SCIENCE CHINA
Technological Sciences

Special Topic: Functional Materials
• **Review** •

July 2016 Vol.59 No.7: 1012–1022
doi: 10.1007/s11431-016-6081-7

Ferroelectric materials for vibrational energy harvesting

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Received January 2, 2016; accepted May 10, 2016; published online June 20, 2016

Energy harvesting is an appealing technology that makes use of the ambient energy which is otherwise wasted. Piezoelectric materials directly convert the elastic energy to the electric energy, and thus have a great advantage in scavenging vibrational energy for simplicity in device structure with relatively high power density. This paper provides an overview on the research of piezoelectric materials in energy harvesting in recent decades, from basics of piezoelectricity and working principle of energy harvesting with piezoelectric materials, to the progress of development of high-performance piezoelectrics including ceramics, single crystals and polymers, then to experimental attempts on the device fabrication and optimization, finally to perspective applications of piezoelectric energy harvesting (PEH). The criteria for selection of materials for PEH applications are introduced. Not only the figure of merit but also maximum allowable stress of materials are taken into account in the evaluation of their potential in achieving high energy density and output power density. The influence of the device configuration on the performance is also acknowledged and discussed. The magnitude and distribution of induced stress in the piezoelectric unit upon excitation by the vibration source play an important role in determining the output power density and can be tuned via proper design of device configuration without changing its resonant frequency. Approaches to address the issue of frequency match accompanying with the resonant mode are illustrated with literature examples. Usage of PEH devices can be extended to a variety of vibration sources in everyday life as well as in nature. Some appealing applications of PEH, such as in implantable and wearable devices, are reviewed.

energy harvesting, ferroelectric materials, piezoelectricity, figure of merit, applications

Citation: Song J D, Wang J. Ferroelectric materials for vibrational energy harvesting. Sci China Tech Sci, 2016, 59: 1012–1022, doi: 10.1007/s11431-016-6081-7

1 Introduction

Energy harvesting is the technology that converts the ambient energy in the form of vibration, heat, light, etc. into the available energy (usually electric power) [1]. Compared with traditional batteries, energy harvesters have widely-spread resources in nature and everyday life, much longer life time, and no hazard to environment [2]. Until now, energy harvesting has not achieved the capability to provide as large power as batteries within the limited space, but it has started to show promising potential for applications in micro-electro-mechanical systems (MEMS) and low-power electronic apparatus. For example, some signal transmitters or environmental monitors need to work in the places which are dangerous or difficult to reach (e.g. desert, underwater or underground). Energy harvesting technique would endow them with self-powering ability, which certainly extends their life span of usage. Energy harvesting devices can also serve as a backup power for artificial heart pacemakers in which the power cutoff is fatal to the patients [3,4].

Among various forms of energy, vibration is ubiquitous and can be used as a stable energy-supplying source with a relatively high power density [5]. There are mainly three types of the energy harvesters for the conversion of mechanical power to electricity, namely electrostatic, electro-

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magnetic and piezoelectric. However, the electrostatic type is inferior in efficiency and requires additional voltage source. The electromagnetic type has complex structure, and hence is not suitable for applications in micro-sized devices [5]. Piezoelectric energy harvesting (PEH) has the advantage of simple construction structure, high power density and no need for extra power supply, thus it has aroused and continues to attract extensive research interest.

Piezoelectricity was first discovered on quartz, Rochelle salt and other minerals [6] in the 1880s, which produces a change of electric dipole when a force is imposed on. Since lead zirconate titanate ($Pb[Zr_xTi_{1-x}]O_3$, or PZT) was reported to exhibit excellent piezoelectric property in the 1950s [7], the widespread exploitation of the piezoelectric materials has been realized, including the development of PEH. By now PZT is still the most extensively used piezoelectric material due to its high piezoelectric constant, low loss factors and high Curie temperature [8]. However, the increasing depletion of lead severely endangered the environment and human health. Governments started to reinforce the legislation to restrict the exploitation of lead-containing materials, and encouraged researchers to devote more efforts to development of lead-free materials [9–12]. In recent years, a broad range of lead-free piezoelectric materials were evaluated as the competitive candidates to replace PZT [8], which opened up a perspective future for environment-friendly applications of PEH.

There has been much research effort dedicated to the development of piezoelectric energy harvesting including both materials and devices, and the progress in this field has been summarized in a number of review articles [1,2,13,14]. Recently, more and more attentions have been paid to the optimization of PEH devices towards high output power density, which requires not only proper selection of materials but also rational design of the device. Therefore, it seems necessary to provide a general view of the properties of relevant materials and device configurations from the perspective of output power density, which is the motivation of this review.

In this paper, we gave a short review on the application of ferroelectric materials including single crystals, ceramics and polymers in vibrational energy harvesting. Besides the figure of merit, we in particular paid attention to the maximum stress allowed in materials which is another important factor in determining the maximum available energy density as well as the output power density the materials can offer. The realization of the potential of materials (the maximum available energy density) relies on the ability of stress collection of the device which is controlled by the device configuration with given vibration sources. Thus the consideration on stress distribution and magnitude is also emphasized in the review of various device configurations in this paper. Specifically, we introduced in Section 2 the theory of piezoelectricity, illustrated the working principle of PEH, and formulated the criteria for selection of piezoelectric materials. In Section 3, several groups of ferroelectrics with superior piezoelectric and/or mechanical properties are reviewed and commented in terms of their relevant properties in the PEH applications. The design of the device configuration is also discussed in Section 3 with literature work as examples. In Section 4, perspective applications of PEH, e.g. in biomedical and wearable devices are discussed. A summary of the whole paper is drawn in the last section.

2 Piezoelectricity and working principle of PEH

Piezoelectricity means induction of a change of electric dipole upon act of force. The coupling between the dipole and the force is linear and reversible. The piezoelectric equations can be introduced to illustrate the relationship between the mechanical quantities and electric quantities in piezoelectric materials, in which the upper one describes the converse piezoelectric effect and the lower one describes the direct piezoelectric effect:

$$\begin{cases} \boldsymbol{x} = \boldsymbol{s}^E \boldsymbol{X} + \boldsymbol{d}_t \cdot \boldsymbol{E}, \\ \boldsymbol{D} = \boldsymbol{d} \cdot \boldsymbol{X} + \boldsymbol{\varepsilon}^X \boldsymbol{E}, \end{cases} \quad (1)$$

where $\boldsymbol{D}$ is a vector which stands for the dielectric displacement, and $\boldsymbol{E}$ the electric field; $\boldsymbol{x}$ is the strain tensor and $\boldsymbol{X}$ the stress tensor in Voigt notation; $\boldsymbol{\varepsilon}^X$ is a second-rank tensor which represents the permittivity under constant stress; $\boldsymbol{d}$ is a third-order tensor of the piezoelectric coefficient and $\boldsymbol{d}_t$ is the transpose of $\boldsymbol{d}$; $\boldsymbol{s}^E$ is a fourth-order tensor of the elastic compliance constant under constant electric field.

Figure 1 shows the atomic structure of Barium Titanate ($BaTiO_3$ or BT), a prototype of the perovskite piezoelectric materials [15]. Above the temperature of 120°C, the equilibrium phase of BT is a cubic structure which does not exhibit ferroelectricity or piezoelectricity. When the temperature decreases below 120°C, BT undergoes a tetragonal-phase transition and Ti ion moves from the center of the unit cell towards one of the oxygen ions. This displacement breaks the centro-symmetry of the crystal and generates a dipole, which can be affected by the applied stress. The

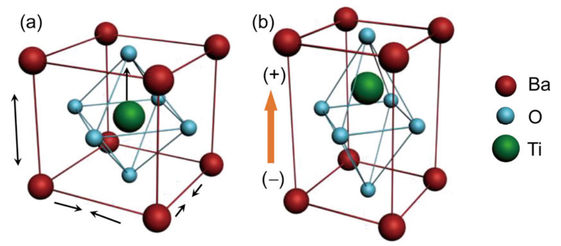

Figure 1 (Color online) Structural transformation $BiTiO_3$ from (a) the cubic phase towards (b) the tetragonal phase when it is cooled below the Curie temperature.

temperature at which a transition from centro-symmetric phase to non-centrosymmetric phase occurs is called Curie temperature (T_c). To acquire piezoelectricity on a macroscopic BT sample (single crystal or ceramic), a poling process is required to rearrange the polarization vectors in all kinds of microscopic regions to be parallel to the direction of the DC electric field.

Similar to appearance of the ionic polarity of BT, β-phase polyvinylidene fluoride (PVDF) can generate a molecular polarization as fluorine locates on the same side of the carbon chain (Figure 2(a)). On the macroscopic level, when the unit cells (Figure 2(b)) are reoriented to the same direction after poling, PVDF displays an obvious piezoelectricity [16]. T_c of the β-phase PVDF is ~120°C [17].

To assess the ability to convert vibration energy to electric energy, the piezoelectric materials is modelled as a parallel plate capacitor, as shown in Figure 3 [2]. When charges accumulate on two electrodes under the alternative force, the electric energy available E_a of the capacitor can be expressed as $\frac{1}{2}CV^2$ [18]. In the expression, C represents the capacitance which can be expressed as $C=\varepsilon\frac{ab}{h}$ and V is the voltage between the two electrodes which can be deduced by $V=\frac{dXab}{C}$, where d, X represents d_{33}, X_3 in the 33 mode and d_{31}, X_1 in the 31 mode. Combined the above expressions, E_a can be deduced as $\frac{1}{2}\frac{d^2}{\varepsilon}X^2\cdot(abh)$ and accordingly the available energy density D_a is

$$D_a=\frac{E_a}{abh}=\frac{1}{2}\frac{d^2}{\varepsilon}X^2. \quad (2)$$

It is seen that $\frac{d^2}{\varepsilon}$ (also expressed as $d\bullet g$ where g is the piezoelectric voltage coefficient) is a material-specific proportionality coefficient representing the dependence of the available-energy density on the applied stress, and it is hence defined as figure of merit (FOM) of the material for PEH applications [19]. Generally, FOM in 33 mode is larger than in 31 mode, while the higher applied stress in 31 mode is easier to obtain than in 33 mode.

The scavenged electric energy density increases with the applied stress. It is very often in the practical application

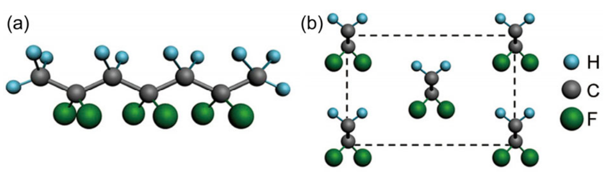

Figure 2 (Color online) (a) β-phase PVDF in all-trans conformation and (b) its unit cell belonging to the m2m point group.

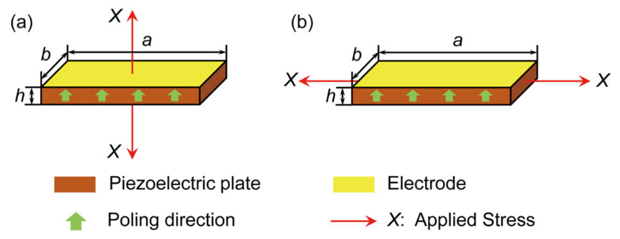

Figure 3 (Color online) (a) 33 and (b) 31 working mode of the piezoelectric materials for PEH.

that the force is not directly imposed on the material. The PEH device picks up vibration from the environment through the inertial force and the induced stress depends on the design of the device. Working in resonant mode helps to magnify the vibration amplitude and thus the induced stress. Note that there is maximum value for allowed X limited by the mechanical strength of the material σ_m (or σ_m divided by a safety factor). The maximum D_a of a piezoelectric material is thus determined by FOM and σ_m as shown in eq. (2). Thus, FOM and σ_m are two important property parameters concerning the material selection for PEH applications.

Subjected to continous vibrational excitation and connected with external circuit, PEH devices transfer the converted electric energy to electric load, and electric power is exported. The generated power depends on many factors, e.g. the connected external electric load, the excitation frequency, vibration acceleration amplitude, material properites, and device configuration. There are abundant literature on these studies [20–24]. Upon the optimization of the device configuration and impedance match, the maximum power density is closely related to the maximum available energy density, usually proportional to the product of the maximum available energy density with the excitation frequency [23]. Thus, optimization of the device configuration towards maximum available energy density agrees with that required by maximum power density.

3 Considerations on materials and configuration towards better-performed PEH devices

As illustrated above, the performance of PEH devices depends on both the properties of functional materials and the design of the device configuration. Regarding the piezoelectric materials acting as the unit to convert mechanical energy to electric energy, FOM and σ_m are good criteria to evaluate its suitability for PEH applications. Therefore, researchers do not need to focus only on the piezoelectric materials with high piezoelectric constant d or high electro-mechanical coupling coefficient k. Accordingly, PZT, which is usually the top choice for actuation applications, might not be the primary choice, while some other lead-free piezoelectric materials could emerge as better candidates. Other properties of the candidate materials, such as the Curie temperature T_c and environmental impact, might also need to be taken into account, subjected to the specific application occasion. In this section, we review several groups of typical ferroelectrics developed for piezoelectric applications, and in particular examine their properties in view of PEH applications.

3.1 Materials selection for PEH

In recent decades, lead-containing ferroelectrics, such as PZT, PMN-PT, and PZN-PT [25], are mainstream materials to construct the functional unit amid the research and applications of PEH. In the meantime, an amount of lead-free ferroelectric materials, via engineering by means of doping, forming solid solutions or microstructure tuning are being extensively explored as candidates to replace PZT in practical applications for the sake of environment [14,26–28]. Most of these candidate materials are lead-free piezoceramics, including BT, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT), $K_{0.5}Na_{0.5}NbO_3$ (KNN) and their derivatives. Piezoelectric polymers such as PVDF and its copolymers are also environmentally benign materials, and very promising in applications of flexible electronics.

PZT was found to have excellent piezoelectric properties due to the discovery of the morphotropic phase boundary (MPB), where the maximum piezoelectric constant exists [8]. Until now various PZT has been developed from the "hard" one which has low losses but small piezoelectric constants to the "soft" one which has high piezoelectric constants with high losses, available for different application requirements. FOM of PZT usually ranges from 5.4–14.4 (10^{-12} Pa^{-1}) [18]. Maximum allowed stress in PZT is about 110 MPa [29]. In 1997, the success in preparation of the relaxor ferroelectric single crystal [30] became a revolutionary breakthrough in the research of piezoelectric materials, which brought about the piezoelectric constant over 1000 pC/N and FOM 7-8 times larger than that of PZT.

BT was discovered in 1940s, earlier than PZT, which has been widely used due to its high dielectric constant [6]. The fracture strength of BT is reported in the range of 100–170 MPa, depending on the sintering condition [31]. The low T_c (120°C) and relatively low d of BT confines its piezoelectric application, so BT is generally researched in the combination with other high T_c ceramics. Besides that, Wang et al. [32] reported that by controlling the grain size of BT, d_{33} can be improved from the traditional 191 pC/N up to over 400 pC/N; Kimura et al. [33] doped BT with a small amount of Li which showed a high d_{33} to 260 pC/N and T_c to 130°C. FOM of BT is usually no more than 5 (10^{-12} Pa^{-1}).

A typical representative of high T_c lead-free piezoceramics is NBT, which was first reported in the 1960s by Hagivev et al. [34]. Compared to BT, NBT has a higher T_c (320°C) but a lower d (72.9 pC/N) [35], so their properties might complement with each other. Therefore, the binary system of NBT-BT was extensively investigated [36–38]. Owing to different processing or dopants, the FOM can be quite diverse from 2 to 8 (10^{-12} Pa^{-1}).

In 2004, Saito et al. [10] achieved the preparation thigh-performance KNN-derived ceramics with $LiTaO_3$ and $LiSbO_3$, through combination of making use of morphotropic phase boundary in an alkaline niobate-based perovskite solid solution and processing textured polycrystals. The obtained properties are comparable to those of the PZT, e.g. d_{33}=416 pC/N and T_c=253°C. Since then, KNN system has become an attractive contender in the development of high-performance lead-free piezoceramics. Wang et al. [39] investigated the MPB of $(K_{1-y}Na_y)(Nb_{1-z}Sb_z)O_3$ and $Bi_{0.5}(Na_{1-w}K_w)_{0.5}ZrO_3$ and obtained a higher d_{33} up to 490pC/N. Zheng et al. [40] investigated $(1-x)(K_{0.40}Na_{0.60})(Nb_{0.965}Sb_{0.035})O_3–xBi_{0.5}Li_{0.5}ZrO_3$ which also showed a relatively high piezoelectric constant (d_{33} is 400 pC/N). The FOM deduced from the reported data can reach 10–14 (10^{-12} Pa^{-1}) and maximum stress is between 68 and 103 MPa [41].

In addition, some other systems were investigated to display the applicable performance for PEH, such as NBT-KBT-BT [42], $Ba(Zr_{0.2}Ti_{0.8})O_3$-$x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-BCT) [11,43] and $BiFeO_3–BaTiO_3$ (BFO-BT) [44].

The ceramics and single crystals exhibit a low fracture toughness and can therefore be prone to brittle failure. In contrast, polyvinylidene fluoride (PVDF), discovered in 1969 by Kawai [45], shows superior flexibility. Among the four phases of PVDF, β-phase structure shows most prominent piezoelectricity but very often has to be obtained via sufficient stretching of the PVDF sheets. In 1993, Wang et al. [46] prepared a kind of copolymers of PVDF namely P(VDF-TrFE), which can be readily formed in the β-phase without stretching meanwhile the piezoelectric properties got enhanced. Although the piezoelectric constants d of PVDF and P(VDF-TrFE) are far lower than those of ceramics [47], their FOM for PEH applications reaches 4–8 (10^{-12} Pa^{-1}), comparable to that of PZT.

Table 1 summarizes the electromechanical properties of the materials reviewed above. From the table, FOM of each material can be calculated and is shown in Figure 4 in combination with T_c which is a measure of the upper limit of application temperature. It is seen that relaxor ferroelectrics such as PMN-PT and PZN-PT possess the highest FOM. It is also worth to note that FOM of some KNN-based or NBT-based lead-free ceramics is fully comparable to that of PZT, enriching PEH a promising future in environment-friendly applications. Piezoelectric polymers also exhibit desirable FOM and definitely can be exploited for vibrational energy harvesting.

Knowing the mechanical strength (maximum allowed stress) of the ferroelectric materials (summarized in Table 2), the maximum available energy density D_{am} can be estimated based on $D_{am} = \frac{1}{2} \cdot \mathrm{FOM} \cdot \sigma_m^2$ as shown in Figure 5. It is seen that materials with high σ_m can compensate low

Table 1 Electromechanical properties of typical ferroelectric materials

Materials	T_c (°C)	ε	tanδ	d_{33} (pC/N)	d_{31} (pC/N)	k_{33}	k_{31}	Ref.
PMN-PT	171	5000		2000	−1000	0.9–0.94	0.7	[25]
PZN-PT	164	6800	<0.01	1400	−1400	0.92–0.94	0.5	[25]
PZT	328	1300	0.004	290	−123	0.7		[2]
	190	3400	0.02	590	−274	0.75		[2]
	300	1000	0.004	225		0.64		[8]
	365	1700	0.02	375		0.71		[8]
$BaTiO_3$	120	1898		191	−79	0.49	0.21	[43]
	130	1744		260				[33]
NBT-BT	280	625	1.3	125				[48]
	280	3000		483	−115		0.397	[37]
	290	1500	0.057	175				[38]
	260	990		208				[9]
	260	420			−59		0.299	[49]
	250	1230		149				[48]
	174	2300		117				[48]
	210	1040		205				[48]
NBT	310	302.6		64				[48]
	315	422		98				[9]
KNN	253	1570		416	−152			[10]
	227	2300		490				[39]
	292	1800		400				[9]
	450	500		250				[9]
	358	1003		104				[9]
PVDF	120	12		−20	18			[47]
	120	12		−24	7			[47]
	135	10		−24	7			[47]
BZT-BCT	100	4050		546	−231	0.65	0.31	[43]
BFO-BT	513	660	0.033	150				[44]

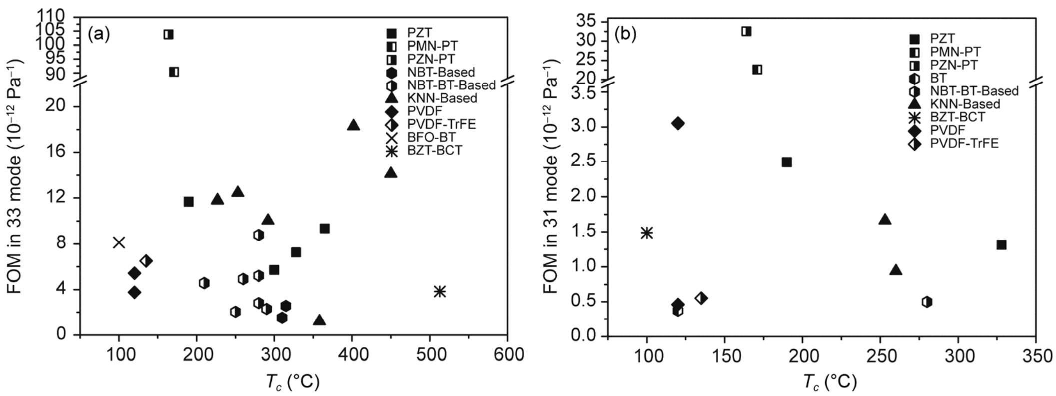

Figure 4 FOM versus T_c of various ferroelectric materials in (a) 33 mode and (b) 31 mode.

FOM for PEH applications.

It should be noted that besides ferroelectric materials in their dense form with a single component as reviewed above, complex structures such as porous ferroelectrics as well as ferroelectric composites could also present competitive properties for PEH. For example, the porosity introduced in ferroelectrics can enhance FOM in certain directions while generally lower the mechanical quality factors, which could be beneficial in some PEH applications. A comprehensive overview of the porous ferroelectrics can be found in the review article by Rescow et al. [51]

3.2 Configuration design and optimization

There are diversified types of PEH device configuration, such as disk-based, beam-based, and other more complicated structures. Resonant mode is usually adopted as it can magnify the displacement and thus the strain, leading to reduced volume of proof mass (thus reduced size of the total device). The cantilever structure is one of the most widely

Table 2 Mechanical strength of typical ferroelectric materials (yield strength σ_s for ductile materials like PVDF and fracture strength σ_f for ceramics)

Materials	σ (MPa)	FOM_{33} (10^{-12} Pa^{-1})	D_{am} (mJ/cm^3)	Ref.
PVDF & PVDF-TrEF	20–45(σ_s)	3.76–6.51	0.752–6.59	[29,46,49]
$BaTiO_3$-Based	101–174(σ_f)	2.17–4.38	11.1–66.3	[41,42]
KNN -Based	68–103(σ_f)	3.14–14.1	7.24–74.6	[9,40]
PZT	96–110(σ_f)	5.71–11.7	26.3–70.7	[8,29,50]
NBT-BT -Based	200(σ_f)	2.82–4.56	56.4–91.2	[48]

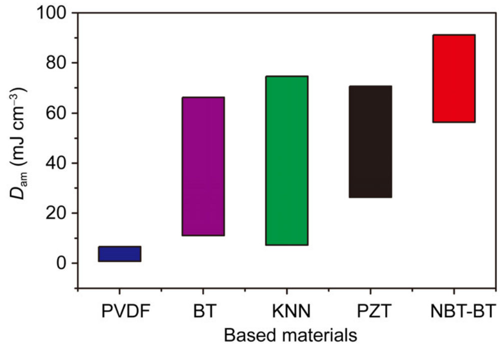

Figure 5 (Color online) D_{am} (in 33 mode) of different piezoelectric materials. Reanalyzed from the data in literature.

used PEH configuration as it is more convenient to match their resonant frequency with the excitation frequency which is usually under 250 Hz. Figure 6 shows a representative scheme of cantilever-type device in which one end of the beam is fixed at the vibration source and the proof mass is attached to the other end. Owing to the brittleness of ceramics, it is usually necessary to bond the ceramic plate to a metallic shim to improve the toughness of the beam. In comparison, the PEH devices using piezoelectric polymers do not necessarily need the shim due to their superior flexibility.

Experimental attempts on fabrication of PEH devices have been widely reported in literature. Jiang et al. [52] fabricated a cantilever energy harvester using PVDF. Magnetic force was introduced to enhance the mechanical load. The device was tested under the acceleration amplitude of 1.2g (g=9.8 m/s^2) at 17 Hz, yielding an output power density of 0.286 mW/cm^3. Wang et al. [53] fabricated a PEH harvester with PMN-PT single crystal bonded on the Al substrate, and obtained a power density of 0.753 mW/cm^3 under the acceleration amplitude of 2.28 m/s^2 at 174 Hz. In addition, they investigated the optimum size ratio between the piezo-

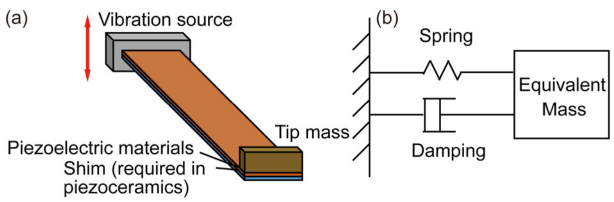

Figure 6 (Color online) (a) Basic configuration of the cantilever beam of the PEH device and (b) its approximated model.

electric layer and the substrate. Liu et al. [54] deposited PZT film on a silicon beam and fabricated an energy harvester via MEM technology. The as-prepared device generated high-level output power density of 41 mW/cm^3 excited by 0.5g acceleration amplitude at 229 Hz. The performance of the reported devices have been summarized in Table 3.

In general, the power output of the PEH device is a function of many configuration parameters, such as the disk/beam shape, proof mass, mechanical boundary conditions. However, fundamentally speaking, these parameters affect the power density through the induced stress in the piezoelectric element, as shown in eq. (2). Within the limit imposed by the mechanical strength of the material, the larger the induced stress, the higher electric energy density and thus higher power density are obtained. Therefore, optimization on the device configuration should be aimed at achieving higher induced stress.

There have also been efforts on the study of the relationship between the performance and the structure of the device for optimization of the device. Cho et al. [21] studied the optimum thickness ratio between the PZT layer and the metallic shim using finite element simulation and designed several energy harvesters in different shapes with the same resonant frequency. The power density measured in the fabricated devices increases with the beam shape towards a square and reaches as much as 13.47 mW/cm^3 under acceleration amplitude of 1g at 29.6 Hz. The best-performing device was shown to bear maximum stress in the beam approaching 100 MPa which is close to the fracture strength of PZT.

There might be still room for improvement of the performance of cantilever-type PEH devices. It is clear that the stress in the conventional rectangular cantilever is not uniform. It reduces as the distance increases from the fixed end. More uniform stress distribution is in favor of design for higher the power density because more fractions of the beam can be stressed up to the maximum allowed level (approaching the mechanical strength of the material). This issue has been paid attention recently. For example, Chen et al. [20] analyzed the different shapes of the beam, showing that from rectangular, to trapezoidal and triangular beam, the stress distribution tends to be more and more uniform, leading to an enhancement in the output signal (Figure 7).

Besides the cantilever structure, some innovative configurations have been proposed recently. To scavenge the vibration energy from insect flight, Aktakka et al. [55]

Table 3 The performance of PEH devices reported in literature

Material	Substrate	Vibration acceleration (m/s^2)	Resonant frequency (Hz)	Output power (μW)	Output power density (mW/cm^3)	Ref.
PZT 5A (ceramic)	Steel	10	29.6	15300	13.47	[21]
PZT 5A (ceramic)	Brass		100	22.5	1.64	[55]
PZT(ceramic)	Be-Cu	6.5	160	0.33		[56]
PZT (film)	Si	5	229	2.25	41.21	[54]
PZT-PZN (ceramic)	Steel	10	85	900	0.85	[22]
PMN-PT (single crystal)	Al	22.8	174	586	0.753	[53]
PVDF (film)	None	5	99.5	1.452	0.266	[24]
PVDF (film)	None	12	17	16	0.286	[52]

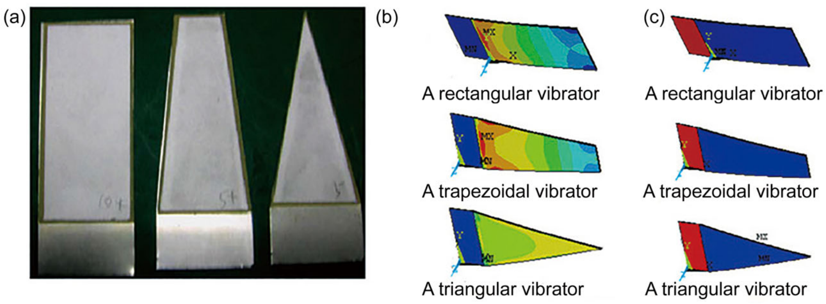

Figure 7 (Color online) (a) Rectangular, trapezoidal and triangular beams and the simulation result of (b) strain distribution and (c) output voltage. Reprinted from ref. [20], with permission from IEEE.

designed a spiral beam to fit the limited space on insects as shown in Figure 8(a), and obtained a power density of 1.64 mW/cm^3. Mo et al. [57] investigated a cymbal-shape shell to cover the piezoelectric plate (Figure 8(b)), which bore the uniform force and output a power density of 0.14 mW/cm^3. Nevertheless, these structures have either the low efficiency or need complicate fabrication.

A potential disadvantage with the resonant mode is that although the PEH device generates a high power density at resonant frequency, the high-level generation drops rapidly once the working frequency deviates from the resonant frequency of the device. This might be adverse in some application occasions which do not have well-defined excitation frequency. Two strategies have been exploited to address this issue. The first approach is to develop broad-band PEH devices. Shahruz [58] designed a multi-beam PEH device in which a series of cantilevers with different resonant frequencies are arranged in an array (Figure 9). This design guarantees at least one beam excited in the resonant state so that the device can scavenge the vibration energy over a wide range of frequencies. Another strategy is the design of a vibration structure with a tunable resonant frequency. For example, Cregg et al. [56] fabricated an energy harvester whose proof mass can move along the beam. A laser sensor was used to reflect the displacement of the beam, so that the proof mass can be fixed where the maximum displacement occurred, i.e. the beam was at the resonance (Figure 10(a)). Challa et al. [59] attached magnets to the proof mass and the applied stress by the mass could be varied by changing the magnetic force which is controlled by the current in the coil, so that the resonant frequency of the device can be tuned to match the frequency of the vibration source (Figure 10(b)).

In practical applications, the mechanical motion sources may supply vibrations in various directions as well as rotation motion and sway motion. Therefore, besides the aforementioned device structures which are usually adapted to

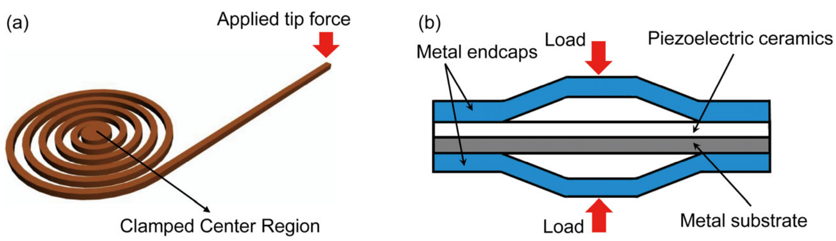

Figure 8 (Color online) The configuration of (a) the spiral beam [55] and (b) the cymbal-shaped PEH structure [57].

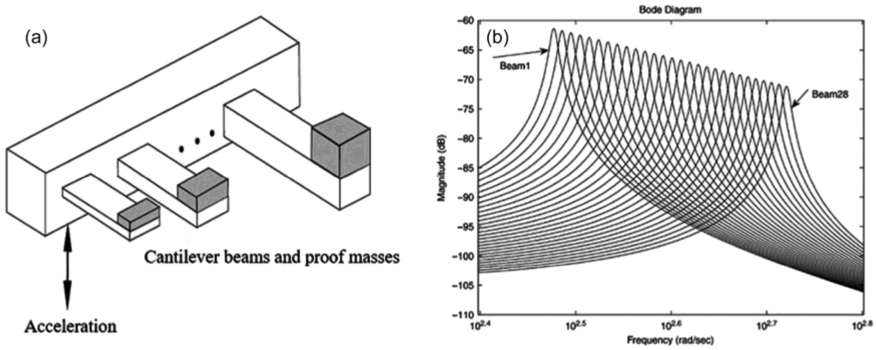

Figure 9 (a) A design of multimodal energy harvesting and (b) the frequency response. Reprinted from ref. [58], with permission from Elsevier.

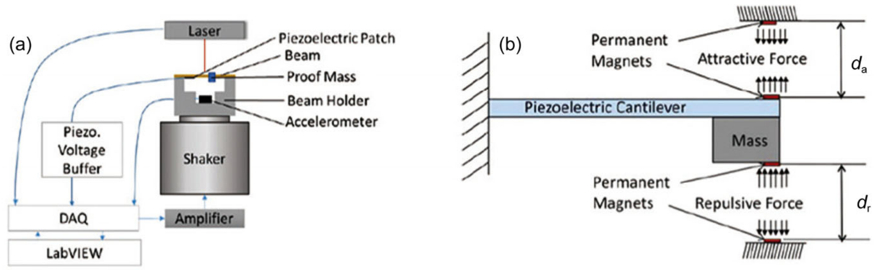

Figure 10 (Color online) The energy harvester with a tunable resonant frequency, which has (a) a movable proof mass (reprinted from ref. [56], with permission from IOP publishing Ltd) and (b) a proof mass controlled by the magnetic force (reprinted from ref. [59], with permission from IOP publishing Ltd).

uni-directional vibrations, efforts have been devoted to designing devices which are capable to exploit all possible mechanical motions. For example, Su and Zu [60] proposed a PEH device which can harvest energy from tri-directional vibrations as illustrated in Figure 11(a). Fan et al. [61] developed a multipurpose energy harvester for scavenging sway and bi-directional vibrations (Figure 11(b)), and recently they realized a nonlinear PEH structure which can scavenge energy from diverse mechanical motions including tri-directional vibrations, rotation motion and sway motion [62]. As the vibration modes in different directions have different resonant frequencies, these multipurpose devices usually exhibit broadened bandwidth.

4 Perspective applications of PEH

PEH can be used in all kinds of application occasions as long as the vibration source exists, among which the biomedical application seems very appealing. An exciting example is to use them in pacemakers. The cardiac pacemaker exerts electric stimulation to regulate the heartbeat which is able to antagonize many heart diseases. However, the limited lifespan of the batteries challenged its long-term operation, and the replacement of batteries would bring a considerable risk to patients. For this reason, Hwang et al. [63] fabricated a single crystalline PMN-PT piezoelectric energy harvester in order to power the pacemaker. The PMN-PT thin film was adhered on a flexible substrate so it can be implanted in the human body (Figure 12(a)). The output power reached 1.83 mW that is sufficient to power the pacemaker. Fadhil et al. [64] intended to scavenge the energy from the artery blood pressure to power small implantable sensors. They embedded the PVDF into a silicon cuff which was attached to the blood wall (Figure 12(b)). The output of the device is only 60 nW with a device volume of 0.3 cm^3, which was needs to be further scaled up to meet the power demand of the sensors.

Besides the application in implantable devices, wearable PEH devices which harvest energy from human motion have been a hot direction. Yang and Yun [65] shaped PVDF into a shell structure which can be set at human's joints such as elbows or fingers (Figure 13(a)). The output power reached 0.87 mW. Zhao and You [66] designed a shoe-embedded multilayer PVDF sheet (Figure 13(b)) and the average output power was measured up to 1 mW. Granstrom et al. [67] designed a backpack equipped with PVDF-based PEH straps to harvest energy when people carry the backpack, as shown in Figure 13(c). The obtained output power was 45.6 mW in their study, which is very promising to power sorts of low-power electronic devices.

PEH devices are also expected to be applied to a variety of vibration sources in routine life such as road, bridge, working electric devices or machines. Table 4 lists the frequency and acceleration amplitude of these vibration sources [5,13]. The harvested energy can be used to power the IC to send information on the environment collected by the sensors, or stored in a battery for future use as a backup

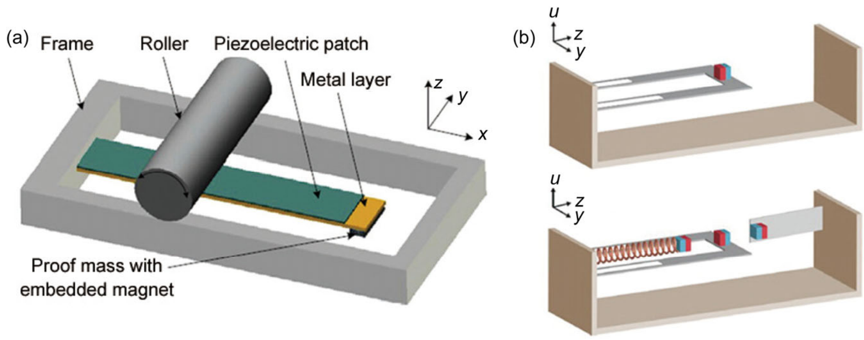

Figure 11 (Color online) (a) A multipurpose energy harvester for scavenging sway and bi-directional vibrations (reprinted from ref. [61], with permission from Elsevier) and (b) a tri-directional broad-band PEH device (reprinted from ref. [60], with permission from AIP publishing).

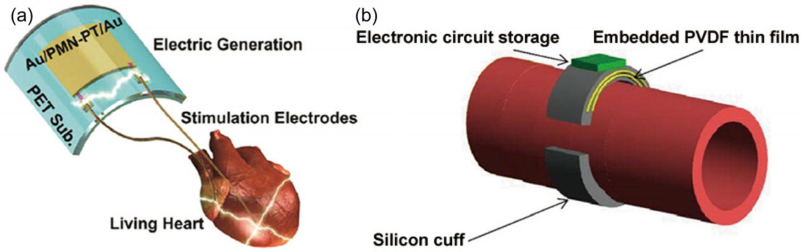

Figure 12 (Color online) (a) The PMN-PT energy harvester powering a pacemaker (reprinted from ref. [63], with permission from Wilay Materials) and (b) the PVDF device scavenging the energy from the pulse of the blood artery (reprinted from ref. [64], with permission from IEEE).

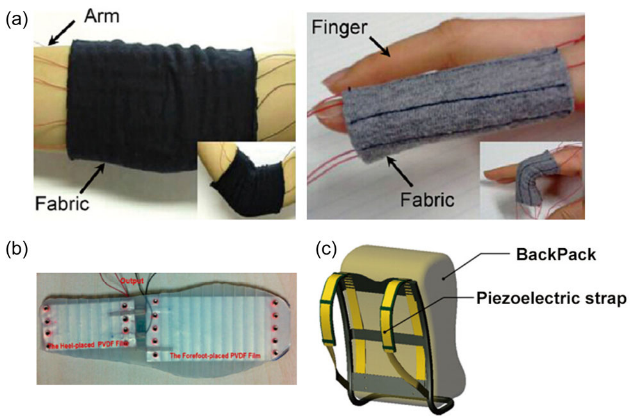

Figure 13 (Color online) Wearable devices scavenging the energy during human walk from (a) bending of body joints (reprinted from ref. [65], with permission from Elsevier), (b) pressure on shoes (reprinted from ref. [66], with permission from MDPI publishing) and (c) strain in the backpack strap (reprinted from ref. [67], with permission from IOP publishing Ltd).

Table 4 The frequency and acceleration amplitude of various vibration sources

Vibration source	Acceleration (m/s^2)	Frequency (Hz)
Car instrument panel	3	13
Car engine compartment	12	200
Clothe dryer	3.5	121
Refrigerator	0.1	240
Blender casing	6.4	121
Small microwave oven	2.5	121
CD on notebook computer	0.6	75
Windows next to a busy road	0.7	100
Person nervously tapping their heel	3	1
Human walking	2–3	2–3

power [68]. Some researchers paid attention to the vibrations in nature, such as wind, raindrops and ocean waves and designed various PEH devices to scavenge the mechanical energy contained in them [69–73].

5 Summary

Energy harvesting is an appealing technology, as it makes use of the ambient energy which is otherwise wasted and can endow MEMS or electronic devices with long-term self-powering capability. Piezoelectric materials directly convert the elastic energy to the electric energy, and thus have a great advantage in scavenging vibrational energy for simplicity in device structure with an acceptable power output. This paper presents an overview on the research of piezoelectric materials in energy harvesting in recent decades, from basics of piezoelectricity and working principle of energy harvesting with piezoelectric materials, to the progress of development of high-performance piezoelectrics including ceramics, single crystals and polymers, then to experimental attempts on the device fabrication and optimization, finally to perspective application occasions of PEH.

In the review, special attention has been paid to the material properties that determine their suitability in PEH applications, such as FOM and the maximum allowed stress of the material. It is worth to note that FOM of some KNN-based or NBT-based lead-free ceramics is as high as that of PZT, thus provoking experimental efforts on fabrication and optimization of environment-friendly PEH devices based on these materials. Piezoelectric polymers such as PVDF also exhibit desirable FOM and can be exploited as vibrational energy harvesting unit in flexible electronic devices where a large strain is required.

The impact of the device configuration on the performance should also be acknowledged. In view of the power density reported in literature, there is still space for further improvement of output power density in many cases, by maximizing the stress magnitude and homogenizing its distribution in the piezoelectric unit via proper design of device configuration without changing the resonant frequency. Approaches to address the issue of frequency match accompanying with resonant mode, such as development PEH devices with broad-band response or a tunable resonant frequency are discussed, together with the review of literature examples.

Applications of PEH in implantabe and wearable devices are very attractive. Their usage can be further extended to a variety of vibration sources in everyday life as well as in nature. Upon improvement of power density, small-scale PEH devices may be directly integrated into micro-scale devices or electronic circuits as the power unit. We believe that as a convenient, stable, and smart power source, PEH devices will find an increasing number of innovative applications.

This work was supported by the National Natural Science Foundation of China (Grant No. 51302143), Shenzhen Special Fund for the Development of Emerging Industries (Grant No. JCYJ20140417115840233), and Shenzhen Peacock Plan (Grant No. KQCX20140521161756228).

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