Mechanical and Electrical Properties of p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and n-type Bi$_2$Se$_{0.6}$Te$_2.4$ Bulk Material for Thermoelectric Applications

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Abstract. This study reports on the fabrication of a chalcogen-based thermoelectric power generation (TEG) device using p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and n-type Bi$_2$Se$_{0.6}$Te$_2.4$ bulk thermoelectric materials. The microstructure of the samples was characterized by field emission scanning electron microscopy (FESEM). The phase composition of the powders was characterized by X-ray diffraction (XRD), revealing a rhombohedral structure. The thermoelectric (TE) properties such as Seebeck coefficient ($S$) and the electrical conductivity ($\sigma$) of the resulting alloys were studied in the temperature range of 300 K to 523 K. The power factor ($P_{\text{factor}}$) for a Bi$_{0.4}$Sb$_{1.6}$Te$_3$ as p-type sample was found to be 4.96 mW/mK$^2$ at 373 K, whereas 2.22 mW/mK$^2$ was obtained at 383 K for a Bi$_2$Se$_{0.6}$Te$_{2.4}$ as n-type sample. Electrical power generation characteristics such as high open circuit voltage ($V_{oc}$) and maximum output power ($P_{\text{max}}$) were monitored by changing the temperature conditions required to generate maximum power. The significance of the resistances including the internal resistance ($R_{\text{in}}$) and contact resistance ($R_{\text{C}}$) between legs and electrodes, are discussed. The maximum output power obtained with the 9 p-n couples device was 39.4 mW under the thermal condition of $T_H$=523 K hot side temperature and $\Delta T$ = 184 K temperature difference.

1. Introduction

A thermoelectric power generation (TEG) device produces voltage when there is a temperature difference ($\Delta T$) between the hot and the cold sides as a result of Seebeck thermoelectric effect (TE) [1]. The following are the advantages of these generators: no moving parts, small and lightweight, maintenance-free, acoustically silent and electrically “quiet”, and environmentally friendly [2]. Bi$_2$Te$_3$-based chalcogenides have attracted great interest due to their promising TE properties [3]. Yet, enhancing in the TE properties is strongly required for empirical applications. One approach to enhance the TE properties is optimization of the doping effective route. For example, recent devices use Bi$_2$Te$_3$, a semiconductor, which when alloyed with antimony (Sb) or selenium (Se) becomes an efficient TE material for power generation as a result of the variations in the carrier concentration and carrier mobility [4, 5]. As an alternate approach, researchers have attempted to improve the efficiency of materials based on Bi$_2$Te$_3$ by creating structures with one or more reduced dimensions [6]. In one case, an n-type Bi$_2$Te$_3$ has been shown to have improved Seebeck coefficient ($S$). However, $S$ and electrical conductivity ($\sigma$) have a trade-off; a higher $S$ results in decreased carrier concentrations and decreased $\sigma$ [7]. The fundamental physical parameters of Bi-Sb-Te and Bi-Se-Te TE materials such as $\sigma$, $S$, and power factor ($P_{\text{factor}}$) are referred in our previous papers [5,8], which reported that the highest $P_{\text{factor}}$ have been obtained for the compositions of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and Bi$_2$Se$_{0.6}$Te$_{2.4}$. For Bi$_2$Se$_{0.6}$Te$_{2.4}$ as n-type materials, the carrier concentration is adjusted by doping with tellurium (Te) which is done in the
present paper. Te atoms exhibit a donor action because they replace Se atoms in the lattice and each contributes one electron to the conduction band [9]. It appears that the ionization energy of a Te atom is very low and therefore this atom in Bi$_{2}$Se$_{0.6}$Te$_{2.4}$ is almost fully ionized. As an extension of our previous work, we fabricated in this paper 9 couples of TEG device using solid-state microwave synthesis. We focused on the thermoelectric properties of the TEG device that use Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$ as p-type and Bi$_{2}$Se$_{0.6}$Te$_{2.4}$ as n-type.

2. Experimental

Bi, Sb, Se, and Te that were used in this study were highly pure powders (99.999%). The typical element ratio for the preparation of p-type Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$ is as follows: 0.2528g Bi, 0.5892 g Sb, and 1.1580 g Te. The n-type Bi$_{2}$Se$_{0.6}$Te$_{2.4}$ with excess Te was prepared by mixing 1.0834g Bi, 0.1228g Se, and 0.7938g Te. The p-type and n-type ingots were grown using a solid-state microwave synthesis that was described in a previous literature [5, 8]. After grinding, the samples were then characterized to determine their crystallization via X-ray diffraction (XRD, PANalytical X’Pert PRO MRD PW3040, Almelo, The Netherlands). Both types of powders were pressed into disk shapes (5 mm diameter and 3.5 mm thickness) through cold pressing at 10 tons. Selected regions of the samples were imaged using field emission scanning electron microscopy (FESEM) (Leo-Supra 50VP, Carl Zeiss, Germany).

$\sigma$ as a function of temperature was measured via the standard 4-terminal DC method under a vacuum of $10^{-3}$ mbar, whereas, $S$ was determined by the slope of the linear relationship between the thermoelectromotive force (e.m.f.) and $\Delta T$ between the two ends of each sample. As shown in Fig.1, the assemblies of 9 (p-n) couples from these pellets were placed between two alumina plates with the corresponding dimensions of 50 mm × 25 mm, which served as hot and cold ends for the relevant TE pellets. By using Ag paste and Cu plates, the Ag paste–Cu plates–Ag paste electrodes were made on the inner surface of the alumina substrates. The device was then dried at room temperature for one day to metalize the electrodes on the devices.

![Figure 1.](image)

Figure 1. (a) connection of p- and n-type samples by Cu plates, and (b) schematic diagram of the thermoelectric generation device.

To evaluate device performance, the top alumina plate was heated up to 523 K by one brass block as a heater for the device, and the bottom plate was cooled by another brass block with circulated cooling water. $\Delta T$ between the hot and the cold sides was measured by two digital K-type E$^0$ Sun (ECS820C) thermocouples near the inner surface of the alumina substrates. The current-voltage ($I$-$V$) lines and the current-power ($I$-$P$) curves of power generation were performed in air by sweeping the load resistance ($R_L$) using the variable resistance box. The open circuit voltage ($V_{oc}$) and many other voltages at the condition of power generation were measured by a voltage meter (Keithley 197).
3. Results and discussion

Typical SEM images of the surface morphology of the samples (ingots and pellets) Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and Bi$_2$Se$_{0.6}$Te$_{2.4}$ are shown in Figure 2(a) to 2(d). In Fig.2 (a), most of the grains were uniformly arranged and formed by the assembly of micro-sheet grains (Bi$_{0.4}$Sb$_{1.6}$Te$_3$ as an ingot). In Fig.2 (b), the FESEM observations revealed the appearance of a typical layered and well-packed structure (Bi$_2$Se$_{0.6}$Te$_{2.4}$ as an ingot). In Fig.2 (c) and (d), small pores notice at the grains boundaries in the samples, explaining that the compact texture was obtained. Therefore, the surfaces show uniform grains and high density (Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and Bi$_2$Se$_{0.6}$Te$_{2.4}$ as pellets).

![Figure 2](image)

**Figure 2.** (a) and (b) are the FESEM images of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and Bi$_2$Se$_{0.6}$Te$_{2.4}$ ingots, respectively, whereas (c) and (d) are the FESEM images of Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and Bi$_2$Se$_{0.6}$Te$_{2.4}$ pellets, respectively.

XRD experiments were carried out to determine the structure of the powder samples, and the results are shown in Figs. 3 (a) and (b). XRD spectra for Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and Bi$_2$Se$_{0.6}$Te$_{2.4}$ powders indicate that the powders are polycrystalline and characterized by a rhombohedral structure, with a dominant peak representing the plane (0 1 5). All of the diffraction peak positions and (hkl) values match very well with the standard diffraction data of pure Bi$_2$Te$_3$ and Sb$_2$Te$_3$ (JCPDS 15-0863 and 15-0874, respectively) for Bi$_{0.4}$Sb$_{1.6}$Te$_3$ (Fig.3 (a)), whereas Bi$_2$Te$_3$ and Bi$_2$Se$_3$ (JCPDS15-0863 and 33-0214, respectively) for Bi$_2$Se$_{0.6}$Te$_{2.4}$ (Fig.3 (b)).
Figure 3. (a) and (b) are the XRD patterns of Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$ and Bi$_{2}$Se$_{0.6}$Te$_{2.4}$ powders, respectively.

The transport properties of p- and n-type samples in terms of $\sigma$, $S$, and $P_{\text{factor}}$ were investigated from 300 to 523 K (Figs. 4 to 6). Both sample types had nearly the same behavior for $\sigma$, which gradually decreased as the experimental temperature increased, that is, a degenerate semiconductor (Figure 4). $\sigma$ for the p-type Bi$_{0.4}$Sb$_{1.6}$Te$_{3}$ sample ($\sigma_p$) varied from $9.6 \times 10^5$ S/m at 300 K to $4.8 \times 10^5$ S/m at 523 K, whereas $\sigma$ for the n-type Bi$_{2}$Se$_{0.6}$Te$_{3}$ sample ($\sigma_n$) was from $1.99 \times 10^4$ S/m at 300 K to $1.74 \times 10^4$ S/m at 523 K.

Figure 4. Temperature dependence values of $\sigma$ of p-type and n-type samples.
As shown in Figure 5, $S$ for the p-type sample ($S_p$) was 90 at 443 K and for n-type ($S_n$) was -330.6 $\mu$V/K at 423 K. The value of $S$ increases almost rapidly with temperature from 300 to 443K for p-type (300 to 383K for n-type), which is consistent with the Mott formula [4]. Due to the thermal excitation of extrinsic charge carriers at higher temperatures a decrease in $S$ (with rising temperatures) is observed for both types of samples.

![Figure 5](image1.png)

*Figure 5. Temperature dependence values of $S$ of p-type and n-type samples.*

As evident in Figure 6, the temperature behaviors of $P_{factor}$ for the p-type and n-type samples were similar. $P_{factor,p}$ values obtained for the p-type samples were larger than those for the n-type samples ($P_{factor,n}$) within the entire temperature range. The maximum $P_{factor,p}$ measured was 4.96 mW/mK$^2$ at 373 K, which is larger than that reported by Li et al. [10], whilst the maximum $P_{factor,n}$ was 2.22 mW/mK$^2$ at 383 K, which is comparable to that reported by Wang et al. [4]. These two maximum values for p- and n-type contribute to a maximum output power for our devices.

![Figure 6](image2.png)

*Figure 6. Temperature dependence values of $P_{factor}$ of p-type and n-type samples.*
The output voltage and the output power of the fabricated 9 couples versus the current were measured by sweeping $I$ at several temperature conditions, as shown in Figure 7. The $V_{oc}$ that is equal to the intercept of the $I$-$V$ line reached 355 mV at $\Delta T$ of 184 K and $T_H$ of 523 K, which are in agreement with the expression $V=V_{oc}-R_L I$. It is lower than that calculated $S$-$T$ curves (Figure 5) of both p- and n-type legs ($V_{calculated} = (S_p-S_n) \times \Delta T \times N$, where $N$ is the number of couples). This voltage loss could have originated from many factors including low thermal conductivity of alumina substrate [11] and unfavorable junctions between the TE legs and the electrodes. $I$-$P$ curves illustrated in Figure 7 exhibit the parabolic curves of the output power ($P_{out}$); an analysis to plots of $I$-$V$ lines allows the observation of an increasing in the $P_{out}$ with the $\Delta T$. The explanation for this observation results from the rise of the $\Delta T$, whose consequence is an increase in the output voltage ($V_{oc}$). The higher the value of this $V_{oc}$, the higher will be the output current ($I_{out}$) for a given $R_L$, and therefore will be the dissipated power in the external load ($P_{out} = R_L I_{out}^2$). The maximum output power ($P_{max}$) values were 39.4 mW at the thermal condition of 523 K $T_H$ and $\Delta T = 184$ K, which means these results could be comparable with the results of Wang et al. [4]. It was investigated that the powers of the devices improved by increasing the temperature. The internal resistance ($R_{in}$) of each device which corresponds to the slope of the $I$-$V$ lines was directly obtained by the measured system. The ideal internal resistance ($R_{id}$) was calculated by the sum of the resistance values of p-type and n-type samples. With $R_{in}$ and $R_{id}$, contact resistance ($R_c$) can be obtained by $R_c = R_{in} - R_{id}$ [2]. The resistance values of the device ($R_{in} = 0.8 \Omega$ and $R_c = 0.4 \Omega$). This result demonstrates that, with the relationship between $R_c$ and $P_{max}$, $R_c$ should be minimized for each device because it plays a key role in TEG device performance. Based on the data obtained, the good TEG properties originally came from the relatively high electrical properties of p-type and n-type samples that were prepared by solid-state microwave synthesis. Two methods were adopted to optimize the device performance. First, the surface of the alumina plates was treated with NaOH solution to increase roughness and to enhance both mechanical strength and electrical contact between the alumina plates and the Cu electrodes. Second, the ends of p-type and n-type samples were grooved to increase the surface area, also improving the mechanical and the electrical properties of the contacts [2]. Based on these results, the device using p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and n-type Bi$_2$Se$_{0.6}$Te$_{2.4}$ worked successfully and it was stable with satisfactory TE performances.

![Figure 7](image-url) Figure 7. The power generation characteristics of the TEG device that comprises 9 couples, where (I) $\Delta T = 27$, (II) $\Delta T = 66$, (III) $\Delta T = 104$, (IV) $\Delta T = 145$, and (V) $\Delta T = 184$ K.
4. Summary
TE materials p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and n-type Bi$_2$Se$_{0.6}$Te$_{2.4}$ were prepared via solid-state microwave synthesis. TEG devices were fabricated and characterized in terms of high open circuit voltage ($V_{oc}$) and maximum output power ($P_{max}$). A maximum $V_{oc}$ and $P_{max}$ of 355 mV and 39.4 mW was achieved in the device with 9 p-n couples with $T_H$ of 523 K and $\Delta T$ of 184 K. $V_{oc}$ and $P_{max}$ systematically increased with $\Delta T$. As a result, the device using p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ and n-type Bi$_2$Se$_{0.6}$Te$_{2.4}$ worked successfully and it was stable with satisfactory TE performances. The successful demonstration of good thermoelectric performances of the as-prepared device suggests the great potential of these low temperature doped thermoelectric materials towards future applications.

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