Pyroelectric waste heat energy harvesting using relaxor ferroelectric 8/65/35 PLZT and the Olsen cycle

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Pyroelectric waste heat energy harvesting using relaxor ferroelectric 8/65/35 PLZT and the Olsen cycle

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Abstract
Waste heat can be directly converted into electrical energy by performing the Olsen cycle on pyroelectric materials. The Olsen cycle consists of two isothermal and two isoelectric field processes in the electric displacement versus electric field diagram. This paper reports on the electrical energy generated by lanthanum-doped lead zirconate titanate (8/65/35 PLZT) subjected to the Olsen cycle. The material was alternately dipped into a cold and a hot silicone oil bath under specified electric fields. A maximum energy density of 888 J l$^{-1}$ cycle was obtained with a 290 $\mu$m thick 8/65/35 PLZT sample for temperatures between 25 and 160 $^\circ$C and electric fields cycled between 0.2 and 7.5 MV m$^{-1}$. To the best of our knowledge, this is the largest pyroelectric energy density experimentally measured with multiple cycles. It corresponded to a power density of 15.8 W l$^{-1}$. The electrical breakdown strength and therefore the energy and power densities of the material increased as the sample thickness was reduced from 720 to 290 $\mu$m. Furthermore, a physical model for estimating the energy harvested by ferroelectric relaxors was further validated against experimental data for a wide range of electric fields and temperatures.

(Some figures may appear in colour only in the online journal)

1. Introduction
Waste heat is rejected as a by-product of power, refrigeration or heat pump cycles as a consequence of the second law of thermodynamics. In 2009, more than 55% of the energy consumed in the United States was lost as low temperature waste heat [1]. For example, the transportation sector contributed to 37% of the total waste heat. This is due to the fact that about 25–35% of the energy contained in the fuel of cars and trucks is typically converted into useful energy while the rest is dissipated as heat through the radiator and the exhaust pipe [2]. In the past decade, direct energy conversion technologies for harvesting low temperature waste heat have received significant attention.

1 www.seas.ucla.edu/~pilon.
This paper reports, for the first time, experimental measurements of the energy harvested by commercially available lead lanthana zirconate titanate (PLZT) subjected to the Olsen cycle. The effects of low electric field $E_L$, cold source temperature $T_{\text{cold}}$, hot source temperature $T_{\text{hot}}$ and high electric field $E_H$ on the energy harvested were systematically investigated. Then, experimental data were compared with predictions made by a recently developed physical model [19].

2. Background

2.1. Pyroelectricity/ferroelectricity

Pyroelectric materials possess a spontaneous polarization defined as the average electric dipole moment per unit volume in the absence of an applied electric field [29]. A subclass of pyroelectric materials known as ferroelectric materials have the ability to switch the direction and magnitude of the spontaneous polarization by reversing the applied coercive electric field [30].

Figure 1 shows the isothermal unipolar hysteresis curves between electric displacement $D$ and electric field $E$ exhibited by a pyroelectric material at two different temperatures $T_{\text{cold}}$ and $T_{\text{hot}}$. These so-called $D$–$E$ loops are traveled in a counter-clockwise direction. The $D$–$E$ loops corresponding to $T_{\text{cold}}$ and $T_{\text{hot}}$ are characteristic of a typical ferroelectric and paraelectric material, respectively. In fact, a ferroelectric material undergoes a phase transition from ferroelectric to paraelectric when it is heated above its Curie temperature, denoted by $T_{\text{Curie}}$. Then, the spontaneous polarization vanishes. The electric displacement $D$ of an isotropic material at electric field $E$ and temperature $T$ can be expressed as [30, 31]

$$D(E, T) = \varepsilon_0 \varepsilon_r(T) E + P_s(T)$$

where $\varepsilon_0$ is the vacuum permittivity ($=8.854\times10^{12} \text{ F m}^{-1}$) and $\varepsilon_r(T)$ is the relative permittivity of the material at electric field $E$ and temperature $T$. The saturation polarization denoted by $P_s(T)$ is estimated as the displacement in the linear fit of $D$ versus $E$ extrapolated at zero electric field. The slope of this linear fit corresponds to the product $\varepsilon_0 \varepsilon_r(T)$ as illustrated in figure 1.

2.2. Olsen cycle

The Olsen cycle consists of two isothermal and two isoelectric processes in the electric displacement versus electric field ($D$–$E$) diagram [7] as illustrated in figure 1. Process 1–2 consists of charging the pyroelectric element (PE) at $T_{\text{cold}}$ by increasing the applied electric field from $E_L$ to $E_H$. Process 2–3 corresponds to discharging the PE by heating it from $T_{\text{cold}}$ to $T_{\text{hot}}$ under constant electric field $E_H$. Process 3–4 consists of reducing the electric field from $E_H$ to $E_L$ under isothermal conditions at $T_{\text{hot}}$. Finally, process 4–1 closes the cycle by cooling the PE from $T_{\text{hot}}$ to $T_{\text{cold}}$ under constant electric field $E_L$. Note that the Olsen cycle, in the $D$–$E$ diagram, is analogous to the Ericsson cycle defined in the pressure versus specific volume diagram.

The area enclosed by the clockwise 1–2–3–4 loop in the $D$–$E$ curve represents the electric energy produced per unit volume of material per cycle denoted by $N_D$ (in J l$^{-1}$/cycle) and defined as [7]

$$N_D = \oint E \text{d}D.$$  

(2)

The corresponding power density $P_D$ (in W l$^{-1}$) produced by the pyroelectric element is expressed as

$$P_D = N_D f$$

(3)

where $f$ is the cycle frequency. Note that $N_D$ is also dependent on the cycle frequency [18, 20].

2.3. Materials

Relaxor ferroelectrics are a promising class of materials which feature exceptional electro-optical, dielectric and piezoelectric properties [32]. These materials can be used in devices such as piezoelectric actuators, pyroelectric sensors, multilayer capacitors and optical shutters [33]. The material investigated in this study is a relaxor ferroelectric composed of 8 mol% lanthanum doped into a 65 mol% lead zirconate and 35 mol% lead titanate solid solution (Pb$_{0.92}$La$_{0.08}$(Zr$_{0.65}$Ti$_{0.35}$)O$_{3}$), also denoted as 8/65/35 PLZT [34]. The lanthanum doping increases the resistivity of the material and contributes to the strong electromechanical coupling [34–36]. At room temperature, the 8/65/35 PLZT crystal structure has rhombohedral symmetry [37]. The material undergoes complex phase transitions which are very sensitive to temperature and applied electric field [35]. It is paraelectric beyond the Burns temperature $T_B \approx 350^\circ\text{C}$ [38]. Upon cooling below $T_B$, the material transforms from the paraelectric phase to the ergodic relaxor phase. In the latter phase, nanoscale polar regions with randomly distributed...
dipoles form and give rise to large dielectric and piezoelectric properties [39].

The phase transition between ergodic relaxor and ferroelectric is field-dependent and occurs at the Curie temperature \( T_{\text{Curie}} \). The latter can be determined from the maximum of the pyroelectric current \( (\partial D/\partial T)_p \) versus temperature \( T \) curve measured under a specified electric field \( E \). The material can revert phase from ferroelectric to ergodic relaxor by heating it above \( T_{\text{Curie}} \) and/or depoling below a critical electric field \( E_{\text{cr}}(T) \). The Curie temperature \( T_{\text{Curie}} \) is expected to become nearly frequency-independent in the vicinity of the ergodic-relaxor–ferroelectric phase transition [40]. This is due to the reduction in dipole thermal fluctuations as the material is cooled below \( T_{\text{Curie}} \) [40–42]. In 8/65/35 PLZT, the ferroelectric phase cannot be established upon cooling under zero electric field [43]. However, the ferroelectric phase can be induced from the ergodic relaxor phase by applying an external electric field \( E \) greater than \( E_{\text{cr}}(T) \) [44–47]. Unfortunately, \( T_{\text{Curie}} \) and \( E_{\text{cr}}(T) \) for the PLZT composition 8/65/35 have not been reported in the literature. Therefore, we can only speculate upon the ferroelectric–relaxor phase transitions in 8/65/35 PLZT based on data reported for 9/65/35 PLZT [47, 48].

Note also that the remnant polarization \( P_r(T) \) of ferroelectric relaxors does not vanish above \( T_{\text{Curie}} \) due to the persistence of nanopolar domains interacting with each other at temperatures between \( T_{\text{Curie}} \) and \( T_H \) [42]. However, the remnant polarization is negligibly small in the relaxor state with respect to its value in the ferroelectric state [42]. The converse of the pyroelectric effect is the electrocaloric effect. It is the change in temperature caused by a change in applied electric field under adiabatic conditions [49]. Lu et al [50] recently demonstrated a large electrocaloric effect on 8/65/35 PLZT thin films. The electrocaloric temperature change of \( \Delta T = 40 \) K was observed for 0.45 \( \mu \)m thick 8/65/35 PLZT at about 45°C under an electric field of 125 MV m\(^{-1}\). In addition, Sebald et al [51] have shown theoretically that materials exhibiting large electrocaloric activity are of interest in pyroelectric energy harvesting. Consequently, the present study aims to experimentally assess the pyroelectric energy harvesting capabilities of 8/65/35 PLZT.

2.4. Physical modeling of the Olsen cycle

Recently, Kandilian et al [19] developed a physical model predicting the amount of energy harvested by relaxor ferroelectric materials undergoing the Olsen cycle. The model accounted for temperature-dependent properties of the material. The energy density \( N_{\text{O}} \) was expressed as [19]

\[
N_{\text{O}}(E_L, E_H, T_{\text{cold}}, T_{\text{hot}}) = (E_H - E_L)
\times \left\{ \frac{\varepsilon_0}{2} \left[ \varepsilon_r(T_{\text{cold}}) - \varepsilon_r(T_{\text{hot}}) \right] (E_H + E_L) + P_r(T_{\text{cold}}) - P_r(T_{\text{hot}}) + \frac{d_{33}x_3}{s_{33}} \right\}
\]

where \( \varepsilon_r(T_{\text{cold}}) \) and \( \varepsilon_r(T_{\text{hot}}) \) are the low frequency relative permittivities of the pyroelectric material at the cold and hot operating temperatures \( T_{\text{cold}} \) and \( T_{\text{hot}} \), respectively. The saturation polarizations of the material at \( T_{\text{cold}} \) and \( T_{\text{hot}} \) are denoted by \( P_r(T_{\text{cold}}) \) and \( P_r(T_{\text{hot}}) \), respectively, and expressed in C m\(^{-2}\). Note that Kandilian et al [19] erroneously called \( P_r(T) \) the spontaneous polarization instead of saturation polarization, as sometimes found in the literature [52]. The piezoelectric coefficient \( d_{33} \) is expressed in C N\(^{-1}\), \( s_{33} \) is the elastic compliance (in m\(^2\) N\(^{-1}\)) and \( x_3 = \alpha_3(T_{\text{hot}} - T_{\text{cold}}) \), where \( \alpha_3 \) is the linear thermal expansion coefficient (in K\(^{-1}\)). Note that this model was based on the assumption that the dielectric contribution to the primary pyroelectric coefficient was negligible compared with the dipole contribution (see equation (8) in [19]). The model successfully predicted the energy density harvested by PMN-32PT [19] and PZN-5.5PT [20]. Here also, the model predictions will be compared with the energy density experimentally measured with 8/65/35 PLZT.

3. Experiments

3.1. Samples

Hot isostatically pressed 8/65/35 PLZT ceramics with grain diameter around 5 \( \mu \)m were acquired from Aura Ceramics, Inc. (New Hope, MN, USA). The specimen was cut into seven samples with thicknesses ranging from 290 to 720 \( \mu \)m using a diamond abrasive saw. Rectangular gold electrodes were sputtered on opposite faces. Electrical wires were bonded to the electrodes using conductive silver epoxy. Table 1 lists the thickness and the cross-sectional dimensions of each sample used in this study. Note that the electrodes in samples 5–7 did not fully cover the faces. This electrode configuration was chosen in order to minimize electrical conduction (leakage current) around the samples’ edges.

3.2. Experimental setup

Two thermally insulated beakers containing Dow Corning 100 cSt silicone oil were maintained at temperatures \( T_{\text{cold}} \) and \( T_{\text{hot}} \) thanks to temperature-controlled hot plates [19, 23]. J-type thermocouples were immersed in each bath to monitor and control their temperature. The samples were alternately dipped between the cold and hot baths to create the temporal temperature oscillations required in the Olsen cycle. Sufficient time (\( \sim 20–60 \) s) was given for the sample’s

<table>
<thead>
<tr>
<th>Table 1. Thickness and cross-sectional area of the different 8/65/35 PLZT samples and their electrodes investigated in this study.</th>
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<tbody>
<tr>
<td>Sample</td>
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electric displacement to reach steady state ($\partial D/\partial t = 0$) during processes 2–3 and 4–1 before varying the electric field and then moving the sample from one bath to the other. This ensures that the cycle was performed under quasiequilibrium conditions to achieve the maximum energy density. Note that the thermal characteristic time constant can be estimated as $\tau = \rho c_p h b$ [53], where $h$ is the heat transfer coefficient and $b$ is the sample thickness, while $\rho$ and $c_p$ are the sample density and specific heat, respectively. For example, the thermal characteristic time constant was estimated to be 2.5 s for a 290 $\mu$m thick 8/65/35 PLZT sample with $\rho = 7900$ kg m$^{-3}$ [54], $c_p = 329$ J kg$^{-1}$ K$^{-1}$ [55] and $h = 300$ W m$^{-2}$ K$^{-1}$, corresponding to convective quenching in an oil bath [56].

The electrical subsystem used to perform the Olsen cycle consisted of a modified Sawyer–Tower circuit [31] to apply the required electric field across the pyroelectric material and to measure the charge $Q$ collected at the electrode surfaces. Details of the circuit used in the present study were provided in [19] and need not be repeated. This circuit was also used to measure the unipolar and bipolar $D$–$E$ loops at various temperatures.

3.3. Experimental procedure

3.3.1. Isothermal $D$–$E$ loops. Isothermal unipolar and bipolar $D$–$E$ loops were collected at 45, 65, 100, 110, 120, 130 and 160 $^\circ$C for samples 4–6 and at 25 and 160 $^\circ$C for sample 7 using the electrical circuit previously discussed. The measurements were taken while the sample was immersed in a silicone oil bath maintained at the desired temperature. For bipolar loop measurements, a continuous triangular voltage signal was applied across the sample at 0.33 Hz, corresponding to the frequency at which the electric field was cycled during isothermal processes 1–2 and 3–4 in the Olsen cycle. The amplitude of the applied voltage corresponded to an electric field cycled between $-2.5$ and 2.5 MV m$^{-1}$. Similarly, the applied voltage for unipolar $D$–$E$ loop measurements corresponded to an electric field varying from 0.0 to 2.5 MV m$^{-1}$. These measurements were taken at 0.66 Hz, corresponding to the same rate of change in electric field as that imposed to collect the 0.33 Hz bipolar $D$–$E$ loops.

Moreover, the saturation polarization $P_s(T)$, the remnant polarization $P_r(T)$ and the relative permittivity $\varepsilon_r(T)$ of 8/65/35 PLZT samples were evaluated by linearly fitting the upper curve of isothermal bipolar $D$–$E$ loops corresponding to a decrease in electric field from $E_H$ to $E_L$ as shown in figure 1.

3.3.2. Olsen cycle. The Olsen cycle was performed on 8/65/35 PLZT at various electric fields and temperatures to investigate their respective effects on the energy harvested. For example, the low electric field $E_L$ was varied between 0.0 and 0.4 MV m$^{-1}$ and the high electric field $E_H$ from 0.4 to 7.5 MV m$^{-1}$. The cold source temperature $T_{\text{cold}}$ was either 25, 45 or 65 $^\circ$C, while the hot source temperature was varied from 100 to 160 $^\circ$C. The Olsen cycles were recorded in the $D$–$E$ diagram and the energy density $N_D$, defined in equation (2), was estimated by applying the trapezoidal rule.

![Figure 2. Bipolar isothermal electric displacement versus electric field ($D$–$E$) hysteresis curves at various temperatures (colored figure). The $D$–$E$ paths travel in a counter-clockwise direction. The electric field was cycled between $-2.5$ and 2.5 MV m$^{-1}$ at 0.33 Hz. The $D$–$E$ loops at 45 and 65 $^\circ$C correspond to the ferroelectric phase while those at 100, 110, 120, 130 and 160 $^\circ$C indicate that the material was in the ergodic relaxor phase.](image-url)
the saturation polarization and relative permittivity varied nonlinearly as a function of electric field and the dielectric properties required in equation (4) were estimated from two piecewise regions of the isothermal bipolar $D$–$E$ loops corresponding to the decreasing electric field branch. The electric displacement was assumed to depend linearly on the electric field in each region corresponding to electric field decreasing (i) from $E_{H}$ to $E_{C}(T)$ and (ii) from $E_{C}(T)$ to $E_{L}$.

4.2. Effect of low electric field $E_{L}$

Figure 3 shows the average energy density harvested by sample 4 for five different Olsen cycles performed with low electric field $E_{L}$ equal to 0.0, 0.1, 0.2, 0.3 and 0.4 MV m$^{-1}$. The high electric field was set as $E_{H} = 1.5$ MV m$^{-1}$ while the cold and hot source temperatures were maintained at $T_{cold} = 65^\circ$C and $T_{hot} = 160^\circ$C, respectively.

![Energy density as a function of high electric field $E_{H}$]({{https://example.com/energy_density_figure.png}})

**Figure 3.** Energy density as a function of low electric field $E_{L}$ varying from 0.0 to 0.4 MV m$^{-1}$. The high electric field was set as $E_{H} = 1.5$ MV m$^{-1}$ while the cold and hot source temperatures were maintained at $T_{cold} = 65^\circ$C and $T_{hot} = 160^\circ$C, respectively.

4.3. Sample variability

Figure 4 shows the energy density as a function of high electric field $E_{H}$ between 0.4 and 1.5 MV m$^{-1}$ collected from four different samples for temperatures $T_{hot}$ equal to (a) $100^\circ$C, (b) $110^\circ$C, (c) $120^\circ$C and (d) $130^\circ$C. The low electric field $E_{L}$ was 0.2 MV m$^{-1}$ while the cold source temperature $T_{cold}$ was maintained at 65°C. The energy harvested represents the averaged values over five cycles performed under quasiequilibrium. Here also, the error bars represent a 95% confidence interval. Figure 4 indicates that sample variation was larger for low values of temperature $T_{hot}$ and electric field $E_{H}$. In fact, the largest sample variation was found for $T_{hot} = 100^\circ$C and $E_{H} = 0.4$ MV m$^{-1}$, with a maximum relative difference among samples of 19.7%. Meanwhile, sample variability was the lowest for $T_{hot} = 130^\circ$C and $E_{H} = 1.5$ MV m$^{-1}$, with a maximum relative difference among samples of 9.1%. These results establish the consistency and repeatability of experimental measurements not only from one cycle to the next but also from one sample to the next.

4.4. Effect of cold source temperature $T_{cold}$

Figures 5 and 6 show the average energy density harvested by sample 4 as a function of high electric field $E_{H}$ ranging from 0.4 to 2.5 MV m$^{-1}$ for cold source temperature $T_{cold}$ equal to 65 and 45°C, respectively. Here also, the hot source temperature $T_{hot}$ was equal to (a) $100^\circ$C, (b) $120^\circ$C, (c) $130^\circ$C and (d) $160^\circ$C. The low electric field was set as $E_{L} = 0.2$ MV m$^{-1}$. Figures 5 and 6 establish that the energy density $N_{D}$ increased as the cold source temperature $T_{cold}$ decreased. For example, for the conditions $E_{H} = 2.5$ MV m$^{-1}$ and $T_{hot} = 160^\circ$C, the energy density increased from 343 to 442 J l$^{-1}$/cycle, or by 29% when $T_{cold}$ was lowered from 65 to 45°C. Indeed, this was attributed to the increase in electric displacement span [$D(E, T_{cold}) - D(E, T_{hot})$]. In other words, more free charges were collected at the electrode surface as $T_{cold}$ was lowered. However, reducing $T_{cold}$ from 65 to 45°C increased the cycle period from 51.9 to 124 s and in turn decreased the corresponding power density from 6.61 to 3.56 W l$^{-1}$. This reduction in power density was attributed to an increase in the time required for isoelectric cooling (process 4–1) to be performed under quasiequilibrium conditions. This may be a consequence of the slow dielectric relaxation of PLZT in the ergodic relaxor phase at $T_{cold}$ [58]. The dipole reorientation contributing to the polarization change slows down at low temperatures due to the increasing energy barrier necessary to activate and reorient the polar nanodomains [59].

4.5. Effect of hot source temperature $T_{hot}$

Figures 5 and 6 also establish that the energy density increased as the hot source temperature $T_{hot}$ was raised from 100 to $160^\circ$C for a given high electric field $E_{H}$. Between $T_{cold}$ and $T_{hot} \geq T_{Curie}$, the 868/35 PLZT samples underwent a phase transition from ferroelectric (polar) to ergodic relaxor (non-polar). In fact, the largest energy density was obtained at $T_{hot}$ near the ferroelectric–ergodic-relaxor phase transition temperatures $T_{Curie} \leq 160^\circ$C. However, increasing the operating temperature difference ($T_{hot} - T_{cold}$) in excess of 135°C resulted in large thermal stresses, causing the sample to crack.
Figure 4. Experimentally measured energy density of 8/65/35 PLZT as a function of high electric field $E_H$ for samples 1–4. The hot source temperature $T_{\text{hot}}$ was equal to (a) 100°C, (b) 110°C, (c) 120°C and (d) 130°C. The high electric field $E_H$ ranged from 0.4 to 1.5 MV m$^{-1}$. The cold source temperature $T_{\text{cold}}$ and low electric field $E_L$ were set as 65°C and 0.2 MV m$^{-1}$, respectively. Sample variability was greatest at low temperatures and low electric fields.

4.6. Effect of high electric field $E_H$

Figures 5 and 6 indicate that, for a given hot source temperature $T_{\text{hot}}$, the energy density $N_D$ increased as the high electric field $E_H$ increased. Indeed, raising $E_H$ increased the electric field span ($E_H - E_L$) resulting in larger energy densities as suggested by figure 1 and equation (4). However, the high electric field $E_H$ was physically limited by the sample’s dielectric strength, which was determined experimentally as 2.5 MV m$^{-1}$ for samples with bare gold electrodes. We speculate that large strains were electrically induced within the samples when they were subject to cyclic high magnitude electrical loading, causing microcracks to develop along the domain boundaries [60]. In addition, electric field concentrations were formed such that the relative permittivity at the crack interior and the ceramic body were different, thus producing a strain [61, 62]. Ultimately, the propagation of these field-induced cracks led to sample failure [35]. Each sample used in this study cracked after ~200–300 Olsen cycles due to a combination of thermal stress and field-induced strains.

Two strategies were explored to increase the electrical breakdown field of 8/65/35 PLZT samples and maximize $E_H$. First, the specimen thickness was reduced from 650 µm (sample 4) to 370 µm (samples 5 and 6) and 290 µm (sample 7), since the electrical breakdown strength of ceramics was reported to increase with decreasing sample thickness [60]. This can be explained by the presence of fewer defects typically contained in thinner samples. Furthermore, a silicone conformal coating was applied to the PLZT samples 5–7 to reduce their susceptibility to cracking as suggested by [63]. Implementation of these strategies in sample 5 resulted in an increase of the material electrical breakdown from 2.5 to 4.5 MV m$^{-1}$ for the operating conditions $T_{\text{cold}} = 45°C$, $T_{\text{hot}} = 160°C$ and $E_L = 0.2$ MV m$^{-1}$. Then, the maximum energy density harvested per cycle increased by more than 50% from 442 J l$^{-1}$ (sample 4) to 668 J l$^{-1}$ (sample 5).

4.7. Maximum energy density

Figure 7 presents four consecutive Olsen cycles performed on sample 7 at 0.0178 Hz, corresponding to the maximum energy density achieved experimentally with this material. The cold and hot source temperatures were 25 and 160°C while the electric field was cycled between $E_L = 0.2$ MV m$^{-1}$ and $E_H = 7.5$ MV m$^{-1}$, respectively. An energy density of $887.5 \pm 8.5$ J l$^{-1}$/cycle was obtained, corresponding to a power density of 15.8 W l$^{-1}$. 

6
Figure 5. Experimentally measured energy density harvested by 8/65/35 PLZT (sample 4) as a function of high electric field. The hot source temperature $T_{\text{hot}}$ was equal to (a) 100 $^\circ$C, (b) 120 $^\circ$C, (c) 130 $^\circ$C and (d) 160 $^\circ$C. The high electric field $E_H$ ranged from 0.4 to 2.5 MV m$^{-1}$. The cold source temperature $T_{\text{cold}}$ and low electric field $E_L$ were set as 65 $^\circ$C and 0.2 MV m$^{-1}$, respectively. The relative error between the model predictions and experimental data is denoted by $\delta$.

4.8. Discussion

The maximum energy density of 888 J l$^{-1}$/cycle produced by 8/65/35 PLZT should be compared with those achieved by other pyroelectric materials. In fact, table 2 compares the maximum energy density generated from the Olsen cycle for different materials, temperature ranges and operating electric fields. Note that a maximum energy density of 900 J l$^{-1}$/cycle using 60/40 P(VDF-TrFE) was reported by Olsen et al [4] for temperatures between 25 and 120 $^\circ$C and electric fields cycled between 20 and 50 MV m$^{-1}$. However, it is unclear whether these experimental results were averaged over multiple cycles and if they were repeatable. In fact, Navid et al [23] produced 204 J l$^{-1}$/cycle averaged over five cycles for the same material, temperature range and operating electric fields. To the best of our knowledge, the maximum energy density reported in the present study for 8/65/35 PLZT is the largest energy density experimentally measured repeatably over multiple cycles. It could be further increased by increasing the electrical breakdown strength of the material. For example, samples can be (i) pre-stressed such as in a thin layer unimorph ferroelectric driver and sensor actuators to increase sample durability [66] or (ii) fabricated into single or multilayer thin film capacitors with thicknesses of the order of nanometers to increase the applied electric field without sample failure [67]. The use of thin film PLZT would substantially reduce the applied voltage delivered to the electrical circuit during the Olsen cycle. For example, only 7.5 V applied across a 10 µm thin PLZT film would be
Figure 6. Experimentally measured energy density harvested by 8/65/35 PLZT (sample 4) as a function of high electric field. The hot source temperature $T_{\text{hot}}$ was equal to (a) 100 °C, (b) 120 °C, (c) 130 °C and (d) 160 °C. The high electric field $E_H$ ranged from 0.4 to 2.5 MV m$^{-1}$. The cold source temperature $T_{\text{cold}}$ and low electric field $E_L$ were set as 45 °C and 0.2 MV m$^{-1}$, respectively. The relative error between the model predictions and experimental data is denoted by $\delta$.

Table 2. Comparison of maximum energy density achieved using the Olsen cycle or different materials, temperature ranges and operating electric fields.

<table>
<thead>
<tr>
<th>Material</th>
<th>$N_D$ (J l$^{-1}$/cycle)</th>
<th>$T_{\text{cold}}$ (°C)</th>
<th>$T_{\text{hot}}$ (°C)</th>
<th>$E_L$ (MV m$^{-1}$)</th>
<th>$E_H$ (MV m$^{-1}$)</th>
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<td>[64]</td>
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<td>81</td>
<td>20.3</td>
<td>37.9</td>
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<td>800</td>
<td>25</td>
<td>120</td>
<td>20.0</td>
<td>60.0</td>
<td>[4]</td>
</tr>
<tr>
<td>61.3/29.7/9 P(VDF–TrFE–CFE)</td>
<td>50</td>
<td>0</td>
<td>25</td>
<td>0.0</td>
<td>25.0</td>
<td>[69]</td>
</tr>
<tr>
<td>PZN-4.5PT</td>
<td>217</td>
<td>100</td>
<td>160</td>
<td>0.0</td>
<td>2.0</td>
<td>[17]</td>
</tr>
<tr>
<td>PZN-5.5PT</td>
<td>150</td>
<td>100</td>
<td>190</td>
<td>0.0</td>
<td>1.2</td>
<td>[20]</td>
</tr>
<tr>
<td>PMN-10PT</td>
<td>186</td>
<td>30</td>
<td>80</td>
<td>0.0</td>
<td>3.5</td>
<td>[51]</td>
</tr>
<tr>
<td>PMN-32PT</td>
<td>100</td>
<td>80</td>
<td>170</td>
<td>0.0</td>
<td>0.9</td>
<td>[19]</td>
</tr>
<tr>
<td>8/65/35 PLZT</td>
<td>888</td>
<td>25</td>
<td>160</td>
<td>0.2</td>
<td>7.5</td>
<td>Present study</td>
</tr>
</tbody>
</table>

required to achieve an electric field of 7.5 MV m$^{-1}$ instead of 2175 V required across a 290 µm thick sample (sample 7). Moreover, the power output of devices using conduction [21], convection [25] or radiation [24] could be significantly improved by employing a multistaging technique [5]. This technique consists of placing pyroelectric materials in the order of increasing $T_{\text{Curie}}$ between the cold and the hot source. The Curie temperature $T_{\text{Curie}}$ of PLZT can be tuned by adjusting the lanthanum doping level ($x$) into PZT along with the Pb/Ti ratio. In fact, $T_{\text{Curie}}$ was reported to be 65, 150,
Table 3. Critical electric field $E_{cr}(T)$, spontaneous polarization $P_s(T)$, remnant polarization $P_r(T)$ and relative permittivity $\varepsilon_r(T)$ of 8/65/35 PLZT (sample 4) retrieved for two piecewise regions of isothermal bipolar $D-E$ loops in the temperature range between 45 and 160°C.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>45</th>
<th>65</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{cr}(T)$ (MV m$^{-1}$)</td>
<td>0.4</td>
<td>0.6</td>
<td>1.2</td>
<td>1.5</td>
<td>1.6</td>
<td>1.8</td>
<td>—</td>
</tr>
</tbody>
</table>

$E_{H} = 2.5$ MV m$^{-1}$ to $E_{cr}(T)$

$\varepsilon_r(T)$

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>45</th>
<th>65</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>160</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_s(T)$ (C m$^{-2}$)</td>
<td>0.265</td>
<td>0.220</td>
<td>0.155</td>
<td>0.151</td>
<td>0.139</td>
<td>0.118</td>
<td>0.0145</td>
</tr>
<tr>
<td>$P_r(T)$ (C m$^{-2}$)</td>
<td>10850</td>
<td>26050</td>
<td>15040</td>
<td>12547</td>
<td>11243</td>
<td>9651</td>
<td>6439</td>
</tr>
</tbody>
</table>

Energy density predicted by the piecewise model can be expressed as the sum of two components:

$$N_D = N_D(E_L, E_{cr}, T_{cold}, T_{hot}) + N_D(E_{cr}, E_{H}, T_{cold}, T_{hot})$$

(5)

where the function $N_D(E_L, E_{cr}, T_{cold}, T_{hot})$ is given by equation (4). The contribution from the region of decreasing electric field from $E_{H}$ to $E_{cr}(T)$ can be predicted by equation (4) using the saturation polarization $P_s(T)$. The contribution from the region of decreasing electric field from $E_{cr}(T)$ to $E_L$ is $0.2$ MV m$^{-1}$ can be predicted by equation (4) using the remnant polarization $P_r(T)$ instead of $P_s(T)$.

Figures 5 and 6 compare systematically the energy density obtained experimentally with predictions of equation (5) for four hot source temperatures $T_{hot} = 100, 120, 130$ and $160$°C and $E_{H}$ ranging from 0.4 to 2.5 MV m$^{-1}$. The cold source temperature $T_{cold}$ was set as $65$°C (figure 5) and $45$°C (figure 6). Note that the thermal expansion term $d_{33,33}/s_{33}$ [31] corresponding to the secondary pyroelectric coefficient was ignored in the model predictions for PLZT. Indeed, Kandalian et al [19] observed that, for PMN-32PT, the Olsen cycle extended beyond the electric displacement bounded by the isothermal $D-E$ loops. This was attributed to the contribution of thermal expansion to the energy density [19]. However, in the case of 8/65/35 PLZT, the Olsen cycles fell within the bounds of the isothermal $D-E$ loops at both $T_{cold}$ and $T_{hot}$. Therefore, the thermal expansion did not contribute to the energy density harvested. Similar observations were made for PZN-5.5PT [20].

Figures 5 and 6 also report the range and the average value of the relative error between experimental data and model predictions, denoted by $\delta$ and $\delta_{avg}$, respectively. For example, the average relative error reached $39\%$ and $28\%$ for $T_{cold} = 65$°C and $T_{cold} = 45$°C at $T_{hot} = 100$°C, respectively. For such a low value of $T_{hot} = 100$°C, a small absolute difference in energy density resulted in a large relative error. However, the model predicted the experimental data reasonably well, for $T_{cold} = 45$°C and $T_{hot} \geq 100$°C and for $T_{cold} = 65$°C and $T_{hot} \geq 130$°C. In these cases, the average relative error between model predictions and experimental data was less than $30\%$.

Figure 8 shows the isothermal bipolar $D-E$ loops collected on sample 4 at $T_{cold} = 45$°C and $T_{hot}$ equal to (a) $100$°C, (b) $120$°C, (c) $130$°C and (d) $160$°C overlaid
Figure 8. $D$–$E$ diagram of isothermal bipolar $D$–$E$ loops and experimental Olsen cycles for 8/65/35 PLZT (sample 4). The temperature $T_{\text{hot}}$ was equal to (a) 100°C, (b) 120°C, (c) 130°C and (d) 160°C while $T_{\text{cold}} = 45$°C, $E_L = 0.2$ MV m$^{-1}$ and $E_H = 2.5$ MV m$^{-1}$. The Olsen cycle was vertically displaced to coincide with the $D$–$E$ curve at $T_{\text{hot}}$.

with the corresponding Olsen cycles measured for $E_L = 0.2$ MV m$^{-1}$ and $E_H = 2.5$ MV m$^{-1}$. Figure 8 illustrates the discrepancies between model predictions and experimental data. In fact, the Olsen cycles did not span the electric displacement between the isothermal bipolar $D$–$E$ loops corresponding to $T_{\text{cold}}$ and $T_{\text{hot}}$. It did not fully overlap either with the isothermal bipolar $D$–$E$ loops at $T_{\text{cold}}$ when the electric field increased from $E_L$ to $E_H$ (process 1–2). This may be attributed to a sudden increase in electric displacement associated with a field-induced phase transition [18] and/or possibly the existence of mixed phases [68] when the applied electric field increased from $E_L$ to $E_c$ during the Olsen cycle. In contrast, this sharp increase in electric displacement was absent in the bipolar $D$–$E$ loop at $T_{\text{cold}}$.

Overall, the model predictions were relatively good given the range of parameters explored, the simplicity of the model which did not account for leakage current and the complexity of the physical phenomena taking place during the Olsen cycle.

6. Conclusion

This paper reports, for the first time, experimental measurements of energy densities generated by ferroelectric relaxor 8/65/35 PLZT undergoing the Olsen cycle. A maximum energy density of 888 J l$^{-1}$/cycle corresponding to a power density of 15.8 W l$^{-1}$ was obtained at 0.0178 Hz for operating temperatures between $T_{\text{cold}} = 25$°C and $T_{\text{hot}} = 160$°C and electric fields cycled between $E_L = 0.2$ MV m$^{-1}$ and $E_H = 7.5$ MV m$^{-1}$. The maximum electric field and temperature swing were limited by electrical breakdown and thermal stress, respectively. Sample variability was relatively small, particularly at high temperatures and large electric fields. Moreover, increasing the operating temperature difference $T_{\text{hot}} - T_{\text{cold}}$ increased the energy density harvested but in turn reduced the power density produced due to an increase in the time required to perform isoelectric cooling and heating (processes 4–1 and 2–3) under quasiequilibrium conditions. Furthermore, the electrical breakdown strength and thus the energy and power densities of 8/65/35 PLZT increased as the sample thickness decreased. Finally, the experimental results confirmed the validity of the physical model [19] developed to predict energy densities of ferroelectric relaxors subjected to the Olsen cycle. Further experiments on the electric-field-induced phase transitions of 8/65/35 PLZT are necessary to better understand the behavior of the $D$–$E$ loops and Olsen cycles obtained in this study.

Acknowledgments

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