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ORIGINAL PAPER

# Thermal and mechanical energy harvester based on flexible PVDF/PLZT polymer-ceramic composites

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## Abstract

The present manuscript focuses on the thermal and mechanical energy harvesting through flexible PVDF/PLZT (Polyvinylidene Fluoride/ Lanthanum doped lead zirconium titanate) composite films prepared using solution-cast technique. The effect of Lanthanum doped lead zirconium titanate (PLZT) ceramic content in the composite was studied in terms of its structural, morphological and dielectric properties. The pyroelectric coefficient, figure of merit and piezoelectric voltage were determined for pure PVDF and PVDF/PLZT composite films. With increasing PLZT concentration in PVDF from 0 to 50%, the pyroelectric coefficient values were found to vary from $0.5 \times 10^{-4}$ $Cm^{-2}$ $K^{-1}$ to $18 \times 10^{-4}$ $Cm^{-2}$ $K^{-1}$ respectively. The maximum piezoelectric voltage of 1.5 V was achieved for PVDF/PLZT (50%) flexible composite films. The obtained pyroelectric coefficient and piezoelectric voltage for the PVDF/PLZT (50%) composite film revealed its importance in terms of performance for thermal and mechanical energy harvesting.

**Keywords** Lanthanum doped lead zirconium titanate (PLZT) · Ferroelectric · Piezoelectric · Dielectric · Pyroelectric

## Introduction

In recent few years, researchers have focused on the development of flexible ceramic-polymer composites [1, 2]. This is because of the fact that embedement of ceramic particles into different organic polymers increase the multifunctionality resulting in wide applications in the field of wearable devices, actuators, sensors, energy harvesters and wireless communication etc. [3, 4]. Amongst the various applications of ceramic/polymer composites, energy harvesting technology is one of the prominent research topic for generating the renewable and green energy due to increasing energy demand and limited energy resources [5, 6]. In order to generate electrical voltage, various number of ambient waste sources such as wind, heat and vibration have been studied. Among these energies, waste mechanical energy and heat are easily available and offer great potential for energy harvesting [7, 8]. The mechanical energy can be obtained from the sources including human activity, vehicle movement etc. Also, Lot of heat obtained from various sources including heat from solar energy, during breathing of living beings, heat due to vehicles movement is wasted which can be harnessed easily [9]. In order to harvest thermal and mechanical energy, piezoelectric and ferroelectric materials are the best candidates and they also have excellent pyroelectric properties [10, 11]. There are some dielectric materials such as potassium sodium niobate (KNN), barium strontium titanate (BST), Strontium barium titanate (SBN), Zinc Oxide (ZnO), lead zirconium titanate (PZT), which are piezoelectric as well as pyroelectric in nature. Said et al. studied ferroelectric and piezoelectric properties of Strontium Barium Niobate ($Sr_{0.53}Ba_{0.47}Nb_2O_6$) and reported that the piezoelectric coefficient ($d_{33}$) value was 14pC/N with saturation polarization of 25 μC/$cm^{-2}$ [12]. Potassium sodium niobate (KNN) is also an efficient multicomponent material and its piezoelectric properties are studied by Mirzazadeh et al. when integrated with flexible polymer. However, the obtained piezoelectric coefficient ($d_{33} = 23.06$ pC/N) was still low [13]. Amongst different multicomponent materials, Lead Zirconium Titanate (PZT) was found to be a potential candidate having good ferroelectric polarization ($P_s = 80$μC/

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cm$^2$), dielectric constant ($\in_r = 1800$), pyroelectric coefficient ($p = 3.52 \times 10^{-4}$ Cm$^{-2}$ K$^{-1}$) and having excellent piezoelectric coefficient material as reported by Sappati and Bhadra [14]. Hence, it was concluded that lead zirconium titanate (PZT), based materials exhibit good piezoelectric and pyroelectric coefficient which can be further explored for energy harvesting purpose [6, 7]. However, it was studied in previous reports that suitable dopants such as $Fe^{3+}$, $Sc^{3+}$, $La^{3+}$, $Nb^{5+}$, $Ce^{3+}$, $Ta^{5+}$, $K^+$, $Na^+$ in "A" or "B" sites of PZT can further improve the ferroelectric properties of PZT. Xu et al. studied effect of lanthanum doping on dielectric properties of PZT ceramic and found maximum dielectric constant of 1502 in 2% La-doped PZT thin film, which increased by 53.9% compared with undoped film [15]. Kathiresan et al. studied the effect of Sr and La on the ferroelctric properties of sputtered PZT films and found that saturation polarization is enhanced from 5.5μC/cm$^2$ to 12 μC/cm$^2$ with Lanthanum doping [16]. Liu et al. studied pyroelectric properties of PLZT ceramic and reported pyroelectric coefficient to be $17 \times 10^{-4}$Cm$^{-2}$ K$^{-1}$ which is appreciable in comparison to pure PZT [17]. Hence, it was concluded that the most suitable dopant in order to enhance the functional properties of PZT is Lanthanum. This is because lanthanum doping in PZT facilitate the motion of domain walls resulting in enhancement in piezoelectric and pyroelectric properties of PZT [11, 18, 19]. Despite good ferroelectric and piezoelectric properties of PLZT ceramics, poor mechanical properties such as brittleness and inflexibility are the major disadvantages which limit the applications of this material in the field of flexible electronics [20, 21]. Therefore, for the fabrication of flexible thermal and mechanical energy harvester based on PLZT, this material should be integrated with ferroelectric polymer. The ferroelectric polymers exhibit weak piezoelectric and pyroelectric properties in comparison to the ferroelectric ceramics [10]. However, the polymers have advantages over ceramics in terms of good flexibility, easy processing and high breakdown strength [18]. Hence, the integration of ferroelectric ceramic and polymers may result in a flexible material exhibiting promising ferroelectric properties. There are different kinds of ferroelectric polymer available such as polyvinyldiflouride (PVDF), polyvinylchloride (PVC), polyurthene (PU), polyvinyldiflouride-tetrafluoroethylene P(VDF-TrFE), polydimethylsiloxane (PDMS) etc. which are used for fabrication of flexible composites [1]. However, amongst all types of polymers, PVDF is used more widely due to its easy commercial availability and low cost. PVDF exhibits excellent abrasion resistance with good thermal stability [11]. It has high breakdown strength with good resistance to creep under long term pressure and high dielectric strength [22]. It is well recognized as mechanically stronger than other kind of polymers. In the present work, the optimized PLZT (6% La doped) ceramic particles, as discussed in our previous reports [23], have been dispersed in flexible polymer in order to obtain polymer/ceramic flexible composite. In the present manuscript, 6% La doped PZT was chosen because of good dielectric, and ferroelectric properties have been obtained in case 6% PLZT in comparison to pure PZT in previous reports [23]. Content of ceramic particles in polymer plays a significant role in tuning the ferroelectric, piezoelectric and pyroelectric properties of PVDF flexible polymer. Research has already been done on the fabrication of polymer/ ceramic composite and used for energy harvesting purpose. Zhang et al. studied pyroelectric properties of PVDF/PZT composite films and reported pyroelectric coefficient value was found to be $0.26 \times 10^{-8}$ C/cm$^2$ K [24]. Similarly, Ponnan et al. studied piezoelectric voltage using PVDF/ POFPA composite and reported peak to peak voltage was achieved to be 1.195 V [25]. The obtained pyroelectric and piezoelectric results were good however, there is scope of improvement in terms of energy harvesting performance of flexible composites. In the present manuscript, PVDF/PLZT flexible thick films with different fractions of PLZT content varying from 0 to 50%, respectively were fabricated using solution-cast method because of simplest and cost effective method for fabrication of flexible films [26–28]. The effect of ceramic content on the structural, surface morphological, dielectric, ferroelectric, pyroelectric and piezoelectric properties of PVDF/PLZT flexible films have been investigated using X-ray diffraction (XRD), Scanning electron microscopy (SEM), P-E hysteresis loop tracer and Keithley 4200 semiconductor characterization unit.

## Experimental section

### Preparation of PVDF and PVDF/PLZT flexible composite films

PLZT ceramic powder was prepared with the help of modified sol–gel technique. The PLZT sol prepared as discussed in our previous work was dried on hot plate at 120 °C overnight to evaporate the solvent [23]. The dried as—deposited powder is crushed in pestle-mortor and calcined in high temperature furnace at 800 °C for 5 h to obtain the pure perovskite phase. Solution-cast technique has been adopted for the preparation of PVDF and PVDF/PLZT flexible composite films. Figure 1 shows the systematic diagram of PVDF and flexible composite film using solution casting technique. For the preparation of flexible composite film, solution is first prepared by mixing ceramic particles with polymer homogeneously. Then the solution is dispersed to form a denser film which is flexible. The PVDF powder (purity ≥ 99.99%), procured commercially from the sigma Aldrich was used as raw powder for preparation of PVDF film. The commercially purchased PVDF powder was dissolved in the dimethylformamide (DMF) solvent using the continuous magnetic

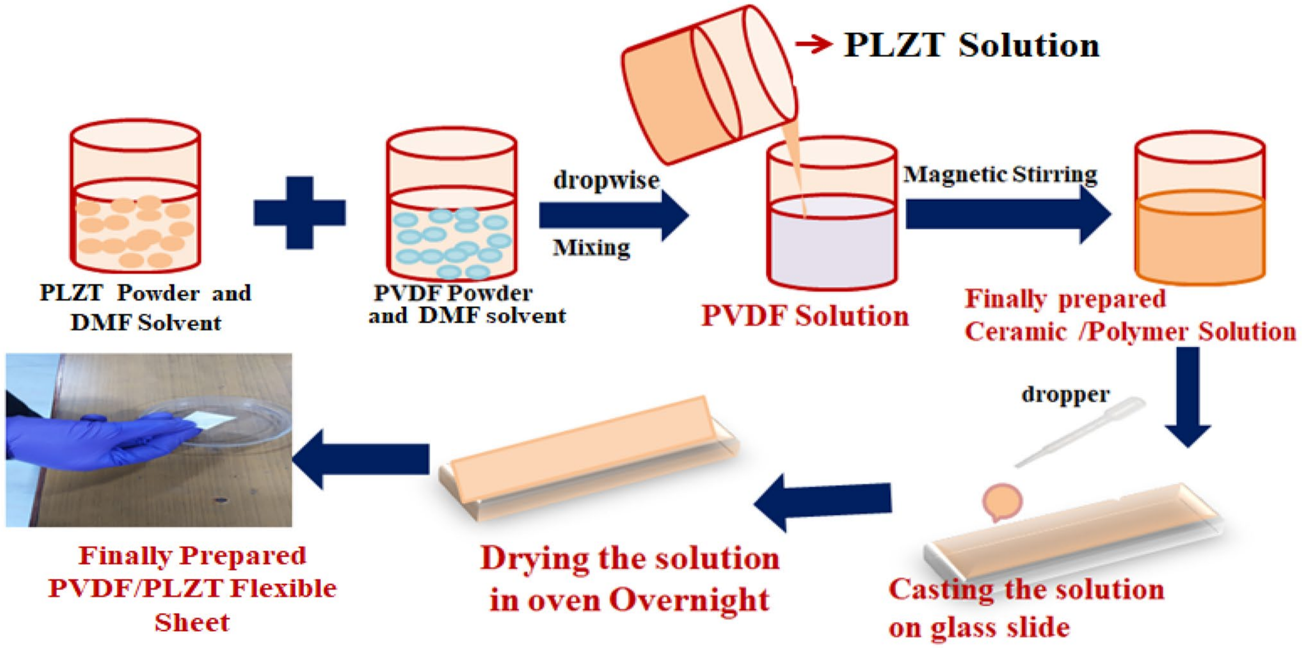


**Fig. 1** Schematic representation of the preparation of the PVDF/PLZT flexible composite film using solution-cast method

stirring at 50 °C. The solution was stirred on magnetic stirrer till the transparent homogeneous solution was obtained. The obtained pure PVDF solution was drop casted on the glass substrate and kept in oven at 60 °C for 1 h. After 1 h of drying, the oven was evacuated and the samples were dried at 110 °C in the vacuum oven for 3 h. The film was then peeled off from the glass substrate. In the similar way, Different concentrations of composites have been prepared by mixing PVDF and certain percentage of PLZT (10%, 30% and 50% by volume) of PVDF. The molar ratio of both constituents has been provided in Supplementary Table 1. PVDF and PVDF/PLZT flexible composite films are structurally and morphological characterized using X-ray diffraction, and Scanning electron microscopy. The pyroelectric properties and piezoelectric voltage measurements were carried out using Keithley 4200 source meter. In the present manuscript, concentration of PLZT has been varied till 50% only. Beyond 50% concentration, incorporation of PLZT in PVDF leads to cracking in the films.

## Results and discussion

### Structural characterization

Figure 2 shows the XRD and SEM micrographs pattern of PVDF/PLZT composite films with varying concentration of PLZT from 0 to 50% respectively. 2θ scan is done starting from 20° to 60° with step size of 3°/ minute respectively. 0% concentration of PLZT corresponds to pure PVDF sample. XRD pattern of pure PVDF shows diffraction peaks at $2\theta = 17.94°$ and 18.50°, which correspond to diffraction planes (100) and (020) of α-phase of PVDF, which is non -polar and hence, does not exhibit dipole moment. The confirmation of β-phase of PVDF corresponds to presence of diffraction peak at $2\theta = 20.30°$ with diffraction plane (110). The diffraction peaks of PVDF matched with JCPDS File # 33–0784 [22, 29]. The structural characterization of the PVDF/PLZT composite films with different PLZT concentration varying from 10 to 50% by volume are also represented in Fig. 2. It is observed from the diffraction spectra of all the composites that peaks corresponding to PLZT and PVDF are only observed. In other words, no other secondary phase is formed as a result of interaction between PLZT and PVDF. The diffraction peaks correspond to PLZT matched well with JCPDS Card Number #00–050-0346 [30]. The crystallographic planes (100), (110), (111), (200), (210) and (211) at 21.89°, 31.09° and 38.34°, 45.12°, 50.27° and 55.51° are the signatures of the perovskite phase corresponding to PLZT. The diffraction angle (2θ) corresponding to (110) plane is slightly decreased with increasing content of PLZT indicating inter planer spacing increases. It is observed from XRD pattern that with increase in PLZT content from 10 to 50% by volume in PVDF, the intensity corresponding to (110) diffraction plane increases indicating the formation of good crystalline structure of the flexible composite film. It was found that non polar phase (α) of PVDF disappear with increase in PLZT content which may be due to incorporation of PLZT in PVDF. It is also noticed that a small diffraction peak corresponding to β phase of

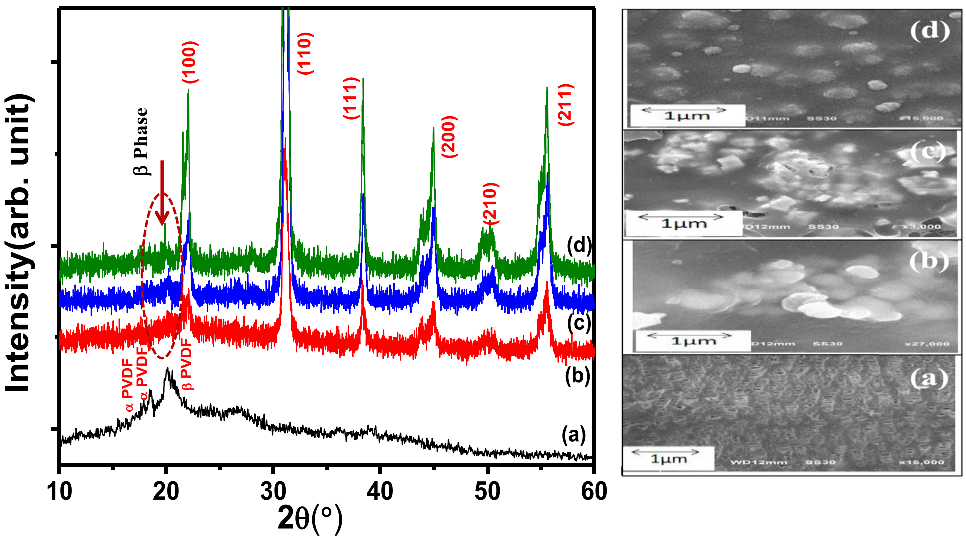


**Fig. 2** X-Ray Diffraction Pattern and Surface micrographs of PVDF/PLZT flexible composite films **a** Pure PVDF **b** PVDF/PLZT (10%), **c** PVDF/PLZT (30%) and **d** PVDF/PLZT (50%)

PVDF starts to evolve in 30% PLZT/PVDF composite. All the diffraction peaks of PVDF phase and PLZT phase are clearly visualized and enhancement of β-phase of PVDF and suppression of α-phase in 30% sample is clearly seen which is slightly enhanced with increase in PLZT content. The degree of texturing (DOT) in percentage for PVDF/PLZT composite films along (110) plane is determined using the following formula

$$\mathrm{DOT}(\%) = \frac{\mathrm{I}(110)}{\mathrm{I}(110) + \mathrm{I}(110) + \mathrm{I}(111)} \times 100\% \tag{1}$$

The values of $D_{\mathrm{texture}}$ (%) for the dominating (110) plane are found to be 39%, 41% and 45% for 10%, 30% and 50% PVDF/PLZT flexible composites, respectively. Degree of texturing of the flexible composite films along (110) plane of PLZT improves with increase in PLZT filler in PVDF matrix.

Crystallite size (D) for the flexible composite films with variation in PLZT content is also calculated along the (110) dominant plane using the Sherrer's formula and tabulated in Table 2. The values of crystallite size along the (110) dominant plane found to be increase from 18 to 23 nm with increase in the content of PLZT filler in PVDF matrix from 10 to 50%, respectively. The surface micrographs of PVDF and PVDF/PLZT (10%, 30%, 50%) flexible composite films are also shown in Fig. 2. It was found from Fig. 2a that a large number of nodules are found indicating proper growth of nuclei and crystallization of PVDF film [31]. However, with the addition of PLZT ceramic particles in PVDF, the growth of nodules get restricted due to increased amount of ceramic content in composite film [32]. In case of PVDF/PLZT composites (Fig. 2b-d), the white contrast corresponds to ceramic particles which are dispersed into the polymer without any agglomeration indicating the presence of good connectivity between ceramic and polymer. Uniform distribution of ceramic particles in PVDF can be clearly seen from SEM micrographs for all flexible composite films. This confirms the formation of homogeneous flexible composite films.

## Dielectric properties

Figure 3 show the frequency dependence of dielectric constant and dielectric loss of all the flexible composite films over a wide range of frequencies varying from 10 kHz to 1 MHz at room temperature.

The obtained variation of the dielectric constant with the variation in frequency is found to be similar to those reported in literature [33]. The dielectric constant values are found to be high in lower frequency range in all flexible composite films which is related to the contribution of different types of polarizations as discussed in previous reports [34]. It is revealed from the Fig. 3 that dielectric constant values for all the composites decreases with increase in frequency and become constant at higher value of frequency

**Table 2** Structural parameters calculated for PLZT/PVDF composite films using XRD spectra

| PLZT (%) | 2θ correspond to (110) plane (°) | FWHM (°) | Crystallite Size (nm) along (110) plane | Degree of texture (%) Along the (110) direction |
|---|---|---|---|---|
| 10 | 31.19 | 0.48 | 18 | 39 |
| 30 | 31.09 | 0.41 | 21 | 42 |
| 50 | 30.80 | 0.39 | 23 | 45 |

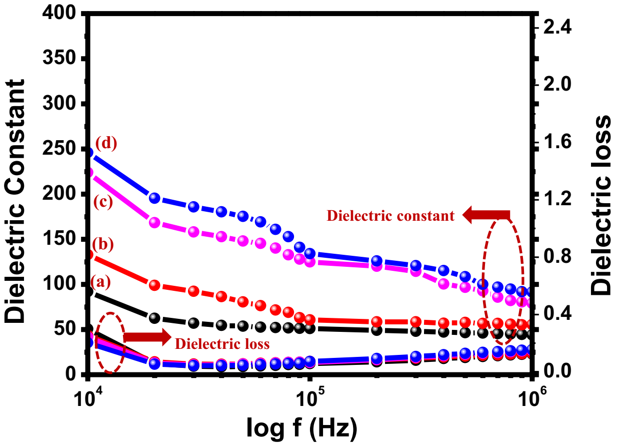


**Fig. 3** Dielectric constant and Dielectric loss of **a** pure PVDF, **b** PVDF/PLZT (10%) **c** PVDF/PLZT(30%) and PVDF/PLZT (50%) flexible composite films

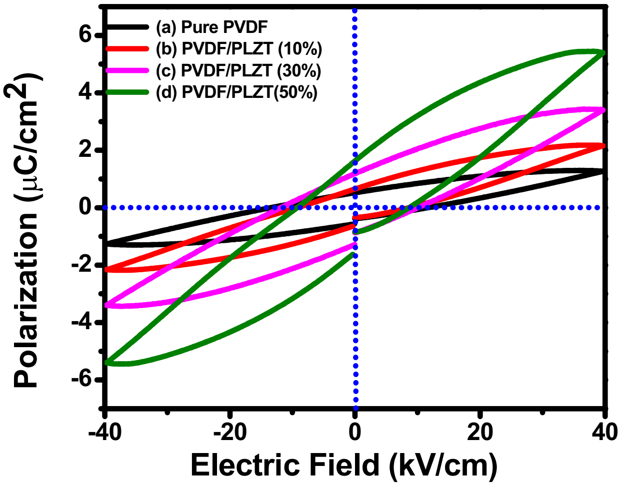


**Fig. 4** Ferroelectric hysteresis loops of all the composite films measured at 100 Hz

(1 MHz). Table 3 displays the dielectric constant and dielectric losses with the variation in PLZT content at 1 MHz.

As frequency is increased, due to a slower response of domains with applied external field, there is reduction in dielectric constant [35, 36]. It is observed from Fig. 3 that dielectric constant values increases from 44 to 91 with increase in PLZT content from 0 to 50% at a frequency of 1 MHz. This increase in the dielectric permittivity with the increase in the ceramic content is as expected because more content of PLZT particles are contributing. Dielectric loss values with variation of frequency of all composite films are also studied (Fig. 3). It is noticed that with increase in ceramic content in composite, the dielectric losses slightly increase which may be due to the particle aggregation in the composite films with high concentration of ceramic content.

## Ferroelectric properties

Figure 4 represents the ferroelectric hysteresis loop of prepared pure PVDF and PVDF/PLZT (with PLZT composition of 10%, 30% and 50%) flexible composite films at room temperature and fixed frequency of 100 Hz and varying electric field varies from -40 kV/cm to 40 kV/cm. The shape of the hysteresis loops indicate the rearrangement of the domains with the application of external applied field and hence confirming the ferroelectric nature of all the prepared flexible films. Polarization ($P_{max}$) and Remanant Polarization ($P_r$) are determined from the P-E loops for all the flexible films and are tabulated in Table 4. It is observed that the maximum polarization is increased from 1.30 μC/cm$^2$ to 5.38 μC/cm$^2$ and remnant polarization is enhanced from 0.55 μC/cm$^2$ to 1.75 μC/cm$^2$ with the increase in the PLZT content from 0% (pure PVDF) to 50% respectively. This is due to the fact that because dipole–dipole interaction increases with increase in ceramic content and hence polarization is increased. Therefore, it can be concluded that PVDF/PLZT with 50% PLZT content showed maximum polarization. Also coercive field is determined for all the flexible composite films and noticed that coercive field is minimum in case of PVDF/PLZT (50%) composite. With further increase in PLZT content, flexible composite films got crack, hence no further increase in PLZT content in PVDF is been studied. The obtained results showed that 50% PVDF/PLZT composite exhibit maximum enhancement in the dielectric and ferroelectric properties. This may be due to fact that as PLZT content is increased in PVDF then due to suppression of α- phase and enhancement in β-phase of PVDF, the ion–dipole interaction increased resulting in the improved ferroelectric, dielectric and piezoelectric properties. In order to compare ferroelectric and dielectric results of 50% PVDF/PLZT with pure PLZT, ferroelectric hysteresis (P-E) loop and dielectric constant variation with frequency have been studied for pure PLZT and shown in Fig. 5.

Figure 5a shows the P-E hysteresis loop of Pure PLZT measured at 100 Hz with varying electric field (-250 kV to 250 kV). The loop is found to be well saturated indicating good domain switching behaviour of Pure PLZT. Saturation and remnant polarization of pure PLZT are extracted from the P-E hysteresis loop at 100 Hz frequency and 250 kV/

**Table 3** Variation in the dielectric constant and loss with the PLZT ceramic content in the composition measured at 1 MHz

| Composite Films | Dielectric Constant | Dielectric Loss |
|---|---|---|
| Pure PVDF | 44 | 0.12 |
| PVDF/PLZT (10%) | 55 | 0.12 |
| PVDF/PLZT (30%) | 79 | 0.14 |
| PVDF/PLZT (50%) | 91 | 0.15 |

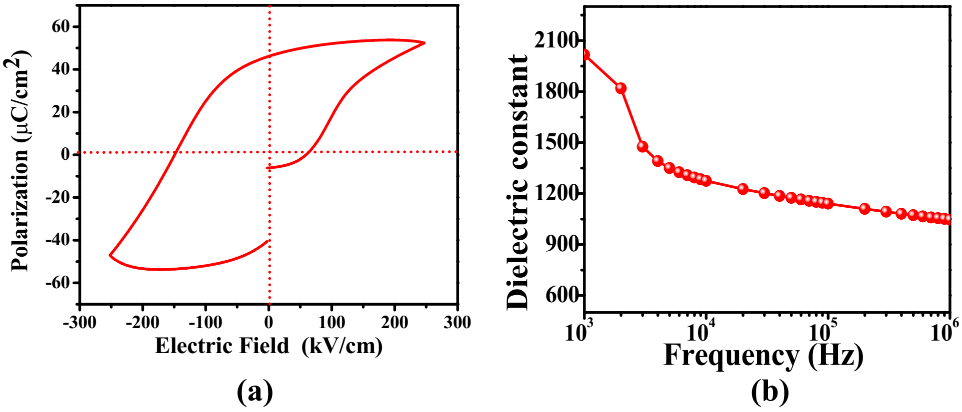


**Fig. 5** **a** Ferroelectric Hysteresis (P-E) loop and **b** Dielectric constant variation with frequency for the 6% pure Lanthanum doped lead zirconium titanate (PLZT)

cm electric field and are found to be 52μC/cm$^2$ ($P_s$) and 46μC/cm$^2$ ($P_r$) respectively. In the similar manner, dielectric constant variation with frequency was studied for pure PLZT (Fig. 5b) and dielectric constant of 1048 at 1 MHz frequency was obtained. It was observed that ferroelectric and dielectric properties of Pure PLZT are far better than flexible PVDF/PLZT based composites (Figs. 3 and 4). However, Pure PLZT is brittle in nature but we can make free standing PLZT films in future work.

## Pyroelectric study

The pyroelectric measurements of all the flexible composite films have been studied for thermal energy harvesting applications. All the pyroelectric measurements are carried out using an indigeneously developed cyclic heating system along with Keithley (4200) semiconducting unit and DC probes as shown in Fig. 6.

DC probes were used to make connections from top and bottom electrodes of the device. Keithley 4200 unit is used to measure the pyroelectric current output from the PVDF/PLZT flexible films with respect to change in temperature with time. Thermal heat is provided to the sample and corresponding change in temperature in the vicinity of the films is measured using a K-type thermocouple placed near to the flexible composite film.

The rate of change of temperature ($\frac{dT}{dt}$= 0.11 °C/s) was kept constant for all the flexible composite films. In order to monitor the effect of PLZT content on the pyroelectric current behaviour of flexible composites, the pyroelectric current with time variation was recorded for all the prepared PVDF/PLZT composite films and is shown in Fig. 7. It is observed from Fig. 6 that with increase in temperature of the sample, the corresponding pyroelectric current is increased and vice versa for pure PVDF and PVDF/PLZT (10%, 30% and 50%) flexible composite films. As PLZT is incorporated, pyroelectric coefficient is increased which is the good signature for realization of energy harvester.

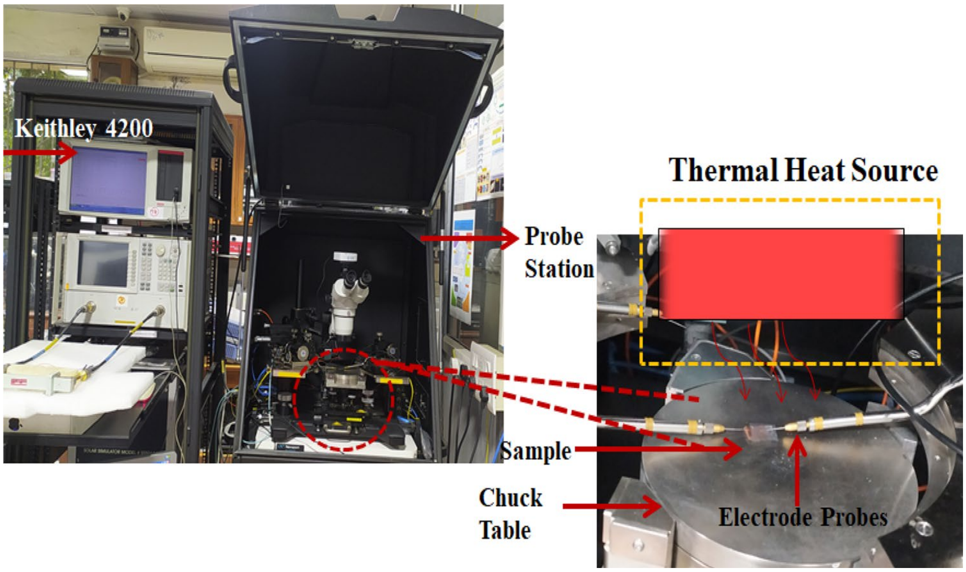


**Fig. 6** Experimental setup used for pyroelectric measurement of flexible composite films

**Table 4** The maximum and remnant polarization values for all the composite films determined from the P-E hysteresis loop

| Sample | $P_{max}$(μC/cm$^2$) | $P_r$(μC/cm$^2$) | Coercive field (kV/cm) |
|---|---|---|---|
| Pure PVDF | 1.30 | 0.55 | 21.62 |
| PVDF/PLZT (10%) | 2.16 | 0.69 | 17.37 |
| PVDF/PLZT (30%) | 3.43 | 1.27 | 21.31 |
| PVDF/PLZT (50%) | 5.38 | 1.75 | 16.81 |

It can also be noticed that pyroelectric current is increased with increase in PLZT content in PVDF matrix. In case of pure PVDF flexible composite film, pyroelectric current is found to be $0.19 \times 10^{-10}$ A which increases to $0.21 \times 10^{-10}$ A for PVDF/PLZT (10%) composite film. The magnitude of pyroelectric current is further increased to $1.61 \times 10^{-10}$ A for PVDF/PLZT film with 50% PLZT content. The increase in pyroelectric current of PVDF film with ceramic content of PLZT is due to polarization change with change in temperature. This is because during thermal fluctuations provided to the sample, then equilibrium position of the domains got disturbed and there is change in alignment of domains resulting change in polarization of the material. As a result of this, the free charges which were attracted to the surface charges got free and participate in pyroelectric current. From pyroelectric current values determined from the pyroelectric current versus time graphs, the pyroelectric coefficient and figure of merits are determined for all the

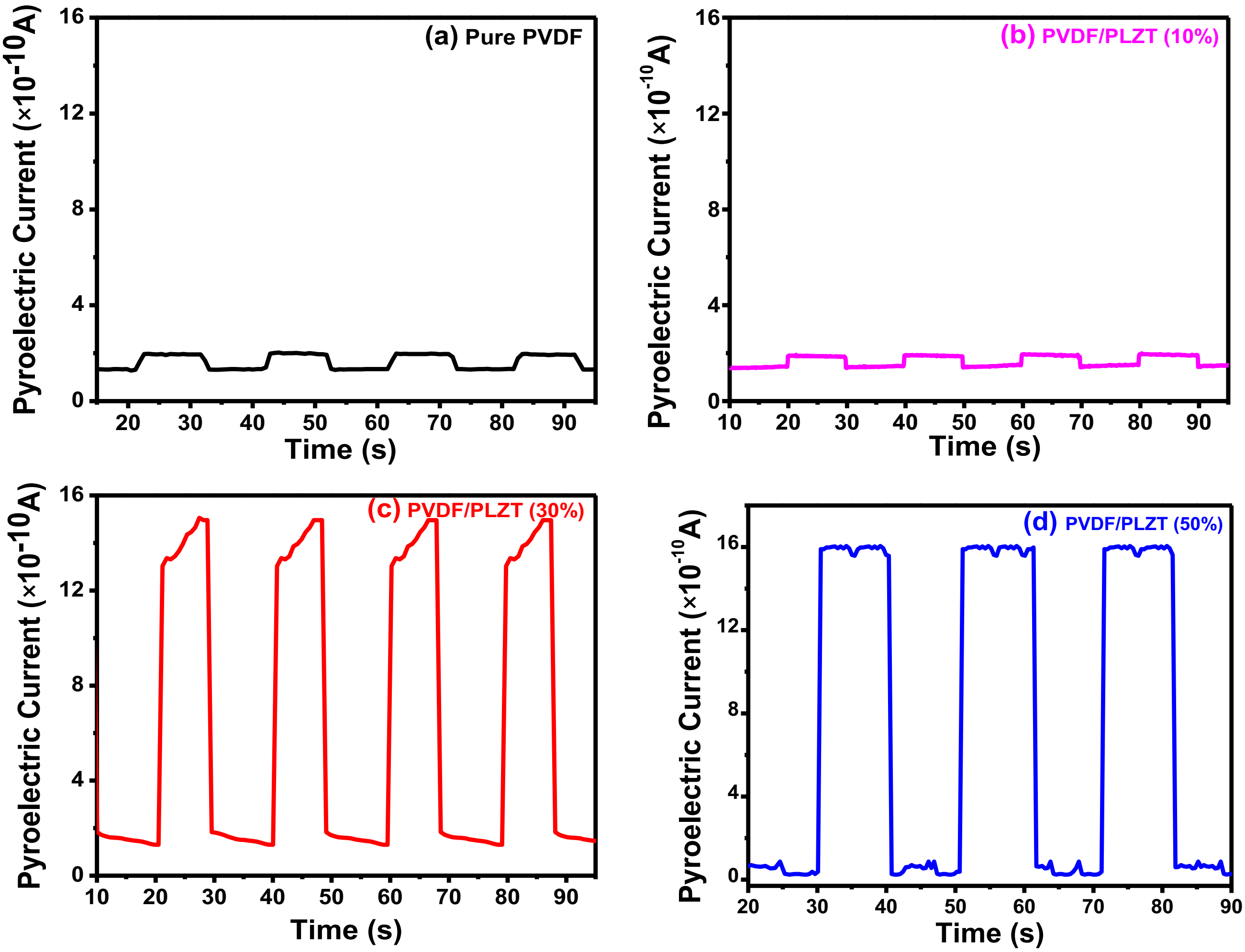


**Fig. 7** Variation in pyroelectric current with time for **a** PVDF/PLZT (0%), **b** PVDF/PLZT (10%) and **c** PVDF/PLZT (30%) and **d** PVDF/PLZT (50%) flexible composite films

**Table 5** Pyroelectric coefficient and figure of merits for flexible composite films with variation in PLZT content

| Composite Film | Pyro electric Coefficient ($Cm^{-2}\,K^{-1}$) | Current Responsivity ($F_i$) $\times 10^{-11}$ $mV^{-1}$ | Voltage Responsivity ($F_v$) $m^2C^{-1}$ | Energy Harvesting Figure of Merit ($F_e$) $\times 10^{-11}$ $m^3J^{-1}$ |
|---|---|---|---|---|
| Pure PVDF | $0.5\times10^{-4}$ | 2.0 | 0.025 | 0.05 |
| PVDF/PLZT (10%) | $0.9\times10^{-4}$ | 3.4 | 0.03 | 0.1 |
| PVDF/PLZT (30%) | $15\times10^{-4}$ | 57.6 | 0.30 | 17 |
| PVDF/PLZT (50%) | $18\times10^{-4}$ | 69.2 | 0.32 | 22 |

composite films and tabulated in Table 5. The variation in pyroelectric coefficient with variation in PLZT content for PVDF/PLZT flexible composite film is also shown in Fig. 8.

The pyroelectric coefficient is found to be $0.5\times10^{-4}$ $Cm^{-2}\,K^{-1}$ corresponding to pure PVDF film. The value get enhanced from $0.5\times10^{-4}$ $Cm^{-2}\,K^{-1}$ to $18\times10^{-4}$ $Cm^{-2}\,K^{-1}$ with increase in PLZT content from 0 to 50% in PVDF/PLZT flexible composite film respectively. The enhancement in the pyroelectric coefficient observed with increase in PLZT content in flexible polymer is due to uniform dispersion of ferroelectric ceramic particles in PVDF resulting in increase in dipolar interaction between the polymer and ceramic particles.. The similar behaviour of pyroelectric coefficient variation with ceramic content was also obtained by Wu et al. in its report where he achieved pyroelectric coefficient value of 96μC/m$^2$K for 50% PZT/PVDF-TrFE composite [37]. The obtained results in the present work found to be superior in comparison to the existing literature.

## Piezoelectric voltage generation in the composite films

In order to fabricate mechanical energy harvesting device, the prepared flexible composite films were enclosed in the polydimethylsiloxane (PDMS) polymer. The PDMS polymer enhance the mechanical toughness of the device without disturbing the flexibility of composite films and can withstand higher input pressure. Figure 9 shows the fabricated device along with the measurement setup of piezoelectric voltage generation.

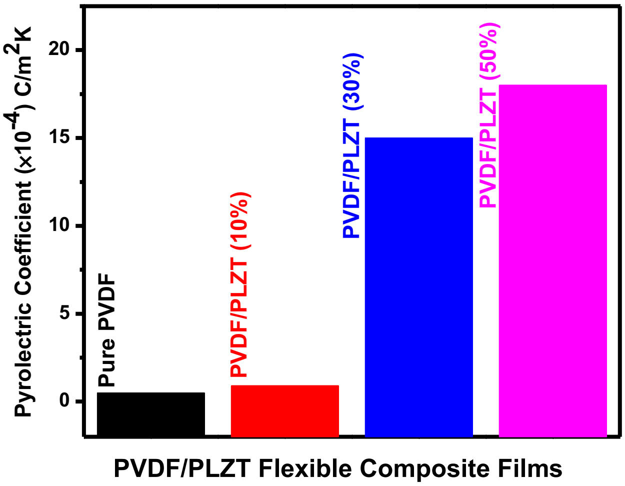


**Fig. 8** Variation in pyro electric coefficient with PVDF/PLZT composite films

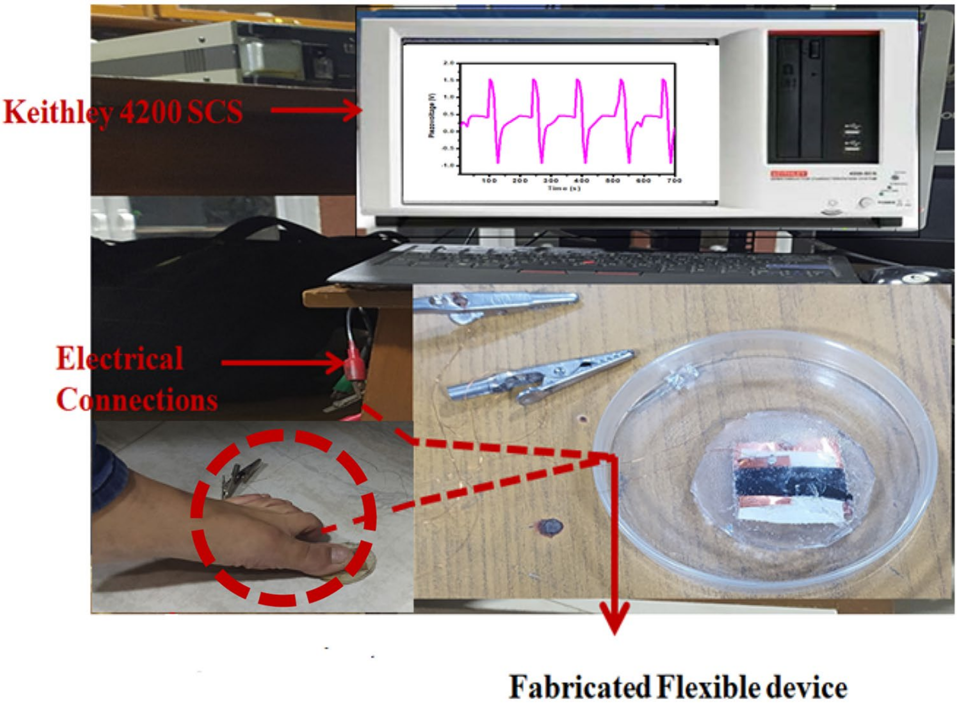
In order to generate piezoelectric voltage, the mechanical force has been applied to the device surface through human feet motion. The amount of force applied to the device through human feet tapping can be determined based on the Kinetic energy –Momentum theorem. During tapping, the momentum of feet is transferred to the device resulting in generation of piezoelectric charge. The following equations can be used to determine the approximated force applied to the device surface:

$$\mathrm{mgh} = \frac{1}{2}\mathrm{m}\,v^2 \tag{2}$$

$$(F - mg)\Delta t = mv \tag{3}$$

where, m is mass of the tip of toe which is approximately 0.5 kg, F is the applied mechanical force, Δt is time difference between initial point and final point of hit measured to be approximately 0.10 s, h is the height from which the object hit the surface of device which is approximately taken to 6.5 cm and g is taken to be 9.8 N/kg. After putting all these values, the approximated value of Force (F) was found to be 50 N. In the similar way, Wankhade et al. calculated the approximated force applied to device through finger tapping during the study of energy harvesting properties of PVDF-PZT nanohybrid in its report [38]. Figure 10 represents the generated piezoelectric voltage for pure PVDF and PVDF/PLZT (PLZT content: 10%, 30% and 50%) flexible composite films. The maximum force applied to the device was approximately 50N. The polarization is induced in the device due to generation of mechanical strain in the film under the application of periodic mechanical force. The potential is developed across the material causing the charge carriers (electrons) to flow through external circuit where load is present to balance the electric field produced in the material due to this induced polarization. Thus, an electrical signal is generated from a piezoelectric material. When the mechanical force is released, it cause potential drop immediately due to which electron gather to electrode and flows

**Fig. 9** Photograph of fabricated composite based flexible mechanical energy harvester alongwith the measurement setup of piezoelectric voltage generation



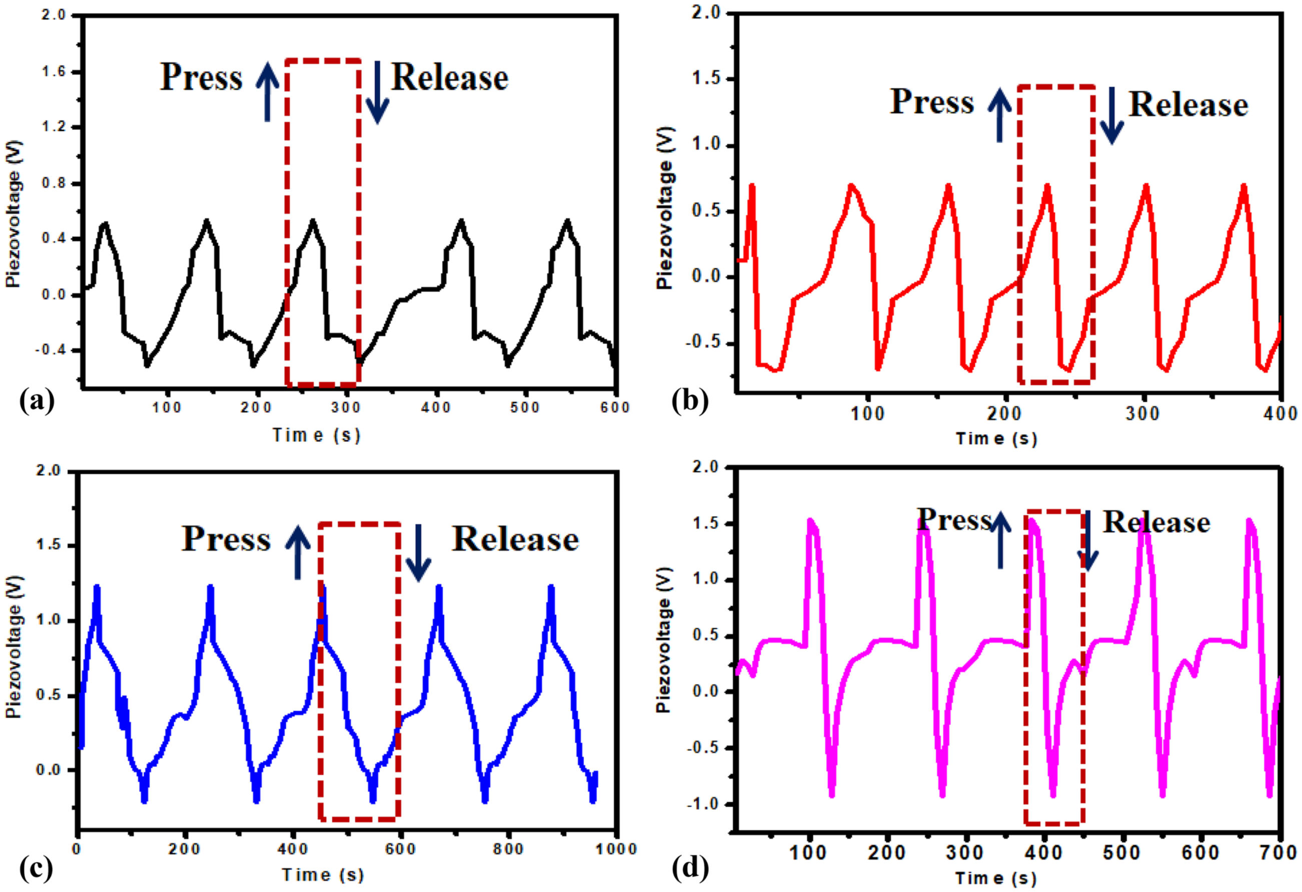


**Fig. 10** Output voltage comparison of different PVDF/PLZT **a** Pure PVDF, **b** PVDF/PLZT (10%), **c** PVDF/PLZT (30%) and **d** PVDF/PLZT (50%) composite films on application of applied pressure

back to it producing a reverse signal. The maximum generated piezoelectric voltage for pure PVDF film is found to be 0.5 V. However, 0.7 V, 1.2 V and 1.5 V is observed for 10%, 30% and 50% PVDF/PLZT, respectively. The β-phase of PVDF is very well known for higher dielectric and piezoelectric response. As discussed above, dielectric and ferroelectric properties of pure PVDF were studied (Figs. 3 and 4). It was found that pure PVDF exhibit both α and β-phases out of which α phase is non-polar in nature (Fig. 2). Since PVDF is flexible in nature but piezoelectric coefficient is less due to the presence of non—polar α phase resulting in poor piezoelectric response resulting poor piezoelectric voltage. However, as Lanthnaum doped PZT (PLZT) ceramic particles which are brittle in nature but known for good piezoelectric coefficient ($d_{33} = 550$pC/N) and high dielectric constant (3500), were mixed in PVDF, the non-polar α phase got diminished and electroactive β-phase of PVDF got enhanced resulting in higher piezoelectric and dielectric response. In the PVDF/PLZT (50%) composite, α -phase of PVDF got fully diminished and hence a maximum piezoelectric voltage (1.5 V) is achieved. The similar explanations was given by Gebrekrstos et al. in its report where the evolution of β-Phase formation in PVDF through nanoparticles dispersion was studied resulting in better piezoelectric response [39]. In the similar way, Mohanty et al. studied dielectric and ferroelectric properties of BNBT/PVDF composites and found that β- phase is enhanced with increasing content of BNBT ceramic particles, thereby enhancing the dielectric and ferroelectric properties [40].

## Conclusions

Pure PVDF and PVDF/PLZT flexible composite films have been fabricated using solution-cast method and are exploited for energy harvesting purpose through thermal fluctations and mechanical deformation. The effect of PLZT ceramic filler on the structural and surface morphological characteristics of PVDF has been studied. On increasing the PLZT content, the crystallinity and degree of texturing of composite films is enhanced. The dielectric and ferroelectric properties of all the composite films are studied and results indicate that maximum dielectric constant of $\in_r = 91$ and maximum polarization of 5.38μC/cm$^2$ are achieved for PVDF/PLZT (50%) flexible composite film. The flexible composite films are explored further for the pyroelectric and piezoelectric studies. The results showed that the maximum pyroelectric coefficient and piezoelectric voltage for PVDF/PLZT (50%) composite film are achieved to be $18 \times 10^{-4}$ Cm$^{-2}$ K$^{-1}$ and 1.5 V respectively.

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**Data availability** The authors declare that the data supporting the findings of this study are available within the paper. The results are found to be original and not published anywhere.

## Declarations

**Conflict of interests** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Competing of interests** The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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