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Review

Thermoelectrics: a review of present and potential applications

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Abstract

Thermoelectric devices are solid state devices. They are reliable energy converters and have no noise or vibration as there are no mechanical moving parts. They have small size and are light in weight. As refrigerators, they are friendly to the environment as CFC gas or any other refrigerant gas is not used. Due to these advantages, the thermoelectric devices have found a large range of applications. In this paper, basic knowledge of the thermoelectric devices and an overview of these applications are given. The prospects of the applications of the thermoelectric devices are also discussed.

Keywords: Thermoelectric device; Application

Contents

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1. Introduction

Thermoelectric devices (thermoelectric modules) can convert electrical energy into a temperature gradient—this phenomena was discovered by Peltier in 1834. The application of this cooling or heating effect remained minimal until the development of semiconductor materials. With the advent of semiconductor materials came the capability for a wide variety of practical thermoelectric refrigeration applications.

Thermoelectric refrigeration is achieved when a direct current is passed through one or more pairs of n- and p-type semiconductor materials. Fig. 1 is a diagram of a single pair consisting of n- and p-type semiconductor materials. In the cooling mode, direct current passes from the n- to p-type semiconductor material. The temperature T_c of the interconnecting conductor decreases and heat is absorbed from the environment. This heat absorption from the environment (cooling) occurs when electrons pass from a low energy level in the p-type material through the interconnecting conductor to a higher energy level in the n-type material. The absorbed heat is transferred through the semiconductor materials by electron transport to the other end of the junction T_H and liberated as the electrons return to a lower energy level in the p-type material. This phenomenon is called the Peltier effect.

A second phenomenon is also important in thermoelectric refrigeration. When a temperature differential is established between the hot and cold ends of the semiconductor material, a voltage is generated. This voltage is called the Seebeck voltage, and it is directly proportional to the temperature differential. The constant of proportionality is referred to as the Seebeck coefficient.

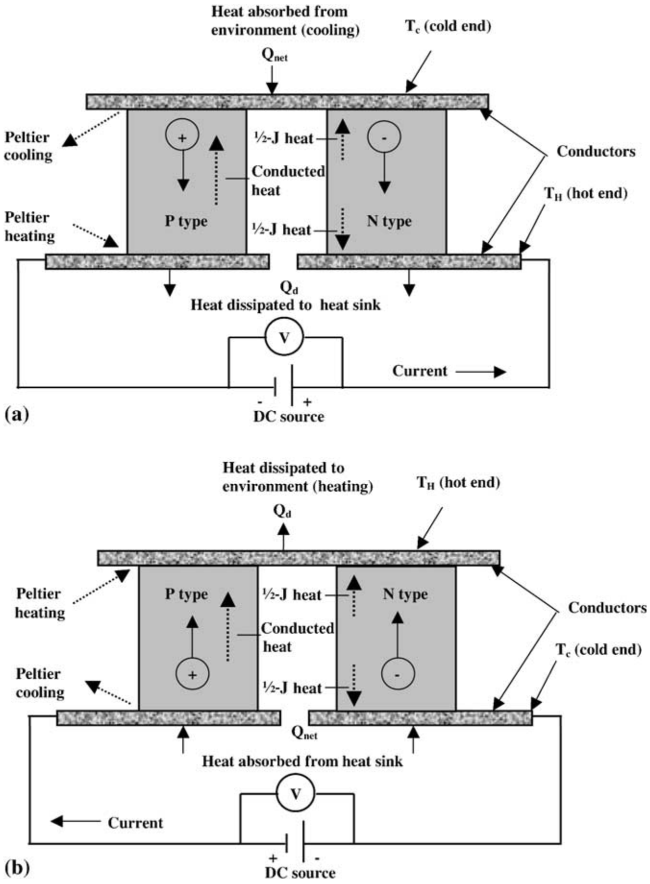

Fig. 1. Schematic of thermoelectric module operation (a) cooling mode; (b) heating mode.

The Peltier effect is controlled by the Peltier coefficient, defined as the product of Seebeck coefficient of the semiconductor material and the absolute temperature. The Peltier coefficient relates to a cooling effect as current passes from the n-type material to the p-type material, and a heating effect when current passes from the p-type material to an n-type material, as shown in Fig. 1. Reversing the direction of the current reverses the temperature of the hot and cold ends.

Ideally, the amount of heat absorbed at the cold end and the heat dissipated at the hot end are dependent on the product of the Peltier coefficient and the current flowing through the semiconductor material. Practically the net amount of heat absorbed at the cold end due to the Peltier effect is reduced by two sources, conducted heat and Joule heat. Due to the temperature differential between the cold and hot ends of the semiconductor material, heat will be conducted through the semiconductor material from the hot to cold end. As the current is increased, the temperature differential, and thus the conducted heat, increases because the Peltier cooling effect increases. However, the other loss, Joule heat, is proportional to the square of the current and, therefore, eventually becomes the dominant factor. At any given current, thermal equilibrium is established at the cold end when the Peltier effect at the cold end is equal to the sum of the conducted heat plus one-half of the Joule heat. The other half of the Joule heat goes to hot end.

As the current continues to increase and Joule heating becomes the dominating factor, a point is reached where additional current will result in less net cooling. The current at which no further cooling can be achieved is the maximum current I_{max}. Maximum voltage V_{max} and maximum temperature differential ΔT_{max} will also occur for any given heat load at the maximum current.

The net heat dissipated at the hot end is the sum of the net heat absorbed at the cold end plus the applied electric power. The coefficient of performance (COP) used to define the cooling "efficiency" is defined as the net heat absorbed at the cold end divided by the applied electric power.

The refrigeration capability of a semiconductor material is dependent on a combined effect of the material's Seebeck voltage, electrical resistivity, and thermal conductivity over the operational temperature range between the cold and hot ends. The Seebeck coefficient squared divided by the product of electrical resistivity and thermal conductivity is called the figure of merit Z. Each of the n- and p-type semiconductor material properties varies as a function of temperature, and therefore the figure of merit for each material is temperature-dependent. It can be shown that the maximum temperature differential that can be achieved by a single pair of n- and p-type material is directly proportional to the "temperature averaged" figure of merit of each semiconductor material. Therefore, maximizing the figure of merit is the major objective in the selection and optimization of thermoelectric materials. The figure of merit of the semiconductor material limits the temperature differential, whereas the length-to-area ratio of each n-and p-type semiconductor material defines the heat pumping capacity. The most widely used thermoelectric material for refrigeration in the temperature range of −120 to 230 °C is a pseudo-binary alloy, $(Bi,Sb)_2(Te,Se)_3$, commonly referred to as bismuth telluride [1].

The thermoelectric devices can also convert thermal energy from a temperature gradient into electric energy—this phenomenon was discovered in 1821 and is called "Seebeck effect". As mentioned above, when a temperature differential is established between the hot and cold ends of the semiconductor material, a voltage is generated, i.e., Seebeck voltage. Actually, the Seebeck effect is an inverse effect of Peltier effect. Based on this Seebeck effect, the thermoelectric devices can also act as power generators. As shown in Fig. 1, if heat supplied at the one junction causes an electric current to flow in the circuit and electrical power is delivered. In practice a large number of such thermocouples are connected electrically in series to form a "module".

More than one pair of semiconductors are usually assembled together to form a thermoelectric device (module). Within the module each semiconductors is called a thermoelement, and a pair of thermoelements is called a thermocouple.

A typical thermoelectric device is composed of two ceramic substrates that serve as a foundation and electrical insulation for P-type and N-type Bismuth Telluride thermoelements that are connected electrically in series and thermally in parallel between the ceramics. Conventional thermoelectric devices have various specifications for various applications; the dimensions vary from 3 mm square by 4 mm thick to 60 mm square by 5 mm thick, the maximum heat-pumping rate from 1 to 125 W. The maximum temperature difference between the hot and cold side can reach 70 °C. The devices contain from 3 to 127 thermocouples. There are multistage (cascade) series thermoelectric devices designed to meet requirements for large temperature differentials (up to 130 °C). The lowest practically achievable temperature is about −100 °C.

Because the cold side of the device contracts while the hot side expands devices with a footprint larger than 50 mm square usually suffer from thermally induced stresses, at the electrical connection points inside the module causing a short, so they are not common. Long, thin devices want to bow for the same reason and are also rare. Larger areas than an individual device can maintain are cooled or have the temperature controlled usually by using multiple modules.

Two types of commercially available multicouple thermoelectric devices are shown in Fig. 2. Type A was originally designed for cooling applications and possesses significant inter-thermoelement separation. In this type of device, n- and p-type semiconductor thermoelements are connected electrically in series by highly conducting metal strips and sandwiched between thermally conducting but electrically insulating plates. Type B has been developed recently for power generation and is densely constructed with very small inter-thermoelement separation to increase the power-per-area. However, the conducting metal strips in the latter device are not insulated and the module cannot be attached directly to electrical conductor, such as aluminium heat sink [2].

Thermoelectric devices can not be used independently. They should be connected with heat exchangers to dissipate heat, which consist of thermoelectric systems. The basic theory and operation of thermoelectric systems have been developed for many years. Thermoelectric systems are usually small heat pumps or power generators, which follow the laws of thermodynamics in the same manner as mechanical heat pumps, vapour compressors associated with conventional refrigerators, or other apparatus used to transfer energy.

The thermoelectric devices offer several distinct advantages over other technologies:

- Thermoelectric devices have no moving parts and, therefore, need substantially less maintenance.
- Life testing has shown the capability of thermoelectric devices to exceed 100,000 h of steady-state operation.

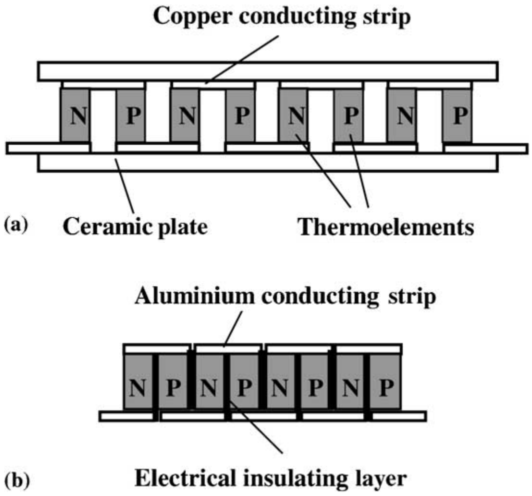

Fig. 2. Schematic diagrams of multicouple thermoelectric modules. (a) Type A configuration with ceramic insulating plates and large inter-thermoelement separation; (b) Type B configuration without ceramic insulating plate and with very small inter-thermoelement separation.

- Thermoelectric devices contain no chlorofluorocarbons or other materials that may require periodic replenishment.
- The direction of heat-pumping in a thermoelectric system is fully reversible. Changing the polarity of the DC power supply causes heat to be pumped in the opposite direction—a cooler can then become a heater.
- Precise temperature control to within ±0.1 °C can be maintained using thermoelectric devices and the appropriate support circuitry.
- Thermoelectric devices can function in environments that are too severe, too sensitive, or too small for conventional refrigeration.
- Thermoelectric devices are not position-dependent.

Due to all the above advantages, thermoelectric devices have found very extensive applications in wide areas, such as military, aerospace, instrument and industrial or commercial products in the past decade. According to the working modes, these applications can be classified into three categories, which are coolers (or heaters), power generators or thermal energy sensors. The details are given below.

2. Applications of thermoelectric devices as coolers

Commercially available thermoelectric devices are very reliable when used as coolers and operated at temperatures below room temperature. However, the results of a recent reliability study indicated that these devices might be less reliable when operated above room temperature as generators [2].

Usually, thermoelectric coolers are used in cases where the cooling system design criteria includes such factors as high reliability, small size, low weight, intrinsic safety for hazardous electrical environments, and precise temperature control. Thermoelectric coolers are more appropriate for niche applications (under 25 W) because their low COP is not an apparent disadvantage.

A thermoelectric cooling system has an electric circuit including a direct current power source providing direct current through the electric circuit, a thermoelectric device has at least one heat sink and at least one heat source capable of being cooled to a predetermined temperature range, and a control assembly. The use of a thermoelectric device in a cooling system has conventionally followed the basic arrangement shown in Fig. 3.

Thermoelectric cooling systems are analogous to conventional refrigeration systems. For example, a conventional cooling system includes an evaporator, a compressor, and a condenser. In the evaporator or cold section, pressurised refrigerant is allowed to expand, boil, and evaporate. During the change of state from a liquid to a gas, energy in the form of heat is absorbed. In the next step, the compressor recompresses the gas into a liquid. Further, the condenser expels the heat absorbed at the evaporator and the extra heat added by the compressor to the ambient environment.

A thermoelectric cooling system has similar subassemblies. However, thermoelectric cooling is specifically the abstraction of heat from electronic components by the Peltier effect. Potential uses

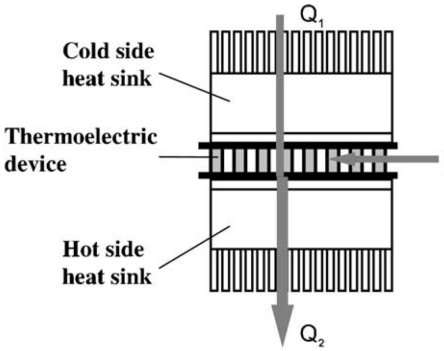

Fig. 3. Conventional arrangement for thermoelectric cooler. Q_1 is the heat to be pumped, P is the electrical power supplied. Q_2 is the heat dissipated to the ambient.

range from the cooling of electronic components to domestic refrigerators and air conditioner for cooling/heating a room space.

2.1. Cooling electronic devices

Electronic devices often have specified cooling requirements. In this area, the thermoelectric coolers have important roles because the conventional bulk cooling systems are not fit for these niche applications. The following are examples of these applications.

One of the applications is cooling the heat-producing device to keep the device in normal operation. By using a thermoelectric cooler arranged as a super cooler, the heat is conducted and the temperatures of the devices are kept close to the ambient temperatures.

Another application is to reduce the thermal noise of the electric components and the leakage current of the electronic devices, which can improve the accuracy of the electronic instruments [3–5]. One of the examples is a cooled CdZnTe detector for X-ray astronomy. Cooling between −30 and −40 °C reduces the leakage current of detector and allows the use of a pulsed reset preamplifier and long pulse shaping times, significantly improving the energy resolution. Although the heat is conducted from the very low temperature (−40 °C) to the chilled water of 10 °C, it is only necessary to use 3W of electrical power for this small capacity application.

In the aforementioned applications, an electronic device to be cooled is usually directly physically mounted on the cold side of one or more thermoelectric devices allowing maximum thermal transfer between the electronic device and the cold side. The hot side of the thermoelectric device is coupled to a heat sink and a fan or water is used to cool the hot heat sink. Nature convection is also used in some cases. A variable source of direct current connected to the thermoelectric coolers to allow them to lower the temperature of the electronic devices.

Applications of thermoelectric devices for cooling electric devices require very small and low current thermoelectric devices. The low-cost, general-purpose thermoelectric devices for cooling instrumentation, laboratory apparatus and consumer appliances etc are commercially available, such as FRIGICHIP CP Series thermoelectric devices provided by Melcor.

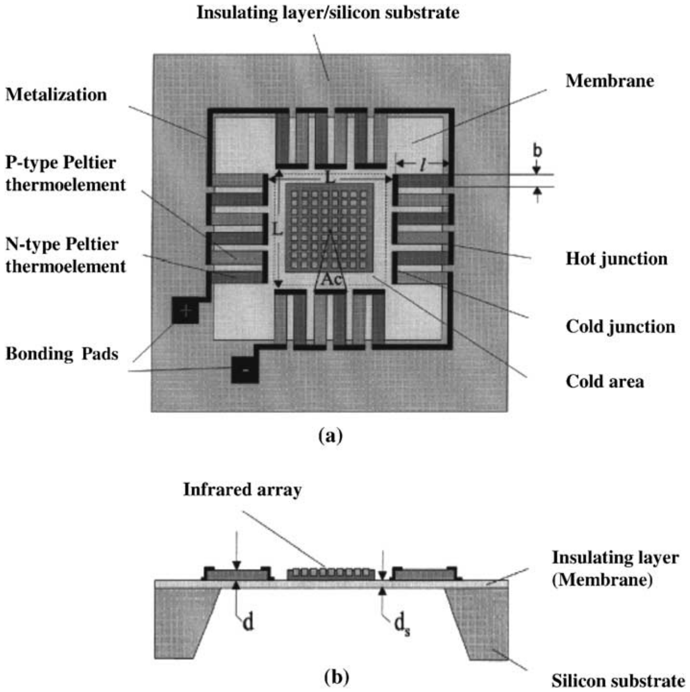

Fig. 4. Schematic diagrams showing an integrated thermoelectric microcooler with infrared components integrated onto cooled central region (a) plane view and (b) cross-sectional view.

Thermoelectric coolers are also widely employed in microelectronics to stabilise the temperature of laser diodes, to cool infrared detectors and charge-coupled devices, and to reduce unwanted noise of integrated circuits. For this application, the conventional thermoelectric coolers are bulk and are incompatible with microelectronic fabrication processes. Therefore, the thin film thermoelectric coolers have been designed by using micromachining technology and can be integrated in microelectronic circuits. Fig. 4(a) and (b) are schematics of a proposed thin film thermoelectric cooler with infrared component integrated into cooed central region. This thin film thermoelectric cooler can be fabricated as follows: a very thin amorphous SiC film is ‘laid down’ on a silicon substrate using conventional thin film deposition and a membrane formed by removing the silicon substrate over the desired regions using micromachining. N- and p-type thermoelements are then deposited on the membrane to form thermocouples. Thermocouples are configured so that the central region which is to be cooled is surrounded by the cold junctions of the Peltier thermocouples, while the hot junctions are located on the outer peripheral area which rests on the silicon substrate rim. Heat is pumped laterally from the central region to the silicon substrate rim and then dissipated vertically through it to an external heat sink. Theoretical analysis indicates that the COP and heat-pumping capacity, when operating at a temperature difference of 20 °C, are 0.6 and 1 mW, respectively. The maximum temperature difference of 30 °C can be obtained for a thermoelement length l of 0.15 mm [6].

2.2. Refrigerator and air conditioner

In addition to cooling the electronic devices, thermoelectric devices are widely used in other niche applications where the cooling demands are not too great (such as portable cooler boxes) or cases in which the energy cost is not the main consideration (such as military applications). However, their applications in cooling large thermal capacity components or spaces have been limited due to the relatively low COP and high energy cost. The COP of a present thermoelectric refrigerator is typically <0.5 when operating at temperature difference $\Delta T \sim 20$ °C.

In recent years, the available air conditioners and refrigerators have become a way of life for millions of people around the world. As the standard of living increases in less developed countries, many more people will demand the convenience and comfort that they offer. At the same time, energy costs and environmental regulations regarding the manufacture and release of CFCs are also increasing. These facts are encouraging manufacturers and their customers to seek alternatives to conventional refrigeration technology. One of the alternative refrigeration systems being used for an increasing number of these solutions is thermoelectric technology [7]. As a unique cooling device in which the electron gas serves as the working fluid, the thermoelectric device is noiseless, inherently reliable and environmentally friendly.

Actually, examples of using thermoelectric devices for refrigerators can be found as early as 1950s–1960s [8–10]. However, their low COP had limited their development. In recent years, due to the aforementioned reasons, the interests in the use of thermoelectric devices for domestic refrigerator have been revived in spite of the drawback of the low COP. Some thermoelectric devices, such as Melcor's Polar TEC$^{\mathrm{TM}}$ series thermoelectric devices, was developed specifically for these low-cost, high volume, commercial applications. Many improved thermoelectric refrigerators have been report frequently. US Patent no. 6,003,319 entitled Thermoelectric Refrigerator with Evaporating/Condensing Heat Exchanger shows an improved heat exchanger with an evaporating surface and a condensing surface, which increase the COP of the current thermoelectric refrigeration system. US Patent no. 5,987,891 entitled Thermoelectric Refrigerator/Warmer Using no External Power shows that a refrigerator/warmer convert a natural energy such as the solar energy into electric power based on difference between the internal and external temperatures to make an external power needless. US Patent no. 5,927,078 entitled Thermoelectric Refrigerator shows a unit, the interior of which can be always maintained at a high humidity by controlling the quantity of electric power to the Peltier device and to the interior fan. This refrigerator therefore can maintain the freshness of perishables, vegetables and the like for a longer time compared to a conventional refrigerator. US Patent no. 5,522,216 entitled Thermoelectric Refrigerator provides a unit which combines the benefits of superinsulation materials and phase change materials to provide an energy efficient and can maintain relatively uniform temperatures for extended periods of time with relatively low electrical power requirements.

Compared to thermoelectric refrigerators, fewer thermoelectric air conditioners are reported. Reports on using thermoelectric devices for air-conditioning on different occasions can be found as early as 1960s. However, after more than 30 years, only a company supplied thermoelectric air-conditioning systems commercially [11]. A few reports can be found in using thermoelectric air-conditioning for small scale or particular case [12,13]. Only one recent report can be found describing a thermoelectric air conditioner for cooling/heating a room space, such as living rooms, restaurants, offices, or the like [14].

Compared to conventional gas compressed air conditioner systems, thermoelectric air conditioner systems have the following features: They can be built into a very flat unit that can be conveniently handed on walls for building air-conditioning. They can be easily switched between cooling and heating and proportionally adjusted to meet requirements for air-conditioning individually. Thermoelectric systems can also efficiently work with a PV panel. Since thermoelectric devices are low voltage driven devices, they can accept a power supply directly from PV panel without conversion. These advantages make thermoelectric devices very attractive for building air-conditioning.

2.3. Specific applications

Some thermoelectric equipment for specific applications in military, areospace, instrument, biology, medicine and industrial or commercial products have been report. The following is some examples.

A solar cell-driven, thermoelectric cooling prototype headgear can be used cool the forehead. As shown in Fig. 5, three pieces of amorphous flexible paper solar cells, which were 90 × 230 mm and weighted 5 g, were mounted on a baseball cap. A 40 × 40 mm thermoelectric element was mounted under the root of the brim (it cannot be seen in the Figure) to cool the forehead by the cold side of the element. A 45 × 47 mm multi-pin fin was attached at the hot side of the thermoelectric element and a 40 × 40 mm axial electric fan was set on the fin. The total weight of this headgear is only 135 g. This headgear can achieve required temperature difference between ambient and cooling temperature (4–5 °C) for thermal comfort [15].

A prototype of thermoelectric "cryoconcentration cell" is developed for obtaining concentrated orange juice, which use Peltier effect as an alternative to the traditional methods of cryoconcentration using the conventional refrigeration cycles based on gases such as NH_3, as shown in Fig. 6 The cryoconcentration cell uses 16 thermoelectric modules (Marlow model DT-1089 and Marlow model DT-1069) on each surface (surface C_1 and surface C_2) to produce the cooling conditions able to convert the excess of water included in the juice into ice so that later it is possible to eliminate it and to concentrate the juice. Cryoconcentration is the process of cooling juice till −8 °C to obtain ice and fruit juice, because the freezing point of fruit juice is around −12 °C. The next step is a mechanical separation of the ice from the juice. The heat exchanger of this

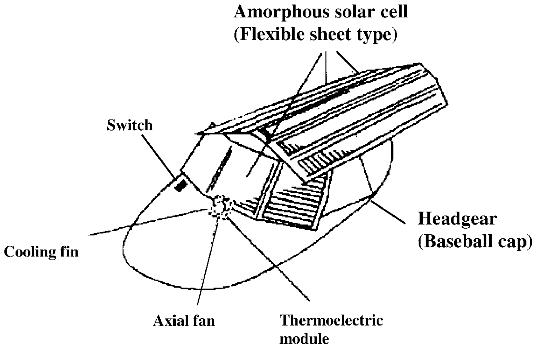

Fig. 5. Solar cell-driven, thermoelectric cooling prototype headgear.

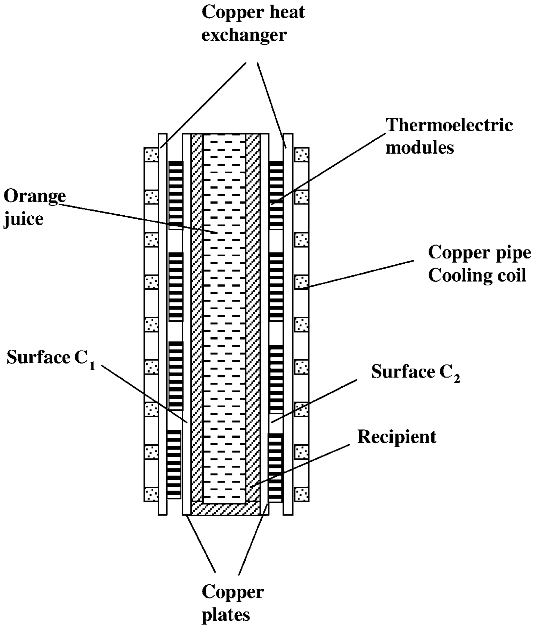

Fig. 6. Schematic diagram of a cryoconcentration cell.

prototype permits the circulation of water coming from the general external water network. It is made of copper squared plate with a cooling coil made of copper pipe running along the surface of the plate [16].

An active thermoelectric intercooler for heating or cooling a fluid passing through the intercooler was reported [17]. The intercooler may be used to cool gases from the compression stage of an engine turbocharger in order to increase engine horsepower. The intercooler could also be used to cool the oil in an engine or transmission. Alternately, the intercooler could be used to heat or cool the air provided to the passenger compartment of a vehicle. As shown in Fig. 7, the active intercooler includes a chamber through which the fluid flows. A thermoelectric heat pump is attached to the chamber in order to remove and dissipate heat from the fluid flowing through the chamber. A control system is provided to control the current supplied to the thermoelectric heat pump and thus the cooling capacity of the thermoelectric heat pump. A heat sink including a plurality of fins is attached to the thermoelectric heat pump on a surface opposite the chamber in order to increase the ability of the thermoelectric heat pump to dissipate heat.

2.4. Current thermoelectric cooling products

The thermoelectric coolers have been used practically in widespread fields. Thermoelectric production costs have decreased steadily and significant consumer markets of thermoelectric coolers have opened. There are an increasing number and variety of thermoelectric products. With each new year, the imaginations of design engineers widen with the immense possibilities of thermoelectric heating and cooling. The reliability of the thermoelectric coolers is very high, but the efficiency remains near 1960 levels (5%–10%) [18]. Over the past four decades, improvement in

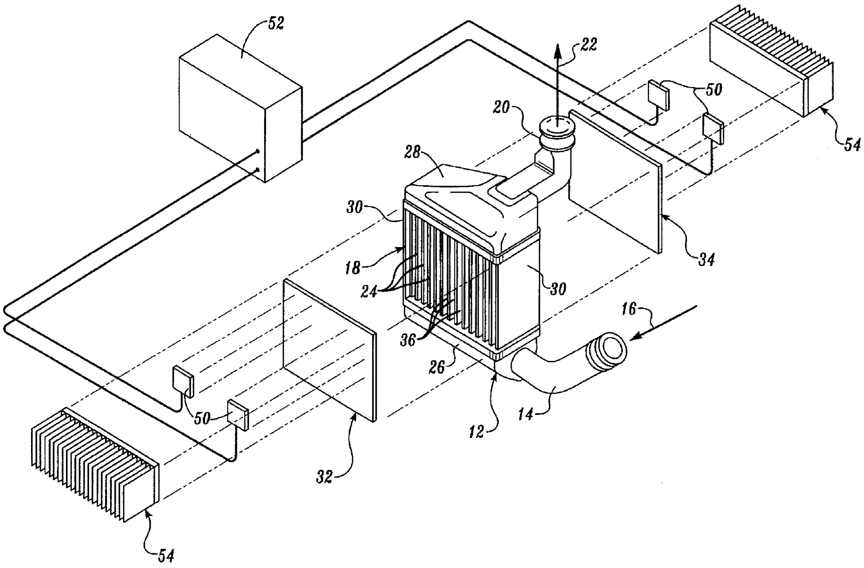

Fig. 7. Schematic diagram of thermoelectric intercooler. (Explanation for the Figure: 12—chamber; 14—inlet pipe; 16—fluid in; 18—body of the chamber; 20—outlet pipe; 22—fluid out; 24—tubes; 26—bottom of chamber; 28—top of chamber; 30—side plate; 32—front plate; 34—back plate; 36—interior; 50—thermoelectric modules; 52—control system; 54—conductive heat sink. ∗ This Figure is from United States Patent, 5547019.)

Table 1
Commercial available thermoelectric cooling products or assemblies

Military/aerospace	Electronic cooling; cooled personnel garment; portable refrigerators; cooling infrared sensors; cooling laser diodes
Consumer products	Recreational vehicle refrigerators; mobile home refrigerators; car refrigerators; portable picnic coolers; wine coolers; beer keg coolers; water coolers; motorcycle helmet refrigerators; insulin coolers (portable); residential water coolers/purifiers; beverage can coolers
Laboratory and scientific equipment	Photomultiplier tube housing coolers; laser diode coolers; charge-coupled device cooler; change induced device coolers; integrated circuit coolers; vidicon tube coolers; laboratory cold plates; stir coolers; cold chambers; immersion coolers; ice point reference baths; microtome stage cooler; electrophoresis cell coolers
Industrial-temperature control	NEMA enclosures; harsh environment protection for critical components; PC computer microprocessors; microprocessor and PCs in numerical control and robotics; stabilizing ink temperature in printers and copiers
Restaurant equipment	Cream dispensers; whipped cream dispensers; butter dispensers; individual portion dispensers
Miscellaneous	Pharmaceutical refrigerators—portable and stationary; hotel room refrigerators; automobile mini-refrigerators; automobile seat cooler; aircraft drinking water cooler; coach coolers; marine cooler; van coolers and refrigerators; trucks coolers and refrigerators; car air conditioners; DNA cyclers; diagnostic medical equipment; hot/cold therapy pads

the conversion efficiency has been marginal. The challenge has been the improving the performance of the thermocouple materials, which could lead to a breakthrough in terms of the efficiency of the thermoelectric device. But less progress is achieved. Table 1 summarises the current commercial available thermoelectric cooling products.

3. Application of thermoelectric devices for power generation

A thermoelectric generator is a unique heat engine in which charge carriers serve as the working fluid. It has no moving parts, is silent in operation and reliable. However, its relatively low efficiency (typically around 5%) has restricted its use to specialised medical, military and space applications, such as radioisotope power for deep space probes, and remote power, such as oil pipelines and sea buoys, where cost is not a main consideration. In recent years, an increasing public awareness of environmental issues and in particular global warming has resulted in broad based research into alternative commercial methods of generating electrical power and thermoelectrics has emerged as a serious contender. Thermoelectrics has attracted increasing attention as a 'green' and flexible source of electricity able to meet a wide range of power requirements [19].

The use of a thermoelectric converter for electrical power generation has conventionally followed the basic arrangement shown in Fig. 8. A thermoelectric module is sandwiched between a heat source and a heat sink. Heat from the source flows though the module and is rejected through the heat sink into the ambient. Provided a temperature difference can be maintained across the module, electrical power will be generated.

3.1. Low power generation

Energy supply for small, independent and wireless system for remote sensing, control, safety surveillance and metering is mostly made with batteries. This presents a number of severe disadvantages: the lifetime of batteries is limited which implies that the system has to be maintained or replaced after a few years. Furthermore, batteries contain chemical substances that are harmful

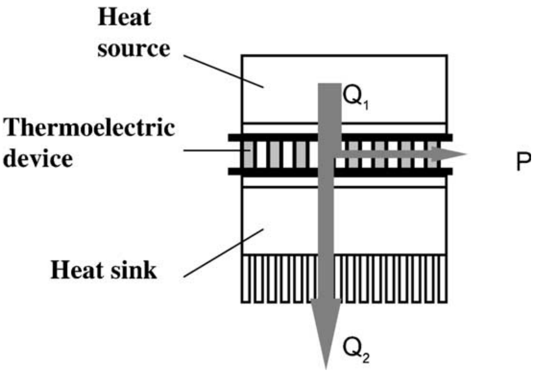

Fig. 8. Conventional arrangement for thermoelectric power generation. Q_1 is the heat supplied by the heat source. P is the electrical power generated. Q_2 is the heat dissipated to the heat sink, which is the thermal energy wasted.

to the environment. For this reason, the disposal of battery operated systems has to be controlled, which is a very expensive procedure. Another common solution is the solar cell as it is used for small calculators or watches. If no light is available the small temperature differences which are present could be used to operate a small thermoelectric generator. Therefore, small, inexpensive and efficient thermoelectric generators are gaining importance as a replacement for batteries in many systems [20]. One of the examples is to operate a small preamplifier and a sensor control system with a thermoelectric generator generating an electrical power of 1.5 μW with a temperature difference of 10 °C.

A large number of studies have been reported on the $(Bi,Sb)_2(Te,Se)_3$-based thermoelectric materials and devices because of their excellent performance in thermoelectric refrigeration and power generation at room temperature. Thermoelements have been usually fabricated from sintered blocks of these materials. There are, however, certain difficulties and limitation in making highly miniaturized modules because of the fragile nature of these materials. Moreover, the number of P/N couples fitting in a limited space available makes it impossible to obtain relatively high output voltage (order of volt) for power generation. To overcome these drawbacks, thermoelectric modules based on thin film technology for both refrigeration and power generation have been studied [21]. Microwatt or milliwatt power level could be obtained by thin film thermoelectric generators. At present, the thin film thermoelectric generators for electronic applications have be commercially available [22].

Any available heat source such as the surface of a water pipe would provide sufficient heat flux to these low power applications.

3.2. High power generation

3.2.1. Waste heat thermoelectric generator

The performance of thermoelectric materials can be expressed as $Z = \alpha^2/kR$, where Z is a figure of merit, α the Seebeck coefficient, R the electric resistivity and k the thermal conductivity. This figure of merit may be made dimensionless by multiplying by T (average temperature of hot side and cold side of the thermoelectric module, K), i.e., $ZT = \alpha^2 T/kR$. In general, a thermoelectric generator exhibits low efficiency due to the relatively small dimensionless figure of merit ($ZT \leqslant 1$) of currently available thermoelectric materials. For low power generation, the low efficiency of the thermoelectric generators is not a main drawback. But for high power generation, low efficiency is a disadvantage and has limited its application to specialised areas.

In recent years it has been realised that in situations where the supply of heat is cheap or free, as in the case of waste heat, efficiency of the thermoelectric generation system is not an overriding consideration. The use of waste heat as an energy source particularly at temperatures below 140 °C substantially increases the commercial competitiveness of this method of generating electrical power [19].

In general, the cost of thermoelectrically producing electricity mainly consists of the running cost and module cost. The running cost is determined by its conversion efficiency, while the device cost is determined by the cost of its construction to produce the required power output. Since the conversion efficiency of a device is comparatively low, thermoelectric generation using waste heat is an ideal application. In this case, the running cost is negligible compared with the module cost because the fuels cost very little or nothing. Consequently, an important objective in thermoelectric power generation using waste heat is to reduce the cost-per-watt of the devices. A figure of about £4/W can readily be obtained using commercially available thermoelectric device with an appropriate thermoelement length. Furthermore, cost-per-watt can be reduced by optimising the device geometry, improving the manufacture quality and simply by operating the device at a larger temperature difference. The power-per-area can also be significantly improved by reducing the inter-thermoelement separation. Although the inter-thermoelement separation may not affect most cooling applications, its reduction will significantly increase the power-per-area of a device when it is used in generating mode.

Currently, a standard device consists of 71 thermocouples with the size 75 mm^2 can have 19 W output (www.hi-z.com). The world's largest supplier of thermoelectric generators, Global Thermoelectric Inc., provide thermoelectric generators range in output from 15 to 550 W, and with the module size from 508 × 279 × 483 mm^3 to 1549 × 1549 × 1016 mm^3 (www.globalte.com).

One investigation of the performance of thermoelectric generating systems powered by waste hot water indicates that, over a three year operating period, electrical power can be produced by this method and at a price which matches that of conventional utilities [19].

Another study carried out by Yodovard et al. [23] assesses the potential of waste heat thermoelectric power generation for diesel cycle and gas turbine cogeneration in the manufacturing industrial sector in Tailand. The data from more than 27,000 factories from different sectors, namely, chemical product, food processing, oil refining, palm oil mills petrochemical, pulp and paper rice mills, sugar mills, and textiles, were used. It is shown that gas turbine and diesel cycle cogeneration systems produced electricity estimated at 33% and 40% of fuel input, respectively. The useful waste heat from stack exhaust of cogeneration systems was estimated at 20% for a gas turbine and 10% for the diesel cycle. The corresponding net power generation is about 100 MW.

Although the economic viability of a thermoelectric generator may be improved significantly when used for waste heat recovery, the generator still dissipates a large amount of unconverted heat from its cold side due to its relatively low conversion efficiency. In order to overcome this drawback, the concept of "symbiotic" generation has been proposed. The idea is to use the thermoelectric generator as a dual function device, heat exchanger/generator. When heat flows through a thermoelectric generator, part of the heat absorbed is converted into electricity, while the rest, instead of being discharged to the ambient, is collected and used for preheating. Fig. 9 illustrates a basic arrangement of a thermoelectric symbiotic cogeneration system. In this arrangement, a thermoelectric device is linked to a fluid heater by attaching the cold side of the thermoelectric device to the cold fluid inlet and the hot side the hot fluid outlet. The main purpose of such a cogeneration system is to produce hot fluid. However, when a thermoelectric device is

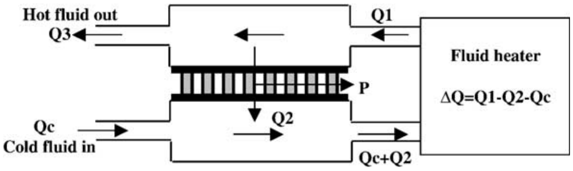

Fig. 9. An example of a thermoelectric generator as a fluid preheating/parasite generation device. The heat dissipated from the thermoelectric generator is used to preheat the fluid, i.e. Q_2 is not wasted.

incorporated, a small portion of heat (Q_1–Q_3) from the outlet of the fluid heater will flow through a bypass, consisting of the thermoelectric module, and is converted to electricity. The heat dissipated from the cold side of the thermoelectric generator (Q_2) returns to the fluid heater inlet and preheats the cold fluid.

It is estimated theoretically that the overall efficiency (including both heat production and electricity generation) of a symbiotic generation system is the same as that of heat production by a conventional heating system. In principle, the input energy (e.g. fuel) can be fully (100%) utilised and converted into heat and electricity. Consequently, the drawback of the relatively low conversion efficiency of a thermoelectric generator becomes rather inconsequential. Since such a system can generate both heat and electricity simultaneously with little or no sacrifice in the overall efficiency of the system, it has potential for wide-scale applications in situations where both electricity and heat are required. Typical of these applications are domestic central heating boilers and conventional fuel or biomass combustion units. Currently, most of these systems require both a fuel supply (for heat production) and electricity supply (for powering pumps, fans or control panels). The proposed symbiotic thermoelectric system only requires a supply of fuel as energy input and the electricity can be generated in situ as a "by product". This is a significant advantage for applications where an electricity supply is not available or unreliable due to severe weather and environmental conditions [24].

3.2.2. Solar thermoelectric generation

The growing demand for energy throughout the world has caused great importance to be attached to the exploration of new sources of energy. Among the unconventional sources, solar energy is one of the most promising energy resources on earth and in space, because it is clean and inexhaustible. Applications of solar thermoelectric generator are attractive. The use of the solar thermoelectric generator usually combines a solar thermal collector with a thermoelectric generator, which delivers the electric energy.

Due to current solar thermoelectric generators having a low conversion efficiency, some researchers are seeking improved methods. Research on solar-powered high-efficiency thermionic/thermoelectric conversion systems has been reported [25]. The system combines a thermionic converter (TIC) with a thermoelectric generator to use thermal energy efficiently and to achieve high-efficiency conversion. The TIC emitter must uniformly heat up to 1800 K. The TIC emitter can be heated using thermal radiation from a solar receiver maintained at a high temperature by

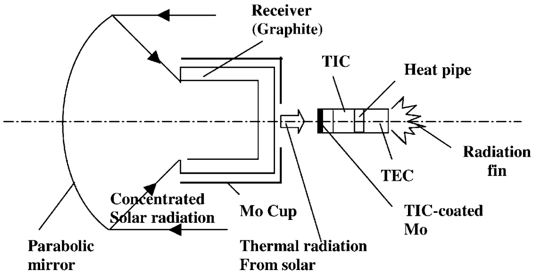

Fig. 10. Schematic view of solar-powered conversion.

concentrated solar irradiation. A cylindrical cavity-type solar receiver constructed from graphite was designed and heated in vacuum by using the solar concentrator at Tohoku University, as shown in Fig. 10. The maximum temperature of the solar receiver enclosed by a molybdenum cup reached 1965 K, which was sufficiently high to heat a TIC emitter using thermal radiation from the receiver. A high-efficiency conversion close to 40% was achieved.

4. Application of thermoelectric devices as thermal energy sensors

Many new types of thermal energy sensors based on Peltier effect or Seebeck effect of the thermoelectric modules have been developed. These novel sensors have improved properties compared to conventional thermal energy sensors. The following are some examples of the thermoelectric thermal energy sensors.

4.1. Cryogenic heat flux sensor

The potential application of the conventional thermoelectric devices as a heat flux sensor at cryogenic temperatures is reported [26]. Commercially available thermoelectric modules were tested at temperatures from 200 K down to 60 K for possible application to in situ radiant heat flux measurement. The 127 P/N junction thermoelectric modules with the surface area of 30 mm × 30 mm show a sensitivity of 27 μV/(W/m^2) at 80 K, which is nearly 10 times higher than that of a conventional heat flux sensor. The sensitivity is still as large as 17 μV/(W/m^2) at 60 K demonstrating promise for practical cryogenic use.

4.2. Ultrasonic intensity sensor

The use of ultrasound is now considered, among other methods, to be a way of activation of kinetics (chemical reaction, mass transfer...) and of yield improvement in chemical engineering processes. A large variety of ultrasonic devices are presently available at the laboratory scale.

The design of ultrasonic reactors lies partly in the description of the ultrasonic intensity space and time distribution. Among other techniques, the thermoelectric sensor seems to be one of the most appropriate tools to measure the intensity available. It consists of a thermocouple embedded in an absorbing material (silicone). An experimental device of ultrasonic intensity measurement is shown in Fig. 11. The thermocouple is mounted on a rack gearing, which allows accurate horizontal and vertical displacement. A second rack gearing permits a precise of positioning of a reactor inside ultrasonic cleaner. During the heating step, the temperature increase of the absorbing material is linked to absorption of ultrasound as it is transmitted in the medium, the decrease of temperature in the absorbing material is caused by stopping the ultrasound emission. The variation of the temperature signal delivered by the sensor is real-time recorded and processed. The modelling of the heat transfer allows the establishment of the relationship between the temperature signal response of the probe and the ultrasound intensity. It is shown that either the initial rate of temperature rise or the difference between the steady-state probe temperature and the medium temperature can be used [27].

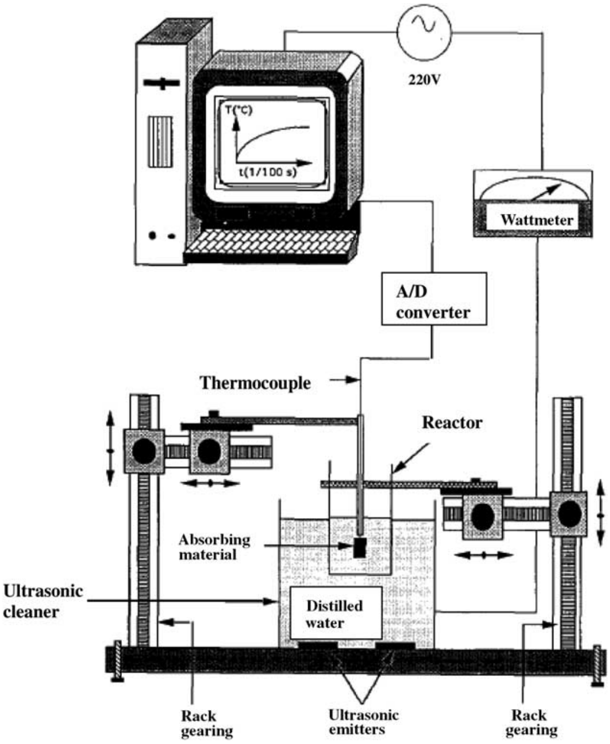

Fig. 11. An experimental device of ultrasonic intensity measurement.

4.3. Detection of water condensation

A new type of integrated microsensor for the preventive detection of water condensation is reported [28]. The sensor operation is based on a thermal oscillation generated by the Peltier effect at a junction. When water droplets form upon cooling of the junction sensitive area, the thermal oscillation is perturbed, resulting in a frequency shift. This shift allows us to determine in advance the conditions for mist formation.

4.4. Fluid flow sensor

A new thermoelectric sensor and a method to measure the low velocity of fluid flow, a fluid flow range from zero to 1.5 m^3/s, are described [29]. The prominent advantage of this device is an average temperature close to the fluid temperature. Then thermal perturbations (natural convection) generated by the sensor are negligible.

4.5. Infrared sensor

Thermoelectric infrared sensors are used in contactless temperature measurement, infrared gas analysis and as passive intrusion alarm sensors.

4.6. Thin film thermoelectric sensor

Thin film thermoelectric devices with very small dimensions, which can be integrated in microelectronics, have been fabricated using micromachining technology as sensors for radiation, electrical AC and DC power, flow and low vacuum [30].

5. The prospects of the applications of thermoelectric devices

5.1. Coolers and power generation

5.1.1. Coolers

It is predicted that every domestic icebox could depend on thermoelectric devices. Thermoelectric domestic heat pumps and air conditioners will become competitive in the world market. This is because energy costs and demands can only increase and environmental concerns can only increase. Also the environmental treaties have banned chlorofluorocarbons. Reduced manufacturing costs of thermoelectric devices have been opening up new markets.

A large market will open for the automotive industry. This is because the compatibility of many thermoelectric devices with automotive voltages, makes them especially suitable for small cooling jobs in that industry [18].

5.1.2. Power generation

Most of the recent research activities on applications of thermoelectric power generation have been directed towards utilisation of industrial waste heat. The Japanese initiated a major waste heat recovery program. High energy costs are more important than capital costs. But waste heat costs very little or nothing. Therefore, where there is abundant waste heat, thermoelectric makes sense.

5.1.2.1. Low power generation. Miniature low powered thermoelectric generators have been fabricated using integrated circuit technology [19]. It is possible to utilise waste human body heat to power a thermoelectric 'watch battery' and to utilise any available heat source such as the surface of a hot water pipe to operate an electronic chip in a domestic gas monitoring system.

5.1.2.2. High power generation. Although a reciprocating piston engine (automobile) efficiently converts the chemical energy in fossil fuels into mechanical work, a considerable amount of energy is dissipated to the environment through exhaust gas, cooling water, lubricating oils and radiation. Typical exhaust output at normal running speed for a family car is 20–30 kW. A comprehensive theoretical study concluded that a thermoelectric generator powered by exhaust heat could meet the electrical requirements of a medium sized automobile [19]. Wide-scale applications of thermoelectrics in the automobile industry would lead to some reductions in fuel consumption but this technology is not yet proven.

In Japan the solid waste per capita is around 1 kg per day and the total amount of energy in equivalent oil estimated at 18 million kilolitre by the beginning of the 21st century. The possibility of utilising the heat from incinerating municipal waste has been considered. A small-scale on-site experiment using a 60 W thermoelectric module was installed near the boiler section of an incinerator plant. The gas temperature varied between 823 and 973 K and with forced air cooling an estimated conversion efficiency of 4.4% was achieved. An analysis of a conceptual large scale system burning 200 ton a day indicated that around 2000 kW could be recovered.

Vast amounts of heat are rejected from industry, manufacturing plants and power utilities as gases or liquids at temperature which are too low for use in conventional generating units (<450 K). Thermoelectric generators offer an alternative and a series of prototype systems, powered by low temperature waste heat, have been constructed at University of Wales, Cardiff and operated for several years. Small prototype generating systems powered by waste warm water are economically competitive at present and their competitiveness will increase further as the technology develops [19].

The use of the waste heat would totally change the economic competitiveness of thermoelectric generating systems. Using available technology a thermoelectric generating system if operated over a three year period will produce electrical power at a cost which matches the major utilities.

5.2. Superconductor application

The increase of the superconducting transition temperature in some of the cuprate superconductors to values higher than 130 K has generated new interest in the exploration of Peltier cooling for the operation of superconducting electronics [31].

The prospects for thermoelectric cooling of superconducting electronic have been reported [31]. A thermoelectric cooling experiment using commercially available thermoelectric modules was carried out. As shown in Fig. 12, in this experiment, two single-stage modules served for cooling an aluminum box. Inside this box a four-stage Peltier cascade was placed. Fixing the temperature on the warm end of this system at 282 K using cooling water, on the cold end of the four-stage cascade module a temperature of 149 K was reached. It is concluded that for Peltier cooling to temperatures appreciably below this value better thermoelectric materials must be developed. Whereas at present the typical value of the figure of merit in a Peltier module is about $z = 3 \times 10^{-3}$ K^{-1}, higher values of z are required. For example, with a figure of merit $z = 5 \times 10^{-3}$ K^{-1} and a

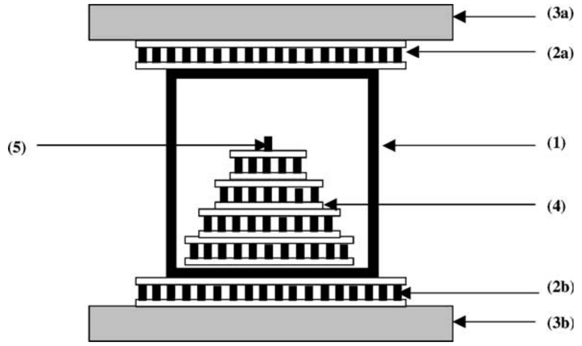

Fig. 12. Arrangement of the Peltier cooling experiment: (1) nearly cubic aluminum box with 5.0 cm on each side; (Fig. 2(a) and (b)) single stage Peltier modules; (Fig. 3(a) and (b)) water cooled copper plates on the warm end; (4) four-stage Peltier cascade; (5) thermometer on the cold end of four-stage module.

temperature $T_0 = 283$ K on the warm end, a three-stage Peltier system will reach 125 K on the cold end. This temperature is close to the supper-conducting transition temperature of 124 K achieved in thin films of $HgBa_2CaCuQ_{6+\delta}$.

5.3. Aeronautics and space applications

Efficient, clean energy conversion for high value-added applications such as space and defence is needed in the future.

Electric and thermal powers have to be available at the base site on the lunar surface before the first lunar crew arrives. Unlimited solar energy is available on the lunar surface. Various options for developing a lunar power plant are proposed. Thermoelectric power plant should be a good candidate.

Mission planners and spacecraft designers, energised by the recent claims of possible discovery of life on Mars and responding to increased public interest in the human exploration of Mars, frequently propose nuclear reactors and radioisotope thermoelectric generators for interplanetary spacecraft propulsion and for power supply on the surface of Mars [32].

5.4. New thermoelectric material

The new thermoelectric materials with large ZT could make a breakthrough on applications of the thermoelectric devices in various fields. There is no easy path to large ZT, but there are many plausible approaches that have yet to be tried. Venkatasubramanian and co-workers (Research Triangle Institute, Research Triangle Park, North Carolina 27709, USA) reported recently in the Journal Nature $ZT = 2.4$ in thin film p-type Bi_2Te_3/Sb_2Te_3 semiconductors. These materials appear to achieve high ZT values thanks to their unusual structure—a superlattice formed by alternating layers of Bi_2Te_3 and Sb_2Te_3 semiconductors. The previous record for ZT at room temperature was around $ZT = 1$, held by a bulk semiconductor alloy based on Bi_2Te_3 and Sb_2Te_3. The superlattice structure appears to enhance the transport of current-carrying holes while inhibiting transport of heat-carrying phonons (quantized vibrations of the crystal lattice). Both effects boost ZT [18].

6. Conclusions

Thermoelectric technology has been used practically in wide areas recently. The thermoelectric devices can act as coolers, power generators, or thermal energy sensors and are used in almost all the fields such as military, areospace, instrument, biology, medicine and industrial or commercial products.

The applications of small capacity thermoelectric coolers are widespread. But the applications of the large capacity thermoelectric coolers and power generators are limited by their low efficiency. However, energy costs and environmental regulations regarding the manufacture and release of CFCs has revived the interest in this area.

In recent years it has been realised that in situations where the supply of heat is cheap or free, as in the case of waste heat or solar energy, efficiency of the thermoelectric generation system is not an overriding consideration.

The increase of the superconducting transition temperature in some of the cuprate superconductors to values higher than 130 K has generated new interest in the exploration of Peltier cooling for the operation of superconducting electronics.

Efficient, clean energy conversion for high value-added applications such as space, defence is needed in the future. Thermoelectric power plant should be a good candidate.

The development of new thermoelectric materials with large *ZT* could make a breakthrough on applications of the thermoelectric devices in various fields.

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