ABSTRACT

HUANG, SHUJIN. Study on Flexoelectric Materials, Structures, and Its Applications. (Under the direction of Dr. Xiaoning Jiang).

Flexoelectricity, the linear coupling between the strain gradient and the induced electric polarization, has been widely studied as a substitution for piezoelectricity among dielectric materials. Recently, the experimental demonstration has widely reported in high permittivity ferroelectric materials, and even thin film materials. Its potential in micro/nano-scale sensing has especially gained attention, outweighing the performance of cutting-edge lead-based piezoelectric materials.

To study the thermal dependence of flexoelectricity, the flexoelectric coefficient of lead-free ceramic BaTiO$_3$-0.08Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ (BT-8BZT) was investigated in the transverse mode at temperatures ranging from 25 °C to 200 °C, and the results were compared with those of Ba$_x$Sr$_{1-x}$TiO$_3$ (BST) ceramics. The effective $\mu_{12}$ of BT-8BZT at room temperature was $\sim$25 $\mu$C/m and remained as high as $\sim$13 $\mu$C/m at 200 °C. This result suggests that BT-8BZT can be effectively used for micro/nano-sensing within a broad range of temperatures.

To broaden the material selection and extend the enhancement method, the flexoelectricity in a 100 nm-thick BaTiO$_3$ (BTO) thin film based metal/ferroelectric insulator/semiconductor (MFS) heterostructure was investigated. The transverse flexoelectric coefficient of the BTO thin film in the heterojunction structure was measured to be 287-418 $\mu$C/m at room temperature, and its temperature dependence shows that the flexoelectric effect in the BTO thin film was dominated in the paraelectric phase. We showed that the BTO thin film capacitance could be controlled at multi-levels by introducing ferroelectric and flexoelectric polarization in the film. These results are promising for understanding of the flexoelectricity in epitaxial ferroelectric thin films and practical applications of the enhanced flexoelectricity in nanoscale devices.
To verify the potential advantages in applications, a novel multi-layer flexoelectric accelerometer was successfully designed, fabricated and tested. The experimental result suggests an improved sensitivity \((8.106 \pm 0.958 \text{ pC/g})\) comparing to the previous bulk ceramic flexoelectric accelerometer. The epitaxial grown BTO thin film on the Nb:STO substrate has been proved its potential in the enhancement of flexoelectric sensing not only at the room temperature, but also above Curie temperature (120 °C).

To study the enhanced electromechanical performance by flexoelectricity, the combined piezoelectric and flexoelectric energy harvesting from the vibration of the bimorph cantilever structure was designed and analyzed. A hybrid bimorph energy harvester in series connection was firstly fabricated with Sm-doped PMN-PT, which has a high piezoelectric coefficient and a high flexoelectric coefficient. The performance of the harvester was characterized, and the results showed that the overall power density of the energy harvesting can reach \(0.093 \text{ mW/cm}^3\).

Future work will be the fabrication of miniature devices for energy harvesting and the study on flexoelectric functional materials.
Study on Flexoelectric Materials, Structures, and Its Applications

by
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DEDICATION

To my Dr. parents, my extended family and friends, as well as myself,

who always love me and stand by me.
BIOGRAPHY

Shujin Huang was born on November 3rd, 1989 in China. She received her Bachelor of Science in Photonic Information Science and Technology from Beijing Institute of Technology in 2012. Following graduation, she went to University of Southern California for her Master of Science in Electrical Engineering. In August 2014, she began her studies toward her Doctor of Philosophy in the Department of Mechanical & Aerospace Engineering at North Carolina State University under Dr. Xiaoning Jiang. Currently, she is working as a Research Assistant at the Micro/Nano Engineering Laboratory directed by Dr. Xiaoning Jiang. Shujin’s research interests include flexoelectric materials and structures, energy transduction, and laser ultrasound applications.

The following publications were authored or co-authored by Shujin Huang in peer-reviewed journals during his study at North Carolina State University:
Journal Articles


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Besides my advisor, I would like to thank the rest of my committee: Dr. Silverberg, Dr. Zhu, and Dr. So, for their insightful comments and encouragement, not only those hard questions which incented me to widen my research from various perspectives, but also those warm greetings in the hall way and at the basketball games.

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stand in my way. Now, after 23 years of school, I am so proud that I have finally met the average education level of my family. Also, I miss the time I would have spent with my grandparents. Growing up, I watched how they cooked and brewed tea, which made me a born foodie. As the only child living in a metropolitan, Beijing, I have made a group of true friends like brothers and sisters, who may not understand any of my research, but warmly listened to my venting, and gave forthright admonition even as we were thousands of miles apart. On the continent of United States, I am not alone either. I have an Extarte in Mississippi, where my homestay family treat me as their oldest child. I have two awesome brothers and two sweet sisters. Last four years I enjoyed the time I was able to spend with them during Thanksgiving and Christmas. And most of all to myself, who did not hesitate a bit to choose this journey, who struggled and procrastinated a lot, who did pillow talks sadly and cheerfully, and who walked through valleys and peaks together, and who made to the finish line together.

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Shujin (Daisy) Huang

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Chapter 1. Introduction

1.1. Principles of flexoelectricity

Flexoelectricity is defined as the generation of an electric polarization in response of a mechanical strain gradient, or the mechanical strain induced by an electric field gradient. The former one is called the direct flexoelectric effect, and the later one is called the converse flexoelectric effect. The existence of flexoelectricity in solid symmetric crystalline materials was originally discussed by Kogan in 1964. [1] As strain gradient can break inversion symmetry, flexoelectricity allows the generation of electric polarization from lattice deformations in all dielectric materials. In mathematics, the flexoelectric effect is usually written in the form of

\[ P_i = \mu^{\text{dir}}_{ijkl} \frac{\partial S_{jk}}{\partial x_i}, \quad P_i = f^{\text{dir}}_{ijkl} \frac{\partial T_{jk}}{\partial x_i} \]

(1.1)

\[ T_{ij} = \mu^{\text{con}}_{ijkl} \frac{\partial E_k}{\partial x_l}, \quad S_{ij} = f^{\text{con}}_{ijkl} \frac{\partial E_l}{\partial x_k} \]

where \( P_i \) is the induced polarization, \( T_{jk} \) is the stress, \( S_{ij} \) is the induced strain and \( E_k, E_l \) is the electric field, \( x \) is the axis of coordinate, \( \mu_{ijkl} \) and \( f_{ijkl} \) are the flexoelectric coefficients caused by strain gradient and by stress gradient, respectively. \( \text{Dir} \) and \( \text{con} \) indicate the direct and converse flexoelectric effect, respectively. The subscripts \( i,j,k,l \) indicates the tensor elements in the matrix.

The relationship between coefficients \( \mu_{ijkl} \) and \( f_{ijkl} \) can be deducted via the stiffness tensor \( c_{ijmn} \):

\[ \mu_{ijkl} = c_{ijmn} \cdot f_{mnik} \]

(1.2)

The concept of flexoelectricity was firstly originated from liquid crystals.[2], [3] The irregularly shaped and polarized molecules existing in liquid crystals will be re-orientated by the mechanical strain gradient. Later, similar strain gradient induced polarization phenomenon was also found in crystalline dielectrics, especially in those perovskites, as shown in Figure 1.1. The
B-site of the lattice will be deviated from the center position, when the material is under an inhomogeneous strain.[4]

Theoretically, the flexoelectric effect in polymers such as PVDF is similar to that in liquid crystals. However, the flexoelectric effect in polymer films is more complicated than that in solid crystals because both residual piezoelectricity effect and the flexoelectric effect should be considered. Thus, the mechanism of flexoelectric effect in polymers has not been adequately understood so far.

![Figure 1.1. Flexoelectric effect origin in solids. (a) 2D structure of elementary charges without dipole moment. (b) Under uniformly tensile strain for each unit cell, the tension gradually varies from one cell to another. (c) Under inhomogeneous deformation, A dipole moment via the flexoelectric effect was induced within the unit cell.[5]](image-url)
In the nanoelectronics, strong strain gradients are often present, which imply the potential promising applications for flexoelectricity.[6]–[8] Huang et al. showed that the flexoelectricity is a size-dependent effects due to the increasing of strain gradient when the size goes down.[9]

1.2. Experimental and analytical methods on flexoelectricity

To discover the materials with advanced flexoelectricity, it is essential to measure the flexoelectric coefficient of dielectrics ceramics, thin films, and semiconductors. In the last decades, experiments on a series of ferroelectrics have been performed due to their high dielectric constants as suggested by the lattice dynamic theory.[4] For cubic crystals, there are only three non-zero independent components of the flexoelectric coefficient matrix, which are \( \mu_{1122}, \mu_{1111}, \mu_{1211} \) corresponding to the transverse, longitudinal, and shear mode. For thin-film polymers, whose behaviour is similar to liquid crystals, there are more non-zero components. In this section, we will summarize the experimental studies in two categories: direct flexoelectric measurement, where mechanical input is applied while the electrical polarization output is measured; and converse flexoelectric measurement, where an external electrical voltage is applied to the materials while the mechanical output is monitored.

1.2.1. Direct flexoelectric measurement

Transverse and longitudinal flexoelectric coefficients \( (\mu_{1122}, \mu_{1111}) \) of dielectric perovskite ceramics were the first two components of the flexoelectric coefficient matrix being characterized. Cross and his co-workers firstly investigated \( \mu_{1122} \) experimentally by using a cantilever system and a four-point bending system, shown in Figure 1.2 (a).[10] Since then, various ferroelectric and paraelectric perovskite materials have been studied, such as Barium Titanate, Barium Strontium Titanate (BST), Lead Magnesium Niobate (PMN), and Lead
Zirconate Titanate (PZT). [10]–[13] Similar method was adopted to study STO by Zubko et al.[14] To eliminate the contribution of longitudinal and shear components, where the sample was constrained to be a slender bar (Length/Width > 5). In addition, due to the single layer plate shape, the remnant piezoelectric contribution is symmetrically cancelled.

\[ \frac{\partial \varepsilon_{11}}{\partial x_1} = \frac{\Delta \varepsilon_{11}}{\Delta x_1} = \frac{\varepsilon_{11}^u - \varepsilon_{11}^f}{h} \]  \hspace{1cm} (1.3)
Other than using continuous stress and strain, many other attempts on measuring the flexoelectric coefficient of ferroelectrics were made. The shock wave method succeeded in measuring the flexoelectric coefficient of bulk barium titanate.[16]

Figure 1.3. Shear mode measurement for PVDF[17]

The shear flexoelectric coefficient (\(\mu_{1211}\)) for bulk ceramic material has not been measured until very recently. It has been a technical barrier to generate a shear strain gradient on bulk ceramics. However, it was easy to generate the shear strain gradient on polymers like Polyvinylindene fluoride films (PVDF), for example shown in Figure 1.3. [17] This material has been the one that was measured for the components of its flexoelectric coefficient matrix, including \(\mu_{1211}, \mu_{3121}, \mu_{2312}, \mu_{1123}\).[17]–[20]

In addition to these shear component, the giant transverse and longitudinal flexoelectric coefficients in PVDF were observed.[7], [21]–[23] The difference apart from the flexoelectric characterization for solid material is that the residual piezoelectricity can’t be ignored for PVDF. The residual piezoelectricity is due to the residual electric polarization, microstructural effects
such as defects, cracks and the interaction between the alpha-phase and the amorphous phase in the film.

**1.2.2. Converse flexoelectric measurement**

Comparing with the direct flexoelectric measurement, the converse flexoelectric measurement is more difficult to achieve mainly due to two critical issues. One is that the flexoelectric deformations have always been in the pico-meter scale for bulk ceramics, which is too small to detect. The other one is that the simultaneous electrostriction effect. Unlike the piezoelectricity, the electrostriction effect has no constraint of structural symmetry. It’s worth to note that centro-symmetric materials are selected to exclude piezoelectricity but not the electrostriction effect. While the flexoelectric effect is a first-order effect, the electrostriction effect is a quadratic effect. It would suggest that the electrostriction effect should be filtered out with a lock-in filter. However, the experiments in Fu’s initial experiments didn’t suggest so.[24]

To verify the converse flexoelectricity in BST ceramics, both longitudinal model and lateral model were adopted. Fu et al reported a longitudinal model by using an optical system to measurement the displacement with the resolution as small as 10E-5 nm. The optical system was based on the scanning Michelson laser beam interferometer, shown in Figure 1.4.

There were two groups composed for the test: one was the flexoelectric group, where the electric field gradient existed; the other was the control group with the uniform electric field. As mentioned above, the flexoelectric group was expected to have first harmonic response, while only the second harmonic response should had appeared in the control group. But significant harmonic responses appeared in both groups. The work was concluded as that the first harmonic response in samples of the control group was due to the first coupling of electrostriction effect with the DC electrical noise signal.[24] The other work on converse flexoelectric effect was
conducted on the SrTiO3 single crystal,[25] which was structured as a cantilever beam. By applying a high voltage (0-3kV) pulse for 2-3 s, the bending curvature was measurement by the deflection angle of the laser beam reflected from the surface of the unfixed edge. Instead of discussing the electrostriction effect, the temperature dependence of the effect within 77 to 450 K was obtained.

![Diagram of optical measurement system](image)

**Figure 1.4.** An optical measurement system based on the scanning Michelson laser beam interferometer. PD: Photodiode; BS: beam splitter.

The lateral model was designed and reported by Shu et al in order to isolate the converse flexoelectric effect from the electrostriction effect.[26] A trapezoid BST block was used and the electrodes were attached to the lateral faces of this structure, where a nonparallel-plate capacitor was created, shown in Figure 1.5. The expected result was that the electrostriction contribution should be cancelled out because the product of the longitudinal electric field (E1) and the transverse electric field (E3) would be zero. However, the first harmonic response showed up in
the response of both trapezoid and rectangle samples. By assuming all the coefficient in different shapes are the same, a calculated shear flexoelectric coefficient of $124\pm14 \, \mu\text{C/m}$ was reported.

![Diagram](image)

Figure 1.5. Schematic for converse flexoelectric measurement for the shear strain along $x_1$ direction generated by the electric field gradient along $x_3$ direction. [26]

In addition to the experimental studies for converse flexoelectric measurement, Shu et al intended to make the converse flexoelectric coefficient inclusive by studying the relation between the converse coefficient and the direct coefficient. [27] Their theoretical derivation with Gibbs free energy density function suggested that the direct and converse flexoelectric coefficients are equivalent in crystalline mediums and systems. This conclusion has assisted researchers to explore applications of converse flexoelectric effects.
1.2.3. Theoretical methods

For flexoelectric (non-piezoelectric and centrosymmetric) dielectrics, the most general bulk thermodynamic potential density considering both polarization gradient and strain gradient is written as

\[
U = \frac{1}{2\chi} P_i P_i + \frac{1}{2} b_{ijkl} P_{i,j} P_{k,l} + \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} + \frac{1}{2} g_{ijklmn} \varepsilon_{ij,k} \varepsilon_{lm,n} + h_{ijkl} \varepsilon_{ij,k} P_i + k_{ijkl} \varepsilon_{ij,k} P_{i,k} - E_i P_i - \sigma_{ij} \varepsilon_{kl} \tag{1.4}
\]

where \( \chi \) is the dielectric susceptibility, \( c_{ijkl} \) is the elastic constant tensor, \( b_{ijkl} \) represents the polarization tensor, \( h_{ijkl}, k_{ijkl} \) are flexoelectric coupling tensors. \( g_{ijklmn} \) represents the purely nonlocal elastic effects and relates to the strain gradient elastic theories. \( P_i, P_{i,j} \) denote the polarization and polarization gradient tensors, respectively. \( E_i \) denotes the electric field and \( \sigma_{ij} \) is the stress tensor. \( \varepsilon_{ij}, \varepsilon_{ij,k} \) are the strain and strain gradient tensors, respectively, defined as

\[
\varepsilon_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i}) \tag{1.5}
\]

Here, \( u_i \) represents the displacement vector and the comma in the subscript indicates differentiation with respect to the spatial variables i.e. \((\cdots)_{,j} = \partial (\cdots) / \partial x_j \).

In the bulk thermodynamic potential density, the terms \( \frac{1}{2} b_{ijkl} P_{i,j} P_{k,l} \) and \( \frac{1}{2} g_{ijklmn} \varepsilon_{ij,k} \varepsilon_{lm,n} \) respectively represent the pure polarization and strain gradients effects, which are not included in the classical piezoelectric theory. The term \( h_{ijkl} \varepsilon_{ij,k} P_i + k_{ijkl} \varepsilon_{ij,k} P_{i,k} \) describes the flexoelectric coupling effect, which can be expressed in other forms using the integration by parts. Here, the most used three other forms are in Equation (1.6). [32]–[34]
\[
\frac{h_{ijkl}e_{ij,k}P_i + k_{ijkl}e_{ij}P_{i,k}}{2} = \frac{h_{ijkl} - k_{ijkl}}{2} (\eta_{ijk}P_i - e_{ij}P_{i,k}) + \frac{h_{ijkl} + k_{ijkl}}{2} (e_{ij}P_i)_{,k}
\]

\[
= \left( h_{ijkl} - k_{ijkl} \right) \eta_{ijk}P_i + k_{ijkl} (e_{ij}P_i)_{,k}
\]

\[
= \left( k_{ijkl} - h_{ijkl} \right) e_{ij}P_{i,k} + h_{ijkl} (e_{ij}P_i)_{,k}
\]  \hspace{1cm} (1.6)

In each form, the last term will be treated as a surface term because the whole derivative cannot be included in the bulk energy density. These expressions lead to the same governing equations but with different natural boundary conditions.

Applying the Euler equations \( \partial H \partial A - \left( \partial H \partial A_j \right)_j = 0 \), where \( A \) stands for \( P_i \) or \( \varepsilon_{ij} \), the bulk constitutive electromechanical equations will be obtained.

\[
P_i - \chi b_{ijkl} P_{k,ij} = \chi E_i + \chi \left( k_{ijkl} - h_{ijkl} \right) e_{ij,k}
\]  \hspace{1cm} (1.7)

\[
\sigma_{ij} = c_{ijkl} e_{ij,k} + \left( k_{ijkl} - h_{ijkl} \right) P_{i,k} - g_{ijklmn} e_{lm,nk}
\]  \hspace{1cm} (1.8)

In Equation (1.7), the first term on the right side describes the classical dielectric response to an electric field. The second term describes the direct flexoelectric response. In Equation (1.8), the first term in the right side describes the classical Hook's law and the second term describes the converse flexoelectric response. In addition, it should be noted that \( \chi b_{ijkl} P_{k,ij} \) and \( g_{ijklmn} e_{lm,nk} \), which are derived from the pure polarization and strain gradients terms respectively, represent the higher-order effects. If the characterize size of the structure (for example the thickness of a dielectric cantilever beam) is comparable to the effective range of these effects, these higher-order effects could influence the polarization field and the stress field in the nanoscale or even in the microscale.[35]–[37] Unfortunately, the coefficients of these higher-order terms are scarcely quantified in most dielectrics. Generally, these higher-order terms are neglected especially in the
experiment (the characteristic size is tens or hundreds of microns). Thus, substituting Equation (1.7) into Equation (1.5) and neglecting the higher-order effects, we find the most general constitutive equations characterizing the flexoelectric effects

\[ P_i = \chi E_i + \mu_{ijkl} E_{jk,l} \]
\[ \sigma_{ij} = c_{ijkl} E_{kl} + \mu_{ijkl} E_{r,k} \]  

(1.9)

Here, \( \mu_{ijkl} = \chi (k_{ijkl} - h_{ijkl}) \) is the flexoelectric coefficient. The tensor \( k_{ijkl} - h_{ijkl} \) is called the flexoelectric coupling coefficients that can be represented by an independent tensor \( f_{ijkl} \). It is obvious that the flexoelectric coefficient is proportional to the relative dielectric constants and the flexoelectric coupling coefficients, the values of which were theoretically estimated to be around several tens volts for simple ideal ionic solids by Kogan, Tagantsev and Hong. [1], [4], [38], [39] This may be called the intrinsic (or lattice-based) flexoelectric coupling coefficients. However, more and more experimental results showed that the apparent (or effective) flexoelectric coupling coefficients in many dielectrics can reach up to several hundred or even several thousand volts.[9], [11], [40] Therefore, it appears there are other dominant origins contributing to the apparent flexoelectric responses.

Many researchers have been investigating the anomaly enhanced flexoelectric responses and some possible origins were proposed.[14], [41]–[47] First, the initial strain gradients formed around the interface, grain boundary or defects have been reported to possibly enhance the flexoelectric responses. These local strain gradients can reach up to as large as \( 10^6 \text{-} 10^7 \text{ m}^{-1} \), which are 7-8 orders of magnitude larger than those reported for bulk solids. For example, using grazing-incidence in-plane x-ray diffraction, Lee et al measured the strain gradient, induced by a strain relaxation with tens of nanometers of the film-substrate interface due to the lattice
mismatch, to be $10^5$-$10^6$ m$^{-1}$.[42] Zubko believed the strain gradient near the defect can be as large as $10^7$ m$^{-1}$.[14] The extremely large strain gradients will induce large local polarization and should contribute to the effective flexoelectric responses. Another main origin of the anomalously large effective flexoelectric responses may come from the residual ferroelectricity, of which the polar nano-region is one important source. Jackeline Narvaez et al found that the ferroelastic switching induced by the stress combined with the intrinsic flexoelectric field may pole the relaxor ferroelectrics such as PMN-PT even at the room temperature.[41] Similar enhancement of apparent flexoelectric responses due to the residual ferroelectricity was also found in the BST ceramics by Lauren M. Garten and much recently in PIN-PMN-PT by Shu et al. [43]–[46]

Due to the complex microscale of nanoscale structures existing in the dielectrics, the effective flexoelectric response may result from mixed effects of many factors. These factors include the surface piezoelectric, intrinsic piezoelectric, residual ferroelectric, defects and still need to be verified in terms of both theory and experiment.

1.3. Flexoelectricity materials

1.3.1. Bulk dielectrics

Both experimental studies and theoretical derivation have suggested that the enhanced flexoelectricity may exist when the materials have a high dielectric permittivity. All measured flexoelectric coefficients up to the date are summarized in Table 1.1, along with their dielectric permittivity value. It is worth mentioning that there weren’t more different topographic structures of dielectric materials been studied to measure the longitudinal or shear flexoelectric component.
Instead, the temperature dependence has caught the attention. It has been reported that flexoelectricity is positively correlated with the dielectric constant in solid crystalline materials.[15] The temperature dependence of flexoelectric coefficients has been investigated since the dielectric permittivity has a peak value at the Curie temperature. Furthermore, comparing to the piezoelectric materials, it is expected that flexoelectric materials can work in a broader temperature. It was found in BST that the flexoelectric coefficient approaches its peak at the phase transition point.[15] Later on the temperature dependence of flexoelectricity in BaTiO3 and SrTiO3 perovskite nanostructures were also measured.[49], [50] For BST, BaTiO3 and SrTiO3, the rapid drop in the dielectric permittivity in the paraelectric phase leads to an inconsistent flexoelectricity as temperature increases. The narrow and sharp dielectric peak occurring at the ferroelectric to paraelectric phase transition limits the enhanced flexoelectric effect within a narrow temperature range. All these experiments characterized the flexoelectricity under 70 °C, which are not qualified for the high temperature application.

Table 1.1. Measured flexoelectric coefficient values and the dielectric permittivity of dielectric materials (at room temperature)

<table>
<thead>
<tr>
<th>Material</th>
<th>(\varepsilon_r)</th>
<th>(\mu_{1122}) ((\mu)C/m)</th>
<th>(\mu_{1111}) ((\mu)C/m)</th>
<th>(\mu_{1212}) ((\mu)C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN</td>
<td>11720</td>
<td>3.4[10]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PZT</td>
<td>2130</td>
<td>1.4[13]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BST</td>
<td>13200</td>
<td>20-100[9], [12]</td>
<td>120[24]</td>
<td>110 ((f_{1212})[26])</td>
</tr>
<tr>
<td>BT</td>
<td>2300</td>
<td>9[11]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMN-PT</td>
<td>~5000</td>
<td>70.8-100.8[48]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Alternatively, a high Curie temperature material can be considered in the flexoelectricity. Very recently, Shu et al have reported the flexoelectric behavior in 0.3Pb(In\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3}-0.35Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}-0.35PbTiO\textsubscript{3} (PIN-PMT-PT) single crystal.\cite{45} The Curie temperature of PIN-PMT-PT is at 229 °C but the crystal undergoes a macro-domain to micro-domain transformation at 209 °C. The maximum effective flexoelectric coefficient is 125 μC/m measured at 209 °C. But above Curie temperature, it decreases to 27 μC/m.

Although significant advances of flexoelectricity have been made in the past decades, the origin of the enhanced flexoelectricity has not been fully understood. In ceramics, interference factors such as the grain boundary was discussed because of its influence to the flexoelectricity.\cite{51} Single crystals, on the other hand, could minimize such effects. But fewer studies on single crystals were reported. It is still in debate whether flexoelectricity is a bulk effect or a surface effect. Catalan’s recent work on BaTiO3 single crystal emphasized the flexoelectricity with enlarged residual surface piezoelectricity.\cite{52} Shu et al discovered the frequency dispersion phenomenon in PMN-PT at a relative low frequency.\cite{48} This dispersion occurred with a time delay but had a positive relationship with frequency. Thus, it proved the flexoelectric effect acts more like a bulk effect rather than surface effect.

1.3.2. Thin films dielectrics

Because the strain gradient is always inversely proportional with the material size, the induced flexoelectricity by strain gradient is expected to be larger in thin films compared with bulk materials. Due to large flexoelectric coefficient of BST bulk ceramics, the flexoelectricity in BST thin film was studied.\cite{53} Also, from the principle, if the deformation applied to one structure is larger, the strain gradient would be larger.\cite{54} Then, the flexoelectric response is
stronger. Polymer thin films, especially PVDF, have its advantages as for this aspect. All the reported components of the flexoelectric coefficient matrix is list in Table 1.2.

<table>
<thead>
<tr>
<th>$\mu_{1122}$ ($\mu$C/m)</th>
<th>$\mu_{1111}$ ($\mu$C/m)</th>
<th>$\mu_{1211}$ ($\mu$C/m)</th>
<th>$\mu_{3121}$ ($\mu$C/m)</th>
<th>$\mu_{1123}$ ($\mu$C/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.5;</td>
<td>-78.19;</td>
<td>7.318 E-4[17]</td>
<td>1.037 E-2[18]</td>
<td>E-3[20]</td>
</tr>
<tr>
<td>37.3[22]</td>
<td>1.6 E-2[55], [56]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 1.3.3. Two-dimensional crystalline membrane:

As mentioned, flexoelectricity is strongly scale dependent. Compared to thin film, 2D crystalline membranes are nearly atomistically thin. Though the flexoelectricity is negligibly small for many dielectrics on the conventional scale, it becomes dominant at the nanoscale. The scaling prediction was firstly proposed by Majdoub et al and recently confirmed by various experimental evidences.[6] Those experimental evidences indicated that the flexoelectricity has a promising application potential in charge transportation, domain engineering, random access memory and nanoscale actuating device.[57] For membranes, flexoelectric polarization can be simplified down to a proportional relation with the mean curvature of the membrane in the direction normal to the membrane. Similar to a thin paper-like structure, it is easy to induce a strain gradient by bending, so that researchers’ have focused on its potentials on applications. There have been rapid computational developments but rare reported experimental results. Piezoelectricity of such materials was firstly explored for an enhanced electromechanically coupling performance. Graphene nitride nanosheet, riddled by triangular holes, was experimentally and computationally shown to exhibit an apparent piezoelectric response.[58] Piezoelectricity in materials such as BN, MoS2, and WS2, were calculated as well.[57], [59] The
characterization data of flexoelectricity in these two-dimensional materials are still missing up to now.

Sharma et al have published a thorough review on this topic including the biological membrane recently and focused on mathematical and computational developments. They pointed out the flexoelectricity has a number of implications in biology including ion transport, electromotility, and mammalian hearing mechanism.[60]–[62] They also summarized experimental findings on organic materials such as lipid bilayers.[63]

![Figure 1.6. Effective flexoelectric behaviour of semiconductive BaTiO3.][52]

### 1.3.4. Semiconductors and its flexo-like response

Although the flexoelectricity has always been studied in dielectric insulators, the insulation is not a formal requirement for the property. Theoretically, the polarization induced by strain gradients would be responsible for the redistribution of the free charge in semiconductors.

Catalan et al reported the significantly enhanced flexoelectricity in the vacuum annealed BaTiO3 semiconductor, which was attributed to a barrier layer mechanism.[52] The mechanism of the enhanced flexoelectricity in semi-conductive treated BTO single crystals is shown in Figure 1.6. As reported, the effective flexoelectric coefficient reached to 1 mC/m, increased by
orders of magnitude since all conventional flexoelectric coefficients were reported in the order of μC/m.

Serry and Sakr reported a semiconductor structure with graphene-metal-silicone for multimodal energy conversion.[64] Flexoelectric behaviour can be observed and further modulated in the fabrication of composite structures. During the fabrication, the mismatch in the mechanical and thermal properties happened between different layers. At the same time, the residual stresses exist at the interface of the structural layers induced from the thin-film deposition processes, which was tested through pure bending and thermos-mechanical tests. Therefore mechanical and thermal energy conversions are achieved through both flexoelectric and thermionic effects.

1.4. Applications

Although the studies of flexoelectricity in materials have been proceeding, it is still difficult to make the flexoelectric effect comparable to the piezoelectric effect in existing structures and devices. Designing new flexoelectric materials has become a fundamental issue in this newly arising field. Engineering the current materials to obtain great flexoelectric coefficient has become one trend to satisfy the standard of real application, especially in passive sensing devices. Meanwhile, people started to introduce the flexoelectricity into energy harvesting devices and structural health monitoring (SHM) sensors. In this section, the work in these two branches will be summarized.

1.4.1. Structure design

The generation of strain gradients should come from the external deformation of the material, or the internal stress of the materials. Characterization techniques always introduce the external force to the materials in order of observing the large deformation. The internal stress of the
material has rarely been engineered. Chu et al have demonstrated a material type named as flexoelectric/piezoelectric metamaterials by using NBBT, PZT-51, PZT-81 and BST ceramics.[65]–[68] The fabrication methods was asymmetric reduction, which was adopted from the fabrication of RAINBOW and THUNDER piezoelectric materials. Because of the reduction induced chemical inhomogeneity, the strain gradient was generated so that the apparent electromechanical coupling effect was enhanced. As results, its effective piezoelectric coefficients approached 57 pC/N at the temperature about Curie temperature, where the nominal piezoelectric device would become absent.

On the other hand, the design of composites using current known flexoelectric material has been undergoing. Chu initially proposed a two-dimensional flexure composite model with BST sheets and tungsten balls.[69] Due to the strain gradient, a giant electric polarization was exhibited in this composite and the effective piezoelectric coefficients was calculated to exceed 4300 pC/N. Shu et al recently followed this model, and systematically designed a flexure composite consisting of BST ceramic and the supporting material based on a parametric sweep finite element method simulation. The design parameters are shown in Figure 1.7.[70] The optimized composite structure can enhance the performance of the initial model up to 50 times by FEM simulation, with the thickness/ length ratio of BST at 1/150, and with silicon carbide as the supporting material at 2.5 mm distance on top and 2.1 mm distance at bottom.
Previously, the potential of nano-generators were summarized and discussed in 2013.[71] Since then, there have been some investigations on materials who exhibit high flexoelectric coefficients like we mentioned in previous sections. However, the proper degradation of nano-scale structures is still required for inventing flexoelectric devices. Up to now, flexoelectric devices have been designed mainly in two applying directions, actuators and sensors, like nominal electromechanical converters by piezoelectricity.

Structural health monitoring in mechanical, architectural, and transport vehicles has been the key area for flexoelectric detections. In such systems, defects like cracks would cause catastrophic accidents. Because of the scaling effect of gradient, the sensitivity and accuracy of flexoelectric sensors could stand out among existed detection technologies. Kwon, Yan and Huang published the flexoelectric strain gradient sensor for structural health monitoring and crack detection.[72]–[75] Due to the stress concentration surrounding a crack, the strain gradient varies abruptly in the vicinity of the crack. The sensor was attached in the neighbor of a cracking site. With varied tension stress, the induced charge due to flexoelectricity was measured to predict the cracking site. Tzou et al have reported a distributed system in structural sensing by flexoelectricity.[76] A group of BST ceramic sensors were distributed on a cantilever
flexoelectric beam and their flexoelectric constant were consistent by the open-circuit model. An alternative of dynamic measurements for mechanical structures was provided.

The performance of micro/nano fabricated sensors can also be improved by adopting the flexoelectric effect. Kwon et al. firstly designed and fabricated a high sensitive flexoelectric microphone, which can work at an extremely wide working frequency range based on barium strontium titanate ceramic.[77]

As for energy harvesting, Zhang et al reported a curved resonant flexoelectric actuator fabricated with PVDF.[78] Tzou et al claimed a static nano-control beams.[79] Catalan et al fabricated a pioneer cantilever actuator with strontium titanate integrated on to silicon, shown in Figure 1.8.[80] A figure of merit (curvature divided by electric field) of 3.33 MV$^{-1}$ was reported to be comparable to that of state-of-the-art piezoelectric bimorph cantilever. Similar structure was also made with PZT which showed the flexoelectricity can either enhance or suppress the piezoelectric response of the cantilever depending on the ferroelectric polarity and lead to a diode asymmetric electromechanically response.

Besides all above known areas that flexoelectricity can show its advantages, thermal gradient induced flexoelectric effects were first studied by Jiang et al in bulk BST ceramics.[81] Wave propagation within the micro-structured solid were observed by Shen et al.[82], [83] These new applications have truly broaden the research in flexoelectricity.
1.5. Dissertation structure

Taking all above knowledges into consideration, the main effort of my research is to investigate the flexoelectricity of the new materials, to test the temperature dependence of their flexoelectricity, as well as to design and fabricate the devices for sensing and energy harvesting. The dissertation is composed in six chapters and references. Each chapter is briefly described as follows.

**Chapter 1** reviews the fundamental principles of flexoelectricity, the current characterization method, the various flexoelectric materials, and up to date applications.

**Chapter 2** presents the flexoelectricity BT-8BZT with a smoothly declined dielectric permittivity. The measurement of transverse flexoelectric coefficient and the temperature dependence study are covered, including the characterization method, testing method and results.

**Chapter 3** reports the flexoelectricity in a metal/ferroelectric/semiconductor heterostructure, including the fabrication, material characterization, experimental set-up, and discussion of its piezoelectricity, flexoelectricity, and capacitance.
Chapter 4 investigates a flexoelectric accelerometer using the heterostructure reported in chapter 3. A unimorph type of a flexoelectric accelerometer with a proof mass at the tip was designed, fabricated, and tested at various temperature.

Chapter 5 focuses on energy harvesting by both piezoelectric and flexoelectric effects. The current technology and limitation of MEMS energy harvesting are taken into consideration. With the new material, the hybrid piezoelectric and flexoelectric bimorph energy harvester was analysed, simulated, fabricated, and tested.

Chapter 6 concludes this dissertation with the summary of my research and the recommendation for further research. Especially, with the collaboration on the theoretical analysis of flexoelectric functional graded materials, the preliminary experimental study is presented here. A novel structure for scaling down devices are proposed and described.
Chapter 2. Flexoelectric effect in response of temperature variation

2.1. Background

As mentioned in Chapter 1.3, it has been reported that flexoelectricity is positively correlated with the dielectric constant in solid crystalline materials. Most materials that were studied for its flexoelectricity (listed in Table 1.1) are ferroelectrics, which are characterized with a high dielectric constant. According to the theoretical model raised by Tagantsev, the flexoelectric coefficient is linear proportional to the dielectric constant. [4] Some of the ferroelectric material have shown a dielectric constant of over ten thousand around the phase transition point at the Curie temperature. [10], [12] Thus, there has been an extensive investigation in materials with their high dielectric permittivity, particularly at the Curie temperature \((T_C)\). [13], [14], [53] Table 2.1 have summarized some materials with their dielectric constant, Curie temperature, and flexoelectric coefficients. Some suggested that the large flexoelectric polarization might be caused by reorientation of the preexisting polar clusters in the relaxor ferroelectrics by the elastic strain gradient. The enhancement is more obvious around the phase transition point. [84]

Table 2.1. Dielectric constant \((\varepsilon_r)\) and Curie temperature \((T_C)\) of reported flexoelectric materials

<table>
<thead>
<tr>
<th>Material</th>
<th>(\varepsilon_r) at (T_t)</th>
<th>(T_C)</th>
<th>(\mu_{1122}) ((\mu)C/m)</th>
<th>Testing Temperature (T_t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMN</td>
<td>11720</td>
<td>-10 °C</td>
<td>3.4[10]</td>
<td>20-25 °C</td>
</tr>
<tr>
<td>PZT</td>
<td>2130</td>
<td>220 °C</td>
<td>1.4[13]</td>
<td>24 °C</td>
</tr>
<tr>
<td>BST</td>
<td>13200</td>
<td>21 °C</td>
<td>20-100[9], [12]</td>
<td>23 °C</td>
</tr>
<tr>
<td>PMN-PT</td>
<td>~5000</td>
<td>150 °C</td>
<td>70.8-100.8[48]</td>
<td>25 °C</td>
</tr>
</tbody>
</table>
It is expected that flexoelectric materials work at a broader temperature range than that of piezoelectric materials. [10], [53] Nevertheless, the rapid drop in dielectric permittivity of piezoelectrics (e.g. BST and BT) in their paraelectric cubic phase may lead to a drawback of persistence of flexoelectricity as temperature rises, showing that some of these materials are not suitable for devices at a broad temperature range.

In section 1.3.1, we have mentioned a high Curie temperature material can also be considered in the flexoelectricity, to avoid the drop of the flexoelectric coefficient in the working temperature range. On the other hand, it would be the direction of material hunting to find a material with a smoothly declined dielectric permittivity to the temperature increasing. Recent studies on \((1-x)\text{BaTiO}_3-x\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\) (BT-BZT) perovskite ceramics have shown promising dielectric properties for high-energy and high-temperature (>300 °C) applications[85]. When \(x = 0.08\), BT-8BZT has exhibited a \(T_c\) of ~25 °C, with a frequency-dependent permittivity and good thermal resistance in dielectric properties against temperatures up to 200 °C. Therefore, it would be promising to investigate the flexoelectricity of BT-8BZT at a broad temperature range.

In this chapter, flexoelectric cantilever beams were fabricated with BT-8BZT and BST ceramics. The dielectric permittivity was examined for BT-8BZT. Then at room temperature, the flexoelectricity of BT-8BZT was measured by using a bending method, while piezoelectricity was directly measured. Furthermore, at different temperatures, the flexoelectric transverse coefficients of BT-8BZT were determined and compared with BST ceramics.

This chapter has some of previously published material authored by S.Huang as shown below. All previously published material was reprinted with permission from the publishers:
Huang, Shujin, Taeyang Kim, Dong Hou, David Cann, Jacob L. Jones, and Xiaoning Jiang. "Flexoelectric characterization of BaTiO3-0.08 Bi (Zn1/2Ti1/2) O3." Applied Physics Letters 110, no. 22 (2017): 222904.

2.2. **Unimorph cantilever method**

For a cubic crystal, the non-zero components of the flexoelectric coefficients $\mu_{ijkl}$ are $\mu_{1111}$, $\mu_{1222}$, and $\mu_{1212}$ in tensor notation, or $\mu_{i1}$, $\mu_{i2}$, and $\mu_{ii}$, in reduced (matrix) notation. Each flexoelectric coefficient is associated with a specific mode: $\mu_{i1}$ for longitudinal, $\mu_{i2}$ for transverse, and $\mu_{ii}$ for shear mode, respectively. Separate experiments have been carried out to determine each component for different materials[15]. Among them, the beam bending method is usually adopted to measure the $\mu_{i2}$. The induced polarization is in response to the axial normal strain gradient in the thickness direction,

$$P_3 = \mu_{i2} \frac{\partial \varepsilon_{i1}}{\partial x_3}$$

(2.1)

where $x_3$ is the normal axis to the electrode surface, and $\varepsilon_{i1}$ is the in-plane mechanical strain.

2.3. **Fabrication of unimorphs with BT-8BZT**

Bulk polycrystalline samples of BT-8BZT ceramics were prepared using a conventional solid state synthesis technique by Cann’s research group at Oregon State University, as described in detail by Triamnak et al.[85]. The sintered pellets were cut into ceramic bars with the size of 1×5×10 mm³ using a diamond wire saw (Well Diamond Wire Saws, Inc., Norcross, GA). The cantilever beams of BT-8BZT were prepared using a dicing process. Parameters of the beam are presented in Table 2.1. Both bottom and top electrodes consist of 100 nm (Au)/5 nm (Ti) were
prepared by the e-beam evaporation (Kurt Lesker Electron Beam Evaporation System, Jefferson Hills, PA).

Table 2.2. Geometric parameters of BT-8BZT cantilever beam

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Length</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>780 µm</td>
<td>6.5 mm</td>
<td>4 mm</td>
</tr>
</tbody>
</table>

The relative permittivity of the BT-8BZT ceramic was measured at 0.1 kHz, 1 kHz, 10 kHz, 100 kHz, and 1000 kHz, respectively, using an impedance analyzer (Agilent Technologies, 4294 A, Santa Clara, CA). Meanwhile, according to Cann et al. [85], a transition in phase from ferroelectric to paraelectric was noted around 25 ºC. Concerning piezoelectricity in BT-8BZT, when the temperature of BT-8BZT sample is above the Curie temperature (25 ºC), the material should theoretically not exhibit any ferroelectricity. However, when the temperature is close to the Curie temperature, a weak persistence of the macro-ferroelectricity may exist due to local nano-domains[86]. A small displacement was observed even at the curie temperature, 25 ºC, which reflected the residual ferroelectricity[11], [41]. So the contribution of piezoelectricity in $d_{33}$ mode to the total electric output was verified at room temperature. The 378 V AC electrical signal was applied across the thickness direction of the unpoled ceramics at 10 Hz, and displacement was detected by a laser vibrometer (Polytec, OFV-5000, Irvine, CA) with a resolution of 100 nm/V.

2.4. Experimental methods

The flexoelectric measurement setup was similar to the one used in our previous work[53]. In addition, a thermal chamber and a thermocouple was used to measure the sample temperature in this work, as shown in Figure 2.1. The ceramic beam was clamped rigidly at one end and
deflected at the other end by a piezoelectric actuator, which was driven by a 10 Hz-excitation from a function generator (Tektronix, Model AFG3101, Beaverton, OR) along with a power amplifier (Brüel & Kjær, type 2706, Nærum, Denmark). The laser vibrometer was also used to measure the vibrating displacement (δ). The generated polarization resulted in the current (I), which was amplified by a charge amplifier (Brüel & Kjær, type 2635, Nærum, Denmark) and then monitored by an oscilloscope (Agilent Technologies, DSO7104B, Santa Clara, CA) at a condition of 1GHz, 4GSa/s.

According to Euler-Bernoulli beam theory, the strain gradient can be calculated as Eq. (2)

\[ \frac{\partial \varepsilon_{11}}{\partial x_3} = \frac{3\delta}{L_0} (L_0 - x) \]  

The measured current, I, can be derived from the induced polarization \( P_3 \).

\[ I = 2\pi fAP_3 \]  

The flexoelectric coefficient is calculated in Eq. (4).
\[ \mu_{12} = \frac{\sqrt{2}II_0^3}{3\pi fA\delta(L_0 - x)} \]  

(2.4)

where \( I \) is the current, \( f \) is the frequency, \( \delta \) is the tip displacement, \( A \) is the electrode area, \( L_0 \) is the cantilever length, and \( x \) is the distance between the electrode and the clamped end.

In addition to the room temperature set-up, an extra thermal chamber built with a ceramic fiber blanket was included for flexoelectric measurements at elevated temperatures, as shown in Figure 2.1. Both the thermal couple (TC) and the infrared thermal meter (TM) were used to monitor the temperature inside the chamber. Hot air generated by a heat gun (Proheat, PH-1300, LaGrange, KY) was blown into the chamber for temperature control.

2.5. Results and discussion

2.5.1. Dielectric permittivity and piezoelectric coefficient

![Figure 2.2. Dielectric properties of BT-8BZT as a function of temperature](image-url)
The temperature dependence of the dielectric permittivity is shown in Figure 2.2. The gradual decline in relative permittivity with respect to the temperature was observed, which corresponds with a previous report[85]. A derivation from classic Curie-Weiss behavior was noticed, which is mainly caused by the diffuse nature of the phase transition due to the addition of BZT[48], [85].

The measured $d_{33}$ was about 39 pm/V, which reflects the residual ferroelectricity. (This value will be discussed later, along with the flexoelectric characterization at room temperature.) However, the piezoelectric contribution to the total electric output were further suppressed at the paraelectric phase as the temperature increased (~200 ºC), suggesting that the polarization output from the bending test described below would be dominated by the flexoelectric effect.

2.5.2. Flexoelectric coefficient of BT-8BZT

Figure 2.3. Electric polarization in response to mechanical displacement at 10 Hz.
Figure 2.3 shows the real time charge output of BT-8BZT under a sinusoidal load with a peak-to-peak value of 1.5 µm at 10 Hz. It can be observed that the charge output is out-of-phase with the applied load. This is because the beam was bent downward, causing the strain gradient direction of the BT-8BZT to be opposite to the electrode connection polarity. The noise was eliminated by a bandpass filter (5~15Hz) in signal processing. At the same time, compared to piezoelectricity and flexoelectricity, the associated electrostrictive effect is of the quadratic dependence of the field, which is featured with a higher frequency \(2f\), 20 Hz in this case, than the exciting signal \(f\), which is 10 Hz, so that it would not interfere with the flexoelectric signal.

![Graph showing polarization vs. strain gradient](image)

Figure 2.4. Flexoelectric polarization as a function of applied strain gradient at room temperature

Figure 2.4 shows that the polarization induced by the flexoelectric effect is linearly proportional to the strain gradient calculated from Eq. (2), which indicates the average \(\mu_{12}\) (slope). The effective \(\mu_{12}\) of BT-8BZT is calculated to be ~25 µC/m at room temperature. The
effective $d_{33}$ is converted from $\mu_{12}$ to be $\sim 67$ pm/V[9]. Because the Curie temperature of BT-8BZT is close to the room temperature, there is still the remnant piezoelectric contribution. Compared to $d_{33}$ value (39 pm/V) from the direct measurement mentioned earlier, the flexoelectric contribution to the effective mechanical-electrical coupling $d_{33}$ is comparable to the part from remnant piezoelectricity at room temperature.

2.5.3. Temperature variation of flexoelectric coefficient of BT-8BZT

![Graph of temperature dependence of flexoelectric coefficient](image)

Figure 2.5. Temperature dependence of the transverse flexoelectric coefficient of BST and BT-8BZT.

Both BST and BT-8BZT cantilever beams were tested at temperatures ranged from room temperature to $200 \, ^\circ C$, where both materials were in the paraelectric phase. The calculated $\mu_{12}$ of BST and BT-8BZT are plotted in Figure 2.5. Both BST and BT-8BZT have high flexoelectric coefficients, $25 \, \mu \text{C/m}$ and $22 \, \mu \text{C/m}$ at $25 \, ^\circ C$, respectively. In BST, an increase in temperature brings the flexoelectricity down rapidly, while the flexoelectric coefficient of BT-8BZT changes
more gradually. As the result, the flexoelectric coefficient $\mu_{t_2}$ of BT-8BZT remains around 12 $\mu$C/m at 200 °C, while $\mu_{t_2}$ of BST is less than 3 $\mu$C/m at 200 °C. Since the temperature range is above the Curie temperature, weak macro-ferroelectric regions may exist due to the presence of local nano-domains which gradually disappear as the temperature is increased.

![Figure 2.6. Temperature dependence of the piezoelectric coefficient $d_{33}$ of BT-8BZT.](image)

To verify the disappearance of this residual ferroelectricity, the direct piezoelectric response of BT-8BZT was measured over the same temperature range and the data is shown in Figure 2.6. As indicated in the figure, the piezoelectric coefficient $d_{33}$ decayed rapidly, which indicates that the piezoelectric effect eventually disappears in the paraelectric phase. Thus, the flexoelectric contribution at high temperatures dominates the mechanical-electrical coupling.

Also, it is worth mentioning that compared with the $\mu_{t_2}$ of lead contained perovskites, such as PZT, PMN, BT and SrTiO3 at room temperature (RT), as shown in Table 1.1, the
The flexoelectric coefficient of BT-8BZT is attractive at both room temperature and elevated temperatures (e.g. 200 °C).

Our experimental results showed there is relatively less variation of $\mu_{12}$ in BT-8BZT compared with that of BST, which is known with the highest $\mu_{12}$ among all reported ferroelectric materials. This finding is believed to correspond with the broad dielectric maximum associated with the diffuse phase transition exhibited by BT-8BZT[85]. Hence, the thermal dependence of flexoelectricity in BT-8BZT is much more stable than in BST. The previous work by Cross’s group[11] showed the flexoelectric coefficient exactly follows the temperature dependent dielectric properties. Our work with BT-8BZT again proved its flexoelectric ability and its dielectric permittivity are correlated in such materials. The broaden ferroelectric-paraelectric peak of BT-8BZT have enhanced the flexoelectric response with good temperature stability[87]. Furthermore, the thermal stability of enhanced flexoelectric response in BT-8BZT would provide a potential candidate for sensing and detecting under high temperatures.

2.6. Summary

The gradual decline of flexoelectric coefficient $\mu_{12}$ with increasing temperature in BT-8BZT was reported in this chapter, confirming the advantage of a high dielectric permittivity of BT-8BZT in paraelectric phase. The measured flexoelectric coefficient $\mu_{12}$ of BT-8BZT is 25 $\mu$C/m at 25 °C and can remain above 12 $\mu$C/m at temperatures up to 200 °C, which suggests potential applications for high temperature micro/nano-sensing. Other compositions in the BiMeO$_3$-BaTiO$_3$ system exhibit temperature stable permittivity over a much wider range.[88] These findings suggest that these materials may be more effective as flexoelectric-based sensors over a broader temperature range.
Chapter 3. Flexoelectric effect in a multilayer structure

3.1. Background

Flexoelectricity has been mostly reported for insulating ferroelectric materials such as BaTiO₃, SrTiO₃, BST, BT-8BST, SrTiO₃, PMN-PT and polyvinylidene fluoride (PVDF).[11]–[13], [18], [22], [52], [71], [80], [89], [90] However, recently, it was found that some semiconducting materials can also yield polarization upon strain gradients, like the oxygen depleted BaTiO₃ (BTO-δ), whose flexoelectric coefficient can reach up to 1 mC/m.[52] In Section 1.3.4, we discussed this research with Error! Reference source not found.. Due to the oxygen depletion process, BaTiO₃ (BTO) became an n-type semiconductor where the surface was fully oxidized and capped by the thin insulating layer. The enhanced flexoelectricity was induced by the surface reduced layer, where the strong electric field was generated in the semiconducting BTO-δ under strain gradients.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mu_{1122}$ (µC/m)</th>
<th>Substrate</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>34.5;37.3</td>
<td>N/A</td>
<td>13.5 µm</td>
</tr>
<tr>
<td>BST</td>
<td>24.5</td>
<td>Si</td>
<td>130 nm</td>
</tr>
<tr>
<td>PbTiO₃</td>
<td>~0.2</td>
<td>DyScO₃</td>
<td>30 nm</td>
</tr>
</tbody>
</table>

Since the flexoelectric effect is expected to be more significant when the material is shrunk down to the nanoscale due to its scaling effect[9], the flexoelectric effects in ferroelectric thin films have attracted a lot of attentions.[54] Table 3.1 summarized the value of flexoelectric coefficient of some reported materials. However, the reported studies focused on the flexoelectric effect in single ferroelectric thin films epitaxially grown on a lattice-matching
substrate. More recently, extremely thin flexoelectric films have been explored showing promising flexoelectricity.[91]

In this chapter, an experimental study on the flexoelectricity in Pt/BTO/Nb-doped SrTiO3 (MFS) heterojunctions is presented. A layer of 100 nm-thick BTO epitaxial thin film deposited on Nb 0.7wt% doped SrTiO3 (Nb:STO) substrate was prepared for the MFS heterojunction and the flexoelectric coefficient of the BTO thin film was then extracted. A ferroelectric tunnel junction (FTJ) was formed by poling the BTO layer, resulting in a resistive switching memory. The flexoelectricity in the BTO thin film harnessed with the ferroelectricity was then studied to control multi-level polarization of the BTO thin film.

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3.2. A metal/ferroelectric/semiconductor heterostructure

Given that the ferroelectric thin film devices such as ferroelectric field-effect transistors[92] or ferroelectric tunnel junction memories[93] require multi-layered film structure, investigating the flexoelectric effect in ferroelectric hetero-junctions is important.[94], [95] Particularly, an interesting thin film based multilayer structure, metal/ferroelectric insulator/semiconductor (MFS) hetero-structure exploiting the ferroelectric tunnel junctions (FTJs), has been extensively studied for a resistive switching memory. [93], [96]–[98] Although the ferroelectric-induced tunneling has been demonstrated experimentally as the dominated transport mechanism in FTJs, it was not
clear whether flexoelectricity played a role in the mechanism of resistive switching memory or not. It is worth to mention that the theoretical mechanism of flexoelectric impacts on ferroelectric switching was predicted using the Landau–Ginsburg–Devonshire phenomenological approach.[99], [100] When the external electrical field applied on the bending beam, the energy profile of the BTO thin film (20 nm) can be recovered. Thus, Zhou et al. predicted the switching mechanism in the epitaxial grown ferroelectric thin film[].

3.3. Fabrication of the heterostructure

3.3.1. Fabrication method

A metal/ferroelectric/semiconductor heterostructure was fabricated and prepared for electrical polarization tests (Figure 3.1). A layer of 100-nm-thick BTO thin film was deposited epitaxially on a [001] -oriented single-crystalline 0.7wt% Nb-doped SrTiO3 (Nb:STO, n-type) substrate by pulsed-laser deposition in a typical epitaxial growth mode.[98] 30 nm thick Pt top electrodes were then sputtered onto BTO/Nb:STO with a dot patterned mask to form the MFS heterostructure.

Figure 3.1. Schematic illustration of the Pt/BTO/Nb:STO metal/ferroelectric/semiconductor heterostructure
heterostructure. Besides, indium electrode and Au electrode were pressed and sputtered to the structure, respectively, to ensure an ohmic contact formed with Nb:STO. The electrical output induced by mechanical bending within the MFS was monitored through a pair of wires connected to the Pt electrode and the Indium ohmic contact pad on the Nb:STO substrate.

Another pair of wire connections were made between the indium ohmic contact and the evaporated Au electrode on the bottom side of Nb:STO substrate, which will be used to monitor the electrical response induced purely from the Nb:STO substrate upon mechanical bending.

### 3.3.2. Material characterization

![Diagram](image-url)

Figure 3.2. Schematic description of the polarization directions induced by bending the sample or by applying an electric field, and the corresponding band diagrams of the MFS structure.

In order to understand the polarization in the MFS structure, three effects were examined here: the ferroelectricity, the piezoelectricity and the flexoelectricity. The deflected end of the samples was vibrated in two directions as shown in Figure 3.2. (A) & (B) represent the ferroelectric layer
is poled as low resistance state by applying a positive voltage (8 V) to the Pt electrode; (C) & (D) represent the ferroelectric layer is poled as high resistance state by applying a negative voltage (-10 V). The mechanical bending direction is shown as the beam deformation. The blue, red, and green arrows denote the flexoelectric, ferroelectric and piezoelectric polarization direction, respectively. A rectangular barrier in the band diagram, denoted by the dashed and solid lines, is assumed before and after the ferroelectric layer is poled, respectively. The arrow in the barrier indicates the dipole induced by ferroelectric (red), flexoelectric (blue), piezoelectric (green), respectively. Therefore, four different polarization states are demonstrated by combining ferroelectric, piezoelectric and flexoelectric polarization as shown in Figure 3.2.

3.4. Experimental Method

3.4.1. Experimental set-up

![Figure 3.3](image)

Figure 3.3. The experimental set-up for electrical polarization measurement.

Figure 3.3 shows the schematic diagram of the electrical polarization measurements. The MFS structured beam was clamped rigidly at one end and deflected at the other end by a piezoelectric actuator, which was driven by a function generator (Tektronix Model AFG3101) at
an excitation frequency of 10 Hz along with a power amplifier (Brüel & Kjær, type 2706, Nærum, Denmark). The displacement of the deflected end was measured using a laser vibrometer (Polytec, OFV-5000), which was connected to an oscilloscope (Agilent model DSO7104B). For a simple cantilever, the induced electrical polarization is represented by:

\[
P_z = \mu_{12} \frac{\partial \varepsilon_{xx}}{\partial x_z} + d_{31} \varepsilon_{xx} + P_r
\]  

(3.1)

where the first term is the flexoelectric polarization, the second term is the piezoelectric polarization and the last term is the ferroelectric polarization. To achieve the controllably bending in two opposite directions, the same displacement of the deflected end was reached by monitoring through the laser vibrometer.

A lock-in amplifier (Stanford Research System Model SR830) was used to record the electrical polarization current induced by bending, for both sets of electrodes. A semiconductor characterization system (Keneith model 4200-SCS) was used to record the capacitance change of the MFS structure upon bending. Similar tests were also conducted at elevated temperatures using a set-up described in our previous work.[50] The temperature range was set to be between 70 °C and 160 °C.

3.5. Results and discussion

3.5.1. Characteristics of MFS heterostructure

To determine the ferroelectric polarization of the MFS structure, the resistance switching effect was tested by measuring current change when external pulsed-train writing voltages were used in the sequence illustrated with a step of 0.2 V, and the read voltage remained unchanged as \( V_{\text{read}} \) of 0.5 V. The positive voltage pulse drives the BTO polarization pointing to NSTO electrode and sets the junction to the ON state (the voltage is applied on the top electrode while
the bottom electrode is grounded). The Pt/BTO/NSTO device is set to the OFF state by applying a negative pulse, which switches the polarization towards the Pt electrode.

![Figure 3.4](image)

Figure 3.4. Current-voltage characteristics of MFS structure before bending.

The results, as shown in Figure 3.4, suggest that the resistance can be varied by applying an external electric field. By sweeping the writing voltage from 8 V to -10 V, two resistance states are obtained. A low resistance state (LRS) is obtained when a positive voltage (8 V) is applied to the Pt electrode while a high resistance state (HRS) is achieved when -10 V is applied. Figure 3.4 shows the two distinct current states obtained at 0.5 V after poling the ferroelectric layer at positive (red) and negative (black) voltages, which confirms the non-volatile resistance switching of the MFS heterojunction.[98]

### 3.5.2. Flexoelectricity

Apart from the ferroelectric effect, the piezoelectric response was checked by measuring the $d_{33}$ value via the piezoelectric $d_{33}$ meter (Institute of Acoustics Academia Sinica, Model ZJ-3D). The observed $d_{33}$ (the effective $d_{33}$) was weaker than 1 pC/N, which can be converted into the
$d_{31}$. The $d_{31}$ is proportional to the effective $d_{33}$ with the square of the length-to-thickness ratio. Since the length-to-thickness ratio of the BTO thin film is in the order of $10^5$, the transverse piezoelectric coefficient $d_{31}$ is extremely small (ten orders smaller than the effective $d_{33}$).[9] Thus, the piezoelectric polarization was neglected throughout the experiment.

Figure 3.5. Induced polarization as a function of strain gradients

Figure 3.5 shows the polarization in the MFS structure as function of a strain gradient. The strain gradient was calculated from the Euler-Bernoulli beam theory.[53] It is worth to note the lattice mismatch between BTO thin film and Nb:STO substrate, which can cause the inhomogeneous in-plane strain inside of BTO thin film.[101] Further discussion will be included later in the chapter. The polarization induced mechanical deflection is linearly proportional to the strain gradient, where the slope indicates the effective flexoelectric coefficient. The estimated (slope) is ~385 μC/m for Case A, ~418 μC/m for Case B, ~339 μC/m for Case C and ~287 μC/m for Case D. This phenomenon agrees with the analysis of the dipole distributions shown in Figure 3.2. It is worth noted that for Case A and C, or for Case B and D, the MFS structure was
set at LRS and HRS, respectively. Even though the mechanical bending direction is the same, the flexoelectric coefficients were different due to the ferroelectric polarization from a capacitor.

### 3.5.3. Capacitance

To understand the different polarization states and interpret the variation of flexoelectric coefficients, the capacitance of the MFS structure for the four different cases (A, B, C, and D) was measured under an accumulation mode (positive bias applied to the Pt electrode) as shown in Figure 3.6.

![Capacitance Graph](image)

Figure 3.6. The capacitance for the four different states induced by combining the ferroelectric polarization with the flexoelectric polarization. The error bars in (b) are added under a calculation of capacitance for 4 samples. A, B, C and D indicate four different combination of polarizations in Figure 3.3 accordingly.

In case of B and C, the directions of the ferroelectric and flexoelectric polarization are same so that the dipoles were lined up in the same direction as shown in Figure 3.3 and hence the capacitance should increase after the bending. In case of A and D, on the other hand, the directions of the ferroelectric and flexoelectric polarization are opposite. The polarization induced by the flexoelectricity compensates that induced by the ferroelectricity and hence the
capacitance decreases after the bending. It is noted that the absolute capacitance for LRS (A and B) is larger than the capacitance for HRS (C and D). Under HRS (C and D), the ferroelectric polarization in the BTO thin film induces a depleted Nb:STO region at the BTO/Nb:STO interface as shown in the band diagram in Figure 3.2. Hence, the total capacitance of the MFS structure is described as:

\[
\frac{1}{C_{BTO}} + \frac{1}{C_{Nb:STO}} = \frac{1}{C_{Total}}
\]  

(3.2)

where the \( C_{BTO} \) is the capacitance in the BTO thin film, \( C_{Nb:STO} \) is the capacitance in the Nb:STO substrate, and \( C_{Total} \) is the total capacitance in the MFS structure. In case of LRS (A and B), the ferroelectric polarization in the BTO thin film attracts the majority carriers in the Nb:STO to the BTO/Nb:STO interface as shown in the band diagram (Figure 3.2). Hence, \( C_{Nb:STO} \) is negligible and the total capacitance is larger compared to the cases for HRS (C and D) as shown in Figure 3.5(b). As a result of the combined effects of resistance states and bending directions, four different capacitance levels could be demonstrated.

3.5.4. Temperature dependence of flexoelectricity

In addition, the bending experiment was performed as a function of temperature from 70ºC to 160ºC. The transverse flexoelectric coefficient of the MFS structure with different poling directions are shown in Figure 3.7.
With the Curie temperature at 120 °C, the flexoelectricity exists in both ferroelectric phase and paraelectric phase, while the ferroelectricity only exists in the ferroelectric phase. Therefore, above the Curie temperature, the crystalline structure of BTO thin film transformed into paraelectric phase so that the ferroelectric effect was gradually eliminated. The flexoelectric effect is dominated in the paraelectric phase so that the effective flexoelectric coefficients of B and D can gradually fall as the same actual flexoelectric coefficient.

3.6. Summary

In this work, the flexoelectric coefficient of BTO thin films with a MFS structure was characterized using the cantilever bending method over a temperature range from 70°C to 160°C. Our work demonstrated that the flexoelectric polarization of the Pt/BTO/Nb:STO MFS structure is purely generated from the BTO thin film layer. Multi-level control of the capacitance in the MFS structure was achieved by combining both ferroelectric and flexoelectric polarizations.
Chapter 4. Multilayer unimorph vibration sensing

4.1. Background

4.1.1. Current MEMS sensor technology

As the development of the smart technology, the requirements for various inertial sensors are becoming increasingly strict in sensitivity and complex in structure. Especially when the Internet of Things (IoT) has been brought up, which refers to the connection of sensors and actuators to the networks and computers over the internet.[102] The IoT applications allows the full integration of sensing products such as wearable devices and self-driving automotive. In other industries, high precision sensing has become an important element in a broad range of applications, such as spacecraft guidance, and inertial navigation, where not only the accuracy and sensitivity are demanded more precisely, but also the dimension, cost, impact resistance and more parameters are required to be customized for various applications. Almost all miniaturized, most of low-power and low-cost sensors are produced using micro-electromechanical systems (MEMS) technology. [103]

An accelerometer is an inertial sensor that detects an electrical signal from the acceleration of the mechanical motion or vibration. Such motion detecting sensors are demanded in automotive, smart wearable devices, industrial monitoring, and military applications. [104] For example, when attached to body, one can monitor the activity during sleep and exercise. One can trigger the air bag when the automotive collides. When attached to industrial architectures, the sensor can be used to detect movement, vibration, and shock during operation or hazard monitoring.
The structures of acceleration sensors can be categorized into three basic transduction modes: compression mode, shear mode, and bending mode, shown in Figure 4.1.[105] Among these, the accelerometers with the cantilever structure are known for the highest sensitivity due to its most compliance to applied mechanical load, like force, vibration, and pressure, etc. The typical principles of cantilevered accelerometers are either detecting the change in capacitance, or the electrical output of piezoelectric or piezoresistive elements. Capacitive accelerometers are less tolerant to the environmental variations such as noise and temperature. Piezoresistive ones are limited in temperature range, which would require an additional compensation circuitry.

Among all MEMS accelerometers, piezoelectric accelerometers have been widely used since they are featured with high output impedance, simplified structures, wide dynamic range and rapid response. The concept of piezoelectric accelerometer was proposed as early as 1964. The first application was on the stress monitoring on the quartz oscillator. [106] The fundamental principle of a piezoelectric accelerometer is that the stress change induces the electric polarization shift. Table 4.1 compares the performance of some of the micromachined piezoelectric accelerometers reported in the literature. These piezoelectric accelerometers have
been used in the atomic force microscopy (AFM) and then been adopted in chemical and biomedical field.

Table 4.1. Key features and performance of some reported piezoelectric accelerometers

<table>
<thead>
<tr>
<th>Sensing material</th>
<th>Structure</th>
<th>Charge Sensitivity</th>
<th>Resonance Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO [107]</td>
<td>Unimorph</td>
<td>0.0447 pC/g</td>
<td>1.03 kHz</td>
</tr>
<tr>
<td>(0.5 µm sputtered)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AlN [108]</td>
<td>Tapered beam</td>
<td>5.2 pC/g</td>
<td>1.1 kHz</td>
</tr>
<tr>
<td>(1.1 µm sputtered)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PZT [109]</td>
<td>Circular membrane (d31)</td>
<td>0.77-7.6 pC/g</td>
<td>3.7-35.3 kHz</td>
</tr>
<tr>
<td>(1.5-7 mm sol–gel)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PZT [110]</td>
<td>Circular membrane with IDE (d33)</td>
<td>0.613 pC/g</td>
<td>15.5 kHz</td>
</tr>
<tr>
<td>(0.6 µm sol-gel)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, the piezoelectric accelerometers have inevitable limitations due to the poor low-frequency response and decreased performance caused by aging and depolarization, which were caused by the intrinsic properties of piezoelectric materials.[105] And the small-scaled piezoelectric structures have shown lower sensing performance comparing with their bulk devices, for example shown in Table 4.1. The PZT circular membrane accelerometer had a lower sensitivity when the thickness of the active material (PZT) is down to 0.6 µm. As a result, new design concepts of accelerometers including new type of materials are needed.

4.1.2. Advantages of flexoelectric sensors

Similar to all piezoelectric sensors, flexoelectric sensors are expected to adopt the fast response time, the wide frequency bandwidth, and the low cost. By introducing the flexoelectric effect, the miniaturized sensors can also overcome several drawbacks of the piezoelectric effect,
such as poling related aging and temperature limitations.[30] Different flexoelectric sensing devices have been developed over years, including vibration sensing, strain gradient sensing, and curvature sensing. The detailed review was covered in section 1.4.

Previously a flexoelectric accelerometer was reported, which was made of Barium Strontium Titanate (BST) ceramics.[111] The reported charge sensitivity of this cantilever accelerometer was 0.84 pC/g. The sensitivity was limited due to the bulk ceramics mechanical and the flexoelectric coefficient of BST. Comparing to the piezoelectric accelerometers listed in Table 4.1,

In chapter 3, we discovered the enhanced flexoelectricity in metal/ferroelectric/semiconductor heterostructure. The transverse flexoelectric coefficient of the BaTiO3 thin film in the heterojunction structure was measured to be at least 287 µC/m at room temperature, which is higher than the reported value of the BST ceramic.

In this chapter, the objective is to design, fabricate and test a flexural mode multi-layer accelerometer based on the heterostructure unimorph with a seismic mass. Static theoretical analysis for the multi-layer was conducted for flexoelectric vibration sensing. Finite element analysis (FEA) was used to simulate the frequency responses of the accelerometer. Experimental measurements were performed, and the result was compared to the one from simulation.

4.2. Configuration of the multilayer unimorph

There are three basic operating modes of electro-mechanical transduction: compression mode, shear mode, and bending mode. Piezoelectric and flexoelectric accelerometers have been configured following these three modes. Instead of applying homogenous strain in the structure for compression and shear mode, generating strain gradient requires more complex geometry
manufacture for the active material. Not only the element needs to be tapered, but also the electrode should be patterned on the side walls for the shear mode sensing. Also, neither compression nor shear mode are compatible with the film deposition. Besides the consideration of fabrication process, bending mode transducers have better sensitivity. [1] Therefore, for the prototype of flexoelectric accelerometer, the bending mode design was adopted. In a typical unimorph, there is a piezoelectric or flexoelectric top layer and a suspension layer underneath. The configuration of our model is shown in Figure 4.2. According to the reported analysis, the strain distribution is close to the base. However, the active flexoelectric material is the thin film, which would not be influenced much by the shape. [112]

![Figure 4.2. The cross section of the multilayer unimorph.](image)

**4.3. Analytical modeling**

As shown in Figure 4.2, the active flexoelectric material is BaTiO3 thin film. Both Nb-doped SrTiO3 and the steel serve as the suspension layer. The vertical deflection of the unimorph along the x direction is
where $\tau$ is the shear force, $L$ is the length of the cantilever and $A$ represents the bending rigidity of the three-layered cantilever beam

$$A = \frac{1}{3} b \left[ E_1 \left( (h_1 - t)^3 + t^3 \right) + E_2 \left( (h_1 + h_2 - t)^3 - (h_1 - t)^3 \right) + E_3 \left( (h_1 + h_2 + h_3 - t)^3 - (h_1 + h_2 - t)^3 \right) \right]$$

(4.2)

In Eq. (2), 1,2,3 denotes the suspension layer, semiconductor layer and ferroelectric thin film, respectively. $h$ is the thickness of the layer, $b$ is the width of the elements, and $E$ is Young’s modulus. $t$ represents the distance between the neutral plane and the lower surface.

$$t = \frac{1}{2 \left( E_1 h_1 + E_2 h_2 + E_3 h_3 \right)} \left\{ E_1 h_1^2 / \left( 1 - v_1^2 \right) + E_2 \left[ (h_2 + h_1)^2 - h_1^2 \right] / \left( 1 - v_2^2 \right) \right. \right. $$

$$+ E_3 \left[ (h_3 + h_2 + h_1)^2 - (h_2 + h_1)^2 \right] / \left( 1 - v_3^2 \right) \left\}$$

(4.3)

where $v$ is Poisson’s ratio. The strain gradient of such multilayer unimorph can be determined as

$$\frac{\partial \varepsilon_{xx}}{\partial z} = - \frac{\partial^2 w(x)}{\partial x^2}$$

(4.4)

which can be calculated from Eq. (2). Then the open-circuit sensitivity $S_Q$ of this flexoelectric accelerometer is as shown in Equation (4.5), where $Q$ is the collected charge, $a$ is the acceleration from base excitation, $b$ is the beam width, $L$ is the beam length, and $\varepsilon_{xx}$ is the strain along the length direction.

$$S_Q = \frac{Q}{a} = \frac{1}{a} \int_0^L \mu_{12} b \frac{\partial \varepsilon_{xx}}{\partial z} \, dx$$

(4.5)
4.4. Fabrication of the vibration sensor

The top heterostructure was fabricated following the same procedure as the described in Chapter 3. A layer of 100 nm-thick BTO epitaxial thin film deposited on Nb 0.7wt% doped SrTiO3 (Nb:STO) subtract. Then the Nb:STO layer was lapped down to 80 µm thick, and the top surface of BTO was then electrode with Cr/Au (5 nm/100 nm) using the E-beam deposition (Thermionics). Au/BTO/Nb:STO forms a structure called metal/ferroelectric/semiconductor heterostructure (MFS). This MFS structure then was diced into the rectangular shape with parameters shown in Table 4.2 using a dicing saw (Disco DAD321). After dicing the MFS structure was bonded onto the 50-µm steel plate with insulated epoxy (Hysol 2039, Hysol 3561, Loctite). Uniform pressure was applied to make sure the bonding layer’s uniformity in thickness and adhesive strength. This composite was diced into the rectangular shape with the dimensions shown in Table 4.2. Finally, a lead block (50 mg) was adhered onto the tip of the accelerometer as a seismic mass using epoxy (Hysol 2039, Hysol 3561, Loctite).

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness</th>
<th>Length</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFS</td>
<td>80 µm</td>
<td>2 mm</td>
<td>3 mm</td>
</tr>
<tr>
<td>Steel</td>
<td>50 µm</td>
<td>3 mm</td>
<td>5 mm</td>
</tr>
<tr>
<td>Lead</td>
<td>~50 mg</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.5. Experimental setup

The experimental setup for sensor test is shown in Figure 4.3. The sensor was attached to a vibration exciter (Model ES020, KCF Technologies). The vibration exciter was driven by the sinusoidal signal with designed frequency and amplitude, which was generated by a function generator (Model AFG3101, Tektronix) and was amplified by a power amplifier (Type 2706,
Bruel & Kjaer). The output charge signal from the sensor was converted and amplified through the signal conditioning circuit then the real-time signal was observed on the oscilloscope. A commercial accelerometer (Model 352C22, PCB Piezotronics) was used as a reference to measure the acceleration from the vibration exciter. This acceleration was also recorded on the oscilloscope through a signal conditioner (Model 482A16, PCB Piezotronics). The generated charge from the flexoelectric accelerometer was recorded as a function of vibration frequency (100–2750 Hz) and base acceleration (0.2–3g). The two channel signals observed on the oscilloscope were expected to be synchronized.

Figure 4.3. Experimental set-up of the dynamic vibration testing

In addition to the set-up for the room temperature measurement, the later section of this work is designed to test the performance above the Curie temperature of BTO thin film. The thermal chamber was inserted above the vibration shaker, which will be around the sensor position. The temperature was elevated by the heat gun. The height between the vibration shaker and the
chamber should be controlled in order to prevent the over heating of the shaker. According to the results in section 3.5.4, the test will be conducted from 20 °C to 140 °C at 300 Hz.

4.6. Results and discussion

4.6.1. Numerical modeling results

The solid mechanics module of COMSOL Multiphysics was chosen to simulate the frequency response of the flexoelectric accelerometer. The detailed methods and steps were reported in previous work [111]. The sensor was meshed automatically with free tetrahedral elements in extremely fine size. The fundamental resonance frequency of the accelerometer was found at 1997 Hz. The Excitation frequency was swept from 50 to 2750 Hz to obtain the frequency response of the sensor. The modeling results are shown in Figure 4.4. The simulated charge sensitivity is 11.864 ± 0.607 pC/g.

Figure 4.4. Finite element analysis of the sensor using COMSOL for the induced charges with frequency variations.
4.6.2. Experimental results

Figure 4.5. Experimental results from the dynamic vibration test of the accelerometer

As shown in Figure 4.5, the experimental results reveal a stable sensitivity of 8.106 ± 0.958 pC/g in the low frequency range. The working frequency with the flat frequency response reaches 750 Hz. The resonance frequency of the sensor system is 1950 Hz. It was assumed that infinitesimal deflection was applied to the cantilever to avoid the large error [22]. The maximum deflection in the test is about 6.5 mm with the angle of 0.2º. Such small deformation could ensure the precision of theoretical estimation. The vibration test was also conducted under different accelerations, which were indicated in different color: black, red, blue, respectively. The average charge sensitivity for the acceleration of 1g, 2g, and 3g was 8.060±0.841 pC/g, 7.637±0.1016 pC/g and 8.619±0.851 pC/g, respectively. Comparing to the FEA and analytical results, the lower induced charge may be caused by the absence of the full strain transmission. The resonance frequency could be decreased by imprecise clamping and additional mass of bonded electric wires.
The sensitivity of the vibration sensor depends on the value of flexoelectric coefficient if the experiment condition is identical. As discussed in chapter 3, the flexoelectric effect of BTO thin film exists in both the ferroelectric and the paraelectric phase. Figure 4.6 shows the charge sensitivity of the vibration sensor at 70-140°C at the vibration frequency of 300 Hz. Within the working frequency range, the charge sensitivity varies when the temperature increasing. It was due to the variation of flexoelectric coefficient at different temperature. However, as tested, the charge sensitivity of this vibration sensor can reach 9.948±1.067 pC/g at 140°C in the paraelectric phase. Comparing with the reported BST flexoelectric accelerometer with a sensitivity of 0.84 pC/g, the sensitivity was enhanced both at the room temperature (in the ferroelectric phase) and at 140°C (in the paraelectric phase).

4.7. Summary

A multi-layer flexoelectric unimorph accelerometer using metal/ferroelectric/semiconductor heterostructure was designed, prototyped, and tested. The static analytic analysis and frequency response based on FEA were conducted. The multilayer accelerometer provides a sensitivity of
8.106 ± 0.958 pC/g in the working frequency of up to 750 Hz. The epitaxial grown BTO thin film on the Nb:STO substrate has proved its potential in the enhancement of flexoelectric sensing not only at the room temperature, but also at high temperature.
Chapter 5. Hybrid bimorph energy harvester

5.1. Background

Over the last decade, the drastic reduction in required power of miniaturized electronics has motivated the study in harvesting the otherwise wasted energy from the ambient environment, such as solar, wind, thermal gradient, and the ubiquitous mechanical vibration, as a substitution of battery. [113] In 1996, Williams and Yates stated that there have been a few critical issues that affect the development of energy harvesting: the size of the system, the efficiency of the system, the compatibility to other electronics, and the output power density.[114] Among all the wasted energy, vibration energy has the largest power density, which can reach up to ~800 µW/cm³. [115] There are three conventional vibration-to-electric energy conversion mechanisms: electromagnetic [116], electrostatic[117], and piezoelectric [118] transductions. Numerous investigation and research based on the three types of transduction have been reported.

Among them, the piezoelectric transduction, as the conversion between mechanical and electrical energy, has been thought as the better candidate due to their high power density (three to five times higher than other two types) and ease of application in the wide range of fields, from human walking to motor rotation. [115], [119] There are mainly three conventional piezoelectric structures investigated: cantilever, cymbal, and stacks, as shown in Figure 5.1a, b, c, respectively.

The cantilever bending mode is the most favored due to the simple fabrication process and relatively large strain generation. A typical piezoelectric energy harvester is a cantilevered beam with a single layer or double layers of piezoceramics, defined as a unimorph or a bimorph respectively. The cantilever is mounted on a vibrating host structure, where the dynamic
deformation generates the strain within the material, then induces the alternating electric potential across the top and bottom surface of the piezoceramics, which are shown in Figure 5.1a.

![Diagram of piezoelectric energy harvesters](image)

Figure 5.1. Structure of piezoelectric energy harvesters: (a) cantilever unimorph (left) and bimorph (right), (b) cymbal, and (c) stack. Green arrows represent the poling direction.

5.1.1. **Current technology of piezoelectric energy harvesting**

![Diagram of piezoelectric modes](image)

Figure 5.2. Two modes of piezoelectric conversion of input mechanical strain into electrical energy.[120]
There are two conversion modes on micro cantilevered piezoelectric energy harvesters. One is the $d_{31}$ mode and the other is $d_{33}$ mode. Figure 5.2 has shown their working mechanism. [121] The $d_{33}$ mode has a higher energy conversion rate since piezoelectric properties of $d_{33}$ mode piezoelectric energy harvester are much higher than that operating in $d_{31}$ mode. [120] PZT film in different thickness and piezoelectric zinc oxide nanowires were also used to fabricate the micro- and nano-scale energy harvesters. [122] The critical difficulty is to effectively convert vibration energy into electricity in low-frequency environment (below 200 Hz) since the nature frequency of the piezoelectric transduction structure is much higher than the low-frequency range.

In terms of analytical modeling for piezoelectric energy harvesting, Erturk and Inman presented the analytical solution to the coupled problem of both a unimorph and a bimorph configuration based on the Euler-Bernoulli assumption. [118] Under a harmonic base excitation, which is in the form of translation in transverse direction with small rotation, the model can obtain both the coupled voltage response across the resistive load and the coupled vibration response of the harvester explicitly.

Although the advantages of piezoelectric energy harvesting are obvious, the common encountered problems cannot be ignored. It is found that the switching polarization decreases significantly in some piezoelectric materials under cyclic loading, which is also known as the electric fatigue. Possible causes include: transition of internal structure into a more stable configuration, the appearance of microcracks in brittle ceramics, and structural inhomogeneity which reduces the domain wall mobility. [123] This problem becomes more serious for systems under high frequency vibration. Other issues like High sensitivity to temperature changes, lead-based materials, and dramatical sensitivity reduction in thin film limit their applications in MEMS, NEMS, and biomedical field. [113], [120]
5.1.2. Current development of flexoelectric energy harvesting

Unlike the piezoelectricity limited in the variety of crystal structures, flexoelectricity can exists in all dielectrics.[124] Using materials with higher fatigue resistance can be an option to overcome electric fatigue in piezoelectric devices. Besides, flexoelectricity is expected to be significant at the sub-micro and nanoscale due to its scaling effect and possibly outperforms piezoelectricity.

![Diagram of flexoelectric cantilever structures](image)

Figure 5.3. Configuration of flexoelectric cantilever structures

The working principle of flexoelectric energy harvester is similar to piezoelectric ones, shown in Figure 5.3. Due to the movement of the clamped base, the cantilever beam undergoes bending vibrations. Dynamic strain gradient associated with vibration results in an alternating potential difference across the electrode. The electrodes are connected to a resistive load to quantify the electrical power output. Even a single layer of flexoelectric cantilever beam can be used for energy harvesting since the strain gradient will not cancel out symmetrically.

Theoretically, Moura and Erturk reported that the electromechanical coupling effect due to flexoelectricity in a strontium titanate (STO) energy harvester can be increased by 6 orders when its thickness decreases from millimeter to nanometer scale. [125] However, at the
nanoscale, there is an argument on the principle of flexoelectricity. Shen and Hu proposed the continuum theory for flexoelectricity with surface effects. [31] As the size of a beam is down to nanometer scale, its natural frequency would probably reach GHz-level, where the flexodynamic effect would become pronounced, which was proposed by Kvasov and Tagantsev in 2015.[126]

On the other hand, experimental validations of flexoelectric energy harvesting was only reported with (Na$_{0.5}$Bi$_{0.5}$)$_{0.92}$Ba$_{0.08}$TiO$_3$ ceramics by Zhang and Chu.[65] The energy harvester made with reduced (Na$_{0.5}$Bi$_{0.5}$)$_{0.92}$Ba$_{0.08}$TiO$_3$ ceramics provided a stable performance to harvest the mechanical energy above the depolarization temperature (140 °C). Their work provided another options to improve the transduction rate of electromechanical coupling. At the same time, looking for the proper material and structure for the energy transduction are still a challenge for pure flexoelectric energy harvesting.

5.1.3. Motivation of hybrid energy harvesting

It is worth to note that piezoelectric and flexoelectric effect may not be always additive. If the single layer of ferroelectric material (poled) is being fabricated into a cantilever, only the flexoelectric effect will appear during vibration while the piezoelectric effect is cancelled symmetrically. However, we can design a structure to take the advantages of both piezoelectric and flexoelectric transduction. The total power density can be increased theoretically. The challenge is to apply the proper material with both high piezoelectric coefficient and high dielectric permittivity, which can be potentially high in flexoelectricity. The recent development of functional piezoelectric materials provides the potential for applications in energy harvesting with enhanced power density. Li’s group designed and synthesized rare-earth-doped Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) by introducing the local structural heterogeneity, which achieved ultrahigh piezoelectric coefficients $d_{33}$ of up to 1500 pC/N and relative dielectric
permittivity above 13000 in a Sm-doped PMN-PT ceramic with a Curie Temperature of 89 °C. [127]

In this chapter, we characterize this type of material for its flexoelectricity. Then the structural design and the analytical model are presented for the proposed hybrid cantilever energy harvester. The experimental verification is presented, and the results are discussed in the end.

![Diagram](image.png)

**Figure 5.4.** Configuration of poling and wire connection for a bimorph with (a) hybrid (both piezoelectric and flexoelectric), (b) flexoelectric (Piezoelectricity was cancelled by tail-to-head wire connection), (c) piezoelectric (Flexoelectricity was cancelled by head-to-head wire connection).

### 5.2. Bimorph structure

In this section, the analysis work is done for both quasi-static and dynamic state, aiming to look for the ratio between the contribution due to piezoelectricity and flexoelectricity for different thickness, as well as the generated power density close to the resonance frequency of
the bimorph. In the following, thin beam theory is used, and it is assumed that the width and thickness of the beam are much smaller than its length. [118] This work is focused on the discussion of bulk electromechanically coupling effect. And for dynamic analysis, static flexoelectricity is applicable since the thickness of the beam is much smaller than the wavelength at vibration frequencies of interest in this study (around the first bending mode).

5.2.1. Quasi-static Analysis

As mentioned in Section 5.1, the piezoceramic layers of a symmetric bimorph can be combined in series or in parallel. However, when the flexoelectric effect is taken into consideration, the electrical response is not all induced by the combination of flexoelectricity and piezoelectricity for both the classic series and parallel connected bimorph. Figure 5.4 shows the configuration for three scenarios. In Figure 5.4a, piezoceramic layers were in series connection, the poling direction was head-to-head. When the cantilever bends, strain induced, and strain gradient induced electric charge would be collected for both piezoceramic layers on the bimorph. In Figure 5.4b, the head of the top layer was connected to the tail of the bottom layer, which made it equivalent to a single layer piezoceramics. When bending, the top half piezoelectric response was canceled with the bottom half piezoelectric response. And in Figure 5.4c, the piezoelectric layers were in parallel connection, the poling direction was pointed downward. When bending, the flexoelectric response of the top layer was cancelled with the flexoelectric response of the bottom layer. Thus, only in the configuration shown in Figure 5.4a, the hybrid device can collect the energy induced by both piezoelectricity and flexoelectricity. This is important to design the fabrication process. The following dynamic discussion was based on the configuration in Figure 5.4a.
Figure 5.5. Configuration of a deflected bimorph with displacement in z direction.

For the cantilever beam bending, \( d \) is the displacement along \( z \) direction. \( B \) is the width of the beam, \( L \) is the length of the beam, and \( h \) is the thickness of the single piezoelectric layer. For bimorph, the thickness of the beam is \( 2h \). \( E \) is the Young’s modulus of the piezoelectric material.

The deflection, \( w \), is expressed as

\[
w(x) = \frac{d}{2L} (3Lx^2 - x^3)
\]  

(5.1)

The strain induced by deflection within the bimorph is

\[
\varepsilon_{xx} = -z \frac{\partial^2 w}{\partial x^2} = -\frac{3d}{L^3} (L - x)z
\]  

(5.2)

The strain gradient in the transverse direction is

\[
\frac{\partial \varepsilon_{xx}}{\partial z} = -\frac{\partial^2 w}{\partial x^2} = \frac{3d}{L} (L - x)
\]  

(5.3)

The collected charge from both piezoelectric and flexoelectric response is
\[ Q_{\text{coll}} = B \int_0^L P_z \, dx = B \int_0^L \left( P_{\text{piezo}}^z + P_{\text{flexo}}^z \right) \, dx = B \int_0^L \left( \frac{h}{2} d_{31} E + \mu_{12} \right) \frac{\partial \varepsilon_{xx}}{\partial z} \, dx \] (5.4)

where \( d_{31} \) is the piezoelectric coefficient, and \( \mu_{12} \) is the transverse flexoelectric coefficient.

Then the induced charge is evaluated separately. The charge induced by piezoelectricity is

\[ Q_{\text{piezo}} = d_{31} E \times \frac{h}{2} B \int_0^L \frac{\partial \varepsilon_{xx}}{\partial z} \, dx = \frac{d_{31} E}{2} \times \frac{3dhB}{2L} = \frac{d_{31} E}{2} \times ABL = k_p \times ABL \] (5.5)

The charge induced by flexoelectricity is

\[ Q_{\text{flexo}} = \mu_{12} \times B \int_0^L \frac{\partial \varepsilon_{xx}}{\partial z} \, dx = \frac{\mu_{12} E}{h} \times \frac{3dB}{2L} = \frac{\mu_{12}}{h} \times ABL = k_f \times ABL \] (5.6)

In Eq. (5) and Eq. (6), \( A \) represents the maximum strain in the cantilever beam

\[ A = \varepsilon_{xx} \bigg|_{x=0, z=h/2} = \frac{3dh}{2L^2} \] (5.7)

Then, with characterized piezoelectric and flexoelectric properties of the specific material, the critical value of \( k_p \) and \( k_f \) can be determined.

### 5.2.2 Dynamic electrical output analysis

We consider the problem of a bimorph with a tip mass under mechanical base excitation for linear transverse (bending) vibration. The electrodes of the cantilever are connected to a resistive electrical load to quantify the electrical power output in the harvester model by accounting for both piezoelectricity and flexoelectricity, as shown in Figure 5.4a.

The partial differential equation governing the forced vibrations of a uniform cantilevered bimorph (with a tip mass) under base excitation is
\[ -\frac{\partial^2 M(x,t)}{\partial x^2} + f(x,t) = \rho A \frac{\partial^2 w(x,t)}{\partial t^2} \]  

(5.8)

where \( M(x,t) \) is the internal bending moment, \( f(x,t) \) is the total external force applied to the element per unit length, \( \rho \) is the density of the beam, \( A \) is the cross-sectional area of the beam, and \( w(x,t) \) is the deflection of the beam in x direction. The boundary condition for a clamped-free \( x = [0, L] \) cantilever without a tip mass can be express as,

\[
\begin{aligned}
  w(x = 0) &= 0, \\
  \frac{dw}{dx}(x = 0) &= 0;
\end{aligned}
\]  

(5.9)

\[
M(x = l) = EI \frac{d^2w}{dx^2} = 0, \\
V(x = l) = \frac{\partial}{\partial x} (EI \frac{d^2w}{dx^2}) = 0.
\]

\( V(x,t) \) is the shear force. At the clamped base, the effective base displacement \( w_b(x,t) \) in the transverse direction is defined in Equation (5.10). The \( g(t) \) and \( h(t) \) denote the translation and the small rotation of the base, respectively.

\[ w_b(x,t) = g(t) + xh(t) \]  

(5.10)

The transverse displacement of the vibration on the beam is

\[ w_r(x,t) = \sum_{r=1}^{n} \phi_r(x) \eta_r(t) \]  

(5.11)

Thus, the govern equation for the forced vibration under the base excitation is

\[
\begin{aligned}
  EI \frac{\partial^4 w(x,t)}{\partial x^4} + c_f \frac{\partial^5 w_u(x,t)}{\partial x^5 \partial t} + c_a \frac{\partial^5 w_u(x,t)}{\partial x^5 \partial t} + m \frac{\partial^2 w_r(x,t)}{\partial t^2} + \omega_V(t) \left[ \frac{d\delta(x)-d\delta(x-l)}{dx} \right] = \\
  - \left[ m + m_r \delta(x-l) \right] \frac{\partial^2 w_b(x,t)}{\partial t^2}
\end{aligned}
\]  

(5.12)
where \( \theta \) is the electromechanical coupling term related to both piezoelectric and flexoelectric effect, \( C_s \) is the equivalent coefficient of strain rate damping, \( I \) is the moment of inertia of the composite cross-section, \( C_a \) is the viscous air damping coefficient.

The mass normalized eigenfunction would be different with the tip mass:

\[
\phi_r(x) = C_r \left[ \cos \frac{\lambda_r}{L} x - \cosh \frac{\lambda_r}{L} x + \zeta_r \left( \sin \frac{\lambda_r}{L} x - \sinh \frac{\lambda_r}{L} x \right) \right]
\]

(5.13)

where \( C_r \) is a modal amplitude constant by normalizing the eigenfunctions according to the orthogonality condition, \( \lambda_r \) is the dimensionless frequency numbers obtained from the characteristic equation and and \( \zeta_r \) can be obtained from

\[
\zeta_r = \frac{\sin \lambda_r - \sinh \lambda_r + \dot{\lambda}_r \frac{m_r}{mL} (\cos \lambda_r - \cosh \lambda_r)}{\cos \lambda_r + \cosh \lambda_r - \dot{\lambda}_r \frac{m_r}{mL} (\sin \lambda_r - \sinh \lambda_r)}
\]

(5.14)

For a hybrid bimorph with a tip mass, the only mechanical source is assumed to be the axial strain due to bending. The electrical circuit of bimorph series cantilever is shown in Figure 5.6. The components of the circuit are the internal capacitance \( C_p \) of the piezoceramic layer, the resistive load \( R_L \) and the current source \( i(t) \).
Figure 5.6 The corresponding electrical circuit of the bimorph series cantilever for a resistive electrical load.

Since only the axial strain due to bending is considered, the electrical displacement can be reduced from the vector form to the scalar equation is:

\[
D_3 = \varepsilon_{311} S_{11}^p + \varepsilon_{33}^3 E_3 + \mu_{1133} \frac{\partial S_{11}^p}{\partial x_3}
\]

(5.15)

Where \(D_3\) is the electric displacement component and \(\varepsilon_{33}^3\) is the permittivity component at constant strain. The other elements in Equation (5.15) can be calculated as Equation (5.16)-(5.18),

\[
e_{311} = d_{311} E
\]

(5.16)

\[
S_{11}^p = -h_p \frac{\partial^2 w(x,t)}{\partial x^2}, \quad \frac{dS_{11}^p}{dx_3} = - \frac{\partial^2 w(x,t)}{\partial x^2}
\]

(5.17)

Substituting all these, the electrical displacement can be rewritten as

\[
D_3 = - \left( \frac{1}{2} d_{311} Eh_p + \mu_{1133} \right) \frac{\partial^2 w(x,t)}{\partial x^2} - \varepsilon_{11}^3 \frac{v(t)}{h_p}
\]

(5.18)
The coupled electrical circuit equation for bimorph is obtained from Equation (5.19), where \( v(t) \) is the voltage across the resistive load,

\[
i(t) = \frac{v(t)}{R_L} = \frac{d}{dt} \left( \int_A D_i dA \right) = -\varepsilon_i^0 bL \frac{dv(t)}{dt} - \left( \frac{1}{2} d_{311} E h_p + \mu_{1133} b \right) \int_0^L \frac{\partial^3 w(x,t)}{\partial x^2 \partial t} dx \tag{5.19}
\]

Then the modal mechanical and voltage response of a bimorph in series connection can be expressed as,

\[
\frac{\partial^2 \eta_r(t)}{\partial t^2} + 2\zeta_r \omega_r \frac{\partial \eta_r(t)}{\partial t} + \omega_r^2 \eta_r(t) - \left( \frac{1}{2} d_{311} E h_p b + \mu_{1133} b \right) \frac{d\phi_r(x = L)}{dx} v(t) = 0
\]

\[
= -m \frac{\partial^2 \omega_r(t)}{\partial t^2} \int_0^L \phi_r(x) dx
\]

\[
\frac{v(t)}{R_L} + \varepsilon_i^0 bL \frac{dv(t)}{dt} + \sum_{r=1}^n \left( \frac{1}{2} d_{311} E h_p b + \mu_{1133} b \right) \frac{d\phi_r(x = L)}{dx} \frac{d\eta_r(t)}{dt} = 0
\tag{5.21}
\]

Then we consider the steady-state response for this bimorph structure. The solution of Equation (5.20) and Equation (5.21) are the multi-mode solutions as they include all vibration modes of the bimorph harvester. At the clamped base, the harmonic excitation is,

\[
w_h(t) = W_0 e^{j\omega t}
\tag{5.22}
\]

If the bimorph cantilever with a tip mass is excited at the frequency close to the \( \omega_r \), the steady-state voltage response is obtained from the modal mechanical and electrical response

\[
V(t) = \frac{\sum_{r=1}^n \frac{j\omega \theta_r F_r}{\omega_r^2 - \omega^2 + j2\zeta_r \omega \omega}}{\frac{1}{R_L} + j\omega C_p + \sum_{r=1}^n \frac{j\omega \theta_r^2}{\omega_r^2 - \omega^2 + j2\zeta_r \omega \omega}} e^{j\omega t}
\tag{5.23}
\]

where the capacitance \( C_p \) for the series connected bimorph is
\[ C_p = \frac{\varepsilon_{\text{eff}} bL}{2h_p} \] (5.24)

Then the power response is calculated out from

\[ P_L(t) = \frac{v^2(t)}{R_L} \] (5.25)

5.3. Experimental methods

5.3.1. Fabrication

Our objective is to experimentally validate the contribution of flexoelectricity in a hybrid bimorph energy harvester. This section provides the detailed fabrication process. Sm-doped PMN-PT ceramics were fabricated by Li et al. with their proposed alternative design to engineer local structural heterogeneity. [127] The fabricated prototype was characterized for its ultrahigh piezoelectric coefficients $d_{33}$ of up to 1500 pC/N and relative dielectric constant above 13000. In this work, the piezoelectric ceramic was synthesized using the same technique, which is the B-site cation precursor method. The $\text{MgNb}_2\text{O}_6$ powders were prepared at 1,200 °C for 6 h. The $\text{Pb}_3\text{O}_4$, $\text{MgNb}_2\text{O}_6$, $\text{TiO}_2$ and $\text{Sm}_2\text{O}_3$ powders were wet-mixed by ball-milling with Y-stabilized zirconia balls for 24 h, and then the mixed powders were calcined at 850 °C for 2 h. On milling with Rhoplex binder for 12 h, the powders were formed into pellets by uniaxial pressing at 30 MPa, followed by binder burn-out at 550 °C and cold isostatic pressing at 300 MPa. The samples were sintered at 1,170–1,270 °C for 2 h. [127]

As for the bimorph structure fabrication, the following process was done for a head to head bimorph series cantilever test device, which will verify the power density for the flexoelectric bimorph and the hybrid bimorph. A poled ceramic disk was first diced into two identical rectangular pieces (7.74 mm by 3.97 mm) by a dicing saw (Disco DAD320, Disco Corporation,
Japan). A thin steel layer (50 μm) was then diced into a rectangular shape of (4 mm by 11 mm). After that, the diced ceramic layers were lapped down to the desired thickness of 50 μm with the lapping machine. Then, the ceramic films were bonded to both sides of the substrate steel layer with conductive silver epoxy (E-solder 3022, EIS Inc, Boston, US) and cured under room temperature for 24 hours. At last, the tip mass and the base were bonded to the bimorph cantilever tip with super glue.

5.3.2. Experimental set-up

First, the dielectric and piezoelectric properties of the given ceramics are characterized and compared with the original properties at room temperature. For bimorph structure, the raw Sm-doped PMN-PT (thickness of 1 mm) was firstly poled before fabrication. And the value of piezoelectric coefficient is used in the analytical estimation. Then, the transverse flexoelectric coefficient is characterized using bending method in house. The set-up is as described in chapter 2 for the ceramic cantilever beam.

![Figure 5.7. Schematic for the energy harvesting test set-up](image)

Then the energy harvester was tested by mounted onto the vibration shaker (Model ES020, KCF Technologies), driven by the function generator (Model AFG3101, Tektronix) and the power amplifier (Type 2706, Bruel & Kjær). Then different electrical load is connected between
the top and bottom electrodes of the bimorph. The output voltage was monitored at the load via the lock-in amplifier (Stanford Research System Model SR830). (Figure 5.7)

5.4. Results and discussion

In this part, the dimension and the electrical load were selected with the consideration on the results of analytical solution. According to the analytical solution in section 5.2, the numerical reference value was calculated with MATLAB. The frequency response and the electrical load response regarding to the power density were tested experimentally. The results are included in the following section.

5.4.1. Basic properties of materials and scaling effect

The dielectric constant, the piezoelectric coefficient, and the flexoelectric coefficient are all listed in Table 5.1. The piezoelectric coefficient of Sm-doped PMN-PT is comparable with it of PZT, while the flexoelectric coefficient of Sm-doped PMN-PT is comparable with it of BST. Thus, this material was qualified to be used in the fabrication of the hybrid energy harvesting device.

Table 5.1. Properties of 2.5%Sm-doped PMN-31PT

<table>
<thead>
<tr>
<th>Properties</th>
<th>Abbreviation [unit]</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>( \varepsilon_r ) [a.u.]</td>
<td>(~8000)</td>
</tr>
<tr>
<td>Elastic compliance</td>
<td>( S_{D33}^{D} ) [m(^2)/N]</td>
<td>(~9.5 \times 10^{-12})</td>
</tr>
<tr>
<td>Piezoelectric coefficient</td>
<td>( d_{33} ) [pC/N]</td>
<td>(~1125)</td>
</tr>
<tr>
<td>Flexoelectric coefficient</td>
<td>( \mu_{13} ) [(\mu)C/m]</td>
<td>(~66.7)</td>
</tr>
</tbody>
</table>
From section 5.2.1, the static solution for the critical value of $k_p$ and $k_f$ can be determined for such material. With different thickness of the ceramic layer, the isolated piezoelectric, flexoelectric and combined effect are predicted as shown in Table 5.2.

Table 5.2. Charge collection by piezoelectric and flexoelectric effect with different thickness

<table>
<thead>
<tr>
<th>h (µm)</th>
<th>$k_p$ (C/m²)</th>
<th>$k_f$ (C/m²)</th>
<th>$k_p+k_f$ (C/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>59.21</td>
<td>133</td>
<td>192.21</td>
</tr>
<tr>
<td>2.5</td>
<td>59.21</td>
<td>53.2</td>
<td>112.41</td>
</tr>
<tr>
<td>10</td>
<td>59.21</td>
<td>13.3</td>
<td>146.3</td>
</tr>
<tr>
<td>25</td>
<td>59.21</td>
<td>5.32</td>
<td>64.53</td>
</tr>
<tr>
<td>50</td>
<td>59.21</td>
<td>2.66</td>
<td>61.87</td>
</tr>
</tbody>
</table>

The induced charge by piezoelectricity remains the same with different thickness of the active layer, while the induced charge by flexoelectricity would increase obviously as the thickness decreases. When the thickness is smaller than 2.5 µm, the contribution of flexoelectricity take the equal part in the overall outcome. Since our fabrication was base on top-down techniques, there was a limitation of minimum thickness. In our fabrication we chose a conservative target thickness (~50 µm) to check the contribution of flexoelectricity ($k_f$) on the overall outcome ($k_p+k_f$).

5.4.2. Frequency response

The dynamic electrical output analysis was carried out in MATLAB to examine the frequency response when only the piezoelectric effect is considered as well as when both the piezoelectric and flexoelectric. The results are shown in Figure 5.8.

The resonance frequency of our device is at 331 Hz. It is obvious that the hybrid device has a larger output voltage and a larger power density than the piezoelectric device. The increase of
power density in simulation is around 6%, from 0.1136 to 0.1202 mW/cm$^3$. The experimental verification of frequency response is shown in Figure 5.8.

Figure 5.8: The comparison of voltage output (top) and power density (bottom) of a piezoelectric and a hybrid energy harvester.
5.4.3. Electrical load response

To look for the largest power output, the electrical load response was taken into consideration. Different electrical load would distribute the voltage differently within the circuit. Here we took a range of electrical load from 50 kΩ to 10 MΩ in order to find an enhanced power generation. As shown in Figure 5.9, the analytical solution suggested that the electrical load of 50 kΩ would collect the most power (0.1202 mW/cm³) with the same energy harvester at the resonant frequency. Then the same trend was observed in the experiment, shown in Figure 5.10.

The resonance frequency of the energy harvester was observed at 330 Hz experimentally, close to the analytical value. The largest power density was collected by the electrical load of 50 kΩ, which matched the expectation from the analysis. The largest power density is 0.093
mW/cm$^3$, which is smaller than the analytical value due to the energy dispassion of the adhesion parts in the actual structure.

Figure 5.10. The power density of the hybrid energy harvester prototype at different frequency with different electrical load.
5.4.4. Potential improvement

As shown in Table 5.2, the static analysis suggests if the thickness of the active layer is close to a few microns, the contribution of flexoelectricity would significantly improve the power density of the hybrid energy harvester. Figure 5.11 shows the power density from simulation of the bimorph energy harvester if the thickness of piezoceramic layer is 2.5 µm. The power density will increase 39% by flexoelectric effect. And the total power density would be 0.5832 mW/cm³.

![Figure 5.11. The power density of hybrid energy harvester with 2.5 µm thick piezoceramic layers](image)

5.5. Summary

Piezoelectric energy harvesting has been investigated by several researchers for the last few years. Flexoelectric energy harvesting has been discussed on its possibility with current materials recently. However, there hasn’t been a flexoelectric material that can perform well in energy harvesting.
In this work, a hybrid bimorph energy harvester was firstly fabricated and tested with Sm-doped PMN-PT, which has a high piezoelectric coefficient and a high flexoelectric coefficient. The combined piezoelectric and flexoelectric energy harvesting from the vibration of the bimorph cantilever structure was designed and analyzed. The bimorph was fabricated in series connection to realize the hybrid energy harvesting from both piezoelectricity and flexoelectricity.

The results showed that the flexoelectric effect increased 6% on the overall power density of the energy harvesting. The size effect was captured at the analysis of static charge collection. It is possible to further increase the efficiency of the energy conversion if the active layer can be thinned at submicron thickness.
Chapter 6. Conclusion and future work

6.1. Conclusions

With the surging research interest on flexoelectricity recently, there have been more findings of large flexoelectric properties in a various of materials with high permittivity. Different from the piezoelectricity, flexoelectricity appears in both ferroelectric and paraelectric phase. Due to the linear relationship with dielectric permittivity, the temperature dependence of flexoelectricity has been explored. Researchers intends to discover the applications for flexoelectric materials beyond its Curie temperature, where the piezoelectricity would disappear. On the other hand, the semiconducting materials and structures have been included into the discussion regarding to flexoelectricity. It was shown that the flexoelectric coefficient was 3-orders higher than that of insulated bulk ceramics. With awareness of materials with the enhanced flexoelectric properties, researchers started to design innovative structures for flexoelectric sensors, actuators, and energy harvesters.

This dissertation has focused on three main topics, including the temperature dependence of the lead-free ceramics, the flexoelectricity in a metal/ferroelectric/semiconductor heterostructure, and the hybrid energy harvester device.

First, the transverse flexoelectric coefficient was characterized for the BT-8BZT ceramics. Then the temperature dependence of the coefficient was measured, which is chosen for its smooth decline after the Curie temperature. The results are in good agreement with expectation that the flexoelectric coefficient is stable in BT-8BZT even with increasing temperature. Therefore, the temperature limitation for the flexoelectric devices can be overcome potentially.

Then, the single sided Schottky barrier model was studied for its flexoelectricity. It was the first time to determine the flexoelectric response of the ferroelectric thin film in an MFS
heterostructure. The enhanced flexoelectricity was obtained in the ferroelectric thin film built on the semiconductor base. Furthermore, this MFS structured material was applied to build a novel multilayer cantilever for vibration sensing. The charge sensing mode of this cantilever was demonstrated, and the sensitivity was observed to be $8.106 \pm 0.958 \text{ pC}/\text{g}$.

Besides discussing the flexoelectricity, there is a possible outcome to check out the contribution from the flexoelectricity to the overall performance of the electromechanical coupling devices. In other words, if the materials have a high piezoelectric coefficient and a high dielectric permittivity at its ferroelectric phase, the energy conversion efficiency can be enhanced. In the last part of my thesis work, the outcome on the combination of piezoelectricity and flexoelectricity was studied in a bimorph energy harvester. The flexoelectric effect increase 6% on the overall power density for the bimorph hybrid energy harvester comparing to the classical piezoelectric bimorph energy harvester. A prototype for the hybrid bimorph energy harvester was fabricated for the first time. The potential improvement for the power density was discussed.

6.2. Future prospects

So far, in the research field of flexoelectricity, the discovery is still mainly limited on bulk dielectrics and some thin films. Few findings have been reported in other material category. Origins of the flexoelectricity and the characterization method for flexoelectric coefficient matrix in bulk dielectric are not thoroughly studied and understood. Meanwhile, Optimization of the flexoelectric devices design and further enhancement in the flexoelectric performance have become critical in this newly arising field. In this section, the preliminary analysis of flexoelectric functional materials and possible prototyping structures is discussed. Later, the potential of scaling-down devices and other related work are summarized.
6.2.1. Flexoelectric functional materials

The definition of functional materials was first raised in the field of homogeneous strain ferroelectrics and piezoelectricity, but in recent years there has been a re-emergence of interest in strain gradients ferroelectrics and flexoelectricity. Experimentally, researchers have successfully synthesized coherently strained, compositionally graded heterostructures of PZT ceramics that change from tetragonal at the substrate interface to rhombohedral at the film surface with a strain gradient of ~40 µm⁻¹. The large built-in potential was observed for this material due to the combination of flexoelectric effects, chemical-gradient effects, and local inhomogeneities that enhance strain gradients.

Then we take the similar ideal into a preliminary analysis of factors that influence the flexoelectric response in functional graded structures. In addition to the classical strain gradient relationship with the stress gradient in uniform materials, it can also be related to the gradient of elastic modulus if the applied stress is uniformly distributed. Thus, the elastic modulus gradient can theoretically enhance the direct flexoelectric response. The larger difference between the elastic modulus of two diffused materials from top and bottom to build the graded structure may lead to a larger flexoelectric coefficient. In the comparison to conventional piezoelectric materials, the effective d33 would increase theoretically. Furthermore, the efficiency of charge collection will be enhanced by engineering the volume ratio between the two diffused materials.

However, it is very challenging to look for the proper materials and the legit method to synthesize the new functional graded flexoelectric material.
6.2.2. Other future work

The growing publication of flexoelectric effect came from the great expectation of researchers. However, there are numerous fields to be explored and more efforts are needed. Based on the findings of this work, following potential aspects can be addressed in the future:

1. For the metal/ferroelectric/semiconductor heterostructure, the transverse flexoelectric coefficient was studied in chapter 3. Furthermore, a few more tasks still need to be addressed. One is to measure the longitudinal flexoelectric coefficient, which would not only complete the study of the flexoelectricity in the ferroelectric thin film, but also would help to understand the build-in strain distribution and contribution to the flexoelectric response. The other is that when the thickness of ferroelectric thin film is down to tens or several nano-meters, the lattice mismatch would induce larger in-plane strain. The thickness dependent study is the other interesting related topic since it can influence both the capacitance of the ferroelectric thin film layer and the strain distribution. Also, it would be interesting to investigate whether the thin film can obey the scaling effect at a thickness of a few unit cells.

2. The scaling down trend of miniature devices or the lab on chip industry needs a new type of electromechanical devices that can be easily integrated with other elements on the chip down in nanoscale. In Chapter 5, we analysed the contribution of flexoelectricity in the hybrid device. As Table 2, the flexoelectric induced charge would over weigh the part induced by piezoelectricity. Compared with piezoelectricity, flexoelectricity is a weak effect of less practical significance in bulk materials. When the devices are down to submicron scale, the scaling effect of flexoelectric shows the advantages. However, the challenges lay on the fabrication of the complex structure in submicron to nano-scale
with top-down techniques.

3. The flexoelectricity can alter the response of materials. Flexoelectric effects of the semiconductor structure was firstly suspected in mechanically induced ferroelectric switching.[92] Previously, the horizontal shifts of ferroelectric hysteresis loops and independent tuning of typically coupled ferroelectric susceptibilities are also reported due to flexoelectricity.[128] Earlier this year, the flexo-photovoltaic effect was reported phenomenally by Yang et al.[129] Flexoelectricity in materials correlated with other effects may open up numerous application possibilities.

Based on the experience with material searching and device prototyping, the author believes that the theoretical quantification, experimental characterization, and application development are equally important in the field of flexoelectricity.
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