

The Pennsylvania State University
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**FLEXOELECTRICITY IN THE BARIUM STRONTIUM
TITANATE (BST) SYSTEM FOR HYDROPHONES**

A Thesis in
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by
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ABSTRACT

The large flexoelectric coefficients ($\sim 100 \mu\text{C}/\text{m}$) in barium strontium titanate (BST) ceramics suggest the possibility of flexoelectric alternatives to piezoelectric sensors and actuators. Flexoelectricity occurs in all insulating materials, including centrosymmetric crystals in which piezoelectricity is forbidden. This wider material selection space provides a pathway towards alternatives to Pb-based piezoelectric devices. Flexoelectricity may also benefit from micro-electromechanical systems (MEMS) and nano-electromechanical systems (NEMS) technologies, based on enhanced performance at these scales. Flexoelectricity is driven by strain gradients inside a material and at the micro and nano scales these gradients may be orders of magnitude larger than at bulk scale.

In this work, the flexoelectric effect of BST was investigated for use in hydrophones. Of interest was whether or not it would be possible to create flexoelectric hydrophones that compete with their piezoelectric counterparts. The flexoelectric effect of BST was studied using cantilever beams. For BST ceramic samples fabricated by Texas Instruments (TI), the maximum relative permittivity at T_c , 33°C , was 18000 and corresponding loss tangent was 0.03. The effective flexoelectric coefficient, $\tilde{\mu}_{12}$, was $105.6 \pm 0.6 \mu\text{C}/\text{m}$ at room temperature over a strain gradient range of 0.0026 - 0.0355 m^{-1} . The ball on 3 ball method was performed on this material to determine biaxial strength limits for BST to match the loading conditions of flexural bending in the application. The data from 20 samples was plotted for Weibull analysis and calculated a Weibull modulus of 14.3 ± 0.2 and a Weibull strength of $130.5 \pm 4.3 \text{ MPa}$.

A prototype hydrophone was built using a TI BST ceramic in a three-point bending configuration with dimensions of the ceramic being $77 \text{ mm} \times 10 \text{ mm} \times 0.67 \text{ mm}$. Tap testing of

the prototype with a calibrated acoustic hammer showed a resonant frequency of 250 Hz and maximum sensitivity of 80 pC/N at this frequency. These results compare to a typical bulk PZT d_{33} value of 200-600 pC/N. Multiple iterations of the initial design were experimentally tested to increase the usable frequency range and increase the sensitivity at higher frequencies. These iterations also provided insight into how different design parameters affected performance. The best sensitivity was achieved on a 40 mm x 10 mm x 0.67 mm TI BST ceramic with a resonant frequency of 500 Hz and peak sensitivity of 140 pC/N. This same design using TPL BST-MgO ceramic achieved a resonant frequency of 590 Hz with a peak sensitivity of 50 pC/N.

Finite element analysis (FEA) was utilized to model the resonant behavior of flexoelectric elements utilizing linear elasticity theory as well as to optimize the flexural bending design to maximize the flexoelectric effect. This was performed using COMSOL Multiphysics® Modeling Software version 5.4. The fundamental resonant frequency was calculated using fixed-fixed and pinned-pinned boundary conditions. The results agreed with analytical models of a fixed-fixed and pinned-pinned beam within 2% error. The difference in fundamental frequency between the FEA model and the original prototype was 7.6% using pinned-pinned boundary conditions. The strain gradient behavior of beams with different arrangements of electrodes and flexural points was utilized to calculate an average output of a device over time given the flexoelectric coefficient of the material. Using this method, it was found that a 3 bending point design with 10 x 5 mm electrodes produced 43% more flexoelectric output than a 1 bending point design with a 10 x 5 mm electrode despite a reduction of strain gradient in each electrode of 52%. This study highlighted the importance of differences between charge-based and voltage-based devices with voltage-based devices needing to apply electrodes in series to avoid a reduction in voltage output with multiple bending points.

FEA also demonstrated greater flexoelectric output at low frequencies based on the greater strain gradients calculated at these frequencies. The tradeoff observed in flexoelectric devices is between flexoelectric output and the available frequency range. A reduction in thickness increases the strain gradient response and therefore the flexoelectric output but decreases the fundamental frequency. A reduction in length decreases the strain gradient response but increases the fundamental frequency.

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Chapter 1

Introduction and Motivation

1.1 Introduction and Literature Review

This study investigated the flexoelectric response of barium strontium titanate (BST) ceramics and their potential use in hydrophones. In order to accomplish this task, several performance milestones were targeted: 1) production of BST samples that demonstrate flexoelectric data equal to or better than the reported literature values, 2) demonstration of prototype hydrophones using the flexoelectric effect, and 3) optimization of the device performance based on an understanding of how parameters affect the output signal (geometry, boundary conditions, materials, and electrodes). The optimization was performed based on a combination of experimental data on multiple iterations of prototypes and finite element analysis (FEA) models.

Flexoelectricity is a fourth-rank tensor property that is present in every insulating material. While a uniform strain cannot induce polarization in a centrosymmetric material, a *strain gradient* acts as a vector field, allowing a net polarization to develop. The resulting polarization vector points from the compressive side to the tensile side, assuming a shift in the cation position. For example, it has been reported that in perovskites, the B-site cation; induces the flexoelectric polarization. This effect is shown schematically in Figure 1-1.¹

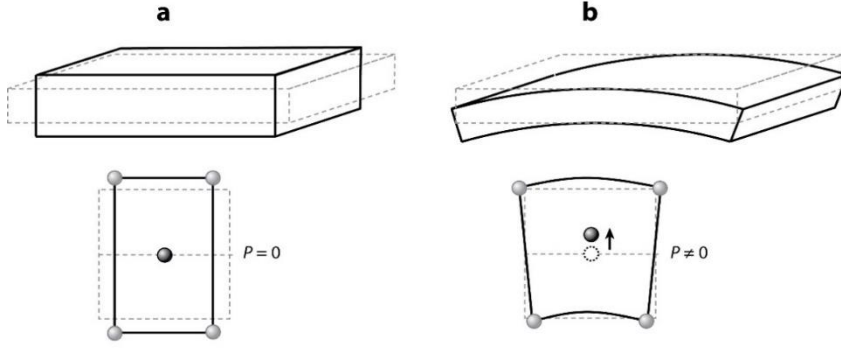


Figure 1-1. Schematic of a) uniform strain that does not break inversion symmetry and b) strain gradient that breaks inversion symmetry and therefore leads to polarization in the material. From reference 1.

Flexoelectricity is governed by Equation 1.1:

$$P_l = \mu_{ijkl} \frac{\partial S_{ij}}{\partial x_k} \quad (1)$$

where P_l is the component of the resultant polarization, μ_{ijkl} are the flexoelectric coefficients (fourth rank polar tensors), S_{ij} is the component of elastic strain, and x_k is the direction of the gradient in S . The flexoelectric coefficients have the same symmetry in a cubic crystal as the electrostriction coefficients Q_{ijkl} so that in a cubic crystal the non-zero components are μ_{1111} , μ_{1122} , μ_{1212} , or μ_{11} , μ_{12} , and μ_{44} in matrix notation.² Unlike other fourth-rank tensors such as Q_{ijkl} , and the elastic stiffness/compliance tensors, c_{ijkl}/s_{ijkl} , the flexoelectric tensor is invariant only through interchanging the two indexes of the symmetrized strain tensor, i.e. $\mu_{ijkl} = \mu_{ijlk}$. Possible relations for the other fourth rank tensors, e.g. $Q_{ijkl} = Q_{jikl} = Q_{ijlk}$ and $c_{ijkl} = c_{jikl} = c_{klij}$, are not applicable to μ_{ijkl} .³ For this reason, there are more nonzero components of the μ_{ijkl} in lower symmetry point groups as shown in Table 1-1.⁴

Table 1-1. Numbers of non-zero independent components for different point groups and Curie groups. From reference 4.

Point groups and Curie groups	Elastic stiffness/compliance tensor (<i>c/s</i>)	Electrostrictive tensor (<i>Q</i>)	Direct/inverse flexoelectric tensor (μ/μ^*)
1, $\bar{1}$	21	36	54
2, m, 2/m	13	20	28
222, mm2, mmm	9	12	15
3, $\bar{3}$	7	12	18
32, 3m, $\bar{3}m$	6	8	10
4, $\bar{4}$, 4/m	7	10	14
4mm, $\bar{4}2m$, 422, 4/mmm	6	7	8
6, $\bar{6}$, 6/m, ∞ , ∞/m	5	8	12
622, 6mm, $\bar{6}m2$, 6/mmm, $\infty2$, ∞m , $\infty/m m$	5	6	7
23, $m\bar{3}$	3	4	5
432, $\bar{4}3m$, $m\bar{3}m$	3	3	3
$\infty\infty$, $\infty\infty m$	2	2	2

The first theoretical work on the flexoelectric effect began with Mashkevich and Tolpygo in 1957.⁵ The first phenomenological theory was formulated by Kogan in 1964, Kogan also derived the first order-of-magnitude estimate of the flexocoupling coefficient, f_{ijkl} , which is simply the flexoelectric tensor, μ_{ijkl} , normalized to the dielectric constant of the material, as described below. In Equation 1.2, the flexocoupling coefficient, f , is estimated to be 1-10 volts based on the permittivity of free space, ϵ_0 , an atomic charge, q , and an atomic spacing, a , which is on the order of angstroms. The estimate is based on a strain gradient on the order of $1/a$.⁶

$$f \approx \frac{q}{4\pi\epsilon_0 a} \cong 1-10 \text{ V} \quad (2)$$

Tagantsev proposed that the dielectric susceptibility, χ , of the material was directly proportional to the measured flexoelectric coefficients, μ , using the flexocoupling coefficient, f , as described in Equation 1.3.^{7,8}

$$\mu = f\chi \quad (3)$$

Therefore, the flexoelectric effect is expected to be the greatest in materials with the highest permittivity. Flexoelectricity is a fourth-rank tensor which allows use of centrosymmetric paraelectric materials for flexoelectric applications with improved performance near the Curie temperature due to the increase in permittivity. The relative permittivity in the paraelectric

region tends to follow Curie-Weiss behavior where C is the Curie constant, T is the temperature, T_0 is the Curie-Weiss temperature, and T_c is the Curie temperature, as shown in Equation 1.4, with some deviations near the Curie temperature depending on residual micropolar regions in the material.^{9,10}

$$\chi = \frac{C}{T - T_0} \quad (T > T_c) \quad (4)$$

The strain gradient provides the driving force for polarization, therefore applying the highest strain gradient prior to mechanical failure produces the largest polarization.

The flexoelectric coefficients, μ_{ijkl} , were predicted and eventually measured in low permittivity dielectrics to be on the order of 10^{-10} - 10^{-11} C/m. These coefficients are small enough that they only developed academic interest. However, Ma and Cross measured μ_{12} values (using matrix notation) of $100 \mu\text{C/m}$ at 2°C above the Curie temperature, T_c , of $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$. These values are six orders of magnitude larger than what had been theoretically predicted and measured, generating greater interest in the phenomenon. The results are displayed in Figure 1-2.

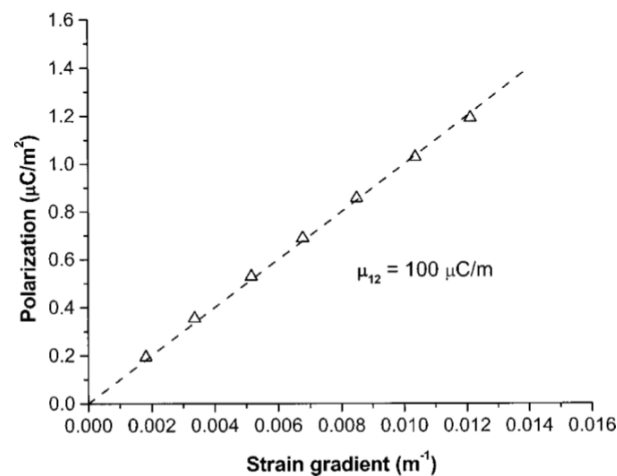


Figure 1-2. Flexoelectric polarization measured as a function of applied strain gradient at 1 Hz. From reference 11.

The enhanced response was theorized to have been caused by the reorientation of micropolar regions occurring above T_c and below the Burns' temperature, T_d .¹¹

Figure 1-3 gives an overview of the flexoelectric testing methods used to collect data in Table 1-2.³ The methods used in this study were cantilever bending (CB) shown in Figure 1-3a and three-point bending (3PB) shown in Figure 1-3d. The CB testing was performed to measure accurately the flexoelectric coefficients of the BST used. The 3PB testing was performed to determine hydrophone bandwidth and sensitivity in this thesis. It is important to note that these methods measure an effective flexoelectric coefficient (denoted by $\sim$) because there are multiple flexoelectric contributions which combine multiple flexoelectric tensor components into one output.

Different flexoelectric coefficients and flexocoupling coefficients from many materials collected by Catalan et al.¹ are shown in Table 1-2. It is apparent that the largest values are observed in BST.

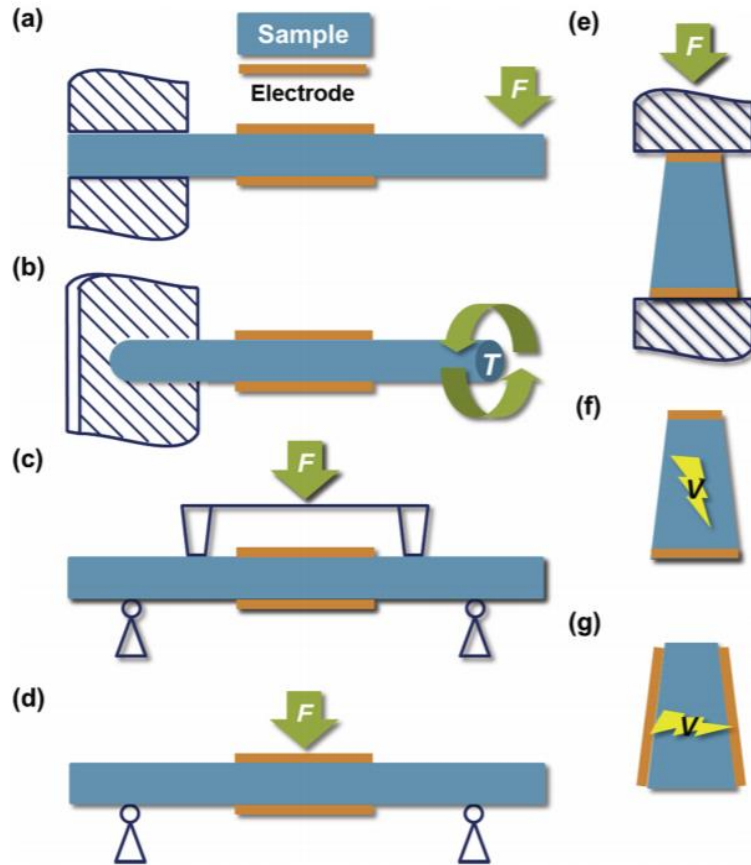


Figure 1-3. Schematics of flexoelectric experimental setups for direct measurements of flexoelectric constants: (a) cantilever bending (CB), (b) cylinder twisting (CT), (c) four-point bending (4PB), (d) three-point bending (3PB), and (e) pyramid compression (PC), and for converse flexoelectric constant measurement: (f) normal-electrode pyramid (NEP) and (g) side-electrode pyramid (SEP). From reference 3.

Table 1-2. Measured experimental flexoelectric coefficients for a variety of materials.^a
From reference 1.

Compound	Coefficient	Method	Value ($\mu\text{C}/\text{m}$)	χ/ϵ_0	$f = \mu/\chi$ (V)
BaTiO ₃	$\tilde{\mu}_{12}$ ($T_c + 3.4$ K)	CB	~50 (12)	~10,000	~560 (12)
Ba _{0.67} Sr _{0.33} TiO ₃	$\tilde{\mu}_{11}$	PC (0.5 Hz)	150 (2)	~20,000	~850
	$\tilde{\mu}_{11}$	CFE (400 Hz)	120 (13)		
	$\tilde{\mu}_{12}$	CB (1 Hz)	100 (11)	~16,000	~700
Ba _{0.65} Sr _{0.35} TiO ₃	$\tilde{\mu}_{12}$	CB	~8.5 (14)	4,100	234
PbMg _{0.33} Nb _{0.67} O ₃	$\tilde{\mu}_{12}$	CB	3-4 (15)	~13,000	~26-45
PMN-PT	$\tilde{\mu}_{11}$	PC (4-10 Hz)	6-12 (16)	21,000	~32-65
		PC (0 Hz)	20-50 (16)		~110-270
Pb _{0.3} Sr _{0.7} TiO ₃	$\tilde{\mu}_{11}$	PC (0.5 Hz)	20 (2)	13,500	170
Pb(Zr,Ti)O ₃	$\tilde{\mu}_{12}$	4PB	0.5 (17)	~2,200	25
		CB (1 Hz)	1.4 (18)		72

^a The values in the last column were calculated from the measured flexoelectric coefficient and the experimental dielectric susceptibilities. References in the fourth and sixth columns are in parentheses. All values are room temperature values unless stated otherwise. Measurement techniques: CB, cantilever bending; PC, pyramid compression; CFE, converse flexoelectric effect; 4PB, four-point bending.

This study had access to high quality Texas Instruments (TI) BST ceramic samples. Given the high reported flexoelectric coefficients found in BST compositions, these samples were tested to determine their dielectric properties and flexoelectric coefficients.

1.2 Barium Strontium Titanate Solid Solution

The BST system is a continuous solid solution exhibited by its end members, BaTiO₃ and SrTiO₃. The addition of Sr into BaTiO₃ lowers the T_c linearly by ~3.4 °C/at% Sr. The Ba·Sr ratio in BST allows control over the relative permittivity at operational temperatures. This has been extensively studied for tunable dielectric applications and is shown in Figure 1-5.¹⁹ BST

has a cubic perovskite structure above the Curie temperature with the larger barium and strontium ions occupying the corners of the unit cell and the smaller titanium ion occupying the middle of the unit cell. The titanium ion is surrounded by an oxygen octahedron. The corner site is known as the A-site and the center site is known as the B-site.²⁰ Therefore, barium and strontium share the A-site in BST and titanium occupies the B-site. This is pictured in Figure 1-4b. In this paraelectric phase above the Curie temperature, the high permittivity of the material derives from the fact that the titanium ion is easily displaced by an electric field generating a large, induced dipole moment.¹⁹

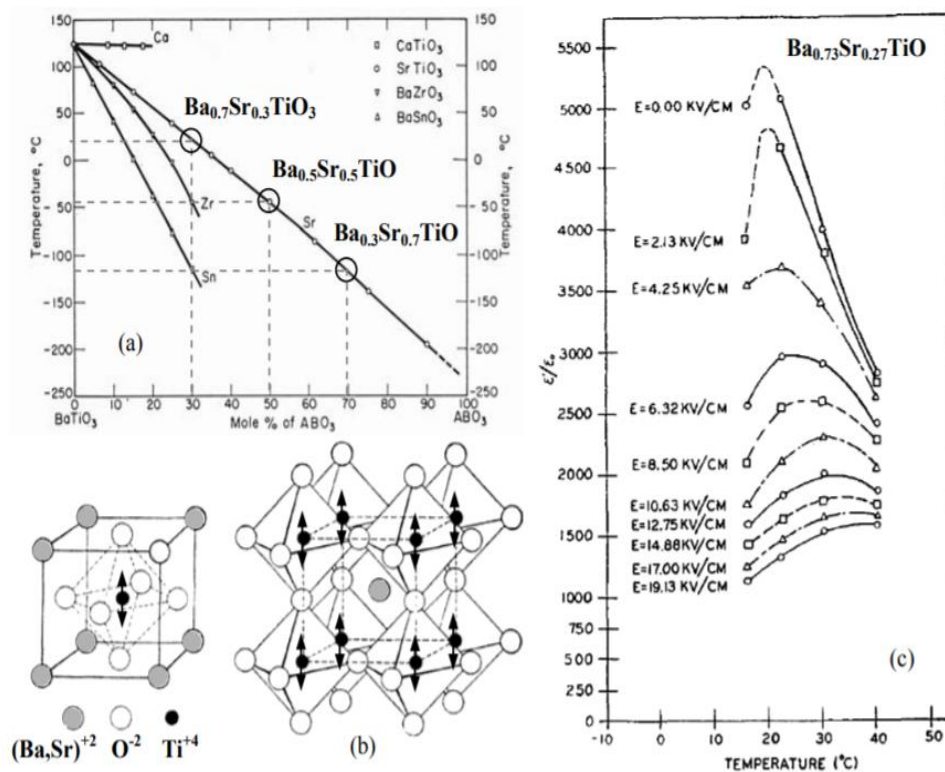


Figure 1-4. (a) Curie temperature of bulk BTO with various additives, (b) BST structure with oxygen octahedra surrounding the titanium ion. (c) Electric field dependence near the Curie temperature for a BST ceramic. From reference 19.

As the T_c is approached, the relative permittivity approaches ~5,000-20,000 for BST depending on composition and processing. The relative permittivity remains high, >3000, even

25° C above the T_c . BaTiO_3 and the barium-rich side of BST exhibit a cubic $\text{Pm}3\text{m}$ space group symmetry above T_c and a ferroelectric tetragonal $\text{P}4\text{mm}$ symmetry below T_c . This phase transition has a first order character.²⁰ The composition chosen for further research in this thesis is $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ which has a T_c of $\sim 0^\circ \text{C}$. This composition was chosen to ensure operation in the paraelectric region for room temperature testing while still exhibiting a large dielectric constant, $\gtrsim 3000$.

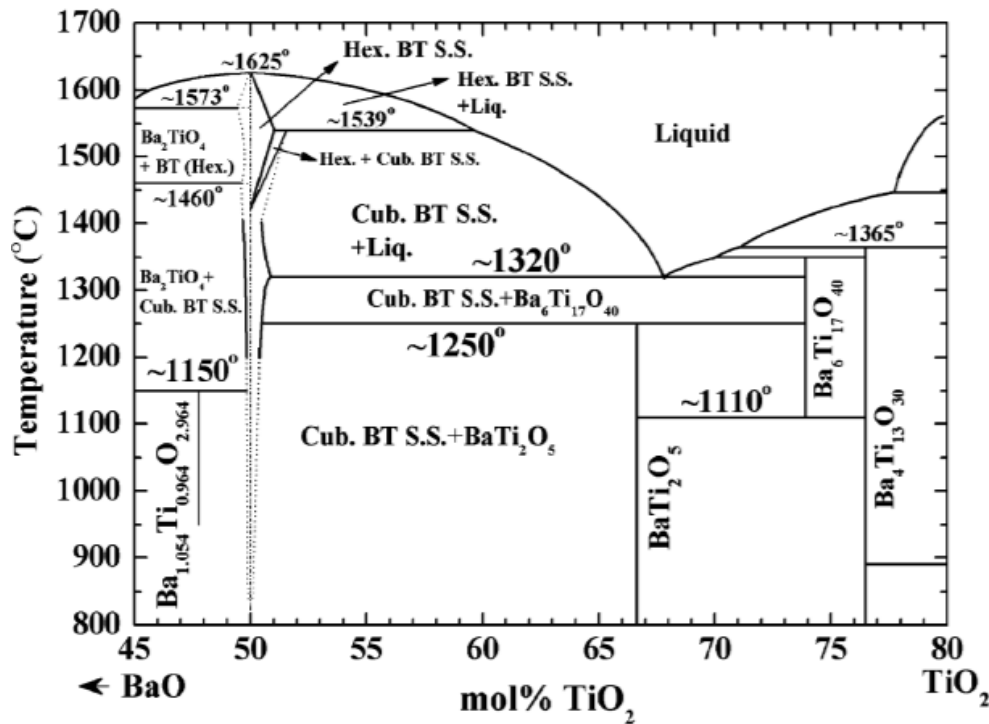


Figure 1-5. Pseudo-binary phase diagram of BaO and TiO₂. From reference 21.

The BaTiO_3 phase diagram is given in Figure 1-5.²¹ The pseudo-binary phase diagram shows the narrow stability range of BaTiO_3 . If there is titanium deficiency, Ba_2TiO_4 may form as a secondary phase. If there is a titanium excess, $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ will form a secondary phase. Both phases lower the permittivity and therefore would reduce the flexoelectric effect^{22,23}.

In Figure 1-6, the pinching nature of Sr addition is shown.²⁴ The phase transitions occur in a narrower temperature range as Sr is added as well as shifting them to lower temperatures.

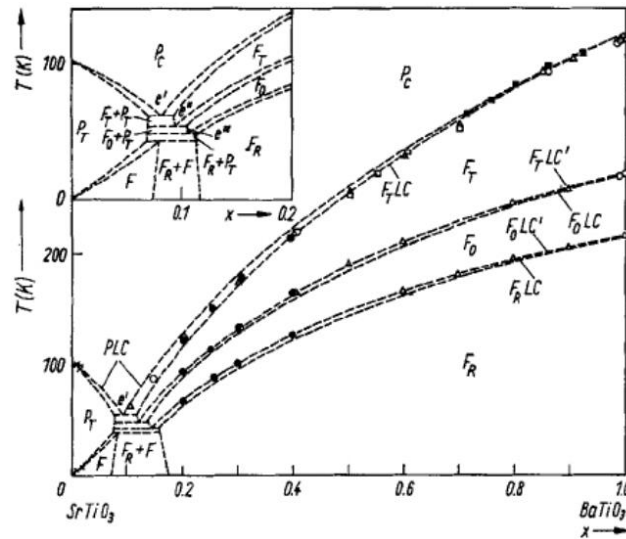


Figure 1-6. Phases of BST as a function of atomic % addition of substitutional cations of Ba. P_C – paraelectric cubic, F_T – ferroelectric tetragonal, F_O – ferroelectric orthorhombic, F_R – ferroelectric rhombohedral, LC – limit curve. From reference 24.

BST may have a wide range of dielectric properties depending on its composition, processing, and homogeneity. BST may exhibit dielectric properties that span the range of normal ferroelectrics to relaxors. Figure 1-7 gives a brief description of the differences in both sides of this range.²⁵

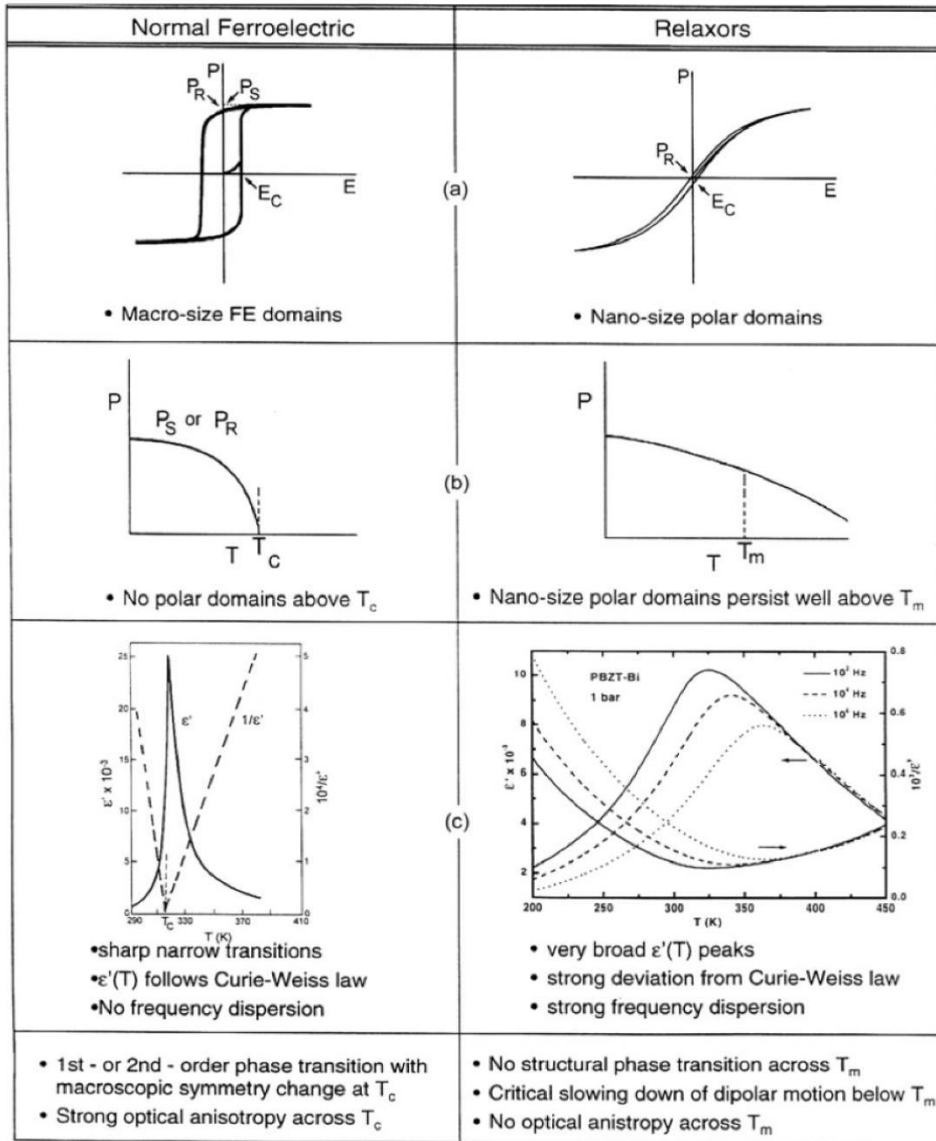


Figure 1-7. Normal ferroelectric versus relaxors ferroelectric behavior. From reference 25.

The explanation for relaxor behavior was summarized by Samara.²⁵ Short range chemical ordering and lattice defects create dipolar entities in some mixed ABO_3 perovskites. At high temperatures, i.e. $T > T_d$, thermal fluctuations are large enough to prevent well-defined dipole moments. On cooling, the dipolar entities manifest as polar nanodomains which increase in size as the temperature decreases. The length scale over which the nanodomains have a similar polarization is called the correlation length, r_c . This is shown in Figure 1-8.

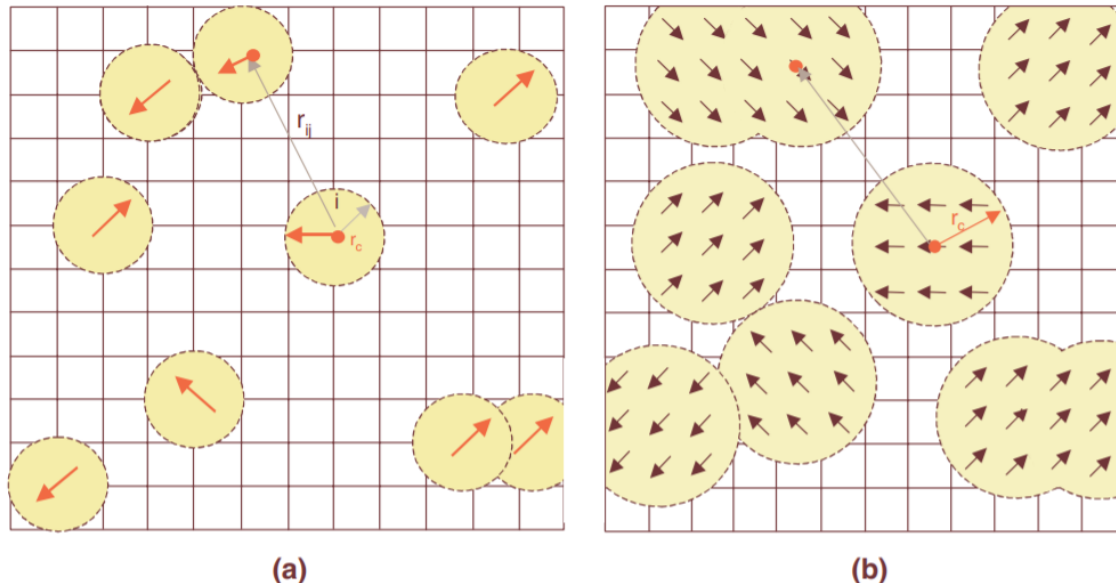


Figure 1-8. The domain structure shown in (a) is for a soft mode ferroelectric lattice with a correlation length, r_c , where the small r_c causes the domain to behave as an isolated dipole. In (b), the domain induces local dipoles around its position increasing r_c and forming a dipolar nanodomain. Adapted from reference 25.

The domains grow as r_c grows with decreasing temperature resulting in two possibilities. When the domains grow large enough (macrodomains) where they percolate over the whole sample, the sample undergoes a static, cooperative ferroelectric phase transition at T_c . However, if the nanodomains grow with decreasing temperature but do not become large enough to percolate the sample, they exhibit a dynamic slowing down of their fluctuations at $T \leq T_m$ leading to an isotropic relaxor state with random orientation of the polar domains.²⁵

In order to differentiate between chemical inhomogeneity and the cause of relaxor behavior, Samara performed hydrostatic pressure experiments with a fixed composition to explore the balance between competing short- and long-range forces with the correlation length model. For example, in PZN-9.5PT, it was found that increasing pressure from 1 bar to 15 kbar induced a normal ferroelectric to relaxor crossover, as shown in Figure 1-9.²⁵ Domains grow as r_c grows with decreasing temperature eventually percolating into a cooperative long-range ordered ferroelectric state at $T < T_c$ on cooling, but increasing pressure reduces r_c and prevents a

ferroelectric transition. This continual reduction in r_c with increasing pressure leads to relaxor behavior and the observed increase in frequency dispersion. This result supports the correlation length model and gives proof that the appearance of relaxor ferroelectricity is not caused entirely by the length scale of chemical inhomogeneity but can be influenced by pressure as well.²⁵

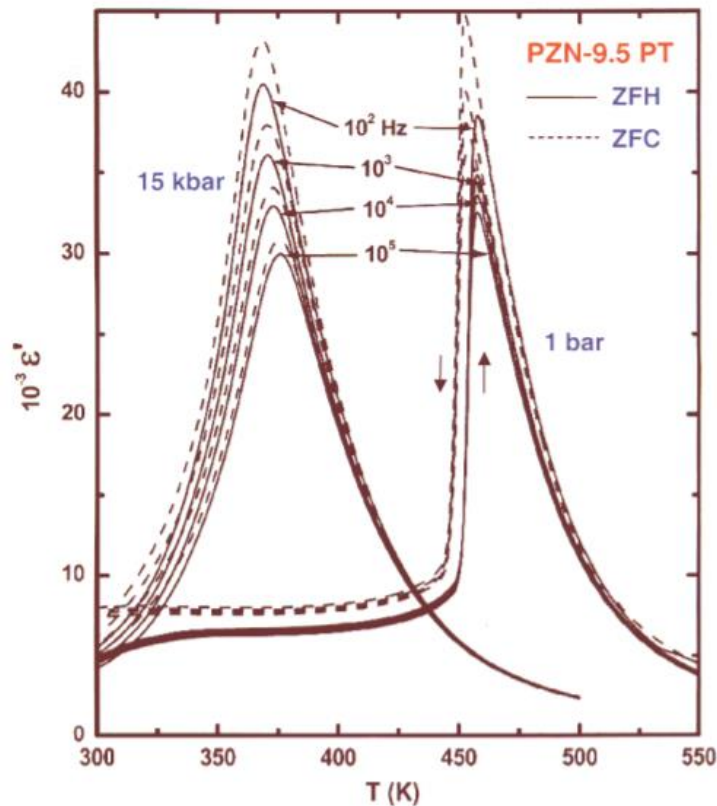


Figure 1-9. Temperature dependence of the real part (ϵ') of the dielectric constant of PZN-9.5 PT at 1 bar and 15 kbar showing the pressure-induced FE-to-relaxor crossover. Data are shown on both heating (H) and cooling (C) in the absence of dc bias, i.e. in zero field (ZF). From reference 25.

1.3 Processing

One of the most challenging problems associated with the processing of BST solid solutions is creating a homogeneous powder or wet chemical solution for fabricating compositionally uniform bulk samples. There are numerous ways to process BST as shown in the literature.^{26–32} The two main methods of synthesis are solid state synthesis through

decomposition of precursor carbonates of BaCO_3 and SrCO_3 with TiO_2 at elevated temperatures of 1100-1200 °C²⁷⁻³⁰ or wet chemical precipitation methods with pyrolysis at lower temperatures of ~750-1050 °C.²⁶ It has also been reported that nanocrystalline BST may be synthesized at ≤ 100 °C using wet chemical methods.^{31,32} The solid state synthesis method tends to be more cost effective than chemical precipitation methods. However, chemical precipitation methods can produce homogeneous and fine powders because of the atomic mixing of the process. Solid state synthesis reactions require the decomposition of BaCO_3 and SrCO_3 and depend on diffusion of Ba and Sr into TiO_2 to create the BST solid solution phase. A common problem is that the Ba and Sr composition is never properly homogenized. The need for fine powders prior to sintering may require additional milling to increase the driving force for sintering and increase the density that may be achieved.

Following preparation of the powder, samples are either uniaxially pressed, cold isostatically pressed (CIP), or both. Samples are sintered conventionally or using alternate techniques such as microwave sintering. The sintering temperatures of these methods generally ranges from 1200-1500 °C²⁷⁻³¹ with better densification toward the higher temperatures. Other techniques such as spark plasma sintering (SPS) can densify the powder at lower temperatures more quickly using added pressure (30 MPa). The sintering temperature was 1000 °C for this method.²⁶

Garten et al.³³ studied the relaxor ferroelectric behavior in BST for both bulk and thin film samples. The methods compared were traditionally processed bulk BST ceramics and chemical solution deposited (CSD) thin films crystallized onto MgO substrates.³⁴ Rayleigh analysis and second harmonic generation (SHG) were used to study the presence of nanoscale polar regions above the global phase transition temperature. It was shown that samples

processed using the two methods showed varying amounts of relaxor-like behavior. The more chemically homogeneous samples showed little relaxor-like behavior while chemically inhomogeneous samples resulted in relaxor-like behavior. This was confirmed using a transmission electron microscope (TEM) through electron energy loss spectroscopy (EELS). The EELS analysis showed more local chemical inhomogeneity using the average Ba:Ti % variation in samples that presented relaxor-like behavior. The samples that showed the lowest amount of local chemical inhomogeneity and the lowest amount of relaxor-like behavior were the bulk BST samples and the samples that showed the highest amount of local chemical inhomogeneity and the highest amount of relaxor-like behavior were the CSD BST thin films on MgO substrates. This work showed the critical importance of the processing conditions in producing a range of chemically homogeneous samples and the influence it had on their final dielectric properties.³³

Zhou and Vilarinho showed the importance of pre-calcination milling time for ensuring chemically homogeneous A-site cation distributions for bulk BST samples. Samples of $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ were milled-mixed for 0, 3, 6, and 9 hours before calcination. The samples that were mixed for 0 and 3 hours showed broad permittivity maxima with temperature while the samples mixed for 6 and 9 hours showed less diffuseness in the permittivity data. Using the X-ray diffraction patterns of each sample set, peak broadening was observed with decreasing milling-mixing time below 6 hours; this was attributed to the inhomogeneity in the Ba^{2+} and Sr^{2+} distribution. The results are displayed in Figure 1-10.³⁵

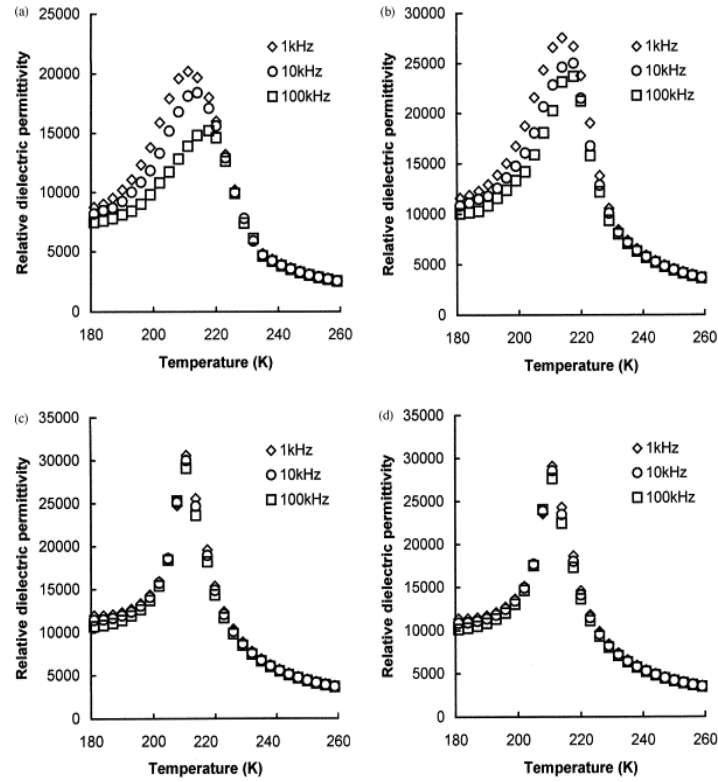


Figure 1-10. Relative dielectric permittivity as a function of temperature for $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ for different pre-calcination milling-mixing times: (a) 0 h, (b) 3 h, (c) 6 h, and (d) 9 h. From reference 35.

1.4 Flexoelectric Design Considerations

The flexoelectric design of the composite device in this work was inspired by the previous work done by Chu et al.³⁶ which followed from the results of Cross. The device is similar in design to the one depicted in Figure 1-11.

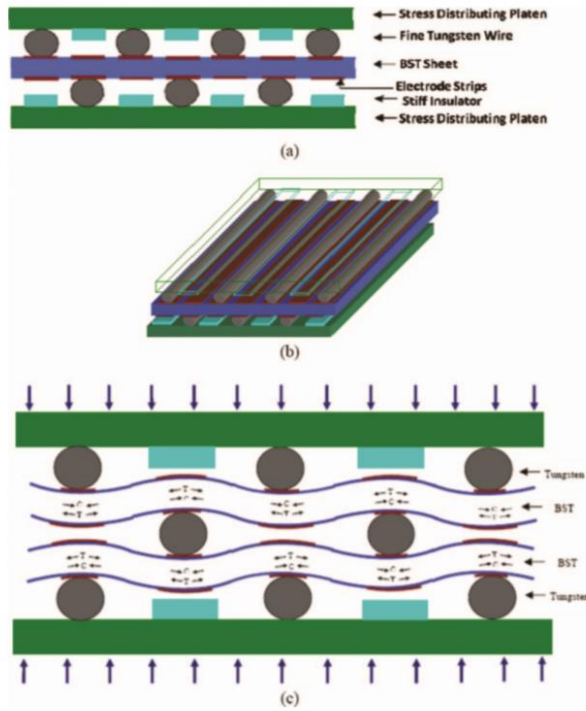


Figure 1-11. The composite flexoelectric device with (a) cross-section design labeled, (b) 3D view from top with top platen removed, and (c) stressed situation showing exaggerated deformation portraying a strong transverse strain gradient that will induce polarization through the $\tilde{\mu}_{12}$ coefficient at the electrodes. From reference 36.

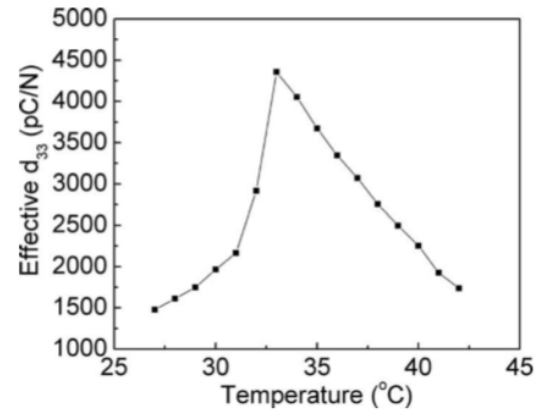


Figure 1-12. The effective d_{33} of a three layer, six unit BST device measured off-resonance at 125 Hz as a function of temperature measured on cooling. The effective d_{33} was measured by taking measured values multiplied by the ratio of capacitance of the ceramic bars to the reference capacitance of the d_{33} meter according to the manual of the meter. From reference 36.

By using extremely well fabricated BST by Texas Instruments (TI) developed for long wavelength IR thermal imaging technology, the composite device showed an effective d_{33} of 4350 pC/N at the Curie temperature as illustrated in Figure 1-12. The use of effective d_{33} is described in Appendix A. This design utilized three layers of the BST to achieve this result, and showed the potential of utilizing the flexoelectric effect for practical use.³⁶

The goal of this work is to provide a more in depth look at how this device might function as a hydrophone. A 60/40 composition BST was used to broaden the flexoelectric response maximum across the ocean temperature range 0-30 $^{\circ}\text{C}$ as well as to allow reproducible fabrication. The material was purchased from TPL Inc. Lastly, the broad design considerations

of the composite device are modeled to provide a quantitative analysis of different design parameters. The design space includes major considerations such as element thickness, nodal spacing, layer count, and electrode size and position as mentioned in Chu et. al.³⁶

Chapter 2

Experimental Procedure

2.1 Pellet Pressing and Tape Casting

Some ceramic samples were created using the solid state method for powder preparation. Homogeneous barium strontium titanate powder with a targeted Curie temperature around 0 °C was synthesized. The Ba/Sr molar ratio was 60/40. A target batch of 40 g was ball milled in a 250 mL Nalgene bottle. The batching details are provided in Table 2-1.

Table 2-1. BST 60/40 solid state synthesis batching; PVA- polyvinyl alcohol, YSZ – Yttria-stabilized zirconia

Material	Supplier	Purity	Size	Lot#	Amount (g)
BaCO ₃	Alfa Aesar	99.8%	1 µm	L03W033	18.405
SrCO ₃	Alfa Aesar	99%, 1% Ba	1 µm	G25T053	9.179
TiO ₂	Alfa Aesar	99.5%	1-2 µm	D04R043	12.415
SiO ₂ (fumed)	Alfa Aesar	99.8%	1 µm	L04K41	1 wt% BST powder
PVA 6 wt%					10 wt% BST powder
Ethanol	Koptec	200 proof		116812	73.3
YSZ media	Inframat	3 mol% Y ₂ O ₃ stabilized ZrO ₂	2 mm		450.0

The batch was processed according to Figure 2-1. Following the calcination step, the powder was assessed by x-ray diffraction (XRD) in a PANalytical Empyrean to ensure phase purity and complete reaction. The calcination temperatures of 1150 and 1100 °C were investigated. Both temperatures produced phase pure powder as assessed by XRD scans. The 1150 °C powder was coarse which prompted the 1100 °C test. The 1100 °C powder reduced coarsening and maintained phase purity. Thus, all future calcinations were conducted at 1100 °C.

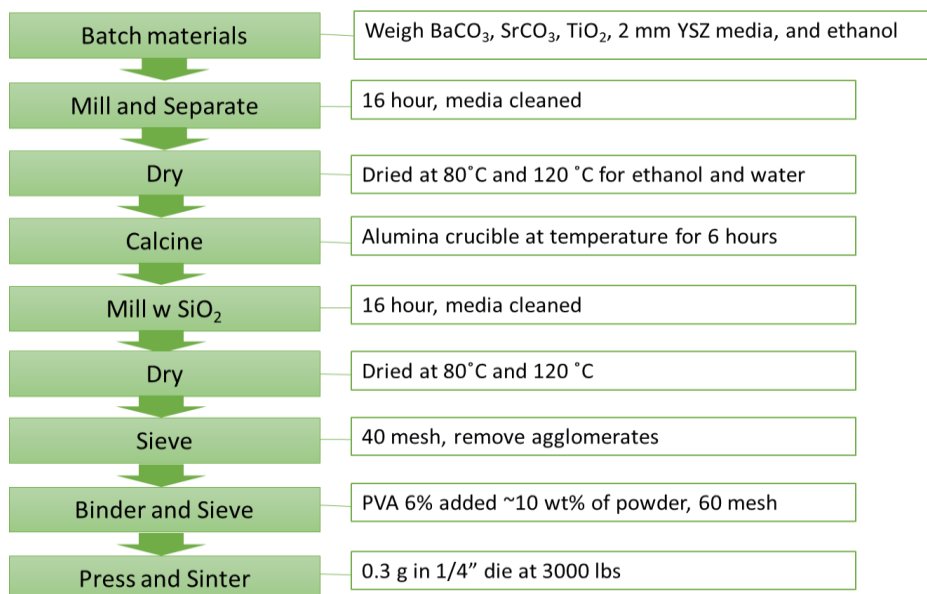


Figure 2-1. Batching flowchart of 60/40 BST

Following calcination, an additional 1 wt% SiO₂ was incorporated in order to promote liquid phase sintering along grain boundaries to enhance densification. The powder was sieved and polyvinyl alcohol (PVA) was added as a binder. The binder promoted dense packing of the powder in the green state after uniaxial pressing.

While this process produced enough powder for sample pellets, production of large cantilever samples was impractical and therefore BST 60/40 powder was purchased from TPL, Inc. in Albuquerque, NM.

Tape casting was utilized in order to create thin 30 mm x 120 mm samples for flexoelectric measurements. The batching details are given in Table 2-2. The processing steps are shown in Figure 2-2.

Table 2-2. BST 60/40 tape cast batching

Material	Supplier	Composition	Size	Amount (g)
BST	TPL	60/40 Ba/Sr	submicron	25.00
Vehicle A	Empower Materials, Fisher Chemical	5 wt % Q-PAC40 95 wt% MEK		8.81
Vehicle B	Sekisui Co. Ltd.	5.3 wt% G-260 28.4 wt% Q-PAC40 66.3 wt% MEK		6.81
YSZ media	Inframat	3 mol% Y_2O_3 stabilized ZrO_2	10 mm	1 every 3 g powder

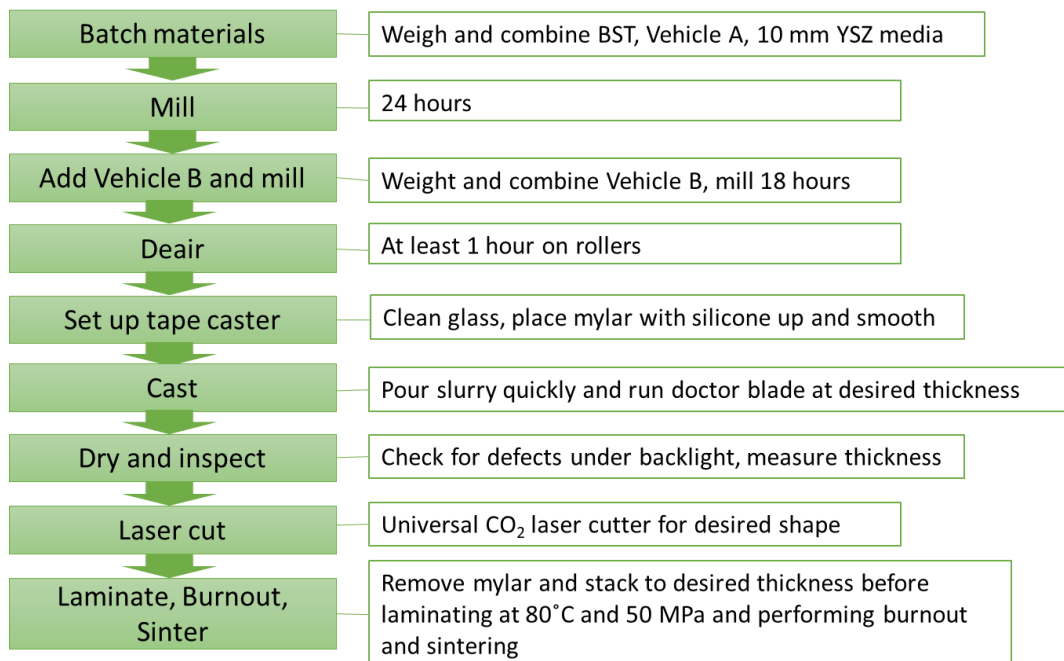


Figure 2-2. Tape casting procedure of BST 60/40

Initial tape casting results seemed promising, but post sintering the BST bars showed extreme warpage. Flexoelectric prototype devices require uniform flat surfaces for the active flexoelectric element in order to ease device manufacturing and ensure compatibility in

cantilever testing. In order to alleviate this problem, green samples were treated in a cold isostatic press (CIP). The CIP pressurizes the sample from all directions through isostatic compression in a fluid (in this case water) reducing stress or density gradients in the material. This procedure showed improved results with a reduction in overall sample warping. The sintered samples only showed problematic warping near the edges and corners of the sample. The relatively flat interior was used to form cantilever samples.

The CIP process is straightforward. Samples were placed in a waterproof material that can be vacuum sealed; latex gloves were initially used for multiple samples until a vacuum food sealer was acquired to ease the process. Using FoodSaver bags, samples were vacuum sealed and placed into the CIP chamber using a metal mesh tube. The samples were pressed at 29,000 psi for 30-60 seconds. The samples were removed from the chamber and the bags, then placed on ZrO_2 setters for burnout and sintering. Figure 2-3 shows the final results. It was found that the resulting parts were flat enough to utilize for cantilever bending experiments. The resulting ceramics were 78.7% of theoretical density; the enormous levels of porosity significantly degraded the dielectric and flexoelectric coefficients, rendering the tape cast materials produced here of low utility.

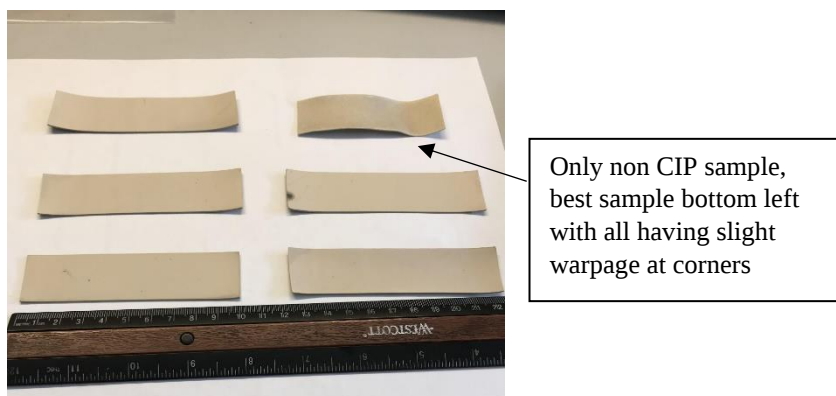


Figure 2-3. Final results of sintering the tape cast, 30 x 120 mm, BST 60/40 samples are shown. The final dimensions are ~ 24 mm x 100 mm. The top right sample was not processed with CIP and shows greater warpage to CIP samples.

2.2 Puck Pressing

In order to improve the relative density of cantilever samples, a 10 cm diameter puck of 60/40 BST was pressed to approximately a 2 cm thickness in the green state. This required 576 g of TPL powder per puck. The powder was pressed using a Tucker Hydraulics 150 ton press in a 10 cm diameter stainless steel die. The sample was placed for burnout in a Lindberg furnace using a 112.4 hour burnout schedule. Following burnout, the sample was transferred to a Keith Company furnace with MoSi_2 heating elements for sintering using a 94.3 hour sintering schedule. Figure 2-4 shows the burnout and sintering profile.

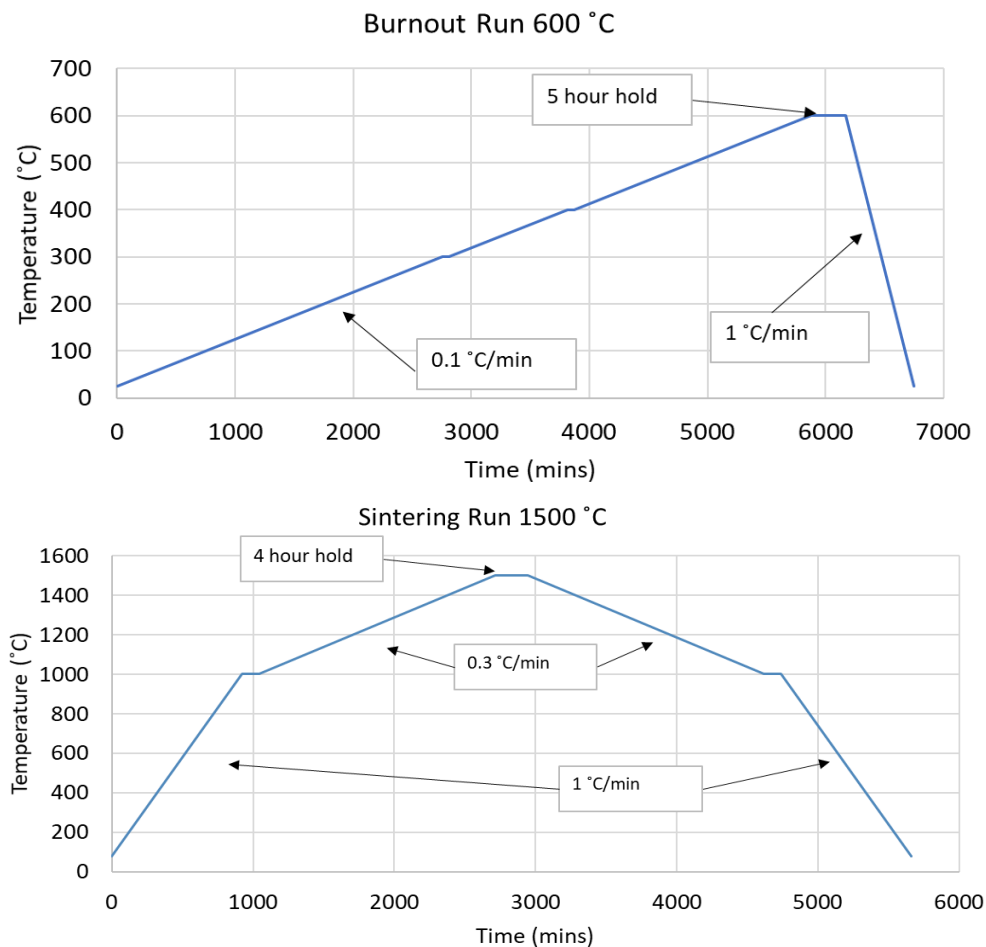


Figure 2-4. Top: 600 °C burnout profile for BST 60/40 10 cm diameter puck;
Bottom: 1500 °C sintering profile for BST 60/40 10 cm diameter puck

Using the sintered puck, the sample was polished at the Applied Research Laboratory (ARL) and cut into different dimensions for the flexoelectric testing. The geometric density was 89.6%.

The relative density is calculated by dividing the measured densities by the theoretical density for 60/40 BST which is 5.683 g/cm^3 .

Due to the low relative density, the BST ceramics were modified with MgO. Mg doping is often studied to lower the loss tangent in BST through acceptor doping of the B site.^{37,38} Cole et al. found benefits in 5 mol% Mg doped BST thin films for tunable device applications from reduced dielectric loss and low leakage current.³⁹ In this case, it was used to improve the relative density of the material with the potential added benefit of reducing the losses. The flexoelectric bending strength and permittivity of BST both benefit from high relative densities (95% +). It should be noted, however, that the MgO second phase dilutes the relative permittivity. In this research, 4 wt% $\text{C}_4\text{H}_2\text{Mg}_5\text{O}_{14} \cdot 5\text{H}_2\text{O}$ (8.4 mol% MgO) was added to the BST as shown in Table 2-3. The sample was prepared as described for the previous puck above with an additional 16 hour dry ball milling step to incorporate the magnesium precursor powder into the BST powder homogeneously. The geometric density of the puck was 94.8% of theoretical density.

Table 2-3. MgO – modified BST 60/40 ceramic batching

Material	Supplier	Composition	Size	Amount (g)
BST	TPL	60/40 Ba/Sr	submicron	576.00
Magnesium carbonate hydroxide pentahydrate, light 98%	Alfa Aesar	$\text{C}_4\text{H}_2\text{Mg}_5\text{O}_{14} \cdot 5\text{H}_2\text{O}$	submicron	24.00

2.3 Machining

In order to prepare polished flexoelectric elements with plane-parallel surfaces for hydrophone testing, sintered BST pucks were sent to the Electro-Optics Center in Freeport, PA. The pucks were trimmed on top and bottom to remove surface impurities using a wire saw from Diamond Wire Technology. The pucks were planarized using a Haas MiniMill to create parallel surfaces. The pucks were then diced into thinner wafers (≥ 800 microns in thickness) using the wire saw and polished to a surface roughness of 5-10 Ra microinches using the MiniMill. Finally, the wafers were cut into elements with the final dimensions for testing using a Disco DAD-321 Automatic Dicing Saw.

2.4 Hydrophone Assembly

These elements were electroded with fired on silver and fixed into the hydrophone structure (described in Ch. 4-2) with epoxy on the walls or supported on small ledge supports. The epoxy is a 100/90 parts mix between EPONTM Resin 828 and EPIKURETM 3140 from Miller-Stephenson. The elements may sit snug between the roller pins with no epoxy needed by using side stops to prevent horizontal movement. This was found not to produce flexoelectric output in tap testing. Instead, the best results were found in samples that used a minimal amount of epoxy to bond the ends to supporting ledges attached to the side walls.

2.5 Ball on 3 Ball

The ball on 3 ball technique is a useful method for measuring the maximum biaxial stress of a material. This method was chosen in order to match the loading conditions of BST in a cantilever flexoelectric device. Texas Instruments BST was diced into 20 samples of 12 mm x 12 mm squares to be tested. The biaxial stress is calculated by Equation 2.1 where f is a dimensionless pre factor, F is the applied force, and t is the thickness of the sample. The pre

factor is calculated using a web application which uses the ratio of the thickness of the sample/disc radius, the ball radius/disc radius, and Poisson's ratio.⁴⁰

$$\sigma_{B3B} = f \cdot \frac{F}{t^2} \quad (1)$$

The technique was performed on an Instron compressive load frame. The sample was placed on top of a stainless steel ball bearing in a die and three additional stainless steel ball bearings were balanced on top of the sample as demonstrated in Figure 2-5. A preload of 2-10 N was applied to balance and ensure contact of all three balls to the load frame. The frame slowly applied a compressive force until failure was achieved. The force at failure was measured. After 20 samples were tested, the data was plotted to a Weibull distribution to determine the Weibull modulus and strength, as shown in Figure 2-6. The Weibull modulus was 14.3 ± 0.2 and the Weibull strength was 130.5 ± 4.3 MPa.

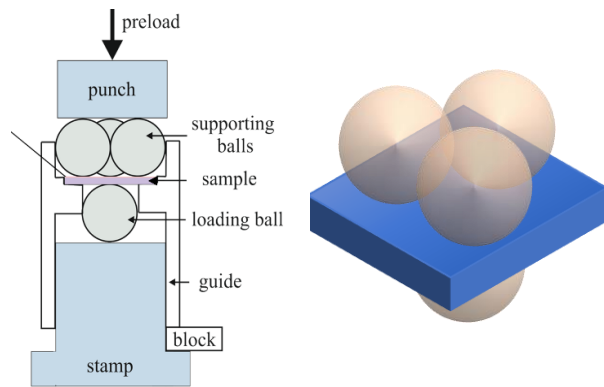


Figure 2-5. Ball on 3 ball experimental diagram

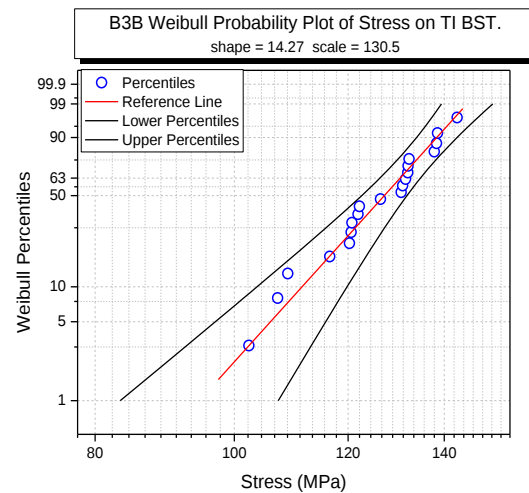


Figure 2-6. Weibull distribution of 20 BST samples

2.6 Scanning Electron Microscope (SEM) Preparation

Both 70/30 Texas Instruments and 60/40 TPL BST samples were polished and prepped for SEM. The samples were polished down to $1 \mu\text{m}$ and showed a mirror finish. Samples were

thermally etched at 1000 °C for 2 hours. Samples were then mounted with carbon tape onto SEM pins and copper tape was used to ground surface charging off the sample. The samples were coated with 5 nm of iridium to prevent charging of the surface using a Leica sputter coater.

Chapter 3

Characterization

3.1 SEM Micrographs

The microstructures of both the TI 70/30 BST and the TPL 60/40 BST were analyzed using a FEI Nova NanoSEM 630. The grain size was calculated using the lineal intercept method from 15 random lines and assuming tetrakaidekahedral shaped grains. As shown in Figure 3-1, the microstructure of the TI sample was dense with no visible porosity. The average grain size was calculated to be $2.3 \pm 0.3 \mu\text{m}$. In comparison, Figure 3-2 shows the TPL 60/40 in-house tape cast BST with open porosity interconnected in the microstructure. This lower density microstructure is proposed to be caused by improper tape casting parameters which introduced porosity during the burnout step that was not removed with conventional sintering.

The TPL 60/40 puck was sampled and analyzed using a Thermo Fisher Scientific Verios 5 XHR SEM. The grain size was calculated using the lineal intercept method from 22 random lines and assuming tetrakaidekahedral shaped grains as shown in Figure 3-3. The average grain size was calculated to be $8.0 \pm 1.1 \mu\text{m}$. A similar TPL 60/40 puck doped with 8.4 mol% MgO was sampled and analyzed. The grain size was calculated using the lineal intercept method from 18 random lines and assuming tetrakaidekahedral shaped grains as shown in Figure 3-4. The average grain size was calculated to be $3.3 \pm 0.5 \mu\text{m}$.

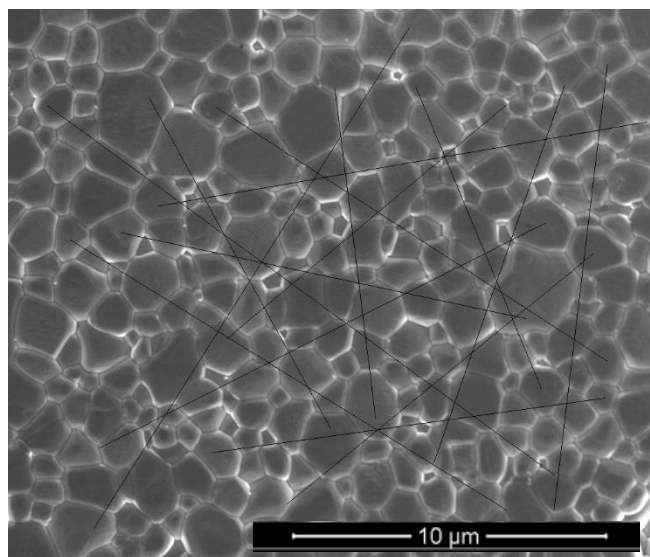


Figure 3-1. TI 70/30 micrograph with 15 random lines drawn to calculate grain size from the lineal intercept method.

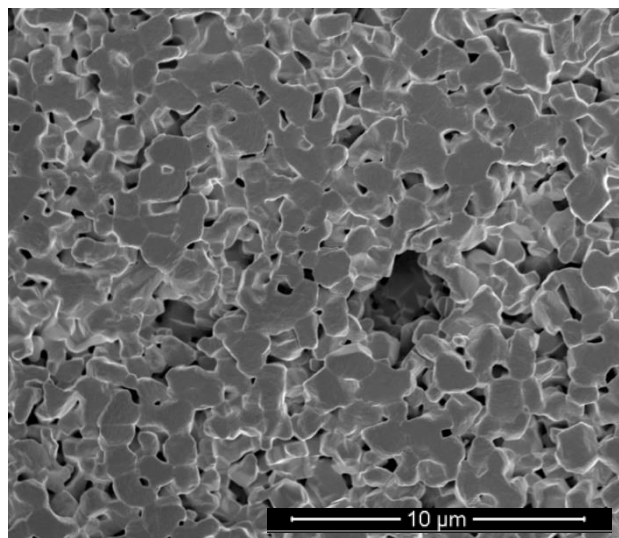


Figure 3-2. TPL 60/40 processed by tape casting micrograph showing interconnected open porosity and therefore lower density.

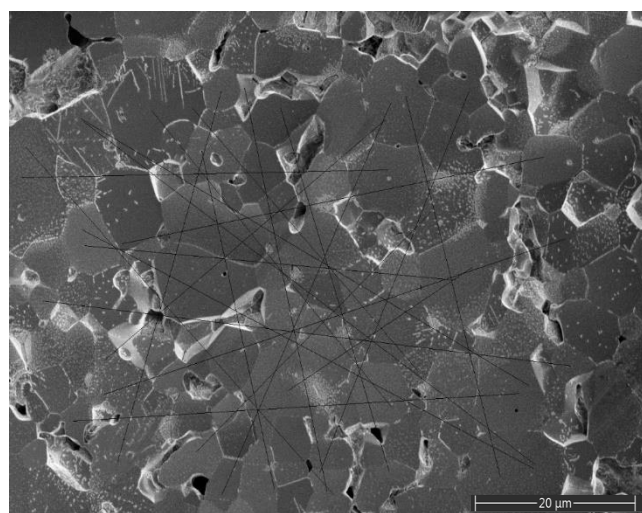


Figure 3-3. TPL 60/40 micrograph with 22 random lines drawn to calculate grain size from the lineal intercept method.

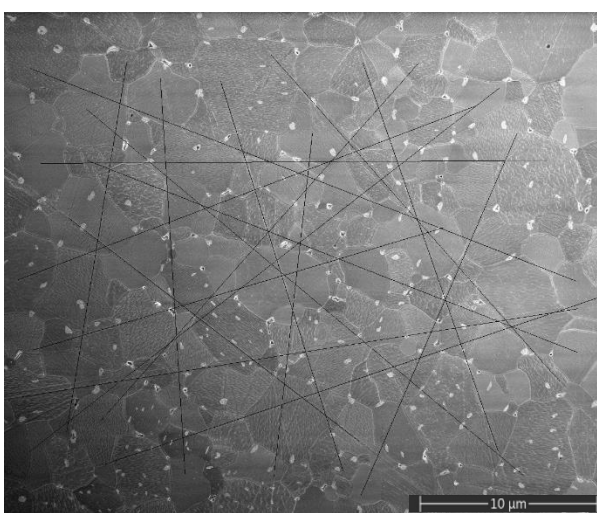


Figure 3-4. TPL 60/40 with additional 8.4 mol% MgO micrograph with 18 random lines drawn to calculate grain size from the lineal intercept method.

3.2 X-ray Diffraction (XRD)

XRD was performed using a Malvern Panalytical Empyrean on a TI BST bulk sample and a polished TI 40 micron thick sample shown in Figure 3-5. Both patterns show the same peak positions within 0.1 degrees 2θ and matched best to a BST 70/30 composition in the

database which is why it was characterized from here on as 70/30. XRD was also performed on TPL 60/40 BST with additional 8.4 mol% MgO displayed in Figure 3-6. The pattern showed phase purity and no secondary MgO peaks. Cole et al. showed no secondary phase of a 5% MgO doped BST film but did see secondary MgO phase in a 20% MgO doped BST film.³⁹ This suggests the 8.4 mol% MgO BST sample is near the detection limit of MgO in BST.

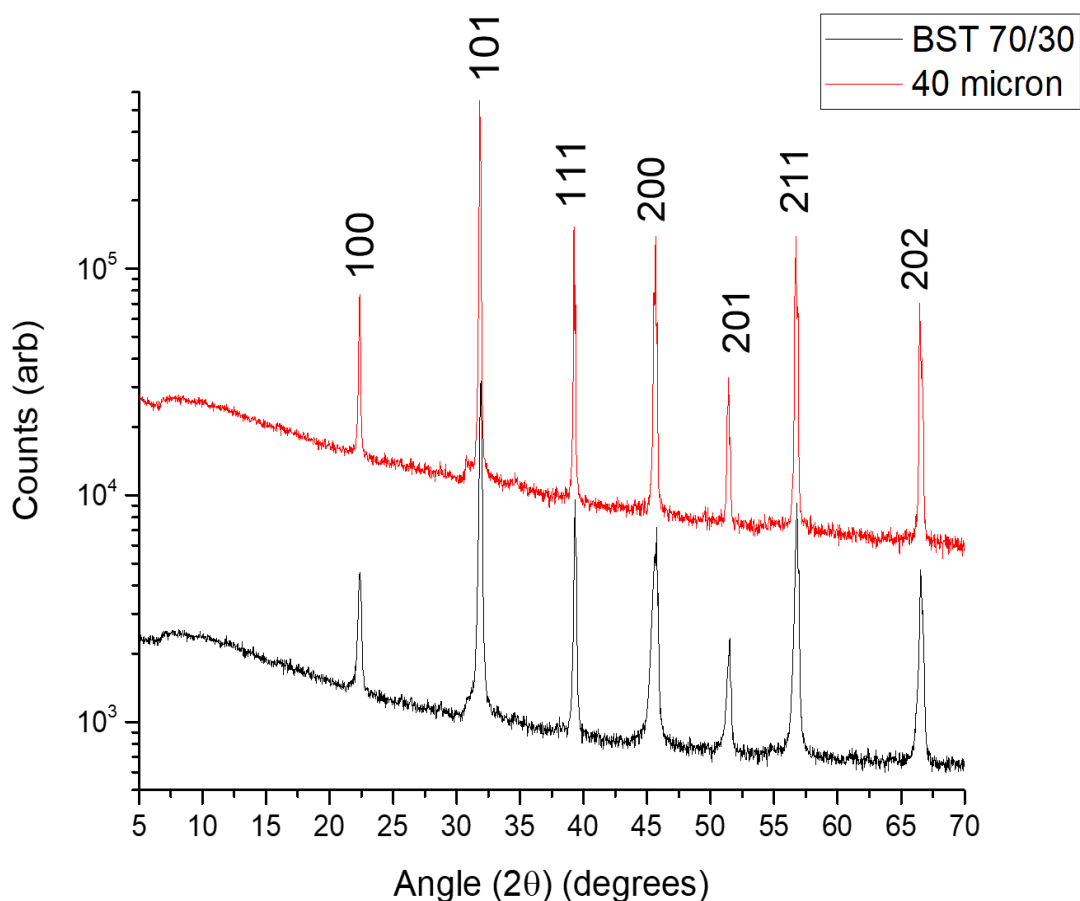


Figure 3-5. XRD pattern of TI 70/30 BST bulk and 40 micron thick overlaid to show peak positions within 0.1 degrees 2θ of each other.

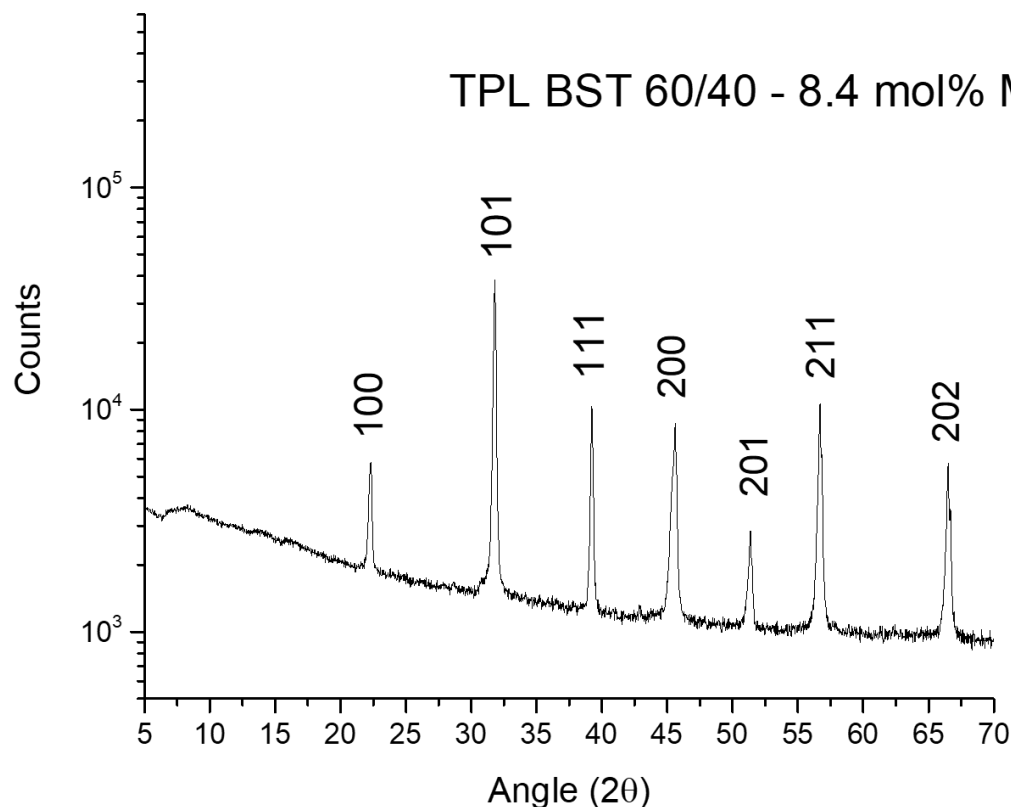


Figure 3-6. XRD pattern of bulk TPL 60/40 BST – 8.4 mol% MgO.

3.3 Dielectric Characterization

The dielectric properties of a material directly affect the flexoelectric response of the material, therefore, characterization of the dielectric properties of a material is necessary to gain insight into the flexoelectric response. The dielectric properties of the TI 70/30 BST and the TPL 60/40 BST were measured using a Delta Design 2300 heating/cooling oven. The sample temperature was measured and recorded from a type-k thermocouple using a digital multimeter (Hewlett Packard 3478). The results are shown in Figure 3-7 and 3-8.

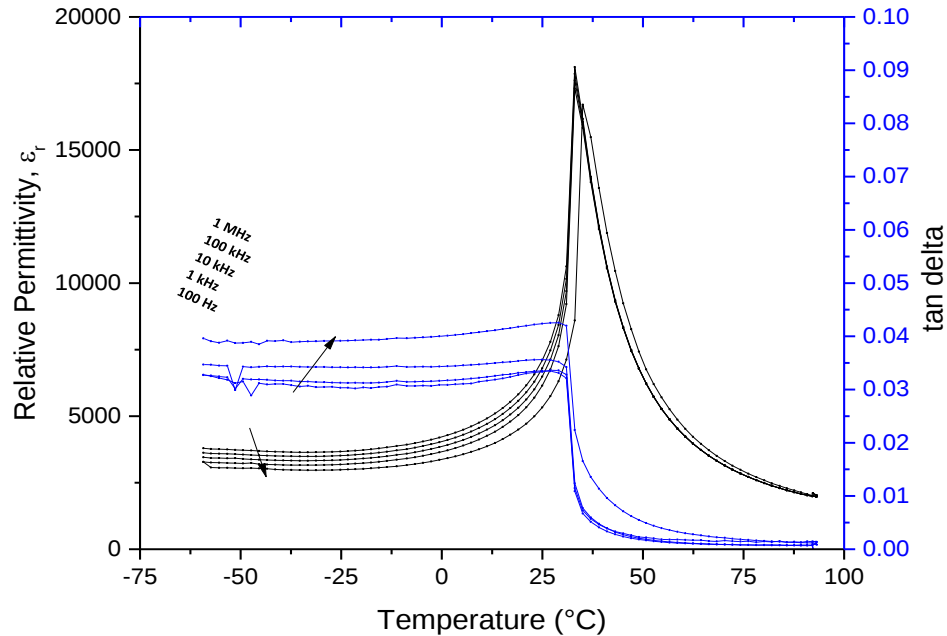


Figure 3-7. TI 70/30 BST relative permittivity as a function of temperature from -60-93 °C measured on cooling with a maximum permittivity achieved at the Curie temperature, 33 °C, of 18000.

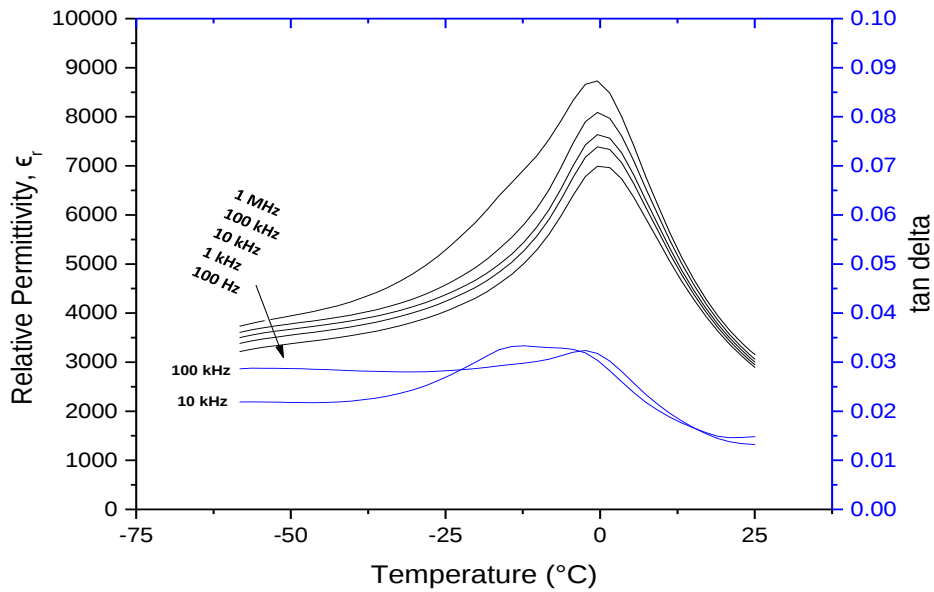


Figure 3-8. Tape-cast TPL 60/40 BST relative permittivity as a function of temperature from -60-25 °C measured on cooling with a maximum permittivity achieved at the Curie temperature, 0 °C, of 8700.

The maximum relative permittivity on cooling in the TI 70/30 was 18000 at the Curie temperature of 33 °C while in the TPL 60/40 it was 8700 at the Curie temperature of 0 °C. The

loss tangent of the TI 70/30 was 0.002 above the Curie temperature in the paraelectric region and increased to 0.03 below the Curie temperature in the ferroelectric region due to the contribution of ferroelectric domain walls. The TPL 60/40 shows a gradual decrease in loss from 0.03 to 0.015 at room temperature above the permittivity maximum temperature of 0 °C. The dielectric behavior of the TPL 60/40 is more heterogeneous, with broader permittivity and loss peaks, along with frequency dispersion characteristic of relaxor behavior.

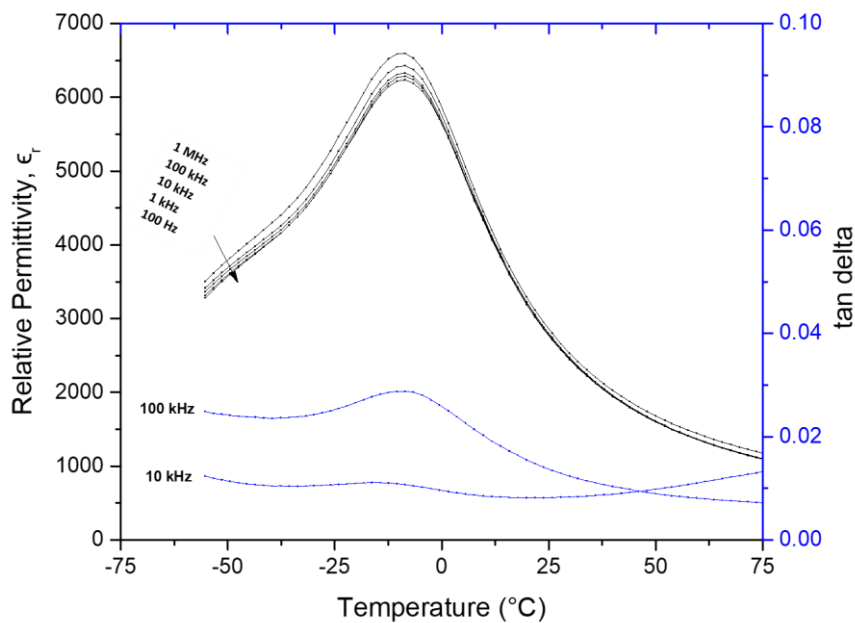


Figure 3-9. TPL 60/40 BST with additional 8.4 mol% MgO relative permittivity as a function of temperature from -60-75 °C measured on cooling with a maximum permittivity achieved at the Curie temperature, -8 °C, of 6600.

Figure 3-9 displays the permittivity results of a TPL 60/40 with additional 8.4 mol% MgO sample. The maximum permittivity was 6600 achieved at the Curie temperature of -8 °C. Therefore, the MgO diluted the permittivity to 6600 and shifted the Curie temperature lower to -8 °C from 0 °C when compared to the pure TPL 60/40 data. The loss was ≤ 0.01 across the range at 10 kHz and from 0.03 to below 0.01 at the Curie temperature to 75 °C, at 100 kHz.

3.4 Curie-Weiss Behavior

The Curie-Weiss behavior of the TI BST was determined by taking the reciprocal of the relative permittivity, which is the dielectric stiffness, and plotting it versus temperature. Curie-Weiss law states that the dielectric stiffness should follow a linear function with temperature in the paraelectric region. If there is deviation from this law in the paraelectric region, it would suggest there is some other contribution to the permittivity and therefore the dielectric stiffness. This could arise, for example from the existence of local micro or nano polar regions above the Curie temperature known as Känzig regions.⁴¹ The temperature range of these regions depends on the homogeneity of the material and the persistence of these regions above the Curie temperature. The temperature at which these regions disappear is known as the Burns' temperature, T_d . The Curie-Weiss behavior of the TI 70/30 BST is given in Figure 3-10.

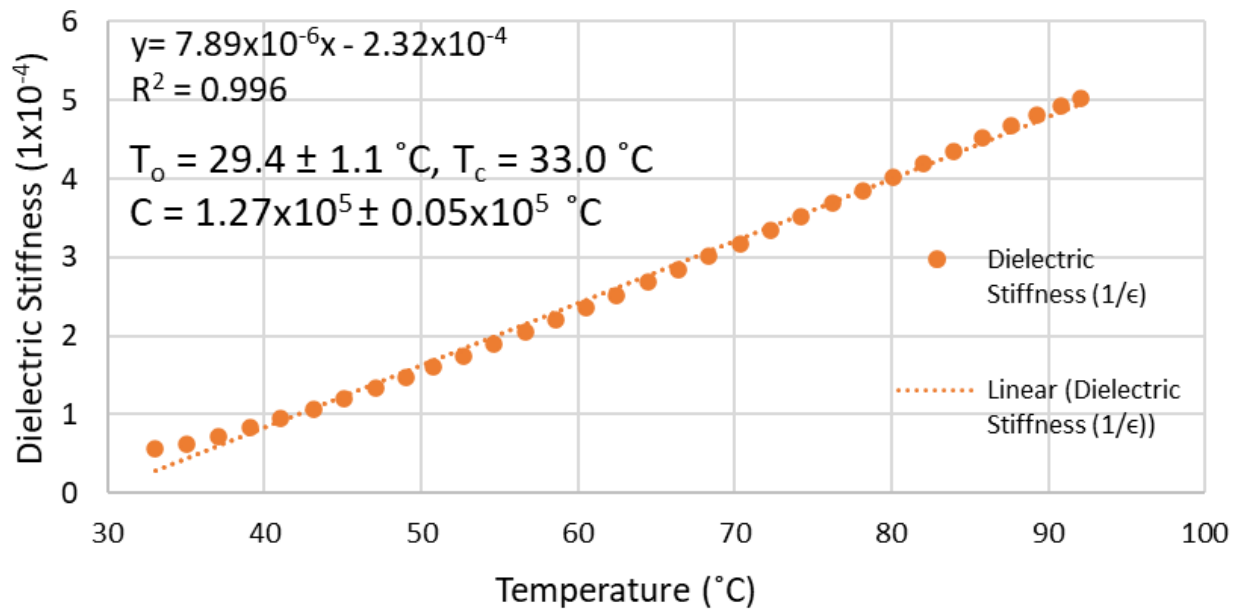


Figure 3-10. TI 70/30 BST Curie-Weiss behavior measured by plotting dielectric stiffness (reciprocal of dielectric permittivity) versus temperature and determining the linear behavior in the paraelectric region. The Curie-Weiss temperature is $29.4 \pm 1.1^{\circ}\text{C}$ and Curie-Weiss constant, C , is $1.27 \times 10^5 \pm 0.05 \times 10^5^{\circ}\text{C}$.

3.5 Elastic Modulus, Shear Modulus, Poisson's Ratio, and Q

The elastic modulus (Young's modulus), E , shear modulus, G , Poisson's ratio, ν , and quality factor, Q , were measured for the TI 70/30 material using a Sonelastic® 3.0 from ATCP Physical Engineering. This technique is based off the Impulse Excitation Technique (ASTM-E1876)⁴² for accurate and nondestructive characterization of elastic moduli (E, G , and ν) as well as damping in the material which gives the quality factor, Q .

The sample is pinged by an impulse pin which is positioned at the correct location on the sample depending on the measurement according to the manual. For flexural measurements, the position is at the center of the bar with the microphone at the end of the sample approximately 1 cm above the sample. For flexural and torsional measurements, the impulse is on the edge 0.32L from an end with the microphone positioned at the opposite edge 0.32L from the other end. From the frequency response function (FRF) graph, the fundamental longitudinal frequency and fundamental torsional frequency can be picked and the E and G can be calculated from Equations 3.1 and 3.2. From these values, the Poisson's ratio, ν , can be calculated according to Equation 3.3 below. The Q factor is calculated by Equation 3.4 and is related to the loss of the signal with each cycle through the damping factor, ζ .⁴²

$$E = 0.9465(mf_f^2/b)(L^3/t^3)T_1 \quad (1)$$

E = Elastic modulus (Pa), m = Bar mass (g), b = Bar width (mm), L = Bar length (mm), t = Bar thickness (mm), f_f = Fundamental frequency of bar in flexural mode (Hz), T_1 = Correction factor

$$G = \frac{4Lmf_t^2}{bt}R \quad (2)$$

G = Shear modulus (Pa), m = Bar mass (g), b = Bar width (mm), L = Bar length (mm), t = Bar thickness (mm), f_t = Fundamental frequency of bar in torsional mode (Hz), R = Correction factor

$$\nu = \frac{E}{2G} - 1 \quad (3)$$

$$Q = 1/2\zeta \quad (4)$$

The calculated E of the TI samples was 124.3 ± 1.8 GPa and G was 48.9 ± 0.7 GPa. The Poisson's ratio, ν , was calculated from these values to be 0.27 ± 0.04 and Q was 19.3.

Chapter 4

Flexoelectric Testing and Results

4.1 Cantilever Beam Flexoelectric Coefficient Study

One of the simplest and most straightforward methods for testing flexoelectric materials is a cantilever bending test. The Cross group used cantilever bending to assess BST from TI and found a flexoelectric coefficient, μ_{12} , of 100 $\mu\text{C}/\text{m}$, which was orders of magnitude greater than expected.¹¹ In this work, the Cross data was replicated to confirm the BST flexoelectric coefficients for elements used in hydrophone prototypes. The samples were created following similar procedures. Electrodes were placed at the clamping position by sputtering 100 nm of platinum through an aluminum shadow mask using a Quorum EMS 150R S. The electrode radii sizes were approximately 200, 300, 460, and 690 μm .

The electrodes were positioned so that the clamping occurred at the edge of the electrodes. The electrodes continued along the length toward the free end for ~ 5 mm. The clamped dimensions were kept to approximately a 1:4 width to length ratio which in this case translated to a ~ 10 mm x 40 mm BST cantilever sample. Two Omega strain gauges (one for longitudinal and one for lateral strain) were attached to the sample on the clamped edge of the electrodes using cyanoacrylate glue. The sample was clamped as rigidly as possible in the setup and the sinusoidal strain measurements were made using a quarter Wheatstone bridge configuration attached to a lock-in amplifier (Stanford Research SR830 DSP) at a 30 second time constant. The charge was measured simultaneously with a custom charge integrator circuit optimized for 4 Hz and using the same lock-in amplifier at a 30 second time constant. The sample was flexed by a shielded piezoelectric stack actuator (Kinetic Ceramics) with the drive signal generated by the

same lock-in amplifier. The setup is given schematically in Figure 4-1⁴³ and with a picture in Figure 4-2.

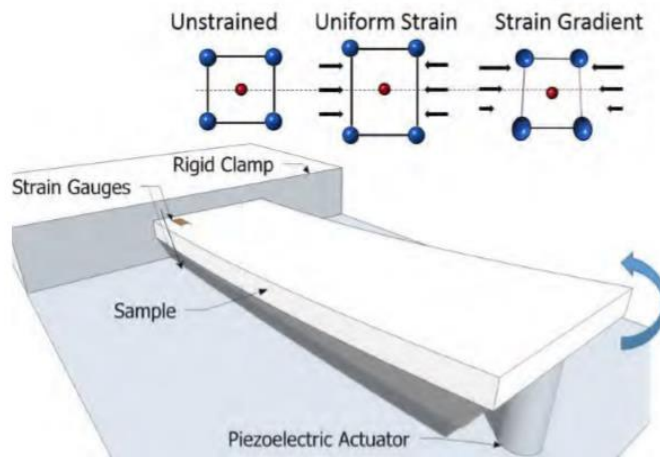


Figure 4-1. Schematic of flexoelectric testing setup showing creation of a strain gradient on a cantilever. From reference 43.

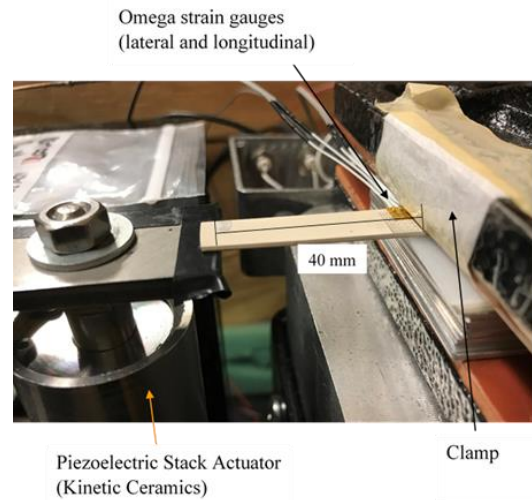


Figure 4-2. Flexoelectric cantilever bending setup with key components labeled. Polarization and strain are measured to calculate the effective flexoelectric coefficient.

The frequency optimized for this system was 4 Hz which was used for this testing. This testing followed previous work by Garten.⁴³ The strain induced on the sample is controlled by varying the AC input voltage to the piezoelectric actuator which in this experiment was 0.1 V increments from 0.1-1 V. The results are shown in Figure 4-3 and are in agreement with previous results¹¹.

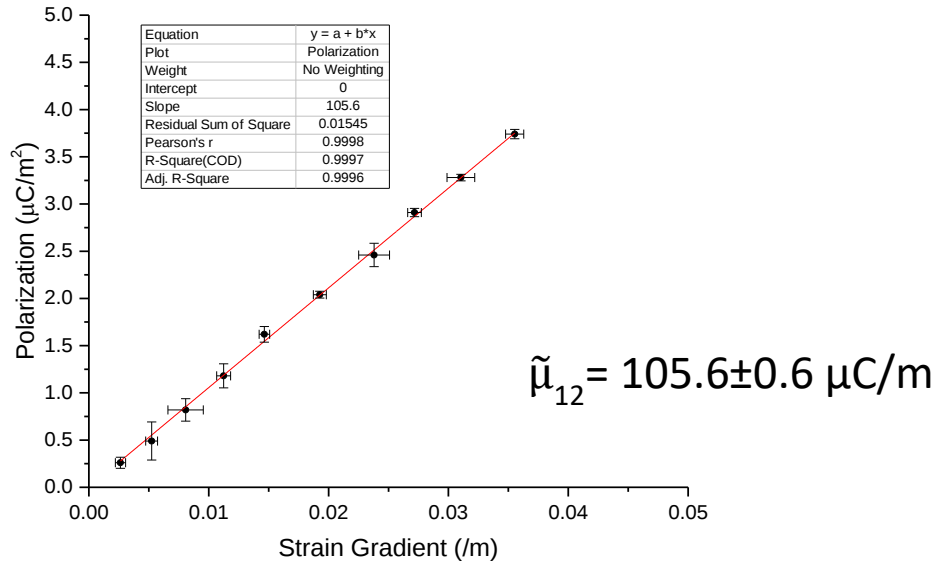


Figure 4-3. Cantilever flexoelectric study of BST 70/30 from TI demonstrating a linear flexoelectric behavior and flexoelectric coefficient, $\tilde{\mu}_{12}$, of $105.6 \pm 0.6 \mu\text{C/m}$.

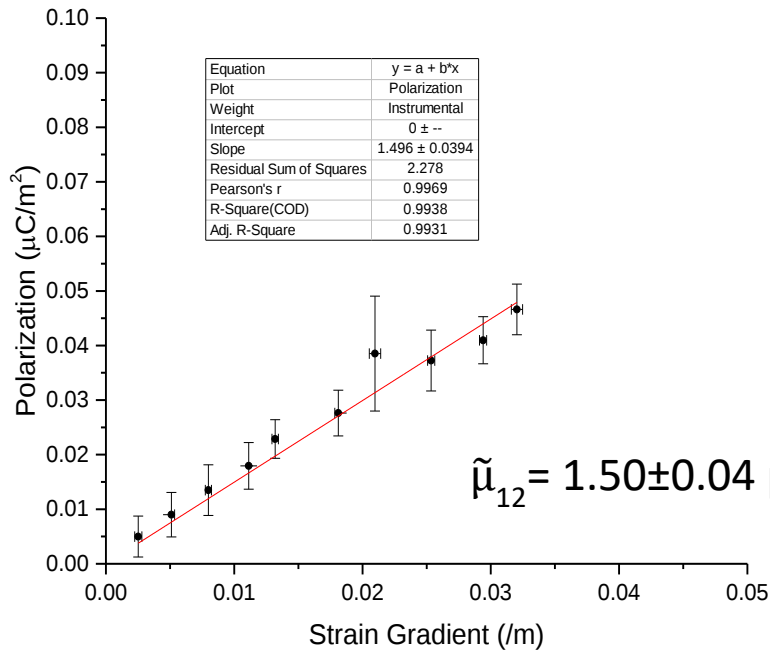


Figure 4-4. Cantilever flexoelectric study of low density tape cast BST 60/40 from TPL demonstrating a linear flexoelectric behavior and flexoelectric coefficient, $\tilde{\mu}_{12}$, of $1.50 \pm 0.04 \mu\text{C/m}$.

The same experiment was performed with the in-house tape cast TPL 60/40 sample; the measured results are displayed in Figure 4-4. The $\tilde{\mu}_{12}$ was $1.50 \pm 0.04 \mu\text{C}/\text{m}$. This value is almost two orders of magnitude lower than the measured values for the TI 70/30 BST. There are two major contributions to this. First, the BST 60/40 is further from T_{max} at room temperature. The expected $\tilde{\mu}_{12}$ is expected to drop in proportion to the drop in permittivity over the temperature range based on the data in Figure 4-5 which shows the temperature dependence of $\tilde{\mu}_{12}$ on BST.¹¹ Second, the sample had a much lower relative density.

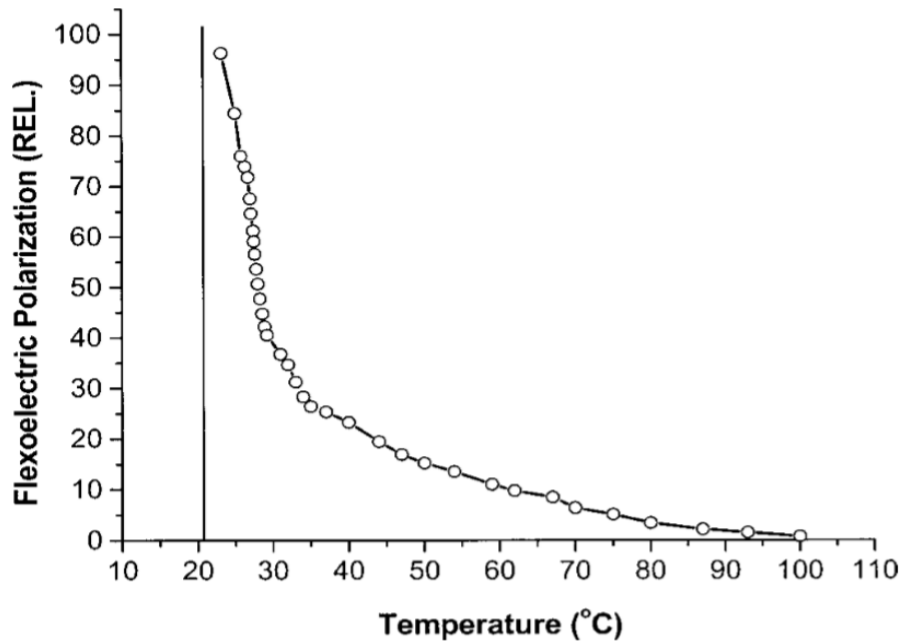


Figure 4-5. Temperature dependence of $\tilde{\mu}_{12}$ in TI BST with vertical line indicating the Curie temperature. From reference 11.

The same experiment was finally applied to the TPL 60/40 with 8.4 mol% MgO. The results are displayed in Figure 4-6. The $\tilde{\mu}_{12}$ was $10.3 \pm 0.2 \mu\text{C}/\text{m}$. The permittivity reduction at room temperature between the TI material and this material was approximately 2 times giving an expected $\tilde{\mu}_{12}$ of $\sim 50 \mu\text{C}/\text{m}$. The measured value was $\sim 10 \mu\text{C}/\text{m}$ suggesting that the flexocoupling coefficient, f , dropped by a factor of 5 giving a net reduction in the flexoelectric effect of 10 times. This is proposed to be caused by the reduction in micropolar regions as the material is

heated further past the Curie temperature.⁴⁴ Since micropolar regions are proposed to cause the enhancement of flexoelectric signal, a reduction or elimination of these regions with increasing temperature greatly reduces the material's flexoelectric effect. If the temperature was decreased to the Curie temperature, the flexoelectric effect should increase greatly in this material with decreasing temperature.

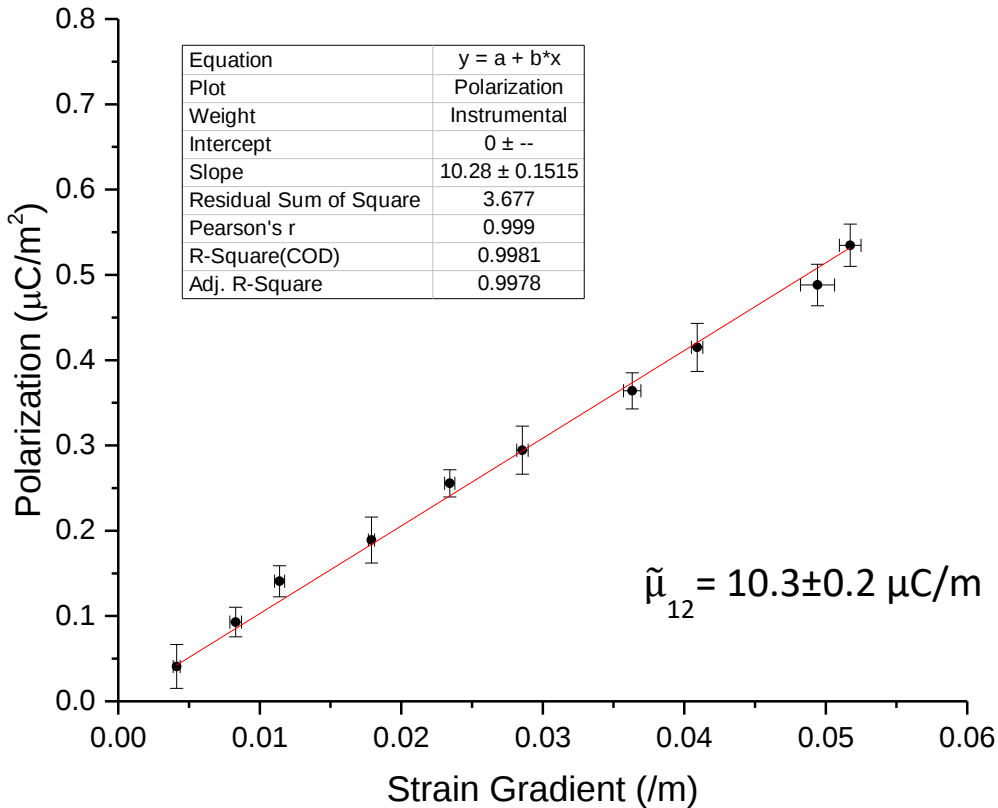


Figure 4-6. Cantilever flexoelectric study of TPL BST 60/40 with 8.4 mol% MgO demonstrating a linear flexoelectric behavior and flexoelectric coefficient, $\tilde{\mu}_{12}$, of $10.3 \pm 0.2 \mu\text{C}/\text{m}$.

Using the measurements done in this study, the table from Chapter 1 has been updated as shown in Table 4-1. There is good agreement between the data of $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ with a $\tilde{\mu}_{12}$ value of $100 \mu\text{C}/\text{m}$ and the current data of $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ with a value of $105.6 \mu\text{C}/\text{m}$ using the cantilever bending (CB) method at room temperature. This is in agreement with Figure 4-5 that

shows a peak in the flexoelectric response as the Curie temperature is approached and a gradual decline in flexoelectric response at higher temperatures.

Table 4-1. Measured experimental flexoelectric coefficients for a variety of materials with this work in the bottom row.^a Adapted from reference 1.

Compound	Coefficient	Method	Value ($\mu\text{C}/\text{m}$)	χ/ϵ_0	$f = \mu/\chi$ (V)
BaTiO ₃	$\tilde{\mu}_{12}$ ($T_c + 3.4$ K)	CB	~50 (12)	~10,000	~560 (12)
Ba _{0.67} Sr _{0.33} TiO ₃	$\tilde{\mu}_{11}$	PC (0.5 Hz)	150 (2)	~20,000	~850
	$\tilde{\mu}_{11}$	CFE (400 Hz)	120 (13)		
	$\tilde{\mu}_{12}$	CB (1 Hz)	100 (11)	~16,000	~700
Ba _{0.65} Sr _{0.35} TiO ₃	$\tilde{\mu}_{12}$	CB	~8.5 (14)	4,100	234
PbMg _{0.33} Nb _{0.67} O ₃	$\tilde{\mu}_{12}$	CB	3-4 (15)	~13,000	~26-45
PMN-PT	$\tilde{\mu}_{11}$	PC (4-10 Hz)	6-12 (16)	21,000	~32-65
		PC (0 Hz)	20-50 (16)		~110-270
Pb _{0.3} Sr _{0.7} TiO ₃	$\tilde{\mu}_{11}$	PC (0.5 Hz)	20 (2)	13,500	170
Pb(Zr,Ti)O ₃	$\tilde{\mu}_{12}$	4PB	0.5 (17)	~2,200	25
		CB (1 Hz)	1.4 (18)		72
Ba _{0.70} Sr _{0.30} TiO ₃	$\tilde{\mu}_{12}$	CB (4 Hz)	105.6 $\pm$ 0.6	~6,000	~1989

^a The values in the last column were calculated from the measured flexoelectric coefficient and the experimental dielectric susceptibilities. References in the fourth and sixth columns are in parentheses. All values are room temperature values unless stated otherwise. Measurement techniques: CB, cantilever bending; PC, pyramid compression; CFE, converse flexoelectric effect; 4PB, four-point bending.

4.2 Prototype Hydrophone Testing (Iteration #1)

In order to test the flexoelectric effect in a hydrophone design, a prototype was fabricated to determine if a mechanical force would generate enough electrical signal to be measured. The method chosen for testing was the tap test where a calibrated impulse hammer struck the structure, imparting flexural bending of the element, leading to the electrical output of the

device. The structure was struck by hand above the roller support attached to the top plate. This was done in order to try to maximize the flexural bending on the BST element at the center electrodes and therefore generate the largest flexoelectric signal. This mimics a three-point bending design used in mechanical materials characterization. In the first prototype design, there were three different electrode pairs: two side pairs and one center pair. Tap testing showed the best results in a tap above the top roller support while collecting electrical signal from the middle pair electrodes. Taps were performed on the sides of the top plate above the other electrode pairs but none of the electrode pairs including the center pair showed coherent signal under these conditions. Another test was performed by tapping the table to see if vibrations transferred through the structure could generate signal from any electrodes. This test again showed no coherent signal in the device for any electrode pairs. Therefore, future iterations were simplified into a single centered electrode pair with one roller support attached to the top plate. The impulse hammer used was a Model 086C02 from PCB Piezotronics using a hard stainless steel tip (Model 084B03) and the data acquisition was collected by a USB-4431 from National Instruments. It is notable that a signal was collected without the use of a preamplifier, which eased data acquisition. Samples were tested with 10 taps and the averaged response was plotted in frequency response function (FRF) plots. Figure 4-7 shows the flexoelectric prototype overall and Figure 4-8 shows the cross-sectional view.

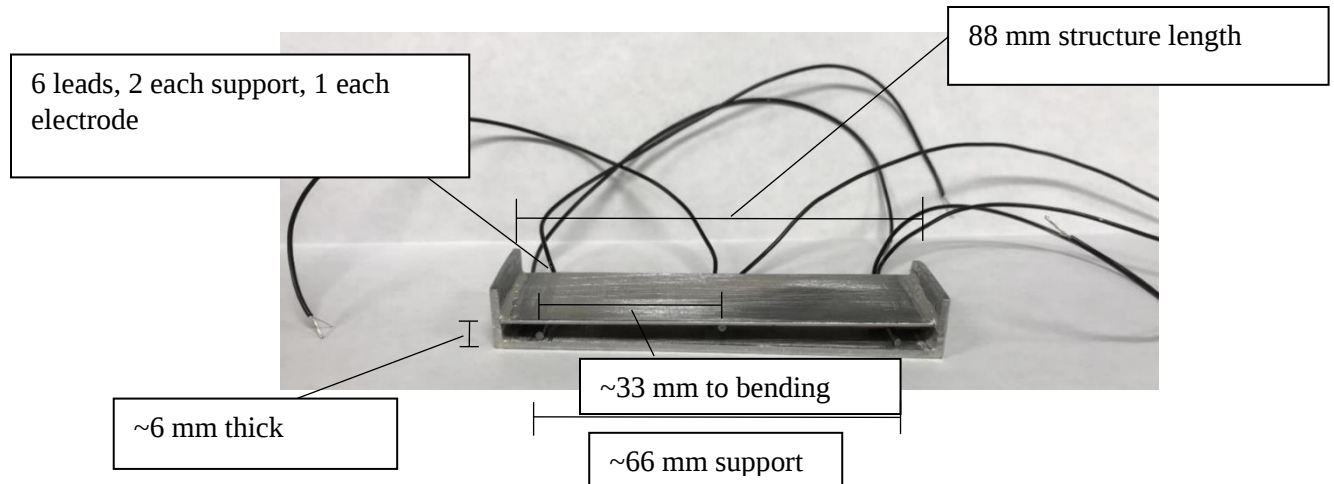


Figure 4-7. Flexoelectric prototype detailing measurements and features

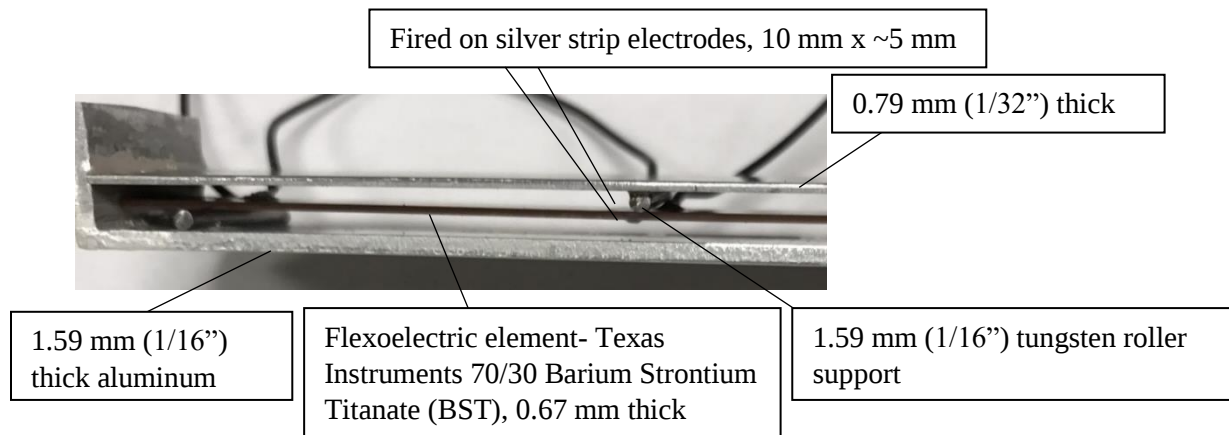


Figure 4-8. Flexoelectric prototype cross-section detailing measurements and materials

By analyzing the frequency response function (FRF) data, the voltage response of the prototype device can be compared to the impulse hammer over the frequency range. Using FRF data shown in Figure 4-9, the sensitivity of the hammer, and the capacitance of the device, the sensitivity of the device may be measured in mV/N and pC/N. This is shown in Figure 4-10.

The coherence of the two signals collected is calculated according to Equation 4.1 where C_{xy} is the coherence, G_{xy} is the cross-spectral density between x and y , $G_{xx}(f)$ and $G_{yy}(f)$ are the autospectral density of x and y . The values for coherence always satisfy $0 \leq C_{xy}(f) \leq 1$.

$$C_{xy}(f) = \frac{|G_{xy}(f)|^2}{G_{xx}(f)G_{yy}(f)} \quad (1)$$

Coherence values closer to 1 provide evidence that the signals are well correlated and that there is a causal relationship between the input and output signal. Any signal with a coherence >0.9 was considered high quality and any signal >0.5 was considered quality. Signal with coherence <0.5 is lower quality and therefore should be studied further before making solid conclusions.

At resonances and antiresonances the coherence dramatically drops. This is due to either the input or output signal being lost in noise at this frequency. At resonance, the input from the hammer is lost and at antiresonance the output from the device is lost. The coherence is quickly recovered around the resonance frequency as signal improves off-resonance. Devices could be studied at their resonant frequencies using an input frequency that matches the resonant frequency to investigate their output behavior instead of just an impulse signal from a tap.

The device was coherent (>0.9) with the hammer up to the first resonance at 250 Hz with a sensitivity at resonance of 80 pC/N. The sensitivity drops below 10 pC/N at the antiresonance located at 300 Hz. The device then maximizes sensitivity at 160 pC/N at a secondary resonance around 530 Hz with low coherence (<0.5) before losing signal in the 600-700 Hz range with no coherence.

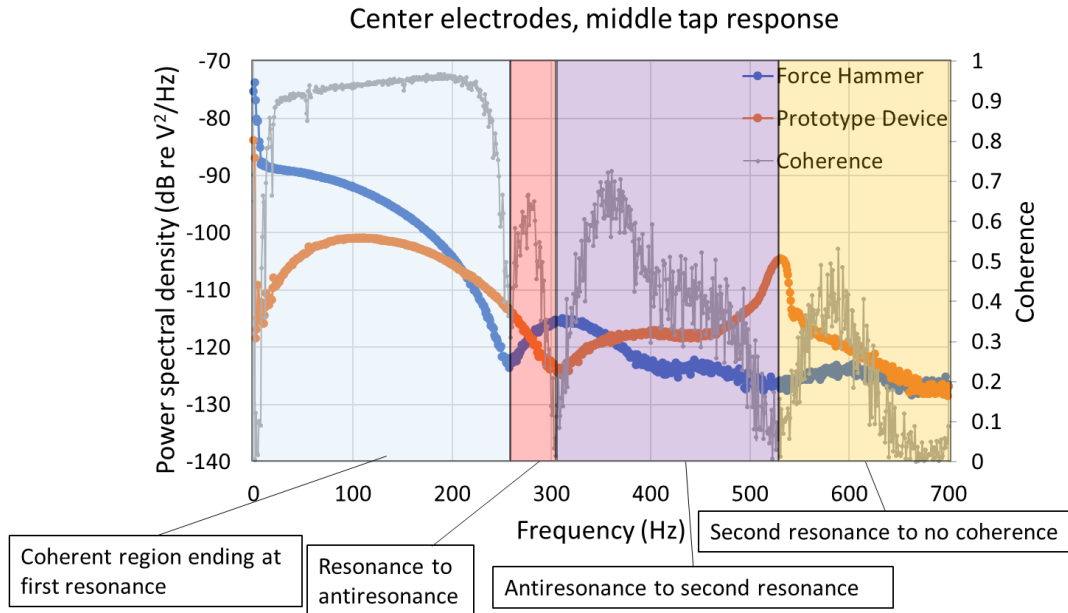


Figure 4-9. Flexoelectric prototype frequency response function (FRF) was measured as power spectral density (PSD) versus frequency. The signals are related through coherence values from 0-1. Regions of interest are labeled.

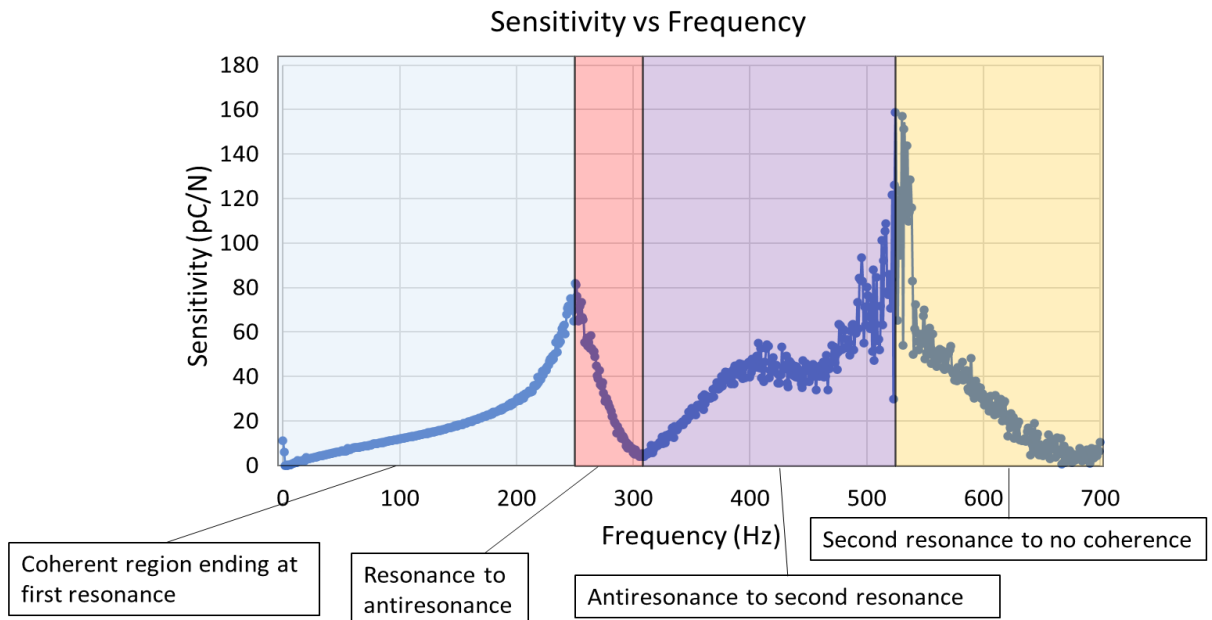


Figure 4-10. Flexoelectric prototype sensitivity (pC/N) as a function of frequency calculated from the FRF using the sensitivity of the force hammer and the capacitance of the device. The sensitivity peaks at 80 pC/N at the resonant frequency of 250 Hz and dips to near 0 pC/N at the antiresonant frequency of 300 Hz. Regions of interest are labeled.

The reduction in beam length for experiments was mainly for practical purposes. The prototype hydrophones devices were hand-built which caused difficulty in precise placement of the pinning roller supports. In theory, the resonant frequency desired for application could be engineered using the pinning roller supports acting as nodes. In practice, it was difficult to precisely place these supports and have them perfectly in contact with the flexoelectric element. Therefore, the designs were simplified to a single centered electrode pair with one roller support centered above the pair to induce bending. This means the fundamental frequency drives the flexoelectric output of the device. By accurately placing roller supports as nodes, targeted frequencies could be achieved by restricting the element to bend in those mode shapes and frequencies.

4.3 Iteration #2

The next iteration tested was a shorter version of the first design approximately ~30 mm in length with the same width and thickness. This was done to try to increase the resonant frequency of the device (where the resonant frequency is inversely proportional to the length squared of the beam). The FRF is shown in Figure 4-11 and the sensitivity is displayed in Figure 4-12. This iteration had weak signal at higher frequency (>600 Hz) and therefore no resonance peaks were observed. This result suggested the device was too stiff and the next iteration was designed to compromise between the large, 77 mm, and short, 30 mm, design at a length of 50 mm.

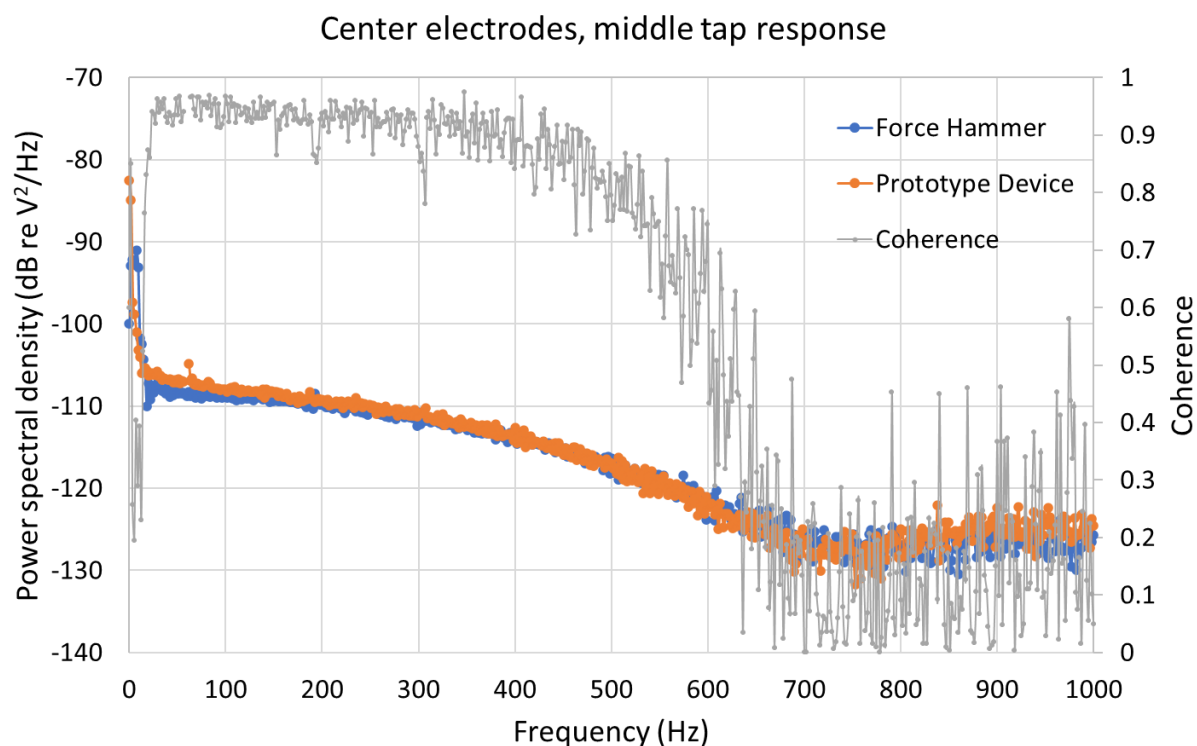


Figure 4-11. Flexoelectric prototype iteration #2 FRF response showing a higher frequency response with no clear resonance.

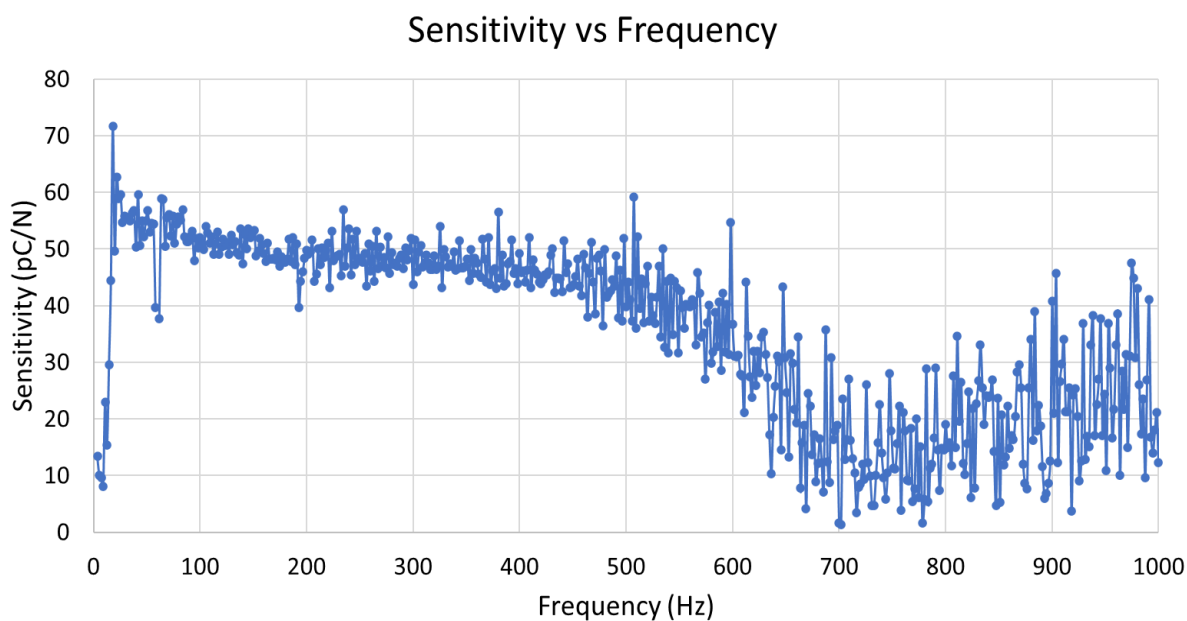


Figure 4-12. Flexoelectric prototype iteration #2 sensitivity as a function of frequency.

4.4 Iteration #3

The next iteration tested was ~50 mm in length with the same width and thickness as previous samples. This length was chosen to increase the resonance frequency measured in the FRF relative to iteration #1. The FRF is shown in Figure 4-13 and the sensitivity is displayed in Figure 4-14. The resonance behavior again was unclear with a broad local maximum response between 200-400 Hz with a sensitivity of 35 pC/N; it is possible that this is a result of imperfect alignment of the stress concentrator with respect to the BST beam. A clear antiresonance was observed at 620 Hz with a peak in sensitivity of 45 pC/N achieved at a secondary resonance of 730 Hz.

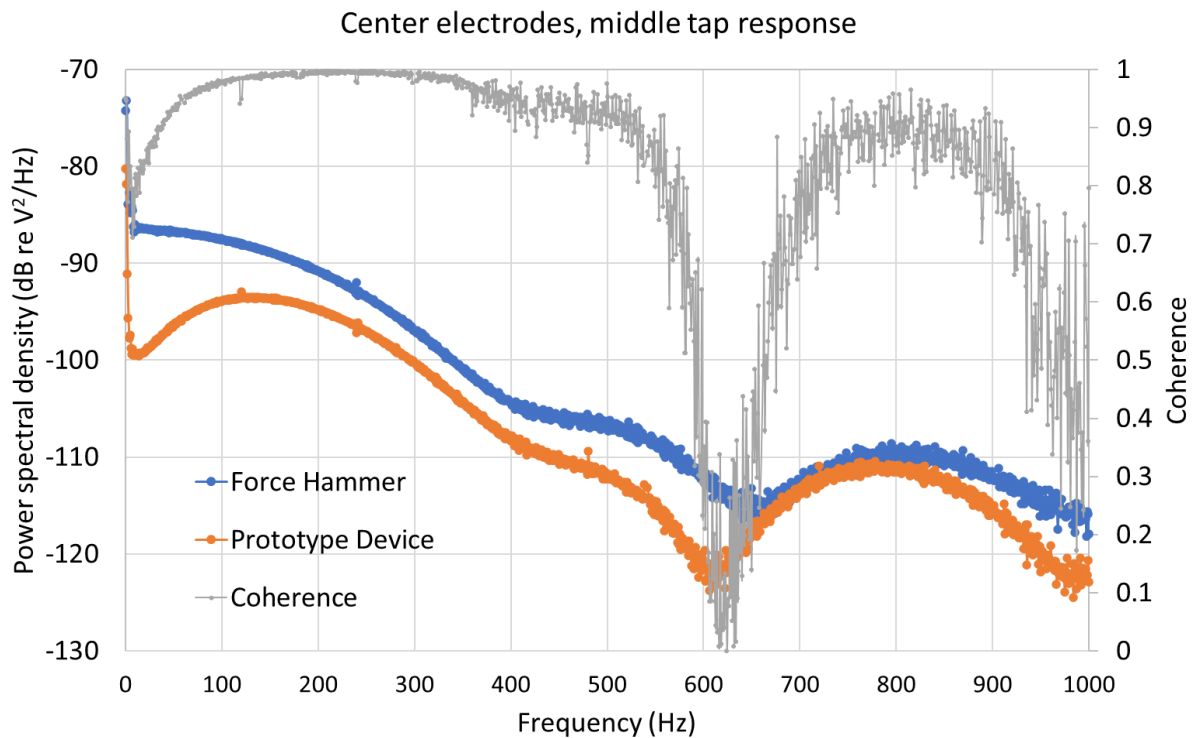


Figure 4-13. Flexoelectric prototype iteration #3 FRF showing a higher frequency response than previous iterations with greater coherence with labeled regions.

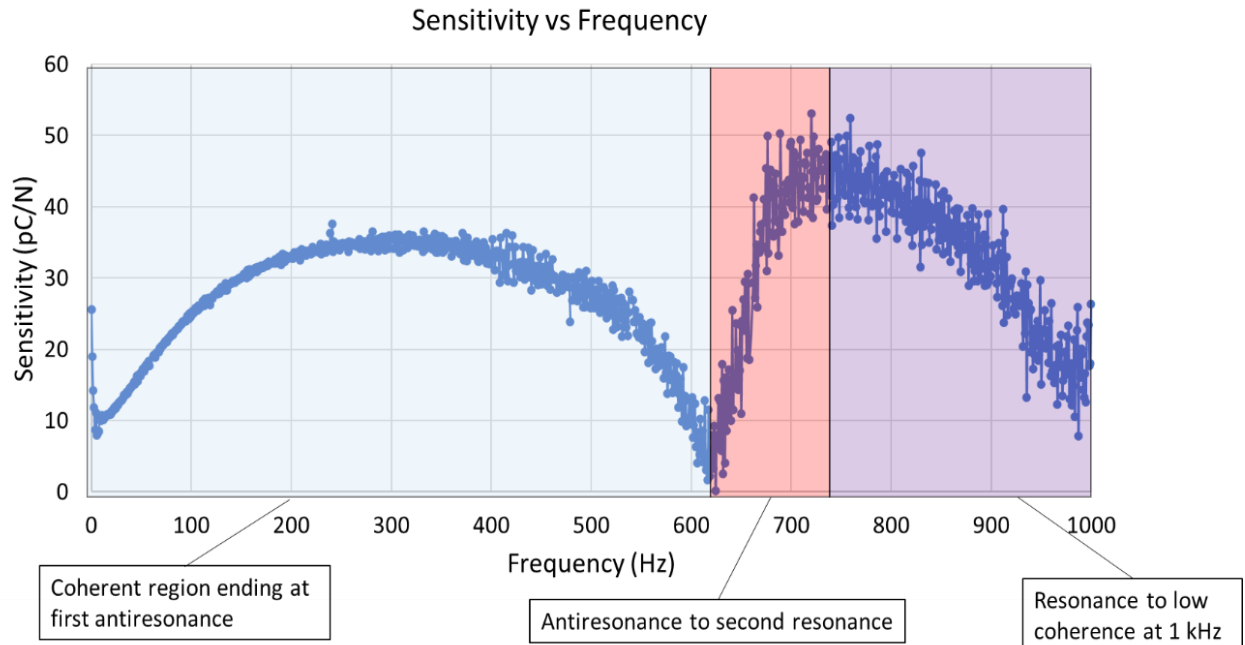


Figure 4-14. Flexoelectric prototype iteration #3 sensitivity as a function of frequency with labeled regions.

4.5 Iteration #4

The next iteration tested was ~40 mm to compromise between iteration #2 and 3 with the same width and thickness as previous samples. The FRF and sensitivity plots are given in Figure 4-15 and 4-16. The iteration showed a fundamental resonance at 500 Hz with peak sensitivity of 130 pC/N and a secondary resonance at 800 Hz with sensitivity of 80 pC/N.

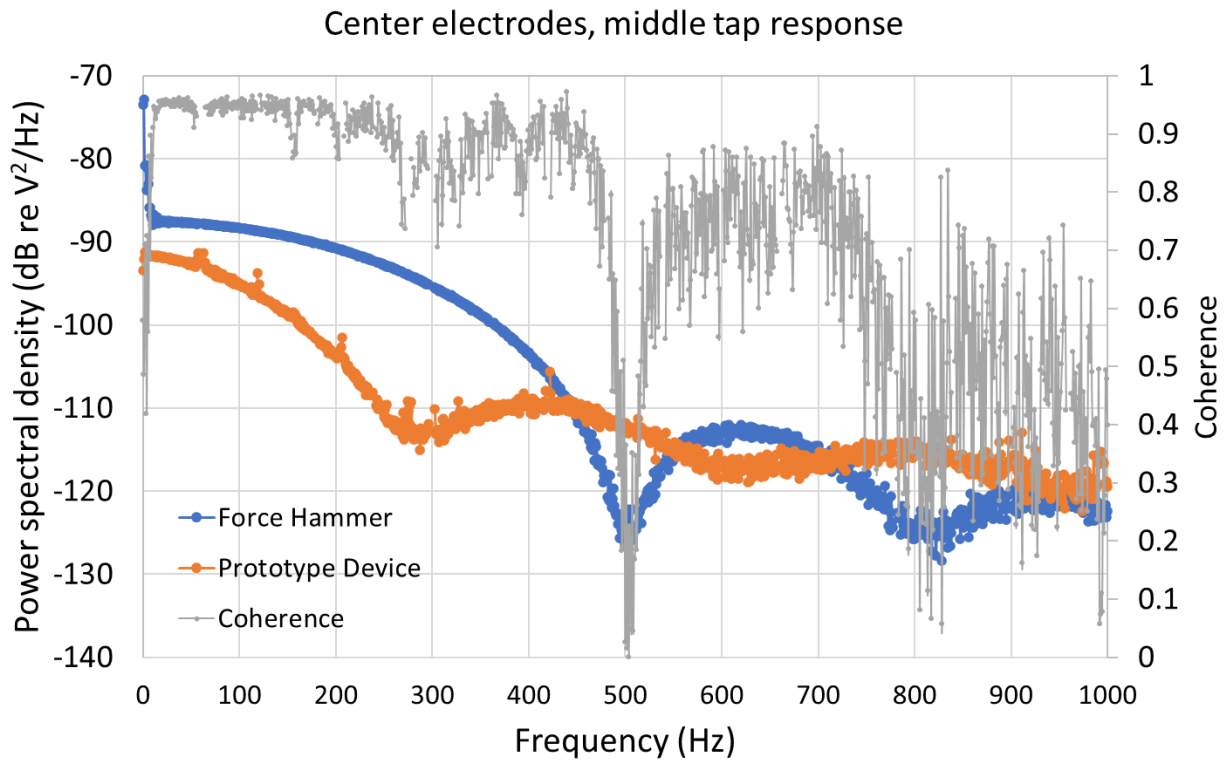


Figure 4-15. Flexoelectric prototype iteration #4 FRF response showing a higher frequency response.

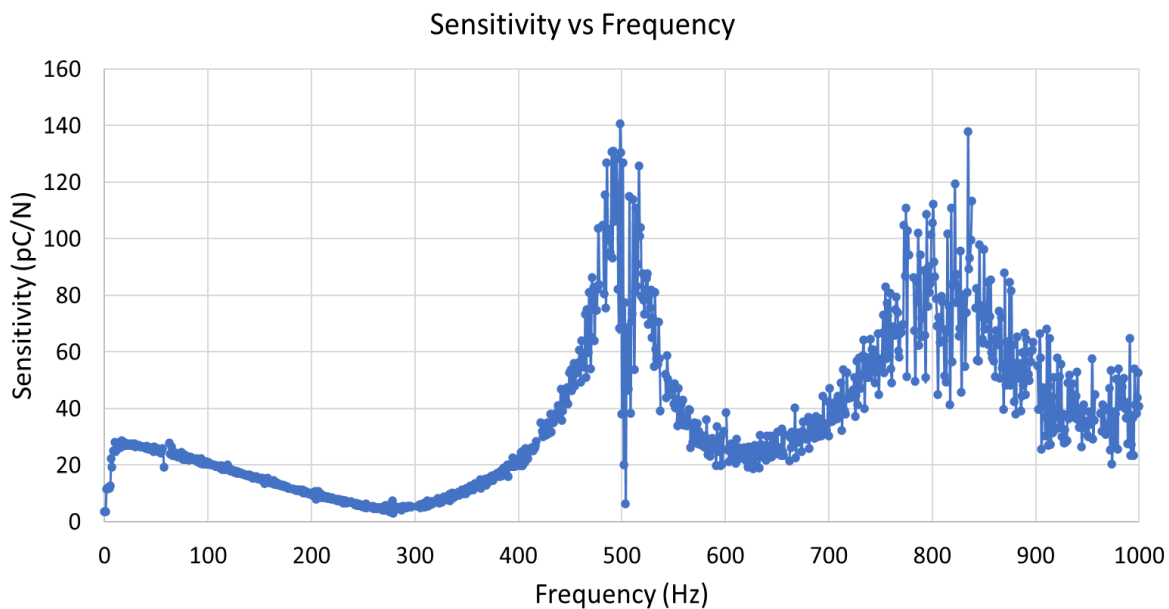


Figure 4-16. Flexoelectric prototype iteration #4 sensitivity vs frequency with peak sensitivity of 130 pC/N at a fundamental frequency of 500 Hz and secondary resonance at 800 Hz with sensitivity of 80 pC/N.

4.6 Electrode Size Study

The next study was intended to study the effect of electrode size (capacitance) on the performance of prototype devices. The study investigated 8 samples with 4 samples using TI 70/30 material and 4 samples using TPL 60/40 with 8.4 mol% MgO. All TI samples were 40 mm x 10 mm x 0.67 mm and all TPL samples were 40 mm x 10 mm x 0.70 mm. The samples had electrode sizes of 3 mm, 5 mm, 7 mm, and 9 mm respectively. FEA results (Chapter 5) suggested an improvement in voltage output for devices with narrow electrodes at the maximum bending position. This is caused by parasitic capacitance that lowers the output voltage of the electrodes as they widen from the maximum bending position. The capacitance per unit area does not change given a homogeneous sample, but the flexoelectric output decays proportionally from the maximum bending point strain gradient to zero strain gradient.

The results of the study were not conclusive to whether the narrower electrodes improved voltage output. The 3 mm and 5 mm samples did not produce signal above the noise making it impossible to compare to the 7 mm and 9 mm samples. One 3 mm sample broke during the tap testing as well. The dielectric properties of the devices are listed in Table 4-2. The hand-built nature of the prototypes is theorized to cause issues with misalignment of electrodes and the tungsten roller stress concentrator. If the components are misaligned, the signal may be too weak for electrical pickup. The large electrode sizes allow more room for error and therefore 3 out of the 4 samples that used 7 and 9 mm electrode widths produced coherent signal. The 7 mm TI, 7 mm TPL, and the 9 mm TPL samples produced FRF responses comparable to the first iteration #4 40 mm sample displayed in Figures 4-17 to 4-22. The 7 mm TI sample was comparable to iteration #4 with a fundamental frequency near 500 Hz and peak sensitivity of 140

pC/N and secondary resonance near 750 Hz with sensitivity of 90 pC/N. The 7 mm TPL-MgO sample showed a similar fundamental frequency of 480 Hz with a peak sensitivity of 40 pC/N. Finally, the 9 mm TPL-MgO sample had a fundamental frequency of 590 Hz with a peak sensitivity of 50 pC/N.

Table 4-2. Electrode size study 7 mm and 9 mm samples' dielectric properties including peak sensitivity and resonant frequency

Material	Electrode Width (mm)	Capacitance (nF)	Relative Permittivity (ϵ_r)	Loss tangent	Peak Sensitivity (pC/N)	Resonant Frequency (Hz)
TI	7	5.261	6300	0.033	140	500
TPL - MgO	7	2.620	2900	0.003	40	480
TI	9	6.137	6300	0.030	-	-
TPL - MgO	9	2.898	2900	0.003	50	590

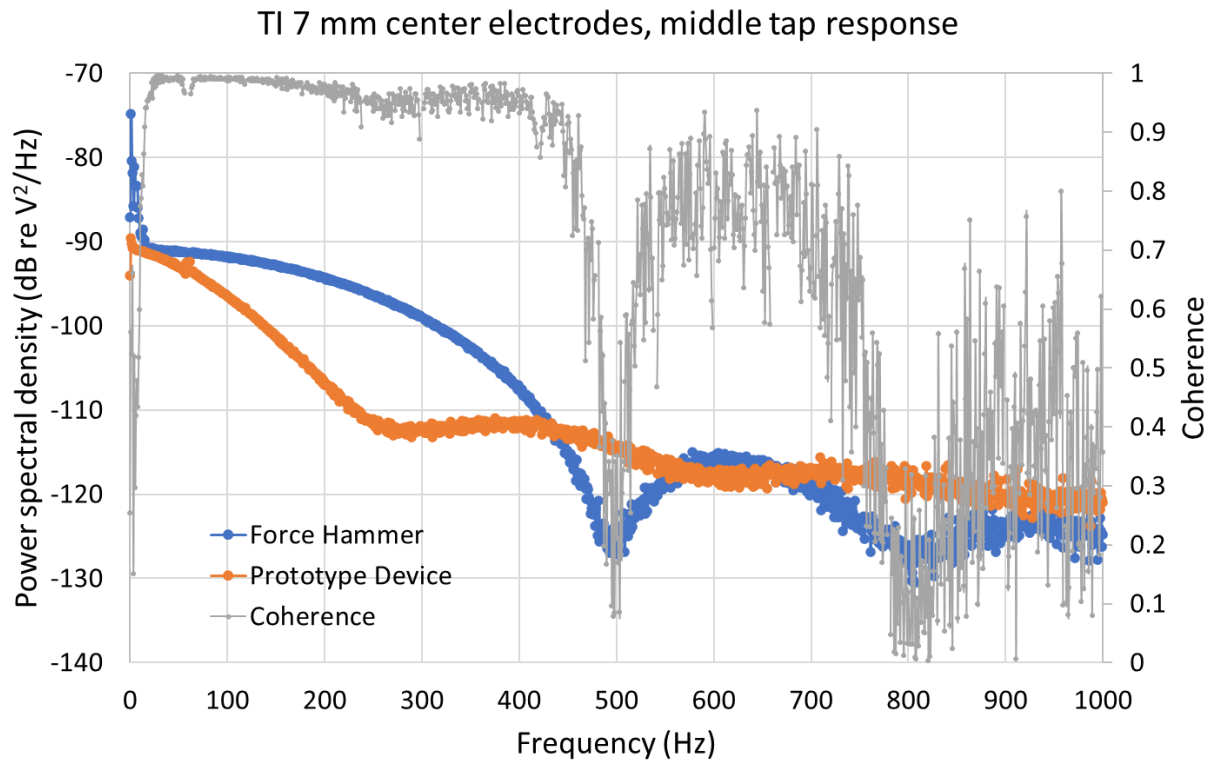


Figure 4-17. 7 mm TI flexoelectric prototype FRF which is comparable to iteration #4.

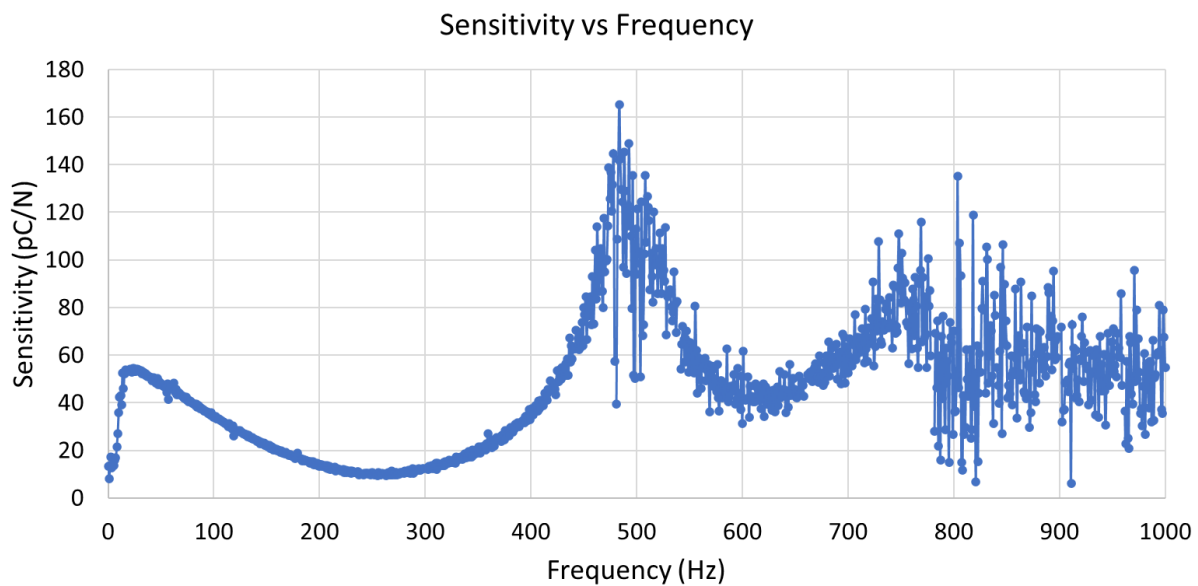


Figure 4-18. 7 mm TI flexoelectric prototype sensitivity vs frequency plot which is comparable to iteration #4.

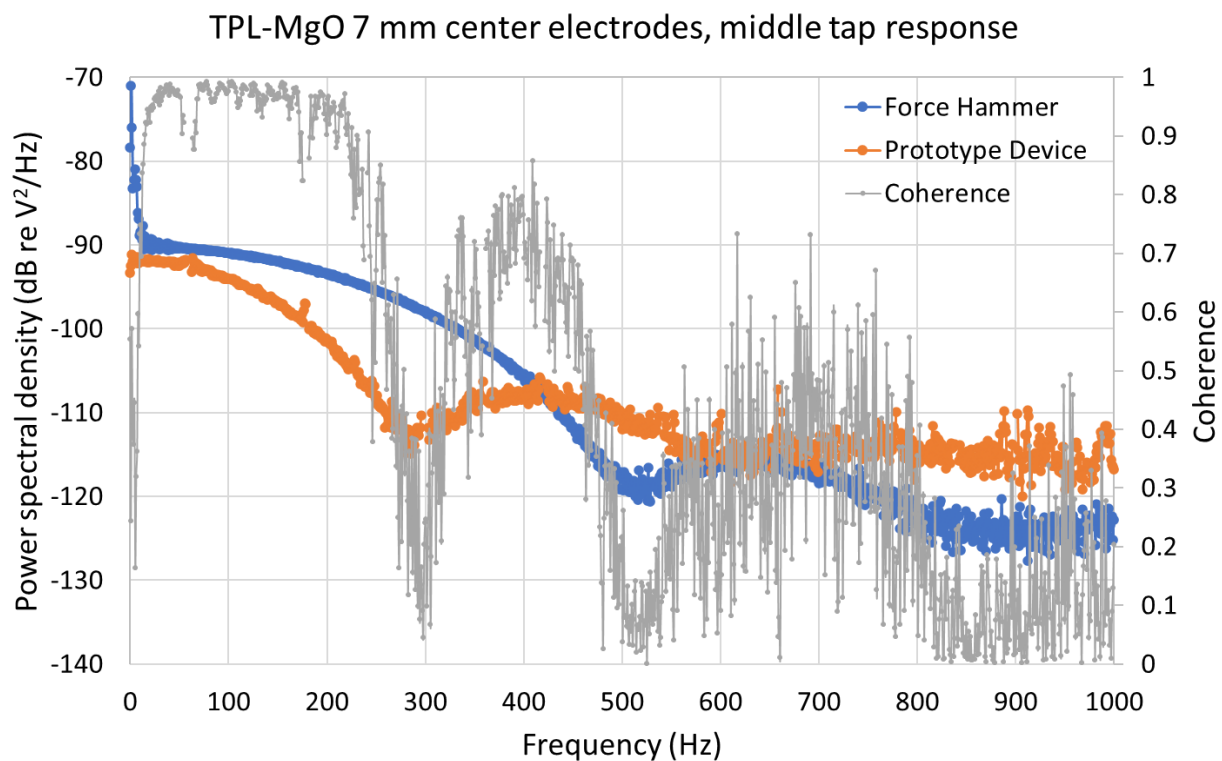


Figure 4-19. 7 mm TPL-MgO flexoelectric prototype FRF.

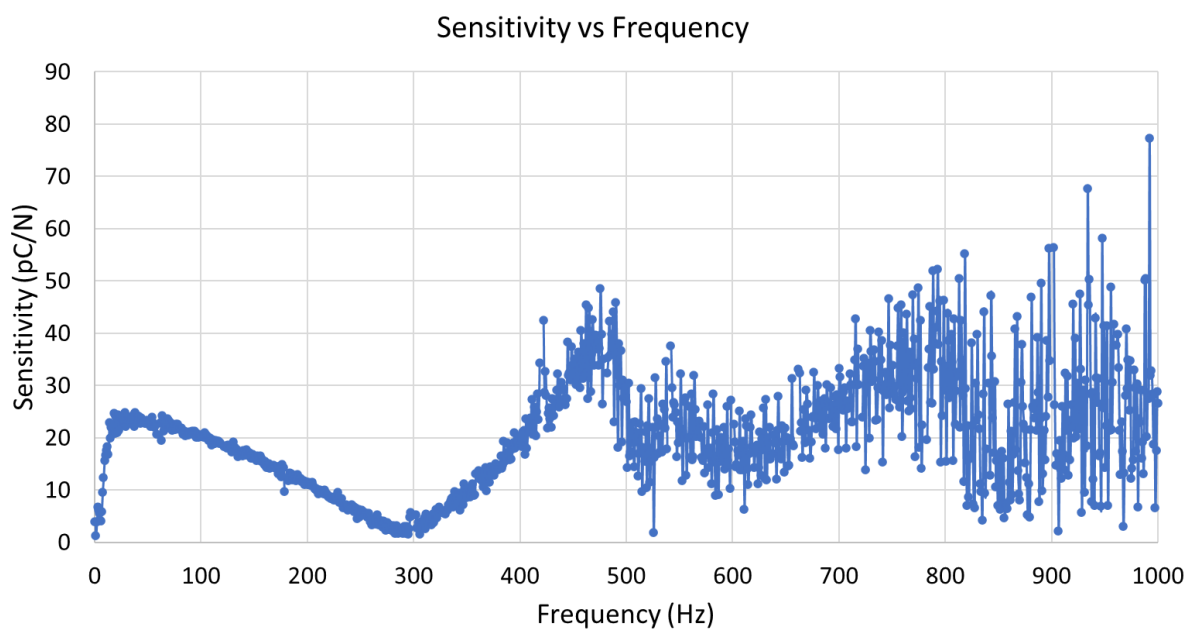


Figure 4-20. 7 mm TPL-MgO flexoelectric prototype sensitivity vs frequency.

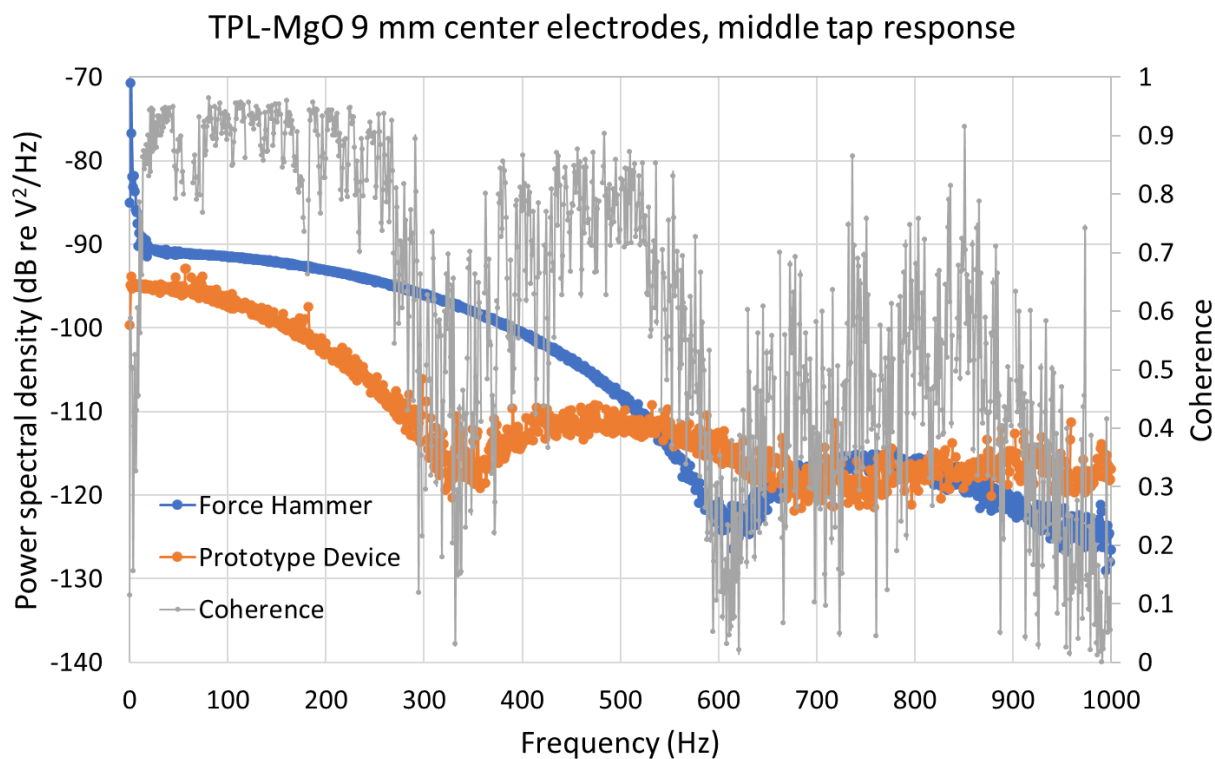


Figure 4-21. 9 mm TPL-MgO flexoelectric prototype FRF.

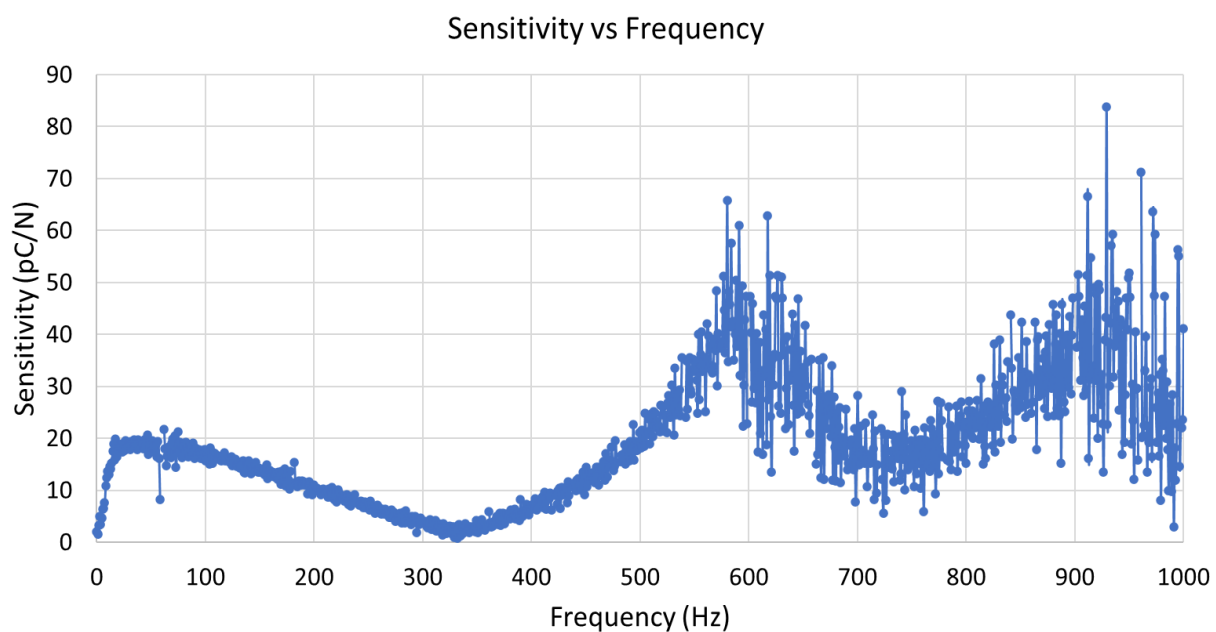


Figure 4-22. 9 mm TPL-MgO flexoelectric prototype sensitivity vs frequency.

4.7 Voltage Output and Mechanical Limits

An example of a single tap's voltage output in the time domain is given in Figure 4-23.

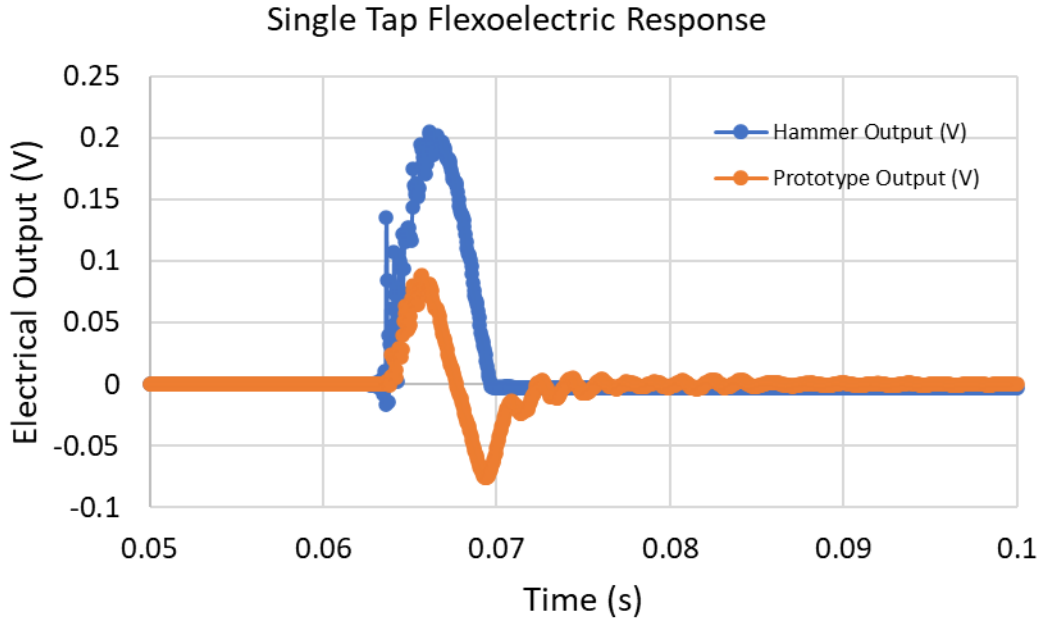


Figure 4-23. Iteration #1's single tap voltage response in the time domain. The peak hammer response is 205 mV (18.3 N) and the peak prototype response is 88.6 mV.

The device produced a peak voltage of 88.6 mV and using the characterization of the material previously, the strain gradient of the material may be calculated that produced the voltage. The capacitance of the electrodes was 3.086 nF so using $Q = CV$ (Q – charge, C – capacitance, V – voltage) the charge produced was 2.734×10^{-10} C. The induced polarization (7.369×10^{-6} C/m²) was calculated by dividing the charge by the area, $A = 0.371$ cm². Finally, dividing the polarization by the flexoelectric coefficient (105 μ C/m) equals the strain gradient which was 0.0702/m. The strain gradient was converted into surface strain by multiplying by the neutral axis thickness which was 0.335 mm. This equals a strain value of 2.35×10^{-5} or 23.5 $\mu\epsilon$. The biaxial strain equation is given in Equation 4.2.

$$\sigma = \frac{E}{1-\nu} \cdot \varepsilon \quad (2)$$

The stress is calculated from Equation 4.1 using material properties values of BST ($E = 161$ GPa, $\nu = 0.35$) and the calculated biaxial strain, $23.5 \mu\epsilon$. The calculated biaxial stress is 5.8 MPa.

Previously, it was determined by the ball on 3 ball method that the Weibull strength of the material is 130.5 MPa. Providing a factor of safety of 2, the maximum biaxial strength is 65 MPa. This implies the material could have been stressed and strained by 10 times the amount of the tap test. This would create a surface strain of approximately $230 \mu\epsilon$ or strain gradient of 0.687/m and therefore a voltage of approximately 0.88 V.

Chapter 5

Flexoelectric Hydrophone Design with Finite Element Analysis

5.1 Design Overview

There are numerous design parameters that will affect the operation of a flexoelectric hydrophone. The first major consideration is how to introduce the strain gradient on the flexoelectric element in order to produce polarization by flexoelectricity. The design chosen was the simplest form of introducing a strain gradient to a material: flexural bending. The design resembled a three point bending configuration. Another option was to introduce the strain gradient through compressing a trapezoidal pyramid element. This is discussed in the next section, but was ultimately not chosen because it requires more fundamental research. The flexural approach has been studied widely in cantilevers and three-point bending configurations⁴⁵⁻⁴⁷. For this reason, there was confidence that a flexural flexoelectric hydrophone would work.

Once it was demonstrated that a flexoelectric hydrophone could work in principle, the goal was to investigate how certain parameters affect the performance. These include: stiffness of the supporting structure, geometry (length, width, thickness), electrode sizes (capacitance), boundary conditions, and flexural supports (tungsten rollers). The performance metrics that were of interest are sensitivity (pC/N), bandwidth (sensitivity as a function of frequency), and resonant frequency (achieving higher frequency limits). An ideal hydrophone would have a high and stable sensitivity across a large bandwidth.

5.2 Finite Element Analysis (FEA)

FEA is used to verify experimental results and develop a positive feedback loop to refine the predictive modeling capability for experiments. FEA has been used to study piezoelectric

and piezocomposite materials to elucidate their frequency behavior and therefore optimize their design.^{48–50}

In order to help target performance requirements and create experiments that will test and verify the modeling results, the modeling parameters were iterated to more accurately predict the experimental results. The first FEA models tried to match the resonant frequency data measured in the FRF tap tests; this is helpful in understanding the relative roles of geometry, material properties, and boundary conditions. FEA also allows investigation of the strain and strain gradient behavior of the flexoelectric element as a function of frequency during the experimental tests as this is not directly measured during tap testing. The final goal of FEA is to accurately model and animate a flexural flexoelectric element functioning as a transducer or in application as a hydrophone by showing the conversion of mechanical energy input into electrical energy output.

FEA was performed using COMSOL Multiphysics® Modeling Software version 5.4. The software allows the creation of either cantilever or three-point bending beams in the structural mechanics module. The geometry is specified, and the mesh may be generated with different sizes depending on the error requirements. The mesh used in this study was the free tetrahedral option. The element size that fit the available computational power and produced the lowest error was with an element size of 0.5 mm. From these conditions the eigenfrequencies and frequency domain studies were chosen. The eigenfrequencies correspond to particular resonant mode shapes while the frequency domain study sweeps through a range of frequencies showing the material's response. This study focused on the first flexural fundamental frequency as this is proposed to be the main contribution to the flexoelectric effect in fabricated prototype

devices. This response may be used to compare to the frequency responses of experimental samples.

The theoretical flexural bending frequency of a fixed-fixed or free-free beam is given below in Equation 5.1.⁵¹ For a fixed-fixed boundary condition, there is no displacement and slope at the ends of the beam. In the functional form $y(x,t)$, this condition is $y(0,t) = 0$ and $\frac{\partial y(0,t)}{\partial x} = 0$.

$$f_n = \frac{\pi\kappa}{8L^2} \sqrt{\frac{E}{\rho}} (3.011^2, 5^2, (2n + 1)^2 \dots) \quad (1)$$

E = Elastic modulus (Pa), κ = radius of gyration (m), L = Bar length (m), ρ = Bulk density (kg/m³), n = mode number (1, 2, 3).

The equation for a pinned-pinned (simply supported) beam is given in Equation 5.2.⁵¹ This condition has no displacement and there is also no moment (torque) at the ends of the beam, $y(0,t) = 0$ and $\frac{\partial^2 y(0,t)}{\partial x^2} = 0$ respectively.

$$f_n = \frac{\pi\kappa}{2L^2} \sqrt{\frac{E}{\rho}} (n)^2 \quad (2)$$

This equation can be used to calculate the error between the analytical model and the FEA result, and acts to provide verification of the accuracy of the FEA model. In particular, the frequency response of the BST beams in different geometries and with different boundary conditions can be used to assess whether the boundary conditions better describe the experimental data.

An example of the FEA modeled frequency response of a fixed-fixed beam corresponding to the geometry of the prototype #1 is given in Figure 5-1 and FEA results for a pinned-pinned (simply supported) beam of the same geometry is given in Figure 5-2.

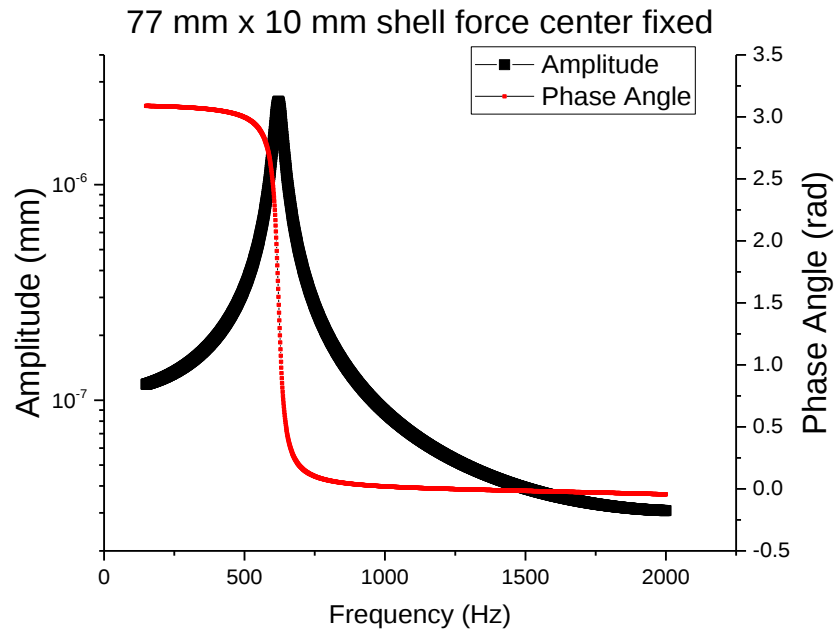


Figure 5-1. Frequency domain response on a cut point (10,5) of a 77 x 10 x 0.67 mm fixed-fixed BST beam using shell elements with a resonant frequency at 620.93 Hz.

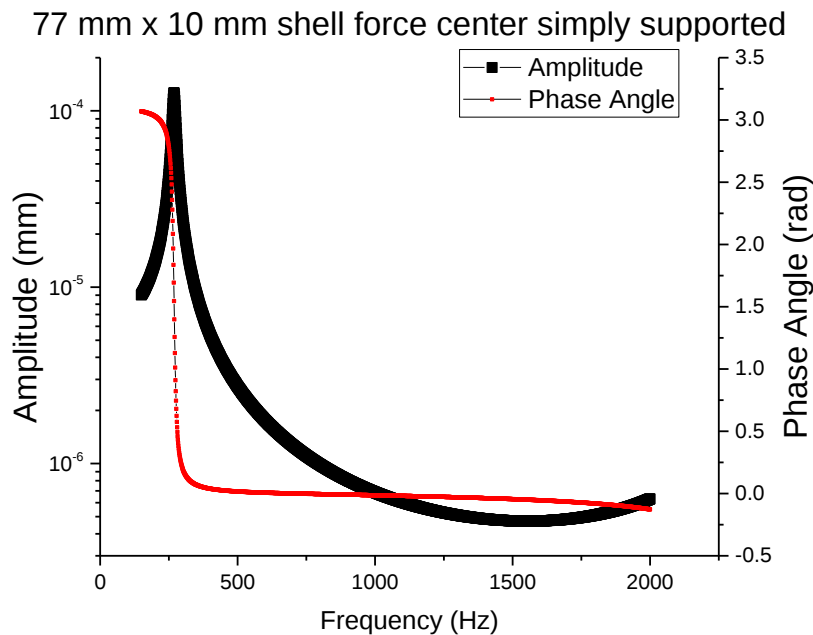


Figure 5-2. Frequency domain response on a cut point (10,5) of a 77 x 10 x 0.67 mm pinned-pinned BST beam using shell elements with a resonant frequency at 268.94 Hz.

The calculated fixed-fixed frequency from Equation 1 is 618.30 Hz giving a percent error of 0.42% for the FEA model relative to the analytical model. Likewise, the FEA calculated

pinned-pinned frequency from Equation 2 is 272.79 Hz giving a percent error of 1.43%. These errors were small enough to show that the FEA model is in close agreement with the analytical model. The FEA model produced a pinned-pinned resonant frequency for the device of 268.94 Hz and the experimental result was 250 Hz or a 7.6% error.

FEA allowed the investigation of the in-plane strain profile in the device during bending. For a beam flexing at 4 Hz, the strain profile is displayed over one cycle in Figure 5-3.

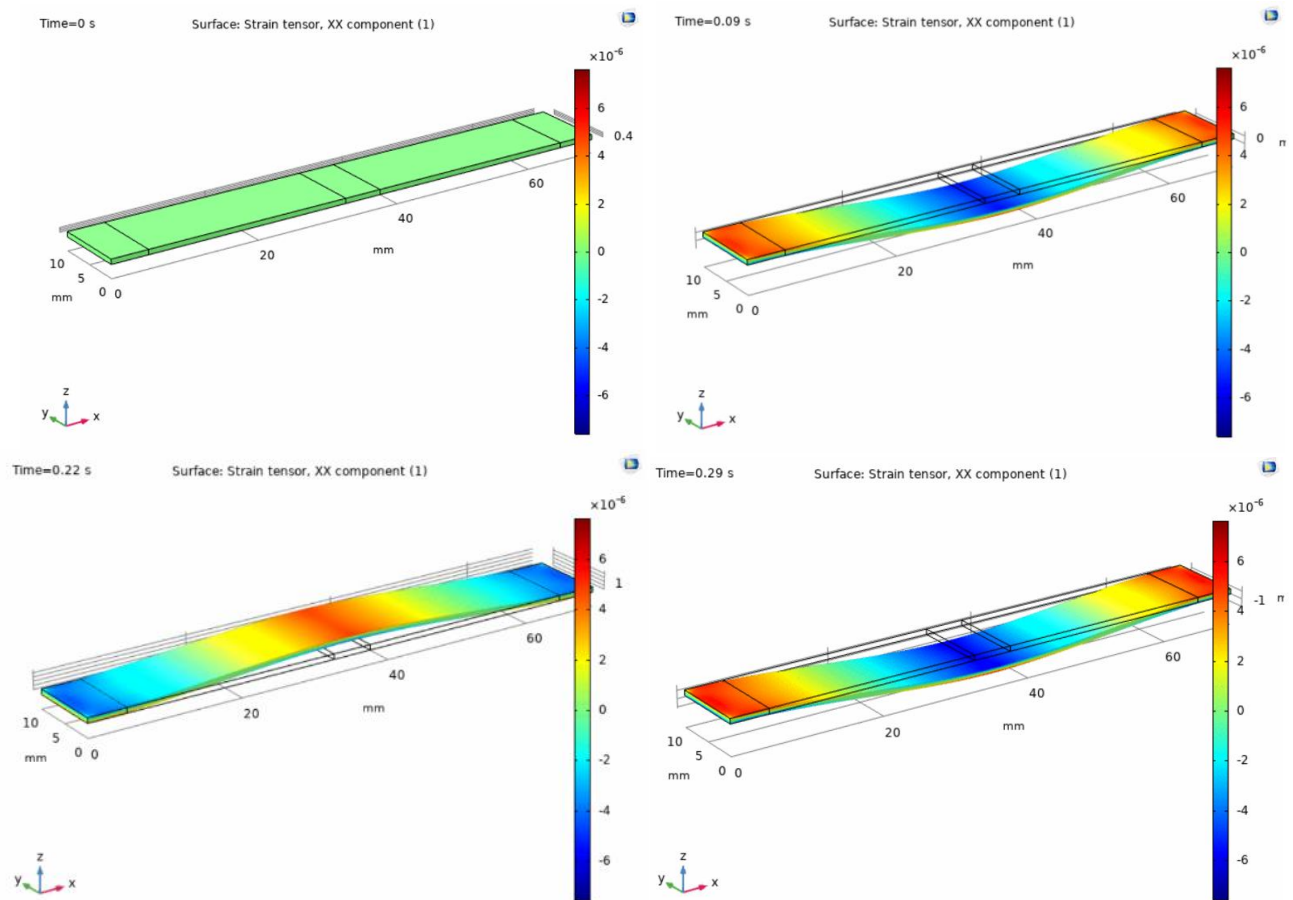


Figure 5-3. X strain component of a 70 mm x 10 mm x 0.67 mm fixed-fixed BST beam using solid elements under a 4 Hz sinusoidal loading showing snapshots in time through one full cycle.

The top surface strain data of the BST beam may be used to determine the strain gradient of any point on the beam when it is assumed that the in-plane strain is linear through the thickness of the beam. By calculating the strain gradient from this assumption, an area of interest such as an

electrode area may be measured to assess the expected flexoelectric output over time given a measured flexoelectric coefficient for a material. This is demonstrated in Figure 5-4 and Figure 5-5. This method allows the study of multiple electrode configurations and designs through modeling to find an optimal output for device design requirements. If the device is charge-based, the surface charge over time may be measured or if the device is voltage-based, the capacitance of the electrode area may be used to calculate the voltage over time.

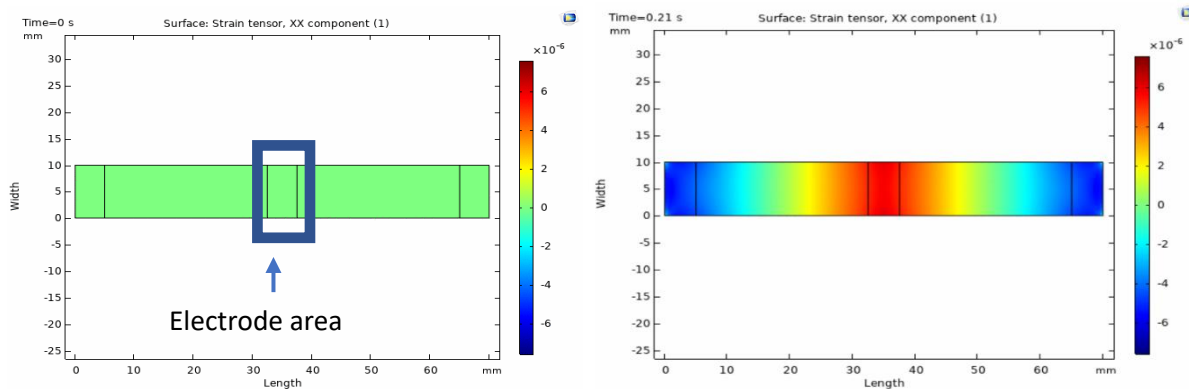


Figure 5-4. An example of a top surface investigated electrode area at the start, $t = 0$, and during bending, $t = 0.21$ s.

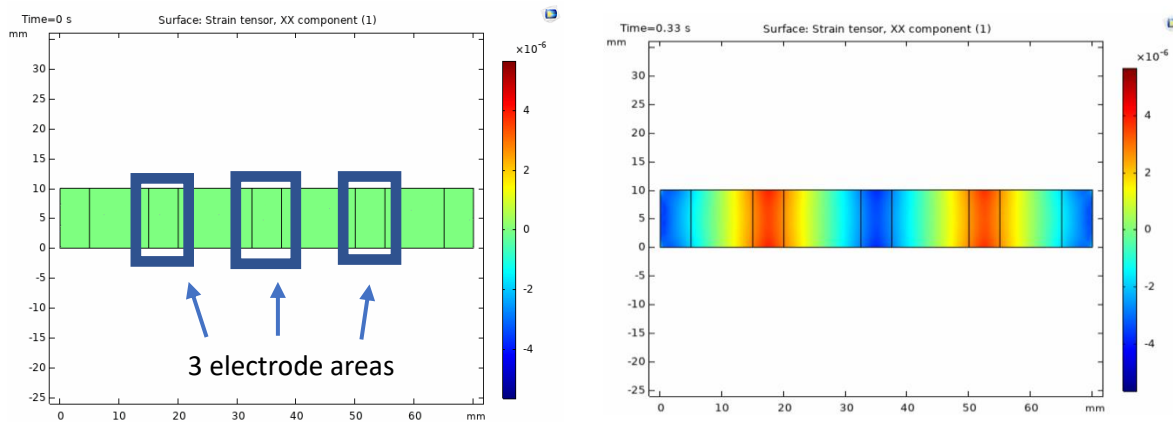


Figure 5-5. A three electrode area strain gradient study with snapshots at, $t = 0$, and during bending, $t = 0.33$.

A FEA study was performed using this method to investigate if multiple electrodes and bending points on the element would increase the output given the same applied force. The

average strain of the one electrode design was 4.21×10^{-6} and the average strain of the three electrode design was 2.01×10^{-6} or about half of the one electrode design over the time frame. However, because the three electrode design harvested electrical output from all three electrodes (three times the area) versus the one electrode design, the total output of the device was over 43% higher.

The multiple bending point study provides insight into design considerations. If the device is a charge-based sensor, larger electrodes and multiple bending points will maximize the charge collected and therefore create greater output resulting in better performance. However, if the device is voltage-based, larger electrodes cause increased parasitic capacitance. The strain gradient is maximized at the center of the electrodes when positioned symmetrically and declines linearly in both directions resulting in weaker voltage as the electrode size increases. This suggests the optimal design for voltage-based devices would utilize the smallest capacitance possible for the electronics to collect the signal. The multiple bending points also lowers the voltage output by decreasing the strain gradient at each electrode pair. This may be an issue unless the voltages can be applied in series to add their output. If series connection is not possible, then multiple bending points will weaken the voltage output in a voltage-based device and would not be recommended.

Another study investigated the tradeoff between the thickness of the beam and the resulting fundamental frequency versus strain gradient output of a center electrode. The thicknesses were varied from 0.30-0.70 mm in 0.05 mm increments with a downward sinusoidal force of $10,000 \text{ N/m}^2$ applied at 1 Hz. The results are plotted in Figure 5-6. The fundamental frequency decreases linearly with decreasing thickness, but the strain gradient response increases exponentially. The strain increases with decreasing thickness due to less flexural rigidity while

the strain gradient is also being enhanced by the $1/a$ size effect of the decreasing neutral axis thickness. This results in almost an 8 times increase in the strain gradient just by halving the thickness from 0.7 mm to 0.35 mm. The x component strain of a 40 mm x 10 mm x 0.30 mm beam flexed at 1 Hz as a function of time is graphed in Figure 5-7. The voltage output is proportional to the strain gradient through the flexoelectric coefficient.

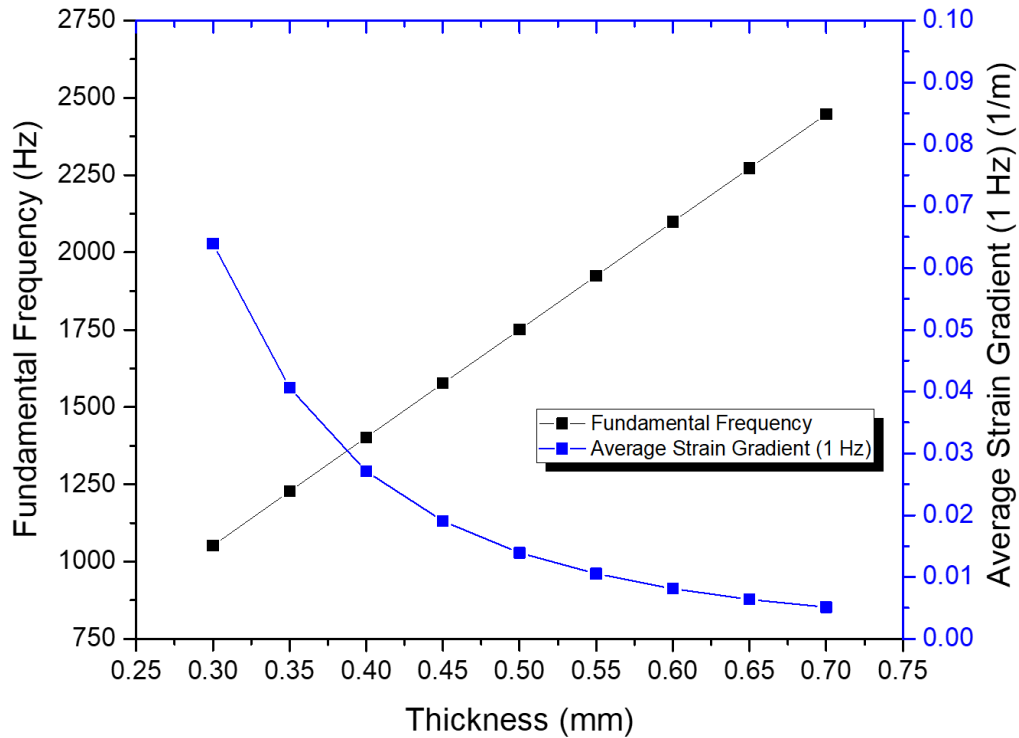


Figure 5-6. The fundamental frequency and strain gradient response of a 40 mm x 10 mm x X mm beam as a function of thickness.

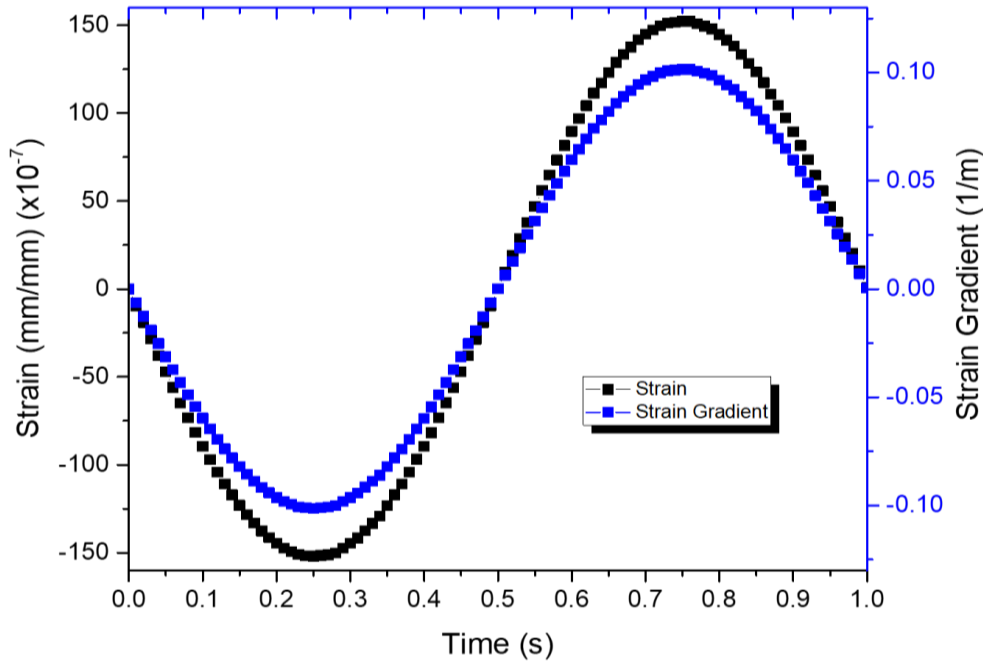


Figure 5-7. The X component strain and strain gradient profile of a 40 mm x 10 mm x 0.30 mm beam flexing at 1 Hz. The voltage is proportional to the strain gradient through the flexoelectric coefficient.

Another bending point study was investigated to understand the effect of adding additional fixed-fixed bending points to an initial beam; the results are plotted in Figure 5-8. The electrode width for the blue data points was normalized to 10 mm as the element length decreased in proportion to the number of bending points to maintain a constant electrode area. The electrode width for white data points was held constant at 5 mm for all bending points resulting in increasing electrode areas (50 mm^2) with increasing bending points. This study used an initial 70 mm x 10 mm x 0.70 mm beam with an electrode width of 10 mm centered at the middle of the beam and flexed using a sinusoidal force of $10,000 \text{ N/m}^2$ at 1 Hz. Subsequent beams were created by dividing the original beam in length, force, and electrode area by the number of bending points. This ensured equal force and electrode area for use in calculating the effective strain gradient as if the beam were divided into multiple subsections. The flexoelectric effect is found to be most effective at low frequency using the fewest bending points as

demonstrated by the large effective strain gradient with a single bending point. The effect quickly decays between 2-4 bending points as the fundamental frequency increases. It continues to decay slower as more bending points are added and approach 0 strain gradient toward infinite bending points. The effective strain gradient decreases slowly between 5-9 bending points as the frequency increases more linearly. This suggests that a device functional at lower strain gradients should be able to function across a much wider frequency range than a device functional only at high strain gradients. The increasing electrode area of the white data points caused the effective strain gradient to drop as more of the beam is utilized but can result in more charge output or voltage output if applied in series. The charge output of the two studies is provided in Figure 5-9 given a flexoelectric coefficient of $100 \mu\text{C}/\text{m}$.

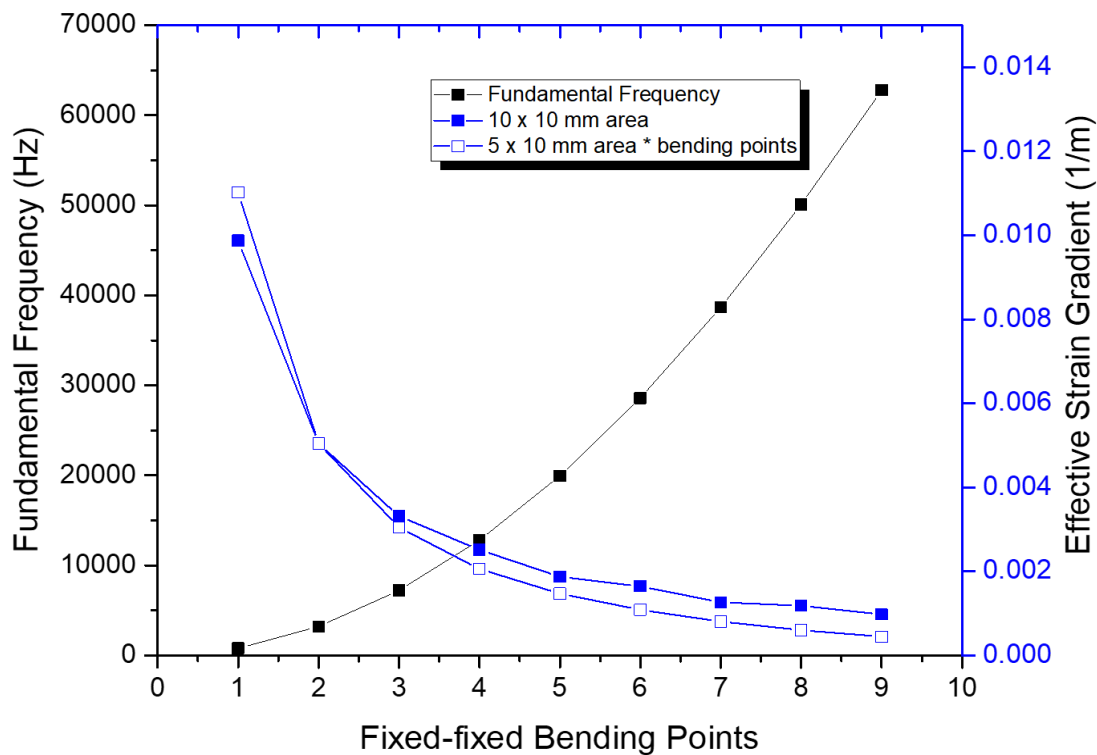


Figure 5-8. The fundamental frequency and effective strain gradient by adding fixed-fixed bending points of a 70 mm x 10 mm x 0.70 mm beam.

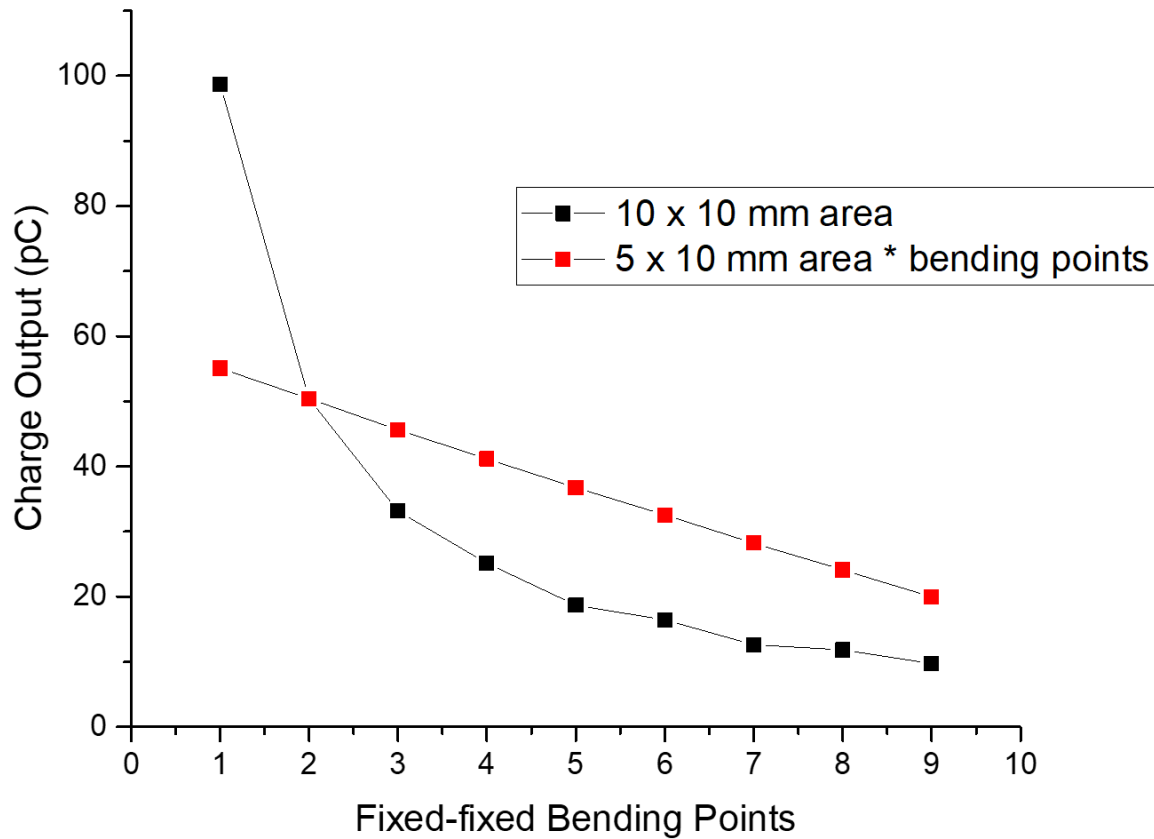


Figure 5-9. The charge output (pC) of a normalized electrode area, 100 mm^2 , as a function of the number of bending points and the charge output of an increasing electrode area of 50 mm^2 * # of bending points as a function of the number of bending points assuming a flexoelectric coefficient of $100 \mu\text{C/m}$.

An FEA study of the thickness dependence of the beam versus frequency response was also performed to observe the effect on the fundamental resonance frequency value. The beam's thickness was decreased in 0.05 mm increments while the length and width dimensions were constant at 40 mm x 10 mm respectively. As the beam's thickness is decreased, the resonance frequency decreases. This is caused by the reduction in stiffness of the beam as the thickness of the beam is reduced. The results are given below in Table 5-1.

Table 5-1. Frequency dependence of a 40 mm x 10 mm beam studied by FEA that demonstrates that the stiffness reduces with decreasing thickness causing a reduction in the fundamental frequency.

Beam Thickness (mm)	Element Type	Boundary Condition	Fundamental Frequency (Hz)	Isotropic Damping	Q
0.67	Solid	Pinned-Pinned	995.5	0.05	20
0.60	Solid	Pinned-Pinned	903.3	0.05	20
0.55	Solid	Pinned-Pinned	835.6	0.05	20
0.50	Solid	Pinned-Pinned	766.4	0.05	20
0.45	Solid	Pinned-Pinned	696.0	0.05	20
0.40	Solid	Pinned-Pinned	624.2	0.05	20
0.35	Solid	Pinned-Pinned	552.1	0.05	20
0.30	Solid	Pinned-Pinned	478.1	0.05	20

5.3 Thickness and Grain Size Dependence

In this research, samples were all fabricated with thicknesses around 670 microns. It is conjectured that the samples could be thinned down to an estimated 300 micron thickness and still be reasonably handled by a person but this would need to be tested. The thinner samples should demonstrate lower resonant frequencies but increased flexoelectric output if agreement is found with FEA calculations. If this was demonstrated, the size effect of flexoelectricity using flexural bending would be strengthened in the literature.

The thickness of the samples in regards to machinability is influenced by the grain size. Smaller grain size provides a greater number of grains through the thickness of long and thin beam designs for flexoelectricity studies. Finer grains generally improve mechanical strength properties by limiting the size of the critical flaws. For the case of a dense ceramic, the critical flaws are grain boundaries. Finer grain size may help improve machinability by reducing the chance of large cracks from running through the material as it is being cut. It has also been demonstrated in BaTiO_3 that relative permittivity is maximized around a 1 micron grain size due to domain wall motion.⁵² However, this effect may be less prevalent in the paraelectric region. Despite this, it is suggested that optimal flexoelectric ceramics in flexural bending applications target a high relative density (>95%) with a grain size of 1 micron for both improved mechanical and dielectric properties as well as good machinability.

5.4 Conclusions

The first prototype device showed a 7.6% difference in the fundamental frequency resonance to FEA modeling. The predicted fundamental frequency using shell elements and pinned-pinned boundary conditions was 268.9 Hz and the measured fundamental frequency was 250 Hz. This result makes clear that the experimental boundary condition is closer to pinned-pinned than fixed-fixed as the fixed-fixed model resulted in a fundamental frequency of 620.9 Hz. The Iteration 4, 40 mm, samples should show resonance near the 1 kHz mark as the pinned-pinned prediction is 995.5 Hz by FEA. The measured results are lower than this prediction similar to the first prototype case. This is due to multiple factors. The elastic modulus of the material in the model used the literature value of 161 GPa⁵³ and the measured elastic modulus of the samples was calculated at 124.3 GPa which would reduce the resonant frequency. The tetrahedral elements used in the models introduce error by error propagation between elements

from the boundary conditions. This error is reduced by decreasing the element size, but this must be balanced with computational cost which increases exponentially with smaller element size. Lastly, the experimental boundary conditions do not perfectly match the fixed-fixed or pinned-pinned boundary conditions. The boundary conditions of the devices could be investigated by directly pinging the flexoelectric element bonded to the supporting structure before completing the entire structure and measuring the FRF to find the resonant frequency. This could provide information on the effect of different assembly configurations on the boundary conditions of the device and help target desired boundary conditions and frequencies matching to the FEA model.

FEA results predict greater flexoelectric responses at lower frequencies either by reducing the thickness of the flexoelectric element and therefore reducing the flexural rigidity or by increasing the flexoelectric element length and keeping the number of bending points to a minimum. The tradeoff is always a decrease in the flexoelectric output by reduction of the strain gradient for an increase in the frequency range. Finally, FEA provides easy visualization of strain in flexoelectric beams. This is both useful for understanding the mechanisms driving flexoelectric response as well as the ability to estimate strain and strain gradient values of real materials that would not otherwise be possible without attaching multiple strain gauges.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

In this work, the flexoelectric effect of BST was investigated for use in hydrophones. A 70/30 BST material fabricated by TI was investigated as it was extremely dense and reported to have a flexoelectric coefficient of $\sim 100 \mu\text{C}/\text{m}$. The permittivity of this material was measured from -60 to 93°C and showed a peak at the Curie temperature of 33°C . The peak permittivity was 18000 and the loss tangent was 0.03 at this temperature. The effective flexoelectric coefficient was measured using cantilever beams. The measured $\tilde{\mu}_{12}$ was 105.6 ± 0.6 . The biaxial strength and Weibull modulus of this material were studied using the ball on 3 ball method. Twenty samples were tested and plotted with Weibull analysis. The Weibull biaxial strength was $130.5 \pm 4.3 \text{ MPa}$ and the Weibull modulus was 14.3 ± 0.2 . The microstructure of this material was dense with no visible porosity and had a grain size of $2.3 \pm 0.3 \mu\text{m}$. Finally, the elastic modulus, E , shear modulus, G , Poisson's ratio, ν , and quality factor, Q , were measured using the Impulse Excitation Technique (ASTM-E1876). E was found to be $124.3 \pm 1.8 \text{ GPa}$ and G was $48.9 \pm 0.7 \text{ GPa}$. The Poisson's ratio was calculated to be 0.27 ± 0.04 . Q was measured to be 19.3. This material was used as the flexoelectric element in prototype hydrophones made using flexoelectric ceramics of different dimensions. The width and thickness were held constant at 10 mm and 0.67 mm respectively. The lengths were 30, 40, 50, and 77 mm for different iterations. The 77 mm design produced a coherent sensitivity of 80 pC/N for a first resonance at 250 Hz, an antiresonance at 300 Hz, and a low coherent maximum sensitivity of 160 pC/N for a second resonance at 530 Hz. The 30 mm design showed no resonance which was proposed to be caused by over stiffness of the flexoelectric element. The 50 mm design showed

high coherence or clear correlation between the input of the hammer and output of the device across the 0-1000 Hz frequency range providing validation in the sensitivity results across this range. The device had an unclear resonance behavior with a broad maximum response between 200-400 Hz and sensitivity of 35 pC/N. This may have been a result of imperfect alignment of the stress concentrator with respect to the BST beam. A clear antiresonance was observed at 620 Hz with a peak in sensitivity of 45 pC/N at a secondary resonance of 730 Hz. The best sensitivity was achieved on a 40 mm design with a resonant frequency of 500 Hz and peak sensitivity of 140 pC/N. A similar design using TPL BST-MgO ceramic achieved a resonant frequency of 590 Hz with a peak sensitivity of 50 pC/N.

Flexoelectric prototype hydrophones were compared to analytical and FEA models. The fundamental resonant frequency of the 77 mm length device was analytically calculated to be 272.79 Hz in the pinned-pinned configuration. The FEA model calculated the fundamental resonant frequency to be 268.94 Hz. The analytical and FEA model were different by 1.4% confirming the FEA model agrees with the analytical model with less than 2% error. The prototype device had a fundamental resonant frequency of 250 Hz or 7.6% difference with the FEA model. This error could be reduced in future iterations by refining material property constants (E and ν), reducing element (mesh) size, and accounting for boundary condition mismatch between experiment and model. FEA models allow the investigation of strain gradient behavior and expected flexoelectric output of flexoelectric elements. This was used to study electrode placement with multiple bending points. The study found that a three bending point design resulted in a charge output of 43% more than a one bending point design with electrode pairs centered above each bending point (maximum strain). This is despite the fact that the average strain decreased by 48% in each electrode pair for the three bending point design. This

drop was overcome by having three times the electrode area. The study also found that this would result in a 48% decrease in voltage across each electrode if the device used a voltage-based design instead of charge-based design based on the voltage proportionality to strain gradient. In this case, the electrode pairs would need to be connected in series for the voltages to be added.

FEA results predicted better flexoelectric output at lower frequencies. The frequency response of the flexoelectric elements were determined by the stiffness of the beams which decreased with a reduced flexural rigidity and with shorter element lengths. The flexural rigidity was reduced by decreasing the thickness of the beams. The lower frequency response of the beams translated into much higher strain gradients which is directly related to flexoelectric output through the flexoelectric coefficient.

The flexoelectric effect has demonstrated promising results in comparison to its piezoelectric counterparts. Chu et al. measured effective d_{33} coefficients caused by flexoelectricity in BST at room temperature of 1480 pC/N which is comparable to piezoelectric single crystals and 4350 pC/N near the T_c of the material.³⁶ These results were obtained using multiple layers of BST in a composite structure. While the output potential in these devices has been measured experimentally, a commercial application has not been demonstrated. The application space for these flexoelectric devices appears to be in sensors, although the nature of the effect could warrant its use in energy harvesting devices as well. The demand for accelerometers has dramatically increased for cars, military applications, consumer electronics, and even biomedical devices. Microflexoelectric accelerometers may be an ideal application for devices utilizing compressive flexoelectricity.

Flexoelectricity has many advantages and disadvantages when compared to piezoelectricity. Flexoelectricity has no symmetry constraints in contrast to piezoelectricity and its non-centrosymmetric symmetry constraint. This has allowed this phenomenon to show great promise in centrosymmetric materials such as BST and opens up the design space to lead-free materials. Piezoelectric materials are dominated by Pb-based materials due to their excellent piezoelectric properties and high Curie temperatures. This leads into another strength of flexoelectric materials: the elimination of poling. Flexoelectric materials require no treatment to function properly while piezoelectric materials need to be properly poled prior to operation. This also eliminates the risk of the material depoling due to temperature or time. The last potential advantage of flexoelectricity is the absence of reciprocity when compared to piezoelectricity. While flexoelectricity does have reciprocity through an electric field gradient and mechanical strain gradient, practically, the mechanical strain gradient is the naturally observable response as electric fields are generally applied uniformly on materials across parallel electrode pairs. Piezoelectricity is more easily observed reciprocally by stressing a material to induce an electric field and applying an electric field to deform the material.

The disadvantages of flexoelectricity versus piezoelectricity are its relatively narrow bandwidth and variable sensitivity in a narrow temperature range. With flexural bending, the resonant frequencies are much lower than longitudinal resonant frequencies in piezoelectric materials. This may be compensated by moving to a compressive flexoelectric design, but has not been fully demonstrated at the current time. The sensitivity of devices may be comparable to piezoelectric materials, however, this sensitivity is only possible in a narrower frequency and temperature range compared to piezoelectric materials. The sensitivity of devices may be improved over time by engineering the design to maximize the flexoelectric effect. The

flexoelectric effect decays substantially as the material is heated or cooled past the Curie temperature. This disadvantage may also be engineered through adjustments of the material's dielectric properties to behave like a relaxor with stable dielectric properties across a broader temperature range. The tradeoff is lower flexoelectric output across the temperature range to achieve this stability. While the disadvantages of flexoelectricity reduce its overall applicability when compared to piezoelectricity, its unique advantages provide design possibilities that are otherwise impossible with piezoelectricity.

6.2 Future Work -Compressive Transducer Design Solution

A proposed solution for creating strain gradients which is an alternative to flexural bending is to create the strain gradient through compression. This is innately beneficial for ceramics as ceramics perform mechanically better in compression than tension. This is due to the fact that tension opens up microscopic flaws or cracks while compression tends to close or inhibit these defects from growing.⁵⁴ In order to create a strain gradient in compression, the area must be nonuniform on the compressive surfaces. The proposed design utilizes a trapezoidal pyramid flexoelectric element displayed in Figure 6-1.²

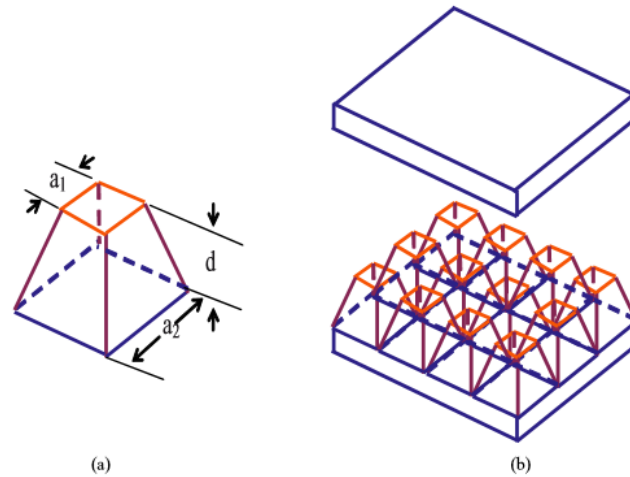


Figure 6-1. Trapezoidal pyramid flexoelectric composite design which shows (a) one element design and (b) a composite array of elements with compression platens. From reference 2.

While flexoelectricity has been demonstrated in pyramidal structures machined in bulk ceramics², the objective of the future work would be to either create these features on thin bulk flexoelectric ceramics or on space charge doped flexoelectric silicon substrates through etching. Morales showed initial results on using space charge in flexoelectric silicon substrates, but did not achieve the large flexoelectric coefficients expected. The highest value achieved was $77.9 \pm 0.3 \text{ nC/m}$ with a dopant concentration of $1.5 \times 10^{17} / \text{cm}^3$.⁵⁵ Work is presently being done to achieve higher flexoelectric coefficients on silicon substrates. These elements could be efficiently stacked together similar to a piezoelectric stack actuator for either sensing or energy harvesting. This would make a more robust device and efficiently use space. However, more validation of strain gradients and flexoelectric coefficients in compressively stressed flexoelectric materials would be required.

6.3 Future Work- Micro and Nanosized Strain Gradient Enhancement

The flexoelectric effect has an inherent scaling effect called the size effect that increases its output at the micro and nano scale which is expected to be applied to highly sensitive

micro/nano-sensors. This is caused by the extremely large strain gradients that may be produced in these regimes. The strain gradient scales as a function of $1/a$ where a is the length scale. For example, a $1\text{ }\mu\text{m}$ thick BST flexoelectric element would be expected to produce 100 times more output than a $100\text{ }\mu\text{m}$ thick BST flexoelectric element given similar dielectric properties and applied strain.⁵⁶ It was demonstrated in Aygün et al. that BST could be produced as a thin film with bulk-like dielectric properties.⁵⁷ This suggests there is no reason that BST flexoelectric output could not be enhanced greatly at micro and nanometer scales. In the simple case of a prototype device in this work that showed 140 pC/N sensitivities near resonance, a reduction of thickness from $670\text{ }\mu\text{m}$ to $335\text{ }\mu\text{m}$ would be predicted to at least double the sensitivity to $\sim 280\text{ pC/N}$ which would be on par with some bulk PZT d_{33} values. A drawback of reducing the thickness is a reduction in resonant frequency. The thinner element produces a reduction in the flexural rigidity lowering the resonant frequency and therefore reducing the usable frequency range of the element.

A drawback of reduction in thickness all the way to the nanometer and micrometer range as seen in thin film processing is the need for a mechanical substrate which clamps flexoelectric films and reduces the dielectric constant. The reduction in dielectric constant decreases the flexoelectric effect proportionally. Also, the introduction of the substrate reduces the applied strain gradient on the film by increasing the distance from the neutral axis of the film during bending.

6.4 Future Work- Alternative Flexible Materials

The flexoelectric material space is still relatively limited and needs to be investigated by targeting the most probable materials that will give enhanced flexoelectric signal. Most studies have been directed towards materials with high relative permittivity (e.g. that are near their Curie

temperature) to exhibit the highest flexoelectric signal. An alternative would be to explore materials that could withstand larger strain gradients, as even small flexoelectric coefficients can be useful at high strain gradient values. This idea could be tested in polymer materials which are extremely flexible and thin and therefore able to handle large strain gradients. A study was performed by Hu et al. on poly(vinylidene fluoride) (PVDF) and composites of PVDF with increasing volume percentages of BST 67/33. The pure PVDF had a μ_{12} of 3.17 ± 0.41 nC/m while the 25 vol% BST composite had a μ_{12} of 13.50 ± 1.76 nC/m.⁵⁸ These coefficients are orders of magnitude lower than pure BST at 100 $\mu\text{C}/\text{m}$. If the strain gradient of the composite material could be 10000 times greater than pure BST, the flexoelectric output of the composite would be on par with pure BST. The major advantage of PVDF or composites of PVDF is the flexibility of the flexoelectric element. If an application warranted the need for curved or flexible flexoelectric elements, then polymers or polymer-ceramic composites could be investigated for performance. Flexible piezoelectric transducers have been demonstrated by transferring thin film PZT from a Si substrate to polyimide using a ZnO release layer.⁵⁹ If a similar process was employed for BST thin films, a flexible flexoelectric transducer may demonstrate applicability due to a high strain gradient applied to the film at micron scale thicknesses with added conformability.

Appendix

Calculation of Effective d_{33} for Flexoelectric Considerations

For a piezoelectric sample, the d_{ij} can relate the strain for an applied voltage or the charge produced from an applied stress. For d_{33} specifically, the polarization is parallel to the applied force or the strain is parallel to the applied field along the polar axis. The typical method for measuring this quantity is called the “Berlincourt Method” after Don Berlincourt, but was first proposed by Jaffe and Cook.⁶⁰ An example system is shown in Figure A-1.



Figure A-1. Commercial Berlincourt d_{33} PiezoMeter which measures the d_{33} of a sample by clamping the sample and subjecting it to a low frequency force to an accuracy of $\pm 2\%$.

The piezoelectric effect in this configuration is generated by a uniform force across the parallel surfaces of a sample where the stress is force divided by area and is measured generally in MPa.

$$\sigma = F/A \text{ (N/m}^2 = \text{Pa)}$$

The d_{ij} coefficient has units of C/N in order to give the polarization (C/m²) induced when a force is applied.

$$P_3 = d_{33} \sigma_3$$

Therefore, the d_{33} is easily measured by measuring the polarization induced by the stress and calculating the coupling coefficient, d_{33} .

For flexoelectric measurements, a d_{33} measurement is not applicable as flexoelectricity is generated by a strain gradient and not a uniform strain. However, comparing the force to polarization output of piezoelectric and flexoelectric materials is desired. This is easily done, since measurements of both the charge output of a sample under a strain gradient with electrodes and the force required to create the strain gradient may be measured for flexoelectric materials and the charge output and stress may be measured for piezoelectric materials. The main difference here, is the force does not have to be applied on the electrodes and can be anywhere along the sample such as at the tip of a cantilever for a flexoelectric sample. This leveraging can create different outputs for the same amount of force, which makes it only an effective d_{33} that depends on the geometric setup.

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