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Yanhua Sun

University of Wollongong, ys460@uowmail.edu.au

Jianguo Chen

Shanghai University, University of Wollongong

Xiaoning Li

University of Wollongong, xl905@uowmail.edu.au

Yun Lu

University of Wollongong, yl544@uowmail.edu.au

Shujun Zhang

University of Wollongong, shujun@uow.edu.au

See next page for additional authors

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Abstract

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Authors

Yanhua Sun, Jianguo Chen, Xiaoning Li, Yun Lu, Shujun Zhang, and Zhenxiang Cheng

**Flexible piezoelectric energy harvester/sensor with high voltage output
over wide temperature range**

**Yanhua Sun^{†,a}, Jianguo Chen^{†, a,b}, Xiaoning Li^a, Yun Lu^a, Shujun Zhang^a,
Zhenxiang Cheng^{a*}**

*^aInstitute for Superconducting and Electronic Materials, Australian Institute
for Innovative Materials, University of Wollongong, North Wollongong, NSW
2500, Australia*

*^bSchool of Materials Science and Engineering, Shanghai University, Shanghai
200072, People's Republic of China*

Corresponding author: Zhenxiang Cheng

***E-mail:** cheng@uow.edu.au

Tel: 61-2-42981406

Address: Institute for Superconducting and Electronic Materials, Australian
Institute for Innovative Materials, University of Wollongong, North
Wollongong, NSW 2500, Australia

Abstract

A flexible piezoelectric energy harvester based on polyimide (PI)/(Bi,La)FeO₃-PbTiO₃ (BLF-PT) 0-3 composite was fabricated by a cost-effective two-step process. The energy harvesting outputs are sensitive to the BLF-PT weight fraction and testing frequency. The flexible BLF-PT/PI composite with 30 wt% BLF-PT exhibits an open circuit voltage of 110 V and a short circuit current of 310 nA under pressure of 0.18 MPa at frequency of 1 Hz. Of particular significance is that the flexible energy harvester exhibits high temperature stability up to 150 °C and a voltage output of 30 V at temperatures as high as 300 °C, showing great potential for capturing mechanical energy or sensor over a wide temperature range at ultra-low frequency.

Keywords: piezoelectric energy harvester, BLF-PT particles, PI composite, flexible electronics

1. Introduction

With development of the “Internet of Things”, where countless numbers of wireless sensing devices are continuously monitoring, detecting, and communicating, the exploration of more sustainable self-powered sensor devices other than battery-powered ones, which need to be periodically recharged and replaced, is highly desired. To power these wireless sensing devices, the continuous generation of electricity converted from ambient energy sources without external interference, such as solar, wind, geothermal, mechanical, and biological forms of energy, has been intensively explored in the past decade [1-6]. Among these energy sources, mechanical energy is ubiquitous, from sources including human activities, vibrations, vehicle operation, etc. [7], although in most situations, it is ignored and wasted.

In order to make use of mechanical energy in the ambient environment, piezoelectric materials, which can directly convert mechanical vibrations into electrical energy, have been

exploited in practical applications. Only in the past decade, however, with the emergence of the energy crisis and global warming, have piezoelectric based energy harvesters for acquiring clean energy started to attract intensive attention. Up to now, different kinds of piezoelectric materials, such as ZnO [8-10] and perovskite ferroelectric materials, have been utilized to fabricate piezoelectric energy harvesters (PEHs) with different structures. Compared with ZnO, perovskite ferroelectric materials with better piezoelectric properties are more suitable for energy harvesting. As one example of piezoelectric materials with the perovskite structure, BiFeO₃-PbTiO₃ (BF-PT) solid solution has recently come to our attention due to the high piezoelectric coefficient at its morphotropic phase boundary (MPB) and its high Curie temperature (T_C) inherited from its two end member compounds BiFeO₃ ($T_C = 820\text{ }^{\circ}\text{C}$) and PbTiO₃ ($T_C = 490\text{ }^{\circ}\text{C}$). The MPB composition of La modified (1- x)BiFeO₃- x PbTiO₃ (BLF-PT) was reported to locate at $x = 0.43$ with Curie temperature of $355\text{ }^{\circ}\text{C}$, possessing good piezoelectric properties [11, 12]. It is worth noting that the Curie temperature of the BLF-PT MPB composition is higher than for most perovskite-structured piezoelectric materials, while it has comparable piezoelectric performance. Therefore, based on the above advantages, the MPB composition of BLF-PT solid solution was chosen in this research for exploration of its energy harvesting properties at elevated temperature, which can be used in harsh environments, such as oil exploration (which operates in temperatures from $150\text{-}200\text{ }^{\circ}\text{C}$).

Among the various kinds of piezoelectric energy harvesters (PEHs), flexible electronic devices are the currently emerging technology and attracting a lot of attention not only because they can harvest electrical power from ambient mechanical energy, but also for their splendid flexibility and robustness with outstanding piezoelectric performance. Flexible piezoelectric energy harvesters with polymers such as polydimethylsiloxane (PDMS) [10, 13, 14], polyvinylidene difluoride (PVDF) [15, 16], poly(methyl methacrylate) (PMMA) [17]) as composite matrix have been paid great attention to due to their high elasticity and acid-

base resistance property, which can enable the integrity of devices without fracturing under high pressure and some kind of harsh environment. However, the working temperatures of PDMS, PVDF, and PMMA are less than 200°C, which is lower than the Curie temperature of a number of piezoelectric materials, and therefore, the low working temperature of a PDMS or PMMA based flexible harvester will seriously restrict the temperature range of the device for application in a harsh environment. To enlarge the operating temperature range of composite device by full utilization of the high temperature working potential of BF-PT, it is of great importance to utilize a polymer matrix with excellent temperature stability. Widely employed in high temperature plastics, dielectrics, photoresists, etc., polyimide (PI) ranks among the most heat-resistant polymers, which can bear wide temperature range from -200 °C to 300 °C [18]. Furthermore PI can be easily peeled off from hard substrates, in contrast to the removal by the complex laser lift-off method for other polymers [19]. Therefore, with its outstanding physical and chemical properties, PI can be a good polymer matrix candidate to fabricate PEHs.

In this work, super-flexible and lightweight free-standing energy harvesters were fabricated from 0.57Bi0.8La0.2FeO₃-0.43PbTiO₃ ceramic powders and PI matrix. The high-temperature piezoelectric BLF-PT particles were synthesized by a conventional solid-state reaction method, and the composite film was prepared by the spin-coating of mechanically mixed ceramic particles and the polymer matrix. To avoid insufficient polarization of thick areas and unexpected breakdown initiated in the thinner areas due to the non-uniform thickness of the composite piezoelectric film, interdigital (ID) electrodes was coated on our device. At room temperature, with the impact from a human hand, a stable voltage output of around 110 V and current density of 220 nA/cm² were obtained. In addition, the electric output property of our PEH subjected to low frequency (~1 Hz) and high temperature (~ 350 °C) conditions, respectively, was also studied.

2. Experiment section

2.1. Fabrication of (Bi, La) FeO₃-PbTiO₃ Nano/micro-particles

0.57Bi_{0.8}La_{0.2}FeO₃-0.43PbTiO₃ (BLF-PT) particles were prepared via a solid-state reaction method, using high purity (99.9%+) bismuth oxide, lanthanum oxide, ferric oxide, lead oxide, and titanium oxide as starting materials. The oxide materials were carefully weighed according to nominal composition and then mixed thoroughly for 12 h in ethanol by ball milling. After drying, the mixed powder was calcined at 750 °C for 4 h in a covered alumina crucible. The calcined powder was ball milled again, after which the binder was added, and the granulated powder was pressed into pellets 12 mm in diameter and 2 mm in thickness. The pellets were sintered in a covered alumina crucible at 1060 °C for 0.8 h with protective powders in order to reduce the volatilization of bismuth oxide. After sintering, the pellets were ground into powder with particle size of about 1 μm, which were measured by a laser particle size analyser.

2.2 Fabrication of piezoelectric energy harvester (PEH)

A polyimide (PI) solution was spin-casted onto glass to form a very thin protective layer (~20 μm) at room temperature, using a spinning rate of 500 rpm for 30 s and then 2500 rpm for 30 s, followed by curing in an oven in order to make high quality PI composite by following a complicated sintering procedure (see **Supporting Figure S1**). After solidification, ID electrodes with gap separation of 150 μm, finger width of 100 μm, and finger length of 1 cm was sputtered on the surface of the PI film via ion sputtering and a shadow mask, with the effective area covered by electrode 1×1.4 cm². Meanwhile conductive wires were attached to the two interdigital electrodes. Then, the BLF-PT powders in different weight fractions of 5, 10, 20, and 30 wt% were uniformly dispersed into the PI solution, followed by spin-casting on the electrode coated PI protective film. The composite film was peeled off from the glass after

solidification. Finally, the device was poled at 185 °C by applying an electric field of 80 kV/cm for 24 h.

2.3 Characterization

The structure of the synthesized BLF-PT was investigated via using X-ray diffraction (XRD, GBC, MMA) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Morphology of the ceramic powders and cross-section of the composite was observed by scanning electron microscopy (SEM, JEOL7500), element mapping was conducted with the same scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy (EDS). The crystal structure of the ceramic powder was analysed by the high resolution transmission electron microscopy (HRTEM, JEOL2010). To measure the electrical properties, the sintered ceramic pellets were polished to a thickness of 1 mm and coated with gold electrode. A precision impedance analyzer (LCR, HP 4980A, Agilent, USA) was used to measure the capacitance of the ceramic pellet. The dielectric constant was calculated from the capacitance. The piezoelectric constant was measured with a quasi-static piezoelectric d_{33} meter. A ferroelectric test system (TF2000E, aixACCT, Germany) was used to collect ferroelectric hysteresis loops. The output current and voltage of the PEHs were in-situ recorded by a source meter (2612B, Keithley, USA), the measurement system is shown in **Supporting Figure S2**.

3. Results and discussion

Figure 1 (a) SEM image of BLF-PT ceramic particles, where the inset shows EDS mappings of a corresponding particle. (b) HRTEM image of a typical portion of a corresponding particle. (c) Rietveld refinement analysis of XRD spectrum of BLF-PT. (d) Polarization – electric field (P - E) hysteresis loops of BLF-PT ceramic pellet. (e) Dielectric constant and loss of BLF-PT as a function of temperature at 10 Hz. (f) Piezoelectric constant as a function of temperature.

Figure 1 shows the basic characterizations of the BLF-PT ceramics. Morphology and local crystallinity of the BLF-PT particles had been investigated by SEM and HRTEM. The BLF-PT particles exhibit polyhedral shape and homogeneous morphology with the size of about 1 μm (**Figure 1(a)**), and the inset EDS mapping images show homogeneously distributed elements of O, Bi, Fe, La, Pb and Ti. **Figure 1(b)** presents the HRTEM image which was used to analyse the crystal structure of the BLF-PT powder used for the following device fabrication. According to the HRTEM image, the interplanar distances of 0.392 nm and 0.275 nm can be

observed, which correspond to the (101) and (110) planes of rhombohedral ($R3c$, $a = b = c = 3.958 \text{ \AA}$) and tetragonal ($P4mm$, $a = b = 3.899 \text{ \AA}$, $c = 4.153 \text{ \AA}$) phases respectively. XRD Rietveld refinement was also carried out with the FullProf package (**Figure 1(c)**). The results show that the XRD pattern of BLF-PT is fitted well when a combination of rhombohedral and tetragonal phases is used with good fitting quality (weighted profile reliability factor, $R_{wp} = 6.4$; profile reliability factor, $R_p = 4.22$), which indicates two phases coexistence for BLF-PT solid solution with 59.2% $R3c$ phase ($a = b = c = 3.961 \text{ \AA}$) and 38.7% $P4mm$ phase ($a = b = 3.899 \text{ \AA}$, $c = 4.167 \text{ \AA}$) at room temperature. The results of XRD and TEM measurement are consistent. **Figure 1(d)** shows room-temperature hysteresis loops at the frequency of 1 Hz for different maximum electric fields. The sample shows typical hysteresis loops with a relatively rectangular shape. The remnant polarization, P_r , and the coercive field are on the orders of $40 \text{ \mu C/cm}^2$ and 28 kV/cm , respectively. **Figure 1(e)** is the temperature dependence of the dielectric constant (ϵ) and loss (δ) at 10 Hz, where the ferroelectric to paraelectric phase transition temperature (Curie temperature) is $355 \text{ }^\circ\text{C}$. The room temperature dielectric constant and piezoelectric coefficient are on the order of 890 and 290 pC/N , respectively. The temperature dependence of the piezoelectric constant d_{33} is given in **Figure 1 (f)**, where it is found that the piezoelectric constant increases with increasing temperature and reaches 528 pC/N at $225 \text{ }^\circ\text{C}$, comparable to the values of soft lead zirconate titanate (PZT) based ceramics.

Figure 2 (a) Schematic illustration of the fabrication process for the flexible energy harvester. (b) Photograph of the fabricated flexible device in the bent state. (c) SEM image of a cross-section of the device. (d) SEM image of the composite film consisting of BLF-PT particles. (e) Schematic diagram of the device with ID electrodes and the polarization distribution from a cross-sectional view. (f) Photograph of the fabricated device and (b) photograph under optical microscope (with the bar in the picture 500 micrometers).

Figure 2(a) shows a schematic illustration of the fabrication of a BLF-PT/PI-based device; detailed information is provided in the Experimental section. The ID electrodes are covered on both sides by PI or composite film, which can prevent them from being damaged during the measurement process. **Figure 2(b)** shows a free-standing composite device being bent by fingers, with only conductive wires attached, which confirms the super-flexibility of the fabricated PEH. **Figures 2(c, d)** show a cross-sectional scanning electron microscopy (SEM) image of the device and microstructure of the composite part, where the whole thickness of the device is around 50 μm, which enables the device to be flexible. As is shown in **Supporting Figure S3**, the average diameter of the piezoelectric BLF-PT particles is 1 μm. Compared to previously reported flexible composite energy harvesters, we employed polyimide as the

matrix, expecting a broader usage temperature range (-200 °C to ~300 °C). In addition, the polyimide can maintain not only its flexibility but also its stiffness after solidification, so that when a force is applied along the vertical direction of the device, the stress can be effectively transferred to all of the BLF-PT particles, thus greatly enhancing the energy harvester's efficiency [20]. **Figures 2(e-g)** show a schematic diagram and photographs of the device with ID electrodes. The positive and negative interdigital electrode fingers are aligned alternately and equidistantly, which will benefit the poling process.

Figure 3. Schematic illustration of dipole alignment during the poling and pressure application process. (a) Dipoles in BLF-PT particle align randomly before poling. (b) After poling, the dipoles align in the same direction as the applied electric field. (c) The piezoelectric potential is generated when a compressive force is applied on the PEH. (d) Electrons flow back along the opposite direction as the compressive force is released from the PEH.

Our device adopted the ID electrode design, since such an electrode design can not only effectively facilitate poling of the device, but also makes it possible to minimize the thickness

of the device, which will reduce the device's weight and improve its flexibility, while maintaining comparable output performance. The poling mechanism and power generation mechanism of the composite energy harvester are described in **Figure 3(a-d)**. The ferroelectric domains align randomly in the BLF-PT within the PI matrix prior to the poling process. The ferroelectric domains tend to align along the direction of applied electrical field when subject to a strong electrical field, as shown in **Figure 3(b)**. In this case, if no external force is applied on the device, the device has no output electric signal because of electrical equilibrium within the device. The distance between two finger electrodes will change when the device is subjected to a vertical compression force, and the total polarization of the composite between the two electrodes will change accordingly, which leads to piezoelectric potential between the two electrodes. Therefore, the free charges will flow through the external circuit to move and gather at the surface of the electrode to maintain balance in the electric potential. As a result, electrical signals will be generated due to the movement of electrons in the external circuit. Furthermore, when the external pressure force is released, the distance between the negative and positive finger electrodes will change back to the initial state, and hence, the piezoelectric potential will disappear. In this case, the gathered charges flow back in the opposite direction, so that a negative electrical pulse is produced. Consequently, repeated positive and negative electric signals are obtained during the continuous tapping and release of external force on the device [21].

Figure 4 (a, b) Time-dependent open circuit voltage and short-circuit current of the fabricated composite with 5-30% BLF-PT weight fractions. (c) The required operating temperature for devices under different specific conditions. (d) Time-dependent output voltage when the device is subjected to different temperatures.

In order to fully understand the influence of the BLF-PT weight fraction on the output signals of devices, a series of devices were fabricated under same procedure with various weight ratios of BLF-PT powders, namely 5, 10, 20, and 30 wt%. Mechanical deformation was produced under application of pressure of ~ 0.18 MPa and frequency of ~ 1 Hz. Under the same test conditions, the time dependent short-circuit current and open-circuit voltage of the devices were characterized. As shown in **Figure 4(a, b)**, with an increasing proportion of BLF-PT powder, the output voltage and current clearly increase, with the highest recorded peak values reaching 110 V and 310 nA for the device loaded with 30 wt% BLF-PT powders. The piezoelectric potential distinctly increases in proportion to the concentration of BLF-PT powders, which can be attributed to the enhanced piezoelectricity of the composite [22].

Energy harvester or sensor application in harsh environments such as high temperature is very important for some specific applications, for example, oil exploration (which operates in temperatures from 150-200 °C), as shown in **Figure 4c**. To characterize the performance of the device at high temperature, the device with 30% BLFPT piezoelectric material was further evaluated under various high temperatures from 50 to 300 °C at the frequency of 1 Hz (**Figure 4d**). Firstly, the device was fixed on the bottom of the glass and immersed in silicone oil for better temperature homogeneity. When the temperature reached the designed value, a stick was used to tap the device at ~1 Hz. The open-circuit output voltage is quite stable, maintaining 100 V when the temperature is below 150 °C, which is much higher than the PEH devices made based on PVDF and PDMS (see **Supporting Figure S4**). Above 150 °C, the output decreases slowly, but is still as high as 30 V at 300 °C, whereas PEH made of PVDF and PDMS showed no obvious output. This result indicates that the device can operate stably below 150 °C and is still workable at temperatures as high as 300 °C. According to the thermogravimetric analysis (TGA) data in **Supporting Figure S5**, the glass transition temperature is around 200 °C, which means that the polymer matrix will not become soft below 200 °C, and then the transferring efficiency of the applied force to the piezoelectric powder may not change obviously. Therefore, the PEH made of PI and BLF-PT ceramic powders show wider workable temperature range than other materials. When the testing temperature is above 200 °C, the piezoelectric particles may experience partial depolarization. In addition, the expansion coefficient of polyimide and BLF-PT ceramic powders are also quite different, leading to the internal stress at the interface between them with the variation of the temperature. Thus, the output voltage potential may decrease obviously above 200 °C.

For BLF-PT/PI composites, the electrical properties are determined by the volume fraction (ϕ) of the BLF-PT particles and the electrical properties of both the ceramic particles and the PI matrix. A model to describe the dielectric ϵ_{33} and piezoelectric d_{33} constants for 0-

3-dimensional composite materials was proposed by Yamada et al. and is expressed by the following formulas [23]:

$$\varepsilon_{33} = \varepsilon_{33}^1 \left\{ 1 + \frac{n\phi(\varepsilon_{33}^2 - \varepsilon_{33}^1)}{n\varepsilon_{33}^1 + (\varepsilon_{33}^2 - \varepsilon_{33}^1)(1 - \phi)} \right\} \quad (1)$$

$$d_{33} = \phi\alpha E d_{33}^2 \quad (2)$$

$$E = \frac{n\varepsilon_{33}}{n\varepsilon_{33} + \varepsilon_{33}^2 - \varepsilon_{33}} \quad (3)$$

where ε_{33}^1 is the dielectric constant of the PI matrix in the poling direction, ε_{33}^2 is the dielectric constant of the BLF-PT ceramic in the poling direction, n is the inverse of the depolarization factor of the particle, α is the poling ratio of the ceramic particles, E is the local electric field coefficient, and d_{33}^2 is the piezoelectric constant of the ceramic. The electric potential is calculated from a simplified simulation model [24] composed of two electrodes with an electrode spacing L of 150 μm (for our device, as shown in **Figure 2e**).

$$V = \frac{Q}{C} \quad (4)$$

$$Q = d_{33}TA \quad (5)$$

$$C = \frac{\varepsilon_0\varepsilon_{33}A}{L} \quad (6)$$

where Q is the induced charge, C represents the capacitance, T is the pressure along the poling direction, and A is the area between the two electrodes. By substituting Eqs. (5) and (6) into Eq. (4), the induced electric potential can be expressed as:

$$V = \frac{d_{33}TL}{\varepsilon_0\varepsilon_{33}} \quad (7)$$

It is obvious that the electric potential is determined by the piezoelectric constant d_{33} , the dielectric constant ε_{33} , and the pressure T . According to the calculations by Yamada's model using the assumed parameters for our device ($\varepsilon_{33} \sim 60$, $\phi \sim 0.7$, $n \sim 8$, $d_{33} \sim 90 \text{ pC/N}$, $T \sim 10 \text{ MPa}$), the device with the concentration of 30 wt% shows the maximum electrical potential of

260 V between the neighboring lateral electrodes. The inconsistency between the experimental and calculated values might be due to the reasons, such as inaccurate parameters used in the calculation or the incomplete poling. However the calculation results indicate that the flexible BLF-PT device can potentially generate even higher output voltage.

For comparison, **Table 1** summarizes the PEHs' energy harvesting performance based on different working materials, active areas and working forms. It indicates that the output electric signal of our super-flexible device made of BLF-PT and PI can be comparable to those of recently studied composite piezoelectric energy harvesters.

Table 1. Output Performance Comparison of Flexible Composite Piezoelectric Energy Harvesters. (RT = room temperature, ~300 K)

Piezoelectric material	Matrix	Active area (cm ²)	Working form	Voltage (V)	Current density (nA/cm ²)	Ref
BaTiO ₃ +Graphitic Carbons	PDMS	4	Bending	3.2 (RT)	62.5-87.5	[25]
PZT+MW-CNTs	PDMS	9	Bending	10 (RT)	144	[26]
BaTiO ₃	PVDF	1	Pressing (1MPa)	35 (RT)	600	[24]
BCZT+Ag NWs	PDMS	9	Bending	15 (RT)	89	[13]
BaTiO ₃ +PVDF	PDMS	2.2	Pressing	75 (RT)	681	[21]
			(0.23MPa)	5 (RT)	272	
			Bending			
ZnO	None	0.32	Bending	0.01 (RT)	31	[27]

NaNbO ₃	PDMS	3.2	Bending	3.2 (RT)	16	[28]
BiFeO ₃	PDMS	1	Pressing	3 (RT)	120	[29]
(Bi,Lu)FeO ₃ -	PI	1.4	Pressing	110 (RT)	220	This
PbTiO ₃			(0.18MPa)	100 (150°C)		work

Figure 5 (a) Time-dependent open circuit voltage of device under different impact frequencies of 0.2Hz, 0.4Hz, and 1.0Hz. (b) Relationship between the peaks of the output open circuit voltage and the impact frequency. (c) Schematic circuit diagram for rectification and energy storage, composed of a PEH, a full-wave bridge rectifier, and a capacitor. (d) Time dependent charging curves of capacitors with different capacitances.

To harvest energy from human motion, the device needs to work efficiently at low frequency, so it is highly important to evaluate the device performance in this specific frequency range. For this purpose, cyclical mechanical tapping with a pressure of 0.02 MPa

was applied on the device with frequency ranges from 0.2 to 1.0 Hz, which is similar to that of human motion. **Figure 5(a)** shows the time-dependent open-circuit voltage of the device with 30 wt% BLF-PT powders. With increasing frequency from 0.2 to 1.0 Hz, the output voltage is 4.5 V for tapping frequency of 0.2 Hz, tending to saturate at 7 V for frequency of 1.0 Hz, which is the maximum frequency of our test facility. The increase of the open-circuit voltage with increasing tapping frequency can be attributed to two possible reasons [30-32], 1) the impedance of the device changes with frequency; 2) at higher frequency, the electrons have less time to balance the piezoelectric potential in the external circuit, which will cause electrons accumulation at the electrodes and thus higher current output (Supporting **Figures S(6-7)**). This measurement verifies that the device can efficiently harvest mechanical energy with frequency below 1 Hz.

To examine the feasibility of storing the charge from the PEH for powering electronic devices, a PEH containing 30 wt% BLF-PT particles was used to charge two capacitors with capacitances of 1.0 and 4.3 μF , just by tapping with an index finger. **Figure 5(c)** shows the schematic circuit diagram for charging which includes a full-wave bridge rectifier, capacitor, and PEH. The AC output generated by the PEH was first converted into DC power through the rectifier, and then the DC power was used to charge the capacitor. As shown in **Figure 5(d)**, in the case of the 1 μF capacitor, its voltage increased gradually and eventually reached its maximum value of 1.5 V within 150 s at a frequency of around 0.6 Hz; and for the 4.3 μF capacitor, it reached 1.6 V within 300 s. These results well demonstrate that our device can be a power source for low energy-consumption electronic devices.

Figure 6 Sensitivity performance of the flexible PEH under different impact forces. (a) Schematic diagram of the test setup. (b-c) Open circuit voltage and short circuit current of the flexible PEH tested by free-falling of table tennis ball from different heights. (d) Relationship between the peaks of output voltage (current) and the free-falling height.

In addition to outstanding output performance and high temperature stability, the flexible PEH can response actively to tiny impact, which indicates its high sensitivity when served as a force sensor. As shown in **Figure 6(a)**, the impact was induced by a free-falling table tennis ball with the mass of 2.5 g and diameter of 4 cm from different height ranging from 3 to 18 cm. The force applied on the device by the ball can be calculated based on the formula $\Delta mgh/\Delta t$, where Δmgh is the momentum change of the ball which is totally transferred to the PEH device and Δt is the interaction time of the ball on the device. Δmgh is calculated as mgh after the ball is completely stopped on the device, where m is ball mass, g is the gravity acceleration, and h is the dropping height. The impact time is assumed based on the output signal width of the device as 0.5 s. Therefore force applied on the PEH device is approximately 1.5×10^{-3} N for dropping from 3 cm height. The open circuit voltage and short circuit current of the device

with 30 wt% BLF-PT powders are shown in **Figure 6(b-d)**, as for the height of 3 cm, the output voltage is as high as 11 V. In addition, the output electrical signal responds actively to the impact force which increases from 11 V/53 nA to 32 V/125 nA when the dropping height change from 3 to 18 cm. These results demonstrate clearly that our flexible device can work as a sensor with excellent sensitivity.

Figure 7 Sensor measurement results: Open circuit voltage and short circuit current outputs when a PEH with 30% BLF-PT was used as a sensor: (a-c) bent by fingers through attached conductive wires; (d-f) attached to the index finger with the poling direction vertical with respect to the finger; (g-i) attached to the finger with the poling

direction parallel to the finger direction. (j) The result of bending durability test for 1000 times bending collected at three different periods when PEH is attached to the finger for 12 hours with finger free motion between test periods. The poling direction parallels to the finger direction.

Figure 7 shows the open circuit voltage and short circuit current outputs from the 30% BLF-PT PEH device when the free standing device was bent by fingers through two attached conductive wires and when it was attached to the index finger joint in two different directions. The open circuit output peak value of 11.5 V and short circuit current of about 87 nA were obtained in response to the bending by fingers, as shown in **Figure 7(a-c)**, and the open circuit peak voltage and short circuit current values of 15.4 V/93 nA and 20.2 V/124 nA were obtained from the finger joint for poling direction vertical to the finger (**Figure 7d, e, f**) and parallel to the finger (**Figure 7g, h, i**), respectively. To verify the mechanical durability of the flexible PEH, the PEH was attached to the finger for 12 hours without limiting the motion of the finger as shown in **Figure 7(g)**, and the output was then collected at different time respectively, morning (8:00 am), noon (14:00 pm) and night (20:00 pm). According to **Figure 7(j)**, the flexible PEH can maintain stable output voltage without obvious change even after 12 hours' free motion of the finger. The results indicate that the device can not only responds actively to human movement but also possesses splendid wearability, which proves its capacity for sensing or harvesting biomechanical energy due to its high flexibility and durability.

4. Conclusion

In summary, we have developed a novel approach to fabricating super-flexible piezoelectric energy harvesters (1 cm × 1.4 cm) based on BLF-PT/PI composite film. The maximum open-circuit voltage and short-circuit current were measured to be 110 V and 310 nA under the pressure of 0.18 MPa, respectively. The flexible device is frequency sensitive below 1 Hz. As the frequency increases, the voltage output tends to be saturated, which means that the device can work under a wide range of frequency. Furthermore, due to the benefits of

unique PI material-based composite, the flexible energy harvester can tolerate high temperatures, which greatly broadens the operating range of the device. Compared with the previously reported piezoelectric energy harvesters, our energy harvester presents remarkable advantages, such as high electrical voltage output and a broad operating temperature range, which enable it to serve as a super-flexible microscale power source and sensor that can work in harsh environments. Moreover, the device responds actively to human movement, which proves its capacity for sensing due to its high flexibility and sensitivity. The approach we report here is simple and cost-saving, so that it can be applied to the fabrication of more flexible energy harvesters based on other piezoelectric materials.

Author Contributions

† Contributed equally to this work.

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TOC Graphic

Author Biosketch

Yanhua Sun received her Master Degree from Southeast University, China. She is currently pursuing her Ph.D. degree in the Institute for Superconducting and Electronic Materials at University of Wollongong. Her research focuses on ferroelectric, piezoelectric, multiferroic materials and flexible devices for energy harvesting and sensing.

Jianguo Chen received his Ph.D. degree in electronic material and device from Shanghai University China, in 2010. He was invited as a Postdoctoral Fellow with Peking University, Beijing, China, from 2011 to 2012. He is currently an Associate professor in the School of Materials Science and Engineering, Shanghai University. He is researching and fabricating Bi(Me)O₃ based ceramics, and designing and fabricating high temperature sensors and

actuators. His current research interests include high-temperature piezoelectric ceramics and multiferroic material for sensor and actuator applications.

Xiaoning Li is currently a Ph.D of University of Wollongong. Her main research interests focus on the transition metal oxide nanomaterials, from synthesis, crystal and electronic structure analysis, to multiferroic and water splitting property characterization.

Yun Lu is a Ph.D. student in Institute for Superconducting and Electronic Materials at University of Wollongong. His current research interests focus on the piezoelectric-magnetostrictive composite for the application of energy harvesting and weak magnetic field sensing.

Shujun Zhang is Professor at ISEM/AIIM of UOW, prior to which, he was Professor at MatSE Department and Senior Scientist at MRI of PSU. He is associate EIC of IEEE Transaction UFFC; associate editor of Science Bulletin; Journal ACerS and Journal Electronic Materials, section EIC of Crystals. He is fellow of ACerS and senior member of IEEE, elected AdCom member of IEEE-UFFC. He holds 8 patents and has coauthored 500 papers, with Google Scholar citation >17,000 and H index of 63. He is now focusing on fabrication-microstructure-property-performance relationship of functional materials for piezoelectric sensor, transducer and energy storage/harvesting applications.

Dr. Zhenxiang Cheng received his BS (Physics, 1995) and Ph.D. (Materials Science, 2001) from Shandong University, China. He worked as a JSPS fellow (Japanese Society for Promotion of Science) in the National Institute for Materials Science, Japan (2003–2005). Then, he worked as a research fellow at the University of Wollongong (2005–2009). He was awarded a Future Fellowship by the Australian Research Council (2009–2013). Currently, he is a Professor at University of Wollongong. His main interest is ferroic materials, including magnetic, ferroelectric, and multiferroic materials, their physics and applications.

Flexible (Bi,Lu)FeO₃-PbTiO₃ based energy harvester/sensor with high voltage output suitable for high temperature application

Yanhua Sun^{†,a}, Jianguo Chen^{†,a,b}, Xiaoning Li^a, Yun Lu^a, Shujun Zhang^a, Zhenxiang Cheng^a

^aInstitute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, Innovation Campus, University of Wollongong, Squires Way, North Wollongong, NSW 2500, Australia

^bSchool of Materials Science and Engineering, Shanghai University, Yangchang Road No. 149, Shanghai 200072, People's Republic of China

This PDF file includes:

Figure S1. Solidification process for the PI and BLF-PT/PI film.

Figure S2. Picture of the measurement system, where the inset shows the corresponding schematic diagram.

Figure S3. Diameter distribution of the BLF-PT particles.

Figure S4. Electrical output of flexible PEHs made of BLF-PT/PVDF and BLF-PT/PDMS at room temperature (RT) and 150 °C.

Figure S5. TGA plot of device with 30 wt% BLF-PT.

Figure S6. (a-d) Output voltage of the PEH with 30 wt% BLF-PT under different impact frequencies with the tapping pressure of ~ 0.02 MPa.

Figure S7 (a-g) Output current of the PEH with 30 wt% BLF-PT under different impact frequencies with the pressure of ~ 0.02 MPa. (h) Relationship between the peaks of the output current and the impact frequency.