figure 6.

Figure 6: Built objects in photocurable resins using the developed prototype system.

We then tested the prototype system by using the PZT slurry that is prepared by following the procedure as described in Section 2.1. The fabrication of different types of ultrasound transducer arrays has been tested. Two of such test cases are shown in Figure 7 and 8 respectively.

The CAD model of a 1-3 composite ultrasound transducer array is shown in Figure 7.(a). The $XY$ extent of the part is 10mm × 10mm. The size of each pillar is 0.2mm × 0.2mm. The height of the pillars is 1.5mm. The built green-part in PZT composite is shown in Figure 7.(b). The test results verified that the developed method can build small features with a big aspect ratio. Note that a small amount of pillars were missing in the fabricated green-part. Such pillars were successfully built; however, they were broken in the post-processing process that include taking the green-part out and washing it to remove extra slurry.

Figure 7: Built objects in PZT composite using the developed prototype system.
Figure 7: A tested 1-3 composite ultrasound transducer array: (a) CAD model; (b) built physical object.

Figure 8: A tested spherically focused 2D segmented annular array: (a) CAD model; (b) built physical object.

3 PYROLYSIS AND SINTERING STUDY OF PZT GREEN-PARTS

A PZT green-part fabricated by the AM-DMD process is a mixture of photocurable polymer and PZT particles. In the pyrolysis process, the PZT green-part is subjected to a raised temperature to drive out the polymer and decompose the organic compounds in the sample. In the sintering process, the PZT green-part will be converted into a fully dense ceramic component in order to achieve the desired functionality. The heat treatment procedure of the pyrolysis and sintering was studied with related material properties measured.

3.1 Use of Sol-Gel Solutions

One of the most important key factors in the piezoelectric characteristics of a piezomaterial is its density. Density has a direct relationship with acoustic impedance of the piezomaterial through characteristic acoustic impedance, which is the product of sound velocity in the material and its density. On the other hand, density in the materials produced by AM processes provides lower density materials by nature due to the addition of photocurable polymers. Hence, the densification of the samples made by AM process is critical. Unfortunately, techniques such as hot uniaxial press cannot be used due to the fact that the axial load and shear forces applied to the brittle PZT samples may destroy the fine features in ultrasonic transducer arrays. We investigated another method, the addition of sol-gel and sintering-aid solutions, for improving the density of the PZT composites.

Numerous studies have been performed on the fabrication of PZT-based thick films [39, 40], thin films [41], and nano fibres [42]. The research results on such processes have showed that the additive of various solutions (e.g. LiBiO$_2$+CuO, PZT, and CuO, Li$_2$CO$_3$+Na$_2$CO$_3$+Bi$_2$O$_3$) can act as “glue” to chemically link the powder together and significantly lower the sintering temperature. The additives can also greatly promote the densification and grain growth.

Dorey et al. [40] demonstrated that the PZT sol–gel solution infiltration into the PZT composite films could reduce partially the porosity in thick PZT films. More recently, Wu et al. [39] used PZT composite solutions to deposit PZT thick films. It was found that increasing of mass ratio of PZT sol–gel solution to PZT powder in the composite solution gives rise to improved piezoelectric and dielectric properties without using any liquid-phase sintering aids.

The sol-gel process has been used in this work for the fabrication of PZT transducer arrays based on the developed AM process. The relative permittivity of the PZT samples in this work was found to be increased by both sol infiltration and the addition of sintering aid, with a slight reduction in dielectric...
loss values. In our work, PZT polymeric precursor (PZT 9103, from Chemat Technology Inc., Northridge, CA) is added in the PZT ceramic slurry. The composition of precursor is Pb(Zr0.52Ti0.48)O3 near the morphotropic phase boundary, which has a high piezoelectric properties. Dopants and liquid-phase sintering aids have been added to improve the rather poor sinterability of porous digitally fabricated parts. These techniques led to an improvement of several of the piezoelectric properties by 40%–80%.

The effect of adding a Cu2O–PbO sintering aid and repeated sol infiltrations have been investigated with the purpose of densifying digitally fabricated PZT bulk parts. In another approach, in order to improve the density of the piezomaterials, a 2-methoxyethanol-based sol–gel Pb(Zr0.52Ti0.48)O3 (PZT) precursor was applied as the matrix. To compensate lead loss during heat treatments, a 10 mol% excess PbO was added to the solution to adjust its concentration. PZT 5H powders from Piezoelectric Technology Inc. (Indianapolis, IN) were procured and used as the loading powder in the composite sol–gel.

3.2 Sintering Procedure

Sintering of green-parts to achieve desired piezoelectric properties is a challenging step in the development of new fabrication methods for functional ceramics. To achieve dense PZT parts, high sintering temperature is required. However, a high sintering temperature may lead to the excessive evaporation of PbO. Consequently the PZT sample will not be functional since the required chemical ratio of Pb, Zr and Ti in the sintered PZT parts cannot be achieved. The addition of sol-gel solution can lower the required sintering temperature. In addition, special procedures are needed for reducing the lead evaporation in the sintering process.

Figure 9: A sintering procedure for functional PZT component fabrication.

Figure 9 presents a thermal cycle used in our process, which includes four steps: organic binder burning, sintering, annealing, and cooling down. First organic binder is burn out by raising the temperature to 550°C. It is important to change the temperature slowly when the organics are most volatile. The oven remains at 550°C for an hour to ensure all organics have been burn out. The temperature is then raised up to 1150°C. As mentioned before, temperatures above ~900°C risk excessive evaporation of PbO in PZT. The use of atmosphere powders such as PbO + ZrO2 would be helpful [43]. Also powder isolation can ensure that no solid state diffusion or liquid phase transfer would occur between atmosphere, powder and sample. Moreover, a certain amount of PZT powder is placed in the chamber to make a PZT-rich atmosphere inside the oven. The digitally fabricated PZT part goes through the sintering process for 90 minutes until it is fully sintered. The sintered sample is then annealed at 750°C for one hour before cooling down to the room temperature. A programmable oven was used in the sintering process. The temperature ramp-up rate was ~10-15 °C/min and the temperature ramp-down rate was ~5 °C/min.

A 2D segmented annular array is designed as shown in Figure 10.a. Sumanaweera et al. [44] showed that the grating lobe level in spiral pattern is lower compared to the rectangular arrangement of array elements. However, such shape is difficult to be fabricated by the dicing approach. A green-part using the DMD-based AM process is shown in Figure 10.b. The sintered PZT array after going through the discussed sintering process is shown in Figure 10.c. Note that the sample shrank 7-8% during the sintering process.

Figure 10: (a) CAD model; (b) Digitally fabricated green-PZT, Before sintering; (c): After sintering and epoxy filling into the kerfs.
3.3 Testing Results of Sintered Samples

To understand the performance of the developed AM process for the fabrication of PZT parts, we quantitatively measured some important dielectric and ferroelectric properties of the sintered samples. The measured properties were also compared with those of commercially available bulk PZT parts.

The structure of the samples was first examined using a Rigaku X-Ray diffractometer (Rigaku Corporation, Tokyo, Japan). As can be seen in Figure 11, the digitally fabricated material has a relatively well-crystallized perovskite phase.

Circular Cr/Au electrodes with a diameter of 1.0 mm were deposited by sputtering as top electrodes onto the sintered PZT plates that were digitally fabricated. The dielectric properties were measured using an Agilent 4294A impedance analyzer as shown in Figure 12. It can be observed that the dielectric constant ($\varepsilon_r$) and the dielectric loss (tg $\theta$) vary slightly with the frequency from 1 KHz to 1 MHz. The values of $\varepsilon_r$ and $\text{tg} \\theta$ of the sample at 1 KHz are 614 and 0.025, respectively. The relative free dielectric constant of the fabricated piezomaterial is higher than Lithium Niobate and around that of Lead-Titanate. The measured piezoelectric constant ($d_{33}$) of the fabricated samples was around $245 \times 10^{-12}$ C/N. The measured electromechanical coupling coefficient ($K_t$) was around 0.44, and the sound velocity about 3140 m/s.

Polarization field (P–E) hysteresis properties were evaluated using a radiant precision materials analyzer (Radiant Technologies, Albuquerque, NM). Figure 13 shows the ferroelectric hysteresis (P-E loop) of the sintered samples. The polarization (P) and the coercive field (E_c) were 29 $\mu$C/cm² and 95 kV/cm, respectively. These results are comparable with Wu et al. [39] and indicate that comparable dielectric properties can be achieved. However, compared to conventionally made bulk PZT samples, the polarization and relative permittivity of the investigated materials is smaller. This might be due to its higher porosity, poor electrical connection, or rough surface finishing.

Figure 12: The dielectric properties of digitally fabricated PZT material after heat treatment.

Figure 13: The P–E loop of a digitally fabricated PZT material.

Figure 14: Variation in relative permittivity with increased levels of sol infiltration.

The effect of adding a Cu$_2$O–PbO sintering aid and repeated sol infiltrations have been investigated with the purpose of densifying digitally fabricated PZT bulk parts. As shown in Figure 14, relative permittivity increases with the addition of sintering aid and increased levels of sol infiltration. Meanwhile, the dielectric loss decreases with increasing of sol infiltration as shown in Figure 15. Measurements of piezoelectric properties indicate that sol infiltrations increased $d_{33}$. Once a critical density has been exceeded (refer to Figure 16). A sample with approximately 10% closed porosity was obtained following the incorporation of sintering aid and three infiltration steps for each sample. This resulted in a relative permittivity of approximately 703 and a $d_{33}$ of 245 pC/N (poling conditions: 5 V/μm for 5 min at room temperature).
Figure 15: Variation in dielectric loss with increased levels of sol infiltration.

Figure 16: The effect on the piezoelectric strain coefficient (\(d_{33}\)) by increased sol infiltrations.

Samples containing the sintering aid exhibit a consistently higher relative permittivity for a given level of sol infiltration. Both sets of results present an initial rapid increase in relative permittivity. At final stages of sol infiltrations, however, the set of results “without sintering aid” show a continuing rise, while the results with sintering aid end up with an almost constant level. This difference in the rate of change of relative permittivity of “with sintering aid” case is due to the efficiency reduction of the later infiltration stages. Initially the structure of the PZT sample is more porous and the sol is able to infiltrate easier and brings about large reductions in pore volume. As the pore size is decreased infiltration becomes more difficult and the rate of pore size reduction becomes less. Although, in the case of having “no sintering aid”, this saturation would not happen at any stage of sol infiltration, due to having much more porosity in the structure than the other case. However, the continued increase in relative permittivity for the case of “no sintering aid” indicates that infiltration and pore size reduction is still happening for these samples.

It can be seen that the dielectric loss is decreased slightly by both sol infiltration and the addition of sintering aid. In all stages dielectric loss mean value in presence of sintering aid is less than the other case with no sintering aid. This is by virtue of having a denser structure as a result of having fewer pores. In the presence of sintering aid we see saturated dielectric loss which is due to having denser structure and consequently less efficient sol infiltration.

For an increased number of sol infiltration steps, the results in Figure 16 indicate an increase in \(d_{33}\) for both cases of with and without sintering aid. However, at the final stages of sol infiltrations, \(d_{33}\) for both cases become close to each other, which indicates a sign of soaking after enough number of sol infiltrations.

Figure 17 shows an increase in the relative density as a function of the amount of CuO contained in the ceramic up to 0.8%. After this percentage, the density reaches to a peak and decreases after that. Thus, the addition of CuO up to 0.8% allows production of PZT digital fabrication ceramics and composites with a high degree of density in final structure.

In another series of experiments, the effects of sintering temperature and external pressure on the density of sintered samples have been evaluated. In addition to various sintering temperatures, external pressures between 15 to 30 MPa were added in the Z axis by using a weight on the samples in the sintering process. The densities of samples using and without using sol-gel solutions have been measured. Figure 18 shows the density values of various PZT samples for the three cases.
As shown in Figure 18, adding sol-gel solution to the curable solvent significantly decreases the sintering temperature. Also, using external stresses improves the density of the samples to roughly 80% of the density value for bulk PZT sample, which is around 7.5-7.9 g/cm³. This improvement is promising, since densification is one of the main challenges to overcome in developing AM processes for PZT component fabrication. However, the external stresses will also lead to cracks of small features and destroy pillars in the ultrasound transducer arrays. Hence an improved method to add pressures without breaking delicate structures in ultrasound transducer arrays is required.

4 CONCLUSIONS AND FUTURE WORK

A DMD-based additive manufacturing (AM) process has been developed for the fabrication of piezoelectric ceramic components with fine features and complex shapes. Since the PZT slurry has different optic and fluidic properties from those of liquid resin, a bottom-up projection system is suitable for the fabrication of PZT composite. Our work has demonstrated that the developed process can quickly fabricate PZT green-parts in various geometries with satisfactory part quality. Our sintering study based on the fabricated green-part shows that the density of sintered components can be increased by adding sol-gel and sintering aid solutions in PZT slurry. The dielectric and piezoelectric properties of sintered samples have been measured. Our work has demonstrated that the density of the fabricated PZT components using the developed AM process can reach ~80% of the density of the bulk PZT ceramics.

The DMD-based additive manufacturing process is promising for the future fabrication of PZT-based piezoelectric components especially high-frequency ultrasound transducer arrays. The digital fabrication process could be a mass production method by sintering a large quantity of PZT green-parts in a single batch. However, two significant fabrication challenges remain, which include: (1) better resolution and accuracy control in the green-part fabrication, and (2) improved sintering procedure to achieve better piezoelectric properties in sintered components and to avoid destroying the fine features in the fabricated components. Such challenges will be targeted in our future research on the fabrication of piezoelectric devices.

REFERENCES


