A novel thermally biased mechanical energy conversion cycle

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This paper demonstrates a new power cycle for direct conversion of mechanical energy into electrical energy under a thermal bias. The cycle consisted sequentially of (i) an electric poling process under zero stress, (ii) an isoelectric process consisting of applying a uniaxial compressive stress \(\sigma_H\) followed by (iii) an electric de-poling process under constant compressive stress, and finally (iv) an isoelectric process consisting of removing the compressive stress. The new cycle was performed at constant bias-temperature \(T_b\). It was demonstrated on [001]-poled 0.72PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\)-0.28PbTiO\(_3\) single crystals. The power density increased with increasing cycle frequency and compressive stress for frequency up to 1 Hz. Maximum energy and power densities of 44 J/l/cycle and 44 W/l were achieved at 1 Hz for bias-temperature \(T_b\) of 80 °C and electric field cycled between 0.2 and 0.8 MV/m with compressive stress \(\sigma_H = 25.13\) MPa. This was attributed to a tetragonal-monoclinic-orthorhombic phase transition sequence. The material efficiency reached up to 87% and exceeded that of a similar thermomechanical power cycle performed on pyroelectric material. Finally, a physical model predicting the power density was derived and yielded accurate predictions of experimental data for all bias-temperatures considered and cycle frequency up to 1 Hz. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4846735]

I. INTRODUCTION

Rising awareness in sustainable and efficient energy technologies has stimulated efforts in scavenging thermal and mechanical energies. In 2012, an estimated 60% of the energy consumed in the United States was rejected mainly in the form of low grade waste heat.\(^1\) Methods for harvesting low grade waste heat include Stirling engines,\(^2\) organic Rankine cycles,\(^3\) and thermoelectric devices.\(^4\) Stirling engines and organic Rankine cycles convert thermal energy into mechanical energy. Thermoelectric devices make use of the Seebeck effect to convert a steady-state temperature difference at the junction of two dissimilar metals or semiconductors directly into electrical energy.\(^4\) Waste mechanical energy in the form vibrations, shocks, or strains can also be harvested.\(^6\) Methods for direct mechanical to electrical energy conversion include electromagnet, electrostatic, and electroactive polymers generators.\(^6\) Electromagnetic generators rely on time-varying magnetic field caused by the relative motion between a magnet and a coil to generate electrical energy.\(^6\) Electrostatic generators rely on temporal variations in the capacitance of a structure caused by mechanical motion to generate electrical energy.\(^6\) By contrast, electroactive polymers generate electrical energy in response to a change in shape due to mechanical deformations.\(^6\) Alternatively, ferroelectric materials have the ability to convert both thermal and mechanical energy directly into electricity. They possess a temperature and stress-dependent polarization and constitute a subclass of pyroelectric materials themselves a subclass of piezoelectric materials.\(^7\)

This study presents a novel cycle performed on ferroelectric materials that converts time-dependent compressive stress oscillations under constant bias-temperature directly into electricity. This new cycle was demonstrated on commercially available [001]-poled lead magnesium niobate-lead titanate 0.72PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\)-0.28PbTiO\(_3\) (PMN-28PT) single crystals.

II. BACKGROUND

A. Dielectric hysteresis loops

Figure 1(a) presents the isothermal bipolar hysteresis curves (\(D-E\) loops) in the electric displacement \(D\) versus electric field \(E\) diagram for a typical ferroelectric material at constant temperature \(T_b\) under compressive stress \(\sigma_H\) equal to 0 and \(\sigma_H\). The \(D-E\) loops under any compressive stress traveled in the counter-clockwise direction. The electric displacement \(D\) of a ferroelectric material at temperature \(T\) under electric field \(E\) and compressive stress \(\sigma\) can be expressed as\(^7,8\)

\[
D(E,T,\sigma) = \varepsilon_0 \varepsilon_r(T,\sigma) E + P_s(T,\sigma),
\]

where \(\varepsilon_0\) is the vacuum permittivity equal to \(8.854 \times 10^{-12}\) F/m and \(\varepsilon_r(T,\sigma)\) is the large-field dielectric constant of the material at temperature \(T\) and under stress \(\sigma\). The saturation polarization \(P_s(T,\sigma)\) is equal to the electric displacement in the linear fit of \(D\) versus \(E\) at large-field extrapolated to zero electric field\(^9\) and the slope of this linear fit corresponds to the product \(\varepsilon_0 \varepsilon_r(T,\sigma)\).

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undergoes a rhombohedral-monoclinic (R-M) phase transition at 0.2 MV/m. In addition, for [001] PMN-32PT, the electric field corresponding to the phase boundary temperature decreases to 85 °C. This phase boundary temperature is represented by the grey area enclosed between 1–2–3–4. The electric field versus temperature (E-T) phase diagram of PMN with h001 phase occurs in [001] PMN-32PT under large uniaxial stress and small electric field. In addition, the authors found that rhombohedral to orthorhombic (R-O) phase transition occurred with the application of compressive stress at temperatures less than 60 °C. However, at temperatures greater than 60 °C, a direct monoclinic \( M_h \) to orthorhombic (\( M_{h-o} \)) phase transition occurred upon application of a compressive stress. Furthermore, the \( O-M_h \) and \( M_{h-o} \) phase transitions occurring at high temperature exhibit small hysteresis characteristic of continuous polarization rotation. This suggests that there are continuous rather than abrupt phase transitions and multiple phases may coexist. Finally, the phase boundaries in PMN-xPT are frequency-dependent typical of relaxor behavior. For example, Chen et al. found the peak of the dielectric constant as a function of temperature to be 27.5 and 33 mol. % and determined that PMN-28PT was the preferred composition for transducer, sensor, and actuator applications due to its advantageous piezoelectric properties. Previous power cycles on ferroelectric materials convert temporal temperature oscillations directly into electricity. This cycle consists of two isothermal and two isobaric processes in the D-E diagram and is analogous to the Ericsson cycle, in which a working fluid undergoes two isothermal and two isobaric processes in the pressure-volume diagram. In addition, time-dependent mechanical deformations imposed on piezoelectric materials connected to an external electrical load can generate electricity. These mechanical deformations can be small deflections at high frequency due to vibrations or can be large strains due to the application of large cyclic compressive stress. Furthermore, the thermomechanical power cycle demonstrated by McKinley et al. performed on ferroelectric materials utilizes time-dependent temperature and compressive stress oscillations to convert both thermal and mechanical energies directly into electricity. The first process consists of an isothermal increase in electric field from \( E_L \) to \( E_H \) at \( T_{cold} \), performed in the absence of compressive stress. The second process corresponds to simultaneously compressing the sample under compressive stress \( \sigma_H \) and heating it up to \( T_{hot} \). The third process consists of an isothermal decrease in electric field from \( E_H \) to \( E_L \) at \( T_{hot} \) under compressive stress \( \sigma_H \). Finally, the fourth process closes the cycle by simultaneously cooling the sample to \( T_{cold} \) and removing the loading under constant electric field \( E_L \). This cycle was demonstrated on 3 mm thick (001)-oriented PMN-28PT single crystals and achieved larger energy and power densities than the Olsen cycle for lower operating temperatures. This was realized (i) by combining both piezoelectric and pyroelectric energy conversion and (ii) by increasing the cycle frequency by quickly forcing the material into a specific state using mechanical stress instead of heating and cooling which are inherently slow. However, the heat input still dominated the energy consumption of the thermomechanical power cycle at low cycle frequencies and negatively affected the material efficiency.

**B. Single crystal PMN-xPT**

Single crystal PMN-xPT possesses large piezoelectric constants near the morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal phases. This MPB corresponds to \( x \) ranging between 27.5 and 33 mol. %. Zhou et al. compared the performance of PMN-xPT with \( x \) equal to 28, 30, and 32 mol. % and determined that PMN-28PT was the preferred composition for transducer, sensor, and actuator applications due to its advantageous piezoelectric properties in a broad temperature range. The electric field versus temperature (E-T) phase diagram of (001) PMN-28PT under zero stress indicates that the material has a monoclinic-tetragonal (\( M-T \)) phase boundary around 90 °C under zero electric field. This phase boundary temperature decreases to 85 °C and 70 °C as the electric field increases from 0 to 0.2 and 0.8 MV/m, respectively. At room temperature under zero electric field, the material is in the rhombohedral phase and undergoes a rhombohedral-monoclinic (R-M) phase transition at 0.2 MV/m. In addition, for [001] PMN-32PT, the electric field corresponding to the R-M and M-T phases boundaries increases with increasing uniaxial compressive stress for a given temperature. McLaughlin et al. found that a depolarized orthorhombic (O) phase occurs in [001] PMN-32PT under large uniaxial stress and small electric field. In addition, the authors found that rhombohedral to orthorhombic (R-O) phase transition occurred with the application of compressive stress at temperatures less than 60 °C. However, at temperatures greater than 60 °C, a direct monoclinic \( M_h \) to orthorhombic (\( M_{h-o} \)) phase transition occurred upon application of a compressive stress. Furthermore, the \( O-M_h \) and \( M_{h-o} \) phase transitions occurring at high temperature exhibit small hysteresis characteristic of continuous polarization rotation. This suggests that there are continuous rather than abrupt phase transitions and multiple phases may coexist. Finally, the phase boundaries in PMN-xPT are frequency-dependent typical of relaxor behavior. For example, Chen et al. found the peak of the dielectric constant as a function of temperature to be 27.5 and 33 mol. % and determined that PMN-28PT was the preferred composition for transducer, sensor, and actuator applications due to its advantageous piezoelectric properties. Previous power cycles on ferroelectric materials convert temporal temperature oscillations directly into electricity. This cycle consists of two isothermal and two isobaric processes in the D-E diagram and is analogous to the Ericsson cycle, in which a working fluid undergoes two isothermal and two isobaric processes in the pressure-volume diagram. In addition, time-dependent mechanical deformations imposed on piezoelectric materials connected to an external electrical load can generate electricity. These mechanical deformations can be small deflections at high frequency due to vibrations or can be large strains due to the application of large cyclic compressive stress. Furthermore, the thermomechanical power cycle demonstrated by McKinley et al. performed on ferroelectric materials utilizes time-dependent temperature and compressive stress oscillations to convert both thermal and mechanical energies directly into electricity. The first process consists of an isothermal increase in electric field from \( E_L \) to \( E_H \) at \( T_{cold} \), performed in the absence of compressive stress. The second process corresponds to simultaneously compressing the sample under compressive stress \( \sigma_H \) and heating it up to \( T_{hot} \). The third process consists of an isothermal decrease in electric field from \( E_H \) to \( E_L \) at \( T_{hot} \) under compressive stress \( \sigma_H \). Finally, the fourth process closes the cycle by simultaneously cooling the sample to \( T_{cold} \) and removing the loading under constant electric field \( E_L \). This cycle was demonstrated on 3 mm thick (001)-oriented PMN-28PT single crystals and achieved larger energy and power densities than the Olsen cycle for lower operating temperatures. This was realized (i) by combining both piezoelectric and pyroelectric energy conversion and (ii) by increasing the cycle frequency by quickly forcing the material into a specific state using mechanical stress instead of heating and cooling which are inherently slow. However, the heat input still dominated the energy consumption of the thermomechanical power cycle at low cycle frequencies and negatively affected the material efficiency.
D. Material efficiency

The material efficiency of a power cycle is typically defined as the ratio of the energy produced by the material to the energy consumed by performing the cycle. Overall, the material efficiency of the thermomechanical cycle can be expressed as

$$\eta = \frac{N_D}{Q_{in} + W_{in}},$$

where $N_D$ is the electrical energy produced per unit volume of the material per cycle while $Q_{in}$ and $W_{in}$ are the thermal energy and mechanical work provided per unit volume of the material during the cycle. The area enclosed by the cycle in the $D$-$E$ diagram corresponds to the generated energy density $N_D$. It is expressed in J/l/cycle (1 J/l/cycle = 1 kJ/m$^3$/cycle) and defined as

$$N_D = \int E dD.$$  

The power density $P_D$ is the amount of energy generated per unit time per unit volume of pyroelectric material. It is expressed in W/l (1 W/l = 1 kJ/m$^3$) and defined as $P_D = N_D f$ where $f$ is the cycle frequency. The overall cycle frequency (in Hz) is defined as $f = (\tau_{12} + \tau_{23} + \tau_{34} + \tau_{41})^{-1}$ with $\tau_{ij}$ corresponding to the duration of process $i-j$.

The thermal energy consumed per unit volume of material during the cycle may be expressed as

$$Q_{in} = \int \rho c_p(T) dT,$$

where $c_p(T)$ and $\rho$ are the specific heat and density of the ferroelectric material expressed in J/kg K and kg/m$^3$, respectively. In addition, the mechanical work $W_{in}$ per unit volume of material can be expressed as

$$W_{in} = \int \sigma(x) dx,$$

where $x$ represents the strain in the longitudinal direction parallel to the polarization. For ferroelectric materials undergoing phase transitions, the relationship between $\sigma$ and $x$ is typically non-linear and should be estimated from stress-strain curves.

Here, we present a new cycle using variable uniaxial compressive stress in addition to electric field cycling but at a fixed temperature. We hope that this new cycle can achieve larger cycle efficiency than the thermomechanical cycle by reducing the required heat input. Single crystal PMN-28PT was chosen to demonstrate the thermomechanical power cycle for its strong piezoelectric response in a broad temperature range. Single crystal samples of PMN-28PT were purchased from Sinoceramics, LLC. The samples were 5 × 5 × 3 mm$^3$ and poled in the [001]-direction. The two 5 × 5 mm$^2$ faces of each sample were entirely coated with Cr/Au electrodes. Two strain gages were mounted to opposite 5 × 3 mm$^2$ faces of one of the samples to measure longitudinal strain (parallel to the polarization direction).

B. Experiments

1. Samples

PMN-28PT was chosen to demonstrate the thermomechanical power cycle for its strong piezoelectric response in a broad temperature range. Single crystal samples of PMN-28PT were purchased from Sinoceramics, LLC. The samples were 5 × 5 × 3 mm$^3$ and poled in the [001]-direction. The two 5 × 5 mm$^2$ faces of each sample were entirely coated with Cr/Au electrodes. Two strain gages were mounted to opposite 5 × 3 mm$^2$ faces of one of the samples to measure longitudinal strain (parallel to the polarization direction).

2. Experimental setup

The experimental setup included an electrical and a thermomechanical subsystem. The electrical subsystem was a Sawyer-Tower circuit identical to that used in our previous studies that simultaneously measured electric field and electric displacement. The subsystem consisted of a spring return air cylinder ( McMaster-Carr 6498K252) vertically actuated using compressed air at a maximum pressure of 469 kPa. A 24 V DC solenoid valve was used to control the extension and contraction of the cylinder rod applying pressure on the sample between two copper rods. The PMN-28PT sample was sandwiched between two copper tapes used to provide electrical contact between the sample’s electrodes and the wires. A 0.14 mm thick Kapton film was used to electrically isolate the sample’s electrodes from the copper rods. The sample was placed inside an acrylic support structure submerged in a heated silicone oil bath. A 100-Watt cartridge heater was imbedded in a 1.27 cm thick aluminum plate serving as a heat source to the oil bath. A type-K thermocouple was embedded at the center of this heating block whose temperature was maintained at $T_H$ with an Omega CN-7823 proportional integral derivative (PID) temperature controller. The corresponding sample bias-temperature $T_b$ was measured by a type-K thermocouple placed on the sample. After the desired steady-state temperature was reached, this second
In addition, the new power cycle was performed at very low cycle frequency \( f \sim 0.004 \text{ Hz} \) in the servo-hydraulic test frame while the electric field, electric displacement, stress, and strain were simultaneously measured. The load frame measured the applied force ranging from 0 to 850 N corresponding to stress of 0 to 34 MPa. The energy density generated per cycle \( N_d \) was evaluated by numerically integrating experimental data for \( D \) versus \( E \) according to Eq. (3) using the trapezoidal rule. The mechanical work done per cycle \( W_m \) was evaluated by numerically integrating experimental data for \( \sigma \) versus \( x \) according to Eq. (5) using the trapezoidal rule. Finally, the material efficiency \( \eta \) given by Eq. (2) was estimated.

C. Physical modeling

Recently, Kandilian et al. developed a model to predict the energy density generated by the Olsen cycle. This model can easily be adapted to predict the power density generated by materials undergoing the present thermally biased mechanical cycle. According to Eq. (1), the large-field dielectric constant \( \varepsilon_r(T, \sigma) \) and the saturation polarization \( P_s(T, \sigma) \) are functions of both temperature and compressive stress. Assuming the \( D-E \) path of the new cycle follows that of the Olsen cycle, the power density of the new cycle at frequency \( f \) can be expressed as

\[
P_D = f(E_H - E_L) \left\{ \frac{\varepsilon_0}{2} [\varepsilon_r(T_b, 0) - \varepsilon_r(T_b, \sigma_H)] (E_H + E_L) + P_s(T_b, 0) - P_s(T_b, \sigma_H) \right\}.
\]

This model could enable the rapid determination of the power density of materials undergoing the new cycle from intrinsic dielectric properties of PMN-28PT without physically having to perform the cycle. But first, it must be validated experimentally.

IV. RESULTS AND DISCUSSION

A. Isothermal bipolar \( D-E \) loops

Figure 3 plots isothermal bipolar \( D-E \) loops measured at 0.1 Hz on [001] PMN-28PT samples for bias-temperature \( T_b \) of (a) 80°C and (b) 100°C under mechanical loading ranging between 0 and 25.13 MPa. The \( D-E \) loops were closed and consecutive \( D-E \) loops overlapped for any temperature and compressive stress considered. This indicates that leakage current through the sample was negligibly small. Figure 3 illustrates that the \( D-E \) loops gradually became slimmer with increasing compressive stress. This behavior is indicative of continuous polarization rotation and was previously observed with [001] PMN-32PT.

Figure 4 shows (a) the saturation polarization \( P_s(T, \sigma) \) and (b) the large-field dielectric constant \( \varepsilon_r(T, \sigma) \) retrieved from the isothermal bipolar \( D-E \) loops for temperatures 22, 80, and 100°C and compressive stress between 0 and 25.13 MPa. Each data point represents the average over three \( D-E \) loops. The error bars have been omitted because they
fell within the data markers. In addition, Figure 4 also shows
the piecewise cubic hermite interpolating polynomial fit of
the properties for each temperature considered. Figure 4(a)
indicates that the saturation polarization $P_s$ decreased nearly
linearly with increasing stress at 22 and 100 °C. This behav-
ior is also characteristic of continuous polarization rotation
 corresponding to continuous phase transitions.\textsuperscript{15,16} On the
other hand, at 80 °C, the saturation polarization was nearly
constant below 6.16 MPa and decreased linearly with com-
pressive stress beyond. This can be attributed to phase transi-
tion from tetragonal to monoclinic at 80 °C and compressive
stress between 6.16 and 10.38 MPa. Indeed, at 80 °C, \[001\]
PMN-28PT assumes the tetragonal phase under zero stress
and electric field above 0.4 MV/m.\textsuperscript{13} In addition, \[001\]
PMN-32PT was reported to assume the monoclinic phase at
80 °C under stress above 10 MPa and electric field below
1 MV/m.\textsuperscript{15} As stress increased from 0 to 25 MPa, the largest
change in saturation polarization occurred at 80 °C, while the
smallest change occurred at 22 °C. Figure 4(b) indicates that
the large-field relative permittivity increased with increasing
compressive stress for all temperatures considered. This
behavior is consistent with bipolar $D$-$E$ loops reported for
\[001\] PMN-30PT (Ref. 23) and \[001\] PMN-32PT (Ref. 16)
at room temperature for compressive stress up to 30 MPa.

B. Thermally biased mechanical power cycle

1. Demonstration

Figure 5 depicts, in the $D$–$E$ diagram, the new mechani-
cal power cycle performed at 1 Hz at bias-temperature
$T_b = 80^\circ C$. The electric field was cycled between $E_L = 0.2 \text{ MV/m}$ and $E_H = 0.8 \text{ MV/m}$ at $T_b = 80^\circ C$ and compressive stress between $\sigma = 0$ and $\sigma_H = 25.13 \text{ MPa}$. The power cycle was vertically displaced to match the $D$–$E$ loop at $T = 80^\circ C$ and $\sigma_H = 25.13 \text{ MPa}$.

2. Effect of temperature and compressive stress

Figure 6 shows the power density generated by the new power cycle as a function of applied compressive stress $\sigma_H$ for bias-temperature $T_b$ ranging between 22 and 100$^\circ C$. Here, the frequency was fixed at 1 Hz while the electric field was cycled between 0.2 and 0.8 MV/m. Each data point represents an average of five cycles and the error bars correspond to one standard deviation or 63% confidence interval. Figure 6 indicates that the power density increased nearly linearly with increasing $\sigma_H$ for any given bias-temperature $T_b$. For $T_b$ above 80$^\circ C$, the power density decreased and was nearly identical for 90 and 100$^\circ C$. In fact, the largest power density of 44 W/l was achieved for bias-temperature of 80$^\circ C$ with a compressive stress of 25.13 MPa. This optimum performance can be explained by the tetragonal to monoclinic to orthorhombic phase transition sequence previously discussed. On the other hand, for bias-temperatures of 90 and 100$^\circ C$, the decrease in power density was more pronounced with $\sigma_H$, indicating that the system is less efficient at higher temperatures.

Given the phase diagram of PMN-28PT reported in Ref. 13 at frequency of 10 Hz, we speculate that, at bias-temperature of 80$^\circ C$, PMN-28PT was in the tetragonal $T$ phase at both state 1 and 2 of the cycle. This is supported by the fact that (i) the coercive electric field in the $D$–$E$ loops at low frequency of 0.1 Hz was around 0.1 MV/m and (ii) the change in electric displacement between these states was small as illustrated in Figure 5. In addition, we speculate that the application of compressive stress during process 2–3 caused the sample to undergo a phase transition into the monoclinic $M_A$ phase, as suggested by the $T$-$M_A$ phase transition occurring in [001] PMN-32PT at 0.8 MV/m and 80$^\circ C$ under $\sigma = 13 \text{ MPa}$. Furthermore, the decrease in electric field during process 3–4 caused another phase transition into the depolarized orthorhombic $O$ phase. This was suggested by the $M_A$-$O$ phase transition in [001] PMN-32PT occurring at 0.2 MV/m and 80$^\circ C$ under $\sigma = 20 \text{ MPa}$. Finally, during process 4–1, when stress was removed at constant electric field 0.2 MV/m, the sample transitioned back to the tetragonal phase. Thus, during the cycle at 80$^\circ C$, the sample successfully alternated between a depolarized state and a highly polarized state corresponding to a large change in electric displacement and a large energy density.
100 °C, the material remained in the highly polarized tetragonal phase away from any phase boundaries for all electric fields considered under zero stress.\textsuperscript{13} At these temperatures, the application of large compressive stress during process 2–3 also caused a phase transition into the monoclinic phase. However, the decrease in electric field during process 3–4 did not lead to a phase transition into the orthorhombic phase. This interpretation is supported by extrapolation of the [001] PMN-32PT phase diagram reported in Ref. 15 to PMN-28PT at 90 °C and 100 °C. This resulted in nearly identical power density generated versus compressive stress at these temperatures.

Furthermore, for cycles performed at 22 °C, the material transitioned from the rhombohedral to the monoclinic phase during process 1–2, as suggested by the PMN-32PT phase diagram reported in Ref. 15 to PMN-28PT at 90 °C and 100 °C. This resulted in nearly identical power density generated versus compressive stress at these temperatures.

However, the decrease in electric field during process 3–4, as suggested by the PMN-32PT phase diagram, did not lead to a phase transition into the orthorhombic phase away from any phase boundaries for all electric fields considered under zero stress.\textsuperscript{13} At these temperatures, the material remained in the highly polarized tetragonal phase. In addition, the compressive stress should be performed at temperatures where the tetragonal phase is present. In addition, the compressive stress $\sigma_H$, the sample transitioned into the orthorhombic phase during process 3–4, as suggested by the PMN-32PT phase diagram.\textsuperscript{15} Overall, the power density with $T_b = 22$ °C was limited by the fact that the sample never reached the highly polarized tetragonal phase. These results indicate that to maximize power generation of PMN-28PT, the new cycle should be performed at temperatures where the tetragonal phase is present. In addition, the compressive stress $\sigma_H$ should be large enough to induce the orthorhombic phase at the temperature and electric field corresponding to state 2 of the cycle.

### 3. Effect of frequency

Figure 7 shows the power density generated by the thermally biased mechanical power cycle as a function of compressive stress $\sigma_H$ for frequency of 0.5, 1, 2, and 3 Hz. The low and high electric fields $E_L$ and $E_H$ were set at 0.2 and 0.8 MV/m, and the bias-temperature $T_b$ was 80 °C. Each data point represents an average over five cycles and the error bars correspond to one standard deviation or 63% confidence interval. It is evident that the power density increased with increasing compressive stress for frequency below 1 Hz. However, at higher frequency, the power density reached a maximum at compressive stress of 23.02 MPa and decreased beyond. This can be attributed to the fact that, at high cycle frequency, the electric displacement did not reach its equilibrium value during processes 2–3 and 4–1. Furthermore, the large error bars for frequency of 3 Hz were due to inconsistent changes in electric displacement during each process from one cycle to the next. Figure 7 establishes that a cycle frequency of 1 Hz yields the largest power density for large compressive stress at 80 °C.

### C. Model predictions

Figure 6 compares experimental data and model predictions obtained from Eq. (6) for the power density $P_D$ at bias-temperature $T_b$ of 22, 80, and 100 °C. Predictions were based on the dielectric properties previously estimated from isothermal bipolar $D$-$E$ loops measured at these temperatures. Analysis of the electric displacement variations $D(t)$-$D_4$ versus time $t$ with $T_b = 80$ °C for cycle frequency ranging from 0.5 to 2 Hz confirmed that the properties extracted from the $D$-$E$ loops at 0.1 Hz can be used in the model given by Eq. (6) (see supplementary material).\textsuperscript{33} However, predictions for $T_b = 90$ °C were not included because isothermal $D$-$E$ loops were not collected at 90 °C. Figure 6 indicates that the model predictions agreed well with experimental data. In fact, the average relative error between experimental data and model predictions was 47.6%, 13.9%, and 2.4% for $T_b$ equal to 22, 80, and 100 °C, respectively. The largest error for $T_b = 22$ °C corresponded to small values of $\sigma_H$. Overall, the model predictions were acceptable.

Figure 7 shows the model predictions of the power density at $T_b = 80$ °C for frequency of 0.5 and 1 Hz. Here also, the model yields reasonable predictions. In fact, the average relative error between experimental data and model predictions at 0.5 and 1 Hz was 29.1% and 13.9%, respectively. Note that the model did not yield accurate predictions for frequencies larger than 1 Hz because then, the cycle did not follow the path of the $D$-$E$ loops at 0.1 Hz. In other words, $D$ did not reach its equilibrium value during processes 2–3 and 4–1 as previously discussed. Overall, these results validate the model for $P_D$ given by Eq. (6). It can be used to predict energy ($N_D = P_D t f$) and power densities from the material dielectric properties.

### D. Material efficiency

Figure 8(a) presents the relative electric displacement $D$-$D_4$ as a function of electric field $E$ experimentally measured during the new thermally biased mechanical cycle performed at $T_b = 80$ °C and $T_b = 100$ °C at low frequency $f \sim 0.004$ Hz with $E_L = 0.2$ MV/m, $E_H = 0.8$ MV/m, and $\sigma_H = 25$ MPa. Figure 8(b) shows the corresponding experimentally measured stress $\sigma$ versus relative strain $\Delta x$.
At 100°C efficiency were obtained at 80°C. The largest energy density, power density, and material converting mechanical energy into electrical energy. The material undergoing the new cycle was very efficient at during the cycle. These large efficiencies demonstrate that taken as zero, thanks to the bias-temperature kept constant.

Finally, the maximum material efficiency of 87.3% ± 5.6% was obtained at low frequency $f \sim 0.004$ Hz with $T_b = 85$ °C, $E_L = 0.2$ MV/m, $E_H = 0.95$ MV/m, and $\sigma_H = 34$ MPa. Under these conditions, $N_D = 47.8 \pm 1.4$ J/cycle and $W_{in} = 54.9 \pm 1.9$ J/cycle. These operating conditions were the same as those that yielded the maximum material efficiency of 64.1% for our thermomechanical power cycle. Thus, the thermally biased mechanical power cycle achieved larger material efficiency by replacing the thermal cycling in the thermomechanical power cycle with a temperature-bias.

**E. Comparison with other direct mechanical energy conversion methods**

Table I compares the operating frequency as well as the power and energy densities experimentally harvested using various direct mechanical energy conversion methods. Roundy et al. used a piezoelectric lead zirconate titanate (PZT) linear bimorph cantilever driven at a resonant frequency of 120 Hz and acceleration of 2.5 m/s² to harvest 0.98 W/l. However, the large beam deflections required to induce large strains in the PZT were only achievable at frequency near the resonance frequency. Alternatively, Wang and Yuan applied a time-varying magnetic field to PZT sandwiched between magnetostrictive Terfenol-D layers to harvest 0.9 W/l at 58 Hz. The outer Terfenol-D layers were able to induce larger strains in the piezoelectric PZT than the traditional bending approach. This resulted in larger energy density than the linear piezo bimorph method. However, the smaller cycle frequency caused the two methods to achieve similar power densities. In addition, Cottinet et al. applied cyclic transverse strain of 0.2% at 100 Hz to electrostrictive terpolymer poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] films containing 1 vol.% carbon black and harvested 0.015 W/l. In this case, a bias electric field of 5 MV/m was applied continuously throughout the cycle. Moreover, Dong et al. applied cyclic compressive stress between 20 and 26 MPa at 1 Hz in the [001] direction to [110]-poled piezoelectric PIN-PMN-PT single crystals at room temperature. The increase in compressive stress induced a phase transition that increased the polarization of the material and its subsequent decrease induced the reverse phase transition. The resulting power density is illustrated in Figure 8 by the fact that increasing compressive stress from 0 to 25 MPa during process 2–3 produced a larger change in (i) strain and (ii) electric displacement at 80°C than at 100°C.

Table I compares the operating frequency as well as the power and energy densities experimentally harvested using various direct mechanical energy conversion methods. Roundy et al. used a piezoelectric lead zirconate titanate (PZT) linear bimorph cantilever driven at a resonant frequency of 120 Hz and acceleration of 2.5 m/s² to harvest 0.98 W/l. However, the large beam deflections required to induce large strains in the PZT were only achievable at frequency near the resonance frequency. Alternatively, Wang and Yuan applied a time-varying magnetic field to PZT sandwiched between magnetostrictive Terfenol-D layers to harvest 0.9 W/l at 58 Hz. The outer Terfenol-D layers were able to induce larger strains in the piezoelectric PZT than the traditional bending approach. This resulted in larger energy density than the linear piezo bimorph method. However, the smaller cycle frequency caused the two methods to achieve similar power densities. In addition, Cottinet et al. applied cyclic transverse strain of 0.2% at 100 Hz to electrostrictive terpolymer poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) [P(VDF-TrFE-CFE)] films containing 1 vol.% carbon black and harvested 0.015 W/l. In this case, a bias electric field of 5 MV/m was applied continuously throughout the cycle. Moreover, Dong et al. applied cyclic compressive stress between 20 and 26 MPa at 1 Hz in the [001] direction to [110]-poled piezoelectric PIN-PMN-PT single crystals at room temperature. The increase in compressive stress induced a phase transition that increased the polarization of the material and its subsequent decrease induced the reverse phase transition. The resulting power density

<table>
<thead>
<tr>
<th>Conversion method</th>
<th>$f$ (Hz)</th>
<th>$\text{Max } P_D$ (W/l)</th>
<th>$N_D$ (J/l/cycle)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear piezoelectric bimorph</td>
<td>120</td>
<td>0.98</td>
<td>0.008</td>
<td>19</td>
</tr>
<tr>
<td>Magnetostrictive</td>
<td>58</td>
<td>0.9</td>
<td>0.0015</td>
<td>31</td>
</tr>
<tr>
<td>Electrostrictive polymer</td>
<td>100</td>
<td>0.015</td>
<td>0.0002</td>
<td>32</td>
</tr>
<tr>
<td>Mechanical phase change</td>
<td>1</td>
<td>0.75</td>
<td>0.75</td>
<td>20</td>
</tr>
<tr>
<td>Thermally biased mechanical</td>
<td>1</td>
<td>44</td>
<td>44</td>
<td>Present</td>
</tr>
</tbody>
</table>
harvested from this cycle was 0.75 W/l corresponding to the largest energy density \(N_0 = 0.75 \text{J/l/cycle}\) among the previously mentioned mechanical energy harvesting methods.\(^{20}\) Note that this solid-state phase change method did not have performance peaks limited to resonant frequency.\(^{20}\) In addition, it differed from the new cycle in that (i) it was performed in the absence of an applied electric field and (ii) compressive stress was used to increase rather than decrease the polarization of the material. Table I indicates that the present thermally biased mechanical cycle generated energy and power densities orders of magnitude larger than other popular methods using piezoelectric materials. However, in the present study, the energy generated was not harvested, unlike the other conversion methods. Thus, it is critical to design an electric circuit to condition the power and to harvest the energy generated by the new cycle.

V. CONCLUSION

This study demonstrated a novel thermally biased mechanical power cycle on ferroelectric [001]-poled PMN-28PT single crystals. Maximum energy and power densities of 44 J/l/cycle and 44 W/l were achieved at 1 Hz for bistemperature \(T_b\) of 80°C and electric field cycled between 0.2 and 0.8 MV/m with compressive stress \(\sigma_M = 25.13\) MPa. In addition, the power density increased with increasing compressive stress for cycle frequency less than or equal to 1 Hz. For higher cycle frequency, the power density reached a maximum for compressive stress equal to \(\sigma_M = 23.03\) MPa. The maximum power density of the new cycle was obtained for temperature bias of 80°C, thanks to tetragonal to monoclinic to orthorhombic phase transition sequence during the cycle resulting in large changes in electric displacement. The material efficiency of this new power cycle exceeded that of the thermomechanical power cycle previously presented.\(^{21}\) The energy and power densities generated by the new cycle were orders of magnitude larger than alternative mechanical energy conversion methods. Finally, a physics-based model predicting the power density was derived and validated against experimental data. It can be used to predict the energy and power densities for any material based on their dielectric properties and the operating electric fields, temperature, and frequency.

ACKNOWLEDGMENTS

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33See supplementary material at http://dx.doi.org/10.1063/1.4846735 for additional discussion on the effect of frequency.