Bio-inspired Materials Research for Improved Sensitivity Low-cost Uncooled Infrared (IR) Detector Focal-plane Arrays

by Wendy L. Sarney, John W. Little, Frank E. Livingston, Melanie W. Cole, Krisztian Niesz, Teyeb Ould-Ely, and Daniel E. Morse

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Bio-inspired Materials Research for Improved Sensitivity Low-cost Uncooled Infrared (IR) Detector Focal-plan Arrays

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**Abstract:**
This report describes the highlights of progress made for the 6.2 project “Improved Sensitivity Low-Cost Uncooled IR Detector Focal-Plane Arrays” during the February–April 2009 time period. The program goals corresponded to the continued expansion of our BaTiO3 nanomaterial synthesis capabilities and deposition methods, laser-induced pyroelectric phase conversion studies and spectroscopic end-point control scheme, and comprehensive material characterization studies. The Aerospace Corporation investigated the laser-induced phase conversion of functionalized thin-films from the pyroelectrically-inactive cubic polymorph to the pyroelectrically-active tetragonal polymorph. The Institute for Collaborative Biotechnologies (ICB) pursued further refinements in the vapor diffusion reactor design. Efforts also focused on the extension of the thin-film methods for the deposition of smooth, high quality functionalized nanoparticles over a range of thicknesses and nanoparticle densities. ARL investigated the application of various binders for the preparation of thin-films. Efforts also focused on the experimental design and instrumentation required for the pyroelectric capacitance measurements and electrical property analysis on both laser-activated and oven-processed thin-films.

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1. Introduction

This report describes the highlights and summary of the year one, quarter four (Y1Q4) progress for the 6.2 project “Improved Sensitivity Low-Cost Uncooled IR Detector Focal-Plane Arrays.” This work occurred during the February–April 2009 time period. A description of the background technical information and earlier progress is discussed in prior technical reports (1–2).

The program goals for Y1Q4 corresponded to the continued expansion of our Barium Titanium Oxide (BaTiO₃) nanomaterial synthesis capabilities and deposition methods, laser-induced pyroelectric phase conversion studies and spectroscopic end-point control scheme, and comprehensive material characterization studies. The respective team tasks included:

**Aerospace:** Conducted further investigations into the laser-induced phase conversion of Institute for Collaborative Biotechnology (ICB)-provided functionalized BaTiO₃ thin-films from the pyroelectrically-inactive cubic polymorph to the pyroelectrically-active tetragonal polymorph. Efforts also focused on the development of a new dual-beam second harmonic generation (SHG) setup that permits phase conversion analysis during both static laser exposures and laser raster patterning, along with the continued implementation of piezoelectric force microscopy (PFM) techniques for pyroelectric/ferroelectric phase contrast studies.

**ICB:** Pursued further refinements in the vapor diffusion reactor design to permit the more rapid and large-scale synthesis of 100-g batches of BaTiO₃ nanoparticles with high quality and crystallinity in 24–48 h. Efforts also focused on the extension of the thin-film methods for the deposition of smooth, high quality functionalized BaTiO₃ nanoparticles over a range of thicknesses from the monolayer to several microns, and over a range of nanoparticle densities.

**ARL:** Investigated the application of various binders such as polyvinyl alcohol (PVA) for the preparation of high quality BaTiO₃ thin-films using the bio-inspired perovskite nanoparticles synthesized by the ICB. Efforts also focused on the experimental design and instrumentation required for the pyroelectric capacitance measurements and electrical property analysis on both laser-activated and oven-processed BaTiO₃ thin-films.

All project teams have accomplished their respective planned milestones for Y1Q4, and highlights of the major activities are provided in this report.
2. Progress by The Aerospace Corporation

2.1 Analysis of functionalized BaTiO₃ thin films

During the fourth quarter, The Aerospace Corporation received two sets of functionalized BaTiO₃ thin films from our ICB collaborators that were prepared via layer-by-layer spin coating. The BaTiO₃ nanoparticles were pre-functionalized with oleic acid and dispersed in a hexane colloidal solution for eventual spin coating on optical quality quartz substrates. One set of samples remained un-annealed, while the companion sample set underwent annealing at 400 °C for 1 h as described in section 3.2. The as-received BaTiO₃ thin-films were of impressive and uniform quality, and profilometry measurements by the ICB team revealed film thicknesses of approximately 330 nm and 380 nm for the un-annealed and annealed samples, respectively. Our optical transmission measurements revealed that the fluctuations in the band gap energies that were observed previously with unfunctionalized BaTiO₃ nanoparticle thin films have been notably reduced, and light scattering during laser processing has been decreased as well. X-ray diffraction (XRD) measurements indicated that the films comprised amorphous barium titanate with no evidence of crystalline cubic domains. The complementary Raman spectra, however, were essentially featureless and were consistent with cubic phase BaTiO₃ as expected. While the band gap energy fluctuations have been reduced, the absolute band gap energy for the functionalized BaTiO₃ thin-films is appreciably blue-shifted compared with the band gap energy for the unfunctionalized BaTiO₃ thin-films; first-derivative analysis of the absorption spectra for the functionalized thin-films yielded band gap energies that ranged from $E=4.02$ eV to $E=4.15$ eV (300-309 nm), while for the unfunctionalized thin-films the band gap energies ranged from $E=3.82$ eV to $E=4.03$ eV (308–325 nm). Interband transitions in the functionalized BaTiO₃ thin-films now occur at wavelengths of less than 360 nm, and the percent transmission remains quite high (approximately 90%) at our current laser processing wavelength of $\lambda = 355$ nm.

Consequently, the laser phase conversion efficiency at our current exposure wavelength of $\lambda = 355$ nm will be significantly diminished and more of the incident energy will be lost to the underlying substrate due to transmission; this effect depends greatly on whether the phase conversion process retains a single- or multiple-photon dependence, and we are currently exploring the linear and non-linear behavior of the photo-induced phase conversion process. To enhance the laser-induced conversion efficiency and help mitigate any potential problems associated with the increased transparency of the functionalized BaTiO₃ films, we intend to investigate and implement several strategies:

- Examine the laser-induced direct-write phase conversion using laser irradiation at wavelengths of $\lambda = 250–290$ nm, where the percent transmission is only approximately 30–35%. With adaptations to our current laser systems and optical configurations, we can examine laser phase conversion under a wide range of wavelengths (250–1100 nm), along
with variations in pulse length (100 fs–5 ns) and pulse repetition rate conditions (5 kHz–80 MHz).

• Explore the use of photosensitizers and dopants to red-shift the band gap energy and enhance photo-absorption in select wavelength regions that correspond to practical harmonic wavelengths and common commercial laser systems. The ICB team has had prior success in doping metal oxide nanoparticles (e.g., lanthanum, samarium, bismuth and manganese), and together we will work closely to establish the doping protocol and spectral characteristics required to optimize the pyroelectric phase conversion efficiency. We will also consult with our U.S. Army Research Laboratory (ARL) collaborators to ensure that the doped thin-films retain the appropriate infrared (IR) responsiveness and electrical properties.

• Investigate the capability of using the IR absorbing overlayer on the BaTiO_3 thin-film to resonantly capture the laser energy for pyroelectric phase transformation. This capability may facilitate enhancements to the IR photosensitizer layer, and permit the formation of IR absorbing layer patterns and pyroelectric phase domains that are in-registry for improved resolution.

• Other plans include the use of thicker, micron-sized BaTiO_3 thin-films to exploit the 1/e fall-off in the optical penetration depth of the laser irradiation, along with the potential implementation of a non-intrusive, benign reflective interlayer located between the BaTiO_3 nanoparticle thin-film and silicon substrate to improve localization of laser energy in the perovskite thin-film and further protect the underlying substrate.

2.2 New Dual-beam SHG Experimental Setup and Methodology

Our fourth quarter efforts have also focused on a new experimental design and setup for additional SHG studies of the laser-induced pyroelectric phase transformation process. During past quarters, we have designed and developed an in situ pump-probe SHG spectroscopic detection scheme for dynamic, real time monitoring of the pyroelectric phase conversion during laser patterning. The intent is to use the SHG activity associated with the non-centrosymmetric tetragonal polymorph to assess the extent of phase conversion from the SHG-inactive centrosymmetric cubic polymorph.

The new dual-beam experimental design permits additional and complementary SHG analysis under static laser exposure conditions. The ultraviolet (UV) laser processing beam (e.g. λ =355 nm) and IR SHG pump-beam (e.g., λ = 1064 nm) are concurrently delivered to the BaTiO_3 thin-film. The laser processing and pump beams are aligned in a collinear fashion, and the BaTiO_3 sample is positioned in a vertical manner. Consequently, the SHG signal (λ=532 nm) can be measured in a transmission mode configuration, where the pump laser beam and the SHG light are propagating in the same direction; this feature is particularly useful for SHG analysis on ultra thin films where high transparency and minimal surface scattering exist. If desired, the UV laser
processing beam and IR SHG pump-beam can be simultaneously delivered to a substrate under dynamic patterning conditions and a substrate under static exposure conditions. These modifications to the optical configuration allow the UV laser processing beam to be derived from either the electro-optic modulator or directly from the laser cavity. The incident IR pump-beam power is modulated using a zero-order half-wave plate in combination with a Glan-Taylor polarizer. This design facilitates examination of the polarization-dependent behavior of the SHG process. The emitted SHG light is focused into a polarization maintaining fiber bundle, guided into a custom-designed in-line filter assembly for laserline extraction and subsequently delivered to the entrance slit of an ultra fast gated charge-coupled device (CCD) coupled to an Acton 300i spectrometer for spectroscopic analysis. In addition, under static exposure conditions, we can more easily measure the time dependent evolution of the SHG signal on a pulse-by-pulse and dose-by-dose basis using uniform intensity modulation or genotype-scripted modulation. The static exposure-SHG detection capability will help to determine the absolute total energy that is required for laser-induced pyroelectric phase conversion, and permit more rapid assessment of whether certain laser pulse scripts can successfully induce phase transformation. These laser pulse scripts correspond to “locally” optimized pulse scripts that can be used as first-generation scripts for future incorporation into the evolutionary algorithm approach to laser-induced transformation control and the eventual determination of the “globally” optimized pulse script.

2.3 Piezoresponse Force Microscopy (PFM) Analysis of Ferroelectric Thin-films

We are continuing to explore and develop the use of scanning PFM techniques for complementary nanoscale analysis of the laser-induced BaTiO₃ phase conversion. PFM permits direct imaging of ferroelectric domain structures with nanometer-scale resolution (~3–10 nm), and is ideally suited for post-processing examination of the BaTiO₃ thin-films due to its relative insensitivity to topography and ease of implementation. Traditional atomic force microscopy (AFM) instruments can be augmented and tailored for specific operational modes like PFM, where the mechanical response of the sample is measured during local electrical excitation by the AFM probe tip. A modulated ac voltage is applied between the underlying substrate and conductive AFM/PFM tip during contact mode scanning. Using lock-in amplifier techniques, the local electromechanical displacement can be decoupled from the topographical displacement via the phase shift between the rapidly oscillating ac field and the slow cantilever displacement feedback. The static cantilever deflection corresponds to the surface profile variations and topography, while the modulated cantilever oscillations are related to the piezoelectric response of the sample.

As discussed in our prior report (2), we intend to develop several new PFM and laser processing approaches to facilitate ferroelectric phase contrast detection in nanostructured perovskite thin-films, including spectroscopy mode operation, localized poling of BaTiO₃ nanoparticles and dynamic polarization control during laser irradiation. During the fourth quarter, we have specifically developed and tested a dual lock-in amplifier mode PFM approach on several model pyroelectric and ferroelectric materials. We have successfully implemented dual lock-in
amplifier assemblies to acquire simultaneous phase-difference (i.e., tip vibration signal vs. reference ac modulation signal) data corresponding to out-of-plane distortions where the polarization is normal to the surface, and in-plane lateral distortions where the polarization is parallel to the surface.

Figure 1 shows PFM piezoelectric phase contrast results measured for a Lithium Niobate (LiNbO₃) sample. The example shown here corresponds to single crystal LiNbO₃ that has undergone recrystallization and hexagonal-to-trigonal phase conversion in the surface layer via chemical-induced surface restructuring. The phase signal profile is displayed in the left panel in figure 1a and reveals that the PFM phase contrast is increased as the probe tip comes into contact with piezoelectric domains on the LiNbO₃ surface. By scanning the sample surface and measuring the amplitude and phase signals, a 3-D map can be generated which corresponds to the piezoelectric moments that are oriented normal to the surface. The piezoelectric domains are readily identified by the bright field contrast in the right panel in figure 1a, where the piezoelectric regions correspond to the gold color and the non-piezoelectric domains appear as a dark brown color.

In the coming quarters we will examine the pyroelectric/ferroelectric phase contrast in standardized sets of nanostructured barium titanate thin-films under a wide range of preparation (film thickness and functionalization) and processing (as-prepared, furnace heated and laser-exposed) conditions.

Figure 1. Piezoelectric force microscopy results measured for a surface-modified lithium niobate single crystal. (a) Phase signal versus scanning distance. (b) 3-D map of piezoelectric moments that are aligned normal to the surface.

3. Progress by the Institute for Collaborative Biotechnologies (ICB)

3.1 Significantly Increased Throughput Synthesis of BaTiO₃ Nanoparticles

By the end of the third quarter of year 1, we had successfully designed, optimized and used reactors to increase the scale of synthesis of BaTiO₃ nanoparticles to the 100-gram scale. This represented a 100-fold increase in the scale of synthesis from the start of the project, using a single-source bimetallic alkoxide with our bio-inspired, vapor diffusion catalysis method to
produce 6-nm single-crystal BaTiO₃ nanoparticles at very low temperatures and in virtually
quantitative yield. However, throughput was still relatively low, as the total synthesis time
required was several days. In this final quarter of year 1, we report a breakthrough in which
sonication and reaction by vapor-droplet collision are used to accelerate synthesis kinetics to
permit significant increase in throughput.

We found that we can significantly accelerate the kinetics and throughput of synthesis by a
combination of sonication and vapor-droplet collision, as described here: concentrations of
catalyst (water/HCl) and precursor (the bimetallic alkoxide) were as previously described, but
the two solutions were placed in separate wells of a double well reactor (figure 2) and positioned
in an ultrasonic bath operated at 40 kHz. A stream of pure N₂ carrier gas at low flow-rate was
used to drive vapor droplets of the water/acid catalyst over the well containing the BaTi(OR)ₓ
precursor and to remove the product. The resulting combination of sonication and vapor droplet
collision significantly accelerated synthesis without affecting the size, crystallinity, high quality
and virtually quantitative yield of the final product. As an example, 3.6 grams of high quality,
phase-pure, cubic BaTiO₃ nanoparticles were produced within 6 h, including the drying process,
in contrast to the previously reported time requiring 2 days. We believe that this new method for
accelerating throughput of synthesis offers several advantages that we will use in designing a
continuous flow reactor for future scale up of production:

1) Sonication produces small vapor droplets with high surface area and high surface energy;
sonication also increases evaporation of the solvent, increasing the precursor concentration
in the reactive droplets;

2) Collision between the highly reactive vapor droplets containing the catalyst (H₂O/HCl) and
those containing the precursor results in rapid hydrolysis and polycondensation to form the
initial product;

3) Sonication also may accelerate dehydration and crystallization by producing local,
microscopic hot spots in the liquid.
Figure 2. (a) Acceleration of synthesis throughput by sonication and vapor droplet collision. (b) XRD spectrum of the final product, showing high crystallinity of ca. 6 nm cubic barium titanate. (c) TEM image of the final product. (d) High resolution TEM image of the final product, showing crystallographic lattices.

3.2 Preparation and Characterization of Uniform BaTiO₃ Nanoparticulate Thin-films, and Provision to Our Partners at ARL and The Aerospace Corporation

As described at the end of quarter 3, we found that functionalization of the BaTiO₃ nanoparticles with simple linear organic carboxylic acids, such as oleic acid, provides sufficient Coulombic repulsion to prevent aggregation of the particles, permitting complete solubilization in organic solvents from which we are able to spin-cast uniform, well-dispersed thin films. We characterized the smoothness and uniformity of these films by SEM and cross-sectional TEM, profilometry and atomic force microscopy, and provided these films to our partners at ARL and The Aerospace Corporation.

Functionalization of the BaTiO₃ nanoparticles with oleic acid prevents aggregation of the particles, permitting complete solubilization in hexane and similar organic solvents. Uniform, well-dispersed films were produced from these solutions by spin-casting on silicon and quartz silica. Analyses by SEM and cross-sectional TEM, profilometry and atomic force microscopy quantified the smoothness and high density of these films. The absence of cracks in these films and their high smoothness confirms the importance of stabilization and dispersion of the nanoparticles with surface functionalities compatible with volatile organic solvents.

Two kinds of samples were prepared and sent to The Aerospace Corporation for investigation of laser-induced site selective phase transformation in comparison to the results of bulk-heating. The first set comprised films produced by layer-by-layer spin coating of pre-functionalized BaTiO₃ nanoparticles from hexane colloidal solution onto quartz or silicon substrates. The second set was identical but annealed at 400 °C for 1 h under air at 2 °C/min heating and cooling rates. Measurements by optical profilometry show that layer-by-layer spin coating did not
significantly increase film thickness beyond the first layer; however, annealing consistently produced thicker films (~380 nm) than the identical films without heating (~330 nm). This observation remains to be explained, and will be investigated in depth in the next quarter.

Samples of the unfunctionalized nanoparticles (as-prepared) also were sent to ARL, for investigation of alternative routes to processing for IR detection. Results will be compared to those obtained with the thin films described above.

4. Progress by the U.S. Army Research Laboratory (ARL)

4.1 Preparation for Pyroelectric Parameter Measurements

In order to progress with our strategy for using the laser-processed, bio-inspired BaTiO$_3$ thin films for uncooled IR detectors applications, we must be characterize the pyroelectric properties of the post laser-induced phase transformed films. We are preparing to do these measurements and have begun the approval and the procurement process for obtaining the needed instrumentation. We will leverage the perovskite thin film research already in progress at the Weapons and Materials Research Directorate of ARL. This group already possesses the expertise and majority of the instrumentation, consisting of $150K of dielectric measurement instrumentation in-house and working, to accomplish most of the dielectric measurements required to evaluate the figure of merit (FoM) for pyroelectric uncooled detectors. An additional $16K of instrumentation is required as an add-on to the existing equipment in order to measure the pyroelectric coefficient, and we have secured the needed approvals for cost sharing between SEDD and WMRD to procure this equipment, and the procurement is now awaiting action by the Army’s contracts department.

Several figures of merit have been developed to assess the performance of pyroelectric materials for use in thermal detectors. The detection limit of a pyroelectric based detector is limited by the thermal noise (Johnson noise) generated in the capacitor elements (3). Therefore, a useful figure of merit that weighs the material properties for optimal signal-to-noise ratio is given by: $F_D = (p/c_v)(\epsilon_0\epsilon_r\tan\delta)^{-1/2}$, where $p$ is the pyroelectric coefficient (representing the amount of electrical current that can be generated per temperature change), $c_v$ the volume specific heat capacity, $\epsilon_0$ the permittivity of vacuum, $\epsilon_r$ the relative permittivity and $\tan\delta$ the dielectric loss (which represent the amount of dielectric noise present in the material during modulation). Since both $\epsilon$ and $\tan\delta$ have a strong dependence on frequency, these properties are measured at the frequency range of the detector. For bulk detectors, the $F_D$ are usually divided by the specific heat of the material, but for thin-film detectors it is not included. The above $F_D$ provides a convenient metric to measure and compare a materials performance for thermal imaging which allows for optimization in fabrication and processing. Thus, the pertinent material parameters to be measured are $p$, $\epsilon$, and $\tan\delta$. Our goal is to enhance $F_D$ by maximizing the pyroelectric
coefficient and minimizing the permittivity and dissipation factor. Measurements of the complex capacitance will be performed with a HP 4194A impedance/gain analyzer. Samples to be measured will be fabricated into parallel plate capacitors by evaporating metal electrodes a few 100-μm in diameter on top of the deposited pyroelectric film. The complex permittivity of a dielectric material is given by \( \varepsilon = \varepsilon' - j\varepsilon'' \), where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary components of the frequency dependent permittivity. The dielectric constant is given by \( \varepsilon_r = \varepsilon'/\varepsilon_0 \), where \( \varepsilon_0 \) is the permittivity of free space and is related to the measured sample capacitance by \( C = \varepsilon(A/d) \), where A is electrode area and d the film thickness. Dielectric loss is given by \( \tan \delta = \varepsilon''/\varepsilon' \).

Pyroelectricity is a phenomenon that occurs in polar materials and refers to a change in the orientation of dipole moments (a change in the spontaneous polarization) due to a change in temperature. When connected into a circuit, the fluctuation of the dipole moments will generate a current given by \( I = pA(dT/dt) \), where \( p \) is the pyroelectric coefficient, \( A \) the electrode area, and \( dT/dt \) the temperature rate of change with respect to time. Therefore, the pyroelectric coefficient can be determined by measuring the current produced during changes in temperature. This measurement can be accomplished by integrating the new instrumentation into ARL-WMRD’s preexisting electrical characterization scheme. The test station is diagrammed in figure 3 and will be used to accurately determine the pyroelectric coefficient in thin-film pyroelectric samples.

An Agilent 33220A function generator will be used in conjunction with a Maxim-IC power driver to modulate the temperature of the Peltier element to a low frequency \( (f < 1\text{Hz}) \) sine wave. This temperature fluctuation will generate a current from the pyroelectric material under test. The current will be fed into a Signal Recovery 7265 lock-in amplifier, which contains an internal current pre-amplifier, locked onto the reference frequency of the function generator. The pyroelectric current will be 90° out-of-phase with the temperature oscillation since it is proportional to the time derivative of the driven sine wave. This makes a phase-sensitive lock-in measurement beneficial since a true pyroelectric current can be determined, while spurious temperature-induced DC or in-phase currents are not registered. Additionally, a sensitive low-
level ammeter, such as a Keithley 6517B electrometer, can be used to digitally record the pyroelectric current vs. time during modulation. This can be beneficial in regards to comparing the unaltered (frequency unfiltered) pyroelectric signal with the amplitude measured from the lock-in amplifier. A Yokogawa 7651 DC source can be switched into the circuit to allow sample biasing for poling optimization experiments. The temperature of the stage will be monitored by platinum RTD using a preexisting Agilent 34401A multimeter. The equipment will be connected to a computer running LabView allowing computer-based control and datalogging.

To implement the pyroelectric measurements the list of required equipment including pricing is given in table 1.

Table 1. Additional pyroelectric equipment to be procured.

<table>
<thead>
<tr>
<th>Item</th>
<th>Model</th>
<th>Vendor</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peltier Modules</td>
<td>TE Technology, Inc. 60W Peltier modules</td>
<td>TE Technology, Inc.</td>
<td>$120.00</td>
</tr>
<tr>
<td>Peltier Driver</td>
<td>MAX1978evkit</td>
<td>Maxim-IC</td>
<td>$100.00</td>
</tr>
<tr>
<td>Function Generator</td>
<td>Agilent 33220A arbitrary waveform generator</td>
<td>TestMart</td>
<td>$1,269.00</td>
</tr>
<tr>
<td>Lock-in Amplifier</td>
<td>Signal Recovery Model 7265</td>
<td>Signal Recovery</td>
<td>$4,795.00</td>
</tr>
<tr>
<td>DC bias source</td>
<td>Yokogawa 7651 Programmable DC source</td>
<td>TestMart</td>
<td>$2,875.00</td>
</tr>
<tr>
<td>DC ammeter</td>
<td>Keithley 6517B</td>
<td>Keithley Instruments</td>
<td>$6,995.00</td>
</tr>
</tbody>
</table>

**Total Cost:** $16,154.00

### 4.2 Thin-film Studies

We continued our research into improving the quality of the BaTiO$_3$ thin films. We have dispersed BaTiO$_3$ particles into PVA [CH$_2$CH(OH)-]$_n$. PVA is a known film-former used in other sol-gel applications. It is a water-soluble insulating polymer, and is resistant to most solvents. Numerous parameters are being explored, such as the molecular weight of the PVA (we have used low: 13000–23000, medium: 50000–85000, and high: 120000 molecular weight solutions), the percentage alcohol-to-water in the solution, the curing temperature (ranging from room temperature to just below the boiling point of water), and the spin speed. We began this study by spinning PVA without nanoparticles, to determine whether the alcohol would adhere to the Si substrate (it does), whether it needed heat treatment (films are slightly higher quality if heated to about 90 °C), and if it would form a smooth crack-free film (yes!). In a parallel study with Antimony Telluride (Sb$_2$Te$_3$) particles for an ongoing thermoelectric materials research project, we found that the PVA tended to sink below the particles and act as glue between the particles.
and the substrate, leaving nearly bare $\text{Sb}_2\text{Te}_3$ particles on the surface. Since PVA decomposes above 200°C, we are hopeful that the remaining organic in the film will dissipate during the laser treatment.

During this quarter we received films consisting of BaTiO$_3$ particles functionalized with oleic acid onto TiPt:Si substrates from the ICB. These films are much improved in terms of smoothness and adherence to the substrate. We are currently setting up capacitance measurements for these samples.

In yet another approach, we are investigating the possibility of depositing films without first forming nanoparticles. ARL has successfully used low-temperature metal organic solution deposition (MOSD) to grow barium strontium titanate (BST) on Pt:Si substrates (5). The MOSD technique is an industry standard for film deposition over large area substrates with high chemical purity, strict control over chemical stoichiometry and low overhead cost. For our experiment, we have the added luxury using the same commercially-available, inexpensive precursor used for the bio-inspired nanoparticles growth at ICB. Having this precursor will save us numerous steps in the MOSD process.

The MOSD process for BST uses a home-made carboxylate-alkoxide precursor, glacial acetic acid, and 2-methoxyethanol. Since ARL has successfully grown multilayered films with this MOSD process, we expect that growing a single BaTiO$_3$ film to be very feasible.

5. Plans and Goals for Year 2 Quarter 1

In the coming quarter, we will continue to expand our nanomaterial synthesis capabilities, laser processing techniques and PFM phase conversion studies, and perovskite thin-film characterization efforts. We also intend to initiate and pursue several new areas of focus: ICB: investigate the deposition of thicker (> 500-nm) BaTiO$_3$ thin films while maintaining film quality and crystallinity and initiate explorations into doping of the BaTiO$_3$ nanoparticles with candidate photosensitizers for selective laser absorption; Aerospace: initiate testing of the static UV laser exposure SHG detection scheme and begin modifications to laser systems for wavelength-dependent studies of the pyroelectric phase conversion process; ARL: perform electrical characterization measurements on ICB-provided functionalized BaTiO$_3$ thin-films and investigate the use of complementary MOSD techniques for the preparation of BaTiO$_3$ thin-films.
6. References


2. Sarney, Wendy L.; Little, John W.; Morse, Daniel E.; Tao, Andrea; Ould-Ely, Teyeb; Niesz, Krisztian; Livingston, Frank E. Progress in Biologically-Inspired Pyroelectric Materials Growth for Improved Sensitivity, Lower-Cost Uncooled IR Detector Focal-Plane Arrays; ARL-TR-4770; U.S. Army Research Laboratory; Adelphi, MD, April 2009.


## List of Symbols, Abbreviations, and Acronyms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>ARL</td>
<td>U.S. Army Research Laboratory</td>
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<tr>
<td>BaTiO₃</td>
<td>Barium Titanium Oxide</td>
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<td>BST</td>
<td>barium strontium titanate</td>
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<tr>
<td>CCD</td>
<td>charge-coupled device</td>
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<tr>
<td>FOM</td>
<td>figure of merit</td>
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<tr>
<td>ICB</td>
<td>Institute for Collaborative Biotechnologies</td>
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<tr>
<td>IR</td>
<td>infrared</td>
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<tr>
<td>LiNbO₃</td>
<td>Lithium Niobate</td>
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<tr>
<td>MOSD</td>
<td>metal organic solution deposition</td>
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<tr>
<td>PFM</td>
<td>piezoelectric force microscopy</td>
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<td>PVA</td>
<td>polyvinyl alcohol</td>
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<td>Sb₂Te₃</td>
<td>Antimony Telluride</td>
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<td>SHG</td>
<td>second harmonic generation</td>
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<td>UV</td>
<td>ultraviolet</td>
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<td>XRD</td>
<td>x-ray diffraction</td>
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<td>year one, quarter four</td>
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