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Nanoporous Bi$_2$Te$_3$ thermoelectric based Knudsen gas pump

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Abstract
The first bi-directional thermoelectric based Knudsen pump is made using a multifunctional nanoporous P-type bismuth telluride (Bi$_2$Te$_3$) thermoelectric material. The nanoporous material has been fabricated using a cold pressing and sintering technique under an argon atmosphere. Analysis of the nanoporous thermoelectric shows the average grain size is 680 nm, the pore radius ranges from 205 to 756 nm, and the average pore radius is 434 nm corresponding to a Knudsen number of 0.075 in the transitional flow regime. Gas flow due to the principle of thermal transpiration was demonstrated using a thermal gradient generated by running current through the thermoelectric, and measuring the gas flow rate and pressure. For an input power of 3.32 W, a maximum of 300 Pa pressure and 1.8 $\mu$m/min flow rate was observed. A reduction of the pore size down to 25 nm, and an improvement of the electrical contact resistance should lead to a 16 time increase in the generated pressure, and reduction in the consumed power respectively.

Keywords: nanoporous, thermoelectric, Knudsen pump, thermal transpiration

(Some figures may appear in colour only in the online journal)

1. Introduction
Thermally driven pumps have a wide variety of applications in the fields of micro electro mechanical systems (MEMS) and nanotechnology. Some of these applications are: gas chromatography [1–3], spectroscopy [4], and microplasma manufacturing [5, 6]. In some other applications, such as filtration, by-pass medical devices, and micro total analysis systems [7], it is desirable that the pump be bi-directional. The Knudsen pump [8–10] is a thermally driven pump that can potentially be used for these applications. It has no moving parts, can pump any liquid regardless of its PH or conductivity through pneumatic pressure, and can operate at low voltages. The gas flow is continuous.

Many membrane materials have been used in the fabrication of the Knudsen pump; some of these materials are naturally occurring zeolite [10, 11], ceramic [12], polymer commercial membrane [13, 14], glass [9], silicon [8], and silicon aerogel [15]. The membrane pore size must restrict the flow to the free molecular or transitional regime. Another critical characteristic that the membrane should possess is a low thermal conductivity; this will ensure a sufficient thermal gradient is established across the membrane for thermal transpiration to take place. Our group has previously published a work on an infusion pump powered by the body heat to pneumatically push the pharmaceutical agent from a reservoir to the wound [16]. Millipore membrane was sandwiched between a heat sink, and a biocompatible stainless steel plate
Figure 1. Two chambers, separated by a narrow thermoelectric channel. When the thermoelectric is powered, gas flow from the cold side to the hot side is initiated.

which facilitate heat transfer from the skin to the Knudsen pump.

Bi$_2$Te$_3$ was used in this work because it is well studied, documented, and possesses the best figure of merit at near room temperature [17–19]. For medium and high temperature applications, materials such as PbTe [20] and silicon-germanium [17] can be used.

The major challenge during the design of a Knudsen pump is to obtain a maximum temperature difference. In a conventional Knudsen pump [21], a heater is placed adjacent to the hot end of the nanoporous material, and the cold end is passively cooled with a heat sink. Optionally, a thermoelectric module may replace the heater/heat sink [13], resulting in an improved temperature difference by actively cooling the cold end. However, in both methods, there are significant temperature drops across the air gaps supporting the air gap between the heater and nanoporous material from the heater/heat sink/thermoelectric module, limiting the pump performance.

In this paper we overcome these challenges by using a multifunctional, nanoporous sintered Bi$_2$Te$_3$ thermoelectric. The thermoelectric properties are used to generate the temperature difference needed for thermal transpiration. The sub-micron pores which extend through the thermoelectric material function as channels for gas flow. This multifunctional material eliminates the air gap between the heater and nanoporous material that exists in a traditional pump, and thus potentially improving the temperature difference and pump performance, and reducing the overall size of the pump.

2. Theory and operation

The Knudsen pump relies upon the principle of thermal transpiration for its operation. If two chambers filled with the same gas are connected by a narrow channel that restricts gas flow to the free molecular regime, and maintained at different temperatures ($T_C$ and $T_H$) (figure 1), a net gas flow from the cold chamber to the hot chamber will be generated. Once steady state is reached in a closed system, the ratio of equilibrium pressures in the two chambers, $P_C$ and $P_H$, is equivalent to the ratio of the square root of respective absolute temperatures. Subscripts $C$ and $H$ refer to the cold and hot sides, respectively:

$$\frac{P_H}{P_C} = \sqrt{\frac{T_H}{T_C}}.$$  \hspace{1cm} (1)

Equation (1) is obtained by equating the molecular flux between the two chambers. For a channel with larger diameter that is in the transitional flow regime, the ratio of absolute temperatures has an exponent that is between 0 and 0.5. The pressure must be in the free molecular flow or transitional flow regimes for proper operation, ideally requiring pore diameter on the order of 100 nm or smaller for operation at atmospheric pressure.

Figure 2 shows a schematic of the device. Once the power is turned on, one side of the thermoelectric material becomes hot, and the other side becomes cold. Gas starts to flow through the nanoporous thermoelectric material from the cold side to the hot side by thermal transpiration. Switching the voltage polarity reverses the pumping direction.

3. Methods

A schematic of the fabrication process is shown in figure 3. Bi$_2$Te$_3$ rectangular pellets (Crystal Ltd. Russia) were placed in a jar with stainless steel balls and the air evacuated using a rotary vane pump. The jar was mounted on a high energy vibratory ball mill (VQ-N desktop Across International LLC, NJ) to create a nanopowder. Milling was performed in 15 min periods followed by 30 min cool down periods. The total milling time was 5 h. The powder was uniaxially pressed in a circular die at 6 MPa for 1 h. The resulting sample was 13 mm in diameter and 2.75 mm in thickness. Sintering was performed in a tube furnace under running argon for 2 h at 200 °C.

Thermal diffusivity, $D$, was measured with a laser flash system (LFA 427 Netzsch Instruments, Inc.). The specific heat, $C_p$, was determined by differential scanning calorimetry analysis (DSC Q20 TA Instruments) using sapphire as the reference material. Density, $\rho_D$, was calculated from the weight and dimensions of the sintered sample. The thermal conductivity was determined from the product of the three parameters [22]: specific heat, thermal diffusivity, and density:

$$k = D C_p \rho_D.$$  \hspace{1cm} (2)

The sample was then cut to a square shape for thermopower and electrical conductivity measurements. A
Figure 3. Schematic of the fabrication process to create the nanoporous Bi$_2$Te$_3$ thermoelectric material used in the bi-directional Knudsen pump. Commercial grade doped Bi$_2$Te$_3$ is ball milled to create a nanopowder, which is then sintered in a die press to obtain the final pellet.

Figure 4. EDS spectrum of the P-type Bi$_2$Te$_3$ material. (A) Initial material. (B) Sintered sample.

A four-probe technique was used to measure the electrical conductivity. The same setup was adjusted to measure the thermopower from the slope of voltage versus temperature.

The milled powder and pressed sample were characterized with energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD, Bruker-AXS, D8 Discovery) using Cu K$_\alpha$ radiation, and scanning electron microscopy (SEM, Zeiss Supra 35 VP).

A Knudsen pump was made using the sintered Bi$_2$Te$_3$ sample. The sample was placed inside a channel machined on a plastic substrate. The channel was drawn using SolidWorks CAD software. The dimensions are 3 cm long, 13 mm wide. The drawing was saved as .igs file and transferred, to the computer connected to the CNC milling machine with VisualMill 6.0 machining program. The machine was set to 3-axis milling and the milling speed was 14 000 RPM. The machining was performed in two parts, horizontal rough machining and parallel finishing machining. An end mill (3.175 mm diameter, 38.1 mm long, and 2 flutes) made out of carbide was used. Epoxy glue was applied on the sides where the sample touches the channel. A plastic cover, with glued tube (0.01” I.D), was used to close the channel. The plastic tube will be connected to the pressure sensor for pressure head measurement.

To measure the pressure difference that may be obtained with the pump, a digital pressure sensor with a dead volume of 0.8 cc is connected to one side of the pump, and the other side was open to the atmosphere. A similar pressure sensor was used to monitor the atmospheric pressure. A custom labView program was written to plot the room pressure, the Knudsen pump pressure, and their difference.

4. Results

Figure 4 shows an EDS spectrum of the starting material and the sintered sample. The material is made up of Bi, Sb, and Te. No additional peaks are present, indicating that no impurities were introduced. XRD patterns of the powder and sintered sample are shown in figure 5. The two patterns have similar peaks indicating that there were no changes in the crystal phases during the pressing and sintering steps. The average crystal size for the powder and the sintered sample was calculated from XRD peak broadening using the Scherrer equation [23]. The average crystal sizes were 226.95 Å and 370.9 Å for the powder and the sintered sample, respectively, indicating that the crystal size increased during sintering.

Figure 6 shows an SEM image of the sintered sample, and the inset shows a picture of the imaged sample. To verify that the pores extend through the thermoelectric sample, the sample was connected through a T-connector to a pressure sensor and a syringe. After a pressure is applied, a drop in pressure due to gas leaking through the pores on the sample was observed. From an analysis of multiple SEM images using ImageJ software, the average grain size is 680 nm, the pore radius ranges from 205 to 756 nm, and the average pore radius is 434 nm.

Figure 5. XRD patterns of the Bi$_2$Te$_3$ powder and sintered sample. (A) sintered sample, (B) 5 h milled powder. Space group R-3m, system rhombohedral, PDF 01-072-1836.
Figure 6. SEM of the sintered sample, inset: sintered nanoporous Bi$_2$Te$_3$ pellet sitting on top of a US dime.

Figure 7 shows a plot of thermal conductivity, electrical conductivity, thermopower, and the $ZT$ value. Thermal conductivity was less than 0.8 W/K.m from room temperature to 475 K, and less than 1 W/K.m between 475 and 550 K. This decrease in the thermal conductivity compared to bulk is believed to be due to enhanced phonon scattering at the grain boundaries. The $ZT$ value was degraded due to the significant reduction in the electrical conductivity.

Thermal infrared (IR) microscopy was used to test the sintered thermoelectric. The sample was placed on a heated stage (60 °C) to permit emissivity corrections to be performed, and a 324 mW (0.36 V, 0.9 A) was applied. A temperature distribution over the surface of the sample was measured (figure 8), showing cooling (<60 °C) on one side, and heating on the other side (>60 °C). When the voltage polarity is reversed, the hot and cold regions are reversed.

Figure 7. (A) Thermal conductivity, (B) electrical conductivity, (C) thermopower, and (D) $ZT$ value of the sintered sample.

The final device (figure 9) has a footprint of 3 × 2 cm$^2$. Its main components are the nanoporous thermoelectric material, channel, connection wires, and the tubing. Plastic material was used for the channel substrate and cover because it has a lower thermal conductivity which helps maintain the temperature gradient necessary for thermal transpiration.
Figure 9. Fabricated nanoporous \( \text{Bi}_2\text{Te}_3 \) thermoelectric Knudsen pump. The nanoporous thermoelectric sample is placed in a rectangular channel. Wires are soldered on the sides. The pump is sealed using vacuum epoxy glue.

Figure 10. Experimental pressure differential obtained with the fabricated Knudsen pump shown in figure 9.

Figure 11. Graph of the pressure versus flow rate that is obtained for three different levels of power in the nanoporous thermoelectric. The marks are the experimentally obtained data, and the lines represent a linear fit to the measurements.

5. Conclusions

A large portion of the consumed power is due to the lower quality of electrical contacts to the nanoporous thermoelectric material. Electroplating \([24, 25]\), the most common technique for making those contacts, was avoided because the electrolyte can clog the pores. Instead, regular tin material was used. New methods for making contacts such as sputtering and evaporation are being investigated. We believe that the consumed power will decrease significantly with improved electrical contact.

Our group has investigated the effect of pore size on the maximum pressure generated through thermal transpiration \([14]\). Membranes with pores ranging from 25 to 1200 nm have been used, and that corresponds to a Knudsen number \(K_n\) from 2.9 to 0.061. The input power, working gas and the membrane thickness were kept unchanged during the testing. For \(K_n = 0.091\) and \(K_n = 2.9\) the measured differential pressures were 9.65 and 157 Pa respectively. This means that reducing the pore radius from 800 to 25 nm will improve the generated pressure about 16 times. Comparison of the derivative of the generated pressure versus time which is proportional to the flow rate showed that as the pore size decreases, the flow rate increases. For a 25 nm and an 800 nm pore radius membrane, the derivatives were 3.97 and 0.201 Pa/s which corresponds to about 20 times improvement in the flow rate.

In summary, a nanoporous p-type thermoelectric material pellet has been fabricated by sintering a nanoporous powder under an argon atmosphere. Experimental measurements revealed a decrease in the thermal conductivity as well as a decrease in the electrical conductivity, compared to bulk thermoelectric material. When a current flows through the thermoelectric, a temperature gradient is established,
and gas flows due to thermal transpiration. For 3.32 W input power to the thermoelectric, a maximum flow rate of 1.8 μl min⁻¹ and a maximum pressure of 300 Pa is obtained, clearly demonstrating the thermal transpiration effect. It is expected that the gas flow rate and pressure will become more pronounced as the pore size is reduced. Although this paper demonstrates that the porous thermoelectric may be used to generate pneumatic power by running a current through the thermoelectric material, it is also possible to simultaneously generate pneumatic power and electric power from a heat source.

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