Energy Harvesting through Pyroelectric Generators

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Abstract

This article endeavors to critique certain issues for enhancing energy conversion efficiency of pyroelectric generators. It discusses criteria for optimal thickness of pyroelectric materials, induction of dopants and plasmons in the pyroelectric generator system, the electrode material and design, efficient circuit design and implementation of Thermal- Electrical cycle. Depending on the application environment for these pyroelectric generators the variables like material type, geometry, dopant quality and quantity, electrode design, load capacitor voltage etc. would need to be adjusted accordingly.

Keywords

Energy harvesting, Pyroelectric effect, Dopant, Plasmonic effect, Hybrid system, Solar energy, Low grade waste heat, Pyroelectric cell, Geometry, Meshed-patterned electrodes, Olsen cycle, Kim cycle, SSHI.

Introduction

It has been estimated that 72% of the global primary energy usage is lost due to inefficient conversion, 63% of which would eventually be released as low-grade waste heat with a temperature below 100 °C. [1] [2] This Low-grade waste heat is often widespread and located near end-use sites.[3] Pyroelectric materials which convert thermal energy into electrical energy can be used to harvest this low-grade waste heat. There are many methods to harvest this low-grade waste heat, such as heat pumps [4], thermoelectric generators and pyroelectric generators. Heat pumps are highly efficient, making them excellent choices for harvesting and recycling low-grade waste heat. However, their efficiency is dependent on their size [5], requiring large installations that lack portability. They also require regular maintenance to prevent operational issues [6]. Additionally, exhaust gases and liquids can cause safety issues [7] [3]. In contrast, solid-state devices can be installed without location constraints due to their compact nature and require minimal maintenance [8]. Similarly, thermoelectric generators based on semiconductor materials are often used to recover waste heat [9] [10] [11] [12] [13]. They generate electricity from spatial temperature gradients. However, to increase their efficiency, the thermoelectric material's electrical conductivity should be maximised, while its thermal conductivity should be minimized [14]. It can be very difficult to optimise these parameters independently, as an improvement in one of the two properties typically results in a corresponding improvement in the other [15].

The pyroelectric materials have several advantages, such as easy integration with on-chip circuitry, ability to operate at room temperature, rapid response, low cost, compact design and high sensitivity across multiple wavelengths of electromagnetic radiation.[16] These advantages make pyroelectric generators very versatile. For example, pyroelectric cells can harvest energy from various sources, such as air currents, braking systems, waste heat from automotive

exhaust gases, and sunlight [17] [18] [19] [20] [21] [22]. They provide high speed response to changes in the environment as well. In addition, they can be easily integrated with on-chip circuitry, making them ideal choices to power low-power autonomous sensors. Similarly, pyroelectric nanogenerators (PyNGs) have demonstrated that temperature fluctuations from human breathing at 5°C can produce up to 8.31 μW with an external load of 50 MΩ [23] [24], demonstrating their room-temperature operation capabilities. Another noteworthy application of PyNGs is in wearable electronics, as they are portable. By storing electrical energy converted from waste heat through the PyNG, and integrating it into flexible wearable electronics, the daily electrical needs of frequently used devices can be met [19].

Through the study of research papers in the field of energy harvesting based on pyroelectric generators, certain issues were assessed that needed further due diligence and understanding. These issues included understanding multiple factors that affect pyroelectric energy harvesting performance. These factors have been categorized under the following five topics; determining optimal thickness of the pyroelectric material, opportunities for performance enhancement arising from introduction of dopants and plasmons, detailing finer points on the geometry and structure of electrodes, use of appropriate pyroelectric material and setups for different application environments and consideration of various setup criteria for energy harvesting through Olsen and Kim's cycle.

The interlinkages between various operational factors like temperature, structural geometry, applied electric field, pyroelectric material characteristics, circuit design etc., are delineated for each of the five issues as described above. These interlinkages have been put to deeper analysis which is missing or is not obvious in the studied research papers on the subject.

Discussion

Optimal Thickness for Pyroelectric Materials used for Energy harvesting

Pyroelectric material's energy harvesting performance is impacted to a large extent by its thickness. There are various factors that need to be taken into account regarding the thickness of the material to realize optimal energy performance. Better thermal stability of thicker materials allows them to withstand higher temperatures.[25] This results in harvesting of increased energy density per cycle of temperature oscillation as the pyroelectric coefficient itself may increase with increase of temperature [24] along with increased current flow that is generated as higher rate of change of temperature can be applied.[26] [27] Doping of pyroelectric materials too can result in a change of optimal thickness for the pyroelectric material. For example, doping of PMN-PT with Manganese results in increase of pyroelectric coefficient by 300% with increase of thickness from 16 to 400 μm.[28] This may happen because, the crystallization defect related adverse impact on the pyroelectric effect is being mitigated with better scaling of the crystallization quality as the pyroelectric material thickness increases (Figure 1). Also, the mobility of domain walls, concentration of surface charges and in-built mechanical stresses, may improve with the increase in thickness of the pyroelectric material. Also, higher thickness allows for 3D pattern etching on the surface of the pyroelectric material resulting in higher radiation absorption and a temperature gradient created based on uneven exposure to the radiation.[16] This results in higher efficiency in energy harvesting. Temperature gradients created in thick

materials due to non-uniform heating can improve the energy performance as tertiary pyroelectric coefficient induces additional charge creation.[29] [30] Thicker materials provide for better radiation absorbance resulting in better energy performance. For example, PVDF thickness of 320 μm yields optimum increase in the radiation absorption.[31] [32] In thicker materials, there may be more opportunities for radiation to scatter internally. Each scattering event can increase the path length that the radiation travels within the material, thereby increasing the probability of absorption. A pyroelectric material with lower pyroelectric coefficient and higher heat capacity that is deployed in a working environment that provides for lower temperature range will generate lower energy output. Such a system will generate a poor energy harvesting performance as the thickness of the material is reduced beyond a certain point, the capacitance of the pyroelectric material will increase resulting in lower voltage generation for the given operating parameters. This lower voltage generation would result in early parity with the load capacitor voltage resulting in lower energy storage. Higher thickness is therefore necessary for maximum voltage generation for the pyroelectric material.

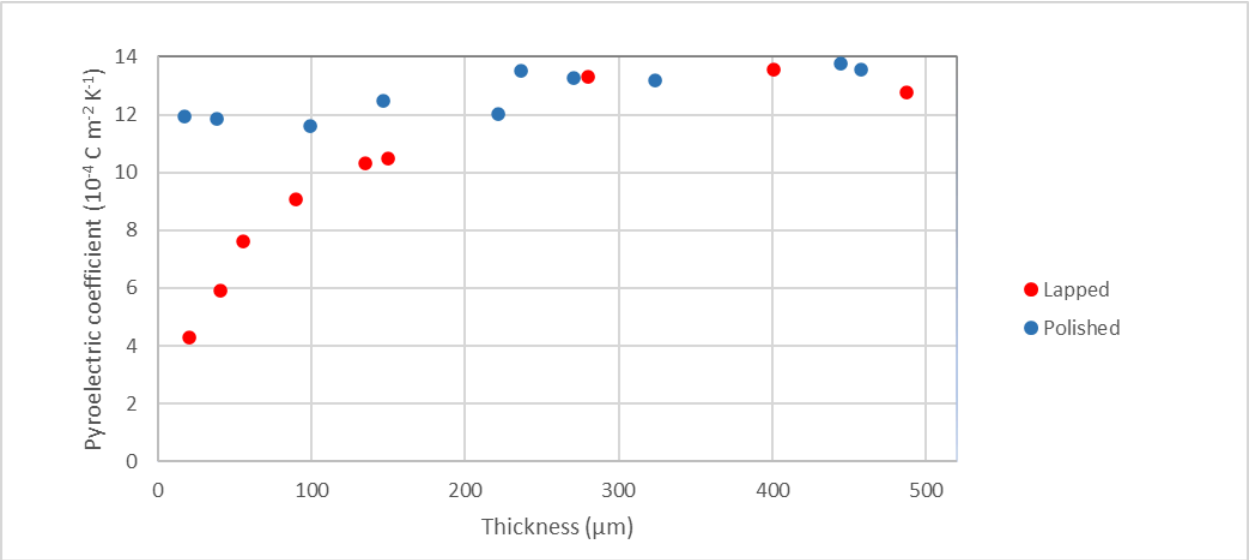

Figure 1: The variation of pyroelectric coefficient with thickness for lapped and polished Mn-doped PMN-PT crystals. Lapped crystals demonstrate an increase in pyroelectric coefficient by 300%. Data reproduced from Zhang *et al*. [28]

At the same time higher thickness makes it difficult to apply quick temperature variations due to higher heat capacity. Therefore, electrical output like current, voltage and power reduce as thickness is increased, as the rate of induced charge reduces due to slower charge build up from delayed temperature increase. [33] Thin film pyroelectrics are inherently low thermal mass, enabling very fast cycling and therefore, high power densities. The optimal energy performance of the thinner materials is achieved for relatively higher temperature oscillation frequency and lower load resistance as compared to thicker materials. The reason for higher optimal temperature oscillation frequency for thinner pyroelectric material is the relatively faster build-up of charges for thinner materials whereas for thicker materials the charge build-up being slow requires more time to reach the maximum charge induction limit.[33] This happens as the thicker materials have higher heat capacity which results in slower increase in temperature for a given time period of thermal exposure. The reason for lower optimal load resistance for thinner

pyroelectric material is based on the relatively rapid fall in the current output, with the increase of load resistance for thinner materials.[33] This may happen as the capacitance is higher for a thinner pyroelectric material (C= ε. A/d (Where d is the thickness of pyroelectric material)). This makes time constant (τ=R.C (R is load resistance and C is capacitance)) for thinner pyroelectric material to be greater and results in bigger decay of current as load resistance is increased. The voltage increases rapidly with increase of load resistance initially and then stabilizes across all thickness parameters.[33] For the thinner materials, the voltage peaks earlier at lower load resistance. Therefore, the power output also peaks at lower load resistance for thinner materials. However, the sensitivity of the electrical output towards the change of period of temperature oscillation or load resistance is higher for thinner pyroelectric materials. For PZT, the material thickness <150 μm results in sharp changes in electrical output values and the associated setup conditions of load resistance and temperature oscillation frequency compared to thickness values higher than 150 μm. If the values of temperature oscillation frequency or load resistance deviate from their optimal values, then the electrical output of the thinner material may fall below the corresponding values of the thicker material, and the advantages of the setup are lost.[33]

Also, if the pyroelectric material doesn't scale well with higher thickness, then more stress may build up along with defects that may trap charges, resulting in drop of charge density and consequent reduction in current output.

Dimensionality also affects the pyroelectric performance, with thin sheets exhibiting higher pyroelectric coefficient than thick ones. As the thickness is decreased, there are fewer restrictions for atoms to be displaced. In a 3D system, atomic displacements are restrained by atoms in all directions. On the other hand, in a 2D system, because such constriction is absent, atomic displacements become more prominent, and they show pyroelectric properties very different from those of a 3D system.[3] On the other hand, thin materials risk reaching curie temperature where the material's pyroelectric effect becomes inactive.[18]

Therefore, depending on the practical energy harvesting setup, the thickness of the pyroelectric material may need to be customised. All the criteria need to be considered before arriving at the optimal thickness for a pyroelectric generator system. An example of such multi factorial consideration can be observed where breathing temperature differential with ambient temperature is harnessed through use of a pyroelectric generator. Depending on the temperature oscillation frequency, a corresponding optimal thickness of pyroelectric material will need to be considered. The thickness of the material should also take into account the range of temperature oscillation frequency which the pyroelectric generator would be subjected to, keeping in mind, the sensitivity of the material's energy harvesting performance to the change in optimal temperature frequency. Another example where pyroelectric generators are used to harvest solar energy, requires thickness of the material to be based on voltage differential criteria. The voltage generated on the pyroelectric system should be sufficiently higher than the load capacitor voltage such that the energy efficiency is optimal. Solar energy-based energy harvesting systems are exposed to a temperature range that is of lower order. Therefore, if the thickness of the pyroelectric material is less than optimal then due to lower amount of charge generation and high capacitance (thinner material have higher capacitance), the voltage generated would also be of lower order. This makes it energy inefficient to pass the generated

charge on to the load capacitor as an early parity is reached between the pyroelectric capacitor and the load capacitor. At the same time, thickness of the pyroelectric material should not result in lower rate of temperature build-up, which causes drop in current generation and consequent voltage development.

Inclusion of dopants and plasmons to enhance energy efficiency

Dopants

The electrical properties of pyroelectric ceramics can be controlled through doping and introduction of certain nano particles called plasmons, into its material structure. In case of doping, for example, doping of Zr in BNT-BZT (BNT is $Bi_{0.5}Na_{0.5}TiO_3$ and BZT is Barium Zirconate Titanate) can change its phase transition temperature, where ferroelectric phase converts into paraelectric phase.[28] This change of phase occurs at a temperature called Curie Point. Zirconium increases the thermal conductivity of the BNT-BZT matrix too.[24] The pyroelectric coefficient of manganese oxide doped NBT-KBT film, increases by ≈750% with an increasing temperature from 20 °C to 75 °C.[28] Doping of PZT with manganese leads to a significant reduction in dielectric constant (~31%) and dielectric loss (~96%), and a significant improvement in the pyroelectric coefficient (~67%).[3] [34] PZT can also be doped with lanthanum or niobium to obtain better pyroelectric characteristics.[3] [20] [35] [19] Doping of BNT-BZT with gallium led to improvement in pyroelectric coefficient due to resonance vibration between gallium, titanium, oxygen and sodium atoms that, lead to higher thermal conductivity.[26] Better lattice heat conduction leads to greater separation of positive and negative charges and thus higher dipole moment. This enhanced dipole moment creates higher polarization density and thus pyroelectric coefficient is improved. The peak performance in thermal conductivity and consequent, pyroelectric coefficient, is achieved when the doping of gallium nitride is at 0.1%. The phase change temperature pertaining to Non-Ergodic to Ergodic, Ergodic to Ferroelectric and Ferro electric to paraelectric states, increases. This results in improvement of polarization characteristics for the BNT-BZT-xGaN matrix. There is a 300% improvement in pyroelectric coefficient, the dielectric constant reduces by 20% and dielectric loss reduces by 25% for doped BNT-BZT-xGaN matrix with x=0.1% compared to pristine BNT-BZT ceramic.[24] Similarly, a giant pyroelectric figure of merit has also been reported for La and Ta co-doped lead-free $0.94Na_{0.5}Bi_{0.5}TiO_3–0.06BaTiO_3$ ceramics.[3] [36]

Doping flexibility is built in perovskite structure-based pyroelectric material. The perovskite ferroelectric ceramic has ABO_3 structure, where A and B are cations, with BO_6 octahedra. Figures 2a and 2b show the ABO_3 structure in more detail. The BO_6 octahedra has oxygen atoms sharing corners. This results in a unit cubic cell structure with voids in the structure.[24] This gives rise to ferroelectric and piezoelectric properties. Therefore, it helps in developing pyroelectric properties easily with ceramics which can provide more flexibility in applying additives without changing the crystal structure.[24] Also, as vacancies in the surface structure are filled, charge density increases, which in turn improves the pyroelectric coefficient.

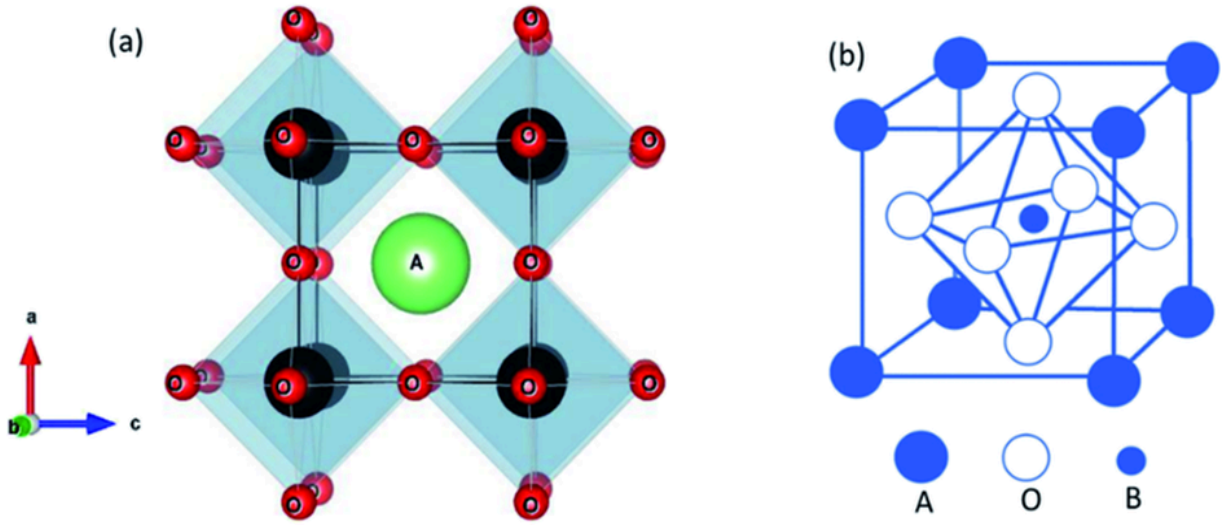

Figure 2: Two different perspectives on the ABO_3 structure. Figure 2a shows the bonding between different ABO_3 cubic units. Figure 2b shows a single ABO_3 cubic unit. In both figures, A and B are cations, bonded with oxygen anions. Reproduced from Yoshimura *et al*.[37]

Vacancies present in the crystal lattice structure create disruption in the dipole alignment of the pyroelectric material. This disruption causes hysteretic loss of energy and a resulting fatigue of the material. Doping can help in filling such vacancies. For example, the pyroelectric properties were enhanced in Mn-doped lead zirconate titanate (PMZT) thin films with excellent ferroelectric (no hysteretic fatigue) and retention properties.[3] The introduction of Mn as part of doping process results in reduction of oxygen vacancies in the lattice structure, wherein the oxygen atoms are missing from lattice structure. The Mn ions as part of the oxidation process create oxygen ions that fill in these vacancies and thus stops these vacancies from moving to different locational parts of the lattice. This vacancy mobility disrupts the dipole alignment leading to less stable polarization and polarization retention property of ferroelectric material. [3] These vacancies may also pin the polarization domains through electrostatic interaction such that the material becomes resistant to polarization change therefore resulting in hysteretic (switching polarization) loss of energy. The ease of switching polarization is thus improved after doping, which means with a small electrical field the polarization states can be switched which leads to lesser degradation or wear and tear of the material. This creates resistance to fatigue of the material as it can undergo many cycles of polarization changes without degradation of the material, while also limiting the dielectric losses in the form of heat dissipation or leakage current when an electric field is applied to the material.

Doping can also enhance the polarization characteristics of the material as more opposite free electrical charges get accumulated on both sides of the material. This happens due to the dipole pinning effect as the two types of dipoles interact with each other. One is electric dipoles that originate from relative displacement between individual ions and within atomic structure. Second is defect dipole formed by defects present in lattice structure. The dipole pinning effect arises when the defect dipoles interact with electric dipoles. For example, use of gallium nitride in BNT-BZT resulted in improved pyroelectric coefficient. [26] The improvement of polarization characteristics also results from better thermal conductivity achieved through dopant that has resonant energy with the pyroelectric constituent atoms as phonon density of state for both

dopant and pyroelectric material synergise at similar frequency of electromagnetic spectrum. Doping also results in phase change of a pyroelectric material to occur at elevated temperatures resulting in better energy harvesting performance. For example, in the case of gallium dopant in BNT-BZT as stated above. [26] However, we can also bring down the phase change temperature of say ferroelectric to paraelectric within our application setup consideration, as it results in high pyroelectric response. For example, doping BNT-BZT with zirconium achieves the said objective.[28]

Therefore, depending upon the end use application, a suitable dopant can be used to improve range of operation across different thermal energy states while improving the energy harvesting performance. Across a certain temperature range, the doped material will have relatively better energy performance compared to the pristine form of the material vis a vis at other temperature points. This may happen as the resonant energy states of the dopant coinciding with the temperature range leads to better lattice vibrational state and therefore better pyroelectric coefficient. This may also happen due to phase change across the temperature range.[26]

The use of dopants to reduce the dielectric loss or dielectric constant can improve the figure of merit for the pyroelectric material resulting in better pyroelectric energy harvesting performance. At the same time, we need to find suitable dopants for a pyroelectric material that can improve the electrical breakdown limit of the pyroelectric material. The improvement of the electrical breakdown limit helps the pyroelectric material to operate at a higher electric field intensity which increases the energy density obtained per cycle of Olsen's method for increasing energy harvesting performance. Therefore, a pyroelectric material's efficacy depends not only on its figure of merit which is the ratio of pyroelectric coefficient with its dielectric constant [38], it also depends on its capacity to bear higher levels of electrical field application without breakdown.

Plasmonic nanomaterials

Plasmonic nanomaterials are capable of generating significant amounts of localised temperature fluctuations instantaneously. They are typically comprised of metal nanoparticles that rapidly heat up due to their miniscule heat capacities and resonant energy states for surface electrons.[29]

As plasmons heat up, they raise the temperature of the surrounding pyroelectric material too, which results in better pyroelectric performance. Since plasmonic nanomaterials offer excellent control over both ΔT and dT/dt, they can serve as a natural and tailorable "handle" to control the pyroelectric response, also providing a degree of wavelength selectivity with respect to the incident light. [29]

Plasmonic materials used mainly include gold or silver metal nanoparticles along with graphene.[29] Though there are others like Al, Cu, Pt, Li, Na, K, Cs, Rb, and Ni.[39] [40] These materials produce plasmonic resonance across visible and near infra-red regions.[29]

The geometry of these materials (nano cubes, nano wires etc) can be changed to provide flexibility in generating resonance across the electromagnetic spectrum. Specific wavelength at which plasmons oscillate depends on size, material type and combined pyroelectric material

used. [29] Aniline Rubrene extended gold nanoparticle's resonant frequency from UV to IR.[41] Also, the temperature change of pyroelectric can be tuned that controls the consequent pyroelectric effect.[29]

The use of plasmonic materials therefore, also helps in providing flexibility in choosing a certain pyroelectric material too. For example, if a pyroelectric material has a low level of pyroelectric coefficient but it compensates for the lack of the same by providing low dielectric loss or dielectric constant properties. It may also compensate by providing better mechanical stability like flexibility or low level of brittleness, better hygroscopic properties etc. For such pyroelectric materials use of plasmonic particles within their structure can result in better thermal performance which will result in higher charge generation as current generation is proportional to the rate of change of temperature, even though the pyroelectric coefficient is not at par with its peer materials. The use of PVDF, a ferroelectric polymer, can benefit from the use of plasmonic material in its structure.

The plasmonic material is induced onto an electrode structure placed on top of a pyroelectric material. As, the photo source of energy falls onto the electrode, wherein, the embedded plasmons generate the required thermal effect which is passed onto the pyroelectric material that lies underneath it (Figure 3). But if a plasmon material that shows resonant frequency in the range of IR radiation is embedded into the pyroelectric structure then, a uniform heating to further higher temperatures can be achieved at a faster rate across the pyroelectric material. This can be a research subject for further due diligence.

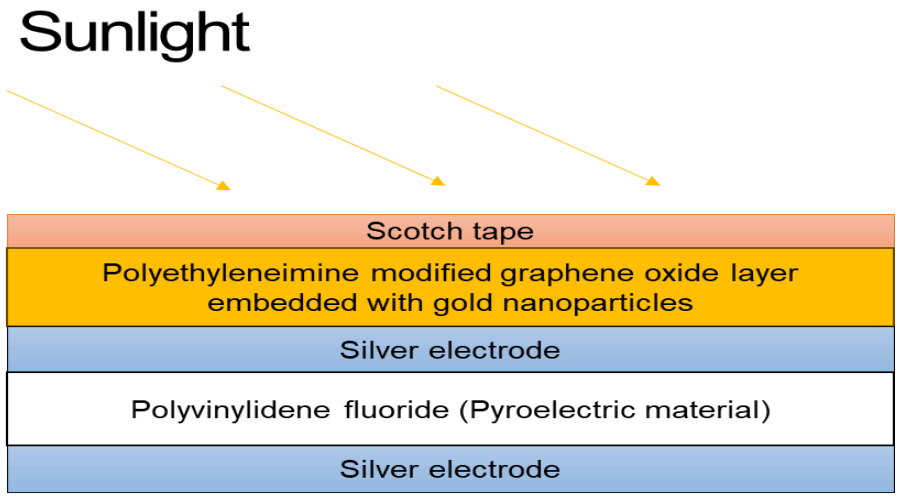

Figure 3: An illustration of the structure of a sunlight-triggered pyroelectric nanogenerator. The embedded plasmons (gold nanoparticles) in the polyethyleneimine modified graphene oxide layer heat up rapidly as sunlight falls on them, due to their extremely small heat capacities. This heat is harvested by the pyroelectric material. Reproduced from Li *et al*.[22]

The density of plasmonic nanoparticles across the substrate also needs to be optimal. Excessive plasmonic nanoparticle loading may lead to detrimental effects to both the light-matter interactions and the related solar-thermal conversions owing to the agglomeration of

plasmonic nanoparticles. Whereas, the lower levels of plasmons would not be able to generate the optimal temperature change for generating the required pyroelectric effect.[22]

The raised thermal effect on pyroelectric material, through use of plasmonic material, can also lead to the electric breakdown of the pyroelectric material. This may happen due to increased molecular vibrations, which make it easier for free electrons to ionize and cause breakdown. Thereby, limiting the density of the plasmonic material across the substrate in accordance with the dielectric properties of the pyroelectric material.

Material design and geometry of electrodes to enhance the pyroelectric performance

The factors affecting the efficiency of pyroelectric generators are surface area and structure of the electrode, thermal and electrical conductivity of the electrode.[24] For example, graphene electrode for PVDF increases current by 7 times as thermal absorbance and electrical conductivity are enhanced.[28] ZrO_2, provides higher thermal conductivity and thus can be incorporated with the upper electrode substrates to increase pyroelectric conversion efficiency.[24] Material used for electrode design should have high radiation absorption coefficient too. For example, aluminium has low radiation absorption coefficient so might be avoided for solar energy harvesting. [31] Geometrical design of the electrode also affects the pyroelectric energy performance. A meshed electrode which has parts of its surface covered with square shaped holes helps improve energy harvesting performance. Use of aluminium meshed electrodes with PVDF pyroelectric material helped improve the voltage and current output by four-fold. [31] Hysteresis loop of pyroelectric material is unchanged in shape when meshed electrodes with different coverage areas are used. [31] This means the energy harvesting performance doesn't change due to hysteretic effects with meshed electrodes.

There is 10 to 15 times improved energy performance as higher electrical output is generated for voltage and current as electrode coverage area is reduced from 100% to 45% (for PVDF) due to quicker charge build up and faster thermal cycles. [31] Any further decrease in electrode coverage area beyond 45% leads to decrease in rate of change of temperature, voltage and current. This may be due to ineffective thermal absorption as metal electrode area reduces and thus can't pass heat to pyroelectric material. A reduced coverage area may also lead to less effective capacitive coupling and electric field distribution, indirectly affecting the material's ability to respond quickly to temperature changes.[31] If electric field becomes weaker then voltage generated will be weakened and therefore the capacitance of the material reduces resulting in lower energy harvesting performance.

If we can use plasmon induced electrodes with meshed structure then the issue of ineffective thermal absorption can be addressed and thus further reduction in electrode coverage area can be achieved, thereby, improving the energy harvesting performance. Engineering three dimensional cavities on the pyroelectric material under the electrode holes will help improve the ineffective thermal absorption issue. These cavities increase surface area and induce a temperature gradient across the shape of the cavity thereby increasing heat absorption and energy harvesting performance. However, it was seen that deeper the cavity and narrower the top electrode square hole width, higher the maximum peak temperature variation rate at the bottom electrode.[16] Higher temperature variation rate at the bottom electrode means that the

thermal energy transfer across the pyroelectric system is more effective resulting in higher energy performance. Therefore, there needs to be an optimal electrode coverage area when using three dimensional cavities, which can further enhance the energy harvesting performance. The ratio of depth of 3D cavity to the meshed electrode square width needs to be assessed for optimal energy harvesting performance. Also, for such a ratio that is optimal, the electrode coverage area can be further reduced from 45%. This would result in better energy harvesting performance.

Also, reducing the thickness of the pyroelectric material can help address the less effective capacitive coupling with meshed electrodes having coverage area less than 45%. This should happen as the capacitance of a pyroelectric material is inversely proportional to its thickness. Aspect ratio of the meshed electrode to pyroelectric material thickness should be kept above 4 so that the capacitance of the material remains unchanged and therefore the energy performance also remains stable. The ratio of the size of the meshed square holes of the top electrode to the pyroelectric thickness is called aspect ratio and this affects the capacitance of the system. For lower aspect ratio below 4, the fringe effect of the electrical field generated by the meshed top electrode is weak thus reducing the capacitance and vice versa. For larger aspect ratios, e.g. greater than four, the fringing electrical fields quickly recover the electrical storage capabilities of the meshed energy harvesting system.[31]

As a further research area, the radiation absorption coefficient of the electrodes and pyroelectric material need to be looked into for better solar energy harvesting. Most of the research literature on pyroelectric materials focus on dielectric properties of the material like dielectric constant, dielectric loss, electric breakdown limit etc, however, we need to also take into account the radiation absorption coefficient into our consideration for optimal energy harvesting performance. A high radiation absorption coefficient along with a high pyroelectric coefficient and a high electrical breakdown limit will result in a high-grade energy efficiency.

Pyroelectric materials and structures for different applications, and efficient circuit design

For optimal energy harvesting performance we need to assess different combinations of pyroelectric material and related energy harvesting setups for different environment usage. For example, in case of solar energy harvesting, with low range of temperature change, we would need to have thinner pyroelectric material (a low thickness to surface area ratio) along with a setup where solar radiation can be concentrated with the use of an optical lens-based system. As a result of using an optical lens-based concentration system, the temperature range of the pyroelectric material can be raised.[20] Also, we can induce plasmonic materials into the pyroelectric structure to improve the temperature range for example when PVDF was induced with plasmonic tungsten oxide and irradiated with infrared radiation for 60 seconds, the temperature of the composite was 41.5 degree Celsius higher than pure PVDF resulting in better charge generation. The voltage produced was 3 times higher. [29] [42] The pyroelectric material made out of ceramic composites have higher dielectric breaking strength and therefore can harvest high energy density.[24] Such materials can be used where high temperatures can be achieved resulting in high electrical polarization levels as is described in the solar energy harvesting setup above. For solar energy harvesting, lower wind speed for rotating the

pyroelectric material will result in higher temperature range and therefore higher voltage, with voltage improvement of 50% at optimal wind speed as voltage generated is proportional to the change in temperature. Consequently, the energy performance improves for the corresponding wind speed. The current remains the same for different wind speeds as the rate of change in temperature remains same for different wind speeds as the rate of change is more dependent on the material characteristics. Optimal wind speed needs to be there to effect optimal temperature fluctuation period and also the optimal range of temperature obtained along with the optimal rate of change in temperature. This can be achieved by deploying a speed reduction unit wherein, the wind speed propelling the rotatory movement of the shutter is adjusted accordingly [43] [21]

The peak value of the generated current and voltage was obtained for $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN). The output voltage was in the decreasing order for the following materials; $(NH_2CH_2COOH)_3{\cdot}H_2SO_4$(TGS), $Pb(Zr_{0.5}Ti_{0.5})O_3$ PZT, $Ca_{0.2}(Sr_{0.5}Ba_{0.5})_{0.8}Nb_2O_6$ (CSBN), $LiTaO_3$, $BaTiO_3$, PVDF. For the same range of operating temperature, SBN is the most promising material for solar energy harvesting applications.[44]

The pyroelectric coefficient changes along different axes of a rhombohedral crystal structure. Due to the presence of a greater number of axes for dipole orientation, the pyroelectric coefficient increases over a larger range of temperature as was observed for [Mn-(94.6NBT-5.4BT)] crystal.[28] Pyroelectric material with such a property can be used to harness energy for high temperature applications like the thermal heat from an automobile's exhaust. Similarly, domain engineering of crystal structure can change pyroelectric properties along with thinner material structure as flatter surface offer fewer restrictions to atomic displacement.[3] [45] [46] Niobium-doped lead zirconate titanate stannate $(Pb_{0.99}Nb_{0.02}(Zr_{0.637}Sn_{0.273}Ti_{0.09})_{0.98}O_3$, PNSZT) ceramic showed high level of energy harvesting performance from the exhaust gas. The energy input required to change polarization of PNZST material is less because of its rhombohedral structure as it has more available orientation states for polarization compared to say a tetragonal structure. Therefore, a small application of electrical field can rotate polarization of the material.[19]

Pyroelectric energy generators can also be used for harvesting heat energy from hot/cold water which widely exists in industrial processes, such as oil refining, steel making and glass making. In such setups, the pyroelectric device contacts a hot flow and cold flow alternatively to produce time-dependent temperature variations. So, the maximum output power increases as the temperature of the hot flow increases, since both voltage and current increases for a given load resistance. This is attributed to the enhancement of the rate of change of the spontaneous polarization under higher temperature difference. It reveals that the output current increases as the contact frequency increases. After reaching the maximum at a certain optimal frequency, the current begins to decrease because the time for the pyroelectric film to contact the flow decreases with the increases in contact frequency. The output current is enhanced as the rate of temperature change rises sustainably (below the optimal frequency point). However, if the frequency is higher than optimal, not much heat could transfer from the flow to the pyroelectric film within a short contact time and then the temperature change rate decreases. Thus, the output current decreases gradually with the increase in the contact frequency of the device.[47] The optimal frequency would depend on the temperature range under which the pyroelectric

system operates and also on the pyroelectric material properties like material's Curie Temperature, heat capacity etc.

The efficiency for energy harvesting performance is based on K square thermoelectric coupling factor [48],

$k^2 = p^2\theta_h / (\varepsilon \cdot C_E)$

p is pyroelectric coefficient, θ_h is high temperature, ε is dielectric constant and C_E is specific heat

Higher the temperature a pyroelectrical material can be raised to, higher will be the efficiency of the energy harvesting process which implies that the pyroelectric applications should consider scenarios where temperature is high and include Curie Point. Also, the temperature difference should be as high as possible to extract maximum energy. The energy harvesting performance of pyroelectric materials would be highest around Curie Temperature as pyroelectric coefficient peaks near Curie Temperature.[38] This is because the thermoelectric coupling factor which impacts the energy performance is proportional to the square of the pyroelectric coefficient. Therefore, increase in coefficient value impacts the factor more than increase of dielectric constant value near curie temperature even though dielectric constant is inversely proportional to the factor. Hence, pyroelectric materials with high pyroelectric coefficients and low dielectric constant, where pyroelectric effect is applied in large temperature variations over time, should be considered. Energy generation has higher sensitivity to pyroelectric coefficient and temperature range under which the pyroelectric material operates compared to area of electrodes or thickness of pyroelectric material or dielectric constant. This conclusion is derived from the following set of formulae [43]:

$Q = p.\ A.\ DT,$ …1

$C = \varepsilon.\ A/d,$ …2

$V = Q/C = p.\ d.\ DT/\varepsilon,$ …3

$E = (1/2)\ .C.V^2 = (1/2).\ (p^2.\ A.\ d.\ (DT^2)/\ \varepsilon),$ …4

Where, Q is the pyroelectric charge, p is the pyroelectric coefficient, A is the surface area of the electrode, d is the thickness of the pyroelectric material, T is temperature, C is capacitance of the pyroelectric material, V is the voltage across the electrodes, E is the energy stored in the pyroelectric material and ε is the dielectric constant of the pyroelectric material.

Based on the above equations, we can see that energy performance is impacted more when pyroelectric coefficient and operational temperature range are maximised compared to area of electrodes or thickness of pyroelectric material or dielectric constant.

The circuit that harnesses the energy generated by the pyroelectric material, has a certain amount of impedance due to the presence of an inductor for minimizing energy loss, and a pyroelectric material-based capacitor for generating electrical energy. The circuit design is optimal when the pyroelectric system operates at a temperature oscillation frequency which

matches the resonant frequency of the circuit.[1] The optimal temperature frequency in turn depends on the pyroelectric material type and thickness.[33] Therefore, we need to design the circuit such that the resonant frequency matches the frequency of pyroelectric system. Very high or low voltage results in degradation of energy performance due to losses in the electrical circuit. The inductor L connected between the active material and the electronic circuit forms a low-pass filter with the ferroelectric material capacitor C.[48] The low-pass filter formed using an inductor regulates voltage frequency to optimize the electronic circuit design. The voltage oscillations can be smoothed as in made almost constant by adjusting the values of inductance and pyroelectric capacitance used such that high voltage frequencies are not allowed to pass through the circuit. This is achieved when for high frequencies the impedance of the inductance and capacitance circuit is increased and there is subsequent drop in the value of output voltage. Secondly, whatever voltage frequency is allowed to pass through the low pass filter can further be regulated by adjusting the Pulse Width Modulator frequency of switching which, at higher frequency, stabilises the voltage oscillations as the capacitor has smaller and further smaller time to discharge its voltage as the time available reduces due to higher pulse modulator frequency. PWM reduces average power that the pyroelectric material generates due to Duty Cycle based switch off operation.[48]

The pyroelectric element is connected to a switched inductor in parallel to the AC side of a rectifier bridge, the DC side of the rectifier being connected to an energy storage cell. After reaching a minimum temperature, the switch is turned ON at a time corresponding to half a period of the electrical oscillations. An oscillating discharge of the pyroelectric capacitor C occurs then through the inductor L, as the polarity is reversed at minimum temperature point. The inductor as a result develops a magnetic field that induces voltage in the opposite direction. This helps in extracting charge which could not be extracted earlier due to response lag in the material to temperature change and thus contributes to enhancing the energy harvesting efficiency. The switch is turned OFF after a small time which is much smaller than the temperature cycle period, as the pyroelectric voltage polarity is reversed. The inductor stores the electrical energy from the time the switch is turned ON till the time it is switched OFF. The stored energy is then released as the voltage across the pyroelectric material is reversed. A small amount of energy is dissipated in the inductor during this operation, so the absolute value of the reversed voltage is reduced by a factor beta compared to its value just before the switch is turned ON ($0 \leq \beta < 1$). This operation is then repeated after each half cycle of electrical oscillation. Since there is small dissipation of energy during the cycle by the inductor, the voltage realised after the inductor starts to conduct electrical current is reduced to that effect which is given by the factor of Beta (Ratio of Reversed Voltage to Original Voltage at start of switching process). This ratio is also called inversion ratio. Lower the inversion ratio for Synchronized Switch Harvesting on Inductor (SSHI) circuit, the optimal DC voltage reduces in value resulting in lower energy harvesting performance. Optimal DC voltage corresponds to the maximum work done by the electrical harvesting device.[48]

The Optimal DC voltage is given by the formula:

$$(V_{dc})opt = p\Phi(\theta_h - \theta_c)/2C(1 - \beta)$$

And, maximum energy harvested per temperature cycle is given by

$W_{MAX} = (p\Phi(\theta_h - \theta_c))^2/2C(1 - \beta)$

Where p, θ, C, Φ are pyroelectric coefficient, temperature, capacitance of the pyroelectric element, and the surface area of its electrodes, respectively. θ_h minus θ_c is the temperature range under which the pyroelectric system operates. [48] The timing of the switch operation relative to the thermal cycles and the inherent response of the pyroelectric material is critical. Proper synchronization ensures that the voltage inversion occurs at the optimal point in the thermal cycle, maximizing the inversion ratio. Therefore, the Duty cycle needs to be optimal. The Duty cycle is the percentage of time the switch is ON compared to the total time period of the input signal. By changing the Duty Cycle value, we can control how much AC voltage becomes the DC voltage. The formula for conversion between AC voltage to DC voltage based on Duty Cycle value, is given by $V_{ac} = V_{dc}(2D - 1)$.[48] Also, dielectric losses of the pyroelectric material should be low so as to maximize the inversion ratio.

Optimal temperature fluctuation frequency depends on radiation intensity, heat capacity and dimensions of the pyroelectric material. The pyroelectric material needs to be of appropriate heat capacity even if it has higher pyroelectric coefficient. Heat conduction rate across the pyroelectric material should be more than the heat transfer rate from environment to the material so that the temperature gradient is not established and a uniform temperature is obtained across the material length.[20]

There is an increase in pyroelectric coefficient and a decrease in piezoelectric coefficient as temperature increases. Stretchable pyroelectric nanogenerators (SPNG) produced by combining poly (vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)] and polydimethylsiloxane (PDMS) helps combine piezoelectric and pyroelectric effects. The output voltage of stretchable pyroelectric nanogenerators is five times that of normal pyroelectric nanogenerators under similar conditions due to additional piezoelectric effect.[24] Other such composites need to be studied that provide higher hybrid energy performance based on piezoelectricity and pyroelectricity for example, PDMS can also be used along with PZT for hybrid energy harvesting. Nanowires formed for ceramic based pyroelectric materials provide mechanical flexibility to the material.[24] Since PVDF presents both piezoelectricity and pyroelectricity, combining both effects for thermal energy harvesting should increase the harvested energy. SMAs (shape-memory alloys) have the ability to convert thermal energy into strain. Consequently, a composite material combining PVDF and SMA has been developed. When the composite temperature increases, the pyroelectric effect displaces electrical charge to the electrodes of the PVDF film, and the SMA deforms the PVDF which adds up to that through the piezoelectric effect. The SMA elements were composed by $Ti_{50}Ni_{25}Cu_{25}$. It is critical that the composite is designed in such a way that the polarity of the piezoelectric and pyroelectric signals is the same, so that they do not offset each other.[49] There is thus an increase of 75% on the output pyroelectric voltage and 200% on the harvested pyroelectric energy. As a result of the flexibility and thinness of the prepared composite and its relatively low-cost production, the use of PVDF with SMAs can be a good candidate for energy harvesting systems where thickness and flexibility are requirements.[49] [50]

When using hybrid energy harvesting systems that combine pyroelectricity with piezoelectricity, we need to use load resistance that allows for optimal energy output as the frequency of

electrical output may be different for pyroelectricity vis a vis piezoelectricity. A high load resistance circuit will respond to a slower frequency source more than a high frequency source. Therefore, one energy source output may dominate over the other depending on the load resistance used.[51] Similarly, when using say hybrid energy harvesting system that uses triboelectricity and pyroelectricity, for certain setups, temperature of the energy harvesting system may become a differentiator with regards to the electrical output from the respective sources.[52]

The hysteresis loop of pyroelectric material changed slightly with increase of temperature [31], as the molecular mobility increases with temperature improving ferroelectric switching i.e. it becomes easier to reduce the polarization to zero. Therefore, look into material structures or a combination of electrode and material structure where increase of temperature can produce bigger shifts in hysteresis resulting in higher energy harvesting performance as hysteretic losses are reduced.

Setup criteria affecting Olsen's and Kim's energy harvesting cycles

A pyroelectric generator solely relying on temperature fluctuations for energy harvesting has a low energy conversion efficiency. Attention has therefore been focused on thermal-electrical (T–E) cycles using pyroelectric materials. In this technique, an electric field is applied synchronously with the temperature variation, enhancing the conversion efficiency of a pyroelectric generator.[53] The reason a higher conversion efficiency is obtained is due to the hysteresis effect of the pyroelectric material. A synchronised application and reduction of electric field with the temperature change for a pyroelectric material helps overcome the response lag in generating optimal polarization or reducing polarization by optimal amount due to only temperature change. Therefore, when an electrical field is applied during phase when temperature is maintained constant then the material is made to reach optimal polarization increase or decrease before the temperature change induces the polarization change on its own. This creates a loop or an enclosed area on the polarization-electric field graph. The area of the loop characterizes energy generated by the process. The T-E cycle follows the electro-thermodynamic equation:

$$dD/dt = \varepsilon . dE/dt + p . d\theta/dt$$

where D, E, θ, ε, t, and p, are the polarization density, electric field, temperature, dielectric permittivity, time, and pyroelectric coefficient, respectively.

During the T-E cycle first an isothermal process is created where temperature is constant but the electrical field increases in intensity. The polarization increases in this phase and then second phase is isoelectric, where the electric field is kept constant and temperature increases which results in polarization drop and then third phase is again isothermal where electric field is decreased resulting in polarization decrease and then last phase is isoelectric, where temperature is decreased resulting in polarization increase. So, this cycle has both electric field and temperature changes resulting in increased energy conversion which can go as high as 50%. This is called Olsen T-E cycle.[53]

There is another T-E cycle called Kim's cycle which has even higher energy conversion than Olsen cycle. The only difference between Kim's cycle and Olsen cycle is that during phase 2, the electric field instead of being constant is increased while the temperature is also increasing. The decrease in polarization due to increase in temperature is compensated for by increase in electric field intensity, resulting in constant polarization. Electrical insulation between the pyroelectric material and the load during this phase ensures constant polarization. This creates a Polarization Electric Field loop which has a larger area and so a higher energy conversion efficiency. Energy density generated from Kim's cycle can be 1.5 times higher than that generated from Olsen's cycle.[53]

The power density of the conversion cycle scales linearly with the applied field, while the primary losses associated with the repetitive charging and discharging of the pyroelectric receiver scale with the square of applied voltage.[1] This means that a peak power density is obtained for a specific voltage. This specific voltage is determined by optimal pyroelectric coefficient value and dielectric loss value for the pyroelectric material for the given voltage.[1] Moderate amount of electric field voltage can enhance the dipole alignment resulting in increase of pyroelectric coefficient but higher voltage levels may result in saturation of the polarization effect thus rendering the material less responsive to temperature induced polarization changes so the pyroelectric coefficient decreases. Similarly, at low voltage the dielectric loss should be constant but at higher values as charge mobility increases the dielectric losses also increase. Therefore, materials with high pyroelectric coefficient and low dielectric loss value will result in best energy harvesting performance in Olsen cycle.

The setup for energy harvesting based on Olsen's cycle includes an inductor which ensures a minimal electrical loss due to resonant frequency-based transmission of charge to the pyroelectric material from the bias capacitor or from pyroelectric material back to the bias capacitor. An additional capacitor (referred as "bias capacitor") is added in series with the device to maintain a relatively stable DC voltage due to its large capacitance during the complete cycle. It is used for charging or discharging the pyroelectric material. A synchronized switch is connected to the inductor, and is in closed state only for half of the resonant period, which ensures that the charging is optimal as it is allowed till the current becomes zero on the inductor. A full-bridge rectifier composed of four semiconductor diodes is applied in order to both clamp the material voltage during isoelectric heating/cooling (diodes have threshold voltage limit above which it allows current to pass through it) and direct the pyroelectric current to a storage capacitor or a battery.[1]

During the first stage of charging of the pyroelectric material, the inductor switch is closed resulting in the high voltage current flow from the bias-capacitor to the pyroelectric capacitor (PEC). As the current flows to the PEC, its voltage rises and the current through the inductor also rises (which creates a magnetic field that opposes the current flow) but as the voltage of the PEC becomes equal to the bias-capacitor, the inductive kickback effect steps in. The energy stored in the magnetic field of the inductor is transferred to PEC, as an E.M.F. is induced in the direction of current flow, due to the inductive kickback effect after current flow is stopped. When the magnetic field in the inductor collapses, the potential difference across the PEC becomes greater than the potential difference across the bias-capacitor and the current in the inductor drops to zero. The inductive kickback effect is aided by the resonant conditions created in the

inductor capacitor circuit. As half resonant period is reached, the switch is set to open and the second stage of isoelectric heating starts. In the isoelectric heating stage, the pyroelectric material is heated and the resultant voltage fluctuation across PEC is passed through the bias-capacitor which has a stable DC voltage. The current passes through the full bridge rectifier that directs it to the storage load capacitor. The clamping by the rectifier stabilizes the voltage and thus maintains the electric field across PEC. As the heating phase is completed, the third phase of discharging the PEC starts, where the inductor switch is closed again resulting in reverse current flow from PEC to bias-capacitor and the voltage across PEC drops till it goes below the stable voltage of bias-capacitor due to the inductive kickback effect and the inductor current again becomes zero. In the fourth stage of isoelectric cooling, again the inductor switch is set to open state, the reverse current flows from PEC and bias-capacitor end to the rectifier and then to load capacitor. In the experiment, the switch is actively controlled by a triggering signal from the laser source (used for heating PEC) to achieve synchronization.[1]

The charging and discharging process conducted with the help of a bias capacitor helps in covering up for the response lag during the pyroelectric energy conversion process, from thermal to electrical, as the temperature is raised or brought down.

To achieve Kim's cycle-based energy harvesting, during the second phase, the pyroelectric system is isolated from the circuit as the switch connecting it to the circuit is put OFF. The temperature still continues to rise and as a result of the equation:

$$dD/dt = e.\ dE/dt + p.\ dT/dt$$

where D is electrical displacement, e is dielectric permittivity, E is electrical field, p is pyroelectric coefficient, T is temperature and t is time;

the electric field within the isolated pyroelectric material begins to rise. The increase in temperature induces a change in polarization but the flow of electrons, as a result of polarization change, is impeded, as the material is not connected to the circuit. Therefore, the electrical displacement is held constant. This makes the internal electrical field of the pyroelectric material to increase in order to counterbalance the change in polarization as per the equation above. When the temperature increase is completed, the switch is turned ON as the pyroelectric material is reconnected to the circuit, the current flows back in the circuit wherein, voltage of the pyroelectric material is clamped by the rectifier diodes as the load capacitor is charged. Thereafter, the discharging process as described above is implemented.[19]

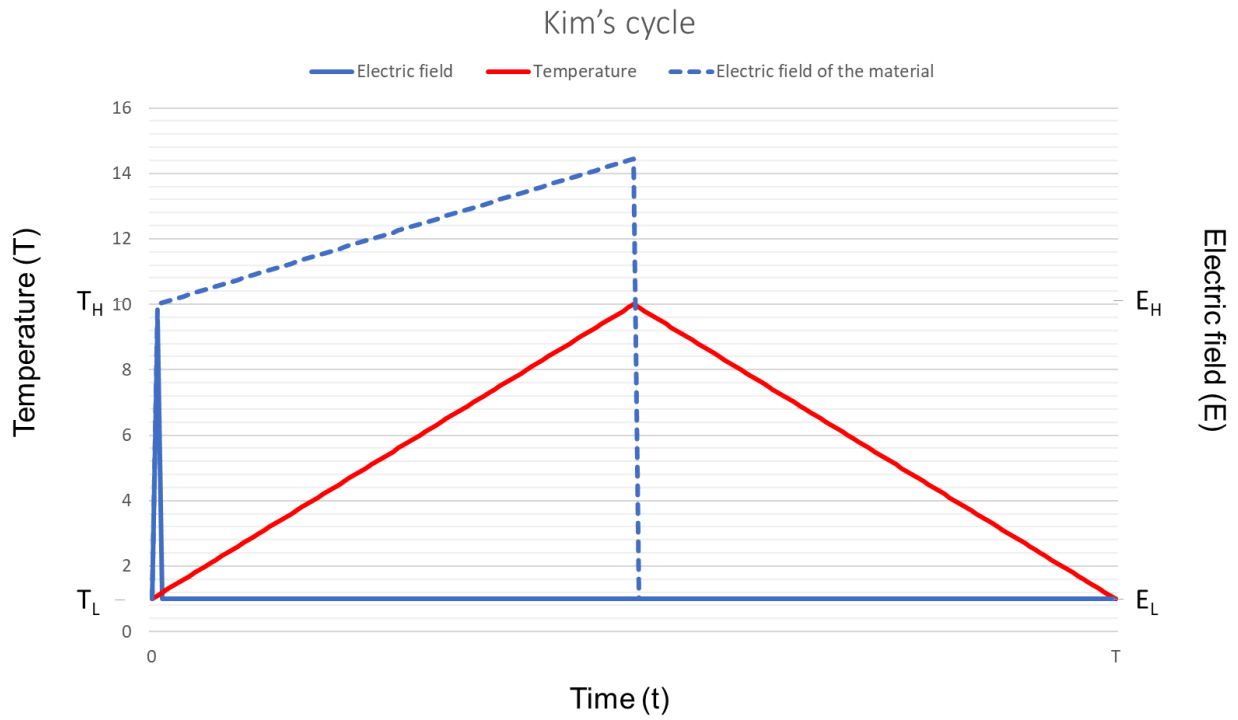

Figure 4: A graphical representation of the changes in temperature and electric field in the Kim's cycle. An external electric field is briefly applied to the system when the temperature begins to rise. After the system is isolated from the circuit (electric field), there is an additional increase in the internal electric field of the material. When the temperature increase is completed, the system is reconnected to the circuit, and current flows back in the circuit. It is important to note the additional increase in the internal electric field of the material, which leads to the increase in efficiency. Reproduced from Kim *et al*.[19]

Energy density per cycle can be maximised in Olsen Cycle if applied electric field, temperature change and pyroelectric coefficient can be maximised. Therefore, higher electrical field values based on higher breakdown voltage of the pyroelectric material would ensure greater energy efficiency. Non-uniform temperature distribution across the pyroelectric material and high leakage current, when dielectric loss is high, can reduce energy density performance per cycle.

Large temperature fluctuations need to be targeted for maximum energy harvesting, preferably near Ferroelectric to Paraelectric (FE-PE) transition phase as change in polarization is maximum. Also, the temperature for phase transition of pyroelectric materials increases with application of electric field. Application of electric field helps pyroelectric materials jump the antiferroelectric region (AFE) and therefore improve energy harvesting performance. The antiferroelectric region is where the dipole alignment is non-parallel to an extent that the net polarization becomes zero. When an electric field above a certain value is applied and the temperature increases, the materials go through Ferroelectric–Paraelectric phase transformation without going through the AFE phase.[19]

Beyond the FE-PE transition phase, the polarization of the pyroelectric material vanishes, so the dipole realignment requires application of electric field. Therefore, extra energy in the form of an

applied electric field would be required to perform the Olsen/Kim cycle when the material undergoes phase transition, in order to repolarize the material. Therefore, for pyroelectric processes where the material is subjected to temperatures beyond Curie Point, an optimal electric field required to effect necessary repolarization would need to be applied.

Olsen cycle includes discharging process so, non-ferroelectric materials won't be good choice for such a cycle, thus mandating the use of only ferroelectric materials. Ferroelectric crystals belong to a group of 10 crystals out of 32 different classes of crystals, which have non-centrosymmetric crystal structure and have permanent electric dipole.[54] Above the Curie point, pyroelectric materials that are not ferroelectric lose their spontaneous polarization and become non-polar. In this non-polar (or paraelectric) phase, they do not exhibit pyroelectric effects and are generally not polarizable by an external electric field. They behave like ordinary dielectrics without the ability to align internal dipoles in response to an external field. Thus, the energy harvesting cycle using non-ferroelectric material will not be optimal. Ferroelectric materials, above the Curie point, lose their spontaneous polarization, meaning they no longer have a built-in electric dipole. However, they remain polarizable in the paraelectric phase. This means they can still align their internal dipoles in response to an external electric field, although this response is now linear and lacks the hysteresis characteristic of the ferroelectric phase.

The losses in implementing Olsen's cycle also comes from damping losses from the operating inductor for charging and discharging process at resonant frequency plus the damping losses at the rectifier diodes. So, within a certain optimal range of voltage accumulation at capacitor, there is highest power generation beyond which the power generation drops significantly.[1]

Conclusion

The optimal thickness for a pyroelectric material is influenced by multiple criteria depending on the application environment, material quality, and its geometry. For example, if the pyroelectric generator is exposed to a high temperature environment, then high thickness of the material is preferred and vice versa. The application environment may also entail operating within a range of temperature oscillation frequency. In these cases, usage of thin pyroelectric materials may result in poor energy harvesting performance as the frequency varies from its optimal value. Any 3D etching on the material surface also requires the material to be of suitable thickness. Meanwhile, a material's crystallization quality may not scale well with increasing thickness, so a suitable dopant may be added to remedy the problem. Therefore, when deciding on the optimal material thickness, multiple operational factors must be considered, and deviating from their criteria may result in subpar energy harvesting performance.

The use of dopants and plasmonic material can change the pyroelectric material's pyroelectric coefficient, curie point, dielectric constant, dielectric loss, phase change temperatures, and hysteretic loss among other properties. These material properties can be optimized to further improve energy harvesting performance. Furthermore, the use of dopant can be customized based on end use application. For example, to provide flexibility in harnessing radiation energy across the electromagnetic spectrum by varying the geometry of these plasmonic structures and their nanoscale particle size. Therefore, a range of pyroelectric materials can be used with the help of such plasmonic materials in optimal quantities.

The structural design of the electrode along with its radiation absorbance and thermal conductivity can change the energy efficiency of the pyroelectric system. Structural changes such as introducing meshed electrodes with optimal coverage area can improve the electrical output of the pyroelectric system severalfold. Additionally, the use of three-dimensional cavities on the surface of the pyroelectric material, as well as plasmon induced electrodes can reduce the optimal electrode coverage area, benefitting the energy harvesting performance. The ratio of depth of 3D cavity to the meshed electrode square width needs to be assessed for optimal energy harvesting performance, as an area for further research in this field.

Different application environments require appropriate setups for optimal performance. Solar energy harvesting requires thin plasmon induced pyroelectric material with high dielectric breaking strength for high energy harvesting performance. Similarly, rhombohedral crystal structure in the pyroelectric material resulted in enhanced energy performance for high temperature applications like the heat from an automobile's exhaust. In case of energy harvesting of hot/cold water from industrial processes, there needs to be optimal oscillation frequency of the pyroelectric device depending on the temperature range under which it operates and pyroelectric material properties. Pyroelectric applications should consider scenarios where temperature is high and include Curie Point as pyroelectric coefficient peaks near Curie Temperature. The pyroelectric circuit using an inductor should be designed such that the resonant frequency of the circuit should match the temperature oscillation frequency of the pyroelectric system. The timing of the switching operation relative to the thermal cycles and the Duty Cycle of switching operation should be optimal so that maximum energy is harvested. Other such composites need to be studied that provide higher hybrid energy performance. Also, we need to look into material structures or a combination of electrode and material structure where increase of temperature can produce bigger shifts in hysteresis resulting in higher energy harvesting performance as hysteretic losses are reduced.

Thermal-electrical (T-E) cycles like Olsen and Kim, help increase the energy conversion efficiency of the pyroelectric system. The energy conversion efficiency can go up to 50% higher. However, there is energy loss due to repetitive charging and discharging of pyroelectric material along with energy dissipation by the inductor and rectifier diodes used in the circuit, which scale up as there is increase in applied voltage. Therefore, optimal applied voltage results in peak power density for the T-E cycle. Further, we can say that if the pyroelectric material has high resistance to fatigue from repetitive charging and discharging, and has ability to bear high electric field intensity then as a result, the energy conversion efficiency would be significantly higher. Ferroelectric materials would be a better option compared to non-ferroelectric material for applications where the material operates at temperatures above Curie Point.

Finally, we see that pyroelectric material's optimal thickness, use of appropriate dopants and plasmons in optimal quantity, use of optimally designed electrodes, efficiently designed energy harvesting circuit, taking into account the application environment parameters, enhances the energy conversion efficiency.

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