Flexible thermoelectric power generation system based on rigid inorganic bulk materials

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HIGHLIGHTS

- We demonstrate that bulk material can be used for flexible thermoelectric system.
- Not only flexible thermoelectric device but also heat sinks are combined together as a system.
- The flexible thermoelectric system produce 80 μW powered by human body heat.

ARTICLE INFO

ABSTRACT

Herein, we demonstrate that conventional inorganic materials can be used in wearable systems despite their bulky and rigid nature. In particular, we proposed a bracelet-like modular design of a thermoelectric (TE) module with a heat sink made of rigid inorganic bulk materials. This device is referred to as the flexible TE system (FTES). Experiments and theoretical analyses were performed to verify whether the FTES performs like a conventional TE module even though it is flexible and wearable. In addition, we performed experiments while the FTES was worn on a subject's wrist for body heat harvesting. The FTES produced a usable power output even when the wearer was at rest. When the subject was running at a slow pace, the FTES generated approximately 80 μW. Our analyses indicate that this value can be further enhanced through future design improvements. Nevertheless, based on the experimental and analytical results, the FTES can deliver a usable power output. This research therefore demonstrates the possibility of using high-performance bulk materials in the design of wearable devices.

1. Introduction

Safe and reliable power sources are essential for flexible and wearable electronics. The power ratings required for wearable medical devices range from a few microwatts to a few milliwatts, as reported by Khan et al. [1]. Energy harvesting from body heat via thermoelectrics (TEs) is a strong candidate technology owing to its reliability, safety, and ability to produce power both in darkness and when at rest. Thus, depending on the required power level, the connection of power plugs to the wearable system may not be necessary.

Numerous approaches for developing future wearable electronics, such as wearable medical devices [2] and electronic skin [3–7], have been developed. Although various approaches [8–10] exist for the implementation of wearable electronics, the efforts related to TE applications can be generally categorized into two approaches. The first approach utilizes organics, which are naturally flexible [11–17]. In contrast, the second approach utilizes printable inorganics, which are flexible materials when printed onto a flexible substrate [18–26].

TE films can be viewed as a combination of both approaches; however, they face several limitations. First, the research directions in the two abovementioned approaches achieve flexibility at the expense of the TE performance. The TE figures of merit (zTs) of both organics and printable inorganics are considerably inferior to those of TE bulk materials, such as BiTe, PbTe, and SiGe. Although rapid progress in organic TEs has been achieved in the past decade, the highest reported zTs of p- and n-type organics at room temperature are 0.42 and 0.3, respectively [1,11,13,15]. Moreover, the zT of printable inorganics is inherently lower than that of their bulk counterparts due to the presence of organic additives such as binders. In contrast, the zT of bulk BiSbTe [27] close to the room temperature has been reported to be as high as 1.86. At higher temperatures, zT as high as 2.6 was reported for bulk SnSe at 923 K [28]. Second, a considerably small power output, P,

is produced due to a negligible drop in the temperature ΔT because $P \approx (\Delta T)^2$. Due to the small thickness of the TE films, the thermal resistance is negligible. For example, the power output of TE films with thicknesses ranging from a few micrometers to approximately 10 μm is four to six orders of magnitude smaller than the power output from bulk materials, which have a thickness of a few millimeters [18,29,30]. The body heat-harvested powers reported using TEs range from 0.3 nW [30] to a few microwatts [18,29]. Third, the specific electrical contact resistance should be sufficiently low in the TE films. If this is not the case, the electrical resistance of the module will be dominated by the electrical contact resistance. Fourth, a flexible heat sink must be devised for the TE films to be practical; however, this has not been previously considered [12,13,18,19].

To the best of our knowledge, there are hardly any reports investigating the development of flexible and wearable TE modules based on rigid inorganic bulk materials, even though the properties of inorganic bulk materials are superior to those of organics and printable inorganics. In addition, inorganic bulk materials are reliable and compatible with existing devices and systems. Herein, we propose a rigid inorganic bulk material-based wearable TE system that comprises both flexible modules and heat sinks. We propose a watch bracelet-like TE power generator based on rigid inorganic bulk materials. Because TE power generators generally require a heat sink [31,32], we also develop heat sinks for the watch bracelet-like power generator. These heat sinks can be readily used in wearable power generators; however, special heat sinks are yet to be developed for thin-film power generators. With the continued increase of the TE figure of merit, i.e., the conversion efficiency [27,28,33–38], and the continued decrease in the power requirements of devices [29,39] [e.g., Lee and Nathan [39] demonstrated a transistor that operated under low supply voltages (< 1 V) and ultralow power (< 1 nW)], our newly proposed rigid bulk inorganic material-based flexible TE system (FTES) is anticipated to serve as an excellent platform for future wearable power systems.

2. Experimental procedures

2.1. Materials synthesis

High-purity raw materials, bismuth (99.999%), tellurium (99.9999%), antimony (99.9999%), and selenium (99.999%), were weighed based on the stoichiometries of $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Te_{2.7}Se_{0.3}$ for the *p*- and *n*-type materials, respectively, and placed in a cleaned quartz tube. The quartz tube was evacuated, sealed, and then placed in a furnace for 10 h at 750 °C for *p*-type materials or 800 °C for *n*-type materials. The ingots removed from the furnace were crushed in a planetary ball mill operated at 500 rpm for 70 min. Subsequently, the crushed powder was placed in a carbon mold and sintered at 450 °C for 10 min using the spark plasma sintering method.

2.2. Thermoelectric properties

The Seebeck coefficient S and the electrical resistivity ρ were simultaneously measured in a helium atmosphere at temperatures ranging from 310 K to 470 K using an ULVAC ZEM-3. The thermal conductivity κ was determined based on the relation $\kappa = \lambda C_p d$, where the thermal diffusivity λ, the heat capacity C_p, and the density d were measured using the laser flash method (NETZSCH LFA 457), differential scanning calorimetry (NETZSCH DSC 200 F3), and the Archimedes' method, respectively. The figure of merit, zT, was calculated using the Seebeck coefficient, electrical resistivity, and thermal conductivity as follows: $zT = S^2T/\rho\kappa$.

2.3. System design and fabrication procedures

Fig. 1 shows the system design and fabrication procedures for the proposed flexible thermoelectric system (FTES). The conventional thermoelectric generator (TEG) shown in the figure is a solid-state heat engine that cannot be bent. The structure of the conventional TEG has rigid *p* and *n* TE semiconductors that are interconnected with conductive metals and covered by ceramic plates. A schematic showing the basic concept of the proposed FTES is shown in Fig. 1(a). The FTES comprises a flexible TEG and heat sinks. The entire FTES comprises 10 units of thermoelectric system; each unit has four TE elements in a 2×2 array and a copper heat sink on top of the elements. The proposed FTES also has *p* and *n* bismuth telluride TE elements, each having dimensions of 3 mm × 5 mm × 5 mm. These elements are connected to polymer links by shafts that penetrate both the elements and the links. In the TEG unit, each *p* and *n* element is connected by a 50-μm-thick copper foil. A copper heat sink can be installed on the TEG unit using the links to secure the heat sink. Given the difficulty associated with installing a heat sink on the flexible substrates of other printed flexible TEGs, the proposed FTES has an advantage: the heat sink can be easily attached with the links. The size of a TEG unit is 14 mm × 12 mm. Overall, the FTES has 40 TE elements that are 156 mm × 16 mm in size, which are therefore suitable for the human wrist.

Fig. 1(b) shows the fabrication procedure for the FTES. First, high-purity raw materials were weighed and transferred to the quartz tube. The quartz tube was evacuated, followed by heating in a furnace to fabricate the melt-grown $Bi_{0.5}Sb_{1.5}Te_3$ and $Bi_2Te_{2.7}Se_{0.3}$ ingots. The ingots were then crushed in a planetary ball mill to obtain a fine powder. After the bismuth telluride powder was sintered in a mold using the spark plasma sintering method, cylindrical-shaped sintered bismuth telluride was obtained. The TE properties, i.e., S, ρ, κ, and zT, of sintered bismuth telluride were measured, as described in Section 2.2, and are presented in Fig. 2. Sintered bismuth telluride was then diced and mechanically manufactured into the intended leg shape. Using electroplating, nickel and gold layers were deposited onto the manufactured TE elements and a copper foil, respectively, as shown in Fig. 1(b).

Subsequently, we assembled the device and soldered using a solder paste. We inserted the heat sink on top of the TEG unit, and an additional copper wire electrode was soldered between two TES units to connect them to each other. Because flexible copper wires were used as the electrodes, the two connected TES units could be bent freely. When the wires were connected, they needed to be slightly longer than the gap spacing because an extra length of electrode was required to accommodate the TES rotating around a pivot point. By repeating the aforementioned processes, the FTES comprising 10 TES units can be fabricated, as shown in Fig. 1(a). Based on the electrical resistance measurements of the FTES (see Section 2.5), approximately 15% of the total electrical resistance was due to the electrode, contact resistance, and non-ideal effects. Although further improvement in the module performance can be achieved by minimizing the electrical resistance, we believe that the current FTES is suitable for demonstrating that rigid inorganic bulk materials can be used for flexible devices.

2.4. Electrical contact resistance

The electrical contact resistance of $Bi_{0.5}Sb_{1.5}Te_3$ (*p*-type) was measured using an in-house contact resistance evaluation apparatus [40]. After surficial polishing, the TE leg was placed between the copper blocks. A gold voltage probe was scanned directly across the interface of the contact between the TE material and the metallic electrode. The contact resistance at the interface between the TE materials and the metallic electrodes should be minimized to prevent the degradation of the TE power output. The specific contact resistance was measured to verify the parasitic resistance during the bonding process. The measurement was performed for three different parallel lines to verify the uniformity of the bonding electrical characteristics, as shown in Fig. 3. The resistance was measured from the copper electrodes to the material side. The measurement result at point A, which is at the edge of the