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High-frequency thermal-electrical cycles for pyroelectric energy conversion

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We report thermal to electrical energy conversion from a 150 nm thick BaTiO3 film using pyroelectric cycles at 1 kHz. A microfabricated platform enables temperature and electric field control with temporal resolution near 1 μs. The rapid electric field changes as high as 11 × 105 kV/cm-s, and temperature change rates as high as 6 × 105 K/s allow exploration of pyroelectric cycles in a previously unexplored operating regime. We investigated the effect of phase difference between electric field and temperature cycles, and electric field and temperature change rates on the electrical energy generated from thermal-electrical cycles based on the pyroelectric Ericsson cycle. Complete thermodynamic cycles are possible up to the highest cycle rates tested here, and the energy density varies significantly with phase shifts between temperature and electric field waveforms. This work could facilitate the design and operation of pyroelectric cycles at high cycle rates, and aid in the design of new pyroelectric systems. © 2014 AIP Publishing LLC.

[I. INTRODUCTION]

Waste heat accounts for more than half the energy produced in the world.1 A significant fraction of this rejected energy is at low temperature which is difficult to harvest efficiently. Thermolectric devices that convert spatial temperature variations into electrical energy are one solution to this problem.2 However, the relatively low efficiencies of thermolectric materials, along with constraints on operating environments have prevented widespread adoption.3 Other solutions include heat exchangers that convert thermal energy into useful work using a liquid or gas based thermodynamic cycle.4 The moving parts and fluid flows required in these systems, however, cannot be easily scaled to small sizes or rapid cycle rates.

Pyroelectric energy conversion utilizes the temperature dependence of electric displacement of polar materials to convert temperature fluctuations into electrical energy.5–8 Initial first principle studies predicted electricity generation from heat using pyroelectric materials to be infeasible due to energy conversion efficiencies less than 1%.9,10 More recent studies have, however, found energy densities up to 1 J/cm3 and efficiencies as high as 5.4% of the Carnot limit using thermodynamic cycles that utilize temperature as well as electric field dependence of the electric displacement of pyroelectric materials.11,12 The four-step pyroelectric Ericsson cycle is one such thermodynamic cycle that consists of two isothermal and two isoelectric processes.12,13 Pyroelectric energy conversion using such thermal-electrical cycles can be particularly attractive for systems with temperature fluctuations, such as internal combustion engines and power electronics that produce low-quality, low-temperature waste heat.14,15

Investigation of pyroelectric energy conversion using thermal-electrical cycles requires a setup that can simultaneously vary the temperature and electric field across the pyroelectric material in time. Published research on pyroelectric energy conversion has commonly used oil baths or pumping fluid to generate temperature oscillations in bulk samples, typically at frequencies less than 1 Hz.11,13,16–19 Other methods of temperature control used thermal contact with hot and cold metal blocks or switchable liquid interfaces.20,21 Desired electric fields required application of voltages as high as a few kV across the thick samples which are impractical for most applications.17,22 Use of bulk samples with large thermal mass and coarse thermal and electrical control limited the investigation of pyroelectric energy conversion to slow changes in temperature and electric field. While some published studies have investigated the effect of temperature oscillation amplitude, electric field range, and cycle frequency on pyroelectric energy conversion, very few have examined the effect of temporal variations in temperature and applied electric field.11,23,24

This paper presents an analysis of the transient thermal and electrical operation of pyroelectric energy conversion cycles with the goal of maximizing the output electrical energy density. We developed a microfabricated platform consisting of a 150 nm thick BaTiO3 film that allows simultaneous, high-frequency thermal and electrical cycling. The device enables investigation of the energy conversion process in the pyroelectric film in response to arbitrary variations in temperature and electric field with microsecond...
temporal control. We studied the effect of phase shifts between heating and electric field at a cycle frequency of 1 kHz, electric field change rates between $1.42 \times 10^5$ kV/cm-s and $11.33 \times 10^5$ kV/cm-s, and temperature change rates around $6 \times 10^5$ K/s on the pyroelectric energy conversion process. Thermal-electrical cycles obtained using different temperature and electric field profiles are compared with the pyroelectric Ericsson cycle.

II. PYROELECTRIC ENERGY CONVERSION TEST PLATFORM

Figure 1 shows the construction and thermal-electrical operation of the pyroelectric energy conversion test platform. The device consists of a BaTiO$_3$ thin-film capacitor with electrical access to top and bottom electrodes. A gold strip placed above the pyroelectric capacitor serves as the resistive heater. A high resistivity SiO$_2$ layer, sandwiched between the top electrode and heater strip, electrically insulates the pyroelectric film and minimizes interference from the heating voltage.

The pyroelectric film was integrated in the test platform using standard microfabrication techniques. Figure 1(a) shows the schematic of the device. The substrate was 5 mm $\times$ 5 mm $\times$ 0.5 mm GdScO$_3$ (110). The films were 40 nm SrRuO$_3$ and 150 nm BaTiO$_3$, and were deposited using pulsed laser deposition. The choice of a GdScO$_3$ single crystal substrate was based on its excellent structural, chemical, and thermal compatibility with BaTiO$_3$. These two layers were then selectively etched by ion milling using a hard-baked photoresist mask to define the bottom electrode and active material of the ferroelectric capacitor. Next, a sacrificial MgO mask was deposited using photoresist lift-off and e-beam evaporation to define the top electrode. The 80 nm thick top SrRuO$_3$ electrode was fabricated using pulsed laser deposition followed by an MgO lift-off step in phosphoric acid. Then, a 150 nm thick layer of SiO$_2$ was deposited over the 500 $\mu$m $\times$ 20 $\mu$m ferroelectric capacitor using plasma enhanced chemical vapor deposition. Freon reactive ion etching of the SiO$_2$ layer and manual scratching of the BaTiO$_3$ layer were used to access the top and bottom electrodes of the capacitor. Finally, we fabricated the 10 $\mu$m wide, 440 $\mu$m long heater strip and contact pads over the SiO$_2$ layer using sputter deposition of 10 nm Cr/100 nm Au followed by a photoresist lift-off process.

Pyroelectric energy conversion cycles rely upon thermal as well as electrical response of the electric displacement. Figure 1(c) shows an illustration of the four-step pyroelectric Ericsson cycle A-B-C-D alongside the corresponding isothermal D-E loops at the maximum and minimum temperatures. A typical pyroelectric Ericsson cycle comprises two isothermal processes, A$\rightarrow$B and C$\rightarrow$D, and two isoelectric processes, B$\rightarrow$C and D$\rightarrow$A. Starting from A, the out-of-plane electric field is first increased at low temperature, increasing the electric displacement. Then, the temperature is increased while the electric field is held constant at a high value, resulting in a decrease in the electric displacement. Next, the electric field is reduced to its low value at high temperature, again...
decreasing the electric displacement. Finally, the clockwise cycle is completed by lowering the temperature to its original value at a constant low electric field. The area of the cycle A-B-C-D represents the total electrical energy density output from the pyroelectric cycle.

A. Electrical characterization

The field-dependence of the BaTiO$_3$ film electric displacement was characterized using room temperature displacement-electric field (D-E) loops shown in Figure 2(a). A 1 kHz triangular voltage waveform was applied to the top SrRuO$_3$ electrode. The resulting current was measured from the bottom SrRuO$_3$ electrode and the film electric displacement change was determined using the virtual ground method. The Curie temperature of the ferroelectric film is about 400°C. All measurements were performed below the Curie temperature, where the film electric displacement decreases with increase in temperature as shown in Figure 1(c).

We characterized the temperature dependence of ferroelectric electric displacement by measuring the pyroelectric current from the device generated due to sinusoidal heating of the thin film. Figure 2(b) shows the pyroelectric coefficient of the BaTiO$_3$ film measured as a function of out-of-plane electric field using a lock-in amplifier based 2o method. A sinusoidal voltage at 1 kHz applied to the heater strip causes a temperature oscillation in the BaTiO$_3$ film at 2 kHz. The temperature fluctuation generates pyroelectric current which was measured from the bottom electrode. The voltage on the top electrode was simultaneously varied with the heating bias at 0.1 Hz to obtain the field-dependence of the pyroelectric response (see supplementary material for details). Measurements were performed at constant background temperatures of 20 and 100°C, controlled using a bulk heating stage. The pyroelectric coefficient was calculated by dividing the pyroelectric current, measured at the temperature oscillation frequency, with the capacitor area and the calculated time rate of change of temperature. The measured pyroelectric coefficient shown in Figure 2(b) increases as the background temperature increases from 20 to 100°C, as is expected for a ferroelectric below the Curie temperature.

B. Pyroelectric film temperature

This section describes the calculation of amplitude of temperature change induced by resistive heating of the gold strip and variation of film temperature with time. For pyroelectric characterization of the BaTiO$_3$ film, we estimated the amplitude of sinusoidal temperature oscillation using a one-dimensional heat diffusion equation in radial coordinates. The gold strip is modeled as a line-source of heat carrying electrical current at frequency $\omega$, over a semi-infinite volume. This current causes a temperature oscillation in the sample at a frequency $2\omega$ due to resistive heating of the metal strip. The frequency-dependent temperature oscillation amplitude of the semi-infinite substrate due to the line heat source of width $2b$ and length $l$ is given by

$$\Delta T_s = \frac{P}{4\pi \Lambda_s} \int_0^\infty \frac{\sin^2(kb)}{(kb)^2(k^2 + q^2)^{1/2}} dk,$$

where $q = (Df/2\omega)^{1/2}$ is the thermal penetration depth, $j = \sqrt{-1}$, $P$ is the input electrical power, $D$ is the substrate thermal diffusivity, and $\Lambda_s$ is the substrate thermal conductivity. The thin films between the metal strip and substrate each add a frequency-independent temperature oscillation given by

$$\Delta T_f = \frac{P}{4\Lambda_f} \frac{t}{2b},$$

where $t$ is the film thickness and $\Lambda_f$ is the film thermal conductivity. The temperature amplitude of the BaTiO$_3$ film, calculated at the mid-point of the pyroelectric film thickness, is given by $\Delta T = \Delta T_s + \Delta T_{SrRuO3} + \frac{1}{2} \Delta T_{BaTiO3}$. The contribution to $\Delta T$ from thin films was significantly smaller than the substrate contribution since the...
films were only ~100 nm thick. Table I shows the thermal property values used for these calculations.\textsuperscript{33} The $\omega$ method was used to measure the room temperature thermal conductivity of the GdScO$_3$ substrate.\textsuperscript{31} The volumetric heat capacity of the substrate was assumed equal to that of the SrTiO$_3$ single crystalline substrate, whose crystal structure and density are similar to that of GdScO$_3$.\textsuperscript{34} The error in the $\Delta T$ calculation due to the SiO$_2$ layer sandwiched between the BaTiO$_3$ film and gold heater was estimated to be <4%, and the error in the $\Delta T$ calculation due to the interfacial thermal resistance (assumed $2 \times 10^{-8}$ m$^2$K/W)\textsuperscript{35} was estimated to be <1%.

We measured the change in BaTiO$_3$ film temperature with time using the temporal pyroelectric response of the film under no applied bias. Figure 3 shows $\Delta T$ profiles for different heating voltage waveforms presented in this paper. The pyroelectric current from the BaTiO$_3$ film was measured from the bottom SrRuO$_3$ electrode, while the top SrRuO$_3$ electrode was grounded. The pyroelectric current depends upon the rate of change of temperature with time ($t$) and is given by $i_p = pA(dT/dt)$, where $p$ is the pyroelectric coefficient and $A$ is the area of the capacitor. We used a constant $p = -20 \mu$C/m$^2$K to evaluate the average $\Delta T(t)$ of the pyroelectric film by integrating $i_p$ with respect to time. The magnitude of $\Delta T$ thus obtained was implicitly calculated from the heat diffusion model described above; variation of $\Delta T$ in time was measured from the pyroelectric response of the thin film.

### III. RESULTS AND DISCUSSION

We used the microfabricated platform to control the temperature and electric field, and monitored the energy conversion cycles by measuring the displacement changes induced due to the pyroelectric and dielectric response of the BaTiO$_3$ thin film. All measurements reported in this section were done at a background temperature of 20°C and the cycle frequency was 1 kHz. Results presented here show how the rates of temperature change, electric field switching and phase lag between thermal and electrical cycles affect the electrical energy density. The phase shift between $\Delta T$ and $\Delta E$ waveforms determines the film displacement at which the isothermal process ends and isoelectric process begins. Different temperature and electric field change rates, on the other hand, lead to processes that are no longer isothermal or isoelectric. In addition, varying $\Delta T$ and $\Delta E$ rates also influences the heat transfer through the sample and dielectric response of the pyroelectric film which affects energy conversion.

#### A. $\Delta T$-$\Delta E$ phase difference

Energy conversion using pyroelectric cycles depends upon the synchrony between thermal and electrical cycles. Figure 4 shows the time-varying heating voltage, temperature change of the BaTiO$_3$ film, three phase-shifted out-of-plane electric field profiles, measured electric current, and the resulting film electric displacement change. In a traditional pyroelectric Ericsson cycle, the electric field switches at the maximum and minimum temperatures to obtain the highest electric displacement change and energy density. The temperature is held constant while the electric field changes. In the measurements shown in Figure 4, identical heating bias waveforms were used to obtain the same $\Delta T$ variation in the pyroelectric film with time. The electric field switches between 200 and 183 kV/cm at a $5.67 \times 10^5$ kV/cm-s ramp rate. The high electric field ramp rate ensures that the temperature is nearly constant. However, unlike the Ericsson cycle, the electric field does not necessarily switch at the highest and lowest temperatures, and depends on the phase of the electric field profile relative to the heating bias profile. Results are shown for phase angles $-42^\circ$, $0^\circ$, and $42^\circ$, where zero phase corresponds to the case when the electric field switches at the mid-point of the heating bias maxima and minima. For $-42^\circ$ phase angle, the electric field switches (at $t = 0.1$ ms) before the corresponding temperature extreme is reached. The $0^\circ$ electric field profile switches at the heating bias extremes which do not coincide with the temperature extremes as shown by the $\Delta T$ profile. For the profile with $42^\circ$ phase angle, the electric field changes from high to low (at $t = 0.3$ ms) near the maximum temperature and from low to high (at $t = 0.8$ ms) before the minimum temperature is reached.

Different thermal-electrical cycles shown in Figure 5(a) for different phase angles are a result of staggered electric field waveforms, and dissimilar heating and cooling profiles.

### Table I. Material properties used for thermal modeling.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity (W/m K)</th>
<th>Heat capacity (J/m$^3$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEVCD SiO$_2$</td>
<td>1.1</td>
<td>...</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>4.8</td>
<td>...</td>
</tr>
<tr>
<td>SrRuO$_3$</td>
<td>3</td>
<td>...</td>
</tr>
<tr>
<td>GdScO$_3$</td>
<td>2.4</td>
<td>$2.7 \times 10^6$</td>
</tr>
</tbody>
</table>

![Image](image-url)
For negative phase angles (shown in blue), the temperature first increases and then decreases at constant low electric field which results in a corresponding decrease followed by an increase in the electric displacement that does not contribute to electrical work out. Maximum electrical energy might be expected for the case when the electric field switches near the highest and lowest temperatures, as is the case for electric field profile phase-shifted by $42^\circ$ (shown in red). Instead, the maximum energy density is observed for phase angles $0^\circ$ or $21^\circ$, as shown in Figure 5(b), where the electric field decreases before the maximum temperature is reached. This counterintuitive result is a consequence of the competition between decrease in displacement due to a decrease in electric field and increase in displacement as the temperature decreases for the $42^\circ$ phase profile. The finite dielectric response time, which depends on the electric field ramp rate, causes the field-driven reduction in displacement to coincide with the counteracting pyroelectric response during the initial cooling phase during which the temperature decreases at the fastest rate and the pyroelectric contribution to electric displacement is highest.

B. Electric field ramp rate

The electric field ramp rates determine the change in film temperature while the electric field varies since the temperature of the pyroelectric film changes continuously in our setup. Electric field switches nearly instantaneously at high ramp rates and the process is nearly isothermal, but the temperature-change-driven pyroelectric contribution can be significant for low electric field change rates when the processes are no longer isothermal. Figure 6 shows the time-varying heating voltage, estimated $\Delta T$, applied electric field with different ramp rates, measured electric current, and the resulting film displacement change. The electric field transitions from high to low at the mid-point of the heating bias extrema corresponding to $0^\circ$ phase angle for all measurements. The $\Delta D$ increase due to a rise in electric field (at $t = 0.7$ ms) is about the same for all cases but the decrease in $\Delta D$ (at $t = 1.2$ ms) is different for different ramp rates. While the dielectric contribution to the displacement change is about the same for an increase or decrease in electric field, the pyroelectric contribution changes depending on the rate of change of temperature. When the electric field increases,
the temperature is decaying slowly as heat is lost to the environment and the pyroelectric contribution is negligible. But when the electric field decreases, the temperature is increasing rapidly with the rising heating power, producing a significant pyroelectric-effect-induced displacement change.

Figure 7 shows the thermal-electrical cycles and measured energy densities for different electric field ramp rates. The isothermal condition is valid for the low temperature top branch of the clockwise cycles as the electric field increases from 183 kV/cm to 200 kV/cm irrespective of the electric field change rate since the accompanying reduction in film temperature is not significant. But the duration over which electric field decreases affects the bottom branch of the cycles as the temperature is changing simultaneously. For the slowest rate of \(1.42 \times 10^5 \text{ kV/cm-s}\) (shown in blue), a decrease in electric field is initially accompanied by a rapid increase in temperature which results in a sharp drop in the electric displacement near 200 kV/cm. However as the electric field approaches 183 kV/cm, the temperature begins to decrease which increases the electric displacement. The temperature-driven increase in \(\Delta D\) counteracts the field-driven decrease in electric displacement that eventually increases the total \(\Delta D\).

The overall energy density, however, is nearly independent of the field change rate since the total temperature change is the same resulting in an identical pyroelectric response superimposed over the dielectric response which does not produce any electrical work by itself.

C. Temperature change ramp rate

We controlled the duration and rate of heating and cooling of the BaTiO\(_3\) film by changing the slope of the heating bias versus time. Figure 8 shows five heating voltage profiles with different ramp rates, corresponding \(\Delta T\), applied electric field, measured electric current, and resulting film electric displacement change. The heating bias was increased linearly from 0 V to 2.5 V at varying rates, held constant at 2.5 V for 0.12 ms, and then decreased to 0 V. There is no temperature change when the voltage along the length of gold heater strip is zero. As the heating voltage \(V\) increases linearly, the temperature increases in proportion with the input heating power which scales as \(V^2\). The temperature continues to increase when the heating bias is held constant due to the sample heat capacity. The maximum temperature is reached just as heating voltage begins to decrease (at \(t = 0.6\) ms).
Thereafter, the sample is convectively cooled but the cooling rate is less than the heating rate and is dependent on the rate of heat transfer to the environment. A steeper heating voltage profile corresponds to a shorter heating period which results in a lower average temperature of the film due to non-uniform heating.\textsuperscript{24} The electric field changes isothermally since the ramp rate is quite high at $5.67 \times 10^5 \text{kV/cm-s}$, and with phase angle of $0^\circ$ relative to the heating bias. The displacement change due to a change in electric field is about the same for all heating profiles, but higher heating bias ramp rates result in smaller $\Delta D$ due to lower $\Delta T$ amplitudes as it decreases the pyroelectric contribution.

Figure 9 shows the thermal-electrical cycles and corresponding energy densities for different heating voltage ramp rates. The average temperature change ramp rate was calculated for each heating profile by dividing the maximum $\Delta T$ with the duration of temperature increase. Steeper heating voltage profiles resulted in lower $\Delta T$ which reduced the magnitude of displacement change due to the pyroelectric effect but did not alter the temperature change rates significantly. The lower average film $\Delta T$ reduced the total displacement change and electrical energy density. We also tried to achieve the same $\Delta T$ for the five heating voltage profiles shown here by varying the maximum applied heating bias to the extent possible, but did not observe any noticeable temperature-change-rate dependence of the output electrical energy density. This observation is consistent with previous studies which reported no significant dependence of the pyroelectric coefficient on the heating frequency.\textsuperscript{30} While we did not observe a dependence of output energy density on the temperature-change-rate itself, we did notice the effect of heat transfer rate on $\Delta T$ and the generated electrical energy. These results highlight the importance of using thin films with small thermal mass and its placement near the heat source with rapid temperature fluctuations. In addition, design of the energy conversion platform should enhance conduction heat transfer within the platform as well as rapid convective cooling from the environment.

IV. CONCLUSION

In summary, we investigated the effect of temporal variations in temperature and electric field on pyroelectric...
energy conversion using a microfabricated platform consisting of a 150 nm thick BaTiO$_3$ film. The platform allowed microsecond control of the temperature and electric field which enabled thermal-electrical cycles at a 1 kHz frequency. With the temperature and electric field profiles for the pyroelectric Ericsson cycle as the starting point, we studied the effect of three parameters: (1) the phase between $\Delta T$ and $\Delta E$ waveforms, (2) $\Delta E$ change rate, and (3) $\Delta T$ change rate. Maximum energy density was obtained when the electric field is switched from its maximum to minimum value before the highest temperature is reached rather than exactly at the $\Delta T$ maxima owing to the finite response time of the dielectric material. The electric field and $\Delta T$ change rates had no direct effect on the energy density, but higher $\Delta T$ change rates cause non-uniform heating of the pyroelectric film which reduced the measured energy density. We measured an energy density of around 3 mJ/cm$^3$ and power density of 3 W/cm$^3$ at representative electric field change rate of 5.67 $\times$ 10$^5$ kV/cm-s and $\Delta T$ change rate of 6.27 $\times$ 10$^5$ K/s from the BaTiO$_3$ films.

This work represents a significant improvement over earlier studies that were typically limited to pyroelectric cycles at frequencies less than 1 Hz due to a lack of precise electro-thermal control and large thermal mass of the pyroelectric materials used. Using the approach outlined in this paper, it should be possible to replicate temperature variations in real-world systems and design thermal-electrical cycles to maximize electrical energy output. The results presented provide a framework for optimizing the energy conversion performance of pyroelectric cycles in systems with high frequency temperature fluctuations, such as internal combustion engines and power electronics. We hope that this work will enable the use of pyroelectric materials for future waste heat harvesting applications.

ACKNOWLEDGMENTS

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1Lawrence Livermore National Laboratory. Energy International.
22M. Ikura, Ferroelectrics 267, 403 (2002).
27See supplementary material at http://dx.doi.org/10.1063/1.4409193 for BaTiO$_3$ film deposition and characterization, dielectric constant measurement versus temperature, and $D$-E and pyroelectric measurements.