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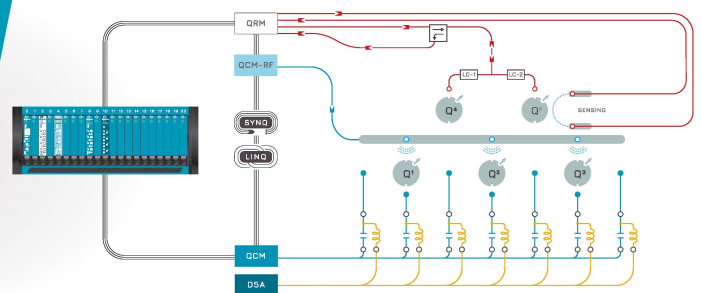
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Dispenser printed circular thermoelectric devices using Bi and Bi_{0.5}Sb_{1.5}Te₃

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This work presents polymer based composite materials used in slurries form to print low cost and scalable micro-scale Thermoelectric Generator (TEG) devices. Bi-epoxy composite is chosen as n-type material and mechanical alloy p-type Bi_{0.5}Sb_{1.5}Te₃ with 8 wt. % extra Te-epoxy composite is used as p-type material. Maximum power factor of 0.00008 W/m-K² is achieved for Bi-epoxy and Bi_{0.5}Sb_{1.5}Te₃ with 8 wt. % extra Te-epoxy composite dispenser printed thick films. A 10 couple dispenser printed circular TEG prototype produced 130 μ W power at ΔT of 70 K resulting in a device areal power density of 1230 μ W/cm². © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4861057>]

Approximately, 90% of the world's power is generated by heat engines that use fossil fuel combustion as a heat source and typically operate at 30%–40% efficiency. A significant proportion of heat is lost to the environment. Co-generation plants have been used to improve the overall efficiency by providing electricity as well as heat for heating purposes. This heat or heated fluids are transported in pipes for many industrial and residential applications. Wireless sensors such as steam/gas-leak sensors, pressure sensors, and temperature sensors are often used for condition monitoring of such pipes. The power requirements for these sensors are few microwatts and primary batteries are used to meet this demand. However, batteries have limited lifetime. Battery replacement cost and labor cost make large scale use of these sensors infeasible. Thermoelectric modules, which utilize the temperature difference between the hot pipe and the ambient air to generate power,¹ can be used for powering these sensors. These solid state thermoelectric generators (TEGs) are reliable, silent, environmental friendly, and could play an important role in a global sustainable energy solution. TEGs utilizing waste heat to generate power should be low-cost in order to be competitive with other technologies.

Existing pick and place and micro fabrication techniques have limited cost-effective scalability for manufacturing of application-specific TEGs. The limitations of the commonly used manufacturing technologies provide an opportunity for printing process. Printing is an additive process, thus reducing materials waste and cost per unit area. It is an automated process that can be used to print high-aspect-ratio devices with minimum labor. Printing involves the deposition of synthesized thermoelectric inks which consist of active TE materials in organic or polymer binders in slurry form.

Therefore, organic thermoelectric composites have attracted considerable attention on account of their mechanical flexibility, cost-effectiveness printability, and scalability.^{2–5} However, figure of merit, $ZT = \alpha^2 \sigma / T$, of these organic based thermoelectric material is 2–3 order of magnitude less than bulk materials.^{2–5} Efficient thermoelectric materials should have high Seebeck coefficients (α) to provide sufficient

voltages, high electrical conductivities (σ) to allow for electric current, and low thermal conductivities (κ) to minimize heat losses. For epoxy based thermoelectric composite materials, the advantages are lower thermal conductivity and high Seebeck coefficient and disadvantage is lower electrical conductivity.^{5,6}

In this work, we have explored Bi as n-type thermoelectric composite material as it is easily and cheaply available and its toxicity is less as compared to commonly used Bi₂Te₃. Bi has high electrical conductivity that may help to improve the electrical conductivity of composite films. We present a unique way of fabricating circular TEGs using dispenser printing methods,^{7,8} which can be easily mounted on hot surface or wrapped around pipe carrying hot fluid to generate electricity to power condition monitoring sensors. In order to realize practical thermoelectric devices, both p-type and n-type elements connected in series are essential to achieve reasonable efficiency. In our previous work, we have shown that the addition of 8 wt. % extra Te to mechanical alloy (MA) Bi_{0.5}Sb_{1.5}Te₃ helps to achieve high ZT for the composite film.⁹ Therefore, Bi-epoxy has been used as n-type composite thermoelectric material and MA Bi_{0.5}Sb_{1.5}Te₃ with 8 wt. % extra Te epoxy composites as p-type thermoelectric material to print circular TEGs.

The preparation of Bi and Bi_{0.5}Sb_{1.5}Te₃ epoxy based thermoelectric slurries are described elsewhere.^{5,10} High aspect ratio circular device design was used to maintain the temperature difference across the device and to achieve reasonable power output. Circular TEG device can be wrapped around heated pipe, one side of the TEG in contact with hot pipe and other in the ambient, generating power output exploiting this temperature difference. A custom made flexible printed circuit board (Flex-PCB) consisted of nickel and gold plated copper traces was fabricated on a flexible polyimide substrate by Rigidflex Technology, Inc.¹¹ A polyimide substrate with metal electrodes was chosen due to its flexibility, electrical insulation, high temperature tolerance, and low thermal conductivity (0.12 W/m-K). N-type Bi and p-type MA Bi_{0.5}Sb_{1.5}Te₃ composite inks were dispenser printed onto the substrate to form lines spanning across the inner and the outer contacts. Thick metal contacts resulted in reduced electrical contact resistance between metal contacts and printed TE elements. Printed lines on the flex PCB were cured in an

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argon/vacuum oven at 250 °C. Custom built test set up for device testing was prepared. Circular thermo-peltier was used as hot side and 10 small rectangular peltiers were connected in series to form a circular shape and maintained as cold side. Circular TEG device was placed in such a manner that one side of thermo elements rested on hot side peltiers and other side on cold side as shown in Figure 1. A schematic of the custom made setup for the power output measurements and the dispenser-printed 10-couple circular TEG prototype is shown in Figures 1(a) and 1(b). Series of temperature differences was applied across the dispenser printed prototype device. Temperatures at the both ends of the elements were monitored to ensure that a steady state was reached and open circuit voltage was measured. Closed circuit voltage measurements were taken at multiple load resistance values. The power output was calculated using the measured voltage and load resistance at various temperature differences.

N-type Bi-epoxy and p-type MA $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ -epoxy slurries were dispenser printed as thick film on glass substrate for thermoelectric characterization purposes and cured at 250 °C. Film properties were measured using a custom built system. The custom built system for thermoelectric property measurement utilizes van der Pauw's method to measure the electrical conductivity. The accuracy of the van der Pauw's method is improved by taking reversed polarity measurements. The electrical conductivity measurements are calibrated against the physical property measurement system (Ecopia HMS-3000). Seebeck coefficient is calculated by measuring the temperature difference across the sample and

the open circuit voltage resulting from the temperature difference. The Seebeck coefficient measurements are calibrated using a sample of known Seebeck coefficient purchased from NIST. The measurements using custom built measurement system matched the standard within 10% error. Figure 2 shows the thermoelectric properties of n-type Bi-epoxy and p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with 8 wt. % extra Te-epoxy dispenser printed films cured at 250 °C, as a function of temperature. Thermoelectric composite material properties are function of polymer matrix and active particles. Given that the electrical conductivity of the polymer binders is significantly lower than that of the active filler thermoelectric material, the effective properties of the composite system are expected to be less than desirable.⁶ Bi has approximately 1 order of magnitude higher electrical conductivity (9000 S/cm) as compare to bulk $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (1300 S/cm).¹² Electrical conductivity of n-type Bi epoxy as

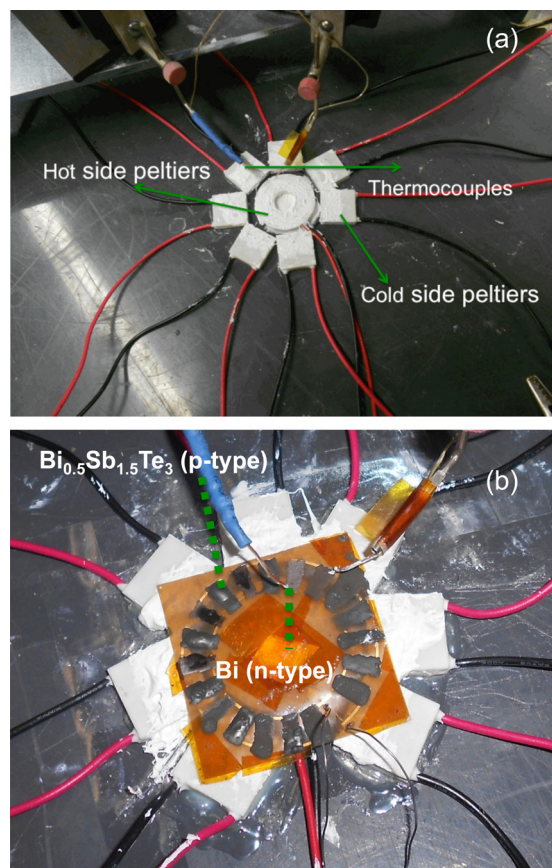


FIG. 1. Image of printed circular thermoelectric device on a custom built measurement set up.

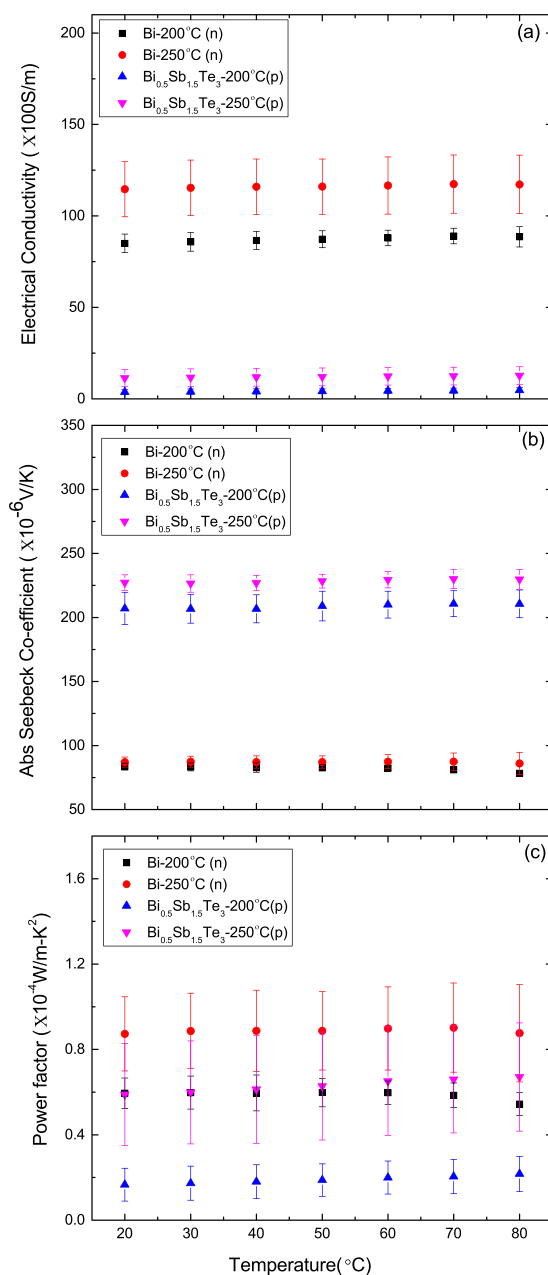


FIG. 2. Thermoelectric properties of n-type Bi epoxy and p-type MA $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ epoxy composite films cured at 250 °C as a function of temperature.

well as MA p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ epoxy composites is almost 2 order of magnitude lower than the bulk due to the insulating nature of epoxy polymer present in composite films. Additionally, Figure 2(a) indicates that Bi epoxy composite has 1 order magnitude higher electrical conductivity (110 S/cm) as compared to MA p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with 8 wt. % extra Te-epoxy films (11 S/cm). Bi epoxy composite films have one order magnitude higher electrical conductivity as compare to MA n-type Bi_2Te_3 dispenser printed films cured at 250 °C.⁶ Almost no variation in electrical conductivity with temperature was observed for n-type and p-type composite films as shown in Figure 2.

Figure 2(b) shows Seebeck co-efficient variation of n and p-type thick films with temperature. For Bi composite films, Seebeck co-efficient is same as bulk (84 $\mu\text{V/K}$) when cured at 250 °C. Similarly, for MA p-type films, Seebeck co-efficient is positive and same as bulk value (250 $\mu\text{V/K}$).¹² This behavior of the composite film can be explained on the basis of effective medium theory Seebeck co-efficient of composite system, which depends on electrical and thermal conductivity. Electrical and thermal conductivity of insulating epoxy polymer is almost zero; so effective Seebeck co-efficient of composite system is same as active filler particles.⁶ Therefore, MA composite printed films cured at 250 °C for 12 h have Seebeck co-efficient same as bulk value. With increase in temperature up to 80 °C, there is almost no change in Seebeck co-efficient was observed in n and p-type composite films as shown in Figure 2(b).

Figure 2(c) shows that power factor ($\alpha^2\sigma$) is same for MA p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ dispenser printed composite films and Bi-epoxy based n-type films ($8.6 \times 10^{-5} \text{ W/m}\cdot\text{K}^2$). As the electrical conductivity and Seebeck co-efficient did not change with temperature, the power factor did not change much with temperature.

Negligible variation in the film properties with temperature is desirable. It indicates that film properties do not deteriorate in the temperature range of 20–80 °C. The device fabricated using these materials can operate in the above temperature range. Similar trends have been previously reported in the literature.^{6,7}

To demonstrate the circular prototype, Bi-epoxy as n-type and MA $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ with 8 wt. % extra Te-epoxy as p-type thermo-element was printed on flex PCB board. For specific applications, it is possible to design the TEG device to optimize the power output for given temperature differences. However, for demonstration purposes, a non-optimized geometry was chosen. The device resistance of the prototype was 100 Ω when cured at 250 °C. Open circuit voltage for 10 couple n and p-type thermo-element connected in series was 230 mV at 70 K temperature difference. It corresponds approximately to sum of thermovoltage of each unit cell $(0.270 + 0.084) \times 10 \times 70 = 245 \text{ mV}$. Maximum power output, P_{max} , open circuit voltage, V_{op} , and internal resistance, R_{in} , of the thermoelectric device are given by the following equations:

$$P_{\text{max}} = \frac{V_{\text{op}}^2}{4R_{\text{in}}},$$

$$V_{\text{op}} = m\alpha\Delta T,$$

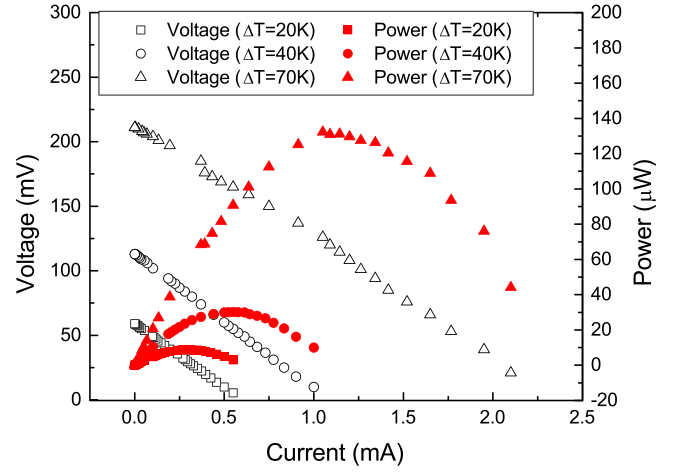


FIG. 3. Characteristics curve of the ten couple circular TEG device at $\Delta T = 20 \text{ K}$, 40 K , and 70 K .

$$R_{\text{in}} = \rho \frac{L}{A},$$

where m is the number of couples (10), α is the Seebeck co-efficient, ΔT is the temperature difference across the device, ρ is the electrical resistivity of the material, L (5 mm) is the element length in the direction of heat flow, and A ($1.5 \text{ mm} \times 120 \mu\text{m}$) is the cross-sectional area of the element. To measure the power output of the device, a variable resistance was attached in series to the device. The maximum power output of the device occurs when the load resistance matches the device resistance. Figure 3 shows the device characteristic curve for a 10 couple circular prototype device measured at ΔT of 20 K, 40 K, and 70 K at various load resistances. At matched load resistance, the device produces approximately 130 μW at 1.145 mA current and 114.5 mV closed circuit voltages at 70 K temperature difference. At 20 K and 40 K temperature differences, maximum power outputs are 8.5 μW and 30.5 μW and closed circuit voltages obtained are 30 mV and 55 mV, respectively.

Figure 4 shows the measured power density (power output per unit area) and fitted model power density of

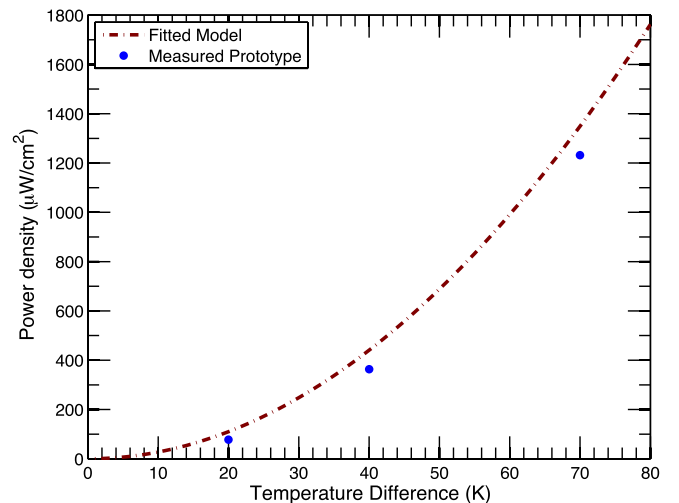


FIG. 4. Power density at matched load resistance as a function of temperature difference across the TEG for fitted model (dotted line) and measured device (circular shape).

TABLE I. Comparison of power density of composite thermoelectric TEGs.

Polymer materials	ΔT	Reference	Power density ($\mu\text{W}/\text{cm}^2$)
PEDOT-PSS	30 K	4	0.27
Bi_2Te_3 -epoxy/ Sb_2Te_3 -epoxy	20 K	7	75
Sb-ethylene glycol/ Bi -ethylene glycol	5 K	3	2
Bi -epoxy/ $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ -epoxy	20 K	This paper	77

the device as a function of the temperature difference. The power density in the fitted model has been calculated using thermoelectric voltage produced by n and p-type dispenser printed composites films and using internal resistance of TEG device and plugging these numbers into power equation written above. The maximum power density of $1370 \mu\text{W}/\text{cm}^2$ can be obtained for TEG devices at ΔT (70 K) using fitted model. However, at ΔT of 70 K actual measured power density ($1230 \mu\text{W}/\text{cm}^2$) is slightly lower than ideal model ($1370 \mu\text{W}/\text{cm}^2$). Similarly, at 40 K temperature difference fitted model power output is ($440 \mu\text{W}/\text{cm}^2$) slightly higher than actual ($365 \mu\text{W}/\text{cm}^2$). At 20 K temperature difference, actual power output ($77 \mu\text{W}/\text{cm}^2$) is same as fitted ($77 \mu\text{W}/\text{cm}^2$). The deviation at higher temperature difference may be due to fluctuations in the temperature across the device during measurement as it becomes more difficult to maintain high temperature difference across the device. It is worth noting that P_{\max} is proportional to $(\Delta T)^2$ as P_{\max} depends on the square of the open circuit voltage and the open circuit voltage is proportional to ΔT .

Table I compares results reported in the literature. The power density of the device fabricated using Bi and $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ is comparable to the previously reported power density for similar composite thermoelectric materials. While Bi_2Te_3 was replaced by relatively inferior thermo-electric material Bi, we achieved similar device performance. Advantage of using Bi over Bi_2Te_3 is that it is cheaper, less toxic, and easily available. The power generated by 10-couple circular TEG device is sufficient to power condition monitoring wireless sensors used at hot surface equipment such as motors, pumps, and steam pipes. The

versatility of printed fabrication processes allows for rapid customization by varying the printed element length, width, and thickness through printing parameters. For future work, we would like to explore cheaper and less toxic alternative for p-type MA $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$.

In summary, Bi is cheaper, easily available, and less toxic compared to Bi_2Te_3 . Bi-epoxy based dispenser printed composite films have power factor similar to Bi_2Te_3 . Therefore, it is preferable to use Bi epoxy based composite materials for printing high aspect ratio devices. In this paper, we demonstrated a unique way of printing circular TEG devices that can be wrapped around pipes carrying heated fluids to power condition monitoring sensors. The maximum power output of $130 \mu\text{W}/\text{cm}^2$ at 70 K temperature difference is achieved for a 10-couple device. Results presented here are promising for use of low-cost and scalable TEGs for various low power applications.

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