PHOTOREFRACTIVE THIN FILMS AND POLYMERS FOR USE IN ORGANIC-INORGANIC HYBRID CELLS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

by

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Steven Harris Buller ENTITLED Photorefractive Thin Films and Polymers for Use in Organic-Inorganic Hybrid Cells BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science.

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Two classes of materials were investigated as possible replacements for the bulk photorefractive windows in inorganic-organic hybrid cells: thin films and polymers. Each material was fabricated and subsequently characterized using two different methods due to their different stages of development. The thin films were characterized by X-ray diffraction while the polymers were characterized by two-beam coupling. Thin films of strontium barium niobate and potassium niobate were grown, using pulsed laser deposition, on four different substrates. It was found that it was possible to grow a thin film of potassium niobate in the correct orientation to replace a bulk photorefractive window. The characterization of the polymers with the use of two beam-coupling showed they required too high of voltages in order to achieve the photorefractive effect and also had sub-optimal phase-shift.
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1 Introduction

The photorefractive (PR) effect is a phenomenon that can occur in electro-optic materials in which the local index of refraction of the material changes due to an incident light intensity pattern [1]. This effect has been demonstrated in both inorganic and organic materials [2, 3]. Models describing the PR effect were originally developed for inorganic materials, however the same basic concepts also apply for the organic materials. Both material classes, organic and inorganic, rely on an ingredient which acts as a source of charge donors and acceptors, with very different transport mechanisms in each material. A simple model for the case of the PR effect in inorganic materials can be described by the ionization of charge donors in the light regions of an inhomogeneous light pattern causing electrons to be promoted to the conduction band, where they are free to move until they become trapped by an acceptor state in a dark region. In the organic materials, which do not have a conduction band, photo-ionized charges use a hopping mechanism to transport charges along a photoconductor until they reach an available acceptor energy level. Photo-ionization continues until illumination ceases or the photo-ionized charges migrate to regions not under illumination where they become trapped. This effect can be used to pattern charges in a more complex manner; for example, an optical interference pattern (alternating light and dark regions) can be generated in a PR material resulting in photo-ionization of donor states in light regions and trapped charges in acceptor states in dark regions. This would cause a separation of charges between the light and dark regions, resulting in an electric field between these regions known as a periodic space charge field. Since the space charge field
is strongest halfway between the two regions, it is shifted out of phase by $\pi/2$ with respect to the incident intensity pattern. This space charge field induces a change in the refractive index via the linear Pockels’ effect (i.e., electro-optic effect). The formation of the periodic space charge field and modulation of a $\pi/2$-shifted refractive index are requirements for beam coupling. A $\pi/2$ phase-shift is optimum for maximizing the conditions for constructive and destructive interference of the laser beams, where one beam is amplified while the other(s) is(are) depleted. This is known as beam coupling, which can be achieved with two or more beams. Without a phase shift, a real transfer of power between the beams would not be achievable, and would lead to just simple diffraction.

The motivation for the work in this thesis was centered around beam coupling applications in both reflection and transmission geometries for the purposes of improving organic-inorganic hybrid cell windows. The hybrid cells were typically used in the transmission geometry. Although the hybrid cells are used in the transmission geometry, the reflection geometry allowed for the study of these materials using much smaller grating spacings, typical of those used in PR applications. The organic-inorganic hybrid cell is comprised of two components: two bulk PR windows (about 1 mm thick each) and a liquid crystal (LC) layer (about 8 $\mu$m) between them. Unlike standard inorganic materials, which are required to be electro-optic in order to generate a periodic refractive index (i.e., grating), windows in the hybrid cell do not need to be electro-optic. When a periodic space charge field is created in the windows, by the mechanism previously described, it extends beyond the surface and modulates the LC’s. Since the LC’s align with the space charge field of the windows, the local refractive index of these molecules will be shifted by $\pi/2$ and it is in this region of the hybrid cell where beam coupling will occur and not in the windows. Therefore, it was not a requirement that the windows be electro-optic materials, however, PR crystals had been proven to provide the necessary space charge field. With the current inorganic bulk windows there are several issues to overcome which include: cost, absorption loss, slow response time, magnitude of the space charge field, durability, and
rigidity.

The most important issue is cost of the device. The current hybrid cells use 2x2x0.1 cm$^3$ cerium doped strontium barium niobate (SBN60:Ce) windows that cost approximately $5,000 each, putting the total device over $10,000 per cell. A larger cell would drive the cost even higher. There were two proposed solutions to cut down the total cost of the cell: crystalline thin films and polymers. The first approach was to grow 2 µm SBN60:Ce thin films to replace the bulk windows. Since the trap density of SBN:Ce was relatively large, the electric field more than 2 µm deep was screened from the surface; therefore, only the first 2 µm at the surface contributed to the space charge field felt by the LC layer. The majority of the window does not contribute to the space charge field, although it does contribute to an unnecessary absorption loss. Thin films can be grown for approximately $100 per window, which would reduce the cost of a hybrid cell by two orders of magnitude. An added benefit of this solution would be its negligible absorption loss by replacing a 1 mm thick window to 2 µm, without sacrificing the full affect of the space charge field.

The second approach was to replace the bulk windows with a PR polymer. Polymers offer greater ease of fabrication and control over their properties [2]. These materials are relatively inexpensive to produce and can be formed into desired shapes and thicknesses. Using polymer materials would also reduce the cost of the cell by approximately two orders of magnitude. An added benefit of this solution would be the flexibility of the window, allowing it to be adhered to curved surfaces increasing its range of potential applications.

It was important to recognize the different aspects being explored for each material class due to the different problem sets of that exist for each. The issues with the thin films were related to its crystallographic nature, whereas with the polymers it was with its optical properties. The results and experimental procedures in this thesis are divided into three subsequent main chapters. Chapter 2 discusses the procedures for growing thin films and fabricating polymers. Chapter 3 describes the methods used for characterization of each material. Chapter 4 provides the results of the characterization for both materials.
Lastly, in Chapter 5 the conclusions for whether or not the thin films or polymers would be a suitable substitution for the bulk PR windows will be discussed based on the results in Chapter 4.
2 Material Fabrication

Two classes of materials were used in this investigation, inorganic thin films and organic polymers, each having different fabrication methods. The thin films were grown by pulsed laser deposition (PLD), which was a process that required ablating a starting material causing the particles to coat and reorient on a substrate. The polymers were synthesized by combining several chemicals required to produce a PR material. The processes for preparing each of these different class materials are described in detail in the following sections.

2.1 Thin Film Fabrication

The thin films were prepared by PLD, which allowed for precise control of the deposition parameters. This was a necessity because even a small change in the deposition parameters would drastically alter the orientation of the final product [4]. Understanding the mechanics of PLD was important in determining the parameters to be used for PR materials. These materials must be well understood to ensure the thin films being deposited were compatible with the selected substrates. Several candidate substrate materials were chosen for this because of their lattice parameters and transparency across the visible spectrum. Depositions of SBN60:Ce were made on magnesium oxide (MgO), lanthanum aluminate (LAO), strontium titanate (STO), and strontium barium niobate (SBN) substrates, while potassium niobate (KN) was deposited on various cut of MgO substrates.
2.1.1 Deposition Process

The process of PLD required a target of starting material and a substrate to be placed in a high vacuum chamber. Vacuum pressures on the order of $10^{-7}$ Torr were achieved using a combination of roughing and turbo pumps. For the case when a partial pressure of oxygen was needed, the chamber was first evacuated then backfilled with O$_2$. This process used high-intensity short pulses (typically 17 ns) that were focused onto a dense SBN60:Ce or KN target, made from pressed powder, inside the chamber [5]. A schematic of the PLD chamber used for this research can be seen in Figure 2.1. In this configuration, the target was attached to a rotation stage to allow for uniform ablation. The energy absorbed by the target from the laser pulse was converted to electronic excitation resulting in thermal, chemical and mechanical energy leading to the release of a cone shaped plume of material containing atoms, ions, electrons, and particulates of the target material in a direction normal to the surface of the target [4]. The plume was shown to have an angular distribution of target material with lighter particles spreading at larger oblique angles from the plume axis while the heavier particles traveled closer to the center [6]. The angular distribution required adjustment of the target-substrate distance as well as the angle of the substrate with respect to the target depending on the elements within the target. The PLD system used for in this research was limited to a 7.1 cm target-substrate distance with little flexibility in the substrate angle. The chamber was equipped with two sets of photo-multiplier tubes (PMTs) set behind narrow band-pass filters mounted to the exterior to monitor emission of excited elements within the plume. The PMTs were used to monitor the time-of-flight (TOF) in order to maintain consistency between depositions. The TOF was the time calculated from initial target impact of the laser pulse to the time of maximum emission of a particular species as the components pass the PMT [7]. TOF was affected by the adjustment of the laser voltage and chamber pressure with higher oxygen pressures decreasing the kinetic energy of the plume and higher laser voltage increasing it [8]. For this research,
Figure 2.1: A diagram of the PLD chamber used for thin film growth.
the substrate was centered in front of the target allowing the plume to travel in line from the target to the substrate.

Once the particles reached the substrate, mobility was limited by their kinetic energy. The resulting structure was dependent on the temperature of the substrate which was typically heated to 700-760 °C creating a favorable energy condition to allow the film to grow in a crystalline structure. Heated substrates transfer energy to the particles allowing them to diffuse throughout the surface of the substrate where they were able to locate low energy sites creating a stable structure. Without an appropriate substrate temperature, the resulting thin film was amorphous which was due to the fact that crystallinity of thin films is determined by the bonding configurations of the atoms at a given temperature with the lowest free energy [9]. At lower substrate temperatures, close to room temperature, the ejected high-energy particles were quenched, rapidly decreasing the energy of the particles, when they reached the substrate preventing them from relaxing into the lowest energy sites. Amorphous thin films become crystalline with the application of post-treatment procedures. The deposition was continued until the desired film thickness of 1-2 µm was reached. Film thickness was determined by a sensor which measured the material deposited per pulse and extrapolated for the total time of deposition. The ideal final result was a single crystal thin film.

Certain materials, such as the oxides used in this research, required a background gas to be present in the chamber during deposition. The oxide materials were prone to losing oxygen if the chamber was under vacuum; a process called reduction. The background gas used for these materials was O₂, allowing for the replacement of lost oxygen in order to obtain the correct stoichiometry of the thin film. The density of the target material was also important to ensure a smooth film was deposited for a given laser fluence. A target that was too dense, such as a bulk single crystal, would not ablate properly without a laser fluence high enough to obtain a plume with a composition congruent with the target, leading to a thin film with improper stoichiometry [6]. It is also possible for the target to have a density
Table 2.1: Thin films grown with deposition parameters

<table>
<thead>
<tr>
<th>Thin Film/Substrate</th>
<th>Atmosphere</th>
<th>Laser Voltage (kV)</th>
<th>Rep Rate (Hz)</th>
<th>Substrate Temperature (°C)</th>
<th>Pulse Energy (mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBN60:Ce/MgO(100)</td>
<td>200 mTorr O₂</td>
<td>16.36</td>
<td>10</td>
<td>760</td>
<td>591.9</td>
</tr>
<tr>
<td>SBN60:Ce/STO(100)</td>
<td>200 mTorr O₂</td>
<td>17.03</td>
<td>10</td>
<td>760</td>
<td>570</td>
</tr>
<tr>
<td>SBN60:Ce/LAO(100)</td>
<td>200 mTorr O₂</td>
<td>18.68</td>
<td>10</td>
<td>760</td>
<td>918</td>
</tr>
<tr>
<td>SBN60:Ce/SBN(100)</td>
<td>50 mTorr O₂</td>
<td>16.00</td>
<td>10</td>
<td>700</td>
<td>402</td>
</tr>
<tr>
<td>SBN60:Ce/MgO(100)</td>
<td>100 mTorr O₂</td>
<td>16.15</td>
<td>10</td>
<td>700</td>
<td>502.4</td>
</tr>
<tr>
<td>SBN60:Ce/MgO(100)</td>
<td>150 mTorr O₂</td>
<td>16.06</td>
<td>10</td>
<td>700</td>
<td>389.4</td>
</tr>
<tr>
<td>SBN60:Ce/MgO(100)</td>
<td>200 mTorr O₂</td>
<td>17.02</td>
<td>10</td>
<td>700</td>
<td>502.7</td>
</tr>
<tr>
<td>SBN60:Ce/MgO(100)</td>
<td>250 mTorr O₂</td>
<td>17.48</td>
<td>10</td>
<td>700</td>
<td>513.8</td>
</tr>
<tr>
<td>SBN60:Ce/MgO(100)</td>
<td>300 mTorr O₂</td>
<td>16.05</td>
<td>10</td>
<td>700</td>
<td>511.8</td>
</tr>
<tr>
<td>SBN60:Ce/Fused Silica</td>
<td>10⁻⁷ Torr Vacuum</td>
<td>20.00</td>
<td>40</td>
<td>22</td>
<td>720</td>
</tr>
<tr>
<td>SBN60:Ce/MgO(100)</td>
<td>10⁻⁷ Torr Vacuum</td>
<td>20.00</td>
<td>20</td>
<td>22</td>
<td>930</td>
</tr>
<tr>
<td>KN/MgO(100)</td>
<td>200 mTorr O₂</td>
<td>16.00</td>
<td>10</td>
<td>760</td>
<td>503</td>
</tr>
<tr>
<td>KN/MgO(110)</td>
<td>200 mTorr O₂</td>
<td>16.00</td>
<td>10</td>
<td>760</td>
<td>503</td>
</tr>
</tbody>
</table>

too low leading to unfavorable ablation, because the target would ablate too easily causing a large distribution of particle sizes to be ejected. The ideal target density (typically 98%) was one that allowed for uniform ablation of all target constituents in order to grow a thin film with proper stoichiometry.

2.1.2 PLD Growth Conditions

The depositions were performed with the use of a LabVIEW program which monitored and controlled all growth conditions. Parameters that were monitored during the depositions included: laser voltage, pulse energy, background gas pressure, laser repetition rate, total deposition time, substrate temperature, and TOF. The LabVIEW program was designed to adjust the laser voltage and energy in order to maintain a set TOF. The target TOF for all depositions was 4.65 $\mu$s which had been shown to provide good quality thin films. The background gas pressure was applied by evacuating the chamber to $10^{-7}$ Torr and back filling it with O₂. Table 2.1 lists the thin films that were grown along with the growth conditions.
2.1.3 Material Considerations

Each substrate was selected for its lattice properties in order to minimize the lattice mismatch between it and the desired thin film orientation (Table 2.2). The lattice structures of SBN and KN were examined and compared to those of several substrates. The objective was to grow a thin film of a PR material with the crystallographic c-axis parallel to the surface of the substrate, i.e., c-axis in-plane, which is the orientation required for the hybrid devices. In an attempt to grow SBN60:Ce and KN thin films with this desired orientation, lattice parameters of the thin films and the substrates were closely matched.

A bulk SBN crystal whose chemical composition is $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ with $0.25 \leq x \leq 0.75$ [10], has a complex tetragonal tungsten bronze (TTB) structure at room temperature as shown in Figure 2.2 [11]. The target used for this research has a value of 0.60 for $x$ and was doped with 0.01 wt% cerium (Ce). In low concentrations, Ce is a common dopant used in
PR materials as it can exist in two valence states ($\text{Ce}^{3+}$ and $\text{Ce}^{4+}$) [12], where one state acts as a charge donor and the other acts as a charge acceptor. The lattice constants and material properties vary slightly depending on the value of $x$. For the case of SBN60 (tetragonal, $a = b \neq c$), the lattice constants are $a = b = 12.467$ Å and $c = 3.938$ Å [13]. The Curie temperature, $T_c$, also varies with the value of $x$ and for SBN60 this value is 75 °C which is well above room temperature and one of the reasons for choosing this composition. Below this temperature the material is ferroelectric having uniformly aligned domains. If the Curie temperature is reached the material becomes paraelectric allowing the possibility for reorientation of the domains which may disrupt the local alignment integrity of the LC’s. $T_c$ for SBN75 is lowered to 56 °C which is still above room temperature; however, it is closer than SBN60. Since our desired result was to have the c-axis of the thin film parallel to the surface of the substrate, a substrate had to be chosen with an in-plane lattice constant close to 3.938 Å. MgO, a cubic crystal ($a = b = c$), has been a commonly used substrate for deposition of SBN because of its transparency and lattice parameters [14], see Figure 2.2. The lattice constant of 4.212 Å provided a lattice mismatch of 6.95%, when matched with the c-axis of SBN. LAO was another selected substrate with a cubic structure and a lattice constant of 3.79 Å, which provided a lattice mismatch of 3.75%. STO, which also has a cubic structure with $a = 3.905$ Å, provided a lattice mismatch of only 0.83%. Deposition of SBN60:Ce was also performed on an undoped SBN substrate to show that it was possible to grow these thin films with the desired orientation (c-axis in-plane) by eliminating the lattice mismatch.

Potassium niobate (KNbO$_3$, KN) was another PR material chosen to be grown as a thin film. KN has an orthorhombic structure ($a \neq b \neq c$) (Figure 2.3) with lattice constants $a = 5.695$ Å, $b = 3.971$ Å, and $c = 5.722$ Å. Since there was a requirement to have the c-axis of this material to be parallel to the substrate, a substrate with an in-plane lattice constant close to 5.722 Å was needed. MgO (100) has been used extensively to grow KN thin films [6, 15, 16], however, its lattice constant of 4.212 Å is closer to the b-axis of KN.
than the a- or c-axis. Examination of the MgO structure showed that if it was tilted along the (110) direction, the surface would no longer have a cubic pattern (Figure 2.4). This would create a pattern with one edge still equal to the original lattice constant of 4.212 Å, while the other would be 5.957 Å. In this configuration there were two lattice constants of KN that were closely matched with that of the substrate, where the mismatch for the c-axis was only 4.10% and for the b-axis was 6.06%. This is a significant improvement compared to the lattice mismatch when using MgO (100) which for the b-axis was still 6.06% but for the c-axis was 26.4%.

Targets were made consisting of potassium niobium oxide powder from Alfa Aesar. Several attempts were made to sinter these targets, a process used to increase the density of target materials. This was done by heating the targets to 1025 °C with and without the presence of O₂. In both cases the densification was shown to decrease by 7.87%. Therefore, an unsintered target was prepared and used for deposition by pressing 6.64 g of material
into a pellet 25.65 mm in diameter and 4.53 mm thick at 15,000 psi. It was calculated to have a densification of 61.47%.

2.1.4 Electric Domain Poling

A useful and necessary procedure used to align domains in a bulk PR crystal is to "pole" it by applying an electric field across the crystal along the c-axis, while the temperature of the crystal is raised to slightly above the Curie temperature for the case of SBN. This allows the crystal to change phase and align the dipoles to orient the c-axis unidirectionally. This procedure was applied to a series of thin films. The typical recipe for poling an SBN crystal is to apply a field of 3 kV/cm at 120 °C over a period of 220 min. It was also found that Y. Xu et. al. [17] were able to orient their SBN thin films by applying fields of 1 and 25 kV/cm across the surface of the substrate during crystallization. This recipe was applied
Table 2.2: Lattice parameters of substrates and deposited materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice Constants (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
</tr>
<tr>
<td>Thin Film</td>
<td></td>
</tr>
<tr>
<td>SBN60:Ce</td>
<td>12.46</td>
</tr>
<tr>
<td>KN</td>
<td>5.695</td>
</tr>
<tr>
<td>Substrate</td>
<td></td>
</tr>
<tr>
<td>MgO (100)</td>
<td>4.212</td>
</tr>
<tr>
<td>MgO (110)</td>
<td>4.212</td>
</tr>
<tr>
<td>LAO (100)</td>
<td>3.79</td>
</tr>
<tr>
<td>STO (100)</td>
<td>3.905</td>
</tr>
<tr>
<td>SBN</td>
<td>12.46</td>
</tr>
</tbody>
</table>

...to the thin films described in this thesis that were deposited at room temperature and later heat treated in an attempt to align the thin film dipoles while the crystalline structure was forming.

2.2 Polymer Preparation

The PR polymer used in this research had five ingredients: photoconductor (poly(9-vinylcarbazole (PVK)), plasticizer (benzyl butyl phthalate (BBP) and 9-ethylcarbazole (ECZ)), sensitizer (Fullerene (C\textsubscript{60})), and birefringent chromophore (4-piperidinobenzylidene malonitrile (PDCST)). All of these components are commercially available except for PDCST, which needed to be synthesized and was provided by Nasser Peyghambarian’s group at the University of Arizona. The process for preparing the polymer was completed in five steps. The global process can be seen in Figure 2.5 and the details of each process will be described in the following sections.
Figure 2.5: Global process for preparing PR polymers.
2.2.1 Preparing the Chemicals

Beakers used to mix the chemicals were thoroughly cleaned and dried with nitrogen to avoid contamination. Each component was measured, yielding 49.5 wt% PVK, 35 wt% PDCST, 10 wt% ECZ, 5 wt% BBP, and 0.5 wt% C\textsubscript{60}; the total mass of the mixture was 100 mg. The BBP and C\textsubscript{60} were added in as solutions with tetrahydrofuran (THF) and toluene, respectively. All components were added to a clean beaker with the exception of the C\textsubscript{60} solution. An additional 12.5 mL of THF was added to the beaker and sonicated for 15-20 min. The C\textsubscript{60} solution was then added to the beaker along with an additional 5 mL of toluene and sonicated for an additional 10 min.

2.2.2 Filtering

The filtering of the prepared chemicals required a piece of 1 µm filter paper to be placed in a filter holder and rinsed with toluene to saturate the filter paper. The solution was then passed through the filter into a clean beaker. The residue from the original beaker was then rinsed with toluene and passed through the filter to keep wasted solution to a minimum.

2.2.3 Evaporating

Once the solution was completely passed through the filter, a piece of aluminum foil was placed over the top with a few small holes in the top about the size of pencil tip to prevent contamination. A Kimwipe was then placed over top and sealed with a rubberband. The beaker was placed in a vacuum oven and the temperature was set to 45 °C. The evaporation time varied depending on the amount of THF added. THF evaporated first from the mixture, taking up to 7 hrs. The evaporation of the THF was known because the level in the beaker dropped by the same amount that was added. Once the THF evaporated, the temperature was increased to 71°C to evaporate the toluene. Evaporation in a vacuum oven was not necessary, although it did decrease the time to evaporate the solvent.
2.2.4 Preparing the Precake

This step was very important in assuring the polymer was the correct consistency. The residue that was left over after the evaporation step was scraped onto a 2 x 3 square inch uncoated glass slide and placed on a hotplate. The target temperature for melting the polymer was 167 °C; it was important not to exceed the melting point in order to avoid damaging the polymer. The polymer became viscous and was collected into one spot in the middle of the slide. At this point it was necessary to roll and mash the polymer to allow for complete homogenization. A second slide was placed on the first, sandwiching the polymer. The slides were pressed together and rotated to further mix the polymer, and then placed on a metal block to facilitate rapid cooling. The cell was separated and the previous step repeated 3 times to further promote a more homogenous mixture and remove any bubbles.

2.2.5 Preparing Individual Cells

Indium tin oxide (ITO) coated slides were prepared by cleaving approximately 1 inch squares. The ITO coating is a transparent conductor used to apply an electric field across the polymer only to portions of the cell with overlapping sections of ITO. These slides were cleaned with acetone and methanol before the polymer was placed on them. To allow for proper spacing, 105 µm spacer beads were added to vacuum grease and lightly applied on the corners of the slides. Small pieces of polymer were cut from the precake and placed on both ITO slides. The polymer was melted again and the slides were pressed together making sure there were no bubbles present. The cell was once again placed on a metal block to facilitate rapid cooling. The polymer cell can be seen in Figure 2.6. It was important that the ITO be etched into strips outlined by the black lines in the figure. It was only in this region of overlapping ITO that an applied electric field would be present in the polymer. An ample amount of polymer was needed to extend beyond this region to prevent arcing between the slides.
Figure 2.6: Final polymer cell showing black outlines where the ITO electrodes overlap.
3 Experimental Procedures

Two different types of materials were being studied at different stages of development. The thin films had crystallographic issues to overcome with the growth parameters while the polymers had already been developed but had optical gain issues to overcome. This required a distinctly different characterization technique for each material. The growth of PR thin films had not been previously studied with a c-axis in-plane orientation, therefore X-ray diffraction (XRD) analysis was required before any optical characterization could be performed. Without the required orientation, the PR effect will not occur. However, the PR effect has already been shown to take place in the polymers, therefore two-beam coupling (TBC) was used to as an optical characterization technique to further probe its PR properties. It was necessary and worthwhile to be aware of the basic concepts of these methods, to understand how they were useful in obtaining the experimental data, which will be discussed in the following sections.

3.1 X-Ray Diffraction of Thin Films

XRD was a very important method used to determine material properties such as lattice orientation and spacing. This method used the basic principles of diffraction and interference of electromagnetic waves. It is well known that diffraction occurs when light passes through a slit with a spacing on the order of the wavelength of the incident light [18]. This was seen in Young’s double slit experiment (Figure 3.1) where by passing light through two
slits, diffraction occurred and constructive and destructive interference took place between the diffracted waves.

This led to the conditions for constructive and destructive interference which are,

\[ n\lambda = d\sin\theta, \quad n = 1, 2, 3... \]  \hspace{1cm} (3.1)

\[ (n + \frac{1}{2})\lambda = d\sin\theta, \quad n = 1, 2, 3... \]  \hspace{1cm} (3.2)

where \( d \) is the spacing between the slits, \( \lambda \) is the wavelength of the incident light. It is seen from the figure that the \( d\sin\theta \) term comes from the difference of the two rays, \( r_1 \) and \( r_2 \), which are the distances from the slit to a point on the screen a distance \( L \) away. These conditions hold true when light is passed through a material with periodic spacing between
the planes in its crystal structure, however, one of the rays must travel $2d \sin \theta$ more than the other as opposed to double slit diffraction. This condition can be seen in Figure 3.2. The adjusted condition for constructive interference when x-rays are diffracted from a set of lattice plane becomes

$$2d \sin \theta = n \lambda, \quad n = 1, 2, 3, \ldots,$$

(3.3)

which is known as Bragg’s Law. This equation allowed for the determination of lattice parameters in a crystal.

XRD was performed using a Rigaku DMAX B diffractometer to obtain the orientation of the thin film samples. The three main components of the diffractometer were an X-ray source, sample mount, and a detector. In the source, a beam of electrons was incident on a copper (Cu) target which emitted CuK$_{\alpha 1}$ radiation with a wavelength of 1.54 Å. CuK$_{\alpha 1}$ was produced by the incident electrons dislodging an electron in the K shell of the Cu and an electron in the L shell dropping to fill the empty level. These emitted X-rays were then projected onto the sample where they interacted with the lattice, diffracting a portion of the
X-rays (Figure 3.2). The detector was attached to a goniometer which allowed it to rotate through a varying range of angles detecting the diffracted X-rays. The detected X-rays were plotted on an intensity vs. angle plot with peaks for every orientation allowing constructive interference to occur. The lattice spacings of the samples were then determined using Bragg’s law with the known wavelength of the X-rays and the $\theta$ terms taken from each peak on the intensity plot. Orientations of the thin films were then found by matching the calculated lattice spacings with a crystallographic database provided by the International Centre for Diffraction Data (ICDD).

### 3.2 Two-Beam Coupling in Photorefractive Polymers

Two-beam coupling (TBC) is a crucial technique for understanding the PR grating dynamics in new materials [2]. Much information can be obtained from this technique to include strength of the space charge field, speed of grating formation, gain through the material, and phase shift of the induced space charge field. This technique was used to determine these properties in the polymer samples. TBC required two coherent beams, a signal and a pump, to be overlapped in the samples which created an interference pattern leading to the formation of the space charge field and refractive index modulation as discussed in Chapter 1 and later illustrated in Figure 3.5. This experimental technique was applied in two different geometries; transmission (co-directional) and reflection (contra-directional) (Figures 3.3 and 3.4). The geometry of the incident beams affected the fringe spacing of the intensity pattern in turn affecting the grating spacing of the space charge field given by:

$$\Lambda = \frac{\lambda}{2n\sin\left[\frac{\theta_2-\theta_1}{2}\right]}$$

(3.4)

where $n$ is the refractive index of the material, $\lambda$ is the wavelength of the incident light, and $\theta_2$ and $\theta_1$ are the angles of the two beams inside the material [2].
Figure 3.3: Transmission geometry of two beams passing through a polymer cell which is tilted to allow a portion of the grating vector, $k_g$, to be in the direction of the applied field, $E_0$.

Figure 3.4: Reflection geometry of a beam passing through a polymer cell interacting with the Fresnel reflection off the back surface placing the grating vector, $k_g$, in the direction of the applied field, $E_0$. 
This shows that smaller angles between the beams produce a much larger grating spacing than larger angles. These large grating spacings are produced in transmission geometry when the beams are incident on one side of the sample while smaller grating spacings are produced when the beams are incident on opposite sides of the sample as in reflection geometry. In the case of the transmission geometry, the laser source was split to create two mutually coherent beams. These beams were incident on the sample using the configuration in Figure 3.3. The reason for the tilt in the sample was that a component of the grating vector, \( k_g \), must be in the same direction of the applied field, \( E_0 \), to promote charge migration along \( k_g \). The beams were overlapped to create an interference pattern inside the sample and as the grating formed, the pump beam transferred energy to the probe through coupling. At this point it is worth mentioning that this geometry was extremely sensitive to vibrations as it behaved just like an interferometer. In the case of the reflection geometry, the two beams are typically incident on opposite sides of the polymer sample at some angle which may vary for each input beam [3, 19]. For this research, only one input beam was required. This beam was incident normal to the surface of the cell which created a Fresnel reflection from the back surface as seen in Figure 3.4, known as self-pumped reflection. The reflected beam was less intense and interfered with the input beam. This geometry was significantly less sensitive to vibrations since the signal beam was a reflection of the pump and was not subjected to fringe movement arising from atmospheric distortions.

A general equation for the space charge field produced by a single charge species was found by solving Kukhtarevs’ equations by using a coupled wave approach. A comprehensive description of this theory and solutions were found in [20]. The space charge field was found to be

\[
E_{sc} = -\frac{E_q(E_0 + iE_d + E_{pv})m(z)}{(E_q + E_d - i(E_0 + (N_a/N_d)E_{pv}))},
\]

where \( E_q \) is the saturation field, \( E_d \) is the diffusion field, \( E_{pv} \) is the photovoltaic field, \( E_0 \) is the bulk electric field, \( m(z) \) is the modulation depth, and \( N_a \) and \( N_d \) are the acceptor and donor concentrations. The grating spacing affects the strength of the space charge field.
through the $E_q$ and $E_d$ terms where $E_q = eN_c\Lambda/2\pi\epsilon_0\epsilon_r$ and $E_d = 2\pi k_B T/e\Lambda$ with $N_c$ being the effective trap density determined by the relative concentrations of $N_a$ and $N_d$ [21].

The temporal response of the PR grating was measured by applying a bias field across the polymer layer to align the components, providing a uniform refractive index, then introducing the pump and signal beams while measuring the transmitted intensity as the PR grating formed. This caused a decay in the pump beam as energy was transferred to the signal beam. The intensity measurements were then fitted to an exponential decay function of the form,

$$P_t(t) = P_0 + \sum_{i=1}^{3} P_i \exp\left(-t/t_i\right),$$

(3.6)

where $P_0$ is the steady state transmitted power, $P_i, i = 1, 2, 3$, are the amplitudes of the exponentials and $t_i, i = 1, 2, 3$, are the respective time constants. The measured intensities are typically fit with $i \leq 3$. The number of exponentials is an indication of how many charge species were present during the grating formation and will be discussed in Chapter 4.

The gain coefficient was another important property of PR materials that was determined through the use of TBC experiments. The gain coefficient is defined as

$$\Gamma = \frac{1}{L} \ln \frac{I_1' I_2}{I_1 I_2'},$$

(3.7)

where $L$ is the interaction length, $I_1'$ is the transmitted intensity of the signal beam, $I_1$ is the incident intensity of the signal beam, $I_2'$ is the transmitted intensity of the pump beam, and $I_2$ is the incident intensity of the pump beam [22]. For this research, the intensity of the pump beam was much larger than the signal beam (order of magnitude), therefore, the
depletion of the pump beam was very small and the gain coefficient reduced to

\[ \Gamma = \frac{1}{L} \ln \frac{I'_1}{I_1}, \]  

(3.8)

where only the signal beam, \( I_1 \) was required.

The phase shift of the space charge field was also an important property to measure as this affects the alignment of the liquid crystals with respect to the incident intensity pattern. Figure 3.5 shows the effect of an interference pattern on the refractive index of a material (as explained in Chapter 1). This shows the space charge field and refractive index are shifted by \( \pi/2 \) relative to the incident intensity pattern. Once the refractive index grating is established, it diffracts the incident beams inducing a \( +\pi/2 \) (constructive interference) phase shift for one beam and \( -\pi/2 \) (destructive interference) \[23\] leading to energy transfer between the two beams. It is important to notice that a \( \pi/2 \) phase shift is an ideal case for complete energy transfer of one beam into the other. The phase shift in both geometries was measured by inducing a known phase shift, with a piezo-mirror, in the pump beam and measuring the change in the transmitted intensity. The changes in transmitted intensity were plotted as gain versus a range of induced phase shifts. The plots were extrapolated to zero gain in order to find the characteristic phase shifts of the polymer at each applied field which were then compared with theory (Figure 3.6). The theory plots were created using a term for the phase shift,

\[ \tan(\phi_0) = \frac{ImE_{sc}}{ReE_{sc}} = \frac{E_d(E_d + E_q) + E_0^2}{E_0E_q}, \]  

(3.9)

which is a function of the real and imaginary parts of the space charge field, \( E_{sc} \), described above \[24\].
Figure 3.5: Effect of the incident light intensity pattern on the refractive index of a PR material with a single charge species.
Figure 3.6: Phase shift vs. applied field in a PR polymer.
4 Characterization

Characterizing the thin films and polymers was an important step in 1) identifying the end state of the fabricated materials, 2) identifying how these materials behave, and 3) determining if they will work for their intended application. These two materials were characterized using different methods due to their different states (i.e., a crystalline film and an amorphous polymer) and stages of development. The current PR polymers have been successfully processed and studied for their diffractive properties [25] thus it was not necessary to re-characterize the internal structure of the polymer. The more important analysis needed to be performed was testing of its PR properties. Characterization of these materials was done by beam coupling in transmission and reflection geometries which is a proven method to study PR grating dynamics [2]. However, growing thin films with the desired orientation (c-axis in-plane) has not been successfully achieved. Many papers have been published discussing the successful growth of c-axis oriented thin films (thin films with the c-axis perpendicular to the surface of the substrate) [10, 26, 27] but never with the c-axis parallel to the surface. Therefore, characterization of the orientation needed to be accomplished, before it is necessary to study its PR properties. XRD was a useful technique to analyze the orientation of the thin films and was the bulk of the thin film characterization. Once proper growth is achieved, more characterization methods can be performed to study the PR properties. The characterization results of both materials will be discussed in the following sections.
4.1 Thin Films

In order for the PR thin films to work in the hybrid cells they must behave similarly to the bulk materials. Therefore the deposited thin films must be single crystal with the c-axis parallel to the surface of the substrate. XRD was used to determine if the thin films had been successfully grown with this preferred orientation. A polycrystalline thin film has an XRD pattern with intensity peaks associated with all lattice planes parallel to the surface of the sample. The desired result was to have intensity peaks only associated with a single lattice plane, which is indicative of single crystal thin films, with the preferred orientation (c-axis in-plane). For the materials researched in this thesis, detection of the a- or b-axis peaks implies that the c-axis is parallel to the surface of the substrate. It was irrelevant whether the a- or b-axis detected so long as the orientation was uniform throughout the film and there was not a combination of the two orientations. Peaks in the XRD patterns of the deposited thin films were compared to ICDD standards to check for proper orientation.

SBN60:Ce thin films were deposited on a several different substrates to include MgO (100), LAO (100), STO (100), and SBN60 (100) while holding all parameters constant between depositions. Each substrate had characteristic peaks present in all XRD data. These peaks were present because the X-rays were powerful enough to penetrate through the thin films and into the substrates. It was important to differentiate between these characteristic peaks and those from the thin film. Figure 4.1 shows the result of growing an SBN60:Ce thin film on an MgO (100) substrate. The characteristic peak of MgO (100) can be seen at 42.95°, representing the (200) plane. The other two peaks at 22.65° and 46.15° are characteristic of an SBN60:Ce film with the c-axis perpendicular to the surface of the substrate [14]. This result can be seen in many papers indicating the peaks are associated with the (001) and (002) planes which describe the perpendicular c-axis orientation. These peaks were also present on the other substrates. The most surprising result was the presence of these peaks when grown on a single crystal SBN substrate with a c-axis in-plane orienta-
Figure 4.1: XRD plot of an SBN thin film deposited on an MgO substrate.
tion. This can be explained by the fact that the length of the a- and b-axis (12.46 Å) is about 3x the length of the c-axis (3.946 Å) which leads to a lattice mismatch of 4.99% in this configuration. This lattice mismatch is larger than 0% which would be the case if the c-axis of the thin film were in-plane, however, the tetragonal unit cell of SBN has the a- and b-axis having a much larger lattice constant compared to the c-axis. It is believed that the thin films prefer growing with the c-axis perpendicular to the substrate because this configuration may require the least amount of energy. This explanation could be attributed to the final orientation of the thin films grown on the other three substrates. Several SBN60:Ce thin films were also grown on MgO substrates while changing the O₂ pressure in the chamber. Depositions were made by increasing the O₂ pressure in the chamber from 50 mTorr to 300 mTorr in increments of 50 mTorr. It was seen that this had no effect on the outcome of the orientation. All thin film orientations matched that of Figure 4.1.

Several thin films were also subjected to the poling procedures discussed in Chapter 2. The first approach was to pole a crystalline thin film that was deposited on MgO at a temperature >700 °C. A 3 kV/cm electric field was applied across the surface of the thin film while heated to 120 °C to ensure the material was above the Curie temperature. The temperature was increased at 50 °C/hr and was stable at 120 °C for 15 min and ramped back down at 50 °C/hr. The voltage was slowly applied just before the temperature started to ramp down and was turned off after the temperature was well below the Curie temperature. XRD analysis showed no change to the orientation of the thin film after the poling cycle. The same poling cycle was also applied with a field of 17.5 kV/cm with no change in the XRD results. Different poling cycles were applied to the amorphous thin films that were grown with no applied temperature to the substrate. These amorphous thin films were subjected to two different electric fields, 1.5 kV/cm and 10 kV/cm, in order to align the c-axis during crystallization. A higher field of 25 kV/cm, as achieved by Y. Xu et al., [17] was unsuccessfully achieved due to arcing across the thin film. Several attempts were made to apply higher fields by immersing the sample in a sulfur hexafluoride (SF₆) filled quartz
Figure 4.2: XRD plot of SBN thin films after undergoing two different poling cycles. Silver, Ag, peaks have been identified from the electrodes applied to the film surface.
crucible. Higher fields can be achieved in SF₆ since it has a higher dielectric strength than air, however, the highest achieved field at 700 °C was approximately 10 kV/cm. These fields were applied across the surface of the thin films while the temperature was increased to 700 °C and dwelled for 1 hr before ramping back down. It can be seen in Fig. 4.2 that the electric fields had no effect on the final orientation of the thin films. These results were compared to an amorphous thin film that was heated to 700 °C with no applied electric field.

Potassium niobate (KN) was another potential PR material to be studied. KN thin films were deposited on two different orientations of MgO; (100) and (110). The XRD results can be seen in Figure 4.3. Several peaks can be seen that do not correspond to crystalline KN. This is attributed to the low quality target used for the deposition most likely causing forms of NbO to be present in the thin film. More important was identifying any peaks which may be associated with the c-axis in-plane orientation. The red plot in Figure 4.3 shows a KN thin film deposited on the typical MgO oriented substrate. There are no peaks present that are associated with an in-plane orientation. It can be seen that by rearranging the pattern of the surface atoms, as in changing from the (100) oriented substrate to a (110) orientation, the resulting thin film had different XRD peaks (blue plot, Figure 4.3). Figure 4.3 is zoomed in to the area of interest. A similar result can be seen in [28] where they use a transition layer of STO to obtain the same result as using a (110) oriented MgO substrate. Figure 4.4 shows a peak related to the (200)/(020) orientation at 31.46° which is in agreement with [28]. The reason these two orientations share an XRD peak is because their a- and b-axes differ by only 0.026 Å. As in [28], it is possible to resolve the percentage of each orientation with a more detailed analysis. A more detailed analysis of the current KN thin films is not worth while since the quality of the thin film was so poor. The thin films had a hazy appearance that is indicative of high surface roughness which is an unfavorable quality of thin films. However, with future research of higher quality KN
Figure 4.3: KN thin films deposited on two different cuts of MgO substrates: (100) and (110).
Figure 4.4: Zoomed in plot of KN thin films showing preferred orientation using MgO (110) substrates.
thin films a more detailed analysis will be quite important in distinguishing between the two orientations and optimizing the deposition procedure to reach a final product with only one orientation. What this crude result allowed us to see is that it is possible to grow a portion of the KN thin film with the c-axis parallel to the surface of the substrate while it still has yet to be successfully achieved using SBN60:Ce.

4.2 Polymers

The polymers were studied using TBC techniques which allowed us to analyze the PR properties to include: speed of grating formation, gain through the material, and phase shift of the induced space charge field. The use of both geometries was not necessary for all cases. For simplicity, the PR grating dynamics were studied only in the reflection geometry while phase shift measurements were taken in both geometries.

Measurements were taken using a linearly polarized CW frequency doubled Nd:YVO$_4$ laser with a 532 nm wavelength (Coherent Verdi V) attenuated to approximately 10 mW output. In order to study the grating dynamics in reflection geometry, the beam was normally incident on the polymer sample [29] (Fig. 3.4). A voltage was applied across the 105 µm sample using a high voltage source. The applied voltage was varied from 1.5 kV to 7 kV in increments of 0.5 kV. The transmitted beam was monitored using a power meter and the data was collected (Fig. 4.5) using a LabVIEW program.

The voltage was applied every 50 sec while the incident beam remained illuminated on the sample. The 50 sec intervals allowed the PR gratings to reach steady state when the voltage was applied and completely erased when the voltage was turned off. It was shown that 50 sec was much longer than the formation of the PR gratings (typically 5-30 sec) and was a sufficient amount of time to allow between measurements. The resulting data was fit using multi-exponential functions. Figure 4.6 shows the resulting data fit with the multi-
Figure 4.5: Experimental result of applying a range of voltages across the polymer every 50 sec in the reflection geometry.
Figure 4.6: Temporal response of applying 20, 40, and 60 V/µm across the polymer.
exponential functions for applied voltages of 2, 4, and 6 kV. For applied voltages less than 4 kV the transmitted power decreased rapidly then reached steady state which is typical for grating formation due to a single charge species (holes). For applied voltages of 4 kV and greater, a rise was seen in the transmitted power after the initial decrease then the signal reached steady state. The rise in the transmitted power is attributed to a second charge species (electrons). This behavior is in agreement with Wang et al., [30]. The variation of the transmitted power was similar even when the direction of $E_0$ was reversed. The unidirectional energy transfer in both cases [23] is indicative of non-negligible diffractive energy coupling between the incident and the (weak) Fresnel reflected beams in the PR polymer, rather than a true energy coupling. This occurs due to suboptimal ($\neq \pi/2$) field-dependent phase shifts measured between the intensity grating and the induced refractive index grating during energy coupling in our PR polymer, in agreement with Grunnet-Jepsen et. al., [31].

As stated in Chapter 3, the transmitted power, which is related to the two-beam coupling response, has been fitted with a multi-exponential function of the form

$$P_t(t) = P_0 + \sum_{i=1}^{3} P_i \exp \left( -t/t_i \right), \quad (4.1)$$

where $P_0$ is the steady state transmitted power, $P_i, i = 1, 2, 3$ are the amplitudes of the exponentials and $t_i, i = 1, 2, 3$ are the respective time constants. For applied fields less than 40 V/µm, the data was fit with a double exponential. The two time constants extracted from the fit are attributed to the alignment of the chromophores and the grating formation due to holes. Above 40 V/µm, the data required a third exponential term which is due to a secondary grating being formed by electrons (i.e., a competing grating). Figure 4.6 shows these two distinct regions. Figure 4.7 shows the extracted amplitudes and time constants of the fitted exponentials as a function of applied field, $E_0$. This shows the electron grating becoming prominent around 40 V/µm and becoming faster as $E_0$ increases. It is possible
Figure 4.7: Plots of time constants and amplitudes vs. applied field extracted from the fitted curves using a multi-exponential function. The squares are attributed to the alignment of the chromophores and the circles and triangles show the grating formations due to holes and electrons, respectively.

The symmetry of the amplitudes, due to the electrons and holes, can be described by the formation of an electron-hole pair when the sensitizer is excited creating both electrons and holes.

The phase shift was also measured in this configuration by placing a 65.5% reflection piezo-mirror between the polymer sample and the power meter. While in transmission geometry, the piezo-mirror was placed in the path of the probe beam. Voltages were applied to the piezo-mirror inducing a range of phase shifts between 10 and 90 degrees, with measurements taken every 5 degrees. The voltages were applied quickly to the piezo-mirror, faster than the response time of the grating, to prevent the formation of multiple gratings.
The measured response was converted to gain and plotted vs. induced phase. A typical plot is shown in Figure 4.8. Phase shift measurements were taken at applied fields between 30 and 70 V/µm every 10 V/µm. The resulting data was fitted with a linear function and extrapolated to zero gain in order to obtain the inherent phase shift of the polymer. Figure 4.9 shows the extracted phase shifts in both geometries which is in reasonable agreement with the theoretical values shown in Figure 3.6 for both geometries. The scatter in the data is attributed to the experiments sensitivity to environmental conditions (i.e., vibrations, air currents, temperature fluctuations, etc.). It can be seen that in both geometries the phase shift was well below 90 degrees ($\pi/2$). This also verifies the above claim that poor energy coupling is achieved due to suboptimal ($\neq \pi/2$) phase shift.
Figure 4.8: Range of induced phase shifts with a field of 70 V/µm applied to the polymer.

Figure 4.9: Experimental and theoretical phase shifts plotted vs. applied voltage for reflection and transmission geometries for 105 µm polymer samples.
5 Conclusions

Two very different classes of materials were investigated for the problem of finding a suitable replacement for the bulk PR windows in an organic-inorganic hybrid cell, which included an inorganic thin film and an organic polymer. Each material was fabricated and characterized in order to verify its suitability as a window replacement. Due to the different material types and stages of development, these materials underwent separate characterization techniques. The aim of this thesis was to investigate possible replacements for the bulk windows without any loss of the space charge field while maintaining a $\pi/2$ phase shift between the incident intensity pattern and the space charge field.

The PR effect of the organic polymers had been previously studied, however, more information was needed since the current application was different. TBC experiments were performed in transmission and reflection geometries to probe the PR properties. It was found that multiple charge species were present during the generation of the space charge field. The holes first began to form a grating which was expected however, signs of a second grating became prevalent which impeded the growth of the hole grating. This extra grating was found to be caused by electrons. Phase shift analysis was also performed to verify the $\pi/2$ ($90^\circ$) phase shift required for complete energy transfer between the two beams. Careful analysis showed the phase shift in the reflection geometry was approximately $40^\circ$ and approximately $8^\circ$ in the transmission geometry. In both geometries the phase shift was much less than $90^\circ$. Another issue found with the polymers was the high voltages required to be applied to the polymer in order to align the components as well as increase the mo-
bility of the charge species. Space charge field formation would not be possible without these high applied electric fields. Such high electric fields would erase the possibility for the space charge field to modulate the LC’s since the high field would dominate the alignment of the LC’s and mask the effects of the space charge field. All these deficiencies combined showed that the organic polymers in their current composition would not be a suitable replacement for the bulk PR windows.

Inorganic thin films were characterized by other means due to their immature processing nature. The hybrid cells require a specific lattice orientation in the windows, in order to modulate the LC’s, which was to have the c-axis in-plane. Successful growth of PR SBN thin films has been achieved and published in many papers with the c-axis out of plane but never in-plane. Several thin films were grown by PLD with varying deposition parameters and on different substrates in order to achieve this desired in-plane orientation. XRD was used to analyze the final orientations of these thin films which showed that the c-axis grew out of plane in all attempts. Poling cycles were performed in an attempt to manipulate the c-axis with no success. Thin films of KN were also grown with two different MgO substrate orientations. It was found that by switching to MgO (110) oriented substrates, successful c-axis in-plane orientations were achieved. However, this result was subtle (small portion with c-axis in-plane) due to insufficient target densities.

It was shown during this research that organic polymers are not suitable for hybrid cell applications. This material had too many issues to overcome. The inorganic thin films showed proper orientation when switching to KN. With more research in this area it will be possible to achieve successful growth of inorganic thin films with the preferred c-axis in-plane orientation. With further analysis of the PR properties of successfully grown PR thin films, it may be possible that they become a suitable replacement for the bulk PR windows in the hybrid cells.

Future work in this area will require some adjustment of each material. In order for the polymer to be suitable for this application, the high applied fields would have to be sig-
nificantly reduced. If the chromophores were pre-aligned, these high applied fields would not be required. There is more promise for the inorganic thin films. Higher density targets of KN have already been obtained and future depositions may show proper orientation of a larger percentage of the thin film. Another possible solution would be to diffuse Ce into a thin undoped crystal of SBN. This would create a doped portion of the crystal at the surface that would generate the necessary space charge field while reducing the absorption.
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