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A novel and stable way for energy harvesting from Bi$_2$Te$_3$Se alloy based semitransparent photo-thermoelectric module

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**Abstract**

In this research, due to the present pandemic of COVID-19, we are proposing a stable and fixed semitransparent photo-thermoelectric cell (PTEC) module for green energy harvesting. This module is based on the alloy of Bismuth Telluride Selenide (Bi$_2$Te$_3$Se), designed in a press tablet form and characterized under solar energy. Here, both aspects of solar energy i.e., light and heat are utilized for both energy production and water heating. The semitransparent PTEC converts heat energy directly to electrical energy due to the gradient of temperature between two electrodes (top and bottom) of thermoelectric cells. The PTEC is 25% transparent, which can be varied according to the necessity of the utilizer. The X-ray diffraction of material and electric characterization of module i.e., open-circuited voltage (VOC) and Seebeck coefficient were performed. The experimental observations disclose that in the proposed PTEC module with an increment in the average temperature ($T_{\text{avg}}$) from 34 to 60°C, results in the rise of VOC ~ 2.4 times. However, by modifying the size of heat-absorbing top electrode and by increasing the temperature gradient through the addition of water coolant under the bottom electrode, an uplift in the champion device results in an increment of VOC ~5.5 times and Seebeck coefficient obtained was ~250 mV/°C, respectively. Results show that not only the selection of material but also the external modifications in the device highly effective the power efficiency of the devices. The proposed modules can generate electric power from light and utilize the penetrating sunlight inside the room and for the heating of the water which also acts as a coolant. These semitransparent thermoelectric cells can be built-in within windows and roofs of buildings and can potentially contribute to green energy harvesting, in situations where movement is restricted locally or globally.

**1. Introduction**

Nowadays especially after the present restricted situation due to COVID-19, researchers are highly devoted to the utilization of sunlight for the production of electricity. The focus is diverted to it, as mostly due to photovoltaics and generators based on solar thermal power the energy production is stable, long-lasting, and not affected by movement limitations. These days many photovoltaic cells are installed, typically as flat panels. Although electricity production through generators based on solar and thermal energy relies on the concentration of light and gradient of temperature, where mechanical heat engines are widely available at large-scale power plants [1]. Though, to realize this energy harvesting phenomenon at micro levels scientists are showing utmost interest towards both important aspects of solar energy, its light, and heat. The shrewdest approach to utilize these features for the generation of electricity, by transforming the light and heat energy our proposed module is solar-thermoelectric cells. However, other than the selection of PTEC’s module, the variations in an external assembly of the cell also aid a lot in increasing the efficiency of the cell as observed in our case.

Recently, numerous scientists are working in the field of power generation by using inorganic and organic semiconductor materials for their thermo-electric (TE) applications and trying to improve its efficiency [2–8]. Mathematically, the TE efficiency ($\eta$) will be presented as mentioned by Eq [9]:

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\[ Z = \frac{\alpha^2 \sigma}{K_{tot}} \]  

where \( \alpha \) represents the Seebeck coefficient, \( \sigma \) is the electrical conductivity and \( K_{tot} = K_e + K_{ph} \) is the cumulative thermal conductivity of electron (\( K_e \)) and phonon (\( K_{ph} \)), respectively. However, equation demonstrates that the \( Z \) increases is highly affected by \( K_{ph} \) decrease. So, while selecting the TE material to achieve high-efficiency materials with lower thermal conductivity are preferred.

Although the market is intensively researching on chalcogenides with multifaceted crystal structures, TEC’s in Ref. [10] are fabricated by utilizing bismuth telluride \( \text{(Bi}_2\text{Te}_3) \)-\( \text{Slb}_2\text{Te}_3 \) (\( \mu \)-type) and \( \text{Bi}_2\text{Te}_3-\text{Bi}_2\text{Se}_3 \) (\( n \)-type), depending on the velocity of flowing gases concerning the \( T_{Avg} \). Low-temperature applications of TEC’s have been designed and characterized by Akshay et al., based on \( \text{Bi}_2\text{Te}_3 \) nanostructures [11]. However, the synthesis of nanostructured \( \text{Bi}_2\text{Te}_3 \) and its thermoelectric properties reveal fascinating results with \( \alpha = -120 \mu\text{VK}^{-1} \) [12]. Then in 2017, authors reported the synthesis of \( \text{Bi}_2\text{Te}_3 \) and their proposed TEC’s \( \alpha \) was \(-135 \mu\text{VK}^{-1}\) and the observed thermal conductivity was about \( 0.95 \text{~W (mK)}^{-1} \) [13]. Another group of scientists fabricated and characterized thin-film based TEC’s based on \( n \)-type nanocrystal-line \( \text{Bi}_2\text{Te}_3 \) and results showed that the obtained Seebeck coefficient was \(-186.1 \mu\text{VK}^{-1} \) [14]. In Ref. [15], \( n \)-type \( \text{Bi}_2\text{Te}_3 \) ultrathin nanowires were synthesized and providing \( ZT \) of 0.96 at 380 K. An alloy of \( n \)-type \( \text{Bi}_2\text{Te}_3 \) with Indium was fabricated to achieve high bandgap, aiding to suppress bipolar conduction and resulting in \( ZT \) of ~1.1 at 625 K in 2018 [16]. In same year Du et al., synthesized flexible \( n \)-type tungsten composites and the obtained Seebeck coefficients vary from \(-11 \) to \(-12.3 \mu\text{VK}^{-1} \) at \(-300 \text{ K} \) [17]. Crackless \( \text{Bi}_2\text{Te}_3 \) film doped with \( n \)-type impurity fabricated by electrophoretic deposition was obtained in 2018, resulting in \( \alpha \) of \(-189 \mu\text{VK}^{-1} \) at 500 K [18]. \( ZT \) about 0.83 was obtained by a sintering process of controlled oxygen content in \( n \)-type \( \text{Bi}_2\text{Te}_3 \) compounds at 473 K in Ref. [19]. Another \( n \)-type \( \text{Bi}_2\text{Te}_3 \) was prepared in Ref. [20] by radio frequency (RF) magnetron sputtering and \( ZT \) of ~0.57 at 375 K was attained. In 2018, again the thermoelectric performance of \( \text{Bi}_2\text{Te}_3 \) with reduced graphene oxide composite was investigated and obtained \( ZT \) (0.29) at room temperature [21].

Thermoelectric modules with semitransparent structure recently under consideration of researchers which plays a significant part in the enlargement of solar energy applications. Some of the innovative advancement in the semitransparent field is semitransparent thermo-electric cells, semitransparent solar cells, and semitransparent solar-thermoelectric cells [22]. The electricity which is produced from light and heat in thermoelectric cells, semitransparent modules are the better choice to entirely utilize it. Not only it produces electricity but also the rest of the light can penetrate through the transparent part resulting in space illumination. Literature showed semitransparent solar cells [23,24] and semitransparent thermoelectric graphene-based cells [25,26] are uplifting the properties of green energy harvesting devices. Recently we also proposed a successful semitransparent photo-thermo-electric cell, where bismuth telluride alloy with antimony was characterized for its thermoelectric properties [27]. The resulted modules were providing a complete setup for installation in green building energy harvesting systems.

In extension to our work, here in this article, the results of the fabrication and characterization of vertical press tablet type semitransparent photo-thermo-electric cell module are being presented with the alloy of \( \text{Bi}_2\text{Te}_3\text{Se} \). The module is designed to utilize both aspects of the solar energy i.e., heat and light as its available vastly and will not get affected due to any restricted conditions. The heat will help in the production of electricity due to the temperature gradient between the top and bottom electrodes of thermoelectric cells. However, under the cell’s bottom electrode there is a transparent water coolant installed which will benefit to enhance the gradient of temperature further. Due to the 25% transparency of the cell, the light will cross through the device and can help in lighting the planetary.

2. Experimental

The photo-thermo-electric cells module is designed in this work. First, the thermoelectric cell is fabricated and then a water coolant is attached under the bottom electrode, however, the top electrode (light receiver) remained moveable, so the effect of its size was also observed. For the fabrication of thermoelectric cells, 99% pure Bismuth Telluride Selenide (\( \text{Bi}_2\text{Te}_3\text{Se} \)) was used purchased from American elements product code (\( \text{Bi}_2\text{Te}_3\text{Se} \)-02-C). It is a grey color amorphous powder and used as it is, without further purifi- cation. It has \( n \)-type properties which are also established from the experimental observations. The particle’s size of \( \text{Bi}_2\text{Te}_3\text{Se} \) powder was \(-11.56 \mu\text{m} \).

To manufacture the thermoelectric cells a semitransparent vertical plastic cylinder was designed with 25% transparency. The height of the cylinder was 20 mm, with an exterior and interior diameter of 6 mm and 5 mm, respectively. However, the two i.e., top and bottom, electrodes diameter was 6 mm (top end of the electrode 1 mm height) and 4 mm from the lower end (2 mm height). The \( \text{Bi}_2\text{Te}_3\text{Se} \) was filled in the semitransparent vertical cylinder with a fixed bottom electrode and covered with the top light-receiving movable electrode as a pressed tablet of 16 \( \times \) 5 mm\(^2\) and then characterized. However, for the water coolant, a self-made transparent plastic box filled with distilled water was used with an area of 8 \( \times \) 8 mm.

Philips PW1830 by Cu-K\(_\alpha\) (\( \lambda = 1.5406 \) \AA\) ) radiation source was used for the X-ray diffraction of the \( \text{Bi}_2\text{Te}_3\text{Se} \). The 100 W filament bulb was used as an illumination source. For temperature measurement Fluke 87 thermocouple and for electronic characterization HIOKI-DT4253 digital multimeter was used. All experiments were performed in a cleanroom.

Fig. 1. X-ray diffraction of \( \text{Bi}_2\text{Te}_3\text{Se} \) sample along with a standard pattern for peak indexing.
3. Results and discussion

The phase identification of Bi$_2$Te$_3$Se powder was performed at room temperature as shown in Fig. 1. The X-ray diffraction (XRD) results were repeated three times for each sample and repeated results were observed. All the peaks in the pattern are well indexed to the rhombohedral Bi$_2$Te$_3$Se standard XRD database JCPDS 15-0863. The major peaks of bismuth telluride Selenide were observed at 2$\theta$ of 27.8° and compared with the literature and similar results were observed [28].

First of all, the vertical thermoelectric cells as shown in Fig. 2(a) were characterized for their electric parameters. The gradient of temperature between two electrodes was obtained by illuminating the top electrode under light source resulting in heating the cell from one side. The obtained gradient of temperature, in this case, was between 3 and 17 °C as seen from Fig. 3, resulting in averaged temperature (T$_{Avg}$) of 34–60 °C between both electrodes demonstrated by Fig. 4. To measure the temperature thermocouple was connected with both the top and bottom electrodes ends next to the probes of the digital multimeter as shown in Fig. 2(b). However, to enhance the temperature gradient a water reservoir as a coolant was attached under the bottom electrode as revealed in Fig. 2(c). To further boost the properties, diameter of the light receiver (top) electrode was increased. Then cell was characterized as demonstrated in Fig. 2(d) resulting in improved electrical properties. Finally, the water coolant is attached to the bottom of PTEC with a larger diameter of the photo-receiver, and the final champion device was obtained as presented in Fig. 2(e).

The transparency of the PTEC was measured by taking the ratio between the squares of the transmitted light part (position 4 in Fig. 2) and the total area square of the plastic sample holder. In our case, its 25%, but according to the requirement, it can be decreased or increased.

Fig. 3 presents the relationship between the intensity of the light to the gradient of temperature. Whenever light falls on the top metallic electrode it increases its temperature resulting in a gradient of temperature (\(\Delta T\)) between the top and bottom electrode. However, Fig. 4 demonstrates the variation in averaged temperature for the same light intensity.

The photo-thermoelectric cells demonstrated in Fig. 2(b)-2(e)
were characterized for its open-circuit voltage ($V_{OC}$) and results can be seen from Fig. 5(a)-5(d). The experimental results showed that when $V_{OC}$ for PTEC as demonstrated in Fig. 2(b) has been measured there was an increment in voltage till $10^\circ C$ ($\Delta T = 10^\circ C$) from Fig. 5(a), and after which the $\Delta T$ starts decreasing resulting in the decrement of $V_{OC}$. This is due to the heating of the bottom electrode. The reason behind the change in voltage due to temperature is phonon.

At first, in overall PTEC when one side temperature is low and other high the charges can move freely as well as there is low thermal conductivity in Bi$_2$Te$_3$Se. Though, as the temperature starts increasing in overall cell and gradient between two electrodes become less, the atoms start vibrating inclusively, resulting in collisions among atoms [29]. Hence, obstacles introduced in the flow of the charges and conduction decreased as thermal conductivity increased which was also observed in our case as observed from Fig. 5 (a). To solve this problem water coolant was attached under the bottom electrode which will help in absorbing excess heat and it increased the $V_{OC}$ as seen in Fig. 5(b) in this case the maximum obtained gradient was 12 $^\circ C$. Then the diameter of the top heat receiving electrode is increased from 6 mm to 23 mm, providing higher voltage and temperature gradient i.e., 14 $^\circ C$ as shown in Fig. 5(c). In the champion device, the water coolant is attached under the bottom electrode of PTEC which is with a larger diameter of top electrode resulting in an enhancement in temperature gradient up to 17 $^\circ C$ as graphically presented in Fig. 5(d). However, short-circuited current to averaged temperature relationship is shown in Fig. 6.

These modules are providing mesmerizing results. The open-circuit voltage is rised from 2.1 times to 5.5 times as presented in Fig. 7. This increase might be attributed to a large receiver which helped in absorbing more heat, resulting in an inflow of more charge. It may be also due to the affect of water coolant which kept the gradient of temperature large.

The PTEC module Seebeck coefficient ($\alpha$) was calculated by Eq. (2) as the ratio between the potential difference ($\Delta V$) and gradient of temperature ($\Delta T$) [9].

$$\alpha = \frac{\Delta V}{\Delta T} \quad (2)$$

By using data from Fig. 5 and Eq. (2) the obtained $\alpha$ from 0.7 times to 0.98 times with the modifications and the maximum $\alpha$ observed is $-250 \mu V^/\circ C$.

The reason for small $V_{OC}$ in the first case was fast heating of the bottom electrode ~2.4, which was the result of heating the surface
under the bottom electrode due to light which was partially passing and partially absorbed by the area under bottom electrode. However, in second case \( \text{VoC} \) increased to 4 as water coolant absorbs the heat, and in the third case enlarged diameter of receiving electrode improves the open-circuit voltage more and utmost voltage was obtained in the last case where water reservoir was attached with case three and that’s our proposed and optimized module.

Usually other than thermoelectric efficiency (\( Z \)) as mentioned in Eq. (1), the other important aspect of thermoelectric cell is the figure of merit (\( ZT \)), which is obtained through the product of efficiency to average temperature. Higher the value of \( ZT \) better the efficiency is considered good, usually, it is around 1 and considered good for thermoelectric applications when between 3 and 4. However, till now best \( ZT \) observed is \( \sim 2 \) [30–32]. Literature showed that the efficiency of TEC’s is better for powdered materials and an increase in dopants of these materials [33,34]. Besides, the thermoelectric properties of the material can be few influenced by the load. The Seebeck coefficients that we measured were also within the range \( \alpha \) is \( > 200–1000 \mu \text{V} \text{C}^{-1} \), which is considered as a decent assortment [14–21]. The \( \alpha \) for n-type materials is negative and positive for p-type materials [35,36]. Seebeck of undoped materials is usually lower than doped one. Although in metals, \( \alpha \) is small \( 0–60 \mu \text{V} \text{C}^{-1} \) and increase gradually with temperature increase and in case of complexes like quasi-one-dimensional crystals i.e., TCNQ \( \alpha \) achieved up to \( 1000 \mu \text{V} \text{C}^{-1} \) [30]. As the growth of the single crystal is a difficult task [37], so the selection of powdered Bi\(_2\)Te\(_3\)Se for its thermoelectric applications and experiments also showed fascinating results as was observed by us recently with another alloy of bismuth antimony telluride [38].

The work presented in this article demonstrates a well-organized experimental symmetry, where the semitransparent PTEC module was designed to analyze and improved keeping real environmental scenarios under consideration. Each step’s advantages and drawbacks were explained in detail and then compared with literature. Although the topic is of great interest as solar energy both aspects i.e., light and heat are utilized at its utmost level. The designed photo-thermoelectric cells provide a substitute between solar PV and solar thermomechanical energy conversions. The research showed that with a better selection of material for thermoelectric applications if external modifications are also designed well then the Seebeck coefficient within an acceptable range can be attained.

4. Conclusions

A well-systemized module for a photo-thermoelectric cell has been demonstrated here in this work. The temperature gradient between two electrodes is created with light and then the point where the gradient starts decreasing reason is assessed and resolved with more modifications. Then finally a device is proposed providing higher open-circuit voltage and Seebeck coefficient \( \sim 250 \mu \text{V} \text{C}^{-1} \) and then results are compared with literature. This work is based on powder-based press tablet type vertical semitransparent photo-thermoelectric cells by using Bi\(_2\)Te\(_3\)Se. There are many applications of this module first energy production through PTEC, second the reservoir water when become hot, it can be used as warm water in houses and the third advantage is due to its semitransparency that will help in lightning the space.

Declaration of competing interest

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.

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