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3D Printing of PZT Piezoelectric Transducer Elements

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Lead zirconium titanate (PZT) piezoelectric ceramic transducer elements are fabricated via an additive manufacturing approach. Commercially available PZT powder is compounded with a polymer binder to make a PZT filled polymer filament. This filament is then fed into a commercial-off-the-shelf desktop 3D printer to additively manufacture green (i.e., unfired) disc preforms. The printed preform parts are pressed into dense discs and sintered to full density for comparison to conventionally processed discs of the same composition. The properties of the sintered discs prepared by both methods are similar and meet or exceed the manufacturer specifications for this composition.

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EXECUTIVE SUMMARY

Lead zirconium titanate (PZT) piezoelectric ceramic transducer elements are fabricated via an additive manufacturing approach. The as-received PZT powder is initially surface treated with a surfactant, then compounded with a thermoplastic binder, and finally extruded into a continuous ceramic filled polymer filament. This filament is then used by an inexpensive commercial-off-the-shelf (COTS) desktop 3D printer to make disc preforms approximately 12mm in diameter and 3mm thick. These 3-D printed preforms are subsequently uniaxially pressed into discs and are compared to discs made from conventional powder processing techniques under the same binder burnout and sintering conditions. This report will show that our additive manufacturing approach can be used to prepare ferroelectric ceramic parts that either meet or exceed the vendor's materials specifications.

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3D PRINTING OF PZT PIEZOELECTRIC TRANSDUCER ELEMENTS

1. INTRODUCTION

The Physical Acoustics Branch (Code 7130) of the Naval Research Laboratory (NRL) is conducting basic research to develop textured ferroelectric ceramic structures for use in Navy sonar applications. In well-textured ceramics, the piezoelectric properties can be comparable to those of single crystals. When the ceramic grains are deliberately oriented in a preferred crystallographic direction, the piezoelectric properties are 2-3 times greater than their polycrystalline ceramic counterparts.

This research program aims to understand the materials science issues associated with synthesizing these textured materials, coupled with developing and perfecting fabrication processes. We envision the potential of a low-cost game-changing fabrication technology such as 3-d printing (additive manufacturing) will make the use of these materials ubiquitous in future Navy sonars.

Ferroelectric ceramics have been manufactured using technologies such as powder injection molding [1,2]. These technologies combine a ferroelectric powder with a polymer that enables the material to flow as a viscous fluid under certain conditions. Previously, additive manufacturing technology was developed for printing high strength ceramic as well as ferroelectric ceramics using a filament containing polymer and ceramic [3,4]. The shear forces in the viscous material can align the particles as the material is deposited through a nozzle [5,6]. Such a rearrangement is necessary for obtaining the alignment of template particles needed for texturing. This method is determined to be an excellent approach towards the texturing of ferroelectric ceramics during additive manufacturing.

Initial steps towards the fabrication of textured ferroelectric materials follows two directions. One is to develop seed crystals to enhance textured growth of the ferroelectric ceramics. The second, which is the focus of this report, is the development of a process to make a ferroelectric ceramic filled polymer filament that is compatible with a desktop 3D printer.

High quality ferroelectric lead zirconium titanate (PZT) powder is commercially available at low cost (~$125/kg). Unfortunately, PZT is not suitable for textured grain growth due to incongruent melting that results in precipitation of ZrO_2 [7]. Because of its low cost and commercial availability, however, PZT powder can be used for developing and refining the 3-d printing fabricating process. The lessons learned using this material can then be transferred to compositions based on lead magnesium niobate (PMN), which will be used in the future to study texturing

2. APPROACH

The stiffness, viscosity, tensile strength, and flexibility of the filament all need to be carefully controlled for successful 3-d printing. These parameters are manipulated by adjusting the chemistry of the ceramic powder and polymer materials.

The first step to fabricate a ceramic-filled polymer filament is to coat the as-received ceramic powder with a surfactant. The surfactant enables mixing of the non-polar polymer with the polar powder. The surfactant used in this study is stearic acid. A molecule of stearic acid consists of a carbon chain attached to an acidic group. The acid group attaches to the polar surface of the ceramic particle leaving the carbon chain pointing outwards where it is attracted to the polymer binder.

The binder is a mixture of multiple polymers used to ensure that the properties of the filament are suitable for 3-d printing. The composition of the binder has four components: a base polymer (elastomer), a tackifier, wax, and a plasticizer [3]. The base polymer has the greatest effect on the binder mixture

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while the other components modify the properties. The wax reduces viscosity at higher temperatures needed for compounding, allowing for a higher fraction of solids in the mixture. The plasticizer enables flexibility of the filament allowing it to be spooled. The tackifier provides tack, allowing the polymer to stick to itself during printing. The tackifier also lowers viscosity and stiffness.

The amount of each component must fall within a certain range to obtain the necessary properties for printing. For example, too much wax causes brittleness and the filament will crack while too much tackifier lowers the elastic modulus causing it to easily stretch. Too much plasticizer results in a soft filament that slowly deforms under stress.

The compounding of the ceramic powder with binder requires high shear mixing to separate individual particles of the ceramic and blend them with the polymer. The compounder is a Haake Rheomix 600 which has a 3-zone temperature controller and a five horsepower motor for high torque. The compounded ceramic and binder mixture is cooled to room temperature and crushed into small pieces using a Granutec 66MM granulator to prepare it for extrusion. The granules are fed into a Filabot EX2 desktop extruder at 90°C and a continuous filament is extruded through a 2.85mm diameter nozzle, air cooled using a fan, collected on a moving conveyor and spooled on a reel. The filament is subsequently 3-d printed using a Lulzbot Mini 2 into green (unfired) disc preforms with dimensions of 12mm diameter and thickness of 3mm.

The printed preform parts are then uniaxially pressed with 250MPa into discs approximately 12mm in diameter and 2mm tall using a cylindrical pellet die. A separate set of discs were made from conventionally pressed PZT powder in order to directly compare their properties to the ones made from the 3-d printed material.

3. EXPERIMENTS

3.1 Surface treatment of PZT powder

The PZT powder (PKI-509, PiezoKinetics, Bellefonte, PA) is prepared for compounding using a surface treatment of stearic acid (Acros Organics). The as-received spray dried powder has large 50-micron diameter granules that must be crushed prior to surface treatment. The powder is dry milled in a FLPE bottle with cylindrical yttria stabilized zirconia media for 24hr. Then 5ml water and 2ml NH_4OH 30% solution are added to the crushed powder and returned to the mill for 3hr. The water is adsorbed by the powder and creates a hydrated surface. The ammonia improves the adsorption of the stearic acid added later. Then 30ml of toluene is added and the mixture is milled for an additional 21hr. Stearic acid is melted on a hot plate and mixed with toluene. Stearic acid is soluble in toluene because it is attracted to the non-polar end of the molecule, while the polar end is attracted to the hydrated PZT surface. The solution is added to the FLPE bottle with the PZT powder. The stearic acid is 1wt% of the PZT and the total amount of toluene added is equal to the mass of the PZT powder. The slurry is milled for 24hr, and then poured into a dish for drying in an oven at 60°C. The water previously added separates from the toluene slurry because it is immiscible.

3.2 Compounding, granulation, and extrusion

The surface treated PZT powder is compounded with the polymer binder using a Haake Rheomix 600 torque rheometer. The polymer consists of a polyolefin base with a wax, plasticizer, and tackifier [3]. The base polyolefin is Vestoplast V2103 (Evonik), the wax is Vestowax SH112 (Evonik), the plasticizer is Indopol H-1900 (Ineos Oligimers), and the tackifier is Escorez 1304 (ExxonMobil). The composition of a printable PZT filament is given in Table 1. The polymers are added to the mixing chamber of the Rheomix 600. The mixing chamber is heated to 150°C and the polymers are melted and blended at 100rpm. The surface modified PZT is added to the mixer in portions of 25%, 25%, 25%, 12.5%, and 12.5% with 15 minutes of compounding between additions. The compounded PZT and polymer is 60% PZT by volume (or 93% PZT by mass).

Table 1 — Composition of the printable filament

Component	Volume (%)	Weight (%)
Lead zirconium titanate	60.0	92.7
Surfactant	5.0	0.83
Elastomer	25.4	4.46
Tackifier	4.4	0.93
Wax	3.4	0.69
Plasticizer	1.8	0.39

3.3 Printing

A Lulzbot Mini 2 desktop 3D printer is used for additive manufacturing. The Mini 2 printer has a direct drive print head that feeds the PZT-filled polymer filament directly to the heated nozzle. The only modification required for printing the PZT filament is to replace the as-received tensioner spring in the print head with a spring of lower stiffness so it does not crush the PZT filament, which is less stiff than typical 3d printing materials such as PLA or ABS. A thin polyester film sheet is taped to the build platform to allow for easy removal of the printed parts. Parts are printed at a nozzle temperature of 160°C using either a 0.5, 1.0, or 1.2mm diameter nozzle. A wide range of lateral movement speed and filament feed speed can be used. Print speeds of 10-100mm/sec are possible. Shear rate, r_s, can be controlled by layer height, h, and lateral movement speed, v, by the equation $r_s = v/h$. For a layer height of 0.1mm and speed of 100mm/sec, the shear rate is 1000/sec, which is achievable using a 0.5mm nozzle. This will be studied in the future for its effect on seed crystal alignment and texturing.

3.4 Post-printing

Post-printing techniques are used after printing because it is difficult to successfully print fully dense green (i.e., unfired) discs that are free of defects. It is possible for printed parts to be shaped by uniaxial pressing into dense discs. A disc preform was printed that consists of four concentric rings printed on top of a 1-layer thick (0.4mm) solid base. The concentric rings have a height of 3mm and wall thicknesses of 1mm as shown in Figure 1.

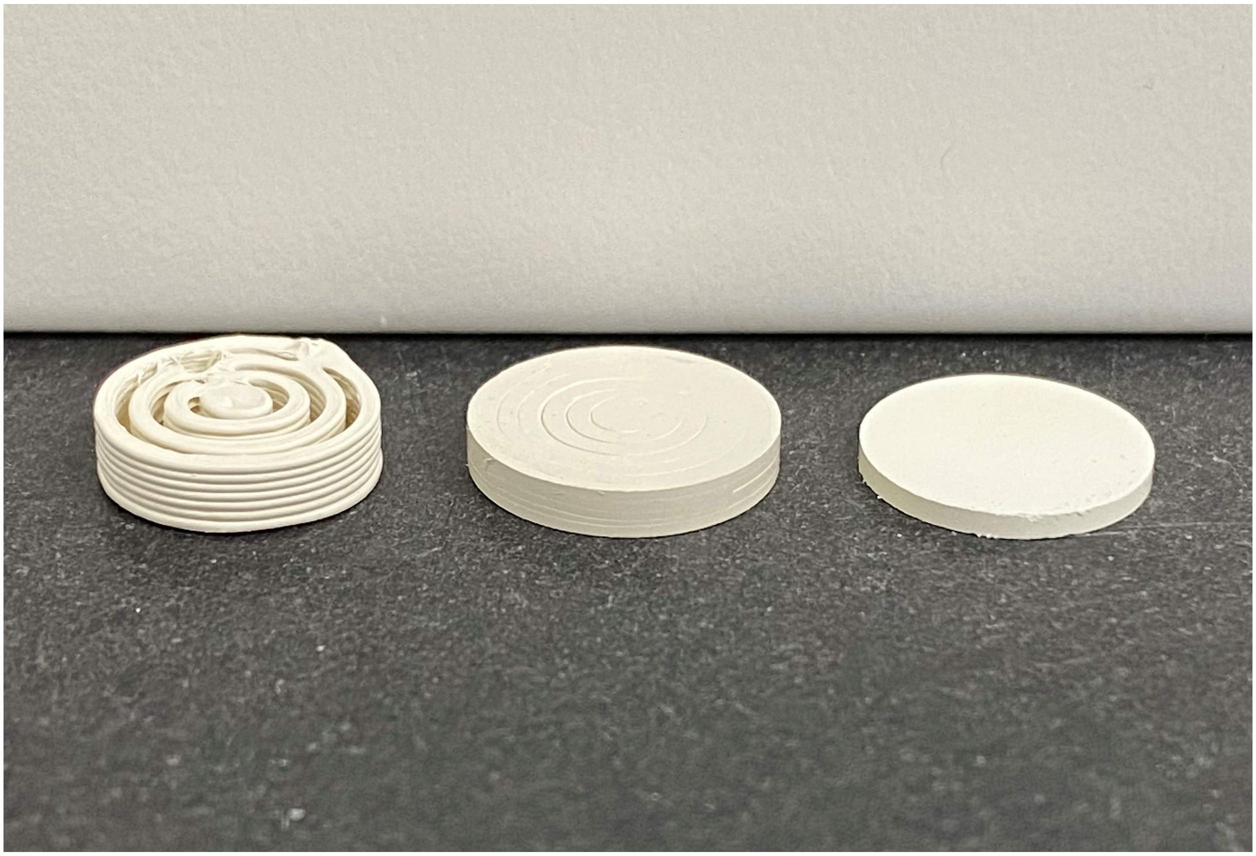

Figure 1. Disc preform consisting of concentric rings (left), disc preform after pressing (middle), and a disc pressed from PZT powder (right).

3.4.1 Shaping and forming

The height, width (i.e., wall thickness), and spacing of the preforms is calculated so that the rings flatten and occupy the full volume of a disc when pressed. As the preform is pressed, it shears laterally and the rings expand. This can be used to further enhance alignment of seed crystals for crystallographic texturing. This effect will be studied in the future for its potential to enhance texturing. The printed parts are placed inside of a steel pellet die. The die is coated in a hydrophilic polymer (RainX anti-fog for interior surfaces) and a thin film of deionized water is used as a lubricant. The printed parts repel water in the film and prevents sticking. The parts are pressed into dense discs without internal voids or defects.

3.4.2 Binder burnout

The printed parts are placed on top of a powder bed of finely milled PZT powder. Binder is removed by slowly heating to 600°C over 60 hr. As the polymer melts, it is removed from the part by capillary forces and drawn into the fine powder at the base. Binder is completely removed from green parts without cracking or blistering.

An interesting footnote: during heating the part softens and curvature can be induced on the part if it is placed on a curved surface. This has been observed when a part was placed on top of a curved alumina crucible.

3.5 Sintering

Discs are sintered at 1250°C for 2hr inside a covered crucible with a lead oxide source. The lead oxide source consists of a PZT powder inside a small platinum crucible and crushed sintered PZT ceramic placed around the perimeter. This minimizes the volatilization of lead oxide from the discs. Both printed and pressed discs are sintered at the same time. The heating and cooling rate is 150°C/hr.

3.6 Piezoelectric properties

The printed parts and the conventionally pressed discs meet the properties defined by the manufacturer PiezoKinetics for PKI-509 [8].

Table 2. Piezoelectric properties of NRL prepared PKI 509 discs compared to the vendors specifications

Composition	**Density (kg/m^3)**	**k_p**	**d_{33} (pC/N)**	**Relative Permittivity**	**Dielectric Loss**
PKI 509 [8]	>7600	0.55-0.63	350-550	1700-2400	0.0200
Pressed discs	7620	0.640	461	2060	0.0193
Printed discs	7710	0.641	477	2060	0.0191

4. CONCLUSIONS

A process for fabricating ferroelectric ceramic parts using additive manufacturing has been developed. Commercially available lead zirconium titanate powder is surface treated with stearic acid and then compounded with a polymer binder. A PZT filled polymer filament is extruded that has the properties of stiffness, elastic modulus, flexibility, and viscosity requisite for printing on a desktop 3D printer. Printed preform parts were pressed into dense discs and sintered to full density for comparison to conventionally processed discs of the same composition. The properties of the sintered discs prepared by both methods are similar and meet or exceed the manufacturer specifications for this composition. Thus, additive manufacturing can be used to prepare ferroelectric ceramics without loss or degradation of properties.

In the future the fabrication process will be adapted for use with lead magnesium niobate (PMN) based ferroelectric powders and will incorporate barium titanate seed crystals for texturing. Alignment of the platelets will be studied using the different shear rates arising from different printing speeds and layer heights. In addition, the effect of shear during uniaxial pressing of the soft printed parts will be investigated with the goal of obtaining highly textured ferroelectric ceramic parts.

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