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A modified figure of merit for pyroelectric energy harvesting

C. R. Bowen^{*1}, J. Taylor¹, E. Le Boulbar¹, D. Zabek¹, V. Yu. Topolov²

¹Department of Mechanical Engineering, University of Bath, Bath, BA2 7AY, United Kingdom

²Department of Physics, Southern Federal University, 5 Zorge Street, 344090 Rostov-on-Don, Russia

* corresponding author: c.r.bowen@bath.ac.uk

Abstract. This paper reports a new figure of merit for the selection of pyroelectric materials for thermal energy harvesting applications, for example, when the material is exposed to heat or radiation of a specified power density. The figure of merit put forward and developed is of interest to those selecting materials for the design of thermal harvesting devices or the development of novel ceramic, single-crystal and composite materials for pyroelectric harvesting applications.

Keywords: pyroelectric; harvesting; thermal; ferroelectric

Introduction

Energy harvesting is a topic of intense interest as a result of the growing energy demands of society and as a potential approach to create autonomous and self-powered systems; examples are energy-harvesting devices for battery-free wireless sensor networks which do not require maintenance or replacement. In the context of thermal energy harvesting, heat remains an almost ubiquitous and abundant ambient source of energy that is often wasted [1] [2]. A significant amount of waste heat is lost as a by-product of power, refrigeration, or heat pump cycles [3]. Pyroelectric harvesting by radiative heating has also been considered by a number of researchers [4] [5] [6].

Thermoelectrics have been widely used and considered as a means to convert temperature gradients (dT/dx , where T is temperature, and x is co-ordinate) into electrical energy using the Seebeck effect. A less widely researched area is ‘pyroelectric harvesting’ in which temperature fluctuations (dT/dt , where t is time) are converted into electrical energy. This has similarities to the way in which piezoelectric harvesters convert mechanical oscillations ($d\sigma/dt$, σ is mechanical stress) into electrical energy. Pyroelectric materials are of interest as they have the potential to operate with a high thermodynamic efficiency and, compared to thermoelectrics, do not require bulky heat sinks to maintain the temperature gradient.

Pyroelectric effect and energy harvesting

All pyroelectrics are polar materials and exhibit a spontaneous polarisation in the absence of an applied electric field, and the spontaneous polarisation is defined as the average electric dipole moment per unit volume [7]. The presence of the spontaneous polarisation leads to a layer of charge on each surface of the material, and free charges, such as ions or electrons, are attracted to the charged surfaces of the poled material. The origin of pyroelectric effect stems from the behaviour of surface charge as the ambient temperature is changed and assuming that polarization level of the material is dependent on temperature [8].

If a pyroelectric material is exposed to radiation of power density W ($\text{J s}^{-1} \text{m}^{-2}$) for a time, Δt , radiation is absorbed onto the surface of the material which results in an increase in the temperature, ΔT (Figure 1). It is assumed that all of the power absorbed in time Δt is rapidly distributed through the pyroelectric element volume, resulting in a uniform temperature increase. In this case, to simplify the process, heat losses from the pyroelectric are neglected. The increase in temperature is related to incident power density by:

$$\Delta T = \frac{W \cdot \Delta t}{c_E \cdot h \cdot \Delta T} = \frac{W \cdot \Delta t}{c_p \cdot \rho \cdot h \cdot \Delta T} \quad (1)$$

where h is the pyroelectric thickness (m), c_p is the specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$), ρ is the density (kg m^{-3}), and c_E is the volume specific heat ($\text{J m}^{-3} \text{K}^{-1}$). As the temperature of the pyroelectric material increases (i.e. $dT/dt > 0$), there is a decrease in its level of the spontaneous polarisation as dipoles within the material lose their orientation due to thermal vibrations. This fall of the polarisation level leads to a decrease in the number of unbound charges on the material surface [8]. The pyroelectric coefficient of an unclamped material, under a constant stress and electric field, is defined by Equation 2,

$$p^{\sigma,E} = \left(\frac{dP_s}{dT} \right)_{\sigma,E} \quad (2)$$

where P_s is the spontaneous polarisation, and the subscripts σ and E correspond to the conditions of constant stress and electric field respectively. While the pyroelectric coefficient is a vector quantity, the electrodes that harvest the charges are often normal to the polar direction, i.e. are on the upper and lower surfaces of the element (figure 1), and therefore, the pyroelectric coefficient is often treated as a scalar quantity [8].

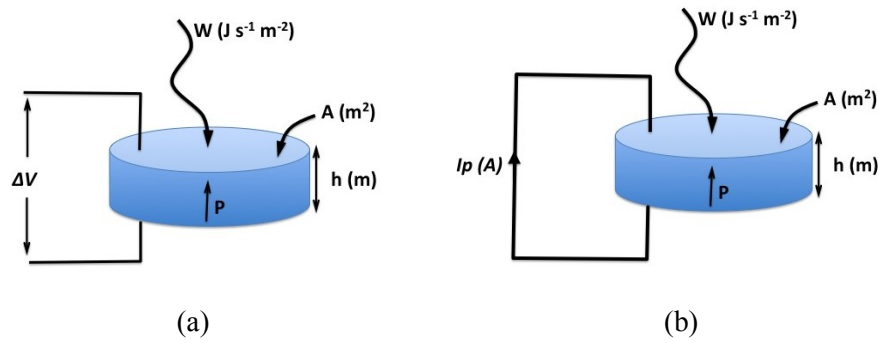


Figure 1. Pyroelectric element subjected to heat flux with (a) open and (b) closed circuit conditions. Polarisation direction (P) is through the thickness as shown and electrodes at the top and bottom faces.

When the pyroelectric is subjected to radiation of power density, W , that results in a temperature increase (ΔT), the charge (ΔQ) released by the area (A) of material due to a decrease in polarisation is given by,

$$\Delta Q = p \cdot A \cdot \Delta T$$

and from Eqn. 1,

$$\Delta Q = \left[\frac{p}{c_E} \right] \cdot \left[\frac{A}{h} \right] \cdot W \cdot \Delta t \quad (3)$$

Under open circuit conditions, as schematically shown in figure 1(a), the charges that are free due to the decrease in polarisation remain at the electrode surface and an electric potential (ΔV) is generated across the material thickness. From the relationship $\Delta Q = C \Delta V$ between charge and capacitance (C) and considering the pyroelectric element as a parallel plate capacitor, where $C = A \epsilon_{33}^\sigma / h$, the potential difference is:

$$\Delta V = \frac{p}{\epsilon_{33}^\sigma} \cdot h \cdot \Delta T$$

and from Eqn. 1

$$\Delta V = \left[\frac{p}{c_E \cdot \epsilon_{33}^\sigma} \right] \cdot W \cdot \Delta t \quad (4)$$

where ϵ_{33}^σ is the permittivity of the pyroelectric material (F m^{-1}).

If the material is under short circuit conditions, as shown in figure 1(b), the change in temperature results in an electric current flowing between the two polar surfaces of the material. Eqn. 5 describes the relationship between generated pyroelectric current (i_p), rate of temperature change (dT/dt), surface area of the element and pyroelectric coefficient (p) [9]:

$$i_p = \frac{dQ}{dt} = p \cdot A \cdot \frac{dT}{dt}$$

and from Eqn. 1

$$i_p = \left[\frac{p}{c_E} \right] \cdot \left[\frac{A}{h} \right] \cdot W \quad (5)$$

Figures of Merit (FOM) for Pyroelectric Materials

A variety of FOMs have been derived for pyroelectric materials selection based on consideration of the thermal and electrical circuits employed [9]. The most common FOMs are based on the generation of maximum current or voltage for a given power input for applications such as thermal imaging sensors [8] [10] [11].

For a high voltage responsivity (F_v) the relevant figure of merit [8] to maximise pyroelectric voltage for a given W value can be seen from Eqn. 4, namely,

$$F_v = \frac{p}{c_E \cdot \epsilon_{33}^\sigma} = \frac{p}{\rho \cdot c_p \cdot \epsilon_{33}^\sigma} \quad (6)$$

To maximise performance of infrared detection devices based on current responsivity (F_i) [8] in order to maximise the pyroelectric current generated for a given value of A , h and W , the FOM from Eqn. 5 is given by

$$F_i = \frac{p}{c_E} = \frac{p}{\rho \cdot c_p} \quad (7)$$

The two FOMs from Eqns. 6 and 7 are often used for selection of materials for heat and infra-red detection, but these are not to be confused with energy-harvesting applications where generated power is a key criterion as well as the overall efficiency of the conversion of thermal energy to electrical energy.

For energy harvesting applications two pyroelectric based FOMs have been proposed [12] [13]. An electro-thermal coupling factor has been defined to estimate the effectiveness of thermal harvesting [12]:

$$k^2 = \frac{p^2 \cdot T_{hot}}{c_E \cdot \epsilon_{33}^\sigma} = \frac{p^2 \cdot T_{hot}}{\rho \cdot c_p \cdot \epsilon_{33}} \quad (8)$$

where T_{hot} is the maximum working temperature.

An energy-harvesting FOM, F_E , has also been proposed as [13]:

$$F_E = \frac{p^2}{\epsilon_{33}^\sigma} \quad (9)$$

The F_E FOM has been widely used for materials selection and materials design [14] [15] [16] [17] [18] for pyroelectric harvesting applications. It is of interest to note that compared to the voltage (F_v) and current (F_i) responsivities, the harvesting FOM, F_E , does not include the volume heat capacity. Atulasimha et al. [19] have also provided a simple but effective analysis of the influence of harvested power on factors such as geometry, clamping conditions and material properties.

We now derive a modified pyroelectric thermal harvesting figure of merit, F'_E , by considering the electrical energy associated with the temperature change or applied power density which gives rise to an increase in electric potential under open circuit conditions as in Eqn. 4. A similar approach has been used to derive criteria for the selection of piezoelectric vibration harvesting materials [20]. Since the change in energy (ΔE) stored in a capacitor is $\frac{1}{2}C(\Delta V)^2$, then

$$\Delta E = \frac{1}{2} \cdot \left[\frac{p^2}{\epsilon_{33}^\sigma} \right] [A \cdot h] \cdot (\Delta T)^2 \quad (10)$$

and from Eqn. 2,

$$\Delta E = \frac{1}{2} \cdot \left[\frac{p^2}{\epsilon_{33}^\sigma \cdot (c_E)^2} \right] \cdot \left[\frac{A}{h} \right] \cdot (W \cdot \Delta t)^2 \quad (11)$$

As follows from Eqn. 10, if the material with specific values of A and h is subjected to a specific thermal cycle (ΔT), then the relevant FOM is p^2/ϵ_{33}^σ as in Eqn. 9; this is valid if the harvesting device is subjected to two specific temperatures via a pumping cycle or if the pyroelectric is used for harvesting of a heat source and heat sink of specific temperatures [16]. However, in a number of cases the harvesting device may be subjected to an incident heat source of specific energy density, W , e.g. as in [21] [22] [23]. The new material FOM is written as,

$$F'_E = \frac{p^2}{\epsilon_{33}^\sigma \cdot (c_E)^2} \quad (12)$$

This particular pyroelectric-harvesting FOM indicates that potential materials operating under these conditions should have a high pyroelectric coefficient to develop a large charge with a temperate change, a low permittivity to develop a large potential difference as a result of the charge generated and a low volume specific heat to ensure the temperature rise due to the incident power density is large. Surprisingly this simple of merit has not used or reported in order to select potential materials for energy harvesting related applications. It is of interest to note that the relation $F'_E = F_v \cdot F_i$ holds, see Eqns. 6, 7 and 12.

At this stage it is of interest to compare the F_v , F_i , k^2 , F_E and F'_E FOMs for conventional pyroelectric materials, see Table 1, which includes a set of parameters of pyroelectric materials employed in heat detectors and thermal energy harvesting. Due to the relatively small difference in volume specific heat between materials the current responsivity, F_i , is largest for the materials with the highest pyroelectric coefficients, such as the poled ferroelectric ceramics (PZT) and domain-engineered relaxor-ferroelectric single crystal (PMN-PT). The low permittivity of PVDF leads to a high voltage responsivity, F_v , for this material. The k^2 coupling coefficient is high for PMN-PT due to the high pyroelectric coefficient. In terms of the p^2/ϵ_{33}^σ energy-harvesting FOM, PMN-PT single crystal material is particularly high in addition to LiTaO₃ single crystal and PZT ceramic; this is due to the high pyroelectric coefficient and strong dependency on p^2 . For the new F'_E FOM from Eqn. 12, PMN-PT remains a material of high performance, however the low squared volume specific heat of PVDF leads to F'_E being almost as large as that of PZT. This is of interest sine PVDF based materials can be relatively low cost, easily manufactured in thin and large area sections, have high breakdown strength, are flexible and damage tolerant. Composite systems, such as those with tailored porosity, may be of interest for achieving a high F'_E value by maintaining a high pyroelectric coefficient but reducing both permittivity and volume specific heat [18].

Table 1. Figures of merit F_i , F_v , k^2 , F_E and F'_E for variety of materials, $T_{hot} = 298K$ for k^2 (%).

Physical parameter	PMN-0.25PT SC ^a	PZT ^b	PVDF ^c	ZnO SC	LiTaO ₃ SC
p ($\mu C m^{-2} K^{-1}$)	1790 [24]	533 [24]	33 [24]	9.4 [7]	230 [9]
$\epsilon_{33}^{\sigma} / \epsilon_0$	961 [24]	1116 [24]	9 [24]	11 [25]	47 [9]
c_E ($MJ m^{-3} K^{-1}$)	2.5 [24]	2.5 [24]	1.8 [24]	2.3 [26]	3.2 [9]
F_i ($pm V^{-1}$)	716	213	18.3	4.1	71.9
F_v ($m^2 C^{-1}$)	0.08	0.02	0.23	0.04	0.17
k^2 (%)	4.5	0.34	0.23	0.01	1.18
F_E ($J m^{-3} K^{-2}$)	376.7	28.8	13.6	0.91	127.2
F'_E ($\times 10^{-12}$) ($m^3 J^{-1}$)	60.3	4.6	4.2	0.17	12.4

^a Relaxor-ferroelectric 0.75Pb(Mg_{1/3}Nb_{2/3})O₃–0.25PbTiO₃ single crystal poled along [111] of the perovskite unit cell; ^b Poled ceramic; ^c Polyvinylidene fluoride, a polymeric ferroelectric.

In summary, the present publication provides the new pyroelectric harvesting FOM, $p^2 / \epsilon_{33}(c_E)^2$, to select and compare materials for pyroelectric energy harvesting when the harvesting element is subjected to an incident power density. The FOM is of interest to those considering the design of thermal harvesting devices or the search and development of new materials and composites for pyroelectric harvesting applications. Additional FOMs that include dielectric loss and diffusivity have been defined for thermal sensing [9] and may be of interest to also adapt for harvesting applications.

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