Next Energy 1 (2023) 100026

Contents lists available at ScienceDirect

Next Energy

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Pyroelectric heat harvesting, what's next

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ARTICLE INFO

Keywords:
Pyroelectric heat harvesting
Pyroelectric materials
Heat mainpulation
Low-grade heat harvesting
Energy sustainability

ABSTRACT

Harvesting all-present environmental waste heat of decentralized, disordered, and diffused forms promises energy sustainability and carbon neutrality to meet the UN's climate target [1]. The non-static waste heat or temporal temperature change (dT/dt), which is of equal importance as the spatial temperature gradient (dT/dx) [2], though commonly existed in the surroundings (e.g., human respiration, water vapours, and exhaust pipes; Fig. 1 and Table S1) according to the second law of thermodynamics, is still far from practice due to inefficiency, intricacy, and instability in powering consumer electronics [3,4]. Providentially, the pyroelectric effect allows for scavenging temporal temperature variations via spontaneous polarization change, making it an attractive approach for direct heat-to-electricity conversion from non-static thermal sources. Pyroelectricity is typically determined by $p = \partial P/\partial T$ ($P = P_S + P_E$, $P_E = \varepsilon E$) [5,6], where p is the pyroelectric coefficient, P_S and P_E are spontaneous and electric polarizations with respect to the applied thermal field and electric field (E), respectively, and ε is the dielectric constant. While tremendous efforts have been made to improve the p of polar materials (up to $\sim$ 10 mC m^{-2} °C^{-1}) [7] and the power density of heat harvesters (up to $\sim$ 10 mW m^{-2}) [8–10] over the past 50 years (Table S2), their large intrinsic impedance (in the level of MΩ) and low energy conversion efficiency (0.1‰) [11] have hindered the potential implications in the sustainable power supply of ever-increasing IoT-based electronics demands. In this short review, we first discuss the fundamental of electric polarization manipulation of typical polar materials for boosting p. Then, the state-of-the-art p versus Curie temperature (T_{Curie}) of various pyroelectric materials is benchmarked. Next, paradigm-changing progress in tailoring the material properties and device configurations, as well as external electric/thermal field modulations, is surveyed. Finally, the review concludes by proposing challenges and opportunities for the next sustainable pyroelectric heat harvesting.

Fundamentals and benchmarks of pyroelectricity

According to the phenomenological theory of free energy of a lattice, pyroelectricity is associated with the electric dipole moment change per unit volume of polar materials under temporal heat varations [12]. The nonlinear temperature dependence of pyroelectricity (Fig. 2a) suggests that the p increases sharply near the T_{Curie} owing to the ferroelectric-paraelectric phase transition. The Born-Szigeti quantum theory states that the primary p consists of two parts [13–15], i.e., rigid-ion displacement (p_1) and electron-phonon renormalization (p_2). Guided by these theoretical commentaries, tremendous ferroelectric and non-ferroelectric materials have been synthesized and investigated in the past five decades, and the p versus T_{Curie} is summarized in Fig. 2b and Table S2. It is notable that the ferroelectric materials provide a high p compared to non-ferroelectrics (e.g., ZnO, AlN, GaN, CdS) owing to the reoriented capability of the spontaneous dipole. The ferroelectric ceramics (orange region), which represent a majority of polar materials, offer a considerably large p of 10–10^3 μC m^{-2} °C^{-1} in a wide T_{Curie} range (room temperature (RT) to 1000 °C), in contrast to PVDF polymers (grey region), and relaxor ferroelectrics (0.7PMN-0.3PT, blue region). However, few polar materials show desirable p at RT, which limits the energy harvesting capability of non-static waste heat from common but overlooked thermal sources such as industrial waste heat, ambient heat fluctuation, solar heat, and body heat, as illustrated in Fig. 1. Therefore, leveraging the p near the T_{Curie} or lowering the T_{Curie} close to the RT, is a pressing research strategy that could prove crucial in achieving efficacious non-static heat-to-electricity conversion, in consideration of low-grade heat sources are of >30% worldwide primary energy consumption present at <100 °C.

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https://doi.org/10.1016/j.nxener.2023.100026
Received 20 March 2023; Received in revised form 18 May 2023; Accepted 19 May 2023

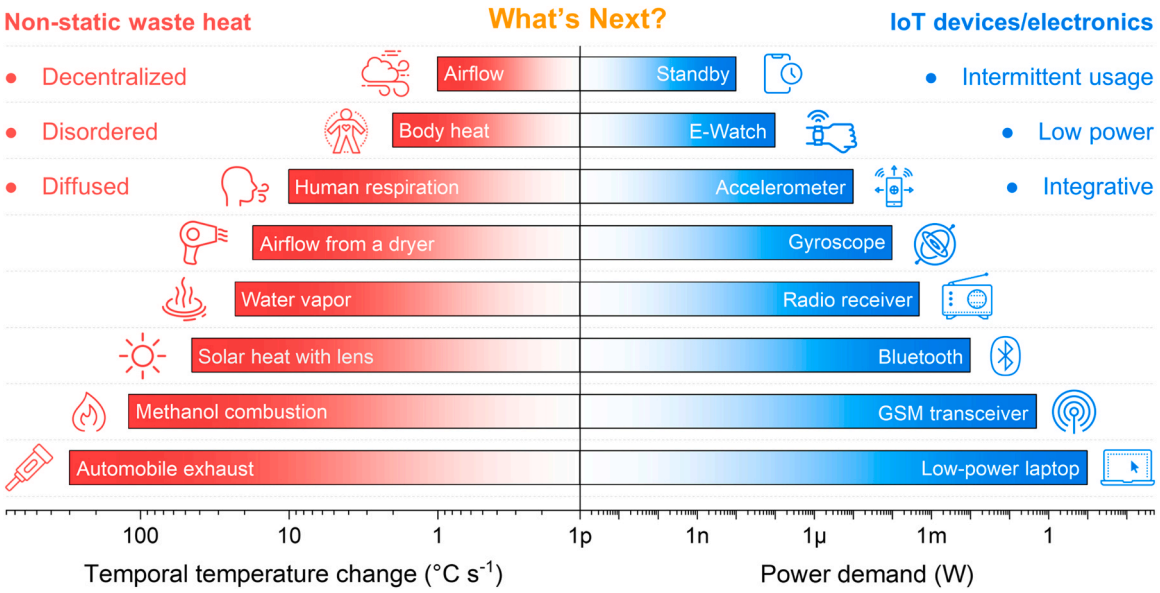


Fig. 1. Next powering solution for IoT devices via non-static waste heat harvesting. Left, typical forms of non-static environmental waste heat; right, commonly used IoT-based electronics/devices [3]. Detailed summaries of non-static waste heat sources, refer to Table S1.

Multiscale manipulations of pyroelectricity

Dimensionality effect and multi-layered capacitors

In order to improve the p of polar materials, one of the typical solutions is to introduce the dimensionality effect into material synthesis. For example, using ZnO nanowire arrays instead of bulk ZnO can increase p by the Schottky contact between the electrode and ZnO nanowires, allowing for improved charge separation under temperature-induced polarization variation [16]. Accordingly, the average p of ZnO nanowires is 2-fold ($\sim$ 15 μC m^{-2} °C^{-1}) larger than that of the bulk ZnO ($\sim$ 7 μC m^{-2} °C^{-1}, Table S2). Also, the dimensionality effect is effective in changing the phonon dynamics when polar materials approach the 2D crystalline limit. In specific, the less restraint of atomic displacement along the out-of-plane/thickness direction in a 2D system has been experimentally examined to contribute to an increase in p [17]. This was not only observed in van der Waals layered In_2Se_3, quasi-van der Waals $CsBiNb_2O_7$ (CBNO), but also in ionic/covalent ZnO crystals (Fig. 3a). The dimensionality effect manifests as giant pyroelectricity in the 2D system was attributed to the electron-phonon renormalization (p_2) resulting from the thickness-dependent mean square displacement. In addition to materials tailoring, the electrode/dielectric configuration is also germane to the pyroelectric output [18,19]. A perfect case study is that a multi-layered capacitor (MLC) with inserted interdigital electrodes inside of low-T_{Curie} lead scandium tantalate (PST) [20] thinning the active layer, thus increasing the capacitance (C) and electric field (V) tolerance (Fig. 3b). Consequently, the energy storage capacity (E) is substantially improved (i.e., $E = 0.5CV^2$), and further enhancement can be achieved by operating the polar material near the T_{Curie} (Fig. 2a).

External thermal/electric field modulations

Aside from tailoring material properties and engineering device configurations, external field manipulation is also vital to spatially tune the dipole moment change of anisotropic polar materials. In specific, the ferroelectricity offers reversible polarization tunability under an applied electric field ($E \neq 0$), thereby increasing the overall polarization change (ΔP, $P_E \neq 0$) towards a high p at low temperatures (Fig. 3c). Recently, electric-field-driven ΔP together with modulated thermodynamic cycles, have been introduced into pyroelectric heat harvesting, offering a joule-level energy output [20,21]. In particular, under isothermal and isoelectric processes, i.e., a thermodynamics cycle (Ericsson cycle, Olsen cycle) associated with DE loop (D, the dielectric displacement) [22], ferroelectric crystals/ceramics can convert waste heat of $\Delta T = 10$ K into electricity with a relative Carnot efficiency of $>$ 19% by applying an electric field of E = 10–100 kV cm^{-1}. The relative Carnot efficiency can be further increased to 40% by thinning the thickness of active dielectric layers (e.g., replacing bulk dielectrics with multi-layered capacitors for a large capacitance and high electric field) [20]. Nonetheless, an ultrahigh electric field may bring forth ferroelectric fatigue due to charge injection, dielectric breakdown, and leakage. Meanwhile, sustaining the modulated polarization and minimizing the leakage after numerous heating/cooling cycles remains challenging. On the other hand, Fig. 2a reveals that p varies nonlinearly with respect to the temperature and increases substantially near the T_{Curie}. In this context, upgrading non-static waste heat from low-grade (low temperature or RT) to high-quality (T_{Curie}) is beneficial for the synergistic increase of dT/dt and p, thus considerably boosting the electricity output. For instance, solar heat generation and dissipation can be successfully decoupled by confining the irradiance onto a focal hotspot via a solar heat manipulator (e.g., Fresnel lens, graded absorbers, or metasurfaces) [10]. This enables transverse non-uniform heat perturbation and polarization ripple propagation from the hotspot to the non-irradiated peripheral part along the x-y plane (Fig. 3d). Unlike conventional pyroelectricity, where spatiotemporally uniform heat absorption and dissipation are thickness-dependent and follow the z-direction, the inappreciable dT/dt comes with a small p at low temperatures and brings forth inefficient heat-to-electricity conversion. The transverse pyroelectricity can convert the manipulated in-plane heat delivery into graded dipole moment changes, providing a record-high power density of 38 mW m^{-2} at 1 sun, which is competitive with solar organic thermoelectrics [23,24] and ferrophotovoltaics [25,26]. Moreover, the solely external thermal field modulation, in the absence of materials tailoring and additional energy penalty, makes transverse pyroelectricity applicable to general polar materials [10], e.g., ferroelectric polymers (β-PVDF), ferroelectric crystals (0.7PMN-0.3PT), and ferroelectric ceramics (PZT). Nonetheless, the microscopic

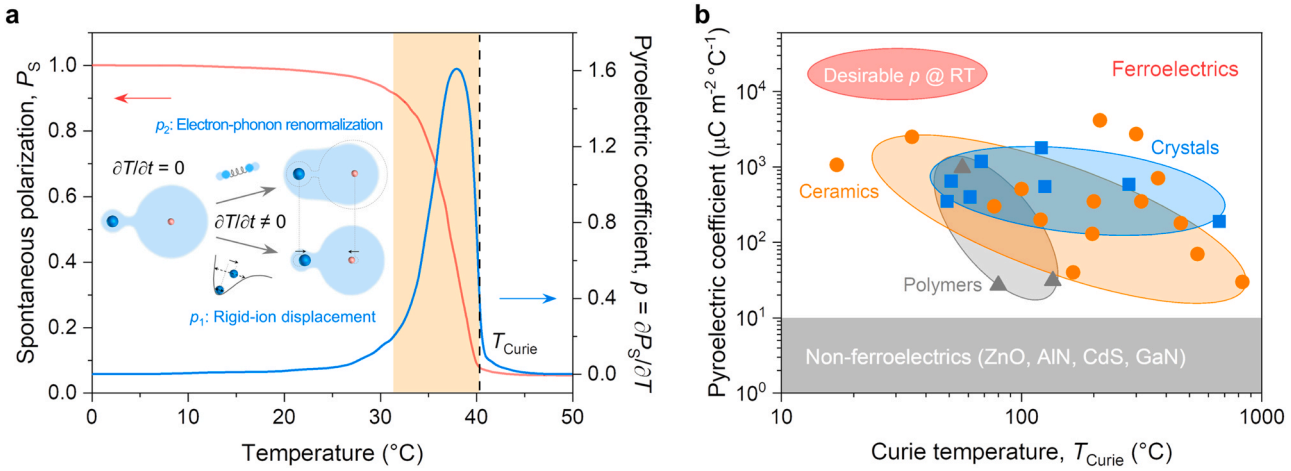


Fig. 2. Pyroelectricity fundamentals and benchmarks for the next pyroelectric materials. (**a**) Temperature dependence of spontaneous polarization and pyroelectric coefficient. Inset, mechanistic insights of rigid-ion displacement (p_1) and electron-phonon renormalization (p_2). Orange block, a first-order phase transition from ferroelectric to paraelectric near the Curie temperature. (**b**) Benchmarks of pyroelectric coefficient with respect to the Curie temperature. The pyroelectric coefficient of non-ferroelectrics (grey block) is significantly lower than that of ferroelectrics. Circle scatters (ferroelectric ceramics), square scatters (ferroelectric crystals), and triangle scatters (ferroelectric polymers). Detailed summaries of the literature, refer to Table S2.

mechanism of dipole moment changes and ferroelectric domain wall evolution under inhomogeneous heat perturbation, as well as the secondary p induced by the non-uniform thermal strain, need further examination.

Toward the next pyroelectric heat harvesting

Pyroelectric heat harvesting is a fundamental research field that deeply roots in the multidisciplinary interaction across physics, chemistry, materials science, and engineering, with a focus on practical applications. Despite its ever-increasing attention from academia and industry over the past 50 years and numerous fruitful developments, pyroelectricity still faces several challenges. These include but are not limited to, the need for a better fundamental understanding of dipole moment changes, complicated materials synthesis, limited eco-friendly materials choices, and low energy conversion efficiency (Fig. 3e) [27]. In order to advance to the next level of pyroelectric heat harvesting, it is necessary to address some key challenges and opportunities as follows:

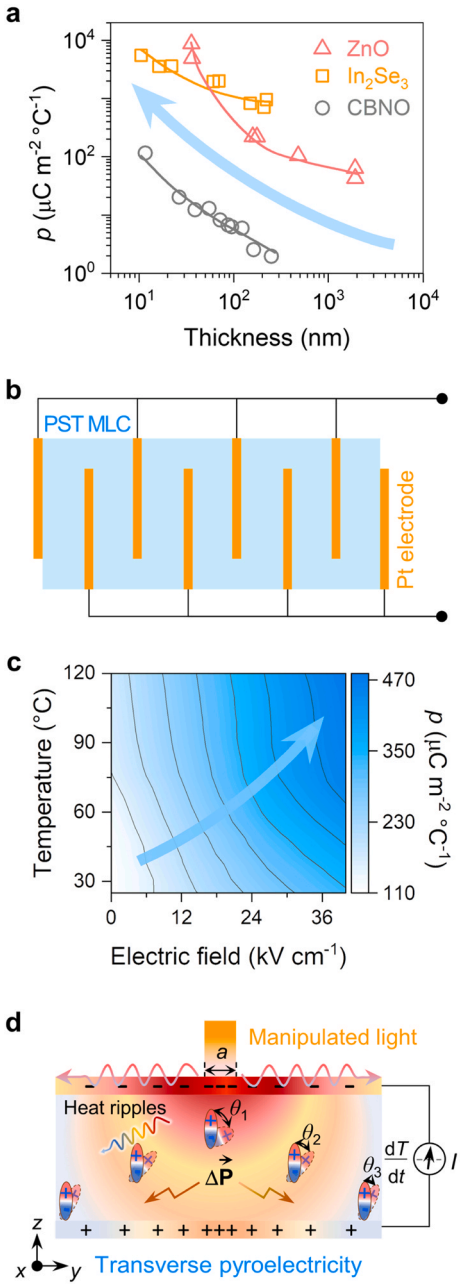
(i) Gaining an in-depth understanding of the origin of pyroelectricity. The theory of pyroelectricity was first introduced by Boguslawski, known as the “monochromatic” theory, nearly ten decades ago. To date, rigid-ion displacement and electron-phonon renormalization have been thought to dominate the primary pyroelectricity. However, the microscopic understanding of pyroelectricity remains unclear. For instance, the polariton-phonon interaction under light triggering and tunable polariton propagation in 2D systems [28], the phonon wavelength dependence of atomic displacement in pyroelectrics (ferroelectrics and non-ferroelectrics) [17], the local ferroelectric domain wall evolution associated with non-uniform thermal strain/gradient, the mechanistic of surface free charge density changes in ferroelectric phase transition [29], and the field-driven spontaneous dipole rotation at the interface are not well-elucidated. Combining atomic-scale in-situ microscopy with computational science is a viable approach to uncover the underlying mechanism and reveal the structure-property relation of the observed phenomena.

(ii) Co-designing demand-oriented devices/systems. In general, the criteria of pyroelectric detectors/sensors and energy/heat harvesters are quite different, especially in the figure-of-merit (FOM), device configuration, and applicable scenarios. Specifically, the sensitivity, detectivity, responsivity, rising/falling time, noise equivalent power, and corresponding frequency ranges are representative parameters/criteria to determine the performance of pyroelectric sensors [30,31]. In contrast, the electrical output of a pyroelectric heat harvester is typically evaluated by the average/peak power/energy density, energy conversion efficiency, Carnot efficiency, harvested energy per cycle, and energy harvesting FOM [6]. Thereby, the system co-design of pyroelectric sensors and harvesters can be optimized/rationalized via physics-guided integration of artificial intelligence and machine learning (ML). For instance, ML-assisted classification can significantly improve the accuracy of detecting human motion (e.g., individual recognition, virtual reality). Also, physics-guided high-throughput materials prediction offers a cost-effective manner to identify high-p polar materials suitable for low-grade heat harvesting. Moreover, the FOM for energy harvesting of pyroelectric devices is not only governed by the p but also by the dielectric constant and heat capacity. As a result, it is necessary to co-design material/device, along with electric/thermal field manipulations to maximize the FOM for demand-oriented implications.

(iii) Balancing the trade-off between lowering the impedance and current leakage for high output. The large impedance of the pyroelectric dielectric is beneficial to suppress the dielectric breakdown and current leakage but limits the generated power, according to Kirchhoff and Ohm’s laws. This far-flung and age-long challenge hinders the implication of dielectric-based energy generation, such as pyroelectricity, piezoelectricity, flexoelectricity, ferrophotovoltaics, and triboelectricity [11,32]. One feasible route is to engineer the electrode/device configuration and topology for instantaneous short-circuit contact at the temperature transition time, which could increase power output substantially.

(iv) Addressing scalability, stability, and flexibility. Sustaining milliwatt-level electronics through pyroelectric heat harvesting requires scalable devices and multiple units, and flexibility is also necessary for powering wearable devices via body heat recovery. Meanwhile, the pyroelectrics in tandem with other energy storage/harvesting systems and circuit interfaces enable stabilization of the electrical output, thus overcoming the intermittency and variability of non-static waste heat sources.

In short, pyroelectric heat harvesting to generate electricity from unused non-static waste heat is vital for promoting energy sustainability and minimizing carbon footprint. The outcome of the research efforts mentioned above is expected to shape the future of the next pyroelectric



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	Fundamentals	Pros and cons
Material/Device engineering (internal)	Dimensionality effect (Electron-phonon renormalization)	• Large p in 2D pyroelectric materials • Abundant material choice • No need of electric field • Complicated material synthesis • Small size for limited practical implications
	Multilayered capacitors (Thinner active layers for increased energy storage)	• Joule-level energy output from macroscopic object • Very low leakage current • Available in other energy conversion frontiers • Complicated material synthesis and device structure • Limited material choice
Electric/thermal field manipulation (external)	Electric-field-driven polarization (Dipole alignment under applied electric field)	• Large P_E and p • No material tailoring required • Flexible design of DE loops • Periodical electric field required, inevitable leakage current • Limited material choice (available only in ferroelectrics)
	Transverse polarization ripples (Decoupled heat confinement and propagation) + (Nonlinear temperature-dependent p)	• Large output from transverse $\partial T/\partial t$ and p • No electric field or material tailoring required, low leakage • Flexible tuning of heat transfer • Abundant material choice • Secondary p from non-uniform thermal strain

Fig. 3. Multiscale manipulation of heat harvesters and discussion on the next generation of pyroelectricity. (**a**) Dimensionality effect of thickness-dependent pyroelectricity [17]. (**b**) Lead scandium tantalate multi-layered capacitors [20]. (**c**) Electric-field-driven polarization for enlarged pyroelectricity [21]. (**d**) Transverse pyroelectricity obtained through manipulated heat ripples [10]. (**e**) Overview of the fundamentals and pros and cons of the discussed multiscale manipulations.

heat harvesting for many years to come and inspire innovative contributions toward building a sustainable community and society.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Author G.W. Ho is a Member of the Advisory Board of Next Energy.

Acknowledgments

This research was supported by A*STAR under its 2019 AME IRG & YIRG Grant Calls, A2083c0059 and the Advanced Research and Technology Innovation Centre (ARTIC), the National University of Singapore under Grant (A-0005947–24-00).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nxener.2023.100026.

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